SOME ASPECTS OF THE CHEMISTRY OF SULPHUR HALIDES AND OXYHALIDES

by

KYRIAKOS C. SYMEONIDES

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SUMMARY

The reactions between thionyl chloride and ketones containing at least one alpha proton, have been shown to give a variety of products depending upon the applied conditions and the structure of the adjacent groups. This work partly deals with the reactions of thionyl chloride with 1,3-diketones which afforded sulphides and α-chlorides. Typically, dimedone gave di-2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl sulphide and 2-chloro-5,5-dimethylcyclohexane-1,3-dione, whereas 1,1-dibenzoyl ethane gave a mixture of products containing an α-sulphinyl chloride, which upon treatment with ethanol gave a disulphide, a trisulphide, or a thiosulphinate according to the conditions employed.

A number of possible intermediates were investigated in an attempt to establish the conditions and structural requirements necessary for the formation of the above products.

A novel synthesis of β-ketosulphinyl chlorides was developed which afforded excellent yields in a simple one stage process. Certain of the chemical and spectral properties of this new class of compounds were examined in an effort to elucidate the role of sulphinyl chlorides as intermediates in the reaction of 1,3-diketones with thionyl chloride.

Ethyl isopropyl ketone afforded a 3-thietanone upon treatment with thionyl chloride, a reaction which possibly involved a sulphinyl chloride intermediate.

Lastly a number of partly saturated cyclic compounds suitably activated by carbonyl groups, were shown to be readily oxidised by thionyl chloride to give aromatic systems.

STATEMENT

The undersigned declares that this thesis has not been carried out in collaboration with others. Neither has the work been submitted for any other award.

Kyriakos Symeonides.

Kyriakos C Symeonides

Acknowledgments.

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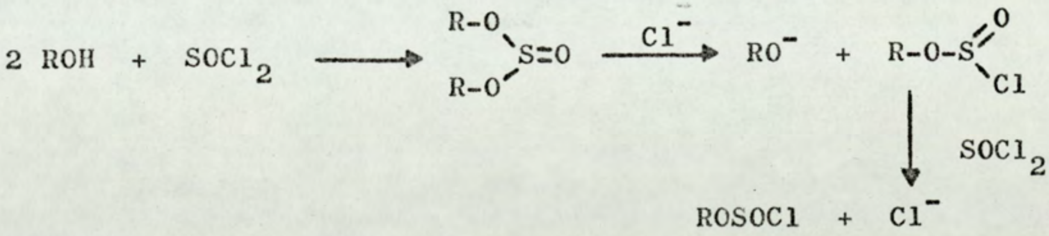
INTRODUCTION

The synthetic applications of the reactions of thionyl chloride with organic compounds have long been recognised and a large number have been reported in the literature. The reagent's versatility is reflected by the numerous products which can be obtained and which depend on the reactive functional group under consideration. It is evident that the driving force for the majority of the reactions of thionyl chloride is provided by an electron withdrawing centre which activates an adjacent proton necessary for the reaction to proceed.

By far the most studied and useful reaction is that between thionyl chloride and the hydroxyl group of an aliphatic compound. The oxygen atom is here responsible for the activation of the adjacent proton. Alcohols and acids can be readily converted to the related chlorides by a single stage process (eq. 1)

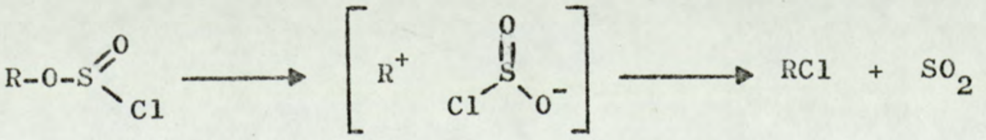
$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl \qquad (1)$$

Barlett et. al.[1] have shown that the reaction proceeds via a sulphite intermediate which affords the chlorosulphinate when attacked by chloride ions (eq. 2)



(2)

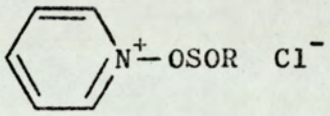
Further rearrangement of the chlorosulphinate produces the chloride with simultaneous evolution of sulphur dioxide(eq. 3)



(3)

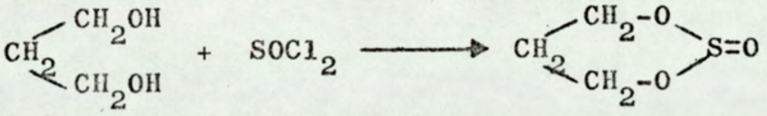
(A)

Both intermediates have been isolated and shown to give the chloride under suitable conditions.[1,2,3] Depending upon the conditions, the configuration of the substrate R may be retained or inverted. Thus in the absence of a base the lifetime of the intermediate ion pair (A) is short and attack of the chloride ion proceeds, with retention of configuration, as soon as the ion pair is formed. In the presence of a base such as pyridine,[4] a complex of the type



is formed. The free chloride ion can then attack the carbonium ion from the rear to bring about inversion of configuration.

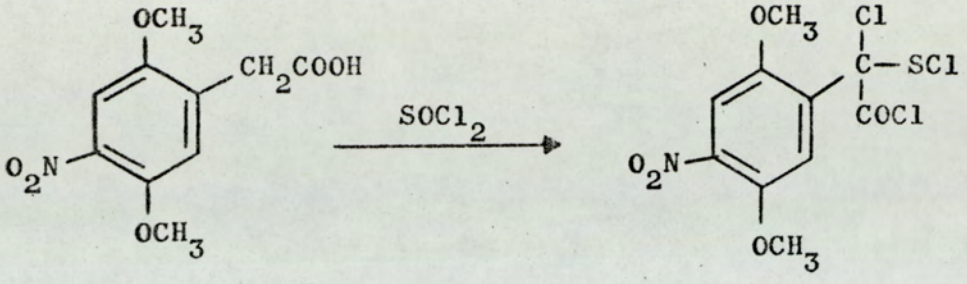
A variety of other products can be isolated whenever two or more active functional groups are present within the same molecule. Such is the case with diols which afford cyclic sulphites.[5] (eq. 4)



(4)

Aliphatic and aromatic carboxylic acids react with thionyl chloride in an analogous way to alcohols. The reaction has been reported[6] to be effectively catalyzed by pyridine. Acid anhydrides have been proposed as intermediates in the reaction and have been isolated under suitable conditions in very good yields.[7]

The presence of an activated proton in the alpha position to the carbonyl group, presents another centre for oxidation to take place. Such an interesting reaction has been reported by Simon et. al.[8] who proposed a sulphinyl chloride intermediate which presumably was then reduced to the α-chlorosulphenyl chloride by a Hell-Vohlard-Zelinsky type addition followed by a Pummerer rearrangement. (eq. 5)

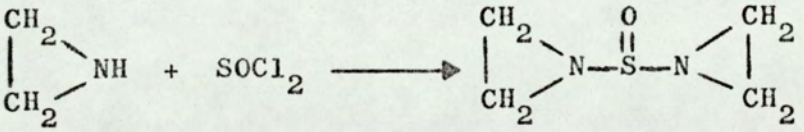


(5)

Protons activated by a nitrogen atom have also been found to be active towards thionyl chloride. Primary amines have been reported to afford N-sulphinyl amines[9] (eq. 6) which are valuable intermediates in the synthesis of certain heterocyclic compounds.

$$RNH_2 + SOCl_2 \longrightarrow R\text{-}N{=}S{=}O + 2\ HCl \qquad (6)$$

The reaction appears to proceed via the N-sulphinyl chloride which decomposes with evolution of hydrogen chloride, a step not feasible in the reaction of secondary amines which afford sulphinyl diamines[10](eq. 7) through intermolecular condensation.



(7)

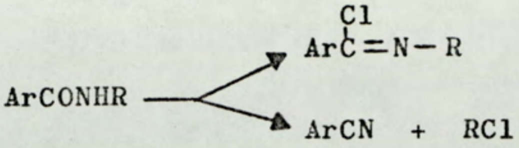
Reduction of the sulpinyl group cannot take place, possibly due to the absence of an alpha proton.

Tertiary aromatic amines react not specifically at the activated aromatic centre.

The reaction of thionyl chloride with amides has been shown[11] to give nitriles in the case of primary compounds.(eq. 8)

$$RCONH_2 + SOCl_2 \longrightarrow RCN + SO_2 + 2\ HCl \qquad (8)$$

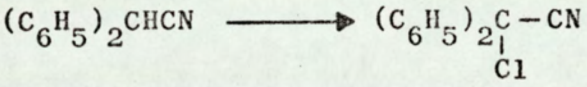
Aromatic secondary amides,depending on the nature of the (R) group, can proceed to the imidochlorides[12] or cleave at the nitrogen atom.[13] (eq. 9)



$$\mathrm{ArCONHR} \longrightarrow \mathrm{Ar\overset{Cl}{C}{=}N{-}R} \;\;\text{or}\;\; \mathrm{ArCN + RCl} \qquad (9)$$

Protons bonded to a carbon atom, undergo a variety of reactions with thionyl chloride when activated by an adjacent strong electron-withdrawing group. The nitrile and carbonyl groups can normally produce such effects, the first through an inductive effect and the latter through a combination of an inductive effect and a possible enolization.[14] Long distance mesomeric effects are also responsible for the activation of protons in unsaturated systems.

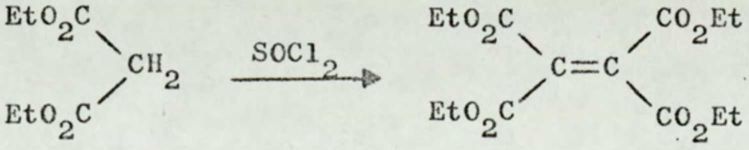
A chlorinated product has been reported by Wilson[15] (eq. 10) from the reaction of benzhydryl cyanide and thionyl chloride.



$$(C_6H_5)_2CHCN \longrightarrow (C_6H_5)_2\underset{Cl}{C}-CN \qquad (10)$$

No mechanism was postulated for the reaction, but it is likely that a sulphinyl chloride intermediate would decompose and form the chloride under the vigorous reaction conditions employed. (30hr reflux.)

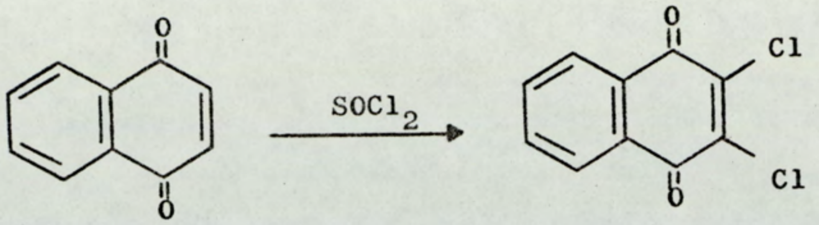
The presence of an activated methylene group in malononitrile[16] and diethyl malonate[17] has been reported to give rise to tetrasubstituted-alkenes. (eq. 11)



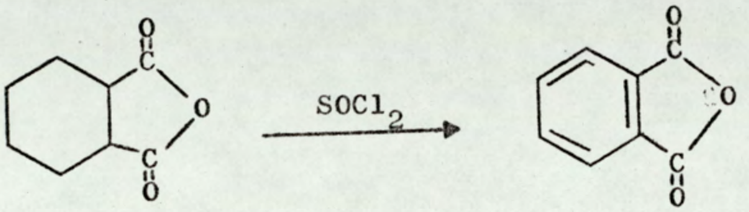
(11)

A sulphinyl chloride, which upon loss of hydrogen chloride forms the sulphine, are the proposed intermediates.

Cyclic systems such as benzoquinones,[18] afford chlorinated products.(eq. 12)


(12)

Aromatization has been shown to take place in preference or in parallel[19,20] to chlorination whenever the structure permits so.(eq. 13)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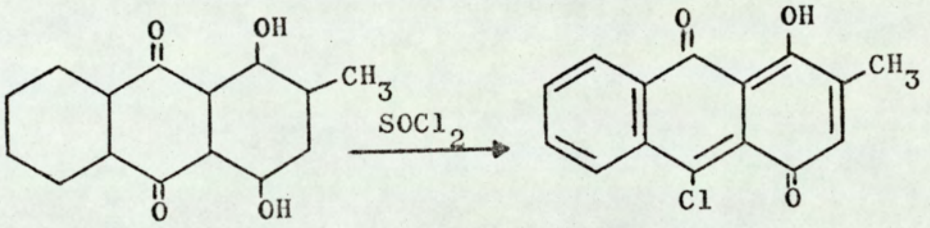
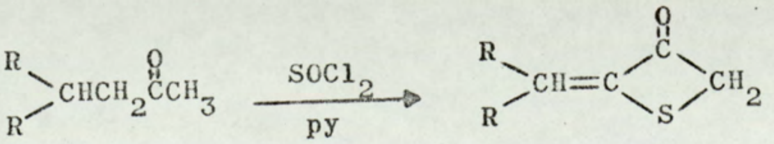
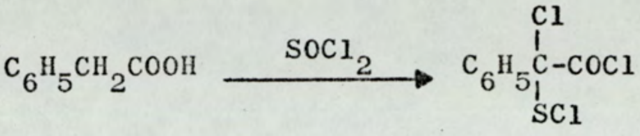

(13)

The reactions between thionyl chloride and ketones possessing at least one alpha proton have not been fully investigated. Complex polymeric products have been obtained from acetone[21] possibly due to the availability of six α-protons all equally activated by the carbonyl function.

An interesting reaction has been reported by Krubsack[22] who obtained a number of 3-thietanones from the reaction of 4-substituted butan-2-ones with thionyl chloride.(eq. 14)

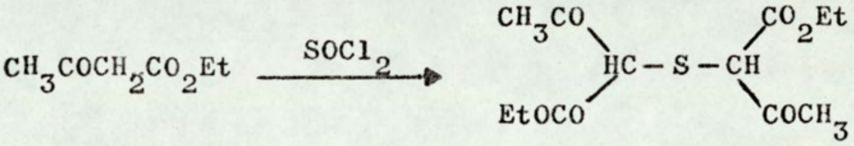

(14)

An α-chloro-α-sulphenyl chloride intermediate has been proposed which can then attack the α-methyl group with subsequent elimination of hydrogen chloride. Such an α-chloro-α-sulphenyl chloride has been isolated by Simon[23] as the major product in the reaction between phenylacetic acid and thionyl chloride.(eq. 15)

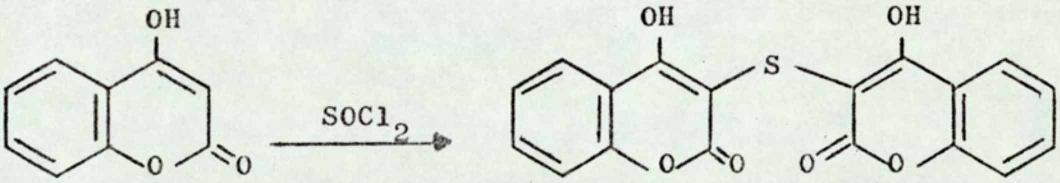


$$C_6H_5CH_2COOH \xrightarrow{SOCl_2} C_6H_5\overset{Cl}{\underset{SCl}{C}}\text{-}COCl \qquad (15)$$

1,3-Diketones such as ethyl acetoacetate[24] and hydroxycoumarin[25] afford symmetrical sulphides upon an uncatalyzed treatment with thionyl chloride.(eq. 16,17)



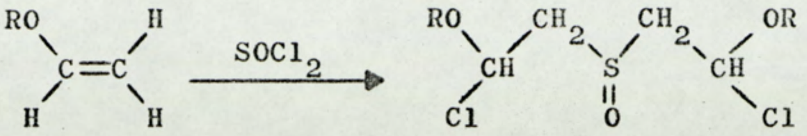
(16)



(17)

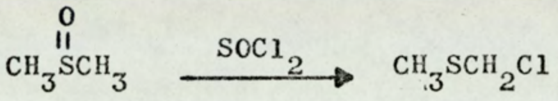
It would seem reasonable to assume that the 1,3-diketo structure is the deciding factor responsible for the formation of such products, but as will be seen later in this thesis such a generalization cannot be fully justified.

In the presence of an activated double bond, addition of thionyl chloride or substitution of the olefinic protons takes place. The intermediate sulphinyl chloride can further react and give a variety of products, depending upon the structure of the alkene employed. A number of enol ethers have been reported[26] to afford β-chlorosulphoxides.(eq. 18)



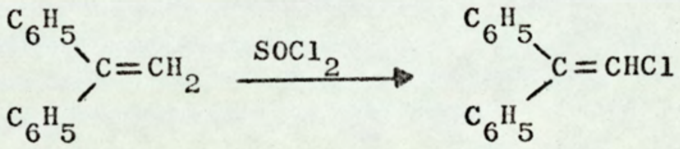
(18)

The authors do not offer an explanation regarding the stability of the sulphoxide, which in the presence of thionyl chloride, should have been rapidly reduced to the sulphide in an analogous manner to the dimethyl sulphoxide[27] reduction. (eq. 19)



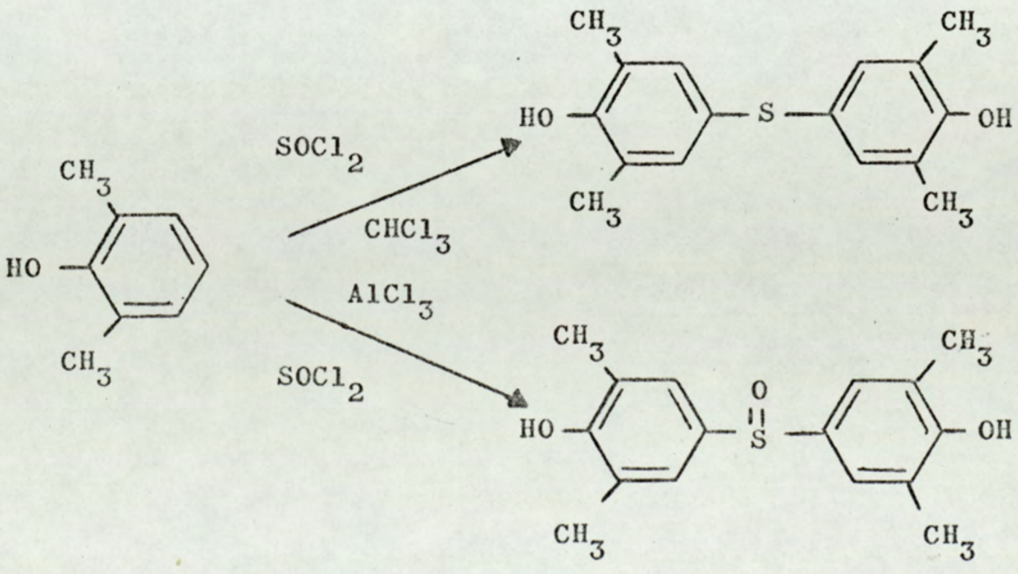
$$CH_3\overset{\overset{O}{\|}}{S}CH_3 \xrightarrow{SOCl_2} CH_3SCH_2Cl \qquad (19)$$

Other alkenes react with thionyl chloride by substitution of the olefinic protons.[28] (eq. 20)



(20)

A number of sulphides have been isolated from the reaction of thionyl chloride and phenols[29] or naphthols.[30] The presence of a catalyst such as copper, zinc or aluminium trichloride has been found in some cases to be necessary for the reaction to proceed. In the absence of a catalyst different products were sometimes isolated.[31] (eq. 21)



(21)

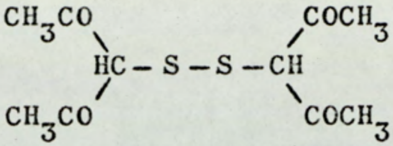
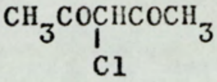
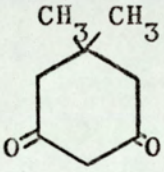
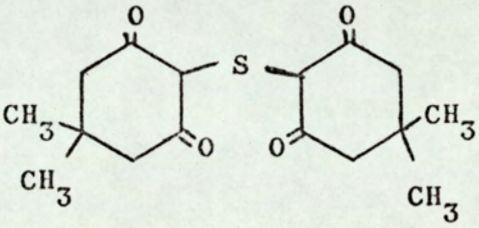
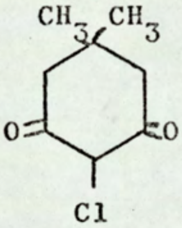
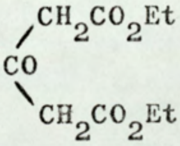
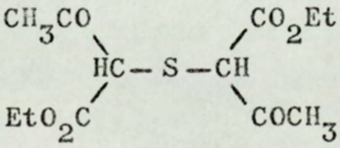
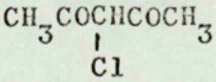
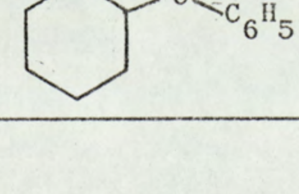
Anisole[31a] afforded a sulphide in the presence of aluminium trichloride thus indicating that the catalyst was not the only factor responible for the sulphoxide formation in the above (eq. 21) reaction.

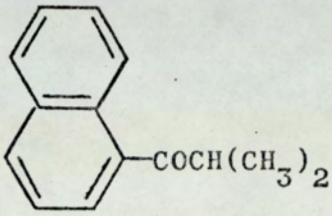
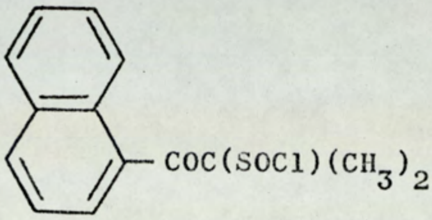
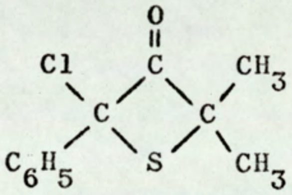
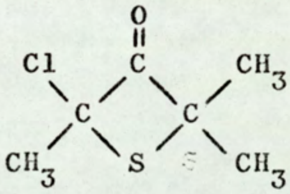
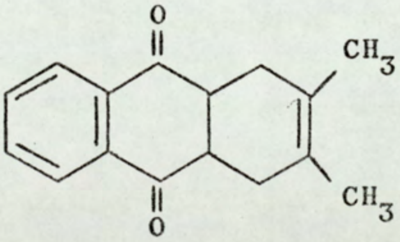
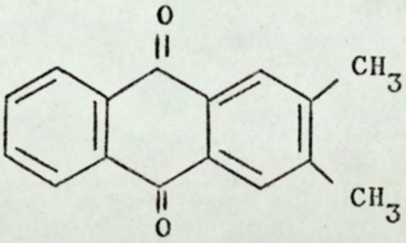
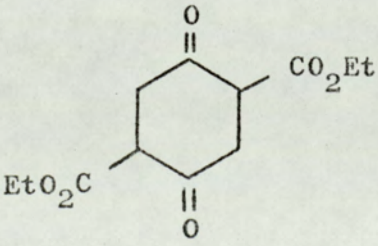
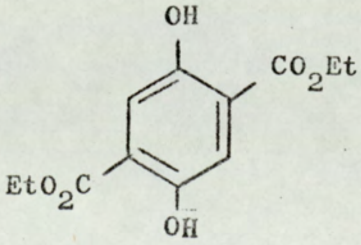
Judging from the numerous reactions of thionyl chloride already mentioned, it is obvious that a lot of reasearch would have to be carried out in order to establish beyond doubt the structural factors which determine the formation of each product.

The work which was carried out in this project dealt with the uncatalyzed reactions of a variety of ketones with thionyl chloride. Compounds like ethyl acetoacetate possessing a 1,3-diketo structure capable of keto-enol tautomerism, were found to afford sulphides. Other 1,3-diketones were therefore treated with thionyl chloride and although sulphides and α-chlorides were sometimes obtained generalizations about the reaction were difficult to make due to a number of side reactions which usually produced non-identified tars. A particular point which was noted was that the sulphides which were isolated or had been reported, existed solely in their enolic form unlike other ketones which incorporated sulphur containing groups, but which existed solely in their keto-form. Such compounds included a number of β-ketosulphinyl chlorides which were prepared by the action of thionyl chloride on β-ketoisopropyl ketones. The synthesis of this new class of compounds was developed to give excellent yields of β-ketosulphinyl chlorides in a simple one stage process.

The presence of a carbonyl group onto or alpha to a ring structure which was capable of aromatization, gave rise to the fully aromatized systems upon treatment with thionyl chloride. Two such reactions were conducted and are listed in the following table along with the other attemted reactions and the products obtained.

TABLE

REACTANT	PRODUCT
$CH_3COCH_2COCH_3$	  $CH_3CO\underset{Cl}{C}HCOCH_3$
$C_6H_5COCH_2COCH_3$	Non-identified tars.
$C_6H_5COCH(CH_3)COC_6H_5$	$C_6H_5COC(CH_3)(SOCl)COC_6H_5$ $C_6H_5C(Cl)=C(CH_3)COC_6H_5$
	 
	Non-identified compounds
$CH_3COCH(CH_3)CO_2Et$	$CH_3COC(CH_3)(SOCl)CO_2Et$ $CH_3C(Cl)=C(CH_3)CO_2Et$
$CH_3COCH_2CO_2Et$	  $CH_3CO\underset{Cl}{C}HCOCH_3$
	Non-identified tars.

REACTANT	PRODUCT
$CH_3COCH(CH_3)_2$	$CH_3COC(SOCl)(CH_3)_2$
$C_6H_5COCH(CH_3)_2$	$C_6H_5COC(SOCl)(CH_3)_2$
$(CH_3)_2CHCOCH(CH_3)_2$	$(CH_3)_2CHCOC(SOCl)(CH_3)_2$
	
$C_6H_5CH_2COCH(CH_3)_2$	$C_6H_5CH_2COC(SOCl)(CH_3)_2$ *  *
$(C_6H_5)_2CHCOCH(C_6H_5)_2$	No reaction.
$CH_3CH_2COCH(CH_3)_2$	
	
	

* These compounds have only been spectroscopically identified

Lastly some mechanistic work was carried out to establish the paths that each reaction followed and so improve on the conditions and general precognition of the structural requirements necessary for the formation of each class of compounds.

CHAPTER 1

1. SYNTHETIC EXPERIMENTAL

1.1 Introduction.

The influence of the purity of the thionyl chloride on the course of the reactions has been examined. It was found that in some cases technical grade thionyl chloride forced the reaction towards a different path and as a result non-identified tars were produced. For this reason, Koch Light puriss A.R thionyl chloride was always employed in subsequent experiments and was found to give satisfactory results. Its purity was checked by gas liquid chromatography which only detected one component. The sulphur dichloride and disulphur dichloride contents in thionyl chloride was checked by titration.(See page 13)

Where an excess of thionyl chloride or a solvent was employed it was removed using a thin film rotary evaporator, the temperature of the bath so arranged to suit the experimental conditions being followed. The products,where liquids, were checked for purity by gas liquid chromatography (a carbo-wax 20M column was employed), and were then identified by spectroscopic means, by titrations, and by elemental analysis. When in doubt, the spectral evidence was correlated to that of authentic samples prepared by known routes.

The nmr spectra were run either in a 60 or in a 100MHz spectrometer, and tetramethylsilane (TMS) was always emloyed internally as the standard. Integration of the spectrum was subject to a ∓5% error and therefore the values recorded for the integration of each signal have been approximated to the nearest integer.

Unless otherwise stated, general purpose reagents and solvents were employed. Uncorrected melting and boiling points have been recorded.

1.2 Purification and analysis of some reagents and solvents.

1.2.1 Purification of solvents.

Benzene, ether and tetrahydrofuran which were some of the solvents employed throughout this work, were suitably dried in sodium. Super-dry ethanol was prepared by distillation over magnesium.

1.2.2 Purification of thionyl chloride.

Triphenyl phosphite[32] (80ml), was slowly added to thionyl chloride (500ml) and the mixture was fractionated through a 12in. dented column. Main fraction between 75.5° and 76°. Colourless liquid. Recovery 69%. Glc showed the presence of only one component. ir(thin film) 1343(w), 1230(s)cm^{-1}

1.2.3 Determination of disulpur dichloride and sulphur dichloride in thionyl chloride.

The method[33] is based on the hydrolysis of a sample of thionyl chloride which produces tri- and tetrathionates according to the following equations:

$$S_2Cl_2 + 2\ SO_2 + 2\ H_2O \longrightarrow H_2S_4O_6 + 2\ HCl$$

$$SCl_2 + 2\ SO_2 + 2\ H_2O \longrightarrow H_2S_3O_6 + 2\ HCl$$

The polythionates can react with bromine quantitatively according to the equations:

$$H_2S_4O_6 + 7\ Br_2 + 10\ H_2O \longrightarrow 4\ H_2SO_4 + 14\ HBr$$

$$H_2S_3O_6 + 4\ Br_2 + 6\ H_2O \longrightarrow 3\ H_2SO_4 + 8\ HBr$$

Bromine was generated in situ by the addition of a bromate solution to an acidic solution of bromide, according to the following equation:

$$^{-}BrO_3 + 5\ ^{-}Br + 6\ H^+ \longrightarrow 3\ Br_2 + 3\ H_2O$$

Because the above equation did not take place quantitatively, an excess of bromate was added and the unchanged bromate was backtitrated by the addition of an excess of potassium iodide which liberated iodine. The iodine was then titrated with a standard solution of sodium thiosulphate. The equations are shown below:

$$^{-}BrO_3 + 2\ I^- + 6\ H^+ \longrightarrow I_2 + 3\ H_2O + Br^-$$

$$I_2 + 2\ S_2O_3^{\ 2-} \longrightarrow S_4O_6^{\ 2-} + 2\ I^-$$

Koch Light puriss thionyl chloride was analyzed for sulphur halides before and after its purification with triphenyl phosphite. The results have been tabulated below. Two titrations were carried out per each sample and the results were averaged out.

	Before purification(%)	After purification(%)
S_2Cl_2	0.237	0.063
SCl_2	0.025	0.022

1.2.4 Purification of 1,1-dibenzoylmethane.

Commercial 1,1-dibenzoylmethane was found to be impure, m.p.68°(lit.78°)[34] and it was therefore decided to purify it before it was utilized in further syntheses. Recrystallization from petroleum spirit(100-120°) did not prove satisfactory and it was therefore distilled under reduced pressure. Yellow liquid, b.p184°/ 2.5mmHg, m.p.77-8°. Recovery 92%.

Preparation of ketones.

1.3.1. 1,3-Diketones

1.3.1.1. 5,5-Dimethylcyclohexane-1,3-dione.(dimedone).

The compound (m.p.147° lit.[35] 148-9°) was prepared by the condensation of diethyl malonate and mesityl oxide according to the method given by Vogel.[35]

nmr($CDCl_3$)	singlet	τ	8.49^{e}	6 protons
	singlet	τ	8.90^{k}	6 protons
	singlet	τ	7.72^{k}	4 protons
	singlet	τ	7.44^{e}	4 protons
	singlet	τ	6.43^{k}	2 protons
	singlet	τ	4.44^{e}	1 proton
	broad singlet	τ	2.30^{e}	1 proton

(e=enol k=keto) Calculated enol percentage in $CDCl_3$ of a 20%v.v solution at 32° = 58%

ir(KBr disc) 2960(broad,s), 2860(broad,s), 2550(broad,s) 1900(m) 1615(broad,s), 1580(s), 1515(s), 1465(s), 1410(m), 1345(s), 1300(s), 1250(s), 1225(s), 1140(s), 960(broad,m).cm^{-1}

1.3.1.2. Diethyl β-oxoglutarate.

The β-ketoester was prepared from citric acid using the method given by Adams et al.[36] in 47% yield. B.p. 100°/0.5mmHg (lit. 131-36°/9-10mmHg). In the esterification step, the hydrogen chloride was generated by introducing concentrated sulphuric acid into a flask containing a paste of sodium chloride and concentrated hydrochloric acid.

nmr(CCl_4)	triplet	τ	$8.77^{e,k}$	12 protons
	singlet	τ	6.75^{e}	2 protons
	singlet	τ	6.39^{k}	4 protons
	quartet	τ	$5.83^{e,k}$	8 protons
	singlet	τ	4.80^{e}	1 proton
	singlet	τ	-2.10^{e}	1 proton

(e=enol , k=keto) Calculated enol concentration in 50%v.v solution in CCl_4 at 32° = 19%.

1.3.1.3. 2-Benzoylcyclohexanone.

The ketone was prepared by the condensation of cyclohexanone and phenyl benzoate in the presence of sodamide.[37] White crystals m.p.87° (lit.88-89°).[37] Yield 46%.

nmr($CDCl_3$)	multiplet	τ	7.50-8.10	8 protons
	triplet	τ	5.56	1 proton
	multiplet	τ	2.10-2.40	5 protons

1.3.1.4. Diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate.

The compound was prepared in 48% yield by the method of Nilsen et al.[38] involving the condensation of diethyl succinate in the presence of strong alkali. Powder m.p.120°(lit. 123,127°)[38]

nmr($CDCl_3$)	triplet	τ	8.50	6 protons
	singlet	τ	6.90	4 protons
	quartet	τ	5.79	4 protons
	singlet	τ	2.10	2 protons

1.3.1.5. 1,1-Dibenzoymethane.

Benzalacetophenone was prepared by the condensation of benzaldehyde and acetophenone in the presence of strong alkali.[39] It was further brominated and then treated with alcoholic sodium methoxide according to the method of Allen et al.[40] Dibenzoylmethane was obtained in 63% yield. m.p.77°(lit.77-78°).[34]

nmr(CCl_4)	singlet	τ	3.30	1 proton
	multiplet	τ	2.15-2.65	10 protons
	singlet	τ	-6.90	1 proton.

The same procedure was adopted for the preparation of aryl-substituted dibenzoylmethanes:

1.3.1.6. 1-Benzoyl-1-p-chlorobenzoylmethane.

m.p.74.5°.

nmr($CDCl_3$)	singlet	τ	3.27	1 proton
	multiplet	τ	2.10-2.55	9 protons
	broad singlet	τ	-6.40	1 proton

1.3.1.7. 1-Benzoyl-1-p-methoxybenzoylmethane.

m.p.129°(lit.132°)[41]

nmr($CDCl_3$)	singlet	τ	6.16	3 protons
	singlet	τ	3.20	1 proton
	multiplet	τ	2.00,2.50	9 protons
	singlet	τ	3.00	1 proton.

1.3.1.8. 1-Benzoyl-1-m-nitrobenzoylmethane.

m.p.130°

nmr($CDCl_3$)	singlet	τ	3.13	1 proton
	multiplet	τ	2.20	9 protons
	singlet	τ	1.20	1 proton.

Preparation of ketones.

1.3.2. α-Substituted 1,3-diketones.

1.3.2.1. Ethyl α-methylacetoacetate.

Methylation was conducted in dimethylformamide solvent according to the method of Zaugg.[42] Sodium hydride was employed in the formation of the sodium salt of ethyl acetoacetate. The solvent was separated from the product by shaking the reaction mixture with water containing a little sodium thiosulphate to remove the free iodine present in solution. A spinning band column was employed in the distillation of the product. Colourless liquid b.p.176-77°(lit.177°).[42] Yield 58%.

nmr(CCl_4)	triplet	τ	8.84	3 protons
	doublet	τ	8.86	3 protons

	singlet	τ	7.85	3 protons
	quartet	τ	6.52	1 proton
	quartet	τ	5.86	2 protons.

ir(thin film) 2985(m), 2940(w), 1740(s), 1715(s), 1450(w), 1358(m), 1330(w), 1240(w), 1200(m), 1152(m), 1100(w), 1070(w), 1050(w), 1020(w)cm^{-1}

1.3.2.2. 3-Methylpentane-2,4-dione.

The compound (α-methylacetylacetone), was prepared from acetylacetone, methyl iodide and potassium carbonate in acetone.[43] b.p.168-72° (lit.170-72°).[43] Yield 85%.

nmr(neat)	doublet	τ	8.75^k	3 protons
	singlet	τ	8.16^e	3 protons
	singlet	τ	7.91^e	3 protons
	singlet	τ	7.85^k	3 protons
	quartet	τ	6.20^k	1 proton
	singlet	τ	-6.30^e	1 proton.

Calculated enol percentage of neat compound at 32° =35%.

ir(thin film) 2990(w), 2940(w), 2880(w), 1720(s), 1700(s), 1600(m), 1420(w), 1360(s), 1275(w), 1160(w), 1080(w), 980(w)cm^{-1}

1.3.2.3. 1,1-Dibenzoylethane.

The compound was prepared by the action of methyl iodide on 1,1-dibenzoylmethane in sodium ethoxide solution. Recrystallized from petroleum spirit(100-120) containing 2% ethanol. White, needle crystals m.p.78°(lit.83°).[44] Yield 75%.

nmr(CCl_4)	doublet	τ	8.50	3 protons
	quartet	τ	4.90	1 proton
	multiplet	τ	2.15,2.60	10 protons.

ir(KBr disk) 3060(m), 2985(m), 2930(m), 1690(s), 1668(s), 1595(m), 1440(m), 1340(m), 1230(m), 1205(m), 970(m)cm.$^{-1}$

1.3.2.4. 1-Benzoyl-1-p-chlorobenzoylethane.

The same proce~~e~~dure as for the methylation of 1,1-dibenzoyl ethane(p.18) was followed. Recrystallized from petroleum spirit (100-120°). m.p.93°(lit.99°).[45]

nmr($CDCl_3$)	doublet	τ	8.48	3 protons
	quartet	τ	4.86	1 proton
	multiplet	τ	2.30,2.82	9 protons.

1.3.2.5. 1-Benzoyl-1-p-methoxybenzoylethane.

A direct synthesis employing methyl iodide and the sodium salt of 1-benzoyl-1-p-methoxybenzoylmethane generated in situ in sodium ethoxide solution, failed. A different approach was therefore followed[41] where silver oxide acted as the base. Yield 68%. m.p.69°(lit.72°).[41]

nmr($CDCl_3$)	doublet	τ	8.50	3 protons
	quartet	τ	4.92	1 proton
	multiplet	τ	2.20,2,90	9 protons

The same method, applied to 1-benzoyl-1-m-nitrobenzoylmethane failed to produce the required ethane.

1.3.2.6. α-Substituted 1,1-dibenzoylmethanes.

A highly α-substituted 1,1-dibenzoylmethane was required in order to facilitate the characterization of the oil obtained from the treatment of 1,1-dibenzoylethane with thionyl chloride. The method adopted, consisted of the preparation of the sodium salt of the 1,3-diketone and subsequent treatment with an alkyl or aryl halide.

To a stirred solution of sodium ethoxide prepared by the addition of absolute ethanol(5ml) to sodium metal(0.01 mole), 1,1-dibenzoylmethane(0.01 mole) was added. The sodium salt precipitated immediately and was broken by means of a glass rod. Cyclohexyl iodide was added and the solution treated under reflux for eighteen hours. Reaction did not proceed at all, as shown by the persistent alkalinity of the mixture.

Triphenyl bromomethane(0.01 mole) was added to the mixture of 1,1-dibenzoylmethane sodium salt and sodium ethoxide(0.01 mole) and the solution immediately turned neutral. The solution was then poured into 50ml of cold water, extracted with ether, the ethereal layer was separated, dried and then evaporated off. The oil left crystallized upon standing for eighteen hours. It was recrystallized from ethanol-1% water mixture. White crystals m.p.81^{o}(lit.84-5^{o})[34] Identified as the ethyl triphenylmethyl ether.

nmr($CDCl_3$)	triplet	τ	8.78	3 protons
	quartet	τ	6.87	2 protons
	multiplet	τ	2.77	15 protons.

Preparation of ketones.

1.3.3. Isopropyl ketones.

1.3.3.1. 2-Methyl-1-phenylpropan-1-one.

The ketone,(isopropyl phenyl ketone), was prepared by the method of Hauser et al.[46] involving the reaction between a Grignard reagent(1 mole) and isobutyronitrile(1 mole).

A solution of bromobenzene(1 mole) in dry ether(80ml) was slowly added to a mixture of magnesium metal(1.2 mole) in dry ether (50ml). When reaction had ceased, isobutyronitrile(1 mole) was added slowly to the reaction mixture, and the resulting solid material was kept overnight at room temperature. It was further hydrolyzed with an excess of 10N sulphuric acid, and the mixture was steam-distilled. The steam distillate was separated from the water, the water layer was extracted with ether, and the combined extracts were dried and distilled under reduced pressure to give the ketone in 72% yield. b.p.116°/ 6.0mmHg (lit. 220-21°).[47]

nmr(CCl_4)	doublet	τ	8.88	6 protons
	septet	τ	6.54	1 proton
	multiplet	τ	2.00,2.50	5 protons.

1.3.3.2. 3-Methyl-1-phenylbutan-2-one.

The ketone,(benzyl isopropyl ketone), was prepared in 58% yield by the same method employed in the preparation of isopropyl phenyl ketone. b.p.116°/ 8mmHg. (lit.83°/ 2mmHg).[48]

nmr(CCl_4)	doublet	τ	9.05	6 protons
	septet	τ	7.45	1 proton
	singlet	τ	6.42	2 protons
	singlet	τ	2.82	5 protons.

1.3.3.3. 2,4-Dimethylpentan-3-one.

The Grignard reagent from isopropyl bromide was treated with isobutyronitrile to give the ketone,(diisopropyl ketone) in 65% yield, using the method employed in the synthesis of isopropyl phenyl ketone. b.p.120-24° (lit. 123-25°).[46]

nmr(CCl_4)	doublet	τ	8.95	12 protons
	septet	τ	7.25	2 protons.

1.3.3.4. 2-Methyl-1-1'-naphthylpropan-1-one.

The Grignard reagent from 1-bromonaphthalene was prepared in a solvent system composed of benzene, ether and tetrahydrofuran in respective ratios 3:2:1.[49] Isobutyronitrile was added and the reaction mixture was treated according to method employed in the synthesis of isopropyl phenyl ketone. Steam-distillation of the reaction mixture only produced a small amount of naphthalene. The reaction mixture was therefore extracted with ether, the ethereal layer was separated and dried and finally the ether was removed. The oil obtained was distilled under reduced pressure to give a fraction of isopropyl 1-naphthyl ketone. b.p.120-24°/ 0.6mmHg (lit. 172-4°/ 8mmHg).[34] Yield 62%.

nmr(CCl_4)	doublet	τ	8.86	6 protons
	septet	τ	6.64	1 proton
	multiplet	τ	1.60,2.40	7 protons.

1.3.3.5. <u>2-Methyl-4-phenylpentan-3-one.</u>

α-Bromoethylbenzene was prepared by hydrobromination of styrene[50]. b.p.96°/ 9mmHg.

nmr(neat)	doublet	τ	8.20	3 protons
	quartet	τ	4.95	1 proton
	multiplet	τ	2.80	5 protons.

The Grignard reagent of the aryl halide was treated with isobutyronitrile under the same conditions employed in the synthesis of isopropyl phenyl ketone. Upon acid hydrolysis of the reaction mixture 2,3-diphenylbutane was isolated. m.p.123°(lit.126°meso form)[34]

nmr($CDCl_3$)	multiplet	τ	9.00	6 protons
	multiplet	τ	7.25	2 protons
	singlet	τ	2.80	10 protons.

ir(KBr disc) 3080(w), 3020(m), 2980(m), 2925(w), 2900(w), 1600(m), 1490(s), 1450(s), 1370(m), 1230(w), 1160(w), 1080(m), 1050(m)cm.$^{-1}$

1.3.3.6. <u>3-Methyl-1,1-diphenylbutan-2-one.</u>

The Grignard reagent from diphenylbromomethane was necessary for the synthesis, but during its preparation in ether, dimerization took place as soon as the halide was added. The reaction mixture was mixed with water and extracted with chloroform. Evaporation of the solvent yielded 1,1,2,2,-tetraphenylethane. Recrystallized from chloroform, m.p.204-06° (lit.211°).[34]

Preparation of ketones.

1.3.4. Miscellaneous ketones.

1.3.4.1. Benzoylmethyl methyl sulphoxide.

The β-ketosulphoxide was prepared from phenyl benzoate and the potassium salt of dimethyl sulphoxide according to Russell's method.[51] m.p.84-85°(lit. 85-86°).[51] Yield 71%.

nmr($CDCl_3$)	singlet	τ	7.39	3 protons
	singlet	τ	5.59	2 protons
	multiplet	τ	2.00,2.40	5 protons.

ir(KBr disc) 3060(w), 2950(w), 2900(w), 1675(s), 1600(m), 1455(m), 1425(w), 1380(w), 1330(m), 1300(w), 1200(m), 1190(w), 1038(m), 1028(m), 1000(w), 975(m), 935(w)cm^{-1}.

1.3.4.2. sym-Tetraphenylacetone.

Ethyl diphenylacetate was prepared by the esterification of diphenylacetic acid(1 mole) with an excess of absolute ethanol in the presence of sulphuric acid(60g.). The mixture was treated under reflux for eighteen hours and was then transferred into a beaker containing 500ml. of water. The aqueous solution was extracted with ether, the ethereal layer was washed twice with sodium bicarbonate solution and the ether was removed to give a white solid, in 58% yield. m.p.54-55°(lit.58°).[34]

sym-Tetraphenylacetone was prepared from ethyl diphenylacetate according to the method given by Dean et al.[52] Recrystallized from ethanol. White needles, m.p. 120° (lit. 133-34°).[34] Yield 11%.

nmr($CDCl_3$)	singlet	τ	4.73	2 protons
	singlet	τ	2.76	20 protons.

ir(KBr disc) 1698(s)(C=O)cm^{-1}.

1.3.4.3. "Ethylidine dimethone anhydride".

The condensation product from the reaction of dimedone and acetaldehyde (m.p.140°, lit.141°),[35] was treated under reflux for five minutes with an ethanolic solution which contained a small amount of hydrochloric acid. The anhydride was isolated in 67% yield, m.p.168° (lit.171°).[35]

nmr($CDCl_3$)	singlet	τ	8.93	12 protons
	singlet	τ	7.76	4 protons
	doublet	τ	7.70	3 protons
	singlet	τ	7.62	4 protons
	quartet	τ	6.43	1 proton.

Preparation of sulphinyl chlorides and related compounds.

1.4.1. β-Keto-isopropylsulphinyl chlorides.

1.4.1.1. 2-Methyl-3-oxobutane-2-sulphinyl chloride.

Thionyl chloride(0.3 moles), was added dropwise to isopropyl methyl ketone(0.1 mole), maintained at 0°, and the resulting red-brown reaction mixture was further stirred for eighteen hours at room temperature. The excess of thionyl chloride was completely removed using a rotary evaporator, and the resulting pungent smelling oil was distilled at reduced pressure(note 1). Distillation at pressures between 10mmHg and 760mmHg, led to decomposition of the product. A yellow fraction boiling at 90°/4mmHg, identified as the sulphinyl chloride was collected in 85% yield.

Found: S = 19.39%, Cl = 20.60%. Calculated for $C_5H_9ClO_2S$ S = 19.00% Cl = 21.05%. Molecular weight by titration with standard sodium hydroxide: found 171, calculated for $C_5H_9ClO_2S$ 168.5 .

nmr(neat) singlet τ 8.42 6 protons
singlet τ 7.71 3 protons.

ir(thin film) 2980(w), 2930(w), 1705(s), 1463(m), 1420(m), 1390(m), 1365(s), 1250(m), 1155(s,S=O), 1110(s), 1015(w), 965(m)cm^{-1}

Note 1. A magnetic stirrer rather than an air-bleed was used during the distillation, as the latter decomposes the oil.

1.4.1.2. 2-Methyl-3-oxo-3-phenylpropane-2-sulphinyl chloride.

Isopropyl phenyl ketone(0.01 mole), was treated with excess of thionyl chloride(0.03 moles), for eighteen hours at room temperature. The excess of thionyl chloride was removed, and the resulting pale-yellow oil was identified as 2-methyl-3-oxo-3-phenylpropane-2-sulphinyl chloride. Distillation of the sulphinyl chloride under reduced pressure resulted in decomposition. Yield of crude product 100%. Found: S = 13.40%, Cl = 16.34%. Calculated for $C_{10}H_{11}O_2ClS$ S = 13.89%, Cl = 15.40%.

nmr(CCl_4) singlet τ 8.18 6 protons
multiplet τ 2.20,2.40 5 protons.

ir(thin film) 3060(m), 2975(m), 2930(m), 2865(m), 1658(s), 1600(m), 1580(w), 1450(m), 1390(w), 1368(w), 1270(s), 1235(m), 1150(s,S=O), 1125(m), 1000(m), 970(s)cm^{-1}

1.4.1.3. 2,4-Dimethyl-3-oxopentane-2-sulphinyl chloride.

2,4-Dimethylpentane-3-one(0.01 mole) was treated with thionyl chloride(0.03 moles) for eighteen hours at room temperature. Strong evolution of hydrogen chloride was observed. The excess of thionyl chloride was removed and the oil was distilled under reduced pressure. A pale-yellow fraction of the sulphinyl chloride was collected at 90-1°/ 1mmHg. Yield 93%. Found: S = 15.86%. Calculated for $C_7H_{13}ClO_2S$ S = 16.28%. Molecular weight by titration with standard sodium hydroxide: found 199, 193.3, calculated for $C_7H_{13}ClO_2S$ 196.5 .

nmr(CCl_4)	doublet	τ	8.90	6 protons
	singlet	τ	8.40	3 protons
	singlet	τ	8.32	3 protons
	septet	τ	6.92	1 proton.

ir(thin film) 2975(m), 2935(m), 2875(w), 1698(s), 1465(s), 1388(m), 1370(m), 1156(s,S=0), 1095(w), 1020(s), 998(w)cm^{-1}.

The monosulphinyl chloride (0.01 mole), was further treated with thionyl chloride(0.03 moles) under reflux for two hours. The excess of thionyl chloride was removed and the nmr and ir spectra of the oil obtained were shown to be identical to that of the starting material-(2,4-dimethyl-3-oxopentane-2-sulphinyl chloride)

A similar experiment carried out in the presence of aluminium trichloride in catalytic quantities also produced no further reaction.

1.4.1.4. 2-Methyl-3-1'-naphthyl-3-oxopropane-2-sulphinyl chloride.

Isopropyl 1-naphthyl ketone(0.01 mole) was treated with excess of thionyl chloride(0.03 moles) at room temperature for eighteen hours. The excess of thionyl chloride was removed and the oil obtained crystallized upon standing for about one hour. It was recrystallized from petroleum spirit(100-120°) containing 5% v.v of benzene to give white crystals of the sulphinyl chloride. m.p.74°, yield 85%. An analysis of the mass spectrum of the sulphinyl chloride showing a molecular ion peak at 280 mass units, is given in table 1.

nmr($CDCl_3$)	singlet	τ	8.35	6 protons
	multiplet	τ	2.20,2.60	7 protons.

ir(thin film) 3055(w), 2980(w), 2935(w), 2870(w), 1680(s), 1590(w), 1506(m), 1455(m), 1384(w), 1365(w), 1276(w), 1245(m), 1210(w), 1152(s,S=O), 1070(m), 1060(m), 1020(w), 940(m)cm^{-1}.

1.4.1.5. 2-methyl-3-oxo-4-phenylbutane-2-sulphinyl chloride.

Benzyl isopropyl ketone(0.01 mole) and thionyl chloride (0.03 moles) were stirred together for eighteen hours at room temperature. The excess of thionyl chloride was removed, and the residual yellow oil was characterized by spectroscopic means,as an attempted distillation produced decomposition products. The oil contained two components that of 2-chloro-4,4-dimethyl-2-phenylthietan-3-one, and that of 2-methyl-3-oxo-4-phenylbutane-2-sulphinyl chloride, in approximately 3:1 ratios.

nmr(CCl_4)	singlet	τ	8.50^{t}	3 protons
	singlet	τ	8.39^{s}	6 protons
	singlet	τ	8.14^{t}	3 protons
	singlet	τ	6.10^{s}	2 protons
	multiplet	τ	$2.3,2.7^{t,s}$	10 protons

t = thietanone, s = sulphinyl chloride.

ir(thin film) 3080(w), 3030(w), 2970(m), 1775(s), 1700(s), 1600(w), 1490(m), 1450(s), 1380(w), 1360(w), 1330(w), 1225(s), 1145(s,S=O), 1120(m), 1080(m), 1055(m), 1035(m), 1000(w), 955(w)cm^{-1}.

The structures of the thietanone and of the β-ketosulphinyl chloride are discussed on page 146

TABLE 1

Mass spectrum: 2-Methyl-3-1-naphthyl-3-oxopropane-2-sulphinyl chloride.

Mass-to-charge ratio	Fragment
280	$C_{10}H_7COC(CH_3)_2SOCl$
198	$C_{10}H_7COCH(CH_3)_2$
156	$C_{10}H_7CHO$
155	$C_{10}H_7CO$
128	$C_{10}H_8$
127	$C_{10}H_7$
76	CS_2
64	SO_2
32	S
28	CO

TABLE 3

Mass spectrum: Ethyl α-methylacetoacetate and thionyl chloride(p.32)

Mass-to-charge ratio	Fragment
226	$CH_3COC(CH_3)(SOCl)CO_2Et$
162	$CH_3C(Cl){=}C(CH_3)CO_2Et$
144	$CH_3COCH(CH_3)CO_2Et$
102	$CH_3CH_2CO_2Et$
83	SOCl
74	$CH_3CO_2CH_3$
43	CH_3CO
36	HCl
29	CH_3CH_2
28	CO or $CH_2{=}CH_2$

1.4.1.6. 2-Methylpentan-3-one treatment with thionyl chloride.

Thionyl chloride(0.03 moles) was slowly added to the ketone (0.01 mole). The rate of addition was such that the reaction mixture was maintained at 20°. It was further stirred overnight at room temperature, and at the end of that period the excess of thionyl chloride was removed at 30°. Upon standing for four days at 5°, the reaction mixture produced white needle crystals which were found to be unstable to atmospheric conditions. Some of the crystals were quickly filtered off and washed with cold ethanol, to give 2-chloro-2,4,4-trimethylthietan-3-one, with an approximate m.p. 45°. Alternatively, the reaction mixture was distilled under reduced pressure to give the thietanone b.p. 80-83°/ 2mmHg. An analysis of the mass spectrum of the thietanone, showing a molecular ion peak at 164mass units is given in table 2.

nmr($CDCl_3$)	singlet	τ	7.97	3 protons
	singlet	τ	8.12	3 protons
	singlet	τ	8.38	3 protons.

ir(thin film) 2980(w), 2930(w), 2860(w), 1783(s), 1453(w), 1438(w), 1370(w), 1182(w), 1136(w), 1078(m), 1054(w), 1010(w)cm^{-1}.

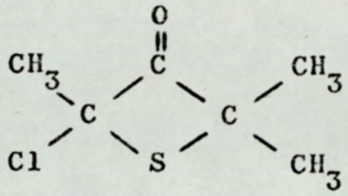
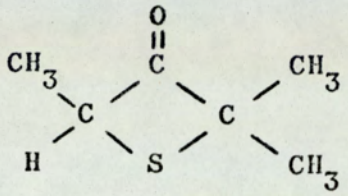
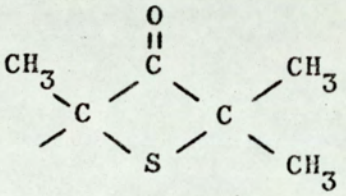
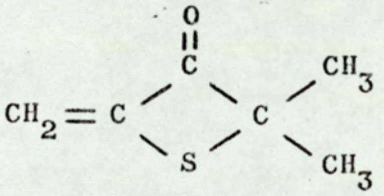
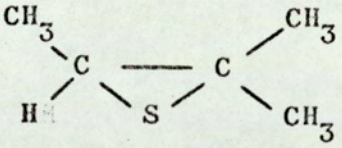
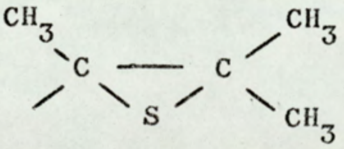
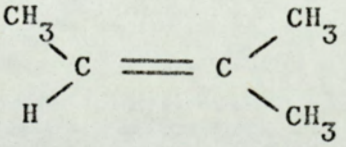
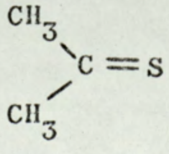
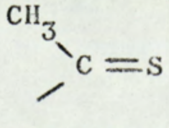
The oil which did not crystallize in the reaction mixture was spectroscopically identified and is thought to belong to 2-methyl-3-oxopentane-2-sulphinyl chloride. It could not be purified by distillation which decomposed it.

nmr(CCl_4)	triplet	τ	8.95	3 protons
	singlet	τ	8.35	6 protons
	quartet	τ	7.35	2 protons.

ir(thin film) 2970(s), 2930(m), 2870(w), 1780(s), 1710(s), 1455(m), 1380(w), 1365(w), 1335(w), 1150(m,S=0), 1120(m), 1080(w), 1055(w), 1000(w)cm^{-1}.

TABLE 2

Mass spectrum: 2-Chloro-2,4,4-trimethylthietan-3-one.

Mass-to-charge ratio	Fragment
164	
130	
129	
128	
102	
101	
70	
74	 or $CH_3CO_2CH_3$
59	 or CH_3CO_2-

1.4.1.7. sym-Tetraphenylacetone treatment with thionyl chloride.

The ketone(0.01 mole) was treated with excess of thionyl chloride(0.03 moles) under reflux for eighteen hours. The excess of thionyl chloride was removed and the oil obtained was recrystallized from ethanol to give needle crystals of starting material. Recovery 86%. Identified by the nmr and ir spectra.

1.4.1.8. 2-Chloro-2,4-dimethylpentan-3-one treatment with thionyl chloride.

The chloride(0.01 mole), prepared by the action of sulphuryl chloride on di-isopropyl ketone, was treated with thionyl chloride (0.03 moles) at room temperature for eighteen hours. Upon removal of the thionyl chloride the oil was shown to consist of unchanged chloride. Thus, its nmr and ir spectra were identical to the starting material.

1.4.1.9. Isopropyl acetate treatment with thionyl chloride.

Thionyl chloride(0.03 moles) was added to the ester(0.01 mole) and the reaction mixture was stirred at room temperature for eighteen hours. Reaction did not proceed under these conditions, shown by the nmr spectrum of the reaction mixture, and it was therefore decided to treat the ester under reflux for eight days. At the end of that period the thionyl chloride was removed by distillation which was further continued to recover the unchanged ester.

Cumene and isobutyronitrile were also treated with thionyl chloride in a similar way. In both cases a quantitative yield of unchanged starting material was recovered.

Preparation of sulphinyl chlorides and related compounds.

1.4.2. β-Keto-sulphinyl chlorides.

1.4.2.1. 1,1-Dibenzoylethane treatment with thionyl chloride.

A mixture of 1,1-dibenzoylethane(0.01 mole) with thionyl chloride(0.1 mole) was refluxed for eighteen hours.(Note 1) The excess of thionyl chloride was removed using a rotary evaporator and the resulting yellow oil was treated with ethanol under the conditions described in page 54. The oil could not be purified by distillation, due to its high boiling point, even at conditions of extremely low pressure. An extensive discussion of its composition is given in page 114.

nmr(CCl_4)	singlet	τ	7.92
	singlet	τ	7.88
	singlet	τ	7.78
	multiplet	τ	2.00,2.70

ir(thin film) 3070(m), 2940(w), 1690(s), 1660(s), 1604(s), 1585(m), 1495(w), 1455(s), 1380(w), 1324(m), 1290(m), 1270(s), 1235(s), 1190(m), 1185(m), 1169(m), 1080(w), 1030(w), 1005(m), 975(m), 960(m), 903(w)cm.$^{-1}$

It was observed that when 1,1-dibenzoylethane was treated under reflux with thionyl chloride for long periods of time, the composition of the products was altered. An experiment was therefore set up where aliquots were taken from the reaction mixture at different time intervals and were investigated by spectroscopic means.

The nmr spectra of the aliquots at 13, 18, 30, 48, and 120 hour intervals, showed that as the refluxing time was prolonged the peak absorbing at τ 7.92 increased its intensity at the expense of the τ 7.88 peak whose intensity decreased. The peak at τ 7.78

remained unaltered.

The ir spectra showed that the peak at 1169cm^{-1} observed at medium to strong intensity after thirteen hours of refluxing time, considerably reduced its intensity as time progressed.

Note 1: Inpure thionyl chloride and/or 1,1-dibenzoylethane, gave rise to tars.

1.4.2.2. 3-Chloro-2,4-dioxopentane-3-sulphinyl chloride.

Bis(diacetylmethyl) disulphide was prepared by the treatment of pentane-2,4-dione(acetylacetone) with disulphur dichloride.(page50) The disulphide was cleaved with chlorine in the presence of acetic anhydride as reported by I.B.Douglass.[53] Stoichiometric quantities of reactants were employed to avoid contamination of the product by inpurities. Carbon tetrachloride was used as a solvent to facilitate mixing of the reactants.

Bis(diacetylmethyl) disulphide(0.1 mole), acetic anhydride (0.2 mole) and carbon tetrachloride(20ml) were mixed together in a round-bottom flask equipped with a dry-ice condenser and immersed in a bath maintained at -20°. Chlorine(0.3 mole) accurately weighed in a tared flask, was passed into the stirred reaction mixture over ninety minutes. The temperature was then allowed to rise to 25° over a further ninety minutes, and finally the reaction mixture was warmed to 40° for fifteen minutes. It was then distilled under reduced pressure. The main fraction of 3-chloro-2,4-dioxopentane--3-sulphinyl chloride was collected at 66-70°/ 0.7mmHg in 43% yield.

Found: S = 13.95%, Cl = 32.13%. Calculated for $C_5H_6Cl_2O_3S$
S = 14.75%, Cl = 32.72%.

nmr(CCl_4) singlet τ 7.55

ir(thin film) 2938(w), 1750(m), 1715(s), 1420(w), 1360(s), 1196(s), 1150(s,S=O), 810(m)cm.$^{-1}$

1.4.2.3. Ethyl α-methylacetoacetate treatment with thionyl chloride.

The β-keto-ester(0.01 mole) was treated with thionyl chloride (0.03 mole) for eighteen hours at room temperature. At the end of that period, the excess of thionyl chloride was removed and the residual pale-yellow oil was shown by gas-liquid-chromatography to be composed of two components. A sample of the crude reaction mixture was mixed with an authentic sample of ethyl α-chloro-α-methylacetoacetate and gave three peaks in the g.l.chromatograph. The same results were given by the nmr spectrum.

The crude reaction mixture was distilled under reduced pressure but poor separation was achieved, possibly due to the necessary low pressure employed to prevent decomposition. b.p.122-24°/ 2.5mmHg. Addition of aqueous silver nitrate precipitated silver chloride immediately.

nmr(CCl_4)	triplet	τ	8.68
	triplet	τ	8.65
	singlet	τ	8.16
	singlet	τ	8.13
	singlet	τ	7.71
	singlet	τ	7.69
	quartet	τ	5.70

ir(thin film) 2990(w), 2943(w), 1750(s), 1710(s), 1630(m), 1445(w), 1378(w), 1360(w), 1248(s), 1199(m), 1168(s,S=0), 1120(m), 1014(w)cm^{-1}.

The mass spectrum of the distillation fraction collected at 122-24°/ 2.5mmHg, contained a peak at 226 mass units which corresponded to the ethyl α-chlorosulphinyl-α-methylacetoacetate, and another at 162 mass units which corresponded to ethyl 3-chloro--2-methylcrotonate. An analysis of the spectrum is given in table 3.

The mixed product collected from the distillation, was eluted through a 30X3 cm silica-gel column with dry A.R. chloroform. - Decomposition of the two products in the column took place, possibly due to small residual amounts of water present in the chloroform, and ethyl α-methylacetoacetate was collected. The ir and nmr spectra of the product eluted through the column were identical to those of an authentic sample of ethyl α-methylacetoacetate.

An attempted isolation of the sulphinamide by the addition of aniline to an ethereal solution of the sulphinyl chloride, only afforded decomposition products. Anilinium hydrochloride precipitated immediately.

1.4.2.4. Aluminium triacetylacetonate treatment with thionyl chloride.

A large excess of thionyl chloride(0.1 mole) was added to the aluminium complex(0.01 mole). The reaction proceeded with vigorous evolution of gas and the crystals which precipitated within five minutes were filtered off and were washed with petroleum spirit(100-120). They were unstable to atmospheric conditions and water in particular.They were spectroscopically identified as aluminium tri-α-chlorosulphinylacetylacetonate.

nmr($CDCl_3$) singlet τ 7.43

ir(KBr disc) 3150(m,broad), 1580(s), 1530(m), 1375(s), 1350(m), 1294(w), 1270(w), 1149(s,S=0), 1025(w), 986(w), 930(w)cm^{-1}.

Spectroscopic data of aluminium triacetylacetonate complex:

nmr($CDCl_3$) singlet τ 8.03 18 protons

singlet τ 4.53 3 protons

ir(KBr disc) 3450(w,broad), 3000(w), 2980(w), 2930(w), 1590(s), 1530(s), 1340(s,broad), 1360(m), 1290(m), 1190(w), 1030(m), 933(m)cm^{-1}.

Preparation of sulphinyl chlorides and related compounds.

1.4.3. Adamantyl-1-sulphinyl chloride.

Adamantane(0.1 mole) was treated with excess of thionyl chloride(1.0 mole) and aluminium trichloride(0.1 mole), according to H.Stetter's method.[54] The reaction mixture was stirred for three hours at -15° and the excess of thionyl chloride was removed. The oil obtained was dissolved in carbon tetrachloride and treated with water. The organic phase was separated and dried, and the solvent was removed to produce an oil which was distilled under reduced pressure to yield the sulphinyl chloride, b.p.110°/ 1.5mmHg, m.p.45° (lit. $42\text{-}44^{\circ}$).[54] Yield 73%.

nmr($CDCl_3$) multiplet τ 8.1

ir(thin film) 2920(s), 2860(s), 1460(m), 1350(m), 1305(m), 1265(w), 1150(s,S=0), 1110(m), 1045(m), 980(w)cm.$^{-1}$

Preparation of sulphinyl chlorides and related compounds.

1.4.4. Sulphinamides.

1.4.4.1. Adamantyl-1-sulphinamide.

Aniline(0.05 mole) was slowly added to adamantyl-1-sulphinyl chloride(0.01 mole) in dry ether(50ml). The reaction mixture was stirred for thirty minutes at room temperature and the crystals which had precipitated were filtered off. They consisted of a mixture of anilinium hydrochloride and the sulphinamide. The crystals were recrystallized from 50% v.v of aqueous ethanol to give white plates of adamantyl-1-sulphinanilide. m.p.155°,(decomposition). Yield 83%.

Found: S = 11.48%. Calculated for $C_{16}H_{21}NOS$ S = 11.64%

nmr($CDCl_3$)	multiplet	τ	8.10	15 protons
	singlet	τ	3.55	1 proton
	multiplet	τ	2.90	5 protons.

ir(KBr disc) 3185(m), 3080(w), 3045(w), 2910(m), 2855(m), 1605(m), 1500(m), 1485(w), 1455(w), 1350(w), 1290(w), 1235(w), 1180(w), 1067(s,S=O), 1038(m), 1000(w)cm.$^{-1}$

1.4.4.2. 1-Chlorosulphinyl-1,1-dibenzoylethane treatment with aniline.

The oil(2g) obtained from the treatment under reflux of 1,1-dibenzoylethane with thionyl chloride, was dissolved in dry ether (50ml). Excess of aniline(6g) was added slowly while the reaction mixture was stirred and cooled in ice. The anilinium hydrochloride was filtered off, the solvent was removed from the filtrate and the oil thus obtained was dissolved in 50ml of 1.5% aqueous ethanol. Upon standing for twentyfour hours, yellow crystals of 1,1-dibenzoyl ethane-1-sulphenanilide precipitated in 21% yield. Recrystallized from boiling ethanol, m.p.160°. Found: S = 9.00% . Calculated for $C_{22}H_{19}NO_2S$ S = 8.86%.

nmr($CDCl_3$)	singlet	τ	8.12	3 protons
	singlet	τ	5.28	1 proton
	multiplet	τ	2.15,2.80	15 protons.

ir(KBr disc) 3340(s), 3050(w), 2975(w), 2935(w), 1678(m), 1650(s), 1600(s), 1575(m), 1498(m), 1450(m), 1405(w), 1374(w), 1290(w), 1260(s), 1233(s), 1180(w), 1075(w), 1026(w), 963(s), 930(w), 900(m)cm.$^{-1}$

The aqueous ethanolic solution which produced the sulphenanilide crystals, gave a second crop of crystals upon standing at room temperature for another fourty eight hours. m.p. 130°. They were identified by tlc,nmr and ir as a two component mixture containing 1,1-dibenzoylethane-1-sulphenanilide isolated before, as well as 1,1-dibenzoylethane-1-sulphonanilide.

nmr($CDCl_3$)	singlet	τ	8.74[a]
	singlet	τ	8.13[b]
	singlet	τ	5.48[a]

singlet τ 5.30^{b}

multiplet τ $2.80^{a,b}$

(a) denotes sulphonanilide, (b) denotes sulphenanilide.

ir(KBr disc) $3415(s)^{a}$, $3340(m)^{b}$, 3050(w), 2910(w), 1668(s), 1650(m), 1618(m), 1600(s), 1500(s), 1450(m), 1405(w), 1355(w), $1320(m)^{a}$, 1290(w), 1260(s), 1240(s), 1175(w), $1155(m)^{a}$, 1075(w), 1025(w), 962(m), 888(m)cm^{-1}.

1.4.4.3. β-Keto-isopropylsulphinyl chlorides treatment with aniline.

A solution of 2-methyl-3-oxobutane-2-sulphinyl chloride(0.01 mole) in dry ether(30ml), was slowly added to a cooled solution of aniline (0.02 mole) in dry ether(50ml). The anilinium hydrochloride which precipitated immediately was filtered off and the reaction mixture was further stirred for thirty minutes at room temperature. The ether was removed using a rotary evaporator, the bath maintained at 30°. The resulting oil was cooled in ice for two hours and the precipitated crystals (approx. m.p.63°) were quickly filtered off under nitrogen, as they were found to be unstable to atmospheric conditions. The ir spectrum exhibited a peak at 1065(s)cm^{-1}.

Piperidine, o-toluidine and N-methylaniline behaved in a similar way and in each case the expected sulphinamide was found to be unstable.

The reaction was also attempted with other β-ketosulphinyl chlorides, namely, 2-methyl-3-naphthyl-3-oxopropane-2-sulphinyl chloride, and 2-methyl-3-oxo-3-phenylpropane-2-sulphinyl chloride, but unstable compounds which quickly changed their physical characteristics at atmospheric conditions, were always obtained.

2-Methyl-3-oxobutane-2-sulphinyl chloride(0.01 mole) was stirred with water(0.01 mole) for thirty minutes. The nmr and ir spectra of the reaction mixture indicated that complete decomposition had taken place and that isopropyl methyl ketone had been formed.

1.4.4.4. 3-Chloro-2,4-dioxopentane-3-sulphinyl chloride treatment with aniline.

Aniline(0.05 mole) was slowly added to a cooled solution of the sulphinyl chloride(0.01 mole) in dry benzene(50ml). The heavy precipipitate of anilinium hydrochloride which immediately appeared was filtered off and the reaction mixture was kept for eighteen hours at room temperature. The solvent was then removed and the red oil was dissolved in 8%v.v of aqueous ethanol(30ml). Crystals of 3,3-dianilinopentane-2,4-dione precipitated within twenty four hours. m.p.115° The mass spectrum gave a molecular ion peak at 282 mass units. (Table 4)

nmr($CDCl_3$)	singlet	τ	7.95	6 protons
	singlet	τ	4.03	2 protons
	multiplet	τ	2.90,3.3	10 protons

ir(KBr disc) 3370(a), 3060(w), 3020(w), 2920(w), 1716(s), 1610(s), 1590(w), 1505(s), 1430(m), 1360(w), 1315(w), 1263(m), 1210(m), 1190(w), 1155(m), 1038(w), 1000(w)cm.$^{-1}$

Preparation of α-chlorides.

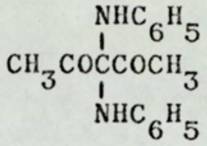
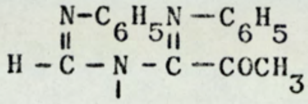
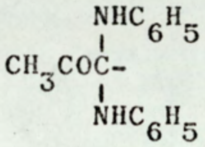
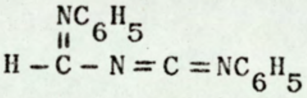
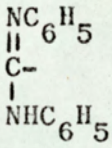
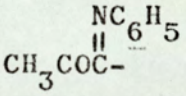
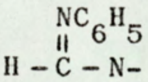
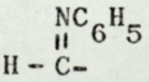
1.5.1. 1,3-Diketones-α-chlorides.

1.5.1.1. Ethyl α-chloroacetoacetate.

Sulphuryl chloride(0.01 mole) was added dropwise over thirty minutes to ethyl acetoacetate(0.01 mole) maintained at 20° The reaction mixture was further stirred at room temperature for eighteen hours and was then distilled. A fraction collected at 192° (lit. 193°)[34] and was identified as the ethyl α-chloroacetoacetate. Yield 83%.

TABLE 4

Mass spectrum: 3,3-Dianilinopentane-2,4-dione.

Mass-to-charge ratio	Fragment
282	 $\mathrm{CH_3CO\underset{NHC_6H_5}{\overset{NHC_6H_5}{C}}COCH_3}$
264	 $\mathrm{H-\overset{N-C_6H_5}{\overset{\Vert}{C}}-\underset{\vert}{N}-\overset{N-C_6H_5}{\overset{\Vert}{C}}-COCH_3}$
239	 $\mathrm{CH_3CO\underset{NHC_6H_5}{\overset{NHC_6H_5}{C}}-}$
221	 $\mathrm{H-\overset{NC_6H_5}{\overset{\Vert}{C}}-N=C=NC_6H_5}$
195	 $\mathrm{\underset{NHC_6H_5}{\overset{NC_6H_5}{C}}-}$
146	 $\mathrm{CH_3CO\overset{NC_6H_5}{\overset{\Vert}{C}}-}$
118	 $\mathrm{H-\overset{NC_6H_5}{\overset{\Vert}{C}}-N-}$
104	 $\mathrm{H-\overset{NC_6H_5}{\overset{\Vert}{C}}-}$
94	$C_6H_5NH_3^+$
93	$C_6H_5NH_2$
77	C_6H_5-
43	CH_3CO-
15	CH_3-

nmr(CCl_4)	triplet	τ	8.70	3 protons
	singlet	τ	7.65	3 protons
	quartet	τ	5.73	2 protons
	singlet	τ	5.19	1 proton.

ir(thin film) 2985(m), 2940(w), 2910(w), 2880(w), 1730(s), 1640(w), 1620(m), 1470(w), 1446(m), 1400(m), 1365(s), 1300(s), 1255(s), 1178(s), 1150(m), 1100(w), 1033(m)cm.$^{-1}$

1.5.1.2. 3-Chloropentane-2,4-dione.

The same synthesis as for ethyl α-chloroacetoacetate was employed. Equimolar quantities of sulphuryl chloride and acetylacetone were employed. b.p.149° (lit. 41-44.5°/ 14mmHg).[55] Yield 89%.

nmr(CCl_4)	singlet	τ	7.76	6 protons
	singlet	τ	-5.55	1 proton

ir(thin film) 2980(w), 2930(w), 1720(w), 1600(s), 1400(m), 1370(m), 1265(m), 1033(m)cm.$^{-1}$

1.5.1.3. Ethyl α-chloro-α-methylacetoacetate.

An ice-cooled solution of ethyl α-methylacetoacetate(0.01 mole) was cautiously treated with sulphuryl chloride(0.01 mole) for thirty minutes, and was further stirred for eighteen hours at room temperature. Distillation afforded the chloride in 92% yield. b.p.72-73°/ 10mmHg. (lit. 42-4°/ 0.1mmHg).[56]

nmr(CCl_4)	triplet	τ	8.72	3 protons
	singlet	τ	8.25	3 protons
	singlet	τ	7.70	3 protons
	quartet	τ	5.75	2 protons.

ir(thin film) 2990(w), 2943(w), 1730(s), 1445(w), 1378(w), 1359(w), 1254(m), 1200(w), 1123(m), 1100(w), 1083(w), 1075(w), 1015(w)cm.$^{-1}$

1.5.1.4. 2-Chloro-5,5-dimethylcyclohexane-1,3-dione.

The α-chloride was prepared by the method of L.P.Hager[57] by the action of sodium hypochlorite on dimedone. Yield 38%. White crystals from ethanol, m.p.159° (lit.164°).[57]

nmr($CDCl_3$)	singlet	τ	8.90	6 protons
	singlet	τ	7.55	4 protons
	singlet	τ	4.63	1 proton.

ir(thin film) 3480(s,broad), 2971(w), 2580(w,broad), 1595(s), 1400(m), 1366(s), 1312(m), 1255(w), 1150(w), 1026(w), 1010(w)cm^{-1}.

1.5.1.5. Dimedone treatment with sulphuryl chloride.

Sulphuryl chloride(0.05 mole) was slowly added to a mixture of dimedone(0.01 mole) in chloroform(20ml). The reaction mixture was stirred for a further thirty minutes, and the solvent was then removed. The solid obtained was recrystallized from ethanol to give white crystals, m.p.108-10° (lit.113°)[57] of 2,2-dichloro-5,5-dimethyl cyclohexane-1,3-dione in 73% yield.

nmr($CDCl_3$)	singlet	τ	8.95	6 protons
	singlet	τ	7.05	4 protons

ir(KBr disc) 2980(m), 2960(m), 2935(m), 2880(w), 1756(s), 1735(s), 1470(w), 1428(w), 1400(w), 1380(w), 1324(w), 1246(w), 1218(m), 1200(m), 1070(w), 1010(w), 932(m)cm^{-1}.

The preparation was repeated using equimolar quantities of dimedone and sulphuryl chloride. The product obtained showed the characteristic nmr absorptions of the 2-chloro-5,5-dimethylcyclohexane -1,3-dione and 2,2-dichloro-5,5-dimethylcyclohexane-1,3-dione, which were formed in approximate ratios of 3:1 respectively. Some unchanged dimedone was also present. The observed absorptions were distinguished through comparison with the spectra of authentic samples.

The monochlorodimedone was isolated in its pure form by fractional recrystallization from ethanol and it exhibited identical spectroscopic properties to an authentic sample prepared by the action of sodium hypochlorite on dimedone, m.p.161-62°(lit.164°).[57] (See p.39).

1.5.1.6. 1,1-Dibenzoylethane treatment with thionyl chloride under mild conditions.

1,1-Dibenzoylethane(0.01 mole) was stirred with an excess of thionyl chloride(0.1 mole) for nine days at room temperature. The excess of thionyl chloride was removed and the nmr spectrum of the oil which was obtained suggested that it consisted of two components.

nmr(CCl_4) singlet τ 7.92
singlet τ 7.78
multiplet τ 2.30,2.80

The oil was also applied to tlc plates which were eluted with benzene to reveal two components which did not further separate when eluted with carbon tetrachloride. Upon standing for thirty hours the oil crystallized. The yellow crystals of 2-benzoyl-1-chloro-1-phenylpropene, m.p.43-44°, could not be recrystallized due to their high solubility even in non-polar solvents like n-hexane. Yield 73% (of crude product). Found: Cl = 11.72%. Calculated for $C_{16}H_{13}ClO$ Cl = 13.05%.

nmr(CCl_4) singlet τ 7.77 3 protons
multiplet τ 2.30,2.80 10 protons.

ir(thin film) 3080(w), 3060(w), 3025(w), 2915(w), 2850(w), 1665(s), 1628(m), 1600(m), 1585(m), 1495(w), 1450(m), 1370(w), 1317(m), 1275(s), 1228(m), 1180(w), 1158(w), 1075(w), 1020(m), 960(w)cm^{-1}.

A sample corresponding to 1-chloro-1,1-dibenzoylethane was prepared by the action of sulphuryl chloride on 1,1-dibenzoylethane.

The ir spectrum of 1-chloro-1,1-dibenzoylethane did not correspond to the ir spectrum of 2-benzoyl-1-chloro-1-phenylpropene and a mixed crystal nmr spectrum showed two absorptions corresponding to the two methyl groups in their dissimilar magnetic environments.

When 1,1-dibenzoylethane was treated with an excess of thionyl chloride and a small amount of pyridine at room temperature for nine days the yield of 2-benzoyl-1-chloro-1-phenylpropene increased to approximately 85-90%.

1.5.1.7. 1-Chloro-1,1-dibenzoylethane.

1,1-Dibenzoylethane(0.01 mole) was treated with sulphuryl chloride(0.01 mole) at room temperature for four hours. Crystallization of the pale green oil obtained, was induced by cooling in ice. The solid obtained was recrystallized from n-hexane to give 1-chloro-1,1-dibenzoylethane in 77% yield. m.p.39°. Found: Cl = 13.48%.
Calculated for $C_{16}H_{13}ClO_2$ Cl = 13.00%.

nmr(CCl_4)	singlet	τ	7.91	3 protons
	multiplet	τ	2.2,2.7	10 protons.

ir(thin film) 3060(m), 3000(w), 2940(w), 1700(s), 1678(s), 1596(s), 1580(m), 1348(s), 1376(m), 1320(w), 1306(w), 1245(s), 1185(m), 1135(w), 1120(w), 1060(m), 1000(m), 980(m), 950(s)cm^{-1}

Preparation of α-chlorides.

1.5.2. Other α-chlorides.

1.5.2.1. 2-Chloro-2-methyl-1-phenylpropan-1-one.

Isopropyl phenyl ketone(0.01 mole) was treated with an excess of sulphuryl chloride(0.03 mole) for eighteen hours at room temperature.

The excess of sulphuryl chloride was removed and the oil obtained was distilled under reduced pressure to give 2-chloro-2-methyl-1-phenylpropan-1-one obtained as a colourless liquid, b.p.69-70°/ /0.4mmHg, (lit.108-08.5°/ 17mmHg).[58] Yield 87%.

nmr(CCl_4) singlet τ 8.20 6 protons
multiplet τ 1.85,2.55 5 protons

ir(thin film) 3060(w), 3000(w), 2940(w), 1680(s), 1598(m), 1580(w), 1450(m), 1388(m), 1372(m), 1270(s), 1170(m), 1116(m), 980(m)cm^{-1}.

1.5.2.2. 2-Chloro-2,4-dimethylpentan-3-one.

The same procedure as for the preparation of 2-chloro-2-methyl-1-phenylpropan-1-one was followed. Thus di-isopropyl ketone(0.01 mole) was treated with an excess of sulphuryl chloride (0.03 mole). Pale-yellow liquid, b.p.145-46°(lit.143-45°).[59] Yield 91%.

nmr(CCl_4) doublet τ 8.88 6 protons
singlet τ 8.33 6 protons
septet τ 6.57 1 proton.

ir(thin film) 2980(m), 2940(m), 2880(w), 1723(s), 1470(m), 1388(m), 1375(m), 1130(m), 1098(w), 1048(m), 1000(w), 910(w)cm^{-1}.

1.5.2.3. 1,3-Dichloro-3-methylbutan-2-one.

2-Methylbutan-3-one(0.01 mole) was treated with sulphuryl chloride(0.03 mole) as described in the previous syntheses. 1,3-Dichloro-3-methylbutan-2-one was obtained in 76% yield. b.p.174-76° (lit.164-65°).[60]

nmr(neat) singlet τ 8.27 6 protons
singlet τ 5.36 2 protons.

ir(thin film) 2990(m), 2945(m), 1738(s), 1455(m), 1388(m), 1362(m), 1300(w), 1120(m), 1058(s), 1000(w), 888(w)cm^{-1}.

1.5.2.4. 1,3-Dichloro-3-methyl-1-phenylbutan-2-one.

Benzyl isopropyl ketone(0.01 mole) was treated with an excess of sulphuryl chloride(0.03 mole) according to the procedure previously described for the preparation of 2-chloro-2-methyl-1-phenylpropan-1-one, to give 1,3-dichloro-3-methyl-1-phenylbutan-2-one obtained as a pale-yellow liquid, b.p.114-16^{o}/ 1.4mmHg,yield 53%.

nmr(CCl_4)	singlet	τ	8.51	3 protons
	singlet	τ	8.25	3 protons
	singlet	τ	3.83	1 proton
	multiplet	τ	2.67	5 protons.

ir(thin film) 3065(w), 3035(w), 2980(m), 2940(m), 2880(w), 1735(s), 1600(w), 1495(m), 1450(s), 1385(m), 1375(m), 1183(m), 1118(m), 1100(m), 1050(m), 1000(m)cm.$^{-1}$

1.5.2.5. sym-Tetraphenylacetone treatment with sulphuryl chloride.

The ketone(0.01 mole) was treated with an excess of sulphuryl chloride(0.1 mole) under reflux for two hours and was further stirred for two days at room temperature. The excess of sulphuryl chloride was removed and the semi-crystalline material thus obtained was recrystallized from ethanol. The unchanged ketone,m.p.120^{o}, which was obtained was identified spectroscopically by nmr and ir.

Preparation of sulphides,polysulphides and related compounds.

1.6.1. Treatment of 1,3-diketones with thionyl chloride.

1.6.1.1. 5,5-Dimethylcyclohexane-1,3-dione.

A mixture of 5,5-dimethylcyclohexane-1,3-dione(dimedone)(4g) and thionyl chloride(25ml) was stirred for three and a half hours at room temperature, during which period hydrogen chloride and sulpur dioxide was evolved. The precipitate which suddenly appeared at the end of that period, was filtered off, washed with petroleum spirit (80-100°) and was recrystallized from ethanol to give crystals of 2-chloro-5,5-dimethylcyclohexane-1,3-dione, m.p.159°(lit.164°),[57] in 63% yield. The mass spectrum showed a molecular ion peak at 174 mass units(table 5).

nmr($CDCl_3$)	singlet	τ	8.90	6 protons
	singlet	τ	7.55	4 protons
	broad singlet	τ	4.63	1 proton

ir(KBr disc) 3480(s,broad), 2970(w), 2580(w,broad), 1595(s), 1400(m), 1366(s), 1315(m), 1255(w), 1150(w), 1026(w), 1010(w)cm^{-1}

When the above reaction mixture was stirred for only ninety minutes and the excess of thionyl chloride then removed on a rotary evaporator, a red oil was obtained which was recrystallized from neat ethanol (30ml of ethanol per gram of dimedone) to give white, fine needle crystals of di-2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl sulphide (dimedone sulphide). m.p.228-29°, (lit.230-31°),[61] yield 32%.
Found: S = 10.42%. Calculated for $C_{16}H_{22}O_4S$, S = 10.32%.

nmr($CDCl_3$)	singlet	τ	8.95	12 protons
	singlet	τ	7.59	8 protons
	singlet	τ	-0.40	2 protons.

ir(KBr disc) 2960(m,broad), 1615(s), 1570(s), 1400(w), 1390(w), 1370(w), 1340(w), 1308(m), 1290(m), 1250(m), 1140(w), 1000(w), 940(w), 780(m,broad)cm^{-1}

The mass spectrum of the sulphide shows a molecular ion peak at 310 mass units and is given in table 5a.

1.6.1.2. Dimedone sulphide treatment with thionyl chloride.

The sulphide(0.01 mole) was treated with a large excess of

TABLE 5

Mass spectrum: 2-Chloro-5,5-dimethylcyclohexane-1,3-dione.

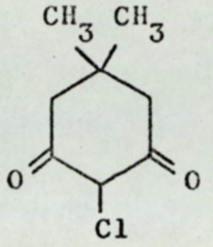
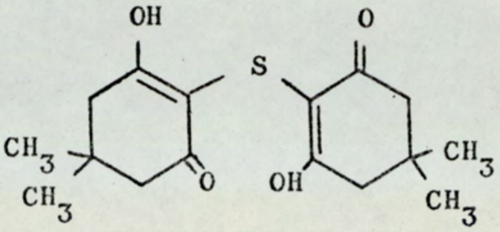
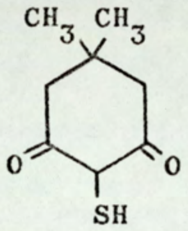
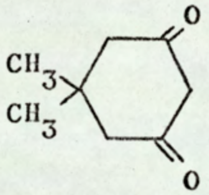
Mass-to-charge ratio	Fragment
174	 = M
159	M-(CH_3)
146	M-(CO)
118	M-(CO+CO)
83	Dimedone-(CH_3CO+CH_2)
56	COCO
43	CH_3CO-
28	CO
29	CH_3CH_2-

TABLE 5a

Mass spectrum: Di-2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl sulphide.

Mass-to-charge ratio	Fragment
310	 = M
295	M-CH_3
172	
140	 = M^*
125	M^*-CH_3
112	M^*-CO
97	M^*-CH_3CO
83	M^*-(CH_3CO+CH_2)
70	M^*-(CH_3+CO+CH_2+CH_2)
56	COCO
43	CH_3CO
29	CH_3CH_2-
28	CO
15	CH_3

thionyl chloride(0.05 mole) at room temperature for five hours. The excess of thionyl chloride was removed from the red solution, and the resulting oil was recrystallized from ethanol. Impure crystals of approx. m.p. 110-20° precipitated upon addition of 5% water. Identification was not conclusive, but the nmr spectrum showed that the mixture contained 50% of unchanged sulphide. New nmr absorptions

singlet	τ	8.87
singlet	τ	7.86

1.6.1.3. Optimization of dimedone sulphide yield.

Having established that the sulphide reacts further with thionyl chloride, it was decided to investigate the conditions which would favour maximum production of the sulphide in the reaction between dimedone and thionyl chloride.

Dimedone(6.752g) was mixed with an excess of thionyl chloride (30ml) and the reaction mixture was stirred at room temperature. Aliquots of 5ml were taken at thirty minute intervals, the excess of thionyl chloride was removed from each one and the resulting oil was recrystallized from ethanol(28ml). Crystallization of the sulphide was effected within fifteen minutes but thecrystals were filtered off eighteen hours later to ensure maximum precipitation. The follwing results were obtained: (Graph 7)

Aliquot taken at(min.)	Yield(g)	M.p. °C
30	0.345	212
60	0.373	212
90	0.350	215
120	0.352	215
150	0.329	215
180	0.288	215

The experiment was repeated and the following results were obtained:

Aliquot taken at(min)	Yield(g)	M.p. °C
30	0.351	213
60	0.383	214
90	0.355	214
120	0.348	213
150	0.340	215
180	0.315	215

The molar equivalents in the reaction between dimedone and thionyl chloride were also varied, in an effort to study their effect on the yield of the sulphide. In each case the reactants were mixed together in the molar ratios stated, and each reaction mixture was stirred at room temperature for four days. Isolation of the sulphide proceeded as before. The results are shown below:

Dimedone(g)	$SOCl_2$(ml)	Molar ratios of Dimedone/$SOCl_2$	M.p. °C	Yield(g) 1st exp.	Yield(g) 2nd exp.
2.00	0.52	2:1	210	0.340	0.359
2.00	1.04	2:2	210	0.539	0.563
2.00	1.55	2:3	-	-	-

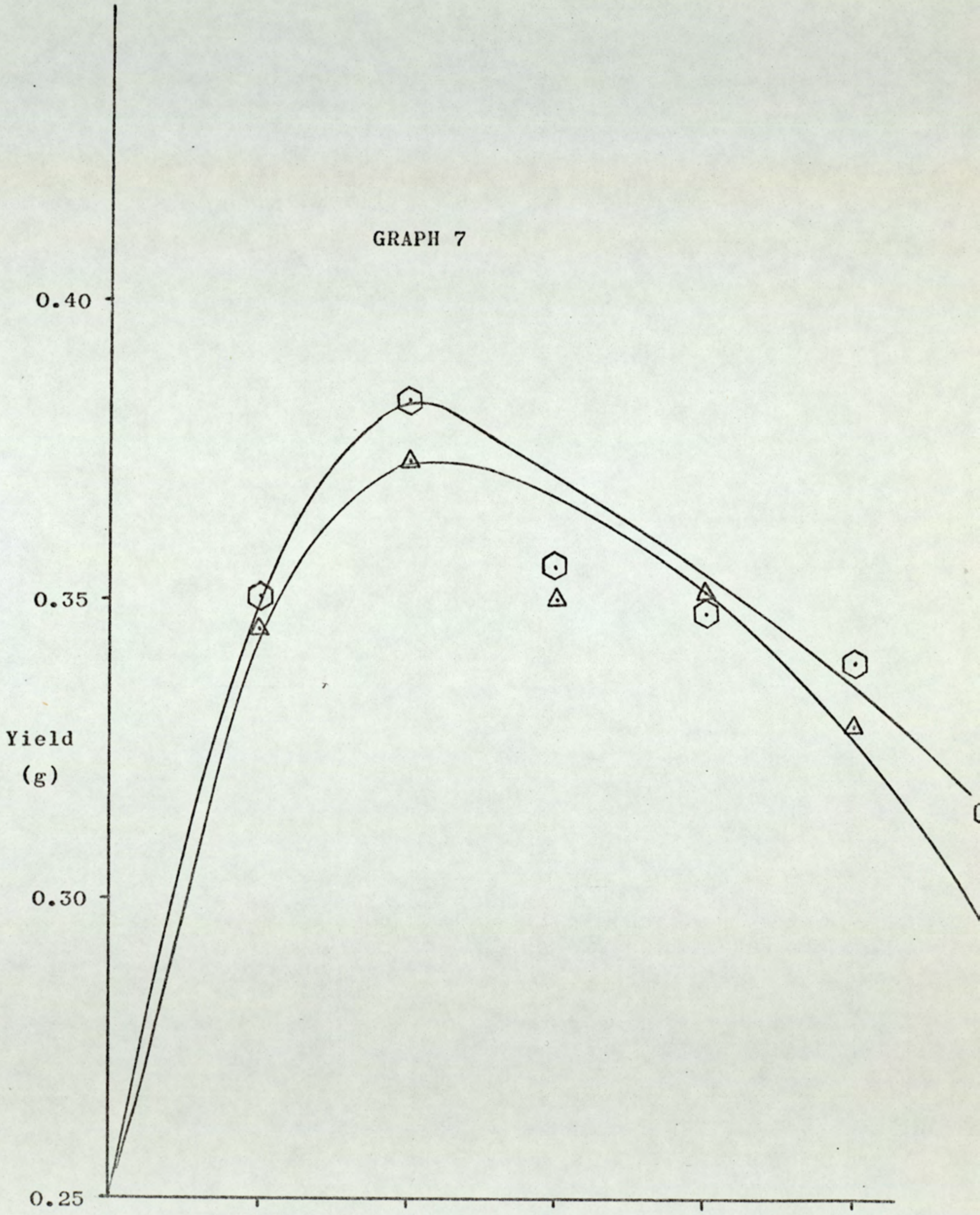
1.6.1.4. Pentane-2,4-dione.

Thionyl chloride (0.1 mole) was slowly added to acetylacetone (0.1 mole) over thirty minutes, and the resulting red-black mixture was kept for eighteen hours at room temperature. The excess of thionyl chloride was removed by distillation which was further continued to give a fraction identified as 3-chloropentane-2,4-dione. B.p.150°(lit.41-44.5°/14mmHg).[55] Yield 23%.

nmr(CCl_4)	singlet	τ	7.75	6 protons
	singlet	τ	-5.55	1 proton.

ir(thin film) 2980(w), 2930(w), 1720(w), 1600(s), 1400(m), 1370(m), 1265(m), 1033(m)cm^{-1}

GRAPH 7



0.40
0.35
0.30
0.25
Yield
(g)
0
30
60
90
120
150
Time(minutes)
△ First experiment
⬡ Second experiment

The tarry material remaining in the distillation, was recrystallized from petroleum spirit(80-100°) to give a crude solid which was further recrystallized from hot ethanol to afford pure bis(diacetylmethyl) disulphide. White, needle crystals, m.p.88°, yield 2%. Found: S = 25.16%. Calculated for $C_{10}H_{14}O_4S$, S = 24.40%.

nmr($CDCl_3$) singlet τ 7.63 12 protons
singlet τ -7.20 2 protons.

ir(KBr disc) 2920(w), 1550(s,broad), 1400(s,broad), 1250(m),
1010(s), 905(m)cm^{-1}.

The mass spectrum shows a molecular ion peak at 262 mass units, and is given in table 6.

1.6.1.5. 3-Methylpentane-2,4-dione treatment with thionyl chloride.

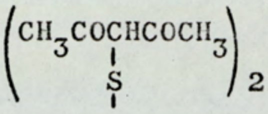
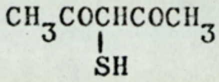
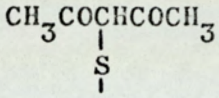
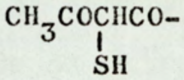
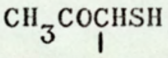
The ketone(0.01 mole) was treated with an excess of thionyl chloride(0.03 mole) at room temperature. A strong evolution of hydrogen chloride and a progressive change of the colour of the reaction mixture from colourless to black, indicated that the reaction had proceeded rapidly. Upon removal of the excess of thionyl chloride, a tarry material was produced which did not crystallize in any of the solvents in which it was dissolved. The reaction was repeated at 0° but non-identified tars were again obtained.

1.6.1.6. Ethyl acetoacetate.

The β-keto-ester(0.03 mole) and thionyl chloride(0.02 mole) were stirred at room temperature for eighteen hours. Hydrogen chloride and sulphur dioxide were given off after thirty minutes, and the reaction mixture progressively changed colour to yellow and green. Crystallization was induced by transferring the reaction mixture into a beaker. The crystals were filtered off and washed twice with petroleum spirit(100-120°) and once with ice-cold ethanol.

TABLE 6

Mass spectrum: Bis (diacetylmethyl) disulphide.

Mass-to-charge ratio	Fragment
262	 $\left(CH_3CO\underset{\substack{\vert\\ S\\ \vert}}{C}HCOCH_3\right)_2$
132	 $CH_3CO\underset{\substack{\vert\\ SH}}{C}HCOCH_3$
131	 $CH_3CO\underset{\substack{\vert\\ S\\ \vert}}{C}HCOCH_3$
117	 $CH_3CO\underset{\substack{\vert\\ SH}}{C}HCO-$
100	$CH_3COCH_2COCH_3$
90	CH_3COCH_2SH
89	 $CH_3CO\underset{\vert}{C}HSH$
85	CH_3COCH_2CO-
43	CH_3CO-
28	CO
29	CH_3CH_2-
15	CH_3-

Rycrystallized from petroleum spirit(100-120). Flower needle crystals of bis(acetylethoxycarbonyl)methyl sulphide, m.p.117-18^{o}, (lit.100-01^{o}).[62] Yield 55%. Found: C = 49.33%, H = 6.51%, S = 10.97%. Calculated for $C_{12}H_{18}O_{6}S$, C = 49.65%, H = 6.25%, S = 11.05%.

nmr($CDCl_3$)	triplet	τ	8.70	6 protons
	singlet	τ	7.57	6 protons
	quartet	τ	5.72	4 protons
	singlet	τ	-3.40	2 protons.

ir(KBr disc) 2980(w), 1610(s), 1475(w), 1410(m), 1380(m), 1335(s), 1270(s), 1160(w), 1070(m), 1023(m), 965(w), 900(s)cm.$^{-1}$

An analysis of the mass spectrum showing a molecular ion peak at 290 mass units is given in table 7.

The filtrate was distilled to give an 85% yield of ethyl α-chloroacetoacetate, b.p.192^{o}(lit.193^{o}).[34]

nmr(CCl_4)	triplet	τ	8.70	3 protons
	singlet	τ	7.70	3protons
	quartet	τ	5.77	2 protons
	singlet	τ	5.20	1 proton.

ir(thin film) 2985(m), 2945(w), 2910(w), 1740(s), 1620(w), 1470(w), 1445(w), 1400(w), 1365(m), 1300(s), 1255(s), 1180(s), 1150(s), 1100(w), 1030(m), 950(w)cm.$^{-1}$

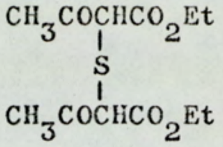
The nmr and ir spectra were identical to an authentic sample of ethyl α-chloroacetoacetate prepared by the action of sulphuryl chloride on ethyl acetoacetate in equimolar quantities.

1.6.1.7. Diethyl β-oxoglutarate.

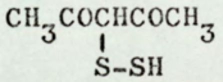
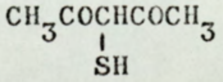
The β-keto-ester(0.1 mole) was treated with a large excess of thionyl chloride(1 mole) under reflux for fourty eight hours. The excess of thionyl chloride was then removed, and the nmr spectrum of the resulting red oil showed that all four active methylene protons

TABLE 7

Mass spectrum: Bis(acetylethoxycarbonylmethyl) sulphide.

Mass-to-charge ratio	Fragment
290	 $\begin{array}{c}CH_3COCHCO_2Et\\ \vert\\ S\\ \vert\\ CH_3COCHCO_2Et\end{array}$ = M
244	M-(CH_3CH_2OH)
130	$CH_3COCH_2CO_2Et$
60	$CH_3CH_2OCH_3$
46	CH_3CH_2OH
45	CH_3CH_2O
43	CH_3CO-
42	$CH_3CH{=}CH_2$
29	CH_3CH_2-
28	CO

Mass spectrum: Bis(diacetylmethyl) trisulphide. TABLE 8

Mass-to-charge ratio	Fragment
294	$(CH_3COCHCOCH_3)_2S_3$
164	 $\begin{array}{l}CH_3COCHCOCH_3\\ \quad\quad\ \vert\\ \quad\quad\ S-SH\end{array}$
132	 $\begin{array}{l}CH_3COCHCOCH_3\\ \quad\quad\ \vert\\ \quad\quad\ SH\end{array}$
100	$CH_3COCH_2COCH_3$
85	CH_3COCH_2CO-
58	CH_3COCH_3
43	CH_3CO-
28	CO

had been substituted.

nmr(CCl_4) set of quartets τ 5.80
set of triplets τ 8.70

Attempts to separate the products by distillation, failed, due to the high boiling point of the oil. Thus a fraction collected at 140°/ 0.5mmHg, produced yellow needle crystals, identified as elemental sulphur, m.p.110°(lit.120,119,112°).[63]

Alternatively, the oil was eluted with benzene through a 30X3cm column packed with silica gel, but no definite separation could be achieved.

Diethyl β-oxoglutarate was also treated with thionyl chloride at a variety of molar ratios and conditions, but in all cases products resembling polymers were obtained. This conclusion arose from the observed high boiling points of the products and from the inability to achieve separation when column chromatography was employed. During this latter technique, a large number of components which possibly corresponded to a range of different molecular weight polymers, were eluted through the column.

1.6.1.8. 1-Phenylbutan-1,3-dione.

The ketone(benzoylacetone)(0.01 mole) was treated with excess of thionyl chloride(0.1 mole) at room temperature for twenty four hours. Aliquots taken at three-hourly intervals and investigated by nmr, indicated that the reaction had proceeded with the simultaneous formation of four to five components, the relative compositions of which continually varied as the reaction progressed.

The black oil obtained upon removal of the thionyl chloride would not recrystallize from any suitable solvent, and an attempted distillation under reduced pressure produced decomposition materials. Column chromatography employing a wide range of eluents was attempted but no definite separation could be achieved.

Variation of the amount of thionyl chloride employed in the reaction,did not appear to affect the composition of the oil, as was shown by nmr.

1.6.1.9. 2-Benzoylcyclohexanone.

The β-keto-ester(0.01 mole) was treated with thionyl chloride (0.03 mole) at room temperature for eighteen hours. Evolution of hydrogen chloride indicated that reaction had proceeded. The black tarry material which was obtained upon removal of the excess of thionyl chloride, would not crystallize, and attempts to distill it under reduced pressure led to its decomposition.

Preparation of sulphides, polysulphides and related compounds.

1.6.2. Treatment of 1,3-diketones with disulphur dichloride.

1.6.2.1. Pentane-2,4-dione.

Disulpur dichloride(0.1 mole) was slowly added to a stirred solution of acetylacetone(0.4 mole) in dry petroleum spirit(60-80°, 150ml), maintained at 0°. Hydrogen chloride was evolved and the powder crystals which precipitated within ten minutes were filtered off, washed with petroleum spirit(80-100°), and recrystallized from neat ethanol. White, needle crystals, m.p.88-89°, of bis(diacetylmethyl) disulphide were thus collected. The nmr,ir and mass spectra were shown to be identical to those of the disulphide(m.p.88°) obtained from the treatment of acetylacetone with thionyl chloride.

nmr($CDCl_3$)	singlet	τ	7.63	12 protons
	singlet	τ	-7.20	2 protons

ir(KBr disc) 1550(s,broad), 2920(w), 1400(s,broad), 1250(m), 1010(s), 905(m)cm.$^{-1}$

The rest of the reaction mixture was left for twenty four hours at room temperature, by which time some more crystals had precipitated. On recrystallization from boiling ethanol, thick, needle crystals were obtained. m.p.130-32°, yield 5%. Found: S = 31.91%. Calculated for $C_{10}H_{14}O_4S_3$, S = 32.40%. Bis(diacetylmethyl) trisulphide.

nmr($CDCl_3$) singlet τ 7.47 12 protons
singlet τ -7.20 2 protons.

ir(KBr disc) 3000(w,broad), 1550(s,broad), 1400(s,broad), 1250(m), 1010(s), 905(m)cm^{-1}.

An analysis of the mass spectrum is given in table 8.

1.6.2.2. Ethyl acetoacetate.

Disulphur dichloride(0.1 mole) was slowly added to a stirred solution of ethyl acetoacetate(0.2 mole) in dry petroleum spirit(150ml) (80-100°). The reaction mixture was maintained at 15° and stirring was continued for forty five minutes. The crystals which had precipitated were filtered off and washed twice with petroleum spirit (100-120°). Recrystallized from petroleum spirit(100-120°) containing 10% v.v. ethanol, to give needle crystals of bis(acetylethoxycarbonyl methyl) sulphide, m.p.118-19°(lit.100-01°).[62] Yield 76%. The nmr, ir and mass spectra of the sulphide were identical to those of the sulphide prepared by the action of thionyl chloride on ethyl acetoacetate.(p.47)

Preparation of sulphides, polysulphides and related compounds.

1.6.3. Treatment of 1,3-diketones with o-nitrophenylsulphenyl chloride.

1.6.3.1. Pentane-2,4-dione.

A mixture of o-nitrophenylsulphenyl chloride(0.01 mole) and

acetylacetone(0.02 mole) was immersed in a water bath maintained at 80-90°. Strong evolution of hydrogen chloride was immediately observed which decreased considerably after thirty minutes. The reaction mixture solidified on cooling in ice. The crystals were filtered off, washed with ethanol and were recrystallized from ethanol, to give diacetylmethyl o-nitrophenyl sulphide, m.p. 128-30°, yield 59%.
A mass spectrum showing a molecular ion peak at 253 mass units, with the correct fragmentation pattern, was obtained, table 9. Found: S = 13.14%, 13.44%. Calculated for $C_{11}H_{11}NO_4S$ S = 12.65%.

nmr($CDCl_3$)	singlet	τ	7.72	6 protons
	multiplet	τ	1.7,2.6	4 protons
	singlet	τ	-7.40	1 proton.

ir(KBr disc) 3100(w), 1600(s), 1575(s), 1525(s), 1460(m), 1410(m), 1345(s), 1310(s), 1260(m), 1115(w), 1060(w), 1045(w), 1010(w), 920(w)cm.$^{-1}$

1.6.3.2. Ethyl acetoacetate.

An attempted synthesis of acetylethoxycarbonylmethyl o-nitrophenyl sulphide via the copper salt of ethyl acetoacetate as reported by Zincke,[64] failed. Best results were obtained by proceeding in exactly the same way as for the preparation of diacetylmethyl o-nitrophenyl sulphide, and cooling the oil in ice for ten-twenty hours to induce crystallization. The purity of the o-nitrophenyl sulphenyl chloride employed in the preparation was found to be critical and if contaminated, crystallization of the sulphide was difficult to achieve. Acetylethoxycarbonylmethyl o-nitrophenyl sulphide, was recrystallized from petroleum spirit(80-100°) containing 5% v.v. ethanol. Golden yellow crystals, m.p. 72-73°, yield 51%. An analysis of the mass spectrum showing a molecular ion peak at 283 mass units is given in table 10. Found: 11.72%. Calculated for $C_{12}H_{13}NO_5S$, S = 11.31

TABLE 9

Mass spectrum: Diacetylmethyl o-nitrophenyl sulphide.

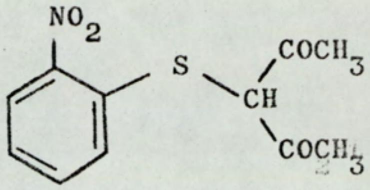
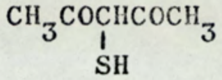
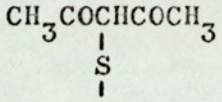
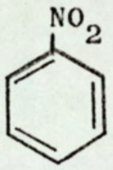
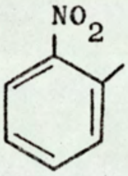
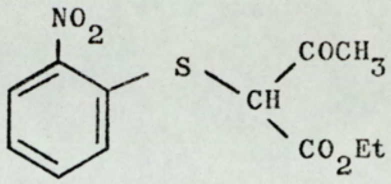
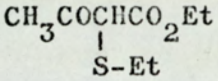
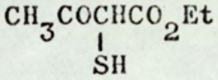
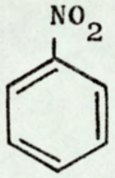
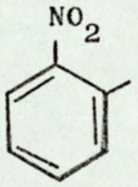
Mass-to-charge ratio	Fragment
253	
132	 $CH_3CO\underset{\overset{\vert}{SH}}{C}HCOCH_3$
131	 $CH_3CO\underset{\overset{\vert}{\underset{\vert}{S}}}{C}HCOCH_3$
123	
122	
100	$CH_3COCH_2COCH_3$
85	CH_3COCH_2CO-
78	C_6H_6
77	C_6H_5-
69	CH_3COCN
43	CH_3CO-
29	CH_3CH_2-
28	CO

TABLE 10

Mass spectrum: Acetylethoxycarbonylmethyl o-nitrophenyl sulphide.

Mass-to-charge ratio	Fragment
283	
190	 $CH_3CO\underset{\text{S-Et}}{\underset{\vert}{CH}}CO_2Et$
162	 $CH_3CO\underset{\text{SH}}{\underset{\vert}{CH}}CO_2Et$
123	
122	
77	C_6H_5-
78	C_6H_6
69	CH_3COCN
45	CH_3CH_2O-
44	$CH_3CH_2CH_3$
43	CH_3CO-
29	CH_3CH_2-
28	CO
27	HCN

nmr($CDCl_3$)	triplet	τ	8.81	3 protons
	singlet	τ	7.65	3 protons
	quartet	τ	5.70	2 protons
	multiplet	τ	1.7,2.6	4 protons
	singlet	τ	-3.90	1 proton.

ir(KBr disc) 3080(w), 2990(w), 2940(w), 1720(w), 1640(m), 1590(s), 1520(s), 1455(m), 1405(m), 1385(m), 1340(s), 1310(s), 1250(s), 1170(w), 1110(w), 1080(w), 1050(w), 1015(w), 960(w)cm.$^{-1}$

1.6.3.3. 5,5-Dimethylcyclohexane-1,3-dione.

A mixture of dimedone(0.01 mole) and o-nitrophenylsulphenyl chloride(0.01 mole) in A.R. chloroform(40ml) was treated under reflux for thirty minutes. The solvent was removed from the reaction mixture and the solid thus obtained was recrystallized from a small amount of ethanol to give yellow plates of 4,4-dimethyl-2,6-dioxocyclohexyl o-nitro phenyl sulphide, m.p.184°, yield 69%. Found: S = 10.54%. Calculated for $C_{14}H_{15}NO_4S$, S = 10.91%. An analysis of the mass spectrum which shows a molecular ion peak at 293 mass units is given in table 11.

nmr($CDCl_3$)	singlet	τ	8.82	6 protons
	singlet	τ	7.45	4 protons
	multiplet	τ	2.70	4 protons.

The enolic proton could not be found in the nmr spectrum due to the insolubity of the sulphide in CS_2, CCl_4, C_6H_6, $CDCl_3$.

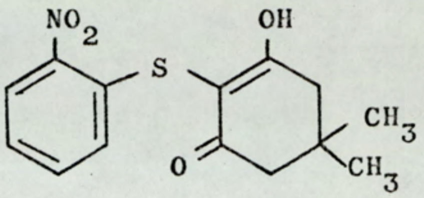
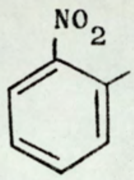
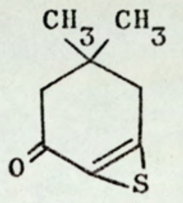
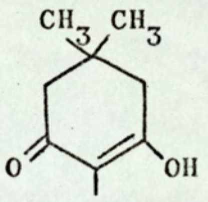
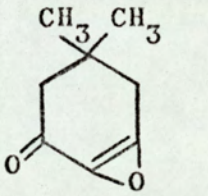
ir(KBr disc) 3450(w,broad), 2960(w), 2930(w), 2530(m,broad), 2980(w), 1593(m), 1570(s), 1518(s), 1471(m), 1455(m), 1400-1200(s,broad), 1150(s), 1100(w), 1048(w), 1010(m), 945(w), 922(w)cm.$^{-1}$

1.6.3.4. 1-Phenylbutan-1,3-dione.

A mixture containing benzoylacetone(0.01 mole) and o-nitro

TABLE 11

Mass spectrum: 4,4-Dimethyl-2,6-dioxocyclohexyl o-nitrophenyl sulphide.

Mass-to-charge ratio	Fragment
293	 = M
246	M-(NO_2+H)
154	 or 
139	
138	
123	$NO_2C_6H_5$
122	$NO_2C_6H_4$-
109	C_6H_5S-
108	C_6H_4S
78	C_6H_6
77	C_6H_5-
69	CH_3COCN
43	CH_3CO-
29	CH_3CH_2-
28	CO
27	HCN

phenylsulphenyl chloride(0.01 mole) was treated according to the method employed in the synthesis of diacetylmethyl o-nitrophenyl sulphide. The product was recrystallized from boiling ethanol to give acetylbenzoylmethyl o-nitrophenyl sulphide. Yellow plates, m.p.118-20°. Yield 73%. The mass spectrum is given in table 12. Found: S = 10.52%, 10.51%. Calculated for $C_{16}H_{13}NO_4S$, S = 10.16%.

nmr($CDCl_3$)	singlet	τ	7.67	3 protons
	multiplet	τ	1.75, 1.60	9 protons
	singlet	τ	-7.90	1 proton.

ir(KBr disc) 3100(w), 3060(w), 3010(w), 1600(s), 1570(s), 1520(s), 1450(m), 1390(m), 1336(s), 1306(s), 1250(m), 1190(w), 1104(w), 1000(w), 925(w)cm^{-1}

Preparation of sulphides, polysulphides and related compounds.

1.6.4. Ethanolic treatment of 1,3-diketone~~s~~-α-sulphinyl chlorides.

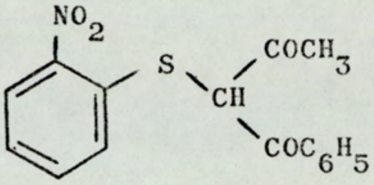
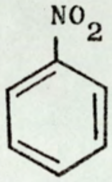
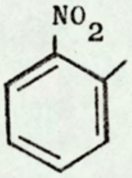
1.6.4.1. 1-Chlorosulphinyl-1,1-dibenzoylethane.

The oil obtained from the reaction of 1,1-dibenzoylethane and thionyl chloride was treated with ethanol in an attempt to crystallize out any of its three components ~~and~~ which were detected in the nmr spectrum.(See page114for discussion). However, it was observed that ethanol acted as a medium in which further reaction of the oil took place.

The oil(1.2g) was dissolved in absolute ethanol(15ml) and the solution was kept at room temperature for forty eight hours. Two to three drops of water were added if precipitation were not complete at the end of that period. The white crystals(m.p.145-50°) were filtered off and washed with cold ethanol. Spectroscopic(nmr) and tlc evidence pointed to two components which were further separated by fractional recrystallization from ethanol. The most

TABLE 12

Mass spectrum: Acetylbenzoylmethyl o-nitrophenyl sulphide.

Mass-to-charge ratio	Fragment
315	
161	$CH_3CO\underset{\vert}{CH}COC_6H_5$
138	C_6H_5COSH
123	
122	
106	C_6H_5CHO
105	C_6H_5CO-
78	C_6H_6
77	C_6H_5-
69	CH_3COCN
43	CH_3CO-
28	CO
27	HCN

soluble of the two components, precipitated in white, long needle crystals of bis(1,1-dibenzoylethyl) trisulphide. m.p.183°, yield 17%. Found: S = 16.32%. Calculated for $C_{32}H_{26}O_4S_3$, S = 16.85%.

nmr($CDCl_3$) singlet τ 8.03 6 protons

multiplet τ 2.2,2.6 20 protons

ir(KBr disc) 3060(w), 2940(w), 1690(w), 1660(s), 1600(m), 1583(w), 1455(m), 1375(w), 1260(s), 1230(m), 1180(w), 960(m)cm.$^{-1}$

The second component corresponding to bis(1,1-dibenzoylethyl) disulphide, precipitated in white, fluffy crystals, m.p.155-56°, yield 22%. Found: S = 12.16%. Calculated for $C_{32}H_{26}O_4S_2$, S = 11.90%.

nmr($CDCl_3$) singlet τ 8.12 6 protons

multiplet τ 2.1,2.7 20 protons

ir(KBr disc) 3060(w), 2940(w), 1690(w), 1660(s), 1600(m), 1583(w), 1455(m), 1375(w), 1260(s), 1230(m), 1180(w), 960(m)cm.$^{-1}$

1,1-Dibenzoylethane oil(1.2g) was dissolved in absolute ethanol(15ml) containing 1.8ml of water.(Note 1) The crystals were filtered off, washed with ethanol and recrystallized from ethanol to give a semi-crystalline material identified as 1,1-dibenzoylethyl 1,1-dibenzoylethanethiosulphinate, m.p. 126°, yield 26%. Found: S = 11.16%. Calculated for $C_{32}H_{26}O_5S$, S = 11.56%.

nmr($CDCl_3$) singlet τ 7.92 3 protons

singlet τ 7.81 3 protons

multiplet τ 2.10 20 protons.

ir(KBr disc) 3060(w), 2940(w), 1660(s), 1595(m), 1580(w), 1448(m), 1375(w), 1250(s), 1225(s), 1180(w), 1100(s,S=O), 1070(w), 1000(w), 960(m)cm.$^{-1}$

Note 1: Methanol also afforded an identical product to ethanol. However, t-butylalcohol did not produce any thiosulphinate.

The treatment of the 1,1-dibenzoylethane oil with neat methanol was follwed by using nmr techniques. Thus, some of the oil was dissolved in methanol in the quantities stated above and the nmr spectrum was observed over forty eight hours. It was found that the composition of the oil changed as a function of time, but at no time could the characteristic thiosulphinate spectral pattern be observed. At the end of the forty eight hour period, crystals corresponding to a mixture of bis(1,1-dibenzoylethyl) disulphide and trisulphide were collected.

1.6.4.2. 1,1-Dibenzoylmethane treatment with thionyl chloride and further treatment of the product with ethanol.

The reaction proceeded in a similar manner to the reaction of 1,1-dibenzoylethane with thionyl chloride(p.30), and the oil obtained was treated with ethanol. Pale-yellow crystals, m.p.185-86°, were isolated and shown by tlc to be composed of two components. Chloroform and benzene were employed as eluents and consistently showed two components. Found: S = 15.50%, 15.62%. Calculated for bis(dibenzoyl methyl) disulphide, $C_{30}H_{22}O_4S_2$, S = 12.55% and for bis(dibenzoyl methyl) trisulphide, $C_{30}H_{22}O_4S_3$, S = 17.70%.

nmr($CDCl_3$) multiplet τ 2.00,2.60

1.6.4.3. 1,1-Dibenzoylethane treatment with thionyl chloride in the presence of dibenzoyl peroxide.

1,1-Dibenzoylethane(0.01 mole), dibenzoyl peroxide(0.01 mole) and an excess of thionyl chloride(0.1 mole) were treated under reflux for eighteen hours. At the end of that period the excess of thionyl chloride was removed and the oil obtained was treated with ethanol under varying conditions. An nmr spectrum of the oil revealed that the amount of 2-benzoyl-1-chloro-1-phenylpropene had decreased significantly.

The oil(1.2g) was treated with 15ml of 12% aqueous ethanol.

Crystals of 1,1-dibenzoylethyl benzenethiosulphonate, m.p. 153°, precipitated within twenty four hours. Yield 24%. Found: S = 15.02 . Calculated for $C_{22}H_{18}O_4S_2$, S = 15.70%.

nmr($CDCl_3$)	singlet	τ 7.76	3 protons
	multiplet	τ 2.3, 2.6	15 protons

ir(KBr disc) 3060(w), 2940(w), 1680(m), 1660(s), 1600(m), 1580(w), 1450(m), 1385(m), 1322(s), 1312(s), 1255(m), 1230(m), 1180(w), 1145(s), 1070(m), 1000(w), 970(m)cm.$^{-1}$

An analysis of the mass spectrum of the thiosulphonate is given in table 13.

The oil(1.2g) was treated with "super-dry" ethanol(15ml) for seven days and did not produce any crystalline compound. Upon addition of one ml of water, immediate precipitation took place. The crystals were collected and washed with ethanol, m.p. 163-65°, yield 37%. The nmr spectrum indicated that the compound consisted of a mixture of bis(1,1-dibenzoylethyl) disulphide and trisulphide, whilst the ir spectrum was identical with that of an authentic sample of the di- and trisulphide.

Preparation of sulphides, polysulphides and related compounds.

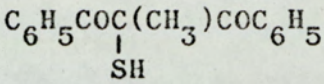
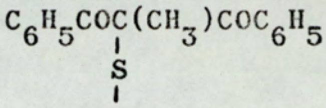
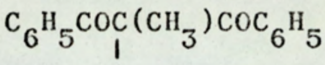
1.6.5. Miscellaneous reactions.

1.6.5.1. Preparation of di-o-nitrophenyl disulphide.

Technical sodium sulphide dihydrate(1 mole) in powder form was treted with sulphur(1 mole) in absolute ethanol(300ml) at room temperature, according to T.Wohlfahrt's method.[65] Vigorous stirring was necessary to affect dissolution(two to three hours required). A solution of o-chloronitrobenzene(2 moles) in absolute ethanol(100ml) was slowly added to the above mixture, the rate of addition controlled

TABLE 13

Mass spectrum: 1,1-Dibenzoylethyl benzene thiosulphonate.

Mass-to-charge ratio	Fragment
270	 $C_6H_5CO\underset{\overset{\mid}{SH}}{C}(CH_3)COC_6H_5$
269	 $C_6H_5CO\underset{\overset{\mid}{\underset{\mid}{S}}}{C}(CH_3)COC_6H_5$
238	$C_6H_5COCH(CH_3)COC_6H_5$
237	 $C_6H_5CO\underset{\mid}{C}(CH_3)COC_6H_5$
170	$C_6H_5COSO_2H$
154	C_6H_5COSOH
142	$C_6H_5SO_2H$
141	$C_6H_5SO_2$-
125	C_6H_5SO-
110	C_6H_5SH
106	C_6H_5CHO
105	C_6H_5CO-
78	C_6H_6
77	C_6H_5-
64	-S-S-
32	-S-
28	CO

by the steady refluxing of the reaction mixture. The solution was further treated under reflux for two hours. The resulting precipitate was filtered off, washed thoroughly with water to remove the sodium chloride, and then washed twice with ethanol. Rycrystallized from boiling acetone to give di-o-nitrophenyl disulphide, m.p.185°(lit. 181°[26], 193-95°[66]). Yield 73%.

nmr($CDCl_3$) multiplet τ 2.2,2.8

1.6.5.2. Preparation of o-nitrophenylsulphenyl chloride.

Di-o-nitrophenyl disulphide(0.3 mole) was mixed with chloroform (200ml) in a flask equipped with a dry-ice condenser and a stirrer. The reaction mixture was saturated with chlorine according to the method employed by Zincke,[64] and it was stirred for a further two hours when it was resaturated with chlorine. Crystallization was induced either by cooling in ice or by standing the reaction mixture overnight. The crystals were filtered off, washed with petroleum spirit and recrystallized from petroleum spirit(100-120°) containing 5% v.v. of benzene, m.p.70°(lit.74.5-75°),[67] yield 89%.

nmr(CCl_4) multiplet τ 2.3,2.9

ir(thin film) 3100(w), 1593(m), 1568(m), 1550(w), 1495(s), 1450(m), 1433(w), 1390(w), 1334(w), 1308(s), 1255(w), 1190(w), 1108(w), 1060(w), 1042(w), 735(s)cm^{-1}

1.6.5.3. Cyclization of di-2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl sulphide.

A mixture of the sulphide(3g) in pyridine(12ml) and acetic anhydride(8ml) was heated to the boiling point and was then immediately cooled down in ice.[25] Prolonged heating resulted in decomposition and afforded a lower yield of the anhydride. The precipitate was filtered off, washed twice with ethanol and was recrystallized from hot ethanol. Golden-yellow plates, m.p.222^{o} of 2,2,7,7-tetramethyl-$-\Delta^{4a,10a}$-perhydro-9,10-oxathia-anthracene-4,5-dione, precipitated. Yield 73%. An analysis of the mass spectrum showing a molecular ion peak at 292 mass units is given in table 14. (Page 72-73)

nmr($CDCl_3$)	singlet	τ	8.92	12 protons
	singlet	τ	7.75	4 protons
	singlet	τ	7.69	4 protons

ir(KBr disc) 2960(m), 2870(w), 1643(s), 1595(m), 1470(w), 1425(w), 1408(w), 1368(w), 1344(w), 1305(w), 1280(w), 1259(w), 1192(m), 1163(m), 1143(m), 1048(w), 1008(w)cm.$^{-1}$

The attempted cyclization of the sulphide, which employed zinc chloride in chloroform afforded a non-identified compound which exhibited eight nmr absorptions.

nmr($CDCl_3$)	singlet	τ	9.24	6 protons
	singlet	τ	9.14	
	singlet	τ	9.00	
	singlet	τ	8.90	
	singlet	τ	7.79	4 protons
	singlet	τ	7.72	
	singlet	τ	7.48	
	singlet	τ	7.43	

Oxidations by thionyl chloride.

1.7.1.1. Diethyl 2,5-dihydroxyterephthalate.

Diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate(0.01 mole) was treated under reflux with an excess of thionyl chloride(0.1 mole) for four hours, during which period hydrogen chloride was evolved. The excess of thionyl chloride was removed and the oil obtained crystallized upon standing for ten minutes. It was recrystallized from a small amount of ethanol. (10ml of ethanol per gram of the ester employed in the experiment.) Yellow, needle crystals, m.p.128° (lit.133°),[34] of diethyl 2,5-dihydroxyterephthalate.

nmr(CDCl$_3$)	triplet	τ	8.58	6 protons
	quartet	τ	5.55	4 protons
	singlet	τ	2.55	2 protons
	singlet	τ	0.02	2 protons

ir(KBr disc) 3300(m), 3020(w), 2980(w), 1755(m), 1725(s), 1685(s), 1493(m), 1468(m), 1405(w), 1370(m), 1320(s), 1285(m), 1200(s), 1100(m), 1060(m), 1020(m)cm^{-1}.

1.7.1.2. 2,3-Dimethylanthraquinone.

1,4-Dihydro-2,3-dimethylanthraquinone(0.01 mole) prepared by the Diels-Alder addition of butadiene to 1,4-naphthoquinone, was treated with an excess of thionyl chloride(0.1 mole) under reflux for eighteen hours. The excess of thionyl chloride was removed and the resulting yellow crystals were recrystallized from boiling ethanol. Yellow, needle crystals of 2,3-dimethylanthraquinone, m.p.209° (lit.210°),[34] yield 49%.

nmr(CDCl$_3$)	singlet	τ	7.60	6 protons
	multiplet	τ	1.8,2.3	4 protons
	singlet	τ	2.13	2 protons.

ir(KBr disc) 3050(w), 2980(w), 1673(s), 1593(s), 1385(w), 1330(s), 1295(s), 1223(m), 1025(w), 958(m), 900(w)cm^{-1}.

MECHANISTIC EXPERIMENTAL

1.1.1. Trapping of intermediates.

1.1.1.1. Dimedone treatment with thionyl chloride in the presence of styrene.

Dimedone(0.01 mole), thionyl chloride(0.02 mole) and antioxidant-free styrene(10ml) were stirred for two hours at room temperature. The excess of thionyl chloride was removed from the reaction mixture by distillation under reducedpressure which was further continued to yield a fraction(8.5ml) corresponding to styrene as shown by the nmr spectrum and by comparison with a gas liquid chromatograph of an authentic sample. The residue left in the flask was recrystallized from ethanol and afforded di-2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl sulphide in 11% yield. m.p.223°. The sulphide showed identical spectral characteristics to the sulphide isolated before.(page 43)

1.1.1.2. Attempted isolation of intermediates in the synthesis of dimedone sulphide.

A mixture of dimedone(0.01 mole), chloroform(15ml) and thionyl chloride(0.01 mole) was stirred at -6° for eighteen hours. Filtration of the reaction mixture afforded a quantitative amount of dimedone in its enolic form.

The reaction was repeated at 0° with similar results apart from the isolation of a very small amount of the dimedone sulphide (approx. yield 2%).

1.1.1.3. Isolation of the enolic form of dimedone.

Thionyl chloride(0.01 mole) was added dropwise to a suspension of dimedone(0.02 mole) in A.R. chloroform(20ml). All of the dimedone dissolved upon addition of the first 0.2ml of thionyl chloride and when more thionyl chloride was added, precipitation of a pale-yellow crystalline material took place. The crystals were filtered off and washed with petroleum spirit(80-100°), m.p.120°. They were found to be composed of a mixture of the ketonic and enolic forms of dimedone, the enolic form being the major component.

The enolic form of dimedone in its pure form was obtained by prolonged treatment(6 days) at room temperature under the conditions mentioned above. m.p.135°. Recrystallization from water afforded the normal keto-enol equilibrium mixture of dimedone, m.p.146°.

nmr($CDCl_3$) spectrum of the pure enolic form isolated:

singlet	τ	8.86	6 protons
singlet	τ	7.49	4 protons
singlet	τ	3.85	1 proton
singlet	τ	-3.95	1 proton.

ir(KBr disc) 2960(m), 2860(m), 2810(m), 2680(m), 2630(m), 2450(m),
1620(s), 1585(m), 1520(s), 1470(s), 1410(w), 1370(m),
1350(s), 1305(s), 1250(s), 1230(s), 1148(s), 880(w)cm^{-1}.

The mass spectrum of the enolic form of dimedone was identical to the mass spectrum of the normal keto-enol equilibrium mixture.

1.1.1.4. Simultaneous treatment of dimedone, acetylacetone and thionyl chloride.

A solution containing acetylacetone(0.01 mole), thionyl chloride(0.02 mole) and dimedone(0.01 mole) in chloroform(50ml), was stirred at room temperature for three days. Dimedone in its enolic form was isolated by filtration and the remaining black solution was evaporated to dryness to yield a tarry material which would not crystallize either from ethanol or petroleum spirit.

1.1.1.5. Ethyl acetoacetate treatment with thionyl chloride in the presence of acetic anhydride.

Ethyl acetoacetate(0.01 mole), was treated with thionyl chloride(0.02 mole) in the presence of acetic anhydride(0.02 mole) at room temperature for eighteen hours. It was hoped that if an intermediate of the type $RSCl_3$ were formed, it would be trapped by the acetic anhydride and transform to the sulphinyl chloride. The product which was obtained upon removal of the excess of thionyl chloride, did not show an ir absorption at $1150cm^{-1}$ indicative of a sulphinyl chloride group and when transferred to a beaker it solidified. The product was identified as bis(acetylethoxycarbonylmethyl) sulphide.

The reaction was repeated under similar conditions using the copper salt of ethyl acetoacetate. It proceeded rapidly and again produced the bis(acetylethoxycarbonylmethyl) sulphide.

1.1.1.6. Ethyl acetoacetate/ copper salt treatment with thionyl chloride.

Thionyl chloride(0.01 mole) was slowly added to a stirred suspension of ethyl acetoacetate-copper salt(0.01 mole) in dry carbon tetrachloride(40ml). Cupric chloride precipitated immediately and the reaction mixture was filtered after thirty minutes stirring at room temperature. An nmr spectrum of the filtrate showed absorptions which corresponded to ethyl acetoacetate and which was possibly formed through the reaction of hydrogen chloride and the copper salt of ethyl acetoacetate. The solvent was removed from the filtrate and the oil obtained was recrystallized from petroleum spirit(80-100°), to give bis(acetylethoxycarbonylmethyl) sulphide, which was characterized spectroscopically. m.p.114°.

A further reaction in which the ethyl acetoacetate-copper salt (0.01 mole) was added to thionyl chloride(0.02 mole) in dry benzene (40ml), again gave the bis(acetylethoxycarbonylmethyl) sulphide rather than the expected sulphinyl chloride. The sulphide was characterized spectroscopically and by its melting point.(116°)

1.1.1.7. Ethyl acetoacetate treatment with 2-methyl-3-oxo-3-phenylpropane-2-sulphinyl chloride.

A mixture of ethyl acetoacetate(0.01 mole) and the sulphinyl chloride(0.01 mole) in A.R. chloroform(30ml) was treated under reflux for twenty four hours. Weak evolution of hydrogen chloride accompanied the reaction.The solvent was removed and the oil obtained was shown by nmr to be composed of unchanged ethyl acetoacetate and the decomposition products of the sulphinyl chloride. The ir spectrum did not show a peak at 1150cm^{-1} indicative of the sulphinyl chloride employed in the reaction,or a peak at 1050cm^{-1} indicative of a sulphoxide.

1.1.1.8. Dimedone treatment with β-ketosulphinyl chlorides.

A mixture of dimedone(0.01 mole), 2-methyl-3-oxo-3-phenyl propane-2-sulphinyl chloride(0.01 mole) and A.R. chloroform(20ml) was refluxed in a water bath for three hours, during which period hydrogen chloride was evolved. The solvent was removed and the viscous yellow oil was recrystallized from ethanol. White, needle crystals of di-2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl sulphide precipitated in 14% yield, m.p.222°. The nmr and ir spectra of the sulphide were identical to a sample prepared by the treatment of dimedone with thionyl chloride.

Spectroscopic examination of the yellow oil(nmr) revealed that it probably contained isopropyl phenyl ketone (septet τ 6.5 doublet τ 8.85). Distillation of the oil under reduced pressure yielded a fraction, b.p.78°/0.5mmHg, corresponding to isopropyl phenyl ketone, (lit. 220-21°).[47]

nmr(CCl_4)	doublet	τ	8.85	5 protons
	septet	τ	6.54	1 proton
	multiplet	τ	2.0,2.5	5 protons.

The presence of 2-chloro-5,5-dimethylcyclohexane-1,3-dione in the yellow oil was also indicated by tlc which consistently produced a component $R_f = 0.62(CHCl_3)$, $R_f = 0.20(C_6H_6)$, which had the same R_f values with an authentic sample of the chloride.

Other β-ketoisopropyl chlorides prepared, viz. 2,4-dimethyl--3-oxopentane-2-sulphinyl chloride, 2-methyl-3-oxo-3-phenylpropane--2-sulphinyl chloride, were found to react with dimedone in an analogous manner.

1.1.1.9. 3-Chloro-2,4-dioxopentane-3-sulphinyl chloride treatment with:

A. Acetylacetone-sodium salt.

The sulphinyl chloride(0.01 mole) was mixed with the sodium salt of acetylacetone(0.02 mole) at 0^o in dry ether(40ml). The heavy precipitate of sodium chloride was filtered off, the solvent was removed from the filtrate and the resulting black-red oil was shown by an nmr spectrum to be composed of many products(four superimposable singlets in the τ 8.00 region). The ir spectrum of the oil showed peaks at $1070cm^{-1}$ and $1040cm^{-1}$ possibly indicative of a sulphoxide group, but the evidence was not conclusive.

B. Acetylacetone or ethyl acetoacetate.

Equimolar quantities(0.01 mole) of the reactants were stirred at room temperature for twenty four hours. Hydrogen chloride was evolved and the rection mixture turned black. The nmr and ir spectra did not present conclusive identification and an attempted recrystallization of the oil failed to produce any crystals.

C. Dimedone.

A mixture of the sulphinyl chloride(0.01 mole) and dimedone (0.01 mole) in A.R. chloroform(40ml) was treated under reflux for three hours. Hydrogen chloride was evolved. The solvent was removed and the red oil was recrystallized from ethanol. Crystals, m.p.224^o

were isolated and spectroscopically identified as the dimedone sulphide. Yield 28%.

1.1.1.10. Adamantyl-1-sulphinyl chloride treatment with dimedone.

A mixture of dimedone(0.01 mole) and the sulphinyl chloride (0.01 mole) in A.R. chloroform(40ml) was treated under reflux for twenty four hours, during which period hydrogen chloride was evolved. The solvent was removed and the oil was recrystallized from ethanol to yield the dimedone sulphide which was spectroscopically identified. m.p.226°, yield 19%. The ir spectrum of the oil showed an absorption at 1730cm^{-1} which is not present in dimedone sulphide or in 2-chloro -5,5-dimethylcyclohexane-1,3-dione.

1.1.1.11. 1,1-Dibenzoylethane treatment with thionyl chloride in the presence of triphenylbromomethane.

1,1-Dibenzoylethane(0.01 mole), triphenylbromomethane(0.01 mole) and an excess of thionyl chloride(0.1 mole) were stirred at room temperature for seven days, during which period aliquots were taken at twenty-four-hour intervals. The reaction proceeded in the same way as in the absence of triphenylbromomethane, as shown by the nmr spectra (singlet τ 7.78, singlet τ 7.90, multiplet τ 2.0,2.6). The excess of thionyl chloride was removed from the reaction mixture and the oil was treated(ethanol-10% water(20ml))for twentyfour hours. Crystals identified as triphenylmethanol, m.p.160-62°(lit.164-65°),[34] precipitated.

nmr($CDCl_3$)	singlet	τ	2.70	15 protons
	singlet	τ	4.92	1 proton

1.1.1.12. 1-Chlorosulphinyl-1,1-dibenzoylethane treatment with EtOH/D_2O

The oil(1.2g) obtained by refluxing 1,1-dibenzoylethane with thionyl chloride for eighteen hours, was treated with absolute ethanol(15ml) containing deuteriated water(1.8ml). The crystals(m.p.118 -20°) which were collected by filtration, corresponded to 1,1-dibenzoylethyl 1,1-dibenzoylethanethiosulphinate. Maximum precipitation was ensured by standing the solution for twenty four hours. The ethanol and deuteriated water were removed from the filtrate and the nmr spectrum of the resulting oil showed that 1,1-dibenzoylethane had been formed during the treatment with ethanol and deuteriated water, and that the proton required for such a process did in fact originate from the deuteriated water.

nmr(CCl_4)	singlet	τ	8.48
	singlet	τ	7.78
	multiplet	τ	2.2,2.8

1,1-Dibenzoylethane(1g) was dissolved in ethanol(20ml) which contained 10% deuteriated water. The solution was cooled in ice until crystallization was complete. The crystals were collected and the nmr spectrum indicated that no deuterium had been incorporated in 1,1-dibenzoylethane.

1.1.1.13. The reaction between a ketone and a sulphinyl chloride.

Isopropyl phenyl ketone(0.01 mole) and 2-methyl-3-oxo-3-phenylpropane-2-sulphinyl chloride(0.01 mole) were heated in a digol bath maintained at 110°. The reaction mixture was treated under these conditions for twenty four hours while hydrogen chloride was evolved. The nmr spectrum of the oil obtained, revealed that isopropyl phenyl ketone did not react (the ketone's absorptions are denoted as a), whereas the sulphinyl chloride (denoted as b) had partly decomposed.

nmr(CCl_4)	doublet^a	τ	8.88	6 protons
	singlet^b	τ	8.52	6 protons
	singlet^b	τ	8.22	
	singlet^b	τ	8.00	

septet[a] τ 6.55 1 proton

multiplet[a,b] τ 2.1,2.6 10 protons

ir(thin film) 3065(w), 2980(m), 2940(w), 1685(s), 1600(m), 1583(w), 1450(m), 1385(w), 1265(w), 1228(s), 1160(m), 980(m)cm^{-1}

1.1.1.14. Bis(diacetylmethyl) disulphide treatment with thionyl chloride.

The disulphide(0.01 mole) was treated under reflux with an excess of thionyl chloride(0.1 mole) for twenty four hours. The excess of thionyl chloride was removed and the resulting semi-crystalline material was recrystallized from ethanol to afford the starting material in 91% recovery.

Detection of intermediates by spectroscopic means.

1.2.1.1. The reaction between n-butyl-lithium and 2-iodopropane.

It has been reported[68] that the reaction proceeds via a free radical mechanism and that the intermediate free radical gives rise to a strong negative absorption in the nmr.

n-Butyl-lithium(0.5ml) was added to an nmr tube filled with dry nitrogen gas and equipped with a suba-seal stopper. 2-Iodopropane (0.15ml) containing 5% tetramethylsilane was injected into the tube and the nmr spectrum was obtained at different time intervals. Formation of a n-butyl radical was indicated by a negative signal at τ 8.23 which consequently formed a triplet, ten minutes after mixing the reactants.

1.2.1.2. Attempted detection of free radical intermediates by CIDNP.

(Chemically induced dynamic nuclear polarization)

Acetylacetone(0.3ml), thionyl chloride(0.3ml) and carbon tetrachloride(0.3ml) containing 5% T.M.S. were quickly mixed in an nmr tube and their reaction was followed, over two hours, using an nmr spectrometer. Reaction proceeded as shown by the constant evolution of hydrogen chloride, but no negative signals, indicative of free radical intermediates could be detected. Similar results were obtained from the reaction between dimedone and thionyl chloride.

1.2.1.3. Ir studies of the reaction between dimedone and thionyl chloride.

Dimedone(0.01 mole) was mixed with an excess of thionyl chloride (0.1 mole) at room temperature. A sodium chloride ir cell with a 0.05mm spacer was constructed. Aliquots at fifteen minute intervals were injected into the cell and the ir spectrum of the solution was immediately obtained. The reaction was followed for three hours but a suphinyl chloride peak at $1150cm^{-1}$ could not be detected at any time during the reaction.

Ethyl acetoacetate was substituted for dimedone and the experiment was repeated again over twelve hours but the same negative results were obtained.

Oxidation of sulphides.

1.3.1.1. Bis(acetylethoxycarbonylmethyl) sulphide / H_2O_2/-V_2O_5.-

Anhydrous hydrogen peroxide in t-butyl alcohol was prepared by N.A.Milan's method.[69] Calculated composition, 5.83% by titration of the liberated iodine with standard sodium thiosulphate solution employing starch as indicator. The iodine was liberated by the addition of a weighed amount of hydrogen peroxide solution to an excess of aqueous potassium iodide solution, containing 4N sulphuric acid.

Bis(acetylethoxycarbonylmethyl) sulphide(0.01 mole) was dissolved in t-butyl alcohol(50ml). Vanadium pentoxide[70](10mg) dissolved in hydrogen peroxide-t-butyl alcohol(0.01 mole) was added dropwise to the stirred solution of the sulphide maintained at 50°, over a period of thirty minutes. It was stirred for a further four hours. The solvent was removed at 30° and the semi-crystalline material left was recrystallized from petroleum spirit. Unchanged sulphide (m.p.117°) was recovered in 77% yield.

1.3.1.2. Bis(acetylethoxycarbonylmethyl) sulphide/ iodobenzene dichloride.

Iodobenzene dichloride was prepared by the action of chlorine on iodobenzene, by the method employed by H.J.Lucas et al.[71]

Iodobenzene dichloride(0.01 mole) in dry pyridine(5ml) was slowly added to a mixture of the sulphide(0.01 mole) in 20% v.v. of aqueous pyridine(10ml) maintained at 20°, according to the method of C.Barbieri et al.[72] When all the solution had been added the black tarry reaction mixture was washed with aqueous sulphuric acid and extracted with chloroform to give a viscous tarry oil which would not crystallize from any solvent mixture.

The reaction was repeated at 0° over eighteen hours but reaction did not proceed and unchanged sulphide was recovered (m.p.116°).

1.3.1.3. Bis(acetylethoxycarbonylmethyl) sulphide/dimethyl sulphoxide.

Organic sulphides can be oxidized by dimethyl sulphoxide to sulphoxides.[73] Bis(acetylethoxycarbonylmethyl) sulphide(0.01 mole) was mixed with an excess of dimethyl sulphoxide(0.1 mole) and the reaction mixture was placed in the rotary evaporator, the bath maintained at 70°. Reaction did not proceed under these conditions and the sulphide was recovered unchanged. When the temperature of the bath was raised to 130°, decomposition of the sulphide took place.

1.3.1.4. Bis(acetylethoxycarbonylmethyl) sulphide/$Na_2Cr_2O_7/H_2SO_4$.

The sulphide(0.01 mole) was treated with an aqueous solution of sodium dichromate-sulphuric acid(0.01 mole) at 70° for two hours. Upon dilution of the reaction mixture with ice-cold water, unchanged starting material precipitated.

The reaction was repeated under the same conditions with an excess of sodium dichromate-sulphuric acid(0.03 mole) but it did not proceed either and the sulphide was recovered unchanged.

1.3.1.5. Di-2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl sulphide/H_2O_2.

The sulphide(0.01 mole) was treated with hydrogen peroxide(0.01 mole) in acetic acid(20ml) for four hours at 50°. The reaction mixture gave unchanged sulphide, m.p.223°, upon cooling. Recovery 87%.

1.3.1.6. Acetylethoxycarbonylmethyl o-nitrophenyl sulphide/H_2O_2.

The sulphide(0.01 mole) was treated with hydrogen peroxide (0.01 mole)(25.4% by titration), in acetic acid(20ml) at room temperature for twenty four hours. The unchanged sulphide precipitated on addition of water. The reaction was repeated under the same conditions but instead 0.03 mole of hydrogen peroxide was employed. The sulphide was again recovered unchanged. Sodium dichromate in sulphuric acid in equimolar quantities with the sulphide, also failed to produce any oxidation products.

Acetic acid and acetic anhydride 50-50% v.v. (30ml) was employed as the solvent mixture. The sulphide(0.01 mole) was treated with hydrogen peroxide(0.03 mole) at room temperature for two and a half hours. The reaction time should not be excessively prolonged as it leads to the formation of decomposition products. Cold water was added to the reaction mixture until it became cloudy. Crystals precipitated within thirty minutes and were recrystallized from petroleum spirit(120-160, 60%) and ethanol(40%). Yellow, needle crystals m.p. 125-26° precipitated in 58% yield. Thought to belong (see discussion) to acetylethoxycarbonylmethyl o-nitrophenyl sulphoxide. Found: S = 10.24%. Calculated for $C_{12}H_{13}NO_6S$, S = 10.70%. The mass spectrum shows a molecular ion peak at 308 mass units which does not correspond to the expected molecular ion peak of 299 mass units, table 15.

nmr($CDCl_3$)	triplet	τ	8.95	3 protons
	singlet	τ	7.66	3 protons
	quartet	τ	5.97	2 protons
	singlet	τ	5.35	1 proton
	multiplet	τ	1.8,2.2	4 protons.

ir(KBr disc) 3120(w), 2960(w), 1745(s), 1720(s), 1602(w), 1525(s), 1370(w), 1350(s), 1290(w), 1240(s), 1200(w), 1155(w), 1115(w), 1070(s), 1040(s), 1012(w), 960(w)$cm.^{-1}$

The crystalline compound which was isolated from the reaction of acetylethoxycarbonylmethyl o-nitrophenyl sulphide with hydrogen peroxide, was treated with an excess of thionyl chloride for twenty four hours at room temperature. At the end of that period the excess of thionyl chloride was removed and the oil which was obtained showed a complex nmr spectrum which indicated the presence of at least four components. The characteristic methine absorption of ethyl α-chloro acetoacetate was absent in the nmr spectrum. Tlc of the oil, carried out in parallel with authentic samples of ethyl α-chloroacetoacetate, o-nitrochlorobenzene and o-nitrophenylsulphenyl chloride, proved that none of these compounds was present in the oil. Carbon tetra chloride and benzene were the eluents employed in the tlc experiment.

1.3.1.7. 4,4-Dimethyl-2,6-dioxocyclohexyl o-nitrophenyl sulphide/H_2O_2-

The conditions discussed in the previous experiment, were employed. Thus, acetic acid and acetic anhydride 50-50% v.v. were

TABLE 14

Mass spectrum: 2,2,7,7-Tetramethyl-$\Delta^{4a,10a}$-perhydro-9,10-oxathia-anthracene-4,5-dione.

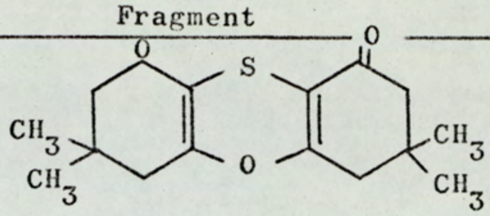
Mass-to-charge ratio	Fragment
292	
83	Dimedone-(CH_3CO+CH_2)
43	CH_3CO-
32	-S-
28	CO

TABLE 15

Mass spectrum: Oxidation product of acetylethoxycarbonylmethyl o-nitrophenyl sulphide.

Mass-to-charge ratio	Fragment
308	Unaccounted.
186	NO_2-C_6H_4-SO_2-
154	NO_2-C_6H_4-S-
78	C_6H_6
77	C_6H_5-
69	CH_3COCN
64	SO_2 or -S-S-
60	$CH_3CH_2OCH_3$
45	CH_3CH_2O-
44	$CH_3CH_2CH_3$
43	CH_3CO
42	$CH_3CH{=}CH_2$
28	CO
27	HCN

employed as solvents and the treatment with hydrogen peroxide was prolonged to eighteen hours. On recrystallization from petroleum spirit(100-120) containing 10% v.v. of ethanol, crystals of 2-acetoxy-4,4-dimethyl-6-oxocyclohex-1-enyl o-nitrophenyl sulphoxide, m.p.100-01°, were obtained. Yield 23%. An analysis of the mass spectrum is given in table 16. Found: S = 9.47%. Calculated for $C_{16}H_{17}NO_6S$ S = 9.12%.

nmr($CDCl_3$)	singlet	τ	8.90	3 protons	
	singlet	τ	8.83	3 protons	
	singlet	τ	7.80	3 protons	
	doublet	τ	6.85	2 protons	J = 15Hz
	doublet	τ	7.55	2 protons	J = 15Hz
	multiplet	τ	2.1,2,4	4 protons	

ir(KBr disc) 3110(w), 2980(w), 2940(w), 2880(w), 1768(s), 1740(s), 1714(s), 1590(w), 1570(w), 1520(s), 1468(w), 1400(w), 1373(m), 1355(s), 1325(w), 1304(w), 1220(s), 1200(m), 1170(w), 1120(w), 1083(w), 1060(s), 1052(s), 930(m)cm^{-1}.

The sulphoxide was treated with an excess of thionyl chloride for eighteen hours at room temperature and then it was refluxed for four hours. Reaction did not proceed as shown by the nmr and ir spectra.

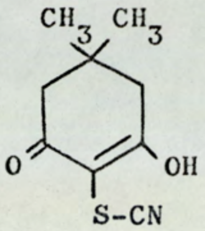
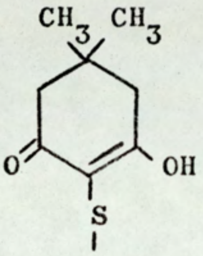
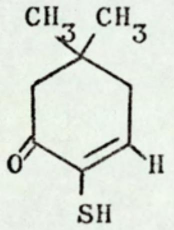
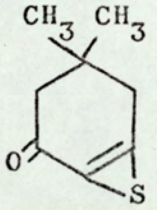
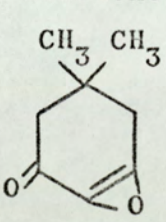
Gas evolution studies and kinetic measurements.

1.4.1.1. Sulphur dioxide evolution in dimedone-thionyl chloride reaction.

Sulphur dioxide was identified by mass spectrometry as one of the gas products of the reaction.A second confirmatory test was carried out by absorbing the gases produced in the reaction, in an aqueous solution containing an excess of hydrogen peroxide. Precipitation of the sulphate ions was then achieved by the addition of an excess of barium chloride. The method gave a qualitative estimation

TABLE 16

Mass spectrum: 2-Acetoxy-4,4-dimethyl-6-oxocyclohex-1-enyl o-nitrophenyl sulphoxide.

Mass-to-charge ratio	Fragment
197	
171	 = M^*
156	
154	
143	M^*-(CO)
139	Dimedone-(H)
138	
106	C_6H_5CHO
69	CH_3COCN
56	COCO
29	CH_3CH_2-
28	CO
27	HCN

of sulphur dioxide. However, a quantitative estimation proved to be impossible due to the inadequate method of collection of the barium sulphate powder. Coagulation of the barium sulphate salt by extensive boiling of the solution did not prove satisfactory.

Quantitative measurement of sulphur dioxide gas in the reaction of dimedone(2g) and thionyl chloride(20ml) was conducted as follows: The gases produced in the reaction mixture, were carried by a constant flow of nitrogen gas through a condenser externally cooled by ice. The gases were then passed through 700ml of 0.1N solution of iodine standarized against a 0.1N arsenic oxide solution. Aliquots(20ml) from the iodine solution were taken at different time intervals and were titrated against a standard 0.1N sodium thiosulphate solution using starch as indicator. A blank reaction containing 20ml of thionyl chloride was carried out in parallel to correct for the amount of thionyl chloride carried by the nitrogen gas. The experiment was performed twice and reproducible results were obtained.

Normality of iodine solution 0.1000N

Normality of sodium thiosulphate solution 0.1015N

20ml of 0.1000N iodine solution required 19.70ml of 0.1015N sodium thiosulphate solution.

The results have been tabulated below:

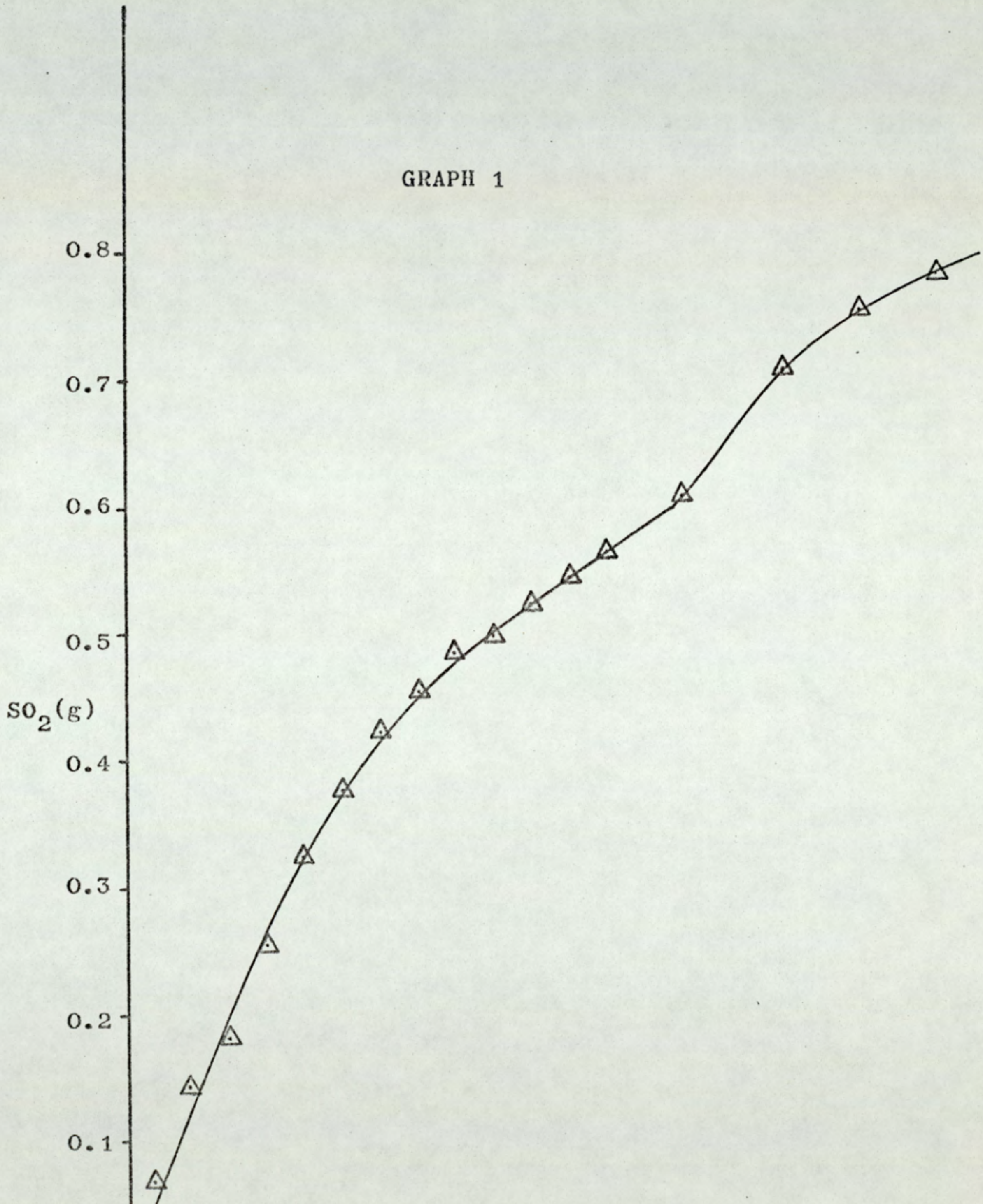
Time(min)	Sodium thiosulphate (ml)		Net	19.70-Net	Caltd. SO_2(g)
	Test sln.	Blank sln.			
10	18.95	19.55	0.60	19.10	0.0687
24	18.23	19.50	1.27	18.43	0.0739
39	17.25	19.09	1.64	18.06	0.0396
54	16.35	18.71	2.36	17.34	0.0748
69	15.40	18.44	3.04	16.66	0.0684
84	14.65	18.23	3.58	16.12	0.0526
99	13.90	17.94	4.04	15.66	0.0433
114	13.32	17.73	4.41	15.29	0.0336

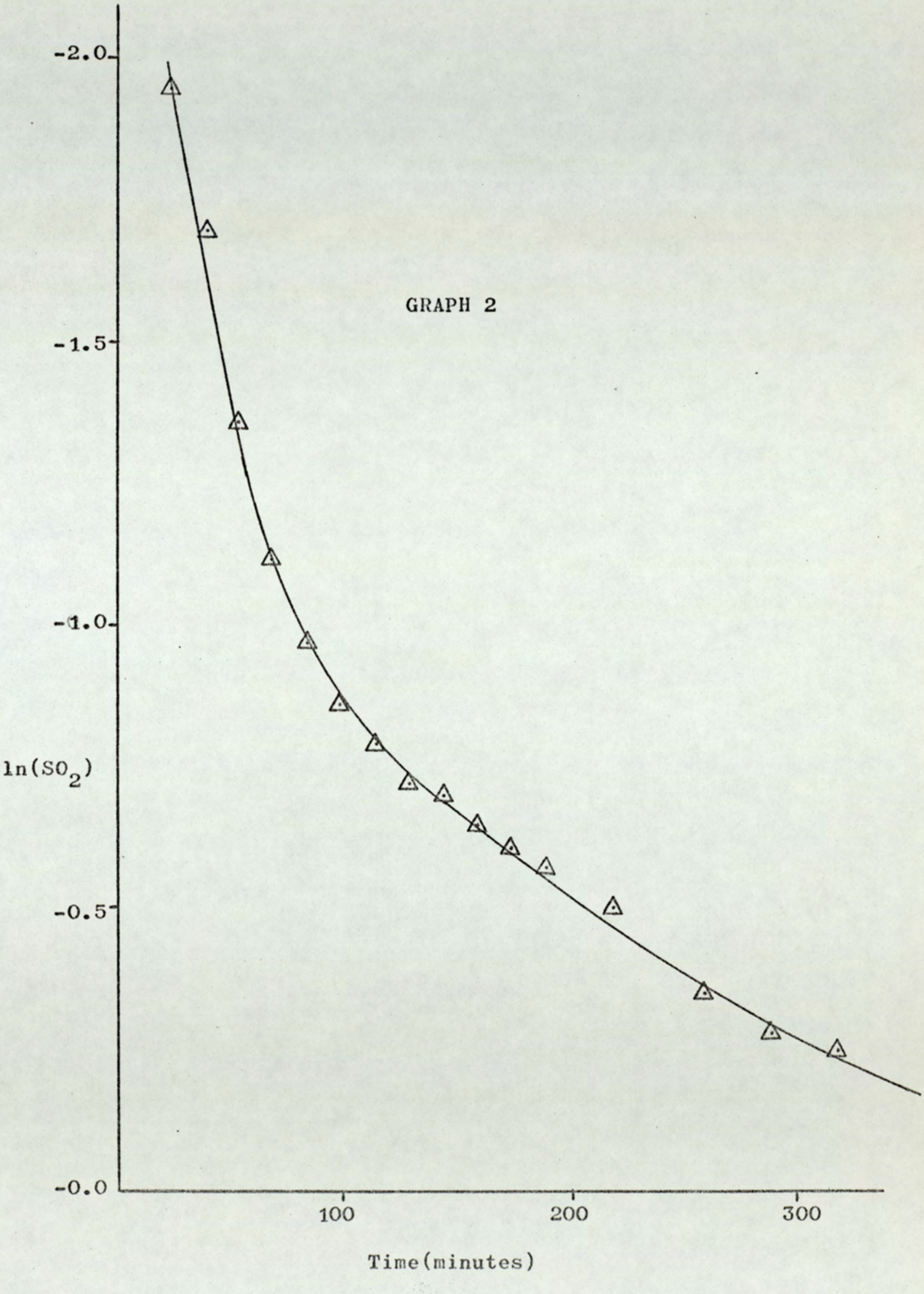
129	12.75	17.51	4.76	14.94	0.0306
144	12.31	17.21	4.90	14.80	0.0118
159	11.78	17.00	5.22	14.48	0.0259
174	11.28	16.77	5.49	14.21	0.0210
189	10.80	16.56	5.76	13.94	0.0201
219	9.81	16.18	6.37	13.33	0.0435
259	8.06	15.84	7.78	11.92	0.0961
289	7.31	15.85	8.54	11.16	0.0493
319	6.84	15.83	8.99	10.71	0.0277

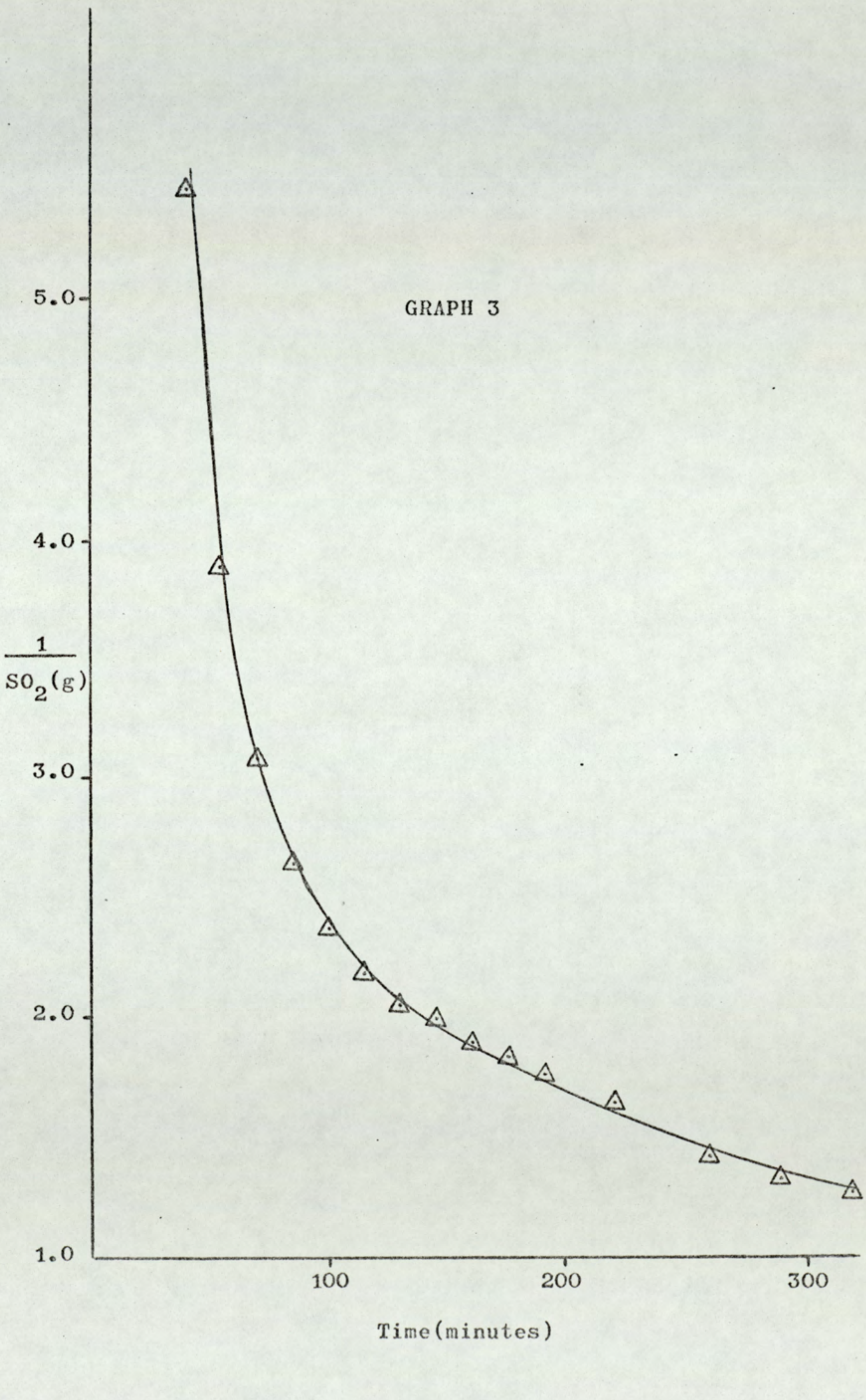
The amount of sulphur dioxide evolved, was plotted in graphs 1,2,3, as of zero, first and second order kinetics. The data for these plots is given below, while the results are discussed on page 111

Time(min)	SO_2(g)	Sum(SO_2)= X	1/x	$\log_e x$
10	0.0687	0.0687	14.555	-2.6780
24	0.0739	0.1427	7.0077	-1.9470
39	0.0396	0.1823	5.4854	-1.7021
54	0.0748	0.2571	3.8895	-1.3582
69	0.0684	0.3256	3.0712	-1.1220
84	0.0526	0.3782	2.6441	-0.9723
99	0.0433	0.4216	2.3719	-0.8636
114	0.0336	0.4552	2.1968	-0.7870
129	0.0306	0.4859	2.0580	-0.7217
144	0.0118	0.4977	2.0092	-0.6977
159	0.0259	0.5237	1.9094	-0.6468
174	0.0210	0.5448	1.8355	-0.6073
189	0.0201	0.5649	1.7702	-0.5711
219	0.0435	0.6085	1.6433	-0.4967
259	0.0961	0.7047	1.4190	-0.3499
289	0.0493	0.7541	1.3260	-0.2822
319	0.0277	0.7818	1.2790	-0.2461

GRAPH 1




-2.0
-1.5
-1.0
-0.5
-0.0
GRAPH 2
ln(SO_2)
100
200
300
Time(minutes)


GRAPH 3
5.0
4.0
3.0
2.0
1.0
$\frac{1}{SO_2(g)}$
100
200
300
Time(minutes)

1.4.1.2. Kinetic measurements of the reactions of para-substituted 1,1-dibenzoylethanes and thionyl chloride.

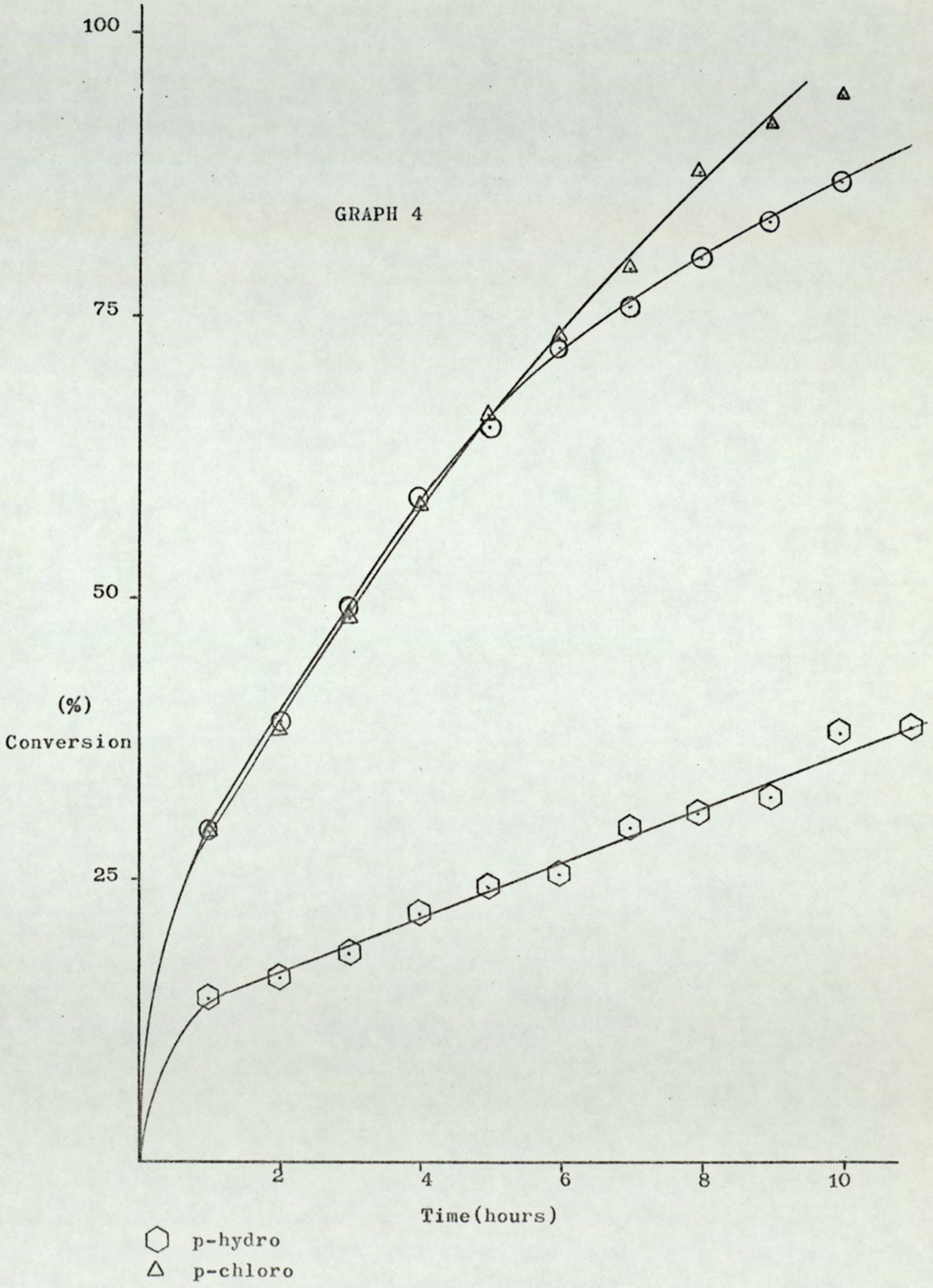
In each case the 1,3-diketone(2g) was treated with a large excess of thionyl chloride(20ml) under reflux for twelve hours. Aliquots(1.5ml), at regular time intervals, were withdrawn from each reaction mixture, the thionyl chloride was quickly removed in the rotary evaporator and the resulting oil was analyzed spectroscopically by nmr. Thus, the integral of the peak corresponding to the unchanged 1,3-diketone was measured against the integral corresponding to the sum of the peaks of the products. The nmr signal due to the alpha methyl was employed in these measurements. The results have been summarized in the following table and have been plotted in graph 4. Each experiment was repeated, but only a limited number of aliquots were withdrawn from each reaction mixture, in order to establish the reproducibility of the results.

	% Product.		
Time(hr)	p-hydro	p-chloro	p-methoxy
1	14.48	29.40	29.88
2	16.21	38.30	39.10
3	18.62	48.10	49.40
4	22.10	58.20	59.00
5	24.20	66.30	65.20
6	25.40	73.10	72.20
7	29.80	79.10	75.78
8	30.90	87.70	79.90
9	32.40	92.00	83.40
10	37.80	94.30	87.00

p-hydro = 1,1-dibenzoylethane

p-chloro = 1-benzoyl-1-p-chlorobenzoylethane

p-methoxy = 1-benzoyl-1-p-methoxybenzoylethane



GRAPH 4

100
75
50
25
(%)
Conversion
2
4
6
8
10
Time(hours)
⬡ p-hydro
△ p-chloro
○ p-methoxy

1.4.1.3. Kinetic measurements of the reaction of 1,1-dibenzoylethane and thionyl chloride in the presence of dibenzoyl peroxide.

The reaction between 1,1-dibenzoylethane(0.01 mole) and thionyl chloride(20ml) in the presence of dibenzoyl peroxide(0.001 mole) was also studied in an analogous manner to the experiment described before. (Page 76) The results have been tabulated below and have been plotted in graph 5.

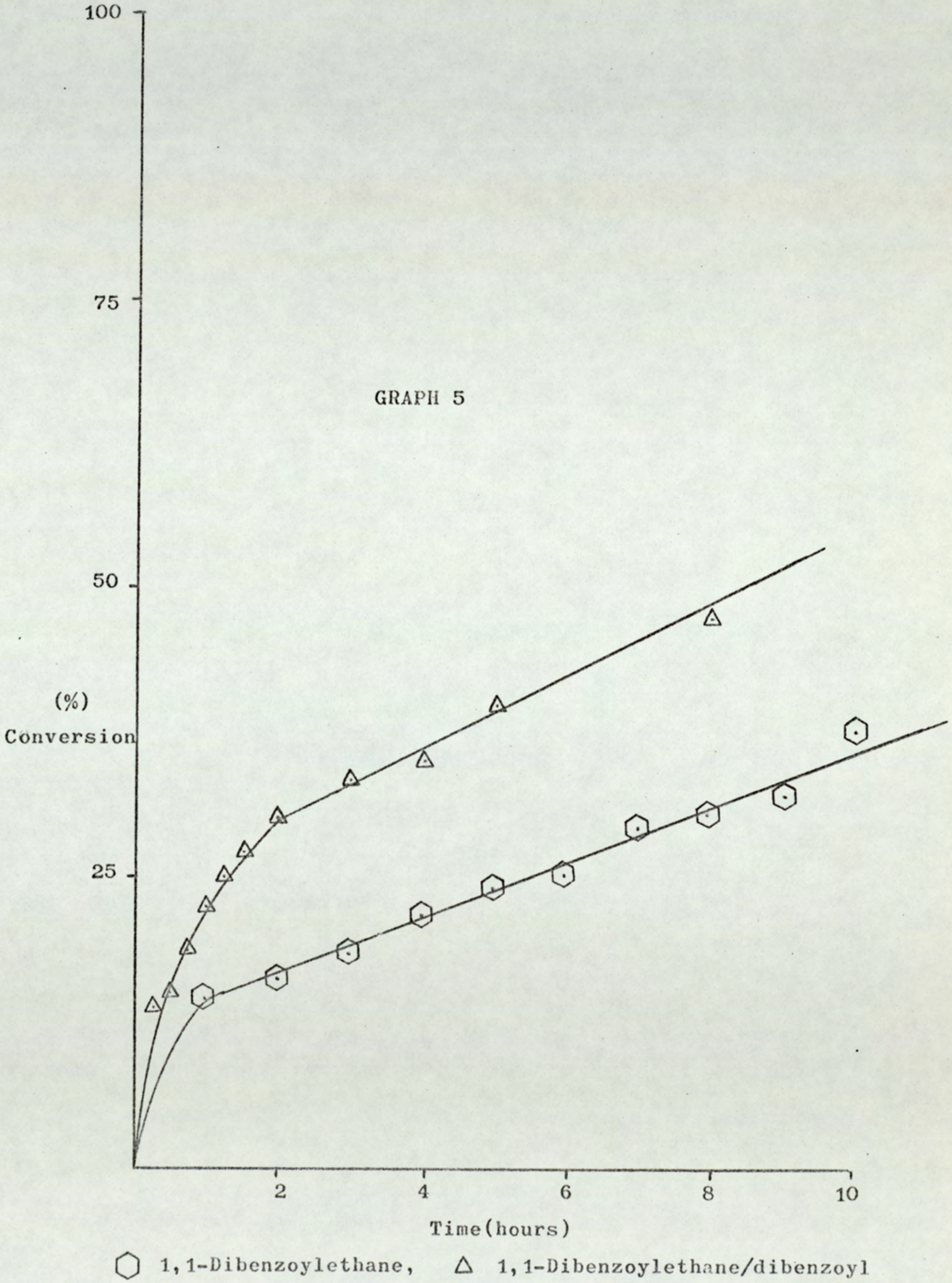
Time(hr)	% Product
1/4	13.20
1/2	15.00
3/4	18.50
1	22.60
5/4	25.00
6/4	27.00
2	30.50
3	33.50
4	35.45
5	40.00
8	48.50

Structural studies.

1.5.1.1. Variable temperature probe nmr studies on β-keto-sulphinyl chlorides.

The nmr spectrum of 2,4-dimethyl-3-oxopentane-2-sulphinyl chloride exhibited an absorption pattern which was found to be dependent on the nature of the solvent employed. Thus in carbon tetrachloride or carbon disulphide, the spectrum consisted of:

doublet	τ	8.90
singlet	τ	8.39



GRAPH 5

100
75
50
25
(%)
Conversion
2
4
6
8
10
Time(hours)
⬡ 1,1-Dibenzoylethane,
△ 1,1-Dibenzoylethane/dibenzoyl peroxide.

singlet	τ	8.31
septet	τ	6.90

In benzene or mesitylene, the spectrum consisted of the following absorptions:

doublet	τ	9.18
doublet	τ	9.21
singlet	τ	8.72
singlet	τ	8.66
septet	τ	7.29

The two doublets at τ 9.18 and 9.21 were superimposed and the septet at τ 7.29 did not show any signs of splitting when expanded. (FIG. 1a) The spectrum shown in fig.1a corresponded to the sulphinyl chloride in mesitylene(50-50% v.v.). Dilution of the solution to 25% sulphinyl chloride and 75% mesitylene altered the shape of the two doublets at τ 9.18 and 9.21, which were transformed into a triplet shown in fig.2b.

Low temperature nmr was employed in order to show that the two doublets at τ 9.18 and 9.21 exhibited in benzene and mesitylene, could also be produced in a relatively non-polar solvent like carbon disulphide by reducing the temperature. At -70° the doublet at τ 8.90 broadened considerably and at -100° it split into four singlets while the other two singlets at τ 8.39 and 8.31 corresponding to the gem-dimethyls adjacent to the sulphinyl chloride group remained unaltered.

The non-equivalence of the gem-dimethyls adjacent to the sulphinyl chloride group was also examined in benzene over a temperature range of 100°. The results are shown in the following table and have been plotted in graph 6.

Temperature (°C)	Separation (Hz)
31	8.60
39	8.45

48	7.85
60	7.65
70	7.40
80	7.10
112	6.30
132	5.70

Figure 1a.

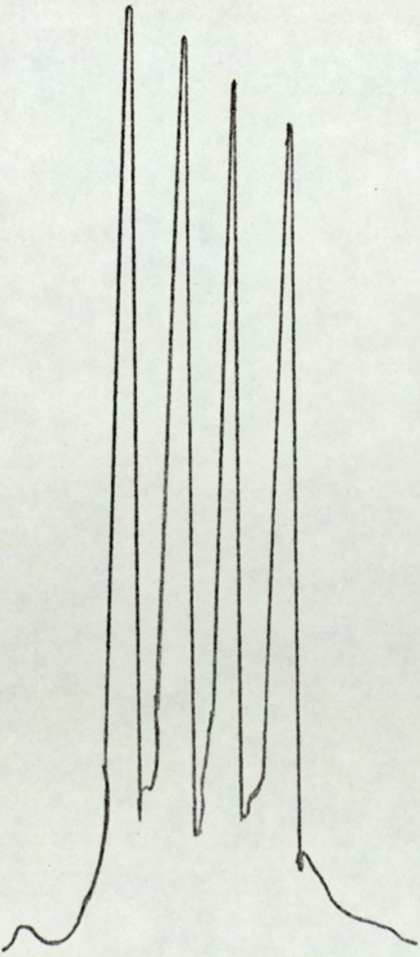
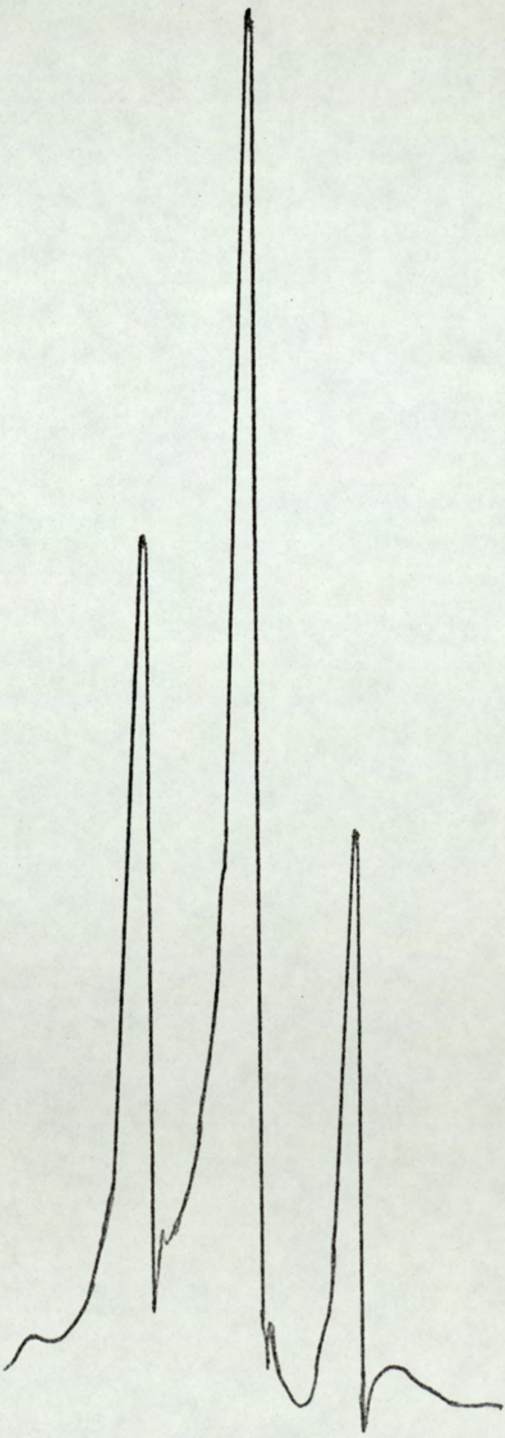
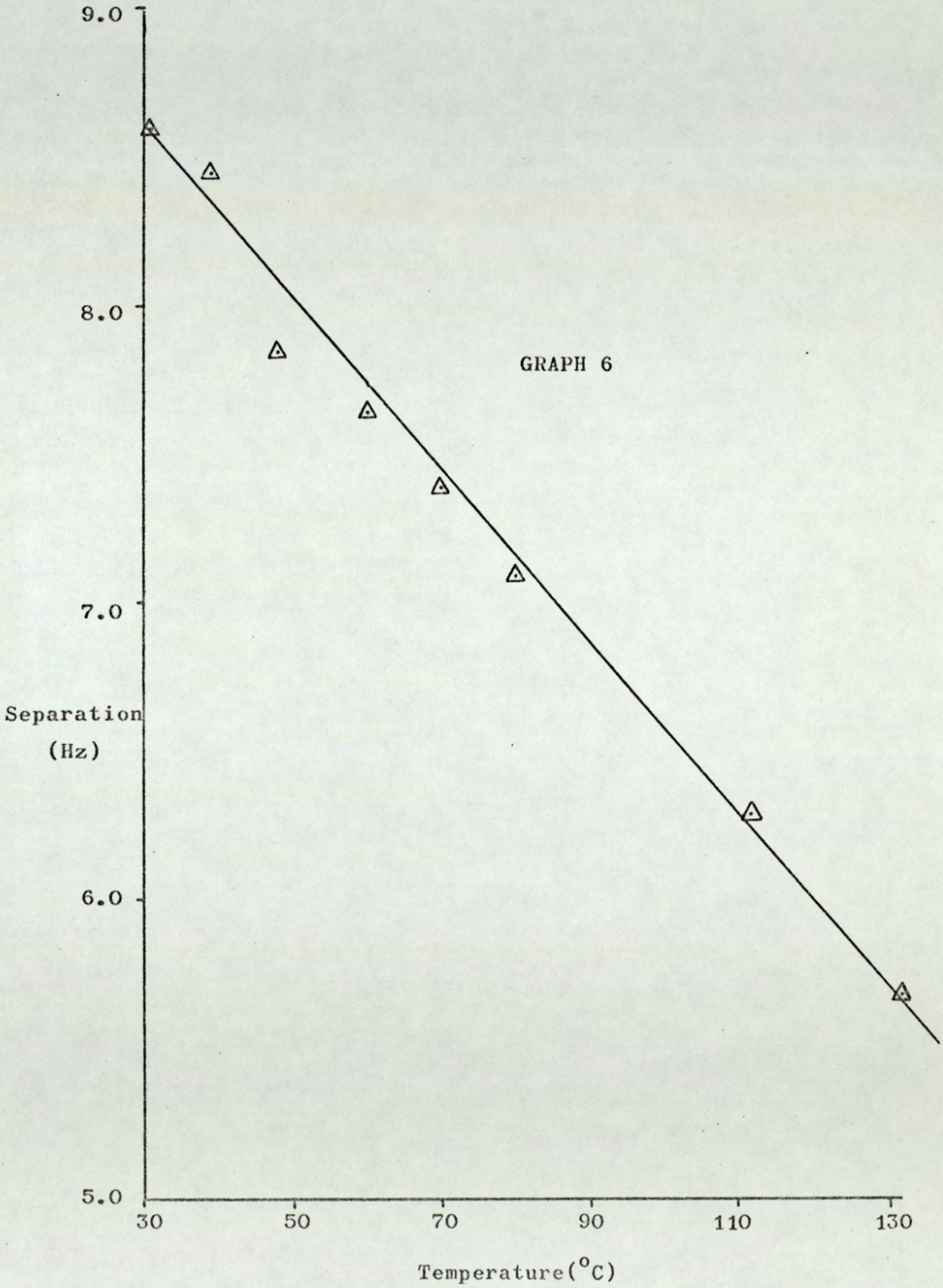


Figure 2b.




9.0
8.0
7.0
6.0
5.0
Separation
(Hz)
30
50
70
90
110
130
Temperature(^oC)
GRAPH 6

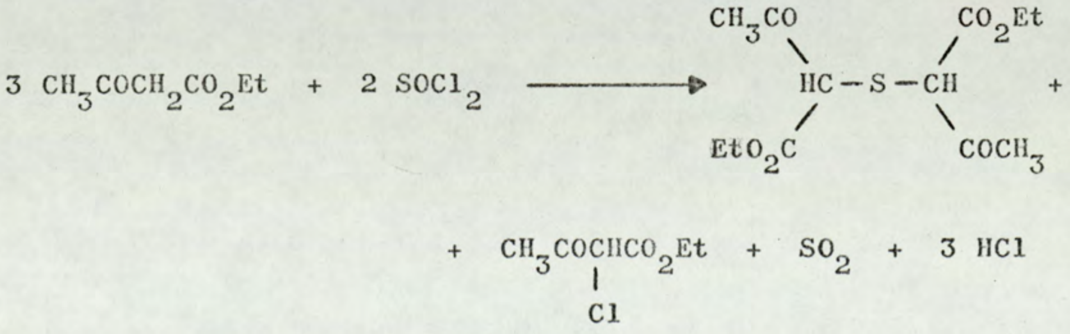
CHAPTER 2

DISCUSSION

2.1. 1,3-DIKETONES AND THIONYL CHLORIDE.

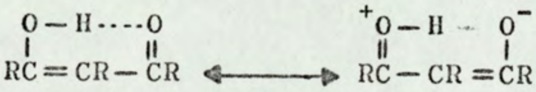
In the previous chapter,no attempt was made to justify and clarify the experimental procedures and results which have been given, as it was felt that such an approach would interfere with the continuity of the text. This chapter therefore deals with the experimental results in more detail and attempts to establish the structural requirements necessary for the formation of each class of compounds. The emphasis has been placed mostly on the formation of sulphides, disulphides and trisulphides, as well as the production of β-ketosulphinyl chlorides a class of compounds which have not been previously reported in the literature. Sulphinyl chlorides have been postulated as intermediates in a variety of reactions of thionyl chloride but have never been isolated as such.

Three examples of the 1,3-diketo-structure which gives rise to sulphides on treatment with thionyl chloride have been reported[24,25] in the literature. The reaction of ethyl acetoacetate with thionyl chloride has been shown to proceed smoothly at room temperature to give bis(acetylethoxycarbonylmethyl) sulphide (ethyl acetoacetate sulphide), as the only reported product. An attempt to reproduce the reaction, afforded a second product which was isolated and identified as ethyl α-chloroacetoacetate. The formation of the chloride offered an explanation for the unaccounted absence of two chlorine atoms from the stoichiometric equation:

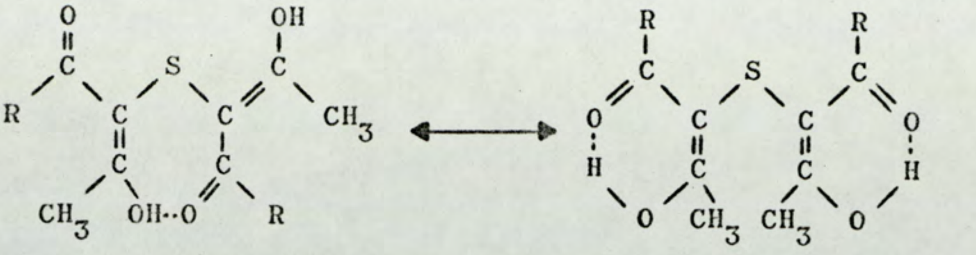


$$3\,CH_3COCH_2CO_2Et + 2\,SOCl_2 \longrightarrow (CH_3CO)(EtO_2C)HC{-}S{-}CH(CO_2Et)(COCH_3) + CH_3COCH(Cl)CO_2Et + SO_2 + 3\,HCl$$

The structure of the sulphide was extensively investigated because it was originally thought that the compound which had been isolated was the sulphoxide rather than the reported sulphide. The formation of a different product from the sulphide was supported by the large deviation between the reported[24] melting point of 100-01° and the observed melting point of 117-19°. It was therefore decided to prepare the sulphide by another route in order to clarify the situation beyond doubt. Disulphur dichloride was employed and the crystalline compound which was isolated from its reaction with ethyl acetoacetate possessed identical spectroscopic and physical characteristics to the postulated sulphide obtained from the reaction between ethyl acetoacetate and thionyl chloride. An absorption peak in the nmr spectrum at $\tau = -3.40$ indicated that the compound existed wholly in the enolic form. Confirmation of the enolic structure also came from the ir spectrum which exhibited a broad weak band at 2730cm^{-1} indicative of an oxygen-hydrogen streching mode. This streching vibration is the normal hydroxyl vibration shown by alcohols at 3333cm^{-1} only it has been shifted through intramolecular resonance in an analogous manner[74] to that encountered in acetylacetone:



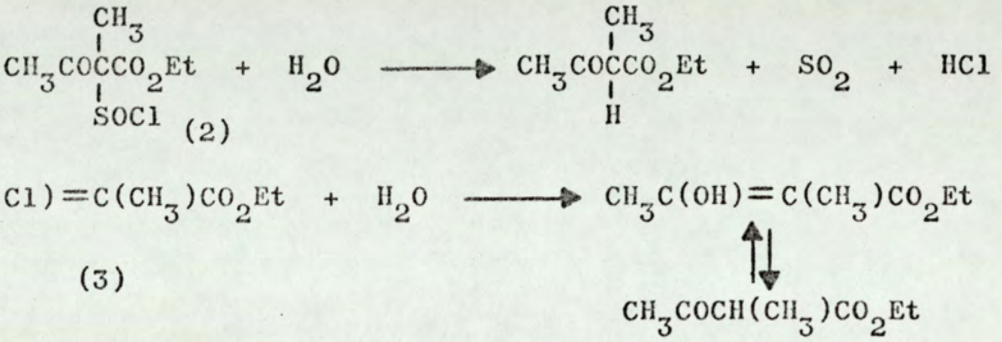
The carbonyl group of the enol form of the sulphide absorbed strongly in the 1615cm^{-1} region thus masking a possible double bond absorption at 1600cm^{-1}. Eventhough no absorptions derived from the keto form were detected in the nmr spectrum, a very small amount of the keto form appears to be present and absorbs weakly at 1750cm^{-1}. No sulphoxide absorption at 1040-1060cm^{-1} could be detected. The mass spectrum (table 7) which exhibited a molecular ion peak at 290 mass units coupled with the elemental analysis (page 48) and the ir and nmr information, confirmed beyond doubt the structure of the sulphide(1):


(1)

R= CH_3CH_2O-

The ethyl α-chloroacetoacetate was also prepared from the reaction of ethyl acetoacetate with sulphuryl chloride, a route proposed by Wyman[59] and frequently employed throughout this work whenever the synthesis of an α-ketochloride was found to be necessary. Comparison of the spectroscopic properties and physical constants of that sample with the ethyl α-chloroacetoacetate isolated from the reaction between ethyl acetoacetate and thionyl chloride proved beyond doubt that the compounds were identical (p.37,48).

The reaction of ethyl α-methylacetoacetate with thionyl chloride afforded a two component mixture which did not correspond to the products obtained from ethyl acetoacetate and thionyl chloride. This deviation from the normal pattern of the reactions of alpha-unsubstituted 1,3-diketones and thionyl chloride, was thought to arise from the alpha substitution as will be discussed later on in this thesis. The ir spectrum of the reaction mixture(p.32), showed a strong peak at 1168cm^{-1} which corresponded to the sulphinyl absorption of the ethyl α-chlorosulphinyl-α-methylacetoacetate(2) and was absent in the starting material. In addition, a medium intensity peak at 1630cm^{-1} revealed the presence of a double bond, which could possibly belong to ethyl 3-chloro-2-methylcrotonate(3). Both of these observations were confirmed from the mass spectrum of the reaction mixture which exhibited a peak at 226 mass units followed by the isotopic peak at 228 mass units belonging to the α-sulphinyl chloride(2). Another peak at 162 mass units could also arise from the substituted ethyl crotonate(3). An attempted distillation of the reaction mixture failed to produce a good separation, whilst column chromatography decomposed the two components and afforded ethyl α-methylacetoacetate in high recovery. Decomposition of (2) and (3) was thought to arise from small amounts of water present in the A.R. solvent employed in the elution process, and a plausible reaction sequence which takes into account the the observed inherent instability of β-ketosulphinyl chlorides is given below:



$$CH_3CO\overset{CH_3}{\underset{SOCl}{C}}CO_2Et + H_2O \longrightarrow CH_3CO\overset{CH_3}{\underset{H}{C}}CO_2Et + SO_2 + HCl$$

(2)

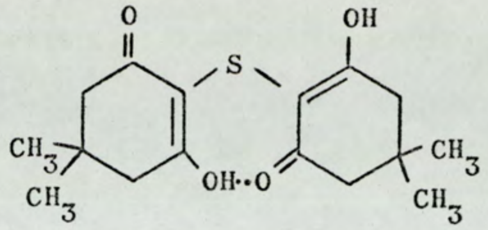
$$CH_3C(Cl){=}C(CH_3)CO_2Et + H_2O \longrightarrow CH_3C(OH){=}C(CH_3)CO_2Et + HCl$$

(3)

$$CH_3C(OH){=}C(CH_3)CO_2Et \rightleftharpoons CH_3COCH(CH_3)CO_2Et$$

Ethyl α-chloro-α-methylacetoacetate was not found amongst the products from the reaction of ethyl α-methylacetoacetate and thionyl chloride. The α-chloride was synthesized by a route employing sulphuryl chloride, and mixed nmr and glc of the α-chloride with the reaction mixture which contained the crotonate (3) and the α-sulphinyl chloride(2) supported the above statement.

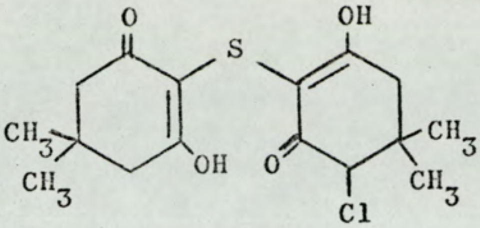
Other compounds possessing the 1,3-diketo-structure might also be expected to afford sulphides and α-chlorides when treated with thionyl chloride. Dimedone satisfied the structural requirements and in addition it was found to exist partly in the enolic form a feature which would be expected to assist the reactivity of the molecule towards thionyl chloride. In fact it was found that dimedone reacted with thionyl chloride at a much faster rate than did ethyl acetoacetate, partly due to the existence of the 58%($CDCl_3$) enol present in equilibrium with the ketone, and partly due to the cyclic nature of the molecule exposing the active methylene group and thus excluding the possibility of steric hindrance from neighbouring groups. The sulphide isolated from this reaction was again found to exist wholly in the enolic form and was assigned the structure(4):



(4)

The characteristic enolic absorption of the hydroxyl group in the nmr spectrum, appeared at τ -0.40 (p.44) whereas the equivalent absorption in the ir spectrum appeared at 2650cm^{-1} as a broad weak band. The carbonyl absorption in the ir showed an interesting pattern composed of two strong peaks at 1615cm^{-1} and 1570cm.$^{-1}$ The former was assigned to the intramolecularly bonded carbonyl of the enolic form, while the second absorption at 1570cm^{-1} was assigned to the intermolecularly [75] bonded carbonyl group. The overall confirmation of the structure and composition of the sulphide was obtained from the elemental analysis and mass spectrum. The second product, 2-chloro-5,5-dimethylcyclohexane-1,3-dione, was found, using the nmr spectrum, to exist solely in the keto-form and showed identical physical and spectroscopic properties to an authentic sample prepared by the action of sulphuryl chloride on dimedone.

The conditions employed in the reaction between dimedone and thionyl chloride had to be carefully controlled in order to minimize further reaction of the sulphide with thionyl chloride. The products of such a reaction were not fully investigated but it was established that the sulphide reacted further with thionyl chloride. It is believed that the 4- and 6- positions of the ring, activated by the adjacent carbonyl groups, can be further substituted as soon as the sulphide is formed. Thus, polymeric sulphides can arise, their formation accompanied by the production of two chlorine atoms per new sulphide link formed. A probable monomeric product from the series of chlorinated polymeric sulphides which could then arise, was identified by mass spectrometry(5):



(5)

A molecular ion peak at 344 mass units was obtained and corresponded to $C_{16}H_{21}ClO_4S$. The mass spectrum also provided more evidence which pointed to further substitution of the ring. The peak at 140 mass units which was encountered in the spectrum of dimedone sulphide and corresponded to dimedone, was replaced by two strong peaks at 136 and 138 mass units in the spectrum of the product obtained from the exhaustive reaction of dimedone with thionyl chloride. The loss of four and two protons respectively could probably be attributed to a polysubstituted dimedone. The elemental analysis of the crude polymeric chlorosulphide gave the following results summarized in the following table:

Polymeric chlorosulphide (%)		Dimedone sulphide (%) Theor.	
C	41.67	C	62.00
H	4.02	H	7.10
S	14.75	S	10.32
Cl	15.31	Cl	NONE

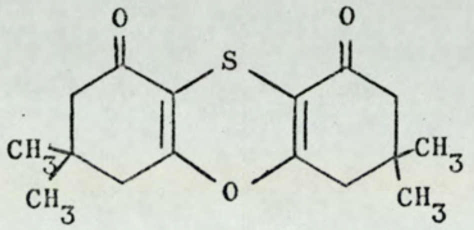
It is clearly seen that the increase in the sulphur and chlorine figures of the polymeric chlorosulphide relative to dimedone sulphide could be attributed to the added sulphur links and substitution by chloride. The added groups increase the molecular weight of the compound thus lowering the carbon and hydrogen analytical figures. The hydrogen analytical results of the polymeric chlorosulphide has been lowered by 38% relative to a 24% decrease in the carbon figure.

The deviation is explained if one considers the loss of hydrogen atoms through substitution by other atoms or groups such as sulphur and chlorine.

Further evidence which pointed to substitution of the 4- and 6-positions of the ring, came from the nmr spectrum of the crude product obtained from the reaction of dimedone sulphide(4) with an excess of thionyl chloride. The integration of the methylene and methyl groups, which should in theory be in the ratio of 4:6 if further substitution did not take place, changed to 3.1:6 in the crude product obtained from the reaction.

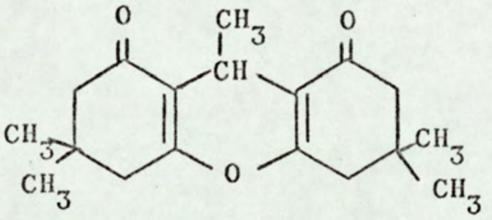
Optimization of the yield of dimedone sulphide(4) was considered to be a necessary step once it was established that further reaction of the sulphide with thionyl chloride took place. The parameters involved in such an investigation were the amount of thionyl chloride used in the reaction, the reaction time allowed, and the temperature of the reaction which was always maintained at $22\mp1^\circ$. Unfortunately a solvent had to be employed when a variety of molar ratios of thionyl chloride to dimedone were examined, which considerably slowed the reaction down. Long reaction times had to be allowed which either produced polymeric chlorosulphides when excess of thionyl chloride was employed, or afforded amounts of unchanged dimedone when the molar ratios of thionyl chloride to dimedone was small. The investigation was therefore concentrated on the reaction time allowed when an excess of thionyl chloride was employed. The results have been plotted in graph 7 while the data is shown in page45, and it is seen that the yield of the sulphide shows a maximum at approximately sixty minutes from the beginning of the reaction. The graph is in accordance with a consecutive reaction, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ where k_1 is slightly larger than k_2, B corresponds to the sulphide(4) and C is the polymeric chlorosulphide.

An attempted cyclization of dimedone sulphide(6) failed to produce definite results when zinc chloride was employed. An impure compound was isolated exhibiting four singlets of equal intensities in the nmr spectrum which possibly corresponded to the dimethyl groups of the cyclohexane rings, and another four similar singlets which corresponded to the methylene groups.



(6)

The nmr spectrum could only be accounted for in terms of two different conformations of (6) and it was decided to prepare another cyclic compound (7) using the reaction between dimedone and acetaldehyde, followed by treatment of the product with acetic anhydride.[35] The anhydride which was thus prepared is shown below:



(7)

The spectral characteristics of (7) consisted of two singlets which corresponded to the methyl and methylene groups. The compound which had been prepared from the reaction with zinc chloride, was therefore believed not to correspond to (6) unless substitution of the sulphur atom by a tetrahedral carbon atom produced such a pronounced effect on the stereochemistry of the molecule.

The anhydride (6) was later prepared by a reported[25] method which employed acetic anhydride in pyridine as the solvent. The compound (6) which was isolated, had a bright golden-yellow colour in contrast to the anhydride (7) which was white. It was concluded that the introduction of the sulphur atom in (6) had some pronounced effect on the electronic structure of the molecule, possibly due to the availability of the unpaired electrons and d orbitals of the sulphur atom.

Acetylacetone reacts with thionyl chloride at a much faster rate than either ethyl acetoacetate or dimedone. Two products were isolated from the tarry reaction mixture, 3-chloropentane-2,4-dione and bis(diacetylmethyl) disulphide, rather than the expected sulphide. The disulphide exhibited the normal spectral characteristics of the sulphides of dimedone(4) and ethyl acetoacetate(1) already discussed and its structure was unambiguously confirmed by synthesis via a route employing disulphur dichloride. During this last preparation, a second product identified as bis(diacetylmetyl) trisulphide was isolated from the reaction mixture. The trisulphide possessed an identical ir spectrum to the disulphide, whilst its nmr spectrum showed a small downfields shift of the methyl group absorption, compared to the disulphide, in accordance with its slightly increased electonegativity due to the added sulphur atom, and analogous to the observed difference between the bis(1,1-dibenzoylethyl) disulphide and trisulphide. 3-Chloropentane-2,4-dione was also synthesized via a route which employed sulphuryl chloride, and exhibited identical spectral and physical characteristics to the α-chloride isolated from the reaction of acetylacetone and thionyl chloride.

A typical property of 1,3-diketones which was early recognised was their ability to sustain an equilibrium between their enolic and ketonic forms. Thus, the compounds exhibit both ketonic and alcoholic properties and in some cases the pure tautomers have been isolated by distillation in quartz apparatus, which is a less basic material than glass, and by other techniques. If an analogous behaviour to that encountered with alcohols were accepted, the enol form would be expected to be less volatile than the keto form. In fact, the opposite effect has been experimentally observed which indicated that the enolic tautomer formed strong intramolecular hydrogen bonds rather than the expected alcoholic intermolecular bonds.

The keto-enol equilibrium of a particular compound is dependent on the solvent employed, the concentration, and the temperature. A quantitative treatment which has been found to produce consistent results and deals with the solvent effects which affect the equilibrium has been reported.[76] Thus, for an equilibrium of the type:

$$\text{Keto} \rightleftharpoons \text{Enol}$$

the equilibrium constant K can be defined in terms of the respective concentrations as:

$$K = \frac{[\text{Enol}]}{[\text{Keto}]} \qquad \text{(eq.1)}$$

Working on the assumption that the concentration of each tautomer is a function of the solubility S of that tautomer in a particular solvent, the constant G can be obtained:

$$G = \frac{[\text{Enol}] / S_{\text{enol}}}{[\text{Keto}] / S_{\text{keto}}} \qquad \text{(eq.2)}$$

and introduction of the constant G in eq.1 gives eq.3:

$$G = K \frac{S_{\text{keto}}}{S_{\text{enol}}} \qquad \text{(eq.3)}$$

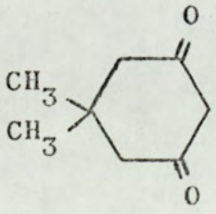
which upon rearrangement gives eq.4:

$$K = G \frac{S_{\text{enol}}}{S_{\text{keto}}} \qquad \text{(eq.4)}$$

Application of equation 4 to α-benzoylcamphor[76] in a number of solvents, indicated that G is fairly constant and therefore the assumption made during the derivation of eq.4 is valid. The results are shown in the following table:

Solvent.	K	S_{enol}/S_{keto}	G
ethyl ether	6.81	6.39	1.06
ethyl acetate	1.98	1.81	1.09
ethyl alcohol	1.67	1.57	1.06
methyl alcohol	0.87	0.75	1.15
acetone	0.85	0.80	1.06

Structural changes in the 1,3-diketo structure have also been found responsible for large deviations in the percentage of keto-enol equilibrium mixtures. Eventhough a quantitative treatment has not been formulated as yet, an obvious conclusion may be drawn. Thus, the introduction of most groups in the alpha position, significantly reduces the amount of the enolic tautomer present. A table of some 1,3-diketones and their percentage enol concentrations in various solvents is given below:[76]

Compound.	% enol		
	Pure liquid.	0.1M hexane	H_2O
$CH_3COCH_2COCH_3$	76-80	91.4-92	15.5
$CH_3COCH(CH_3)COCH_3$	30-31	58.5-59.4	2.80
$CH_3COCH(CH_2CH_3)COCH_3$	26-27	26.2-26.7	-
$CH_3COCHBrCOCH_3$	-	-	8.1
$CH_3COCH_2CO_2Et$	7	49	-
$CH_3COCH(CH_3)CO_2Et$	4	11	-
$CH_3COCH_2CO_2Et$	6	-	-
	-	-	95.3

This part of the thesis deals with the mechanistic aspects of the formation of sulphides and α-chlorides from the reaction between 1,3-diketones and thionyl chloride. In the majority of cases, the reaction proceeded to the formation of sulphur containing conpounds eventhough the isolation of the compounds could not always be achieved due to the large number of by-products present. The only 1,3-diketones which have been shown to behave in a different way, were malonic esters which gave tetra-alkoxycarbonylethylenes, possibly via a carbanion reaction as will be explained later in this chapter.

The mechanism of the reaction of 1,3-diketones and thionyl chloride could proceed by either an ionic or by a free radical route. It was therefore decided to investigate these possibilities before any further mechanistic work was performed. Addition of styrene to the dimedone-thionyl chloride reaction did not produce any change in the products and at the end of the reaction the unchanged styrene was recovered in good yield. If a free radical step were involved during the reaction, it would have been expected to initiate the polymerization of styrene. However, the life time of the free radical would almost certainly determine its reactivity towards styrene.

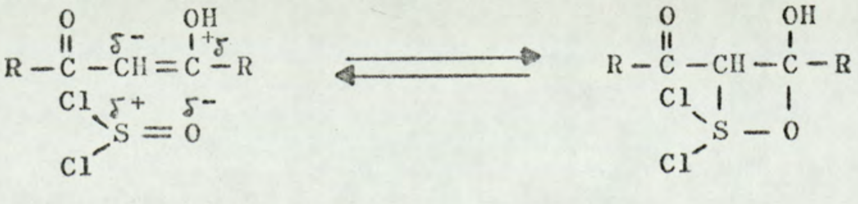
Chemically induced dynamic nuclear polarization (CIDNP), is a fairly new procedure which involves nmr techniques in the detection of free radical intermediates. Classical quantum theory predicts that a proton which has a spin quantum number of a half, can possess two orientations in space once it is placed in a static magnetic field. These are the so-called upper and lower spin states of the proton. Transitions can be induced between these two spin states by the application of a rotating magnetic field perpendicular to the static magnetic field. The probability of an upward transition accompanied by absorption of energy is equal to the probability of a downward transition followed by emission. The net effect would therefore be nil if it were not for a slight excess of nuclei in the lower spin state, and governed by the classical Boltzmann distribution law. The excess of nuclei in the lower spin state, always maintained by relaxation processes, is responsible for the observed absorption of energy. CIDNP,[77] is based on a perturbation of the two spin states which is brought about by the formation of an intermediate free radical. The net result is a small excess of nuclei in the upper spin state, which gives rise to a negative nmr signal. The method has been succesfully applied to the reaction of n-butyl-lithium and isopropyl iodide[68] which is known to proceed by a free radical mechanism. This reaction was simulated in order to establish the experimental technique, and strong negative signals were observed. However, when CIDNP was applied to the reaction of dimedone or acetylacetone with thionyl chloride, no signs of free radical intermediates were detected, a strong indication that the reaction proceeded via an ionic rather than a free radical mechanism.

The reaction of 1,3-diketones with thionyl chloride can proceed via the keto or enol form, depending upon the acidity of each form and upon the approach of the thionyl chloride molecule. A rough estimate of acidities in organic compounds can be obtained from their nmr spectra, eventhough paramagnetic effects act in parallel to diamagnetic effects and they sometimes have a strong influnce on the absorption positions(eg benzene). The overall trend shows that low-field absorptions can be associated with higher acidities once only diamagnetic effects are in operation. Thus, aldehydes and acids appear tp obey this rule and 1,3-diketones also give hydroxyl absorptions between $\tau=0$ and $\tau=-7$, in accordance with the previous arguments. The acidity of 1,3-diketones is also shown by the ready formation of salts.

Acetylacetone was the first compound to be studied and it was shown that the addition of thionyl chloride shifted the equilibrium completely to the enol, before reaction had commenced. Similarly when dimedone was treated with thionyl chloride in chloroform the enolic tautomer of the compound precipitated out immediately and subsequent isolation of the compound indicated that recrystallization from water changed the enolic form to give the normal keto-enol equilibrium mixture. Thionyl chloride was therefore considered to be responsible for the observed effect on dimedone. A simple explanation which involved the polarity of thionyl chloride was dismissed when the reported data[76] on the effect of the polarity of the solvent on the keto-enol equilibrium percentages of ethyl acetoacetate were examined. A table of these effects is shown below:

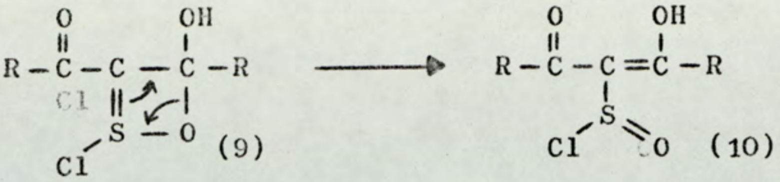
Solvent	% Enol	Solvent	% Enol
Water	0.4	Ethyl alcohol 50%	2.18
Acetic acid	5.74	Propyl alcohol(0°C)	12.45
Methyl alcohol	6.87	Ethyl acetate	12.9
50% Methyl alcohol	1.52	Amyl alcohol	15.33
25% Methyl alcohol	0.83	Benzene	16.2
Acetone	7.30	Toluene	19.8
Pure ester	7.71	Xylene	23.4
Chloroform	8.19	Ethyl ether	27.1
Nitrobenzene	10.1	Carbon disulphide	32.4
Ethyl alcohol(0°C)	12.00	Hexane	46.4
Ethyl alcohol(18°)	10.52	Vapour phase	45.3-51.6
Ethyl alcohol 96%	8.7		

It is clearly seen that the percentage enol concentrations increase quite drastically by decreasing the polarity of the solvent. Thionyl chloride is a very polar molecule and it would therefore be expected to favour the keto rather than the enol form. A more reasonable explanation would involve an electrostatic complex(8) between the polarized sulphur-oxygen bond of thionyl chloride and the double bond of the enolic form of the 1,3-diketone:

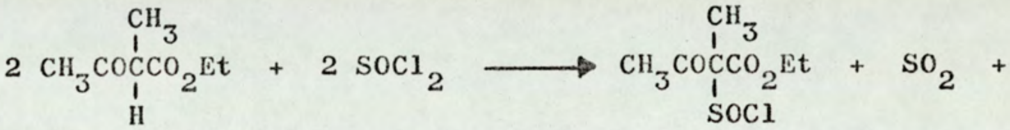


(8)

Elimination of hydrogen chloride from (8) can then give (9) which on a subsequent shift of electrons produces the α-sulphinyl chloride(10)

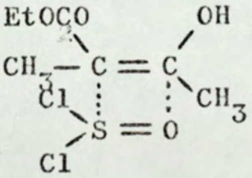


The mechanism is supported by the reaction of ethyl α-methylaceto acetate and thionyl chloride which gave ethyl α-chlorosulphinyl-α-methylacetoacetate and ethyl 3-chloro-2-methylcrotonate according to the equation:



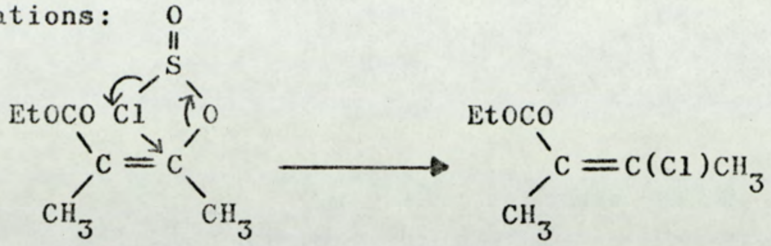
$$2\ CH_3CO\underset{H}{\overset{CH_3}{C}}CO_2Et + 2\ SOCl_2 \longrightarrow CH_3CO\underset{SOCl}{\overset{CH_3}{C}}CO_2Et + SO_2 + CH_3C(Cl){=}C(CH_3)CO_2Et + 2\ HCl$$

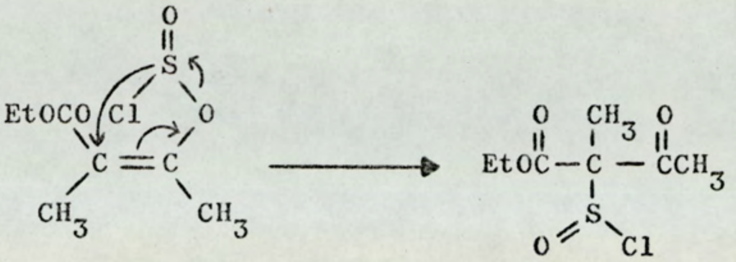
Here the introduction of the methyl group in the α-position excludes the possibility of elimination of a molecule of hydrogen chloride during the steps (8)→(9), and the reaction subsequently follows a different path. The formation of a complex (11) is still considered feasible but the complex is not likely to be as stable as (8) since the methyl group can donate electrons to the α-carbon of (11) and hence make it less electronegative than the unsubstituted compound(8).



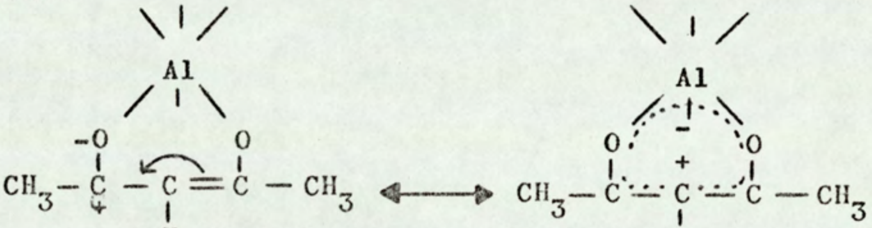
(11)

The complex (11) is thus open to attack by another molecule of thionyl chloride on the hydroxyl group, in the same manner encountered in the reactions of alcohols with thionyl chloride. Elimination of a molecule of hydrogen chloride can then afford the chlorosulphite (12) which can rearrange in two ways. Evolution of a molecule of sulphur dioxide produces the chloride (13) whilst rearrangement of of the chlorosulphite produces the sulphinyl chloride(14) according to the equations:

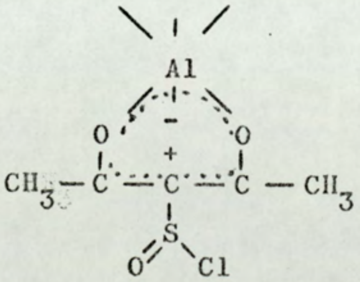

(12) (13)


(12) (14)

Another point in support of the electrostatic complex(8) came from the reaction of the aluminium triacetylacetonate complex (15) (16) with thionyl chloride. The nmr spectrum of the complex indicated that it existed in the isomeric forms (15) and (16) which contained one α-proton:

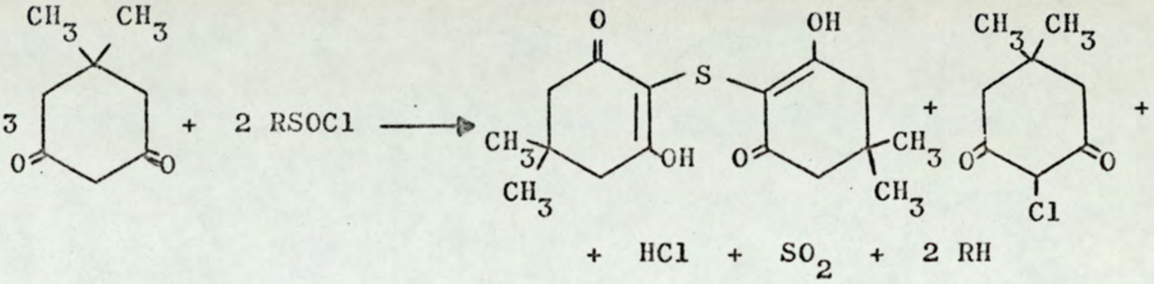

(15) (16)

The complex reacted readily with thionyl chloride to afford the sulphinyl chloride(17) which unfortunately decomposed in air. However the ir spectrum showed a strong sulphinyl absorption at 1149cm^{-1} whilst the nmr spectrum indicated that the α-protons had been substituted.


(17)

The complex (17) could well be formed through interaction of the double bond with a molecule of thionyl chloride according to the proposed mechanism (8) → (9) → (10). The direct elimination of a molecule of hydrogen chloride from the enolic species (15) is impossible due to the existing aluminium-oxygen bonds.

Eventhough ethyl α-chlorosulphinyl-α-methylacetoacetate and aluminium tri-α-chlorosulphinylacetylacetonate(17) were identified, the analogous α-sulphinyl chlorides of dimedone and ethyl acetoacetate could not be detected as intermediates in the formation of sulphides. However, their presence as intermediates was strongly indicated in the reaction between dimedone and a sulphinyl chloride, preferably a β-ketosulphinyl chloride:



The ketone RH was isolated and identified(p.64) but 2-chloro-5,5-dimethylcyclohexane-1,3-dione could not be isolated. Indirect evidence for its formation was obtained through thin layer chromatography. Thus, an authentic sample of the chloride gave the same R_f value as a sample of the reaction mixture which was thought to include the chloride. Two solvent systems were employed as eluents to avoid coincidental occurence of identical R_f values belonging to different compounds. An equilibrium of the type

$$RSOCl + R'H \rightleftharpoons R'SOCl + RH$$

was formulated for the reaction, which proceeded to completion more readily with a β-ketosulphinyl chloride than with adamantyl-1-sulphinyl chloride. The observed reactivity agrees well with the weak carbon-sulphur bond of the β-ketosulphinyl chlorides which have been shown to cleave much more readily than other sulphinyl chlorides. Thus, adamantyl-1-sulphinyl chloride is stable in water which is employed during its isolation from the reaction mixture, whereas all β-ketosulphinyl chlorides react with water according to the proposed equation:

$$RSOCl + H_2O \longrightarrow RH + HCl + SO_2$$

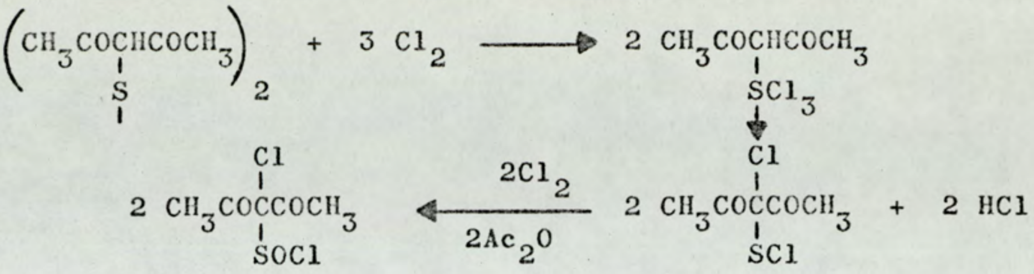
The proposed α-sulphinyl chloride intermediate involved in the reaction of 1,3-diketones and thionyl chloride should show a strong ir absorption if it possessed a detectable lifetime. However, when the reaction of ethyl acetoacetate and thionyl chloride was followed by ir, at no time could the sulphinyl absorption peak be detected, eventhough the reaction proceeded normally. The inability to observe the intermediate was attributed to the rapid reaction of the α-sulphinyl chloride not allowing a detectable concentration to occur.

Once it was indicated from the reaction between dimedone and a sulphinyl chloride, that the α-sulphinyl chloride of the 1,3-diketones could be a possible intermediate in the formation of sulphides, it was decided to prepare the α-sulphinyl chloride by a different route and study its reactios with 1,3-diketones. A reported[53] synthesis of sulphinyl chlorides involved the reaction of the disulphide or thiol with chlorine and acetic anhydride in stoichiometric quantities:

$$RSSR + 3\,Cl_2 + 2\,Ac_2O \longrightarrow 2\,RSOCl + 4\,AcCl$$

$$2\,RSH + 4\,Cl_2 + 2\,Ac_2O \longrightarrow 2\,RSOCl + 4\,AcCl + 2\,HCl$$

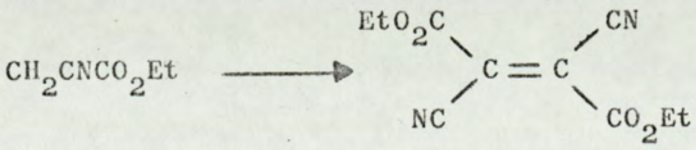
Preparation of bis(acetylethoxycarbonylmethyl) disulphide from the reaction between ethyl acetoacetate and disulphur dichloride only afforded the sulphide and it was therefore decided to prepare the bis(diacetylmethyl) disulphide. Acetylacetone has been found to give the disulphide when treated with disulphur dichloride. However when the disulphide was treated with acetic anhydride and chlorine it produced 3-chloro-2,4-dioxopentane-3-sulphinyl chloride(p.31) rather than the expected 2,4-dioxopentane-3-sulphinyl chloride. It is suggested that some of the chlorine required for the cleavage of the disulphide was utilized in further substitution of the active enolic proton:



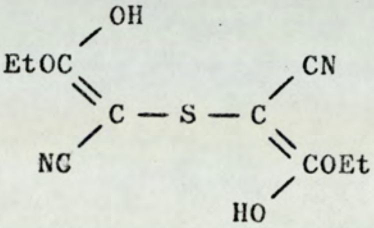
The observed reactivity of the α-proton of the disulphide was not surprising in view of the reported [53] reactivity of other protons α to the disulphide link and not activated by carbonyl groups.

Unfortunately when 3-chloro-2,4-dioxopentane-3-sulphinyl chloride was treated with ethyl acetoacetate or acetylacetone, it only afforded non-identified tars whereas its reaction with dimedone produced dimedone sulphide(4) and the other products stated before (page 96).

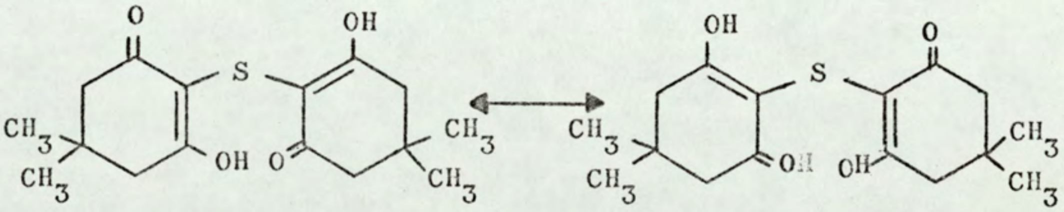
At this point the nature and reactivity of the α-sulphinyl chloride of 1,3-diketones will be considered. As it has been shown in the previous treatment(p.92), the α-sulphinyl chloride exists completely in the enolic form which has been attained from the beginning of the reaction when a molecule of thionyl chloride formed the electrostatic complex (8) through interaction with the double bond of the enolic form of the 1,3-diketone. It is believed that the enolic form provides the distinction between the formation of sulphides and alkenes. Thus, compounds similar to diethyl malonate, malononitrile and ethyl cyanoacetate all form the respective alkenes, eg ethyl cyanoacetate gives diethyl dicyanofumarate[17]:



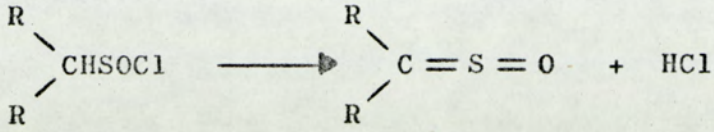
These compounds can react with thionyl chloride through their enolic or ketonic forms but it has been proposed[17] that the reactions proceed via a carbanion type intermediate of the ketonic form. If enolization took place and the α-sulphinyl chloride were formed, the reaction would be expected to proceed to the sulphide(18) which should exist solely in its enolic form, in accordance with the other sulphides here prepared and which behave similarly.


(18)

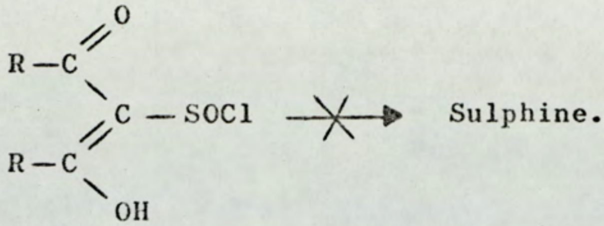
The sulphide(18) would be unlikely to be stable in its enolic form, and formation of the ketone would provide a second activated α-proton, a new site for further reaction. A second point against the formation of (18) is the absence of other carbonyl groups, in compounds similar to ethyl cyanoacetate, which would assist in the delocalization of charge. Such groups exist in dimedone sulphide(4) and the magnetic equivalence of the methylene groups of the sulphide provides evidence to support a tautomeric equilibrium of the type:



Thirdly, malononitrile which gave the alkene, cannot exist in the enolic form and there is no reason to believe that the compound proceeds to the alkene via a different mechanism to ethyl cyanoacetate. The ketonic α-sulphinyl chloride of ethyl cyanoacetate can then proceed to the alkene via the postulated[17] sulphine intermediate (19), a process not feasible for 1,3-diketones similar to dimedone which already exist in their enolic form(20):

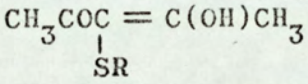
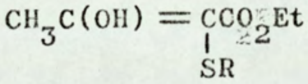
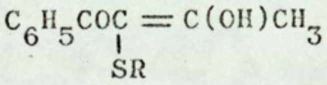
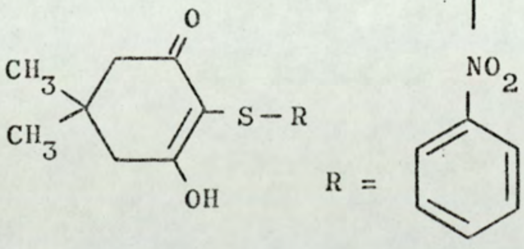


(19)



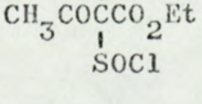
(20)

As ~~it~~ has been mentioned before, all the sulphides isolated from the reactions of 1,3-diketones with thionyl chloride existed solely in their enolic form. This observation is quite significant in view of the known tendency of 1,3-diketones and their α-derivatives to exist in an equilibrium mixture of both keto- and enol-forms. Another series of sulphides possessing an o-nitrophenyl moiety were prepared and showed exactly analogous behaviour. A table of these compounds together with their O-H nmr absorption shifts is given below:

Compound.	nmr O-H absorption(τ)
 $CH_3CO\underset{\substack{\mid\\ SR}}{C}=C(OH)CH_3$	-7.4
 $CH_3C(OH)=\underset{\substack{\mid\\ SR}}{C}CO_2Et$	-3.9
 $C_6H_5CO\underset{\substack{\mid\\ SR}}{C}=C(OH)CH_3$	-7.9
	Undetermined due to insolubility.

It would at first appear that the introduction of an electron-withdrawing atom similar to sulphur, in the α-position of the ketone was responsible for the shift of the equilibrium to the enolic form. The argument was disproved when α-chloro- and α-bromo-acetylacetone were shown to exist mainly in their ketonic forms. Some other explanation was therefore sought, and electron delocalization probably provided the answer. The ground state electronic configuration of sulphur can be considered as $3s^2 3p^4$ whilst the 3d orbitals can be involved in the hybridization of covalently bonded sulphur. This behaviour is unlike that shown by oxygen atoms which cannot utilize their d-orbitals and consequently show less tendency for charge delocalization to take place than sulphur.

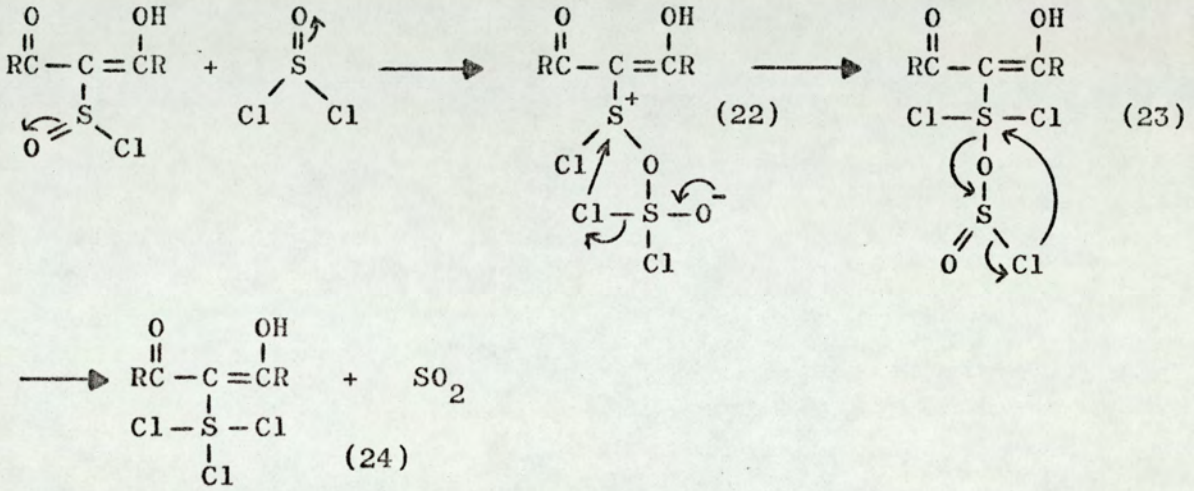
Delocalization of charge of the enolic form of the sulphides can readily take place not only within each radical but also within the whole molecule including the sulphur bridge. The effect that this delocalization has is to provide the so-called resonance energy and thus stabilize the molecule in an analogous manner to that found in aromatic systems. Delocalization has been known to be favoured by planar systems where the effect is at a maximum. Examination of molecular models of the sulphides of 1,3-diketones revealed that the enol could exist in a planar form, and it is only through such a planar form that the anhydride (6)(page 87) of dimedone sulphide could be formed. Consideration of the ketonic form of the sulphides of 1,3-diketones, revealed that delocalization of charge and therefore resonance stabilization, was unlikely to take place due to the following two reasons. Firstly, the introduction of the proton in the α-position of the molecule provides a tetrahedral carbon atom which would destroy the planarity of the molecule and hence its delocalization. Secondly, the absence of the enolic double bond would also stop the delocalization of charge between the carbonyl groups. It is believed that the inability to delocalize the charge system, due to the impossibility of enol formation, is responsible for the stability of ethyl α-chlorosulphinyl-α-methylacetoacetate(21):



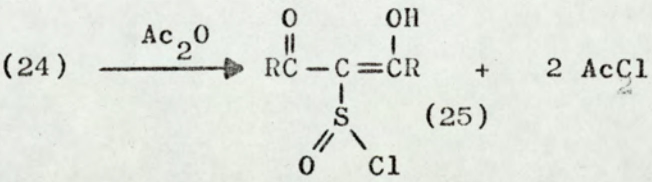
$$CH_3CO\underset{\displaystyle SOCl}{\overset{\displaystyle CH_3}{C}}CO_2Et \qquad (21)$$

The compound(21), does not give the sulphide as do other α-non-substituted 1,3-diketones, because it lacks the driving force which is provided by charge delocalization in the final product.

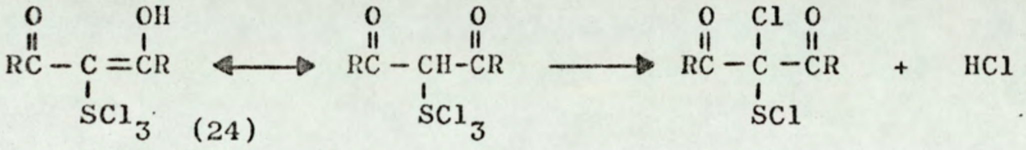
The mechanistic paths through which the α-sulphinyl chloride intermediate could proceed to the sulphide will now be discussed. The α-sulphinyl chloride was considered to react with another molecule of thionyl chloride and form a sulphur trichloride intermediate through the following steps:



Such intermediates(24) have been isolated from the reactions of disulphides or thiols with chlorine and they are known to react with acetic anhydride to give a sulphinyl chloride:



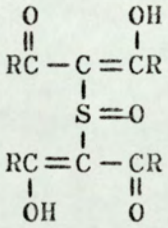
In the absence of acetic anhydride they(24) readily decompose to the sulphenyl chloride and molecular chlorine. Molecular chlorine could then give the α-chloride by reaction with another molecule of 1,3-diketone, whilst the sulphenyl chloride could give the sulphide by a similar reaction. The proposed mechanism (22) ⟶ (24) was studied by introducing stoichiometric quantities of acetic anhydride in the reaction mixture of ethyl acetoacetate and thionyl chloride. It was hoped that if an intermediate of the type(24) were formed, it would react with the acetic anhydride present and produce the α-sulphinyl chloride. The reaction of (24) with the acetic anhydride is a very fast process and would therefore be expected to take place in preference to the decomposition of (24). At the end of the reaction bis(acetylethoxycarbonylmethyl) sulphide and ethyl α-chloroacetoacetate were obtained and the ir spectrum indicated that no sulphinyl chloride had been formed. Another observation which disproved the mechanism was the absence of α-chlorination products which would be formed if the intermediate (24) decomposed:



$$\underset{(24)}{\mathrm{RC(=O)-C(SCl_3)=C(OH)R}} \longleftrightarrow \mathrm{RC(=O)-CH(SCl_3)-C(=O)R} \longrightarrow \mathrm{RC(=O)-C(Cl)(SCl)-C(=O)R} + \mathrm{HCl}$$

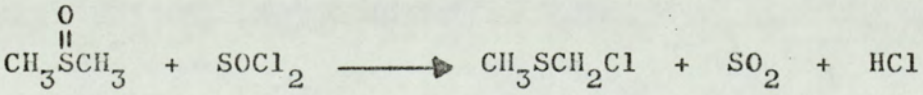
These products were observed when acetylacetone disulphide was treated with chlorine and acetic anhydride.

Once the α-sulphinyl chloride of 1,3-diketones was formed elimination of a molecule of hydrogen chloride between the α-proton of the enolic form of another molecule of 1,3-diketone and the α-sulphinyl chloride could produce the sulphoxide (25):



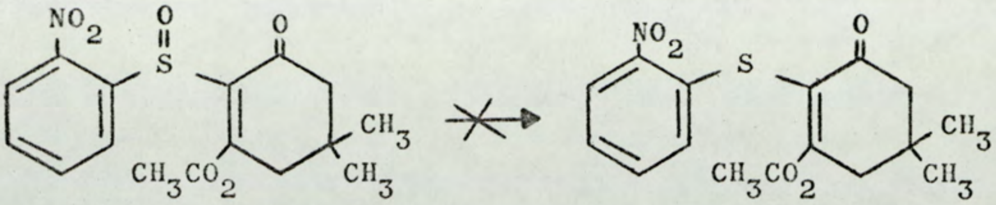
$$\mathrm{RC(=O)-C(=C(OH)R)-S(=O)-C(=C(OH)R)-C(=O)R} \qquad (25)$$

Thionyl chloride is well known to effect reduction of sulphoxides possessing at least one α-proton. For example, dimethyl sulphoxide is readily reduced[27] according to the equation:

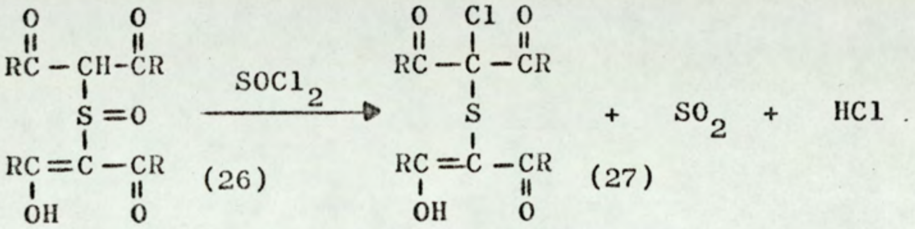


$$\mathrm{CH_3\overset{\overset{\displaystyle O}{\|}}{S}CH_3} + \mathrm{SOCl_2} \longrightarrow \mathrm{CH_3SCH_2Cl} + \mathrm{SO_2} + \mathrm{HCl}$$

Reduction is always followed by α-chlorination and in the absence of an α-proton reduction does not take place as was shown by the reaction:

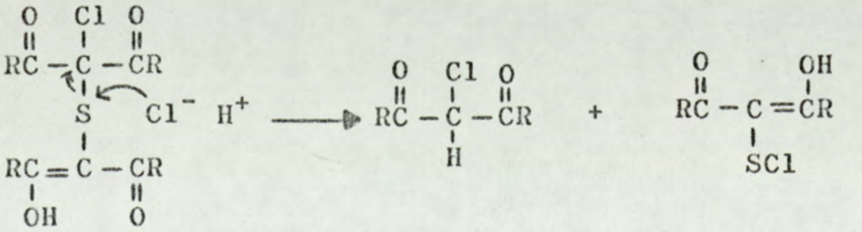


According to the above arguments, it would be expected that the sulphoxide (25) would not reduce to the sulphide, unless the tautomeric equilibrium shifted towards the ketonic form (26) in which case the α-chlorosulphide (27) would be formed:



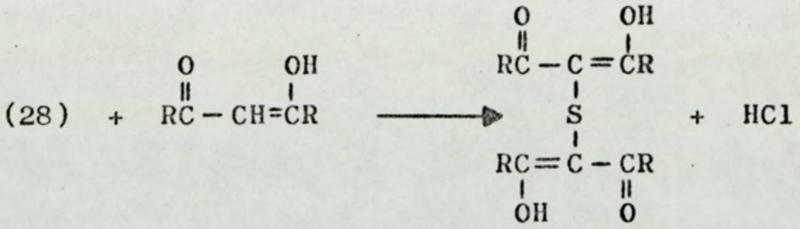
(26) (27)

The α-chlorosulphide (27) was never found amongst the products of the reactionof 1,3-diketones with thionyl chloride, and its stability would be questionable in view of the proposed stability of these compounds through delocalization of charge which cannot fully take place in (27) due to the introduction of the α-chloro-group. Hence the carbon-sulphur bond of the α-chlorosulphide would be expected to be weak due to the three electron-withdrawing groups, the two carbonyl groups and the chlorine atom, bonded to the carbon atom. Consequently, attack of chloride ions from a molecule of hydrogen chloride, produced during the reduction sequence, could cleave the carbon-sulphur bond and form the α-chloride and the α-sulphenyl chloride(28):

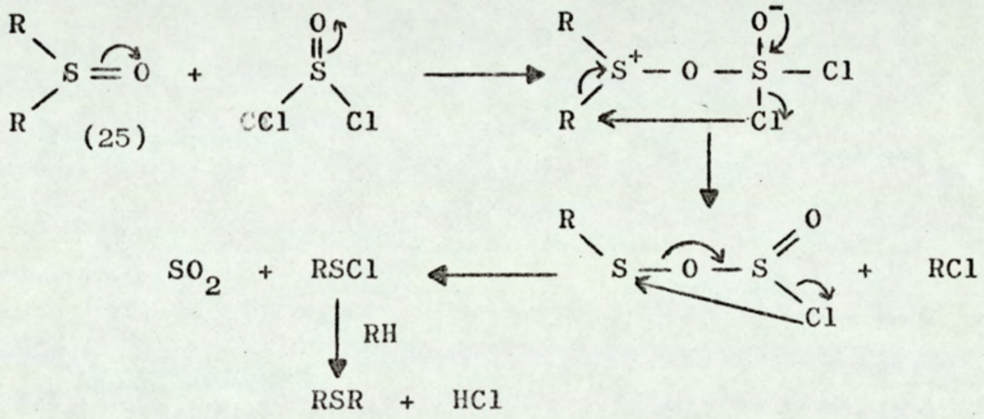


(28)

Elimination of a molecule of hydrogen chloride between the α-sulphenyl chloride (28) and another 1,3-diketone molecule would then give the sulphide:



A somewhat similar mechanism which did not involve the α-chlorosulphide(27) but gave the same products was formulated in terms of an addition of a molecule of thionyl chloride to the sulphoxide group of (25):



Both mechanistic schemes presented above depend on an inherent instability of the intermediate sulphoxide(25) in the presence of thionyl chloride. The reasons as well as the evidence to support such a statement are discussed here. It has been shown that electronic transmission through the sulphur link of sulphides can readily take place, and that such an effect is much more pronounced in sulphides than in sulphoxides or sulphones. Thus, studies[78] of the acidity of compounds(29,30,31) revealed that when the pK_a of the acids of each particular group (29), (30) or (31) was plotted against the Hammett constant σ of the substituent Y, a linear relationship was obtained.

$$Y-C_6H_4-S-CH=CH-COOH \qquad (29)$$

$$Y-C_6H_4-SO-CH=CH-COOH \qquad (30)$$

$$Y-C_6H_4-SO_2-CH=CH-COOH \quad (31)$$

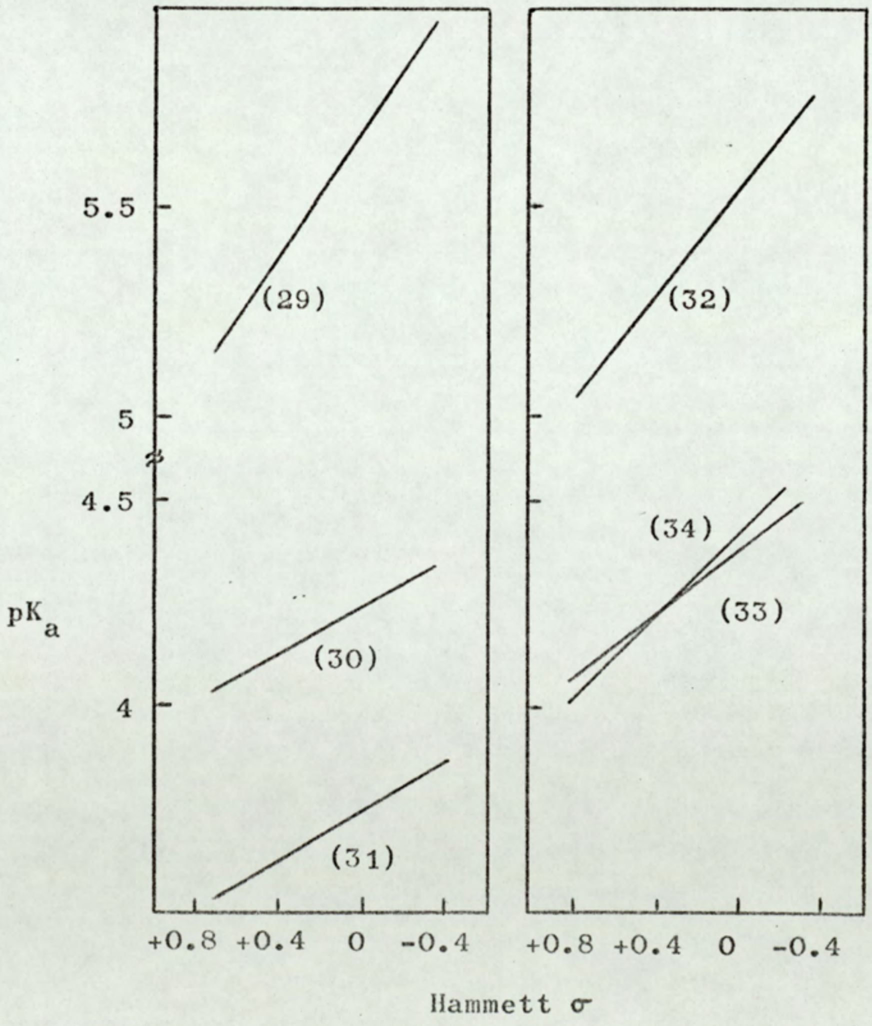
Analogous results were also obtained for another series of compounds:[78]

$$Y-C_6H_4-S-CH_2-COOH \quad (32)$$

$$Y-C_6H_4-SO-CH_2-COOH \quad (33)$$

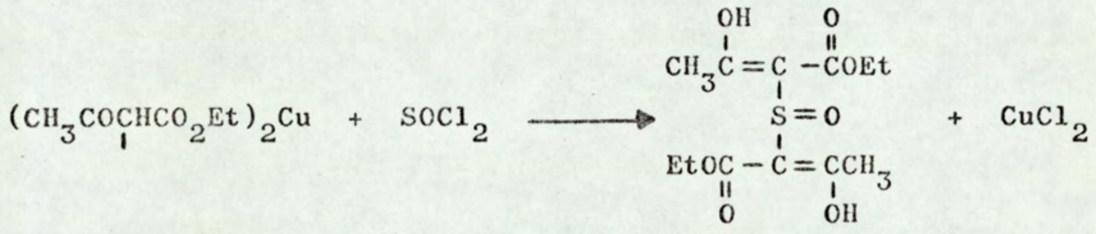
$$Y-C_6H_4-SO_2-CH_2-COOH \quad (34)$$

The data plotted below, shows the consistency of the two sets of results reported by the two authors.[78] Hogeveen[79] remarks that charge transmission through the sulphide link is 1.7 times more efficient than the observed transmission through the sulphoxide or sulphone link.



Consideration of the above arguments points to a higher stability, conferred by the more pronounced resonance stabilization, of the sulphides of 1,3-diketones compared to the proposed sulphoxide intermediate(25). This stabilization is possibly responsible for the experimentally observed resistance to oxidation of the sulphides of 1,3-diketones. Thus, normal oxidation conditions did not have any effect on the sulphides and if more forcing conditions were employed decomposition of the sulphides took place. In addition, the reaction of a sulphinyl chloride with 1,3-diketones did not give a sulphoxide whereas under similar conditions sulphenyl chlorides afforded sulphides.

An experiment designed to trap the sulphoxide (25), failed to produce the desired intermediate. Thus the copper salt of ethyl acetoacetate was treated with equimolar quantities of thionyl chloride according to the equation:



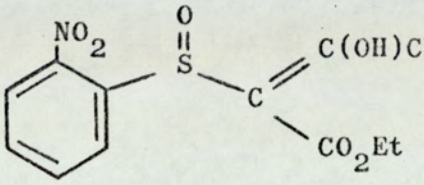
$$(CH_3CO\underset{|}{C}HCO_2Et)_2Cu + SOCl_2 \longrightarrow [CH_3C(OH)=C(CO_2Et)]_2S{=}O + CuCl_2$$

The reaction proceeded very rapidly, unlike the reaction of ethyl acetoacetate with thionyl chloride, and afforded the normal products, the sulphide and the α-chloride. It is possible that the sulphoxide was produced but its rate of formation k_1 was smaller than the rate k_2 of its further reaction with thionyl chloride. The overall reaction sequence is given below:

$$\begin{aligned}
&\text{RH(keto)} \rightleftharpoons \text{RH(enol)}\\
&\text{RH(enol)} + SOCl_2 \longrightarrow RSOCl + HCl\\
&RSOCl + \text{RH(enol)} \xrightarrow{k_1} RSOR + HCl\\
&RSOR + SOCl_2 \xrightarrow{k_2} RCl + RSCl + SO_2\\
&RSCl + \text{RH(enol)} \longrightarrow RSR + HCl
\end{aligned}$$

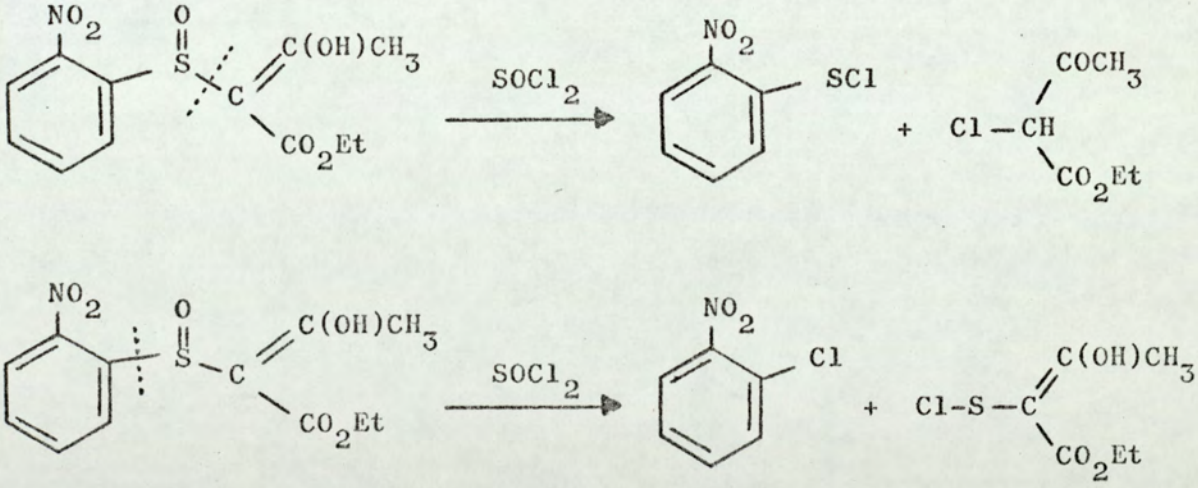
$$R = XCO\underset{|}{C}HCOY$$

As has been mentioned before, the attempted oxidation of the sulphides of 1,3-diketones to the related sulphoxides failed when hydrogen peroxide, hydrogen peroxide/ vanadium pentoxide,[70] benzene iodonium dichloride,[72] sodium dichromate/ sulphuric acid or dimethyl sulphoxide[73] were employed as the oxidizing agents. Hence, it was decided to prepare another sulphoxide(35) which had been reported[64] to be stable and which carried a 1,3-diketone moiety:



(35)

The products of the reaction of the sulphoxide(35) and thionyl chloride could then be studied to see if they corresponded to the postulated products. Depending upon the position of cleavage of the carbon-sulphur bond of the sulphoxide, four different products could in theory be obtained (page 105):

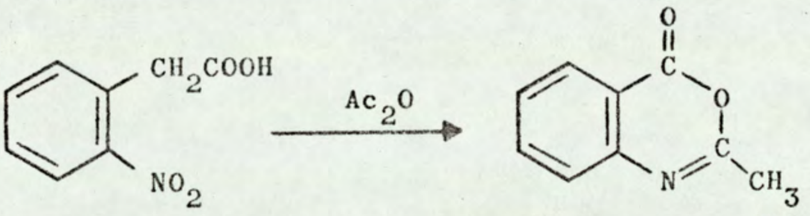


Preparation of the sulphoxide(35) involved a tedious synthesis outlined below:

$$\mathrm{RCl} \xrightarrow{\mathrm{Na_2S/S}} \mathrm{RSSR} \xrightarrow{\mathrm{Cl_2}} \mathrm{RSCl} \xrightarrow{\mathrm{R'H}} \underset{(36)}{\mathrm{RSR'}} \xrightarrow[\mathrm{Ac_2O}]{\mathrm{H_2O_2}} \underset{(35)}{\mathrm{RSOR'}}$$

R= o-nitrophenyl-
R'= acetylethoxycarbonylmethyl-

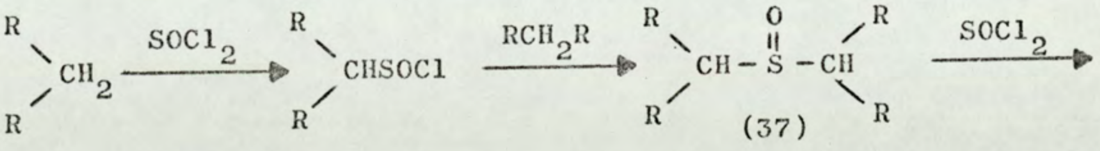
However, the last step in the synthesis involving oxidation of (36) with hydrogen peroxide in acetic acid solvent, did not produce the reported sulphoxide and thus the solvent system was altered to acetic acid, acetic anhydride and an excess of hydrogen peroxide. A compound which resembled the sulphoxide(35) in all spectroscopic properties except for the mass spectrum was obtained. Unfortunately the mass spectrum could not be interpreted and the exhibited molecular ion peak was 9 mass units higher than the theoretical molecular ion peak which corresponded to (35). A number of other irregular reactions which involved intramolecular condensation between the o-nitro group of an aromatic compound and the aromatic substrate which contained active protons, have been reviewed.[80] The reactions can take place both in acidic or basic media and the presence of acetic anhydride has been shown[80] to afford acetylated condensation products:



An analogous reaction is thought to have taken place during the treatment of the sulphide(36) with hydrogen peroxide in acetic acid-acetic anhydride mixture but the exact product was not identified. The unidentified product did not show an enolic nmr absorption as would have been expected if the sulphoxide(35) were formed. It was further treated with thionyl chloride and afforded a number of decomposition products which did not include the postulated ethyl α-chloroacetoacetate, o-nitrochlorobenzene or o-nitrophenylsulphenyl chloride. These results were found by tlc measurements of the mixed products stated above and of authentic samples of the chlorides and sulphenyl chloride. The nmr spectrum also lacked the distinct absorption peaks corresponding to the methine proton of the ethyl α-chloroacetoacetate.

Acetylacetone gave bis(diacetylmethyl) disulphide and 3-chloro pentane-2,4-dione when treated with thionyl chloride. These two products were isolated from the tarry reaction mixture and were compared with authentic samples. Unfortunately other products could not be identified and no conclusive statements can therefore be made regarding the mechanism of formation of the disulphide.

During the work carried out on the reactions of 1,3-diketones and thionyl chloride, it was observed that in many cases tarry products which resembled polymers were obtained. Thus, diethyl β-oxoglutarate, α-benzoylcyclohexanone, acetylacetone and others, all produced tars and in most cases the formation of the by-products was attributed to the possession of more than one activated methylene group. Acetylacetone posed an interesting problem because it was thought that its methyl groups participated in the reaction with thionyl chloride. However, it was shown that 3-chloro-2,4-dioxo pentane-3-sulphinyl chloride(page98) did not react with thionyl chloride and bis(diacetylmethyl) disulphide behaved similarly. It is now thought that the intermediate α-sulphinyl chloride in the reaction of 1,3-diketones with thionyl chloride forms polymeric materials through reaction with unchanged ketone and the whole sequence is further propagated by formation of more sulphinyl chloride groups. A diagrammatic reaction sequence is given below:



The dimer(37) can either be reduced by thionyl chloride and give an α-chlorosulphide or react with thionyl chloride to give an α-sulphinyl chloride.

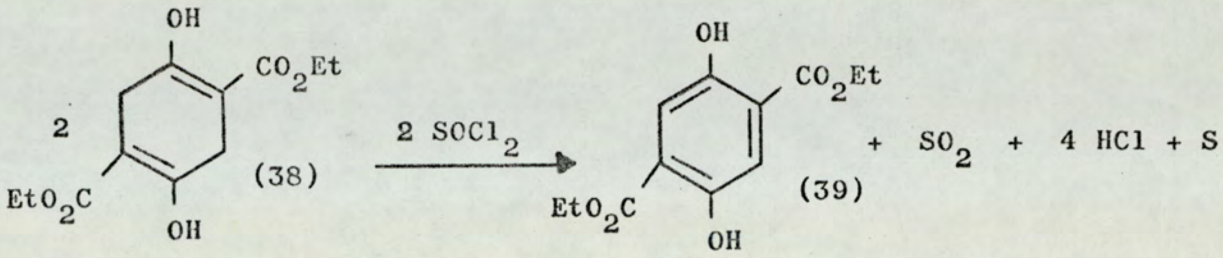
Sulphides have been reported[81] to form stable complexes with mercury salts. This technique was therefore applied, but without success, in cases where a sulphide product was suspected but could not be isolated from the tarry reaction mixture. The formation of sulphides was also shown not to be caused by inpure thionyl chloride as claimed by Goldman[82]. Thus very pure thionyl chloride was prepared by distillation over triphenyl phosphite[32] and subsequent reaction of this reagent with ethyl acetoacetate or dimedone afforded the usual products in comparable yields. The above author had claimed that inpure thionyl chloride afforded sulphides because it contained sulphur chlorides. The postulated[83] equilibrium:

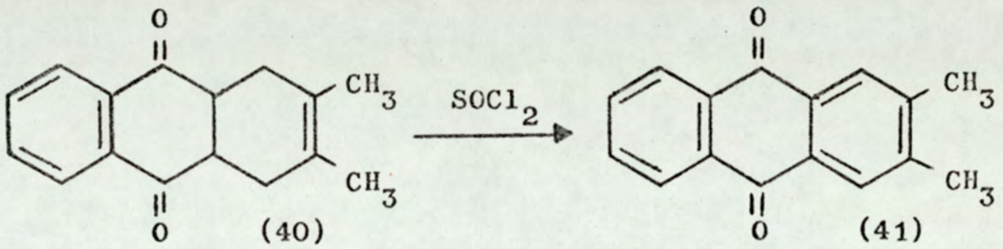
$$2\ SOCl_2 \rightleftharpoons SO_2Cl_2 + SCl_2$$

did not apply to the reactions of 1,3-diketones with thionyl chloride as it was found that equimolar quantities of sulphuryl chloride and dimedone afforded both mono- and dichloro-compounds whereas no trace of an α-dichloride was ever detected in the reactions of 1,3-diketones with thionyl chloride.

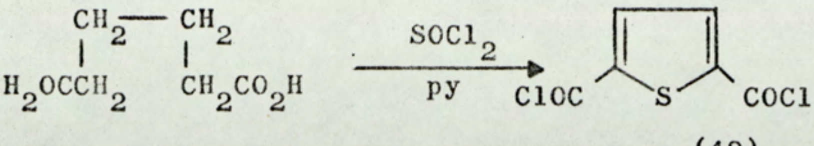
Lastly, the evolution of sulphur dioxide from the reaction between dimedone and thionyl chloride was studied. The method which was employed consisted of passing the gaseous products of the reaction through a standard solution of iodine and backtitrating aliquots of the iodine solution with a standard sodium thiosulphate solution. Nitrogen was employed as the carrier gas and another blank reaction containing thionyl chloride was set up in parallel to the reaction under investigation. The object was to eliminate the error which arose from small amounts of thionyl chloride carried over by the nitrogen gas and the other gaseous products of the reaction. The results have been plotted in graphs (1,2,3) as zero, first and second order reactions. A straight line was not obtained in any of these graphs, an indication of the complexity of the mechanism.

The oxidative action of thionyl chloride was exhibited in its reactions with some cyclic ketones which unexpectedly aromatized rather than afforded sulphides and α-chlorides. Thus 2,5-dioxo cyclohexane-1,4-dicarboxylate(38) gave diethyl 2,5-dihydroxyterephthalate (39), whilst 1,4-dihydro-2,3-dimethylanthraquinone(40) afforded 2,3-dimethylanthraquinone(41):





The presence of sulphur was shown in these reactions, in accordance with the stoichiometric equation put forward. The products of these reactions were readily isolated and identified spectroscopically and by comparison of their physical constants. Thus, a large downfield shift from τ 6.90(p.16) to τ 2.55(p.60) of the methylene group of (38) was observed in the nmr spectrum, a typical absorption position of protons bonded to aromatic rings. The ir spectra gave analogous results. It is believed that aromatization, if possible, takes place in preference to sulphide formation as a result of the extra energy obtained by the system through the resonance energy of the product. Such resonance energy leading to stabilization, is also present in all sulphides of 1,3-diketones prepared, but it is possibly not as effective as the aromatic resonance stabilization. The oxidation(41) mentioned above can be affected by other reagents eg. KOH/O_2[35] and another reported[84] reaction of the same type, involves a cyclization followed by aromatization to give the substituted thiophene (42):



(42)

Other oxidations involving thionyl chloride have been reported in the literature[19,85] but will not be discussed here as it is felt that such a treatment would be beyond the scope of this thesis.

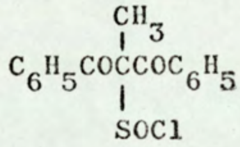
D I S C U S S I O N

2.2. 1,1-DIBENZOYL ETHANE.

In view of the previously discussed reactions of 1,3-diketones with thionyl chloride which afforded sulphides and α-chlorides, 1,1-dibenzoylethane was expected to behave in a similar manner. In fact when the compound was treated with excess of thionyl chloride under reflux, it gave a viscous oil(X), the composition of which was examined by gas liquid chromatography. Unfortunately a large number of peaks were obtained in the chromatograph, possibly due to decomposition of the components at the elevated temperature employed ~~and~~ which was found to be necessary for the components to be eluted through the column. Decomposition products were also obtained when the crude product was distilled under reduced pressure.

1,1-Dibenzoylethane possesses an alpha methyl group, the chemical shift of which was found to be sensitive to the alpha substituents in the nmr spectrum. This property which possibly arose from the alteration in the electron densities at the α-position brought about by the different substituents in that position, was very useful for the estimation of the number of products of the reaction, eventhough it was appreciated that an error could be introduced in the case of two components having exactly the same absorption values in the nmr spectrum. Three components were thus shown to be present and alteration of the sweep width from 600Hz to 100Hz failed to show a further peak. Their absorption peaks appeared at τ 7.92, 7.88, and 7.78 and they were all of different intensities. In addition, their absorption positions were found to be identical in the 60 and 100MHz spectra. Both these observations excluded the possibility of one molecule giving rise to two or three of the peaks observed, either through interaction of magnetically non-equivalent nuclei or through possession of methyl groups in dissimilar environments. The nature of the three components will be discussed later on in this chapter.

Because variable results were obtained when 1,1-dibenzoylethane was treated with thionyl chloride for different refluxing times, it was decided to further investigate the composition of the crude reaction mixture(X). It was found that prolonged heating altered the intensities of the two peaks at τ 7.92 and τ 7.88 in the nmr spectrum, and that the peak at τ 7.92 increased its intensity at the expense of the other one at τ 7.88 whose intensity decreased. The third peak at τ 7.78 remained unchanged. The exactly analogous investigation which was carried out using ir, revealed a progressive decrease of the intensity of the 1169cm^{-1} peak as the refluxing time was prolonged. This peak was assigned to the sulphinyl group streching frequency of 1,1-dibenzoylethane-α-sulphinyl chloride(1), suspected as being one of the three products of the crude reaction mixture(X):

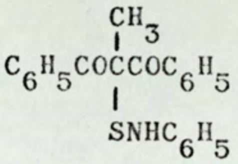


$$\mathrm{C_6H_5CO}\overset{\mathrm{CH_3}}{\underset{\mathrm{SOCl}}{\mathrm{C}}}\mathrm{COC_6H_5}$$

(1)

It was thus found that prolonged refluxing time decomposed the sulphinyl chloride(1). Similar behaviour of other β-ketosulphinyl chlorides has been observed(page 24).

Once it was indicated that the sulphinyl chloride(1)(αMe=τ 7.88) could be one of the products of the reaction of 1,1-dibenzoylethane and thionyl chloride, it was decided to prepare the anilide, the isolation of which would assist in the indirect identification of the compound. Addition of excess aniline to an ethereal solution of the crude reaction mixture(X), resulted in the immediate precipitation of anilinium hydrochloride which helped substantiate the presence of an acid chloride. Upon removal of the solvent the residual oil did not crystallize and therefore a number of solvents were employed for the attempted recrystallization of the oil,but with no success apart from ethanol which yielded a crystalline compound twenty four hours later upon addition of water. This behaviour of the reaction was quite unusual and unlike the preparation of adamantyl-1-sulphinanilide which ~~was~~ readily and easily formed from the appropriate sulphinyl chloride and aniline. The anomalous behaviour was confirmed when the solid component isolated from the reaction of the oil(X) with aniline followed by treatment with aqueous ethanol, was identified as 1,1-dibenzoylethane-1-sulphenanilide(2):



$$C_6H_5CO\overset{CH_3}{\underset{SNHC_6H_5}{C}}COC_6H_5 \qquad (2)$$

A disproportionation of the type:

$$2\ RSONHC_6H_5 \longrightarrow \underset{(3)}{RSO_2NHC_6H_5} + RSNHC_6H_5$$

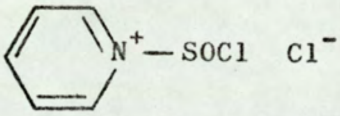
$$R = C_6H_5COC(CH_3)COC_6H_5$$

was indicated and confirmed when 1,1-dibenzoylethane-1-sulphonanilide (3) was spectroscopically identified. The ir spectrum of the sulphonanilide(3) showed three new absorption peaks at 1320, 1155 and 3415cm^{-1} compared to that of the sulphenanilide(2). The literature values[86] for sulphonamides are 1160 and 1325 cm^{-1} and adamantyl-1-sulphinanilide showed a sulphinyl absorption at 1067cm.$^{-1}$ In addition the nitrogen-proton streching frequency of the sulphonanilide(3) absorbed sharply at 3415cm^{-1} while that of the sulphenanilide(2) absorbed sharply at 3340cm.$^{-1}$

The formation of the two disproportionation products discussed above, presented a complication in view of the fact that 3-chloro--2,4-dioxopentane-3-sulphinyl chloride only afforded 3,3-dianilino pentane-2,4-dione when treated with aniline followed by treatment with aqueous ethanol. It is possible that the carbonyl groups in 1,1-dibenzoylethane-α-sulphinyl chloride(1) do not exert their full electron-withdrawing properties due to the presence of the phenyl groups which offer centres for charge delocalization. Consequently, the carbon-sulphur bond of the sulphinamide is quite strong and gains stability by disproportionation rather than by cleavage to form the α-anilino-1,1-dibenzoylethane as in the case of 3-chloro-2,4-dioxopentane-3-sulphinyl chloride.

The component of 1,1-dibenzoylethane oil(X) the methyl of which absorbed at τ 7.78 in the nmr spectrum and was not affected by variations of the refluxing time, was thought to belong to α-chloro-1,1-dibenzoylethane for the following reasons:

a). When the reaction of 1,1-dibenzoylethane with thionyl chloride was carried out in the presence of a small amount of pyridine, the intensity of the peak at τ 7.78 increased. This observation was in accordance with the known mechanism of the reaction of alcohols with thionyl chloride in the presence of pyridine which liberates free chloride ions through formation of the ion pair:



Promotion of chloride formation would be therefore expected to occur in preference to substitution at the α-position of 1,1-dibenzoyl ethane by other sulphur-containing groups.

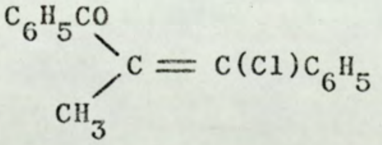
b). When the reaction of 1,1-dibenzoylethane and thionyl chloride was carried out in the presence of dibenzoyl peroxide, the intensity of the peak at τ 7.78 decreased significantly. A reaction between dibenzoyl peroxide and thionyl chloride has been reported[87] to afford benzoyl chloride amongst other products:

$$(C_6H_5CO_2)_2 \xrightarrow{SOCl_2} C_6H_5Cl + C_6H_5COCl + C_6H_5SO_2Cl + (C_6H_5)_2 + C_6H_5CO_2C_6H_5 + (C_6H_5CO)_2O + CO_2$$

The formation of benzoyl chloride offered a plausible explanation regarding the decrease in the intensity of the τ 7.78 peak which belonged to α-chloro-1,1-dibenzoylethane.

An attempted isolation of α-chloro-1,1-dibenzoylethane from the crude reaction mixture(X) failed when column chromatography, recrystallization or distillation techniques were employed. It was therefore decided to treat 1,1-dibenzoylethane with thionyl chloride but at room temperature rather than under reflux. The advantage of this method lay in the fact that the decomposition product of 1,1-dibenzoylethane-α-sulphinyl chloride(1) was eliminated and that a two component mixture was obtained instead. Long reaction time though had to be allowed and a chlorine-containing solid of low melting point was isolated.

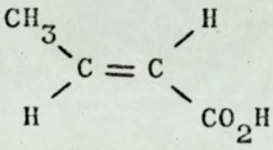
An authentic sample of α-chloro-1,1-dibenzoylethane was prepared by the action of sulphuryl chloride on 1,1-dibenzoylethane. This compound possessed different spectral characteristics from the sample isolated from the reaction between 1,1-dibenzoylethane and thionyl chloride. A mixed nmr spectrum of the two products prepared by the two routes, showed two methyl absorption peaks indicative of two methyl groups in dissimilar magnetic environments. The product obtained from the reaction with thionyl chloride was therefore assigned the structure: (4)

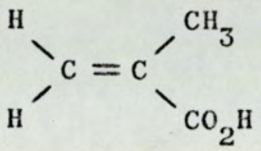


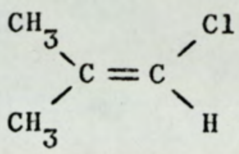
$$(C_6H_5CO)(CH_3)C=C(Cl)C_6H_5 \qquad (4)$$

Its ir spectrum showed a peak at $1628cm^{-1}$ indicative of an olefinic double bond which was absent in the spectrum of α-chloro-1,1-dibenzoylethane. The double bond of non-symmetric tetrasubstituted alkenes absorbs at $1670cm^{-1}$ in the ir, but the presence of groups which can conjugate with the double bond could be expected to shift the absorption to lower wavelenghts.[88]

The singlet observed in the nmr spectrum at τ 7.78 is a typical absorption of a methyl group bonded to a double bond. A number of structurally similar alkenes have been reported[89] and are shown below with their methyl absorptions:

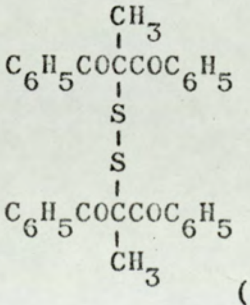

τ 8.10

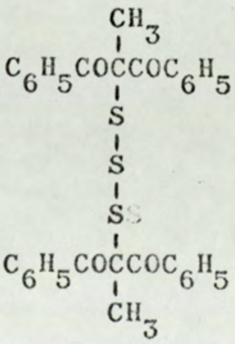

τ 8.03


τ 8.23

It would be expected that strong electron-withdrawing groups like benzoyl, phenyl and chloride, would further deshield the methyl group of the chloride(4) and shift its absorption downfields towards the observed value of τ 7.78

During an attempted recrystallization of the product(X) obtained from the reaction of 1,1-dibenzoylethane with thionyl chloride it was observed that when an alcoholic solvent such as ethanol or methanol were employed, crystalline materials precipitated within two days. Isolation of the crystalline products and comparison of their spectra to those of the crude reaction oil(X) which was initially dissolved in ethanol, indicated that they were products of further reaction of the oil(X) in the presence of the alcoholic solvent. The crystalline products were isolated and identified beyond doubt as bis(1,1-dibenzoylethyl) disulphide and bis(1,1-dibenzoylethyl) trisulphide(5 and 6 respectively):

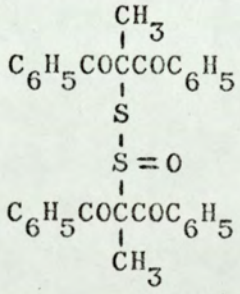

(5)


(6)

Unfortunately mass spectrometry did not prove very informative due to the high molecular weight of the compounds and the ready cleavage of the carbon-sulphur bonds. Thus a strong peak at 237 mass units was assigned to the $C_6H_5CO\dot{C}(CH_3)COC_6H_5$ fragment. The observed fragmentation pattern of the disulphide and trisulphide is similar to that of 1,1-dibenzoylethyl benzene thiosulphonate.(Table 13 p.57-58)

The ir spectra of the two compounds (5) and (6) were identical but not very informative whereas in the nmr spectra the methyl group in the α-position was found to be sensitive to the added sulphur linkage in the trisulphide(6) compared to the disulphide(5). The observed chemical shift of τ 0.1 of the methyl groups in the di- and tri sulphide was in accordance with the deshielding effects expected to be found in such molecules. Analogous behaviour was observed in the nmr spectra of bis(diacetylmethyl) disulphide and trisulphide(p.88).

Treatment of the product(X) obtained from the reaction of 1,1-dibenzoylethane with thionyl chloride, with 12% aqueous ethanol or methanol, afforded another product identified as 1,1-dibenzoylethyl 1,1-dibenzoylethanethiosulphinate(7):



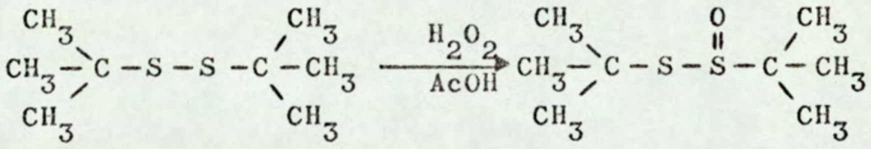
$$\begin{array}{c} CH_3 \\ | \\ C_6H_5COCCOC_6H_5 \\ | \\ S \\ | \\ S=O \\ | \\ C_6H_5COCCOC_6H_5 \\ | \\ CH_3 \end{array}$$

(7)

The compound exhibited some interesting spectroscopic properties. Thus, its nmr spectrum showed two singlets at τ 7.81 and τ 7.92 of equal intensities, the absorption positions of which did not change in the 100 or 60MHz spectra, and the intensities of which did not alter by further recrystallization. It was thus established that a molecule containing two magnetically non-equivalent methyl groups had been formed. Such an effect could be produced either by a molecule which contained some source of asymmetry or by a molecule which possessed a rotational or conformational barrier. Examination of the ir spectrum of (7) revealed that all but one peak were present in the spectra of the disulphide(5) and trisulphide(6) of 1,1-dibenzoyl ethane. The new peak absorbed strongly at 1100cm^{-1} and was assigned to the sulphinyl streching frequency of the thiosulphinate group.[88]

Other workers[90] have noted similar nmr spectral patterns of thiosulphinates and thiosulphonates. Thus, [91] benzyl disulphide, thiosulphinate and thiosulphonate showed that introduction of one or two oxygen atoms in the disulphide link, produced loss of symmetry which was strongly exhibited in the chemical shifts of the benzyl methylene groups.

Alkyl thiosulphinates have been previously prepared by oxidation of disulphides by per-acids but tertiary disulphides could not be oxidized by this method.[91a] Such oxidations have been recently reported[92] to be effected by the use of a hydrogen peroxide-acetic acid mixture eg:

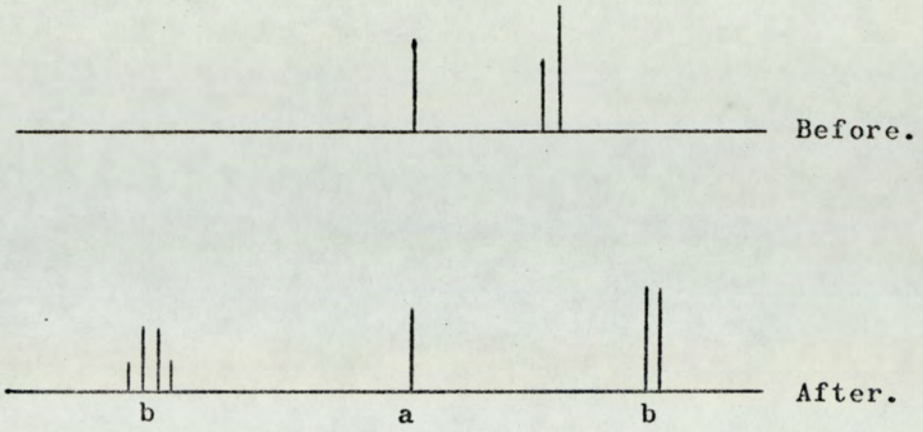


During the treatment with ethanol of the product obtained from the reaction of 1,1-dibenzoylethane and thionyl chloride(X), the following points were noted:

a). Both peaks at τ 7.92 and τ 7.88 present in the crude reaction mixture(X) before it was treated with ethanol, disappeared when the disulphide(5), trisulphide(6) or thiosulphinate(7) were formed after treatment with ethanol or aqueous ethanol.

b). After the thiosulphinate(7) was removed, the ethanol was evaporated off to yield an oil which contained the chloride(4) and some 1,1-dibenzoylethane. The latter was not unchanged starting material.

These points can be seen in the nmr spectrum of 1,1-dibenzoyl ethane oil(X) before and after treatment with aqueous ethanol:



a = 2-benzoyl-1-chloro-1-phenylpropene(4)

b = 1,1-dibenzoylethane.

The formation of 1,1-dibenzoylethane during the treatment with aqueous ethanol, required a source of protons which could be provided by any of the following routes:

a). By a rearrangement of the oil(X)

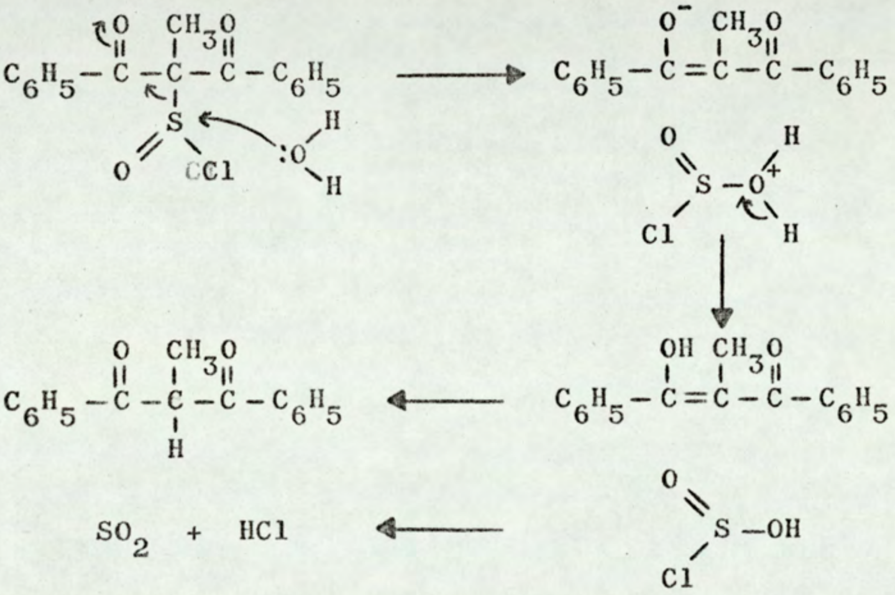
b). From the water employed

c). From the ethanol.

If rearrangement of the oil(X) took place and protons were thus provided, other rearrangement fragments would have shown absorptions in the nmr spectrum an event which was not observed in practice.

The second possibility was tested by carrying out the alcoholic aqueous treatment of the oil(X) in deuteriated water. If water were the source of protons, α-deuteriated-1,1-dibenzoylethane would be formed, and the characteristic nmr coupling of the methyl-methine groups which gave rise to a quartet and a doublet would instead give a singlet. This behaviour was experimentally observed and strongly indicated that the water played a part in the decomposition of the sulphinyl chloride(1). The possibility of an exchange of protons between 1,1-dibenzoylethane and the deuteriated water was tested by recrystallization of the former from D_2O. It was observed that no deuterium was incorporated in 1,1-dibenzoylethane. An analogous decomposition of a β-ketosulphinyl chloride by water was observed during the treatment of 2-methyl-3-oxobutane-2-sulphinyl chloride with water which afforded 3-methylbutan-2-one.

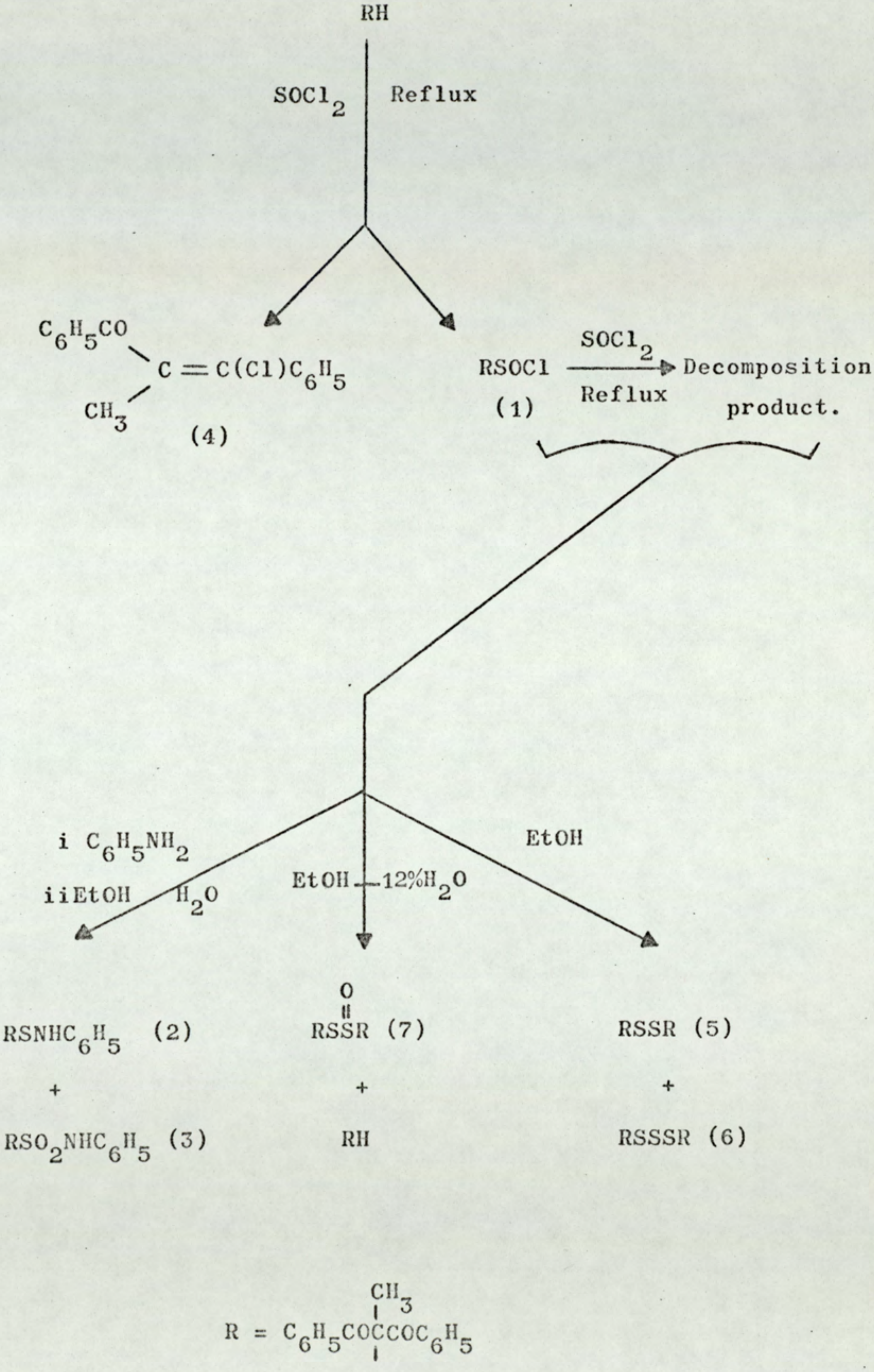
Nucleophilic attack of the lone pair of the oxygen atom of the water molecule onto the weak carbon-sulphur bond of 1,1-dibenzoyl ethane-α-sulphinyl chloride(1) would explain the formation of 1,1-dibenzoylethane, especially in view of the observed instability of β-ketosulphinyl chlorides in the presence of a base such as water and aniline(see page 36):



The overall reaction scheme of the reactions of 1,1-dibenzoyl ethane is shown in figure 1.

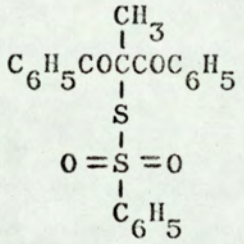
The effect of the addition of dibenzoyl peroxide in the reaction between 1,1-dibenzoylethane and thionyl chloride was also studied. It was found that catalytic quantities of the peroxide did not have an appreciable effect on the rate of the reaction whereas when the amount of the peroxide was increased the rate of the reaction changed. These results have been plotted in graph 5 (page 77). It is believed that the benzoyl peroxide initiates a free radical reaction which cannot propagate itself and therefore terminates when all the benzoyl peroxide has been used up.

FIGURE 1


RH
SOCl2
Reflux
C6H5CO
C = C(Cl)C6H5
CH3
(4)
RSOCl
(1)
SOCl2
Reflux
Decomposition product.
i C6H5NH2
ii EtOH H2O
EtOH - 12%H2O
EtOH
RSNHC6H5 (2)
+
RSO2NHC6H5 (3)
O
RSSR (7)
+
RH
RSSR (5)
+
RSSSR (6)
R = C6H5COCCOC6H5
CH3

The crude oil(Y) which was obtained from the reaction of equimolar quantities of 1,1-dibenzoylethane and dibenzoyl peroxide with excess of thionyl chloride, only showed a singlet at τ 7.88 and the expected aromatics, in the nmr spectrum. The ir spectrum exhibited a strong peak at 1169cm^{-1} indicative of 1,1-dibenzoylethane α-sulphinyl chloride(1), which had not decomposed due to the shorter reaction time. The 1169cm^{-1} peak did not belong to any of the products of the reaction of dibenzoyl peroxide and thionyl chloride[87] (p.117).

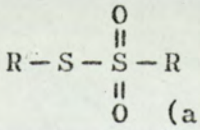
The oil(Y) which only contained the sulphinyl chloride(1) did not produce any crystalline material when it was treated with aqueous ethanol. However, when the refluxing time was prolonged and the oil(Y) had partly decomposed, treatment with aqueous ethanol afforded a new compound identified as 1,1-dibenzoylethyl benzene thiosulphonate(8):



$$\begin{array}{c} CH_3 \\ | \\ C_6H_5COCCOC_6H_5 \\ | \\ S \\ | \\ O=S=O \\ | \\ C_6H_5 \end{array}$$

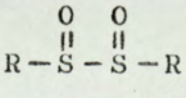
(8)

If neat ethanol were employed, the normal products, namely bis(1,1-dibenzoylethyl) disulphide(5) and trisulphide(6) were obtained. The thiosulphonate(8) was identified by elemental analysis and by its characteristic ir absorptions of the sulphonate group which appeared at 1322cm^{-1} and at 1145cm^{-1}. Similar absorptions have been reported[93] to occur at 1311 and 1128cm^{-1}. Electron spectroscopy[94] and nmr techniques[90,91] have established beyond doubt that thio sulphonates exist in the isomeric form (a) rather than (b):



$$R-S-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-R$$

(a)

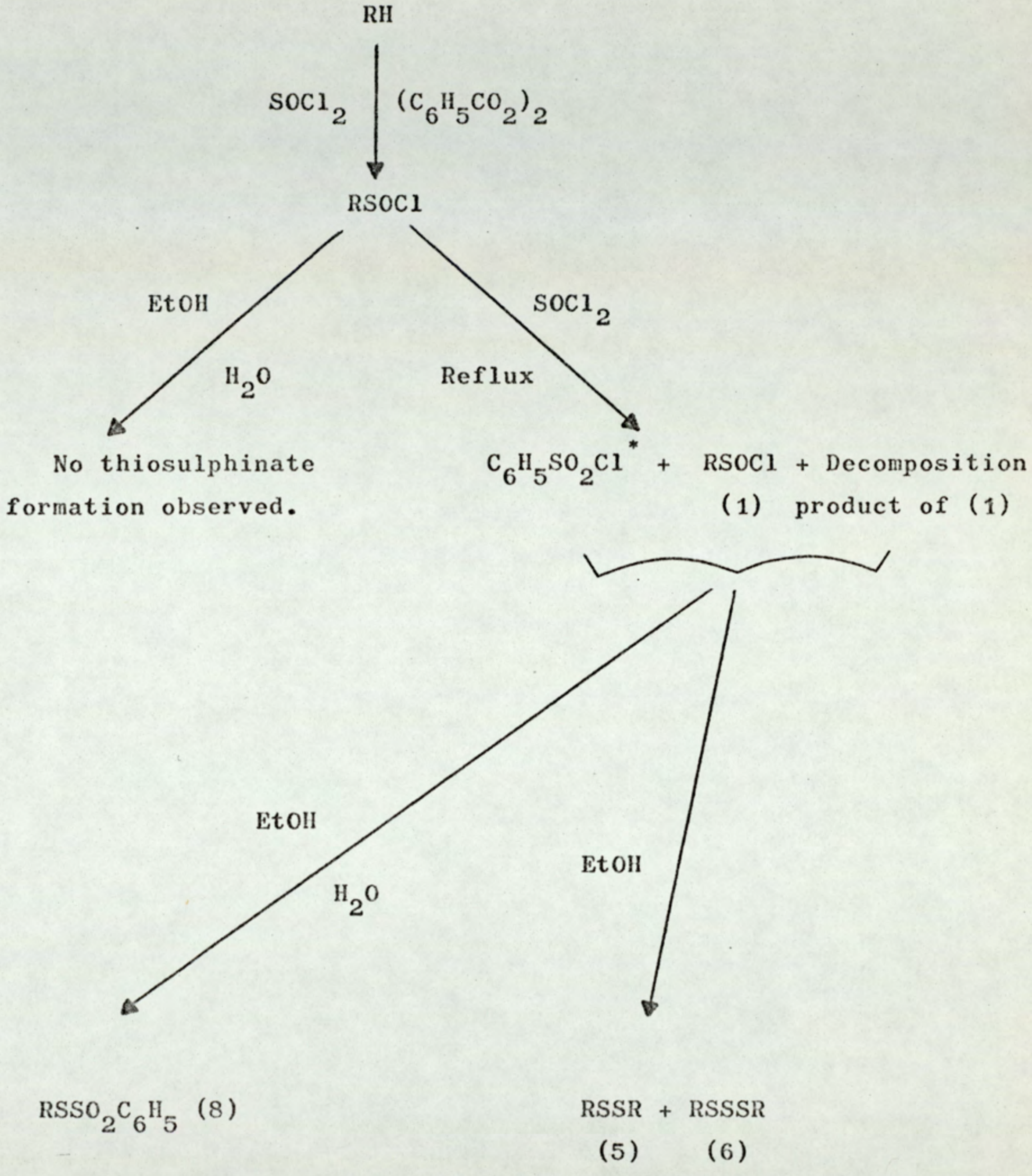


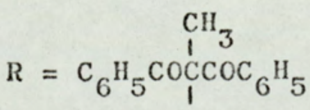
$$R-\overset{O}{\overset{\|}{S}}-\overset{O}{\overset{\|}{S}}-R$$

(b)

The overall reaction scheme of the reaction of dibenzoyl peroxide, 1,1-dibenzoylethane and thionyl chloride is shown in fig.2:

FIGURE 2



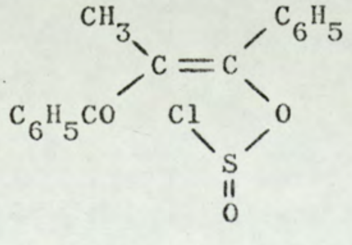

$R = C_6H_5CO\overset{CH_3}{\underset{|}{\overset{|}{C}}}COC_6H_5$

* Reported product from the reaction of dibenzoyl peroxide and thionyl chloride.

1,1-Dibenzoylethane, which normally exists solely in the keto form, possesses an alpha proton which is activated by the adjacent carbonyl groups and deactivated by the inductive effect of the methyl group. The readily obtained sodium salt of the compound indicates that the influence of the methyl group is largely outweighed by that of the two carbonyl groups which enable the compound to enolize. In fact the enolic form of 1,1-dibenzoylethane can be prepared[95] in its pure form through formation of the copper salt which possibly chelates with the two oxygen groups of the compound in the same way that other 1,3-diketones like acetylacetone form similar complexes.

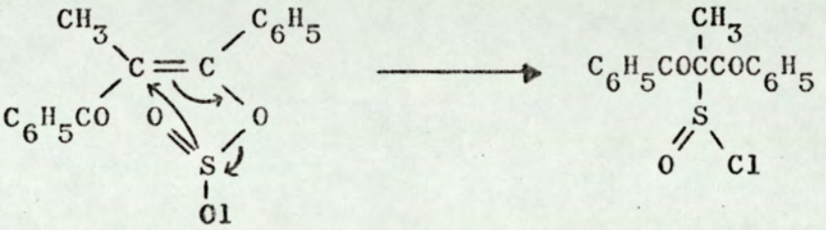
It is postulated that during the treatment of the keto form of 1,1-dibenzoylethane with thionyl chloride, enolization is the first step in the reaction. The experimental evidence for this postulate lies in the observed formation of 2-benzoyl-1-chloro-1-phenylpropene(4) which can only be formed through a reaction analogous to the formation of chlorides from alcohols. (Page 1). In addition, other compounds like dimedone and acetylacetone, which also possess the 1,3-diketo-structure, have been found to react with thionyl chloride via their enolic form. (Page 92) It would therefore appear that 1,1-dibenzoylethane might also react in an analogous manner, in view of the fact that the compound possesses similar structural characteristics to acetylacetone and dimedone.

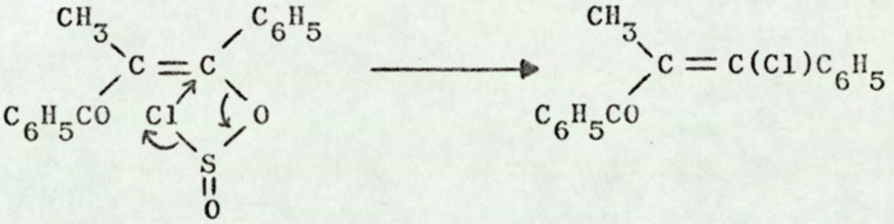
Electrophilic attack of the sulphur atom of thionyl chloride onto the oxygen atom of the hydroxyl group of the enolic form of 1,1-dibenzoylethane, followed by elimination of a molecule of hydrogen chloride produces the chlorosulphite(9):



(9)

The chlorosulphite(9) can then rearrange by two different routes with subsequent formation of two possible products which have been identified. Polarization of the double bond, followed by a nucleophilic attack of the electronegative sulphur atom onto the α-electropositive carbon atom would afford the α-sulphinyl chloride(1) whereas evolution of a molecule of sulphur dioxide followed by nucleophilic attack of chloride on the β-carbon atom would give the chloride(4). The formation of the sulphinyl chloride(1) is believed to proceed via a concerted process:

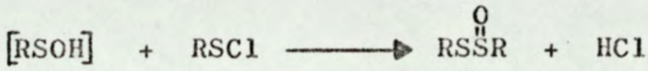

(1)


(4)

During the treatment of 1,1-dibenzoylethane with thionyl chloride, it was established that decomposition of the sulphinyl chloride(1) occurred when the mixture was refluxed for the long time necessary for the reaction to go to completion. The nature of the decomposition is not as yet known but it is thought that a possible product could be the α-sulphenyl chloride. Working on that assumption an attempt is made here to explain the formation of the different products obtained during the treatment with aqueous or neat ethanol. The mechanisms advanced here for the formation of the compounds (5), (6) and (7) are speculative, yet it must be emphasized that they are based on the known chemistry of these compounds and on the experimental evidence already outlined.

The reaction of sulphenyl chlorides with water has long been believed[96] to proceed through a sulphenic acid to give disulphides sulphinic acids and other products. The isolation of a sulphenic acid has been reported by Fries[97] who synthesized the compound by an indirect route and not by a simple hydrolysis of the sulphenyl chloride. It would be therefore plausible to assume that 1,1-dibenzoylethane-α-sulphenyl chloride reacts with the water during its treatment with aqueous ethanol to give the sulphenic acid intermediate which further rearranges to form the thiosulphinate according to the equation:

$$RSCl \; + \; H_2O \longrightarrow [RSOH] \; + \; HCl$$

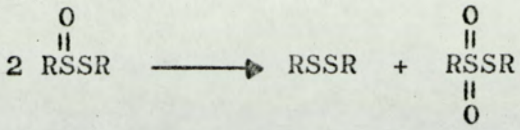


$$[RSOH] \; + \; RSCl \longrightarrow RS\overset{O}{\overset{\|}{S}}R \; + \; HCl$$

An analogous reaction has been proposed by J.I.Cunneen[98] and co-workers who proposed a sulphenic acid intermediate which proceeded to the thiosulphinate, the process encountered in the oxidation of rubber. The sulphinyl chloride(1) which was the primary product of the reaction of 1,1-dibenzoylethane and thionyl chloride simply hydrolyzed to 1,1-dibenzoylethane,when treated with aqueous ethanol, according to the proposed hydrolysis(page123). 1,1-Dibenzoylethane was indeed found amongst the products obtained by the treatment of the oil(X) with aqueous ethanol, and it was shown that the proton required for the process originated from the water employed in the reaction.

The formation of bis(1,1-dibenzoylethyl) disulphide(5) and trisulphide(6) from the reaction of the oil(X) with ethanol or methanol could be accounted for by two different routes.

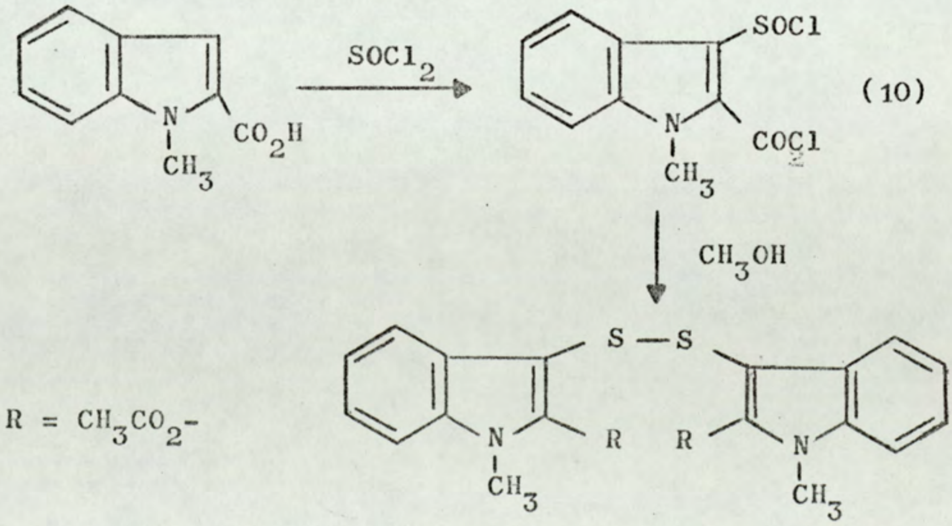
1,1-Dibenzoylethyl 1,1-dibenzoylethanethiosulphinate(7) could have been formed as an intermediate during the treatment with ethanol and in the absence of water it could rearrange to the disulphide(5) rather than precipitate out. A possible rearrangement could most certainly involve the disulphide(5) and the thiosulphonate[98] according to the equation:



$$2\ \mathrm{R}\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}\mathrm{SR} \longrightarrow \mathrm{RSSR} + \mathrm{R}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}}\mathrm{SR}$$

This route was disproved when the methanolic treatment of the oil(X) was carried out in an nmr tube and the reaction was followed by observing the nmr spectrum at different time intervals. It was found that eventhough the spectrum of the oil(X) changed significantly the characteristic methyl absorptions of the thiosulphinate(7) could not be seen at any time. The proof was not fully conclusive, as the thiosulphinate could have actually been formed as an unstable intermediate and hence reacted very rapidly. A second point against this theory of rearrangement involved the absence of the postulated 1,1-dibenzoylethyl 1,1-dibenzoylethanethiosulphonate, which was not found amongst the products. Its presence should have been readily detected by its characteristic nmr and ir absorptions.

An indole derivative has been found[99] to react with thionyl chloride to form the sulphinyl chloride(10) which was isolated and afforded the disulphide(11) upon treatment with methanol:



(10)

(11)

An exactly analogous reaction could take place in the case of 1,1-dibenzoylethane-α-sulphinyl chloride, although the fate of the chloride and oxygen atoms of the sulphinyl chloride would be difficult to account for. The role of the alcohol in these reactions, which was found to be necessary for the formation of the disulphide(5) and trisulphide(6) could provide an explanation. Thus the alcohol could be oxidized to the corresponding aldehyde and acid and so balance the equation:

$$\begin{aligned} 2\ \mathrm{RSOCl} + 2\ \mathrm{CH_3CH_2OH} \longrightarrow \mathrm{RSSR} + \mathrm{CH_3CHO} + \mathrm{CH_3CO_2H} &+ \\ + \mathrm{H_2O} + 2\ \mathrm{HCl} \end{aligned}$$

This theory was supported by the observed inability of t-butyl alcohol, which cannot oxidize, to produce the disulphide or trisulphide.

Bis(1,1-dibenzoylethyl) trisulphide(6) could be formed from the decomposition product of 1,1-dibenzoylethane-α-sulphinyl chloride (1). This hypothesis would agree with the experimentally observed increase in the amount of trisulphide formation during the prolonged refluxing of 1,1-dibenzoylethane and thionyl chloride.

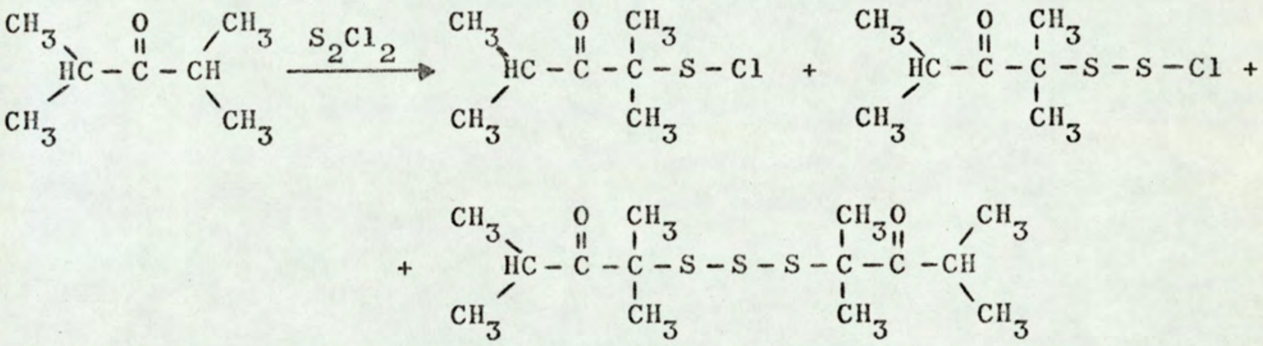
Thus, in summation, 1,1-dibenzoylethane on treatment with thionyl chloride gives 1,1-dibenzoylethane-α-sulphinyl chloride, further treatment with ethanol gives bis(1,1-dibenzoylethyl) disulphide(5) and trisulphide(6), and aqueous ethanol gives 1,1-dibenzoylethyl 1,1-dibenzoylethanethiosulphinate(7). In the presence of large quantities of dibenzoyl peroxide the reaction is modified to give 1,1-dibenzoylethyl benzenethiosulphonate(8) upon an aqueous treatment with ethanol.

The kinetics of the reactions of ring-substituted 1,1-dibenzoylethanes and thionyl chloride were followed by nmr techniques. Thus, examination of 1,1-dibenzoylethane, 1-benzoyl-1-p-chloro benzoylethane and 1-benzoyl-1-p-methoxybenzoylethane indicated that substitution on the aromatic ring accelerated the rate of the reactions with thionyl chloride. The results have been plotted in graph 4(page 76).

DISCUSSION

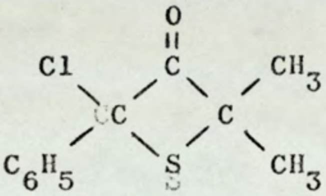
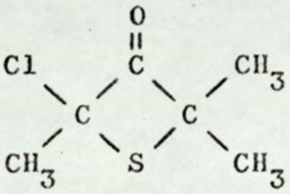
2.3. β-KETOSULPHINYL CHLORIDES.

The intermediates in the reactions of thionyl chloride and 1,3-diketones were believed to include a β-ketosulphinyl chloride. Such an intermediate was never isolated fron the above reactions possibly due to its high reactivity in the presence of unchanged ketone. It was therefore considered desirable to prepare a β-keto sulphinyl chloride and treat it with ethyl acetoacetate or dimedone (cf page98). The opportunity arose when a sulphenyl chloride, a thiosulphenyl chloride and a trisulphide were reported[100] to be produced from the reaction between di-isopropyl ketone and disulphur dichloride:



An analogous reaction of the α-methine proton towards thionyl chloride was thought to be possible and hence could lead to the formation of the desired β-ketosulphinyl chlorides. Thus, isopropyl methyl ketone and a series of other isopropyl ketones were treated with thionyl chloride and in the majority of cases the β-ketosulphinyl chloride was isolated in excellent yield in a one-step simple synthesis. A table of the reaction products together with certain properties and spectra is shown below:

COMPOUND	ir(S=O)	nmr(τ)	bp./m.p.
$CH_3COC(SOCl)(CH_3)_2$	1155cm^{-1}	8.42(s) 7.71(s)	90/4mmHg
$C_6H_5COC(SOCl)(CH_3)_2$	1150cm^{-1}	8.18(s) 2.30(m)	-

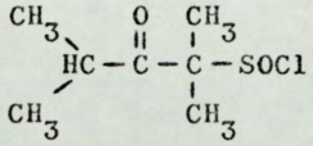
COMPOUND	ir(S=O)	nmr(τ)	b.p./m.p.
$(CH_3)_2CHCOC(SOCl)(CH_3)_2$	1156cm^{-1}	8.90(d) 8.40(s) 8.32(s) 6.92(sp)	90/1mmHg
$C_{10}H_7COC(SOCl)(CH_3)_2$	1152cm^{-1}	8.35(s) 2.40(m)	74°
$C_6H_5CH_2COC(SOCl)(CH_3)_2$	1145cm^{-1}	8.39(s) 6.10(s) 2.50(m)	*
	-	8.50(s) 8.14(s) 2.50(m)	*
	-	7.97(s) 8.12(s) 8.38(s)	80-83/2mmHg 45°

* These compounds have only been spectroscopically identified.

(s)= singlet, (d)= doublet, (m)= multiplet, (sp)= septet.

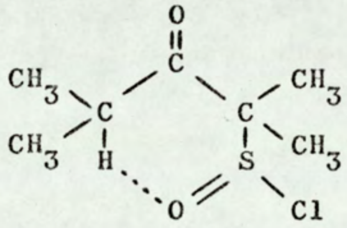
In all cases three molar quantities of thionyl chloride to one mole of the ketone were employed and the structure of the sulphinyl chlorides, purified by distillation or recrystallization, was determined by spectroscopic means and by analysis. Valuable information was obtained from the ir spectra which consistently showed a strong absorption at 1150±6cm^{-1} corresponding to the streching frequency of the sulphinyl group. Other workers have reported[53] similar values which range between 1140cm^{-1} in α-toluenesulphinyl chloride to 1155cm^{-1} in 4-chlorobenzenesulphinyl chloride and ethane-1,2-disulphinyl dichloride.

The nmr spectra of the sulphinyl chlorides provided much information of great assistance for the assignment of each structure. In all cases but one, the gem-dimethyl group adjacent to the sulphinyl chloride group, absorbed as a singlet in the region of τ 8.00. The odd exception belonged to 2,4-dimethyl-3-oxopentane-2-sulphinyl chloride (di-isopropyl ketone sulphinyl chloride) (1):



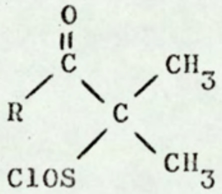
(1)

The sulphinyl chloride(1) exhibited two singlets at τ 8.40 and 8.32 corresponding to the two methyl groups adjacent to the sulphinyl chloride group. An analogous behaviour has been reported[101] for propane-2-sulphinyl chloride. The abnormality was initially thought to arise from chelation between the sulphinyl chloride group and the methine proton:



Construction of molecular orbitals showed that if such a cyclic sructure were formed, both the methyl groups adjacent to the sulphinyl chloride group would have been magnetically equivalent due to the plane of symmetry which coincides with the plane of the ring. Another possible and more likely explanation involved the four conformers shown in figure 3, the interconversion of which would possibly be difficult at room temperature. To test the theory, variable temperature nmr work was carried out on the sulphinyl chloride(1), as it was believed that a conformational barrier could be overcome at elevated temperatures in the same way that other conformations have been frozen at low temperatures.[102] A linear decrease in the separation of the two peaks which corresponded to the two methyl groups adjacent to the sulphinyl chloride group, was observed, when the spectrum was run at temperatures ranging between 30 and 130°(graph 6, page 79). Extrapolation of the straight line indicated that the two peaks would coincide at the theoretical temperature of 347°. A conformational isomer would not be expected to exist at such elevated temperatures and any possible chelation would also give way to free rotation.

The nmr spectrum of 2-chloro-2,4-dimethylpentan-3-one exhibited only one singlet which corresponded to the two methyl groups adjacent to the chloride group, in contrast to di-isopropyl ketone sulphinyl chloride(1) which exhibited two singlets. The obvious conclusion which could be drawn was that the sulphinyl chloride group was partly responsible for the observed abnormality. The unchanged isopropyl group was also considered to be responsible, in view of the fact that other β-ketoisopropyl sulphinyl chlorides(2) only exhibited a singlet corresponding to the gem-dimethyl group alpha to the sulphinyl chloride group.

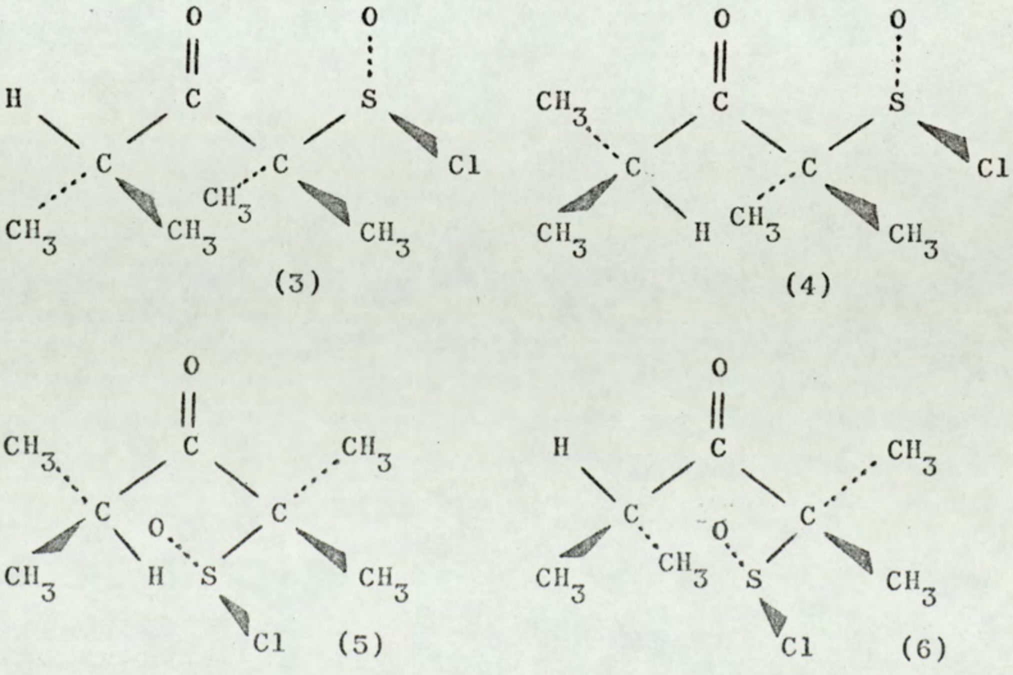


R= CH_3-
C_6H_5-
1-naphthyl-

(2)

The influence of the sulphinyl chloride and the isopropyl groups was investigated once it was recognized that they interacted with each other.

FIGURE 3



(3) (4) (5) (6)

A possible source of interaction could arise between the carbonyl and the sulphinyl or chloride groups in rotamers(3) and (4) shown in figure 3. Such an interaction would be easily avoided if rotamers (5) and (6) were formed which would also give minimum interaction between the two pairs of methyl groups. Rotation of the carbon-carbon bond between the isopropyl and carbonyl groups would interconvert rotamers (6) and (5) the latter being the most stable since the two gem-dimethyl groups are as far apart as possible. The result of the free rotation of the isopropyl group would be to push the oxygen and the chlorine atoms of the sulphinyl chloride group out of the plane defined by the carbonyl group and the two carbon atoms alpha to it. As a result the two methyl groups adjacent to the sulphinyl chloride group, become non-equivalent and they thus show different nmr absorptions.

The inability of variable temperature probe nmr work to overcome the rotational barrier can be justified if one considers the effect of temperature on the rotational frequencies. When the temperature is increased, the sulphinyl chloride group will be expected to rotate at a higher frequency and thus overcome the rotational barrier which the isopropyl group imposed. But the isopropyl group will also undergo an analogous change of rotational frequency and the net result will be to maintain the same nmr spectral characteristics at low or elevated temperatures.

The nmr spectrum of di-isopropyl ketone sulphinyl chloride(1) presented another interesting complication when it was found that the appearance of the spectrum was a function of the solvent employed. Thus, in non-polar solvents (eg carbon tetrachloride, carbon disulphide) the spectrum consisted of a septet, two singlets and one doublet, whereas in aromatic solvents (eg benzene, mesitylene) it consisted of a septet, two singlets and two doublets. (Fig 1a p.79) An intermolecular complex which arose from the interaction between the π-electrons of the benzene ring and the carbonyl or sulphinyl group, was suspected and its formation was verified when it was observed that the appearance of the spectrum in mesitylene changed as a function of the concentration. Thus the two doublets at τ 9.18 and 9.21 gradually altered their shape into a triplet, upon altering the concentration of the sulphinyl chloride from 75% to 25%.

The formation of such a complex is analogous to the reported[103] complexes between benzene and chloroform. The effect that the complex had on the sulphinyl chloride molecule could be considered to be equivalent to a conformational barrier which would prohibit the rotation of the isopropyl group. If this is the case, a similar effect should be observed when the spectrum of di-isopropyl ketone sulphinyl chloride(1) is examined at low temperatures in a non-polar solvent. In fact the spectrum of the sulphinyl chloride in carbon disulphide which at room temperature exhibited a septet, two singlets and one doublet, produced a septet, two singlets and two doublets at -100°. This evidence supported the theory of an intermolecular complex with the benzene solvent giving rise to a sterically hindered structure.

Other workers[104] have observed similar nmr effects in some isopropyl compounds. Van der Vlies[105] concluded that two structural requirements were necessary for the "doubling effect" to take place in some isopropyl esters. Firstly the molecule should possess an asymmetric centre and secondly it should possess a phenyl ring. Once these requirements were fulfilled doubling occurred but the chemical shift between the two doublets ν, varied as a function of solvent and of the other substituents in the molecule. A table of some of the compounds which have been examined is given in the next page.

It is evident that apart from an asymmetric group which is necessary for doubling to take place, the presence of a phenyl ring also plays an important role, with the exception of (12). Thus when a phenyl ring in (7) is substituted by a cyclohexyl ring in (10) doubling disappears, the behaviour pointing to an electronic effect through the π- electrons of the phenyl ring, rather than to steric effects.

No	Compound.	Ref.	Chemical shift(ν) in		
			CCl_4(Hz)	C_6H_6(Hz)	o-$C_6H_4Cl_2$
7	$C_6H_5CH(OH)COOCH(CH_3)_2$	105	10.5	9.5	10.8
8	$C_6H_5CH(Cl)COOCH(CH_3)_2$	105	4.5	4.0	5.0
9	$(C_6H_5)_2C(OH)COOCH(CH_3)_2$	105	0	0	0
10	$C_6H_{11}CH(OH)COOCH(CH_3)_2$	105	0	0	0
11	$C_6H_5CH(OH)CH(CH_3)_2$	105	10.8	12.7	11.5
12	$CH_3CH(OH)CH(CH_3)_2$	105	1.2	3.0	2.3
13	$C_6H_5CH(CH_3)OCH_2CH_2CH(CH_3)_2$	106	2.5	1.8	
14	$(CH_3)_2CHCOCH(CH_3)_2$		0	0	
15	$(CH_3)_2CHCO(Cl)(CH_3)_2$		0	0	
16	$(CH_3)_2CHCOC(SOCl)(CH_3)_2$		0	3.0	

All spectra have been run in a 60MHz spectrometer.

Another point which the authors did not explain was the 2.5 fold increase in the doubling effect of (12) in benzene solvent compared to the doubling of the same compound in carbon tetrachloride solvent. It is suggested that the aromatic ring in (7,8,11,13), forms an intramolecular electrostatic complex with the isopropyl group through an interaction of the π-electrons with the relatively positively charged methyl groups of the isopropyl group. An asymmetric centre is a necessary requirement for the formation of a dissymmetric intramolecular complex, otherwise the formed complex will not exhibit doubling effect.

An analogous behaviour was observed in the case of di-isopropyl ketone sulphinyl chloride(1) but it was attributed to an intermolecular complex with benzene. It was therefore decided to further examine some isopropyl ketones in order to establish the structural requirements necessary for the formation of such complexes with benzene. Comparison of the chloride(15) to the sulphinyl chloride(16) revealed that the centre of asymmetry is provided by the sulphinyl chloride group. The conclusions which can be drawn from the consideration of the compounds in the previous table are summarized below:

a). An asymmetric centre is necessary for doubling to take place.

b). If the asymmetric centre contains an aromatic ring, interaction of the ring with the methyl groups of the isopropyl group produces doubling.

c). In the absence of the aromatic ring, doubling sometimes takes place if benzene is employed as the solvent and if an asymmetric centre is present in the isopropyl compound.

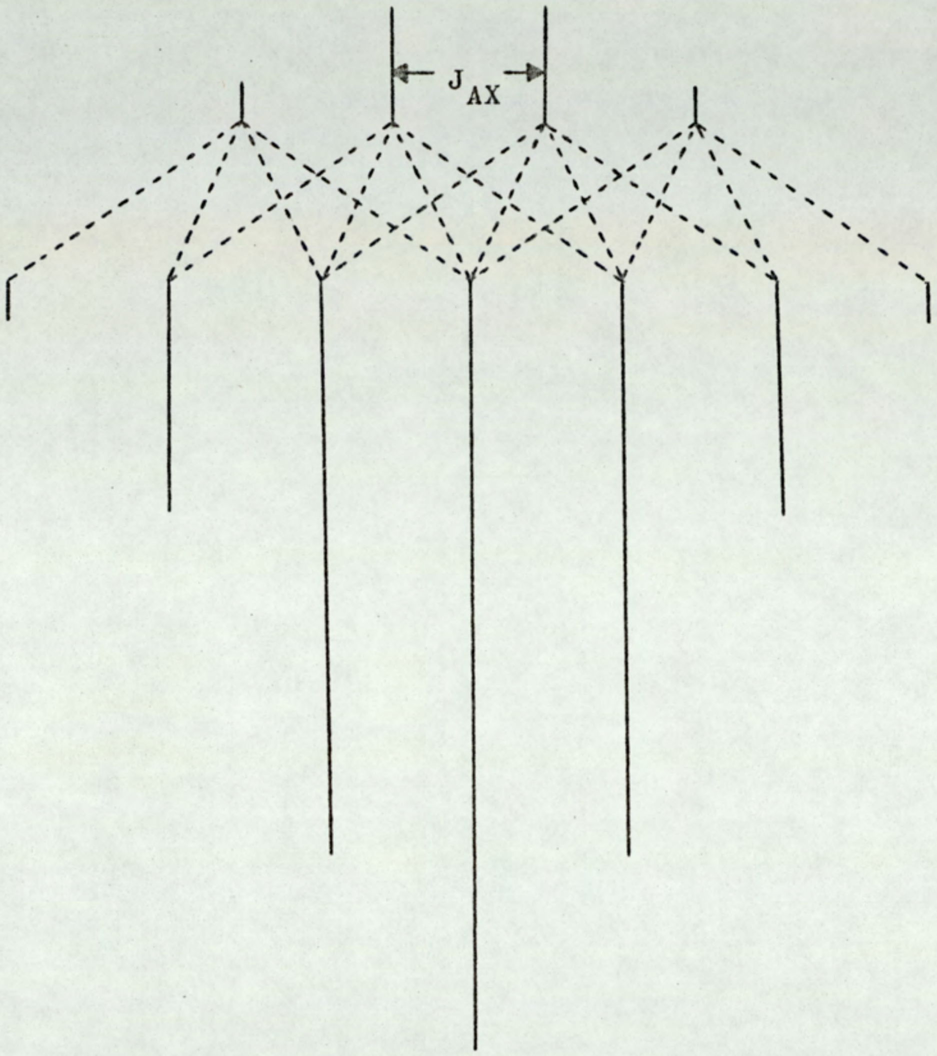
The isopropyl group normally exhibits an A_3B_3C nmr spectrum which gives rise to a septet and a doublet. When doubling takes place due to a rotational hindrance, the spectrum is altered to a A_3M_3X type[107] where J_{AX} is about equal to J_{MX}. The methine proton is then split by the A group into a quartet, each line of which is further split into another quartet by the M group. The net result is a septet of 1:6:15:20:15:6:1 intensities, unlike the methyl groups which each splits into a doublet of quite different chemical shift but with approximately the same coupling constant values $J_{AX} \simeq J_{MX}$.

The observed behaviour of di-isopropyl ketone sulphinyl chloride(1) in benzene solvent, which altered the appearance of the spectrum as a function of dilution, can be explained in terms of a change of the chemical shift which partly depends on the solvent-solute interactions and partly on the structure of the molecule. Figure 5 (page 140) analyzes the observed spectral patterns mentioned above.

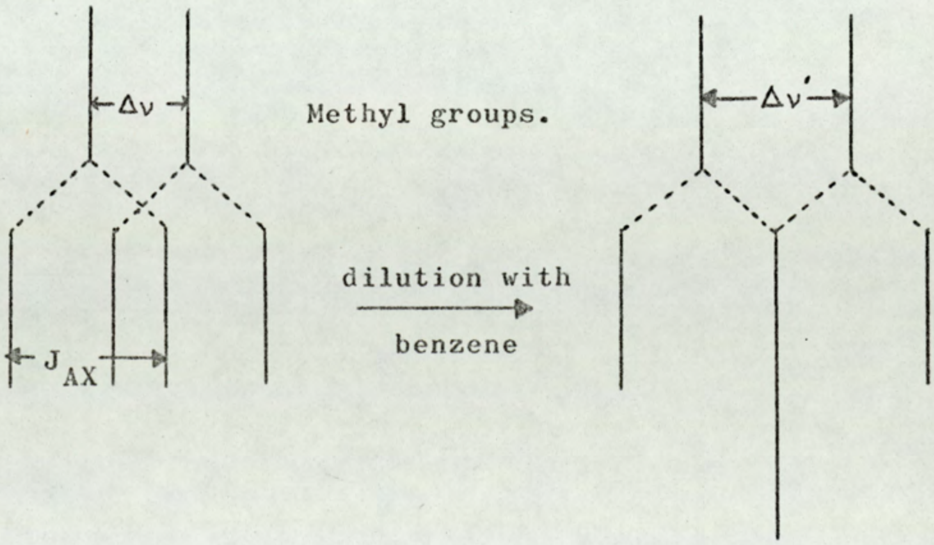
Di-isopropyl ketone posed an interesting question when it was treated with an excess of thionyl chloride and afforded only the mono-sulphinyl chloride(1) rather than the expected di-sulphinyl

FIGURE 5

Methine proton.

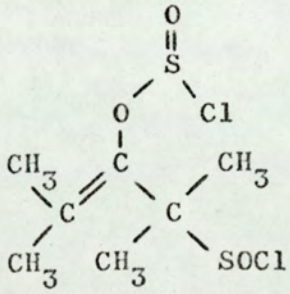


Methyl groups.



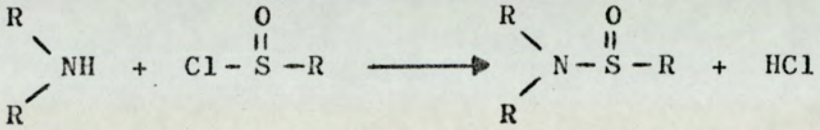
chloride. An analogous reaction of the ketone towards excess of molecular oxygen has also been reported[108] to give the mono-hydroperoxide but the authors did not offer an explanation for the stability of the second isopropyl group. Chelation of the sulphinyl chloride group to the carbonyl or to the unchanged methine proton would be expected to prohibit the proposed enolization step thought to be necessary for the reaction to proceed. Di-isopropyl ketone was therefore treated with excess of thionyl chloride under reflux but it still afforded the mono-sulphinyl chloride(1) eventhough the forcing conditions employed would not be in favour of a stable chelate or a hydrogen-bonded complex.

The sulphinyl chloride is a bulky group and when once incorporated in the molecule it could sterically hinder the approach of another molecule of thionyl chloride. In addition, some steric interaction can take place between the chlorosulphite group in the proposed intermediate, and the already present chlorosulphinyl and methyl groups:



Di-isopropyl ketone monochloride(15) was therefore prepared by the action of sulphuryl chloride on di-isopropyl ketone, and in subsequent treatment with thionyl chloride, even under reflux, it totally resisted further substitution of the methine proton of the isopropyl group. It was deduced that a steric effect or a chelation were not responsible for the non-reactivity of the second isopropyl group of di-isopropyl ketone. An excess of sulphuryl chloride also gave only the monochloride of di-isopropyl ketone, which further supported the conclusions stated above.

The properties of sulphinyl chlorides are very similar to those of acid chlorides due to the presence of the active chloride group. Thus treatment with primary or secondary aliphatic or aromatic amines affords the sulphinamides according to the equation:



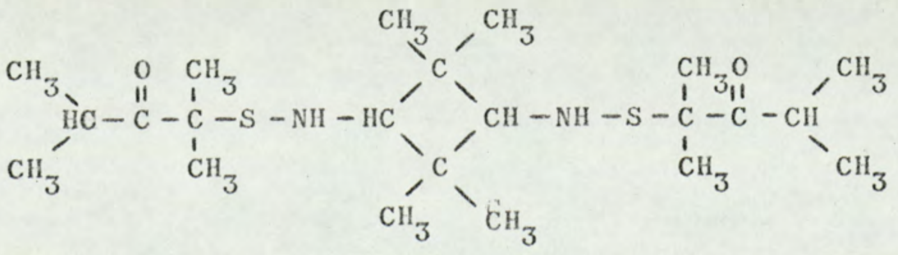
$$\begin{matrix} R \\ & NH \\ R \end{matrix} + Cl-\overset{O}{\overset{\|}{S}}-R \longrightarrow \begin{matrix} R \\ & N \\ R \end{matrix}-\overset{O}{\overset{\|}{S}}-R + HCl$$

This reaction of sulphinyl chlorides with amines has often been employed in their characterization as it readily affords crystalline compounds. Unfortunately, when the β-ketosulphinyl chlorides were treated with aniline, the compound which was isolated and supposedly corresponded to the sulphinamide, was found to be unstable to atmospheric conditions. Secondary aromatic amines also gave unstable products. At first it was thought that a disproportionation of the type

$$2\ RSONHR \longrightarrow RSNHR + RSO_2NHR$$

had taken place and that the sulphenamide and the sulphonamide were the products. The ir spectrum of the tarry decomposition products did not show any sulphonamide streching frequency and if a disproportionation of the above type took place, the products should have been readily identifiable in their crystalline form.

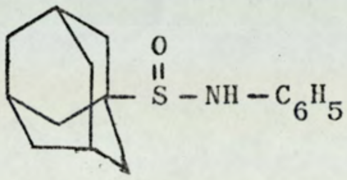
The instability of the β-ketosulphinamides can be attributed to the presence of the carbonyl group and/or to the presence of the tertiary carbon atom in the α-position to the carbonyl group. A literature survey indicated that β-ketosulphinamides had not been reported whereas a β-ketosulphenamide(17) has been shown to arise[100]



(17)

from the condensation between 2,4-dimethyl-3-oxo-2-pentane sulphenyl chloride and 2,2,4,4-tetramethyl-1,3-cyclobutanediamine.

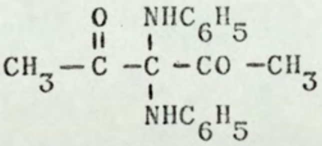
Adamantyl-1-sulphinyl chloride was prepared from the reaction between adamantane and thionyl chloride in the presence of aluminium trichloride[54] and its stable sulphinamide(18) was prepared:



(18)

The presence of a tertiary carbon atom alpha to the sulphinyl group did not appear to affect the stability of the compound and it is therefore suggested that the main factor responsible for the instability ot the β-ketosulphinamides is the presence of the carbonyl group, the electron-withdrawing properties of which coupled with those of the sulphinyl and N-H groups may assist in the rupture of the carbon-sulphur bond.

Some more information relating to the decomposition products of the β-ketosulphinamides was obtained from the reaction of 3-chloro-2,4-dioxopentane-3-sulpinyl chloride and aniline. The isolation of 3,3-diaminopentane-2,4-dione(19) from the tarry reaction mixture

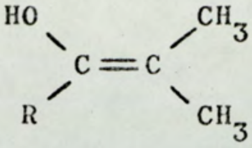


$$CH_3-\overset{\overset{\large O}{\|}}{C}-\underset{\underset{NHC_6H_5}{|}}{\overset{\overset{NHC_6H_5}{|}}{C}}-CO-CH_3$$

(19)

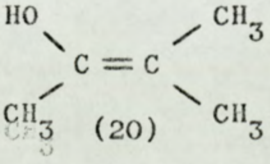
gave further evidence which supported the theory of a weak carbon-sulphur bond in β-ketosulphinamides.

The reactivity of the isopropyl ketones towards thionyl chloride was also investigated in order to establish the factors which were responsible for the activation of the methine proton. The carbonyl group could be considered to have a dual role in the reaction, it could act as a strong electron-withdrawing group and thus increase the acidity of the methine proton, or it could assist in the enolization of the ketone:

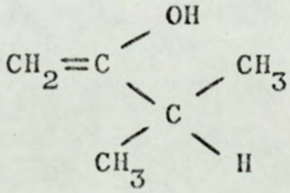


1,3-Diketones have been shown to react with thionyl chloride via their enol form as has been described in a previous part of this thesis (page 92). Further evidence which supported the theory of enolization came from the treatment of cumene, isobutyronitrile and isopropyl acetate with thionyl chloride. None of these compounds reacted with thionyl chloride when treated under similar or more forcing conditions than those employed with the isopropyl ketones. The nitrile and the carbonyl groups possess comparable electron-withdrawing properties and it is therefore deduced that enolization of the carbonyl group is the main factor responsible for the reaction of the isopropyl ketones with thionyl chloride.

The nature of enolization would have to be established once it was indicated that it was the first step in the reaction between isopropyl ketones and thionyl chloride. The phenyl- or naphthyl isopropyl ketones presented no real complications since they only possessed one α-hydrogen atom, but in the case of methyl or ethyl isopropyl ketones, enolization could follow two different and possible paths:

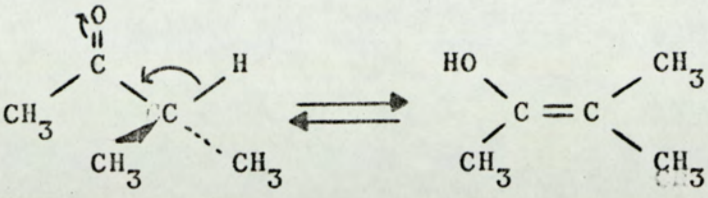


(20)



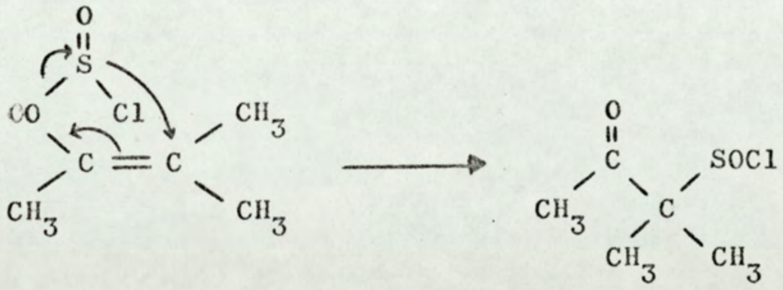
(21)

Formation of (20) would be expected to be favoured over (21) since enolization involves a shift of electrons towards the carbonyl group a process which will be greatly assisted by the two methyl groups which can inductively donate electrons:

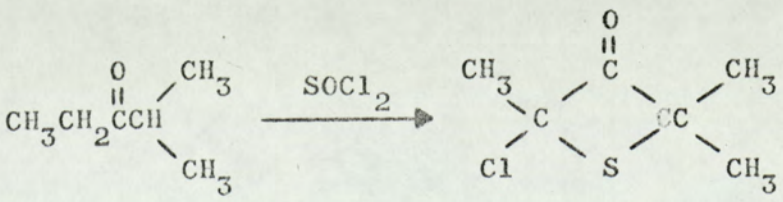


In contrast 1,1,3,3-tetraphenylpropan-2-one did not react with thionyl chloride even under forcing conditions possibly due to the inductive effect of the phenyl groups which act in opposite direction to that of the alkyl groups, and would be expected to hinder the enolization step. The nmr and ir spectra of the ketone did not show any evidence of enolization.

Electrophilic attack of the sulphur atom of thionyl chloride onto the lone pair of the oxygen of the enol form, folowed by elimination of hydrogen chloride, could then produce the proposed chlorosulphite intermediate in a similar manner encountered in the reactions of alcohols with thionyl chloride. Chlorosulphites are unstable compounds and in addition the presence of the adjacent double bond would provide a high negative charge concentration which would provoke a nucleophilic attack of the sulphur atom onto the α-carbon:



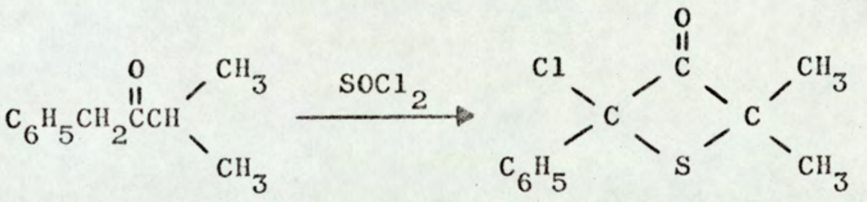
The presence of a second suitably activated methylene group in ethyl isopropyl ketone and benzyl isopropyl ketone has given rise to the formation of 3-thietanones:



(22)

The ir spectrum of the 3-thietanone(22) which was isolated and identified, showed an absorption at 1783cm^{-1} typical of a carbonyl group in a strained ring structure, whilst the nmr spectrum of the same compound consisted of three singlets indicative of a cyclic structure which produced magnetic non-equivalence of the methyl groups. In addition the mass spectrum showed a molecular ion peak at 164 mass units and another one at 166 with the correct isotopic ratios when the isotopic abundance of chlorine, sulphur and oxygen were taken into account.

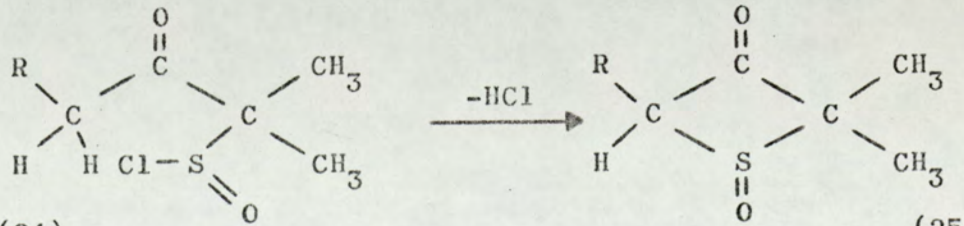
The product from the reaction of benzyl isopropyl ketone and thionyl chloride, exhibited analogous nmr and ir absorptions to the 3-thietanone(22), namely ir(C=0 1775cm^{-1}) and nmr(τ 8.50,8.14) and is believed to correspond to (23) eventhough it was only identified spectroscopically in the reaction mixture:



(23)

The ir spectrum of the crude reaction mixture from the above reaction also showed a strong absorption at 1145cm^{-1} indicative of a sulphinyl chloride group.

In view of the readily obtained β-ketosulphinyl chlorides from other isopropyl ketones, the mechanism of 3-thietanone formation can be formulated in terms of an elimination reaction between the sulphinyl chloride group in (24) and the α' methylene proton, which upon loss of hydrogen chloride gives the cyclic sulphoxide(25):



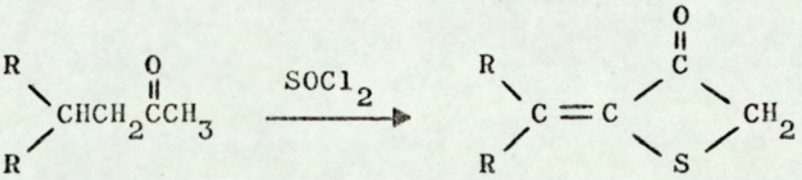
(24) (25)

R= C_6H_5- , CH_3-

The cyclic sulphoxide(25) can then be readily reduced to the 3-thietanone by a Hell Vohlard Zelinsky type addition followed by a Pummerer rearrangement, in an analogous fashion to the dimethyl sulphoxide reduction and chlorination by thionyl chloride.[27] The chloro thietanone would then be the resulting product.

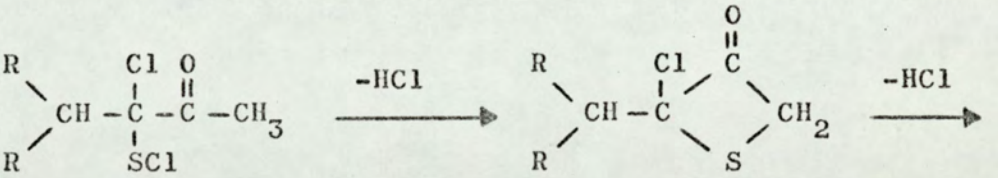
The introduction of a methyl group in the α' position of the cyclic sulphoxide(25) would be expected to render it stable towards reduction by thionyl chloride, but an attempted synthesis of 4-methyl-2-phenylpentan-3-one from isobutyronitrile and the Grignard reagent from 2-bromo-2-phenylethane, failed to give the desired starting material.

A number of 3-thietanones have been reported[22] to be produced by the reaction of 4-substituted butan-2-ones:



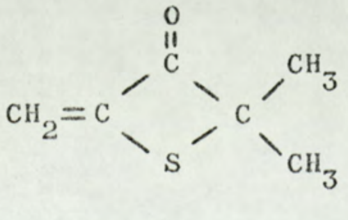
(26)

The authors proposed an α-chloro-α-sulphenyl chloride as the intermediate, which upon loss of two molecules of hydrogen chloride affords the 3-thietanone:



(26)

A similar process was not encountered in 2-chloro-2,4,4-trimethyl-3-thietanone possibly due to the instability of the terminal olefinic methylene group which would be formed(27):



(27)

CONCLUSIONS

During the course of the research which has been described in this thesis, a number of interesting conclusions regarding the reactions of thionyl chloride with ketones containing activated methylene or methine protons, were reached. Thus, the reactions with 1,3-diketones generally gave sulphides and α-chlorides eventhough the products could not always be isolated due to the formation of intractable tars. The formation of such a number of by-products presented many complications and obstructed the development of the reaction as a useful synthetic route. Eventhough a great deal of mechanistic work was carried out, it is felt that more research would have to be undertaken on this aspect of the reaction in order to establish beyond doubt the factors which influence the reaction and which are responsible for the formation of the side reactions.

However, the production of β-ketosulphinyl chlorides from the reaction between isopropyl ketones and thionyl chloride, not only afforded excellent yields but also opened the way to the preparation of this new class of compounds. It is hoped that more research will be carried out in the future, in order to investigate the complex chemistry of β-ketosulphinyl chlorides which is much influenced by the ready rupture of the carbon-sulphur bond. The formation of 3-thietanones is another interesting aspect of this work and may in future have a great potential in the preparation of these cyclic compounds.

The versatility of thionyl chloride was exhibited by its oxidative reactions with some cyclic ketones which unexpectedly aromatized rather then produced sulphides and α-chlorides. These reactions are thought to be governed by the stability conferred on the products by aromatization, and are opposite to the known and fairly well studied reductions of sulphoxides possessing alpha protons by thionyl chloride.

Lastly, a more complete investigation of the reaction of 1,1-dibenzoylethane and thionyl chloride, followed by treatment of the product with aqueous or neat ethanol, should be undertaken and this would possibly assist in the understanding of the chemistry of disulphides, trisulphides and thiosulphinates which are often encountered as intermediates or products in polymer chemistry.

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