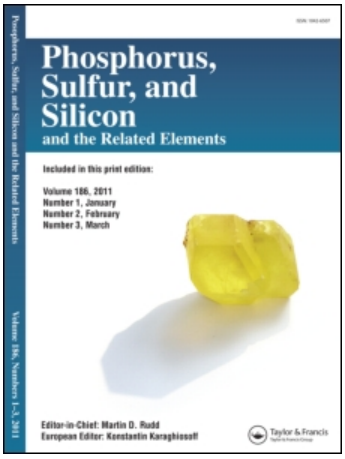

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THE REACTION BETWEEN KETONES AND THIONYL CHLORIDE

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THE REACTION BETWEEN KETONES AND THIONYL CHLORIDE

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The reaction between thionyl chloride and ketones gives rise to a variety of products depending both on the structure of the ketone and on the reaction conditions. Two rules have been formulated enabling the initial reaction product to be predicted. Some reactions involving sulphuryl chloride have also been discussed.

INTRODUCTION

A number of products has been obtained when ketones are treated with thionyl chloride. Thus certain aliphatic ketones possessing both α- and α′-protons produce thietan-3-ones,[1,2] whilst other ketones containing an activated electron-rich phenyl ring beta to the carbonyl group afforded benzo-*b*-thiophens.[3] Acetophenone has been reported[4] to react vigorously with thionyl chloride to give intractable mixtures of products. However recently these mixtures have been shown to contain α-keto-acid chlorides by treating the impure product with ethanol and isolating the α-keto-ester.[5] Deoxybenzoin on treatment with thionyl chloride has been said to yield a thiiran,[6] an oxathiole,[7a,b] or the α-diketone.[8,9] Our earlier work[2] on the reaction between certain isopropyl ketones and thionyl chloride has shown that β-ketosulphinyl chlorides are initially produced in high yields and cyclisation to the thietan-3-one can take place when α′-protons are available. The formation of α-chloro-α-sulphenyl chlorides from hindered[10] and other ketones[11] has been reported.

DISCUSSION

In view of the diversity of the products obtained in this reaction and our general interest in the chemistry of thionyl chloride we decided to study the reaction of a large number of ketones containing all possible combinations of α- and α′-protons with thionyl chloride and we have formulated two rules which are applicable to these reactions. In the following discussion our results have been tabulated according to the number of α- and α′-protons available in the ketone. It may be seen that, depending upon the structure of the ketone, a number of products, sulphinyl chlorides, chlorosulphenyl chlorides, chlorothietan-3-ones, and thietan-3-ones may be obtained. Our results can be rationalised by the following rules:

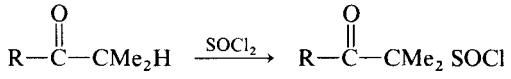
RULE 1. Selective Reactivity of α-Protons towards Thionyl Chloride. The reactivity of α-protons of the ketones follows the sequence tertiary > secondary > primary.

RULE 2. Extent of Reactivity of α-Protons towards Thionyl Chloride. α-Protons of aliphatic acyclic ketones react with thionyl chloride provided two alpha tertiary groups are not formed as a result of the reaction.

Rule 2 does not apply to ketones containing a phenyl group in the alpha-position, i.e., aryl ketones. The phenyl group does not exert a steric effect comparable in magnitude to a tertiary alkyl or similarly substituted group and hence the reactivity is not comparable. Thus isopropyl phenyl ketone (**1**) for example, afforded the sulphinyl chloride (**1a**) whilst propiophenone (**4**) gave the α-chloro-α-sulphenyl chloride (**4b**) on treatment with excess thionyl chloride, in contradistinction to Rule 2.

The ketones in the following tables are classified according to the number of α- and α′-protons present in the molecule.

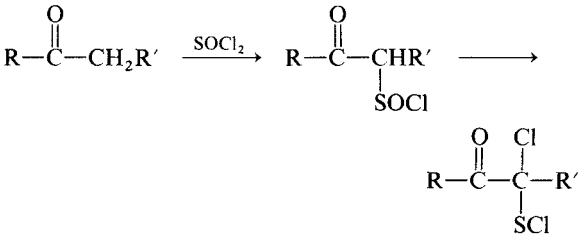
One α-Proton



1	R=C_6H_5	1a
2	R=α-$C_{10}H_7$	2a
3	R=*t*-butyl	no reaction

We have reported previously[2] the formation of the β-ketosulphinyl chlorides (**1a, 2a**) from the reaction between phenyl or α-naphthyl isopropyl ketones and thionyl chloride at room temperature. Thus in this case the aromatic rings did not possess sufficient steric hindrance to prevent a reaction occurring and hence the sulphinyl chloride was formed. In contrast *t*-butyl isopropyl ketone (**3**) did not react with thionyl chloride under any conditions in accordance with Rule 2.

Two α-Protons

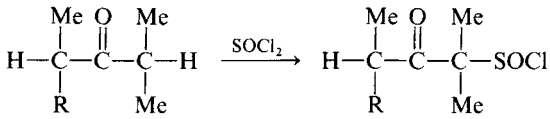


4	R=C_6H_5, R′=Me	4a	4b
5	R=m—$NO_2C_6H_4$, R′=Me	5a	
6	R=t—Bu, R′=Me	6a	

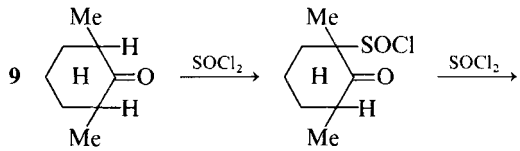
Treatment of propiophenone (**4**) with thionyl chloride rapidly gave the sulphinyl chloride (**4a**) which was only slowly converted to the α-chloro-α-sulphenyl chloride (**4b**) at room temperature after eighteen hours. Spectroscopic analysis showed that almost complete conversion to the sulphinyl chloride occurred within one hour at room temperature. Formation of **4b** presumably occurred by a Hell–Volhard–Zelinsky addition to **4a** followed by a Pummerer-type rearrangement. It was thus clearly indicated that whilst the aromatic ring did not prevent formation of the sulphenyl chloride, as did the *t*-butyl group in **6**, it did appreciably slow down the rate of formation of **4b**.

Substitution of a meta-nitro-group into the aromatic ring (**5**) resulted in formation of the sulphinyl chloride (**5a**) only, after treatment with excess thionyl chloride for seven days at room temperature. The aliphatic ketone, *t*-butyl ethyl ketone (**6**), strictly obeyed Rule 2 and only afforded the sulphinyl chloride (**6a**) on treatment with thionyl chloride.

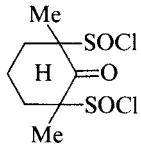
One α- and One α′-Proton



7	R=Me	7a
8	R=C_6H_5	8a



9a

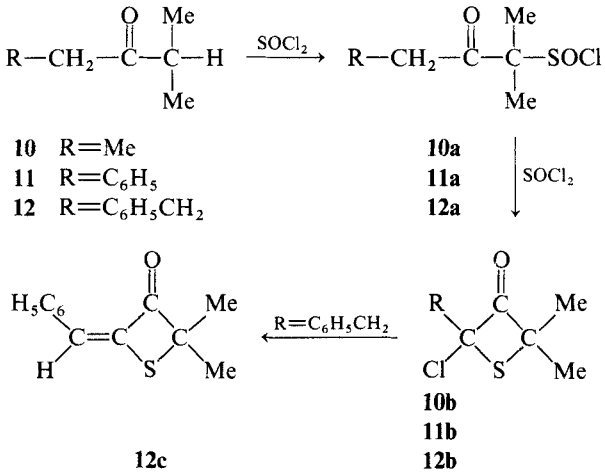


9b

Di-isopropyl ketone (**7**) on treatment with thionyl chloride, even under forcing conditions,[2] gave only the monosulphinyl chloride (**7a**) in agreement with Rule 2. This behaviour was initially attributed to the bulky nature of the chlorosulphinyl group but it was found later that treatment with sulphuryl chloride gave similar results, i.e. the monochloride formed initially (**7b**) did not form the dichloride on further treatment with sulphuryl chloride nor would it react with thionyl chloride even under forcing conditions. Similarly isopropyl α-phenylethyl ketone (**8**) gave only a monosulphinyl chloride (**8a**) on treatment with thionyl chloride.[12] However the cyclic ketone 2,6-dimethylcyclohexanone (**9**) possessing a structure similar to that of (**7**) gave a monosulphinyl chloride, identified spectroscopically, after a few hours at room temperature with thionyl chloride and then gave the disulphinyl chloride (**9b**) upon further treatment with thionyl chloride at room temperature for three days. Similar behaviour was shown when this molecule was treated with sulphuryl

chloride. This anomalous reaction was due presumably to the cyclic structure and hence less steric hindrance in the molecule.

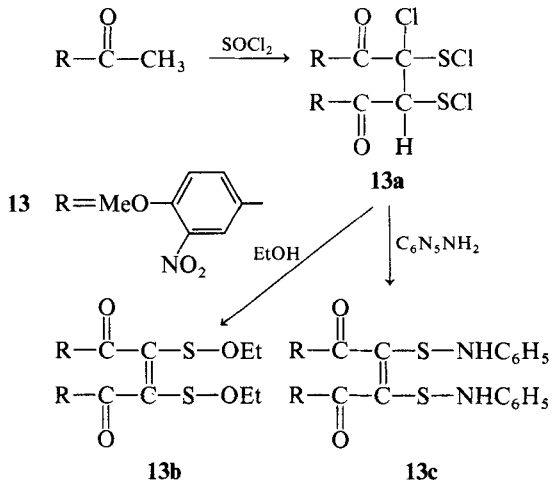
Two α- and One α′-Protons



The presence of three protons, two α and one α′, in a ketone produces two possible reaction sites. However we have found that reaction invariably occurs at the tertiary carbon atom producing the α-sulphinyl chloride (**10a**,[2] **11a**,[2] **12a**), Rule 1, which then cyclises to the chlorothietanone (**10b**,[2] **11b**[2]). Cyclisation probably proceeds via the cyclic sulphoxide which is then converted by further thionyl chloride to the chlorothietanone. If the group R contains protons then dehydrohalogenation may ensue to give the unsaturated compound (**12b** → **12c**). Compound **12b** has not been isolated but is presumed to be an intermediate in the formation of **12c**. If cyclisation of the sulphinyl chloride did not take place then further reaction of the two α′ protons, via an α′-sulphinyl chloride, to give an α′chloro-α′-sulphenyl chloride could be envisaged. However this reaction would give rise to two tertiary carbon centres on either side of the carbonyl group, in contradistinction to Rule 2, and this appears to be energetically less favourable than the alternative cyclisation which affords a secondary carbon centre.

Cyclisation to the thietanone may be spontaneous or may require catalytic quantities of a base such as pyridine. Thus the sulphinyl chloride derived from benzyl and ethyl isopropyl ketones cyclised in the absence of added base whereas (**12a**) required a small amount of pyridine for cyclisation to occur.

Three α-Protons



Acetophenone (**13**, R = C_6H_5) has been reported[5] to give an α-keto-acid chloride on treatment with thionyl chloride at 50–60°.

$$C_6H_5COCH_3 \xrightarrow{SOCl_2} C_6H_5COCOCl$$

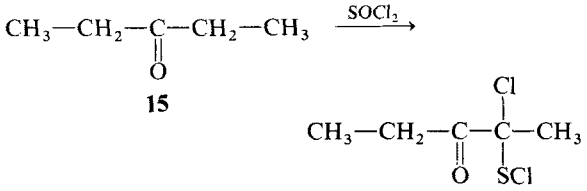
However, when we treated 4-methoxy-3-nitroacetophenone (**13**, R = 4-MeO-3-NO_2-C_6H_3-) with excess thionyl chloride at room temperature for two days the crystalline disulphenyl chloride (**13a**) was isolated. When we treated acetophenone with thionyl chloride at room temperature rather than at 50° as employed by the Russian workers, spectroscopic investigation of the crude reaction product gave similar infrared and nuclear magnetic resonance spectra to those obtained from (**13**). Spectroscopic evidence for the production of α-chloroacetophenone-α-sulphenyl chloride has also been found by Oka and Hara.[13] The crystalline disulphenyl chloride (**13a**) did not further react with thionyl chloride even under forcing conditions. However when (**13**) was treated with thionyl chloride at 60° the infrared spectra showed evidence of the presence of a 1,2-dicarbonyl compound. It thus appears that two reaction paths may be followed depending upon the reaction conditions.

The disulphenyl chloride (**13a**) was then treated with ethanol to give the unsaturated disulphenic ester (**13b**). On treatment with aniline (**13a**) gave the unsaturated sulphenanilide (**13c**) which formed an interesting molecular complex (**13d**) with benzene. Thus when the sulphenanilide was recrystallised from ethanol a bright yellow crystalline material was obtained whereas recrystallisation

from benzene gave a deep red crystalline compound. Both chemical and spectrometric analysis showed this to be a 1:1 molecular complex with benzene. This complex could be destroyed by recrystallisation from ethanol and would reform on recrystallisation from benzene. Further study of the structure of this complex is in progress.

t-Butyl methyl ketone gave a complex reaction with thionyl chloride, in the presence or absence of catalytic quantities of pyridine, and only trimethylacetyl chloride, isolated as the anilide (**14**) could be identified. It is possible that the bulky tertiary butyl group is responsible for the anomalous behaviour of this ketone.

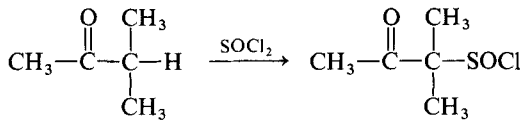
Two α- and Two α′-Protons



15 **15a**

Diethyl ketone (**15**) on treatment with thionyl chloride gave the α-chloro-α-sulphenyl chloride, presumably via the sulphinyl chloride. The sulphenyl chloride on prolonged heating or in the presence of pyridine would then give the thietanone. However this reaction was not pursued further.

Three α- and One α′-Proton

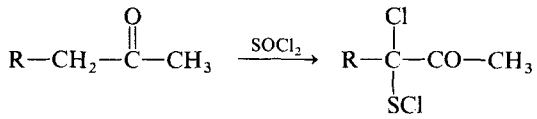


16 **16a**

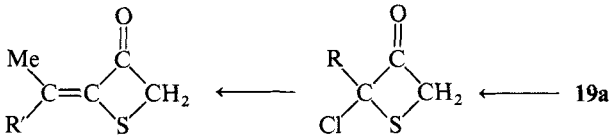
In accordance with Rule 1 the α′-proton is substituted first on treatment with thionyl chloride to give the α′-sulphinyl chloride. Thus isopropyl methyl ketone on treatment with thionyl chloride for fifteen hours at room temperature gave 2-acetylpropane-2-sulphinyl chloride[2] (**16a**) which on treatment with pyridine gave 4-chloro-2,2,4-trimethylthietan-3-one.[8]

Methyl ketones possessing two α′-protons on treatment with thionyl chloride at room temperature are substituted at the α′-position to give the α′-chloro-α′-sulphenyl chloride (**17a**, **18a**, **19a**) in accordance with Rule 1. Cyclisation to the chlorothietanone (e.g. **19b**) may then be achieved using pyridine.

Three α- and Two α′-Protons



17 R=Me **17a**
18 R=Et **18a**
19 R=Me_2CH **19a**



19c R′=Me **19b**

Thus the α′-chloro-α′-sulphenyl chloride (**19a**) was isolated from the reaction between 4-methylpentan-2-one and thionyl chloride and then on further treatment with thionyl chloride and pyridine a mixture of the chlorothietanone (**19b**) and the unsaturated molecule (**19c**)[1] was obtained. The chlorothietanone could be isolated in low yield by treating (**19**) with thionyl chloride and redistilling the residue.

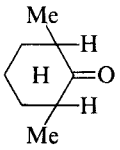
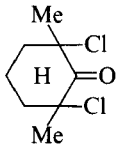
In certain cases the derived thietanone possessing an exocyclic double bond (**12c**, **18c**) was shown to give a dichloro-adduct (**20**, **21**) on further treatment with thionyl chloride in the presence of pyridine. The dichlorocompound (**21**) was assumed to arise from (**18c**) as this compound was not

12c R=C_6H_5, R′=H **20**
18c R=Me, R′=H **21**

isolated from the reaction mixture as it decomposed on distillation.

It has been shown in the preceding discussion that the reaction of ketones with thionyl chloride at room temperature follows two different routes depending on the number and distribution of the α- and α′-protons. Thus ketones possessing a tertiary α-proton and primary or secondary α′-protons give the α-sulphinyl chloride which may then cyclise to the chlorothietanone via the cyclic sulphoxide. Ketones possessing secondary methylene α-protons and other secondary or primary α′-protons may proceed via the α-chloro-α-sulphenyl chloride to the chlorothietanone. In this

The Reaction of Ketones with Sulphuryl Chloride

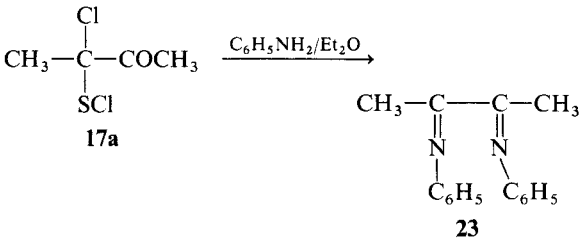
Protons	Ketone		Chloro-compound	
α	$C_6H_5COCMe_2H$	**1**	$C_6H_5COCMe_2Cl$	**1b**[2]
αα′	$Me_2CHCOCMe_2H$	**7**	$Me_2CHCOCMe_2Cl$	**7b**[2]
		**9**		**9c**
αα	$C_6H_5COCH_2CH_3$	**4**	$C_6H_5COCHClCH_3$	**4c**
			$C_6H_5COCCl_2CH_3$	**4d**
ααα′	RCH_2COCMe_2H		$R-CHCOCMe_2Cl$ (Cl)	
	R=Me **10**		**10c**	
	$R=C_6H_5$ **11**		**11c**[2]	
	R=Et **22**		**22a**	
ααα′α′	$CH_3CH_2COCH_2CH_3$	**15**	$CH_3CHCOCCl_2CH_3$ (Cl)	**15b**
αααα′	CH_3COCMe_2H	**16**	$CHCl_2COCMe_2Cl$	**16b**

case pyridine is generally necessary for cyclisation to occur.

In addition to the reaction between ketones and thionyl chloride we also studied the reactions of ketones with sulphuryl chloride. It was found, within the limited number of ketones examined, that the two rules previously postulated were also applicable even though forcing conditions had to be employed to effect trichlorination of pentan-3-one (**15**). The table gives our results.

The formation of (**4d**) once again illustrates our contention that Rule 1 should only be applied strictly to aliphatic ketones; in aryl aliphatic ketones the formation of the tertiary substituted aliphatic group is possible although the rate of formation is much slower than that of the initial substitution.

An interesting reaction occurred when we attempted to form the sulphenanilide from 2-chloro-3-oxobutane-2-sulphenyl chloride (**17a**) by treating the sulphenyl chloride with aniline. We obtained the 2,3-diphenylimino compound (**23**) rather than the expected sulphenanilide.



17a **23**

EXPERIMENTAL

α-Chlorosulphinylpropiophenone **4a.** This compound was detected spectroscopically during the reaction of propiophenone with excess thionyl chloride at room temperature cf. (**4b**). NMR (CCl_4) δ 8.3, 7.3 (m, 5H), 5.3 (q, IH), 1.7 (d, 3H). IR (thin film) ν_{max} 1142 cm^{-1} (S=O).

2-Chloro-3-oxo-3-phenylpropane-2-sulphenyl chloride **4b.** Thionyl chloride (0.25 mole) was added over a one hour period to propiophenone (0.1 mole) in a magnetically stirred vessel at room temperature. The yellow-red reaction mixture was stirred overnight and was subsequently eluted through a silica-gel colum using benzene (300 ml.). The solvent was then removed using a rotary evaporator at 40–45° to give the sulphenyl chloride as a yellow oil, yield 86%. NMR (CCl_4) δ 7.7 (m, 5H), 2.27 (s, 3H). IR (thin film) ν_{max} 1670 cm^{-1} (C=O). (Calc. for $C_9H_8Cl_2OS$: Cl, 30.21; S, 13.62. Found: Cl, 29.8; S, 13.7%).

2-Chloro-1-phenylpropan-1-one[14] **4c.** Sulphuryl chloride (0.15 mole) was slowly added to propiophenone (0.1 mole) over a period of one hour. The reaction mixture was further stirred at room temperature for two hours and was then distilled to give a 93% yield of the chloro-compound, b.p. 78° (1.5mm). NMR (CCl_4) δ 7.8 (m, 5H), 5.25 (q, IH), 1.6 (d, 3H). IR (thin film) ν_{max} 1690 (C=O) cm^{-1}. (Calc. for C_9H_9ClO: C, 64.09; H, 5.34; Cl, 21.07. Found: C, 63.8; H, 5.1; Cl, 21.4%).

2,2-Dichloro-1-phenylpropan-1-one[15] **4d.** A mixture of propiophenone (0.1 mole) and sulphuryl chloride (0.5 mole) was refluxed for two days. Excess sulphuryl chloride was then removed using a rotary evaporator. The dichloride was obtained in an 88% yield on distillation, b.p. 72° (0.1 mm). NMR (CCl_4) δ 8.3, 7.3 (m, 5H), 2.28 (s, 3H). IR (thin film) ν_{max} 1690 (C=O) cm^{-1}. (Calc. for $C_9H_8Cl_2O$: C, 53.20; H, 3.94; Cl, 34.97; Found: C, 53.05; H, 3.9; Cl, 34.6%).

1 - 3' - Nitrophenyl - 1 - oxopropane - 2 - sulphinyl chloride **5a.** 3-Nitropropiophenone (0.1 mole) and thionyl chloride (0.3 mole) were stirred together at room temperature for three days. The pale yellow reaction mixture contained the sulphinyl chloride in quantitative yield. The excess thionyl chloride was removed under high vacuum for three hours and the resulting pale yellow oil was identified as the sulphinyl chloride. NMR (CCl_4) δ 8.2 (m, 4.H), 5.4 (q, 1H), 1.75 (d, 3H). IR (thin film) ν_{max} 1660 (C=O), 1143 (S=O) cm^{-1}. (Calc. for $C_9H_8Cl\,NO_4S$: Cl, 13.57; S, 12.24; Found: Cl, 13.9; S, 12.6%).

4,4-Dimethyl - 3 - oxopentane - 2 - sulphinyl chloride **6a.** The procedure as employed for compound **5a** was used. The sulphinyl chloride was obtained as a pale yellow liquid. NMR (CCl_4) δ 4.85 (q, 1H), 1.6 (2d, 3H), 1.2 (s, 9H). IR (thin film) ν_{max} 1690 (C=O), 1150 (S=O) cm^{-1}. (Calc. for $C_7H_{13}Cl\,O_2S$: Cl, 18.07; S, 16.2; Found: Cl, 18.3; S, 16.5%).

2,6 - Dichlorosulphinyl - 2, 6 - dimethylcyclohexanone **9b.** The procedure as described for **5a** was used to give the dichlorosulphinyl compound as a dark yellow oil. NMR (CCl_4) δ 1.9 (m). IR (thin film) ν_{max} 1700 (C=O), 1150 (S=O) cm^{-1}. (Calc. for $C_8H_{14}Cl_2O_3S_2$: Cl, 24.23; S, 21.84. Found: Cl, 24.8; S, 22.1%). 2,6-Dimethylcyclohexanone was obtained by the sodium dichromate/sulphuric acid oxidation of the corresponding alcohol. NMR (CCl_4) δ 2.25 (m, 2H), 1.79 (m, 6H), 0.95 (d, 6H).

2,6 - Dichloro - 2,6 - dimethylcyclohexanone **9c.** Sulphuryl chloride (0.4 mole) was slowly added to the ketone (0.1 mole) at room temperature. The reaction mixture was then further stirred for twenty-four hours at room temperature and the excess sulphuryl chloride was then removed under high vacuum. The crystals obtained were recrystallised from a small quantity of hot hexane to give an 83% yield of the dichloride as white needle crystals, m.p. 37–38°. NMR (CCl_4) δ 2.2 (m, 6H), 1.78 (s, 6H). IR (thin film) ν_{max} 1735 (C=O) cm^{-1}. (Calc. for $C_8H_{12}Cl_2O$: C, 49.23; H, 6.15; Cl, 36.41; Found: C, 48.9; H, 5.9; Cl, 36.1%).

2,4 - Dichloro - 2 - methylpentan - 3 - one **10c.** Ethyl isopropyl ketone (0.1 mole) and sulphuryl chloride (0.5 mole) were refluxed together for twenty-four hours and the excess sulphuryl chloride was then removed using a rotary evaporator. Distillation afforded the dichloro-compound in 93% yield, b.p. 130° (20 mm). NMR (CCl_4) δ 5.1 (q, 1H), 1.85 (s, 3H), 1.70 (s, 3H), 1.68 (d, 3H). IR (thin film) ν_{max} 1735 (C=O) cm^{-1}. (Calc. for $C_6H_{10}Cl_2O$: C, 42.60; H, 5.92; Cl, 42.01. Found: C, 42.4; H, 5.6; Cl, 42.3%).

2 - Methyl - 3 - oxo - 5 - phenylpentane - 2 - sulphinyl chloride **12a.** A mixture of thionyl chloride (0.3 mole) and 2-methyl-5-phenylpentan-3-one (0.1 mole) was stirred at room temperature for 5–6 hours until evolution of gases had ceased. The excess thionyl chloride was removed under high vacuum and the resulting viscous yellow oil was then recrystallised from petroleum ether/ether to give an 86% yield of the sulphinyl chloride as white crystals. NMR ($CDCl_3$) δ 7.1 (s, 5H), 2.9 (s, 4H), 1.58 (s, 6H). IR (thin film) ν_{max} 1695 (C=O), 1143 (S=O) cm^{-1}. (Calc. for $C_{12}H_{15}ClO_2S$: Cl, 13.73; S, 12.38. Found: Cl, 13.5; S, 12.0%). 2-Methyl-5-phenylpentan-3-one (**16**) was prepared by the action of isobutyronitrile on 2-phenylethylmagnesium chloride, b.p. 100–101° (0.5 mm). NMR (CCl_4) δ 7.1 (s, 5H), 2.7 (s, 4H), 2.2 (sp, 1H), 1.0 (d, 6H). IR (thin film) ν_{max} 1709 (C=O) cm^{-1}.

4 - Benzylidene - 2,2 - dimethylthietan - 3 - one **12c.** A mixture of thionyl chloride (0.5 mole) and 2-methyl-5-phenylpentan-3-one (0.1 mole) was stirred at room temperature for six hours. Pyridine (2 ml) was added and the reaction flask was then maintained at 60° for six hours. The excess thionyl chloride was then removed using a rotary evaporator and the precipitated pyridinium hydrochloride was quickly filtered off. The resulting oil either crystallised slowly to give the thietanone or the thietanone could be obtained by distillation, b.p. 138–140° (0.7 mm). The crystals were then recrystallised from the minimum amount of petroleum ether (40–60°) to give a 68% yield of the thietanone m.p. 46–47°. NMR ($CDCl_3$) δ 7.3 (s, 5H), 7.25 (s, 1H), 1.7 (s, 6H). IR (thin film) ν_{max} 1743 (C=O) cm^{-1}. (Calc. for $C_{12}H_{12}OS$: C, 70.59; H, 5.88; S, 15.69; Found: C, 70.7; H, 5.6; S, 15.5%).

2 - Chloro - 1,4 - di - (4 - methoxy - 3 - nitrophenyl) - 1,4 - dioxobutane - 2,3 - disulphenyl chloride **13a**. 4 - Methoxy - 3 - nitroacetophenone (0.1 mole) was treated with thionyl chloride (0.43 mole) and antibumping granules were added. After an initial induction period the reaction proceeded rapidly at room temperature. After forty-eight hours precipitation of the product took place. The crystals were filtered off, washed ×2 with benzene and recrystallised from a small amount of hot benzene to give a white amorphous compound, the disulphenyl chloride in 39% yield, m.p. 159°. NMR (acetone) δ 7.8 (m, 6H), 6.55 (s, 1H), 4.0 (s, 6H). IR (KBr disk) ν_{max} 1675 (C=O) cm^{-1}. (Calc. for $C_{18}H_{13}Cl_3N_2O_8S_2$: C, 38.88; H, 2.34; N, 5.04; S, 11.52; Cl, 19.17; Found: Cl, 39.2; H, 2.5; N, 5.0; S, 11.5; Cl, 18.7%).

Diethyl 1,4 - di - (4 - methoxy - 3 - nitrophenyl) - 1,4 - dioxobut - 2 - ene - 2,3 - disulphenate **13b.** The disulphenyl chloride (**13a**, (0.01 mole) was refluxed with a large excess of ethanol (50 ml) until dissolution took place, ca. one hour. The excess ethanol was then removed and the resulting yellow oil was recrystallised from a small quantity of hot petroleum ether (60–80°) to give yellow plates of the ester, m.p. 69–70°, yield 73%. NMR ($CDCl_3$) δ 7.6 (m, 6H), 4.8 (q, 4H), 4.05 (s, 6H), 1.5 (t, 6H). IR (thin film) ν_{max} 1688 (C=O) cm^{-1}. (Calc. for $C_{22}H_{22}N_2O_{10}S_2$: C, 49.07; H, 4.09; N, 5.20. Found: C, 49.1; H, 4.0; N, 5.3%).

2,3 - Disulphenanilino - 1,4 - di - (4 - methoxy - 3 - nitrophenyl) - but-2-ene-1,4-dione **13c.** A mixture of the disulphenyl chloride (**13a**, 0.01 mole) and aniline (0.07 mole) in dry diethyl ether (100 ml) was stirred at room temperature for three hours and was then refluxed for one hour. The red precipitate, which formed on cooling, was filtered off, washed ×2 with water and then recrystallised from benzene to give red needle crystals of a 1:1 molecular complex of **13c** with benzene (**13d**), m.p. 130°, yield 72%.

13d. NMR (acetone) δ 11.6 (s, 2H), 7.8 (m, 16H), 7.3 (s, 6H), 4.0 (s, 6H). IR (KBr disc) ν_{max} 3295 (NH), 1660 (C=O) cm^{-1}. (Calc. for $C_{36}H_{30}N_4O_8S_2$: C, 60.84; H, 4.22; N, 7.89. Found: C, 61.1; H, 4.2; N, 7.9%).

If a small amount of ethanol was employed in the recrystallisation yellow crystals of the sulphenanilide (**13c**) were obtained m.p. 143°, yield, 65%.

13c. NMR (acetone) δ 11.6 (s, 2H), 7.8 (m, 16H), 4.0 (s, 6H) IR (KBr disc) ν_{max} 3260 (NH), 1660 (C=O) cm^{-1}. (Calc. for $C_{30}H_{24}N_4O_8S_2$: C, 56.95; H, 3.80; N, 8.86; S, 10.13; Found: C, 56.5; H, 3.7; N, 8.8; S, 9.9%).

Trimethylacetanilide. **14.** A mixture of *t*-butyl methyl ketone (0.1 mole), thionyl chloride (0.5 mole), and pyridine (2 ml) was refluxed for two days. The resulting dark red oil was then fractionated to give trimethylacetyl chloride, b.p. 95–98°. The acid chloride was then dissolved in dry ether, cooled to −30° and a slight excess of aniline was carefully added. The precipitate was washed with water and the anilide was recrystallised from ethanol to give white needle crystals, m.p. 128° (lit. 127–129°)[17], yield 20%. NMR (CD Cl_3) δ 7.3 (m, 6H), 1.3 (s, 9H).

2 - Chloro - 3 - oxopentane - 2 - sulphenyl chloride **15a.** Thionyl chloride (2 moles) was slowly added over a one hour period to pentan-3-one (1 mole) in a magnetically stirred flask in an ice-bath. After the initial vigorous reaction had ceased the reaction mixture was stirred at room temperature for eighteen hours. The mixture was then degassed and distilled from an oil bath at 120° to give the sulphenyl chloride, yield 49%, b.p. 66–72° (6 mm). NMR (CCl_4) δ 2.94 (q, 2H), 2.09 (s, 3H), 1.17 (t, 3H). IR (thin film) ν_{max} 1720 (C=O) cm^{-1}. (Calc. for $C_5H_8Cl_2OS$: S, 17.11; Cl, 37.96; Found: S, 16.8; Cl, 38.3%).

2,2,4-Trichloropentan-3-one **15b.** A mixture of pentan-3-one (0.1 mole) and sulphuryl chloride (0.5 mole) was refluxed for five days and the excess sulphuryl chloride was removed using a rotary evaporator. The trichloro-compound was obtained in a 90% yield on distillation, b.p. 53–54° (0.5 mm). NMR (CCl_4) δ 4.8 (q, 1H), 1.75 (s, 3H), 1.2 (d, 3H). IR (thin film) ν_{max} 1740 (C=O) cm^{-1}. (Calc. for $C_5H_7Cl_3O$: 31.66; H, 3.69; Cl, 56.20. Found: C, 31.9; H, 3.7; Cl, 55.9%).

1,1,3 - Trichloro - 3 - methylbutan - 2 - one[18] **16b.** A mixture of 3-methylbutan-2-one (0.1 mole) and sulphuryl chloride (0.5 mole) was refluxed for seven days and the excess sulphuryl chloride was removed using a rotary evaporator. The trichloro-compound was obtained in a 97% yield on distillation, b.p. 136° (5 mm). NMR (CCl_4) δ 6.85 (s, 1H), 1.80 (s, 6H). IR (thin film) ν_{max} 1740 (C=O) cm^{-1}. (Calc. for $C_5H_7Cl_3O$: C, 31.66; H, 3.69; Cl, 56.20. Found: C, 31.8; H, 3.7; Cl, 56.1%).

2 - Chloro - 3 - oxobutane - 2 - sulphenyl chloride **17a.** Thionyl chloride (2 moles) was slowly added at room temperature over a one-hour period to ethyl methyl ketone (1 mole) contained in a magnetically stirred reaction vessel. Hydrogen chloride was evolved and the mixture turned brown-black. It was then stirred for a further two hours at room temperature until the evolution of gases had finished. Any residual gases were then pumped off. Distillation under reduced pressure using an oil-bath afforded a yellow oil, b.p. 50° (3 mm) in a 47% yield. NMR (CCl_4) δ 2.5 (s, 3H), 2.10 (s, 3H). IR (thin film) ν_{max} 1710 (C=O) cm^{-1}. (Calc. for $C_4H_6Cl_2OS$: Cl, 41.04; S, 18.49. Found: Cl, 40.9; S, 18.3%.

3 - Chloro - 2 - oxopentane - 3 - sulphenyl chloride **18a.** Methyl n-propyl ketone was treated with thionyl chloride using the conditions described for the preparation of **15a**. The sulphenyl chloride was obtained as a yellow liquid, b.p. 60–68° (0.5 mm), yield 62%. NMR (CCl_4) δ 2.48 (s, 3H), 2.37 (q, 2H), 1.08 (t, 3H). IR (thin film) ν_{max} 1720 (C=O) cm^{-1}. (Calc. for $C_5H_8Cl_2OS$: Cl, 37.96; S, 17.11. Found: Cl, 37.8; S, 17.3%).

3-Chloro-2-methyl-4-oxopentane-3-sulphenyl chloride **19a.** 4 - Methylpentan-2-one (0.1 mole) was stirred overnight at room temperature with thionyl chloride (0.2 mole). The flask was placed under vacuum for one hour and the resulting oil was distilled under reduced pressure to give a 58% yield of the sulphenyl chloride, b.p. 66–70° (0.6 mm). NMR (CCl_4) δ 2.46 (s, 3H), 2.40 (sp, IH), 1.25–0.88 (m, 6H). (Calc. for $C_6H_{10}Cl_2SO$: Cl, 35.32; S, 15.92; Found: Cl, 34.9; S, 16.5%).

2 - Chloro - 2 - isopropylthietan - 3 - one **19b.** The procedure as given for **19a** was employed. The chlorothietanone was obtained in a 5% yield, b.p. 82° (10 mm). NMR (CCl_4) δ 4.32 (2d, 2H), 2.22 (sp, 1H), 1.1 (d, 6H). (Calc. for C_6H_9ClSO: Cl, 21.58; S, 19.45; Found: Cl, 21.3; S, 19.8%).

2 - Chloro - 2 - α - chlorobenzyl - 4,4 - dimethylthietan - 3 - one **20.** 4-Benzylidene-2,2-dimethylthietan-3-one (**12c**) was refluxed for 48 hours with a large excess of thionyl chloride and a few drops of pyridine. The oil obtained, on removal of the excess thionyl chloride, was eluted from a silica gel column using petroleum ether (40–60°) and diethyl ether in a 9.1 ratio. NMR (CCl_4) δ 7.5 (m, 6H), 1.75 (s, 3H), 1.5 (s, 3H). IR (thin film) ν_{max} 1785 (C=O) cm^{-1}.

2 - Chloro - 2 - 1' - chloroethyl - 4,4 - dimethylthietan - 3 - one **21.** Thionyl chloride (0.5 mole) was slowly added to a mixture of *n*-propyl isopropyl ketone (0.1 mole) and 2 ml. of pyridine. The mixture was then refluxed for twenty hours, the excess thionyl chloride was removed using a rotary evaporator, and the resulting oil was then distilled under reduced pressure. A yellow oil was obtained, b.p. 80° (0.5 mm), yield 37%. NMR (CCl_4) δ 4.5 (q, 1H), 1.9 (s, 3H), 1.67 (s, 3H), 1.65 (d, 3H). IR (thin film) ν_{max} 1780 (C=O) cm^{-1}. (Calc. for $C_7H_{10}Cl_2OS$: Cl, 33.33; S, 15.02; Found: Cl, 33.8; S, 15.0%).

2,4 - Dichloro - 2 - methylhexan - 3 - one **22a.** A mixture of *n*-propyl isopropyl ketone (0.1 mole) and sulphuryl chloride (0.5 mole) was refluxed for twenty-four hours. The excess sulphuryl chloride was removed using a rotary evaporator and the dichloro-compound was obtained on distillation, b.p. 40° (0.1 mm), 95% yield. NMR (CCl_4) δ 4.9 (t, 1H), 1.8 (s, 3H), 1.7 (s, 3H), 1.2 (m, 5H). IR (thin film) ν_{max} 1730 (C=O) cm^{-1}. (Calc. for $C_7H_{12}Cl_2O$: C, 45.90; H, 6.56; Cl, 38.80. Found: C, 46.0; H, 6.6; Cl, 38.6%).

2,3 - Diphenyliminobutane **23.** Aniline (0.5 mole) was added to a solution of 2-chloro-3-oxobutane-2-sulphenyl chloride (**17a**, 0.1 mole) in dry diethyl ether (100 ml) maintained at 10–15°. The reaction mixture was then stirred at room temperature for a further two hours and the precipitate was filtered off. The filtrate was then connected to a vacuum source and upon concentration precipitation took place. The crystals were filtered off, washed with ethanol and the filtrate and washings were then concentrated. The crystals were recrystallised from hot ethanol by decanting the mother liquor and discarding the undissolved powder. Yellow plates of the diphenylimino-compound were obtained, m.p. 127–129°, (lit. 139°)[19], yield 50%. NMR ($CDCl_3$) δ 7.0 (m, 10H), 2.1 (s, 6H). IR (KBr disc) ν_{max} 1635 (C=N) cm^{-1}. (Calc. for $C_{16}H_{16}N_2$: C, 81.36; H, 6.78; N, 11.86. Found: C, 80.9; H, 6.7; N, 11.4%).

REFERENCES

1. A. J. Krubsack, T. Higa, and W. E. Slack, *J. Amer. Chem. Soc.*, **92**, 5258 (1970).
2. J. S. Pizey and K. Symeonides, *Phosphorus and Sulfur*, **1**, 41 (1976). K. Symeonides, Ph.D. Thesis, Univ. of Aston in Birmingham, (1973).

3. A. J. Krubsack, R. Sehgal, and W. Loong, *J. Org. Chem.*, **40**, 3179 (1975).
4. F. Loth and A. Michaelis, *Ber. Otsch. Chem. Ges.*, **27**, 2540 (1894).
5. A. S. Bespalyi, V. V. Krut, I. N. Zhukov, and S. A. Panaeva, U.S.S.R. 390,069 (1973), *Chem. Abs.*, **79**, 126104.
6. C. J. Ireland and J. S. Pizey, *J. Chem. Soc. Chem. Comm.*, **4** (1972). A further study of this reaction has shown the product to be benzil rather than the thiiran, cf. Ref. 8.
7a. U. Jacobsson, T. Kempe and T. Norin, *J. Org. Chem.*, **39**, 2722 (1974).
7b. A. Senning, *Bull. Soc. Chim. Belges*, **86**, 675 (1977). This paper describes the isolation of 2,2,4-tribenzoyl-5-phenyl-1,3-oxathiole by treating dibenzoylmethane with thionyl chloride.
8. J. S. Pizey, unpublished observations. We have compared the sample of oxathiole kindly sent to us by Prof. T. Norin and agree with him that he has obtained an oxathiole. However the compound isolated by us has been shown by infrared analysis to differ from his sample and to have a ^{13}C NMR spectrum identical to that of benzil.
9. K. Oka and S. Hara, *Tetrahedron Letters*, 695 (1977). The initial compound isolated was the α-chloro-α-sulphenyl chloride which was transformed into the α-diketone on treatment with morpholine and subsequent hydrolysis of the α-chloro-α-sulphenamide.
10. I. Crossland, *Acta Chem. Scand.*, **30B**, 787 (1976).
11. J. S. Pizey and K. Symeonides, VII Internat. Symposium on Organic Sulphur Chemistry (1976), Abstracts p. 134.
12. R. P. Gupta, Ph.D. Thesis, Univ. of Aston in Birmingham, (1976).
13. K. Oka and S. Hara, *Tetrahedron Letters*, 2783 (1976).
14. Luong Thi, N. T., H. Riviere, and A. Spassky, *Bull. Soc. Chim., France* 2102 (1973).
15. M. Ballister and J. Riera, *Anales real Soc. Espan. fis. y quim*, **56**, 897 (1960).
16. R. Jacquier, M. Mousseron, and S. Boyen, *Bull. Soc. Chim. France*, 1653 (1956).
17. I. Heilbron and H. M. Bunbury, *Dictionary of Organic Compounds*, Vol. 4, p. 224, Eyre and Spottiswoode, (1953).
18. G. F. Hennion and G. M. Wolf, *J. Amer. Chem. Soc.*, **62**, 1368 (1940).
19. H. von Pechmann, *Ber. Ostch. Chem. Ges.*, **21**, 1411 (1888).