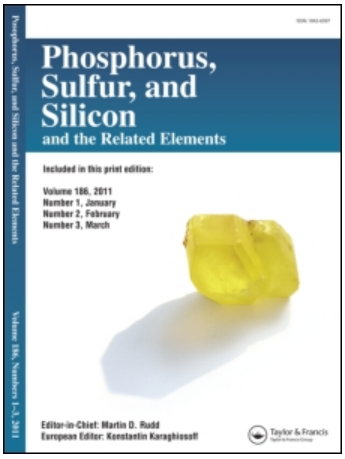

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β-KETOSULPHINAMIDES: THEIR PREPARATION AND PROPERTIES

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β-KETOSULPHINAMIDES: THEIR PREPARATION AND PROPERTIES

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A number of β-ketosulphinamides has been prepared by treating the approriate β-ketosulphinyl chloride with the amine. The ketosulphinamides on treatment with water or ethanol undergo an abnormal cleavage to give the parent ketone rather than the sulphinic acid or ester. A disproportionation to the sulphenamide and sulphonamide has been observed in only one case. A novel rearrangement occurs when certain ketosulphinamides are treated with diethylamine.

INTRODUCTION

The chemistry of β-ketosulphinamides has not been previously examined in any detail and we decided to study these compounds further after attempting to characterise β-ketosulphinyl chlorides[1] by treatment with a number of amines. Corey and Durst in an early paper[2] suggested that β-ketosulphinamides may be produced from β-hydroxysulphinamides and would be rapidly decomposed by water. However they did not isolate or study these compounds.

RESULTS AND DISCUSSION

Our initial study[1] on the reaction between β-ketosulphinyl chlorides and aniline, *N*-methylaniline, and piperidine suggested that the sulphinamides were extremely unstable and we were unable to obtain them in a pure state. However more recent work, outlined in this paper, has shown that both alkyl and aryl sulphinamides may be obtained and their chemistry studied. A number of sulphinyl chlorides derived from isopropyl ketones were treated with a variety of amines and the appropriate β-ketosulphinamides were obtained in good yields. Thus aliphatic (**1**,**2**,**3**,**4**,**7**,**8**,**9**,), cycloaliphatic (**6**) and aromatic (**5**) ketones containing an α-isopropyl moiety could be readily converted to the α-sulphinyl chloride on treatment with thionyl chloride,[1] and then the chloride gave the β-ketosulphinamide on treatment with the amine. Both aliphatic (**3**) and aromatic (**1**,**2**,**4**,**5**,**6**,**7**) primary amines and also secondary amines, diethylamine (**8**), *N*-methylaniline (**9**), and piperidine (**10**), were used in the preparation of the sulphinamides.

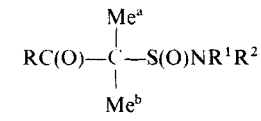
Thus the β-ketosulphinamides may be obtained pure and in excellent yield by using anhydrous conditions, i.e. the dry amine (0.2 mole) in dry ether was slowly added to the β-ketosulphinyl chloride (0.1 mole) in dry ether at ice-bath temperatures. The precipitated amine hydrochloride was then rapidly filtered off and the excess ether was removed using a rotary evaporator. Precise details are given in the Experimental Section. It should be noted that the sulphinamides often decompose on distillation and are rapidly hydrolysed by water.

Spectral Properties

The β-ketosulphinamides showed the characteristic infrared absorption for the sulphoxide group generally at 1060 ± 10 cm^{-1}. An nmr study of isopropyl β-ketosulphinamides showed the diastereotopic effect caused by the chiral sulphoxide group making the gem-dimethyl groups non-equivalent. The chemical shifts shown by certain β-ketosulphinamides are given in Table I. A diastereotopic effect has also been found in both sulphinamides[3] and β-ketosulphinyl chlorides.[4]

TABLE 1

Characteristic absorption of sulphinamides

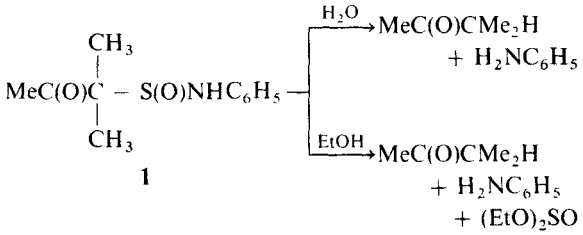


No.	R	R^1	R^2	γso	γco	τMe_a	τMe_b	ΔMe_a-Me_bH_2
1	Me	H	C_6H_5	1068	1700	8.62	8.48	14
2	Me	H	$mCH_3C_6H_4$	1060	1696	8.60	8.45	15
3	Me	H	Et	1100	1660	9.10	8.90	20
4	Me_2CH	H	C_6H_5	1062	1690	8.45	8.45	0
5	C_6H_5	H	C_6H_5	1060	1710	8.20	8.20	0
6	C_6H_{11}	H	C_6H_5	1060	1680	8.50	8.42	8
7	$C_6H_5(CH_2)_2$	H	C_6H_5	1060	1710	8.60	8.42	18
8	Me	Et	Et	1070	1690	8.72	8.60	12
9	Me	Me	C_6H_5	1055	1700	8.75	8.65	10
10	Me	—$(CH_2)_5$—		1083	1700	8.62	8.55	7

CHEMICAL PROPERTIES

a) Reaction with Water or Ethanol

Treatment of the β-ketosulphinamides with either water or ethanol led to cleavage of the carbon-sulphur bond to give the parent ketone and the amine rather than hydrolysis to the sulphinic acid in the case of water or conversion to the sulphinate, as is observed with sulphinamides in the presence of acids,[5] in the case of ethanol.



1

The presence of a tertiary carbon atom to the sulphinyl group does not appear to be responsible for the anomalous reactions. Adamantane-1-sulphanilide,[1] for example, undergoes the "normal" reactions of a sulphanilide. Hence we suggest that the main factors responsible for the reactivity of β-ketosulphinamides in the presence of nucleaphiles is the presence of the neighbouring carbonyl group, the electron-withdrawing properties of which, coupled with those of the N-R and sulphinyl groups, may well assist in the rupture of the carbon-sulphur bond.

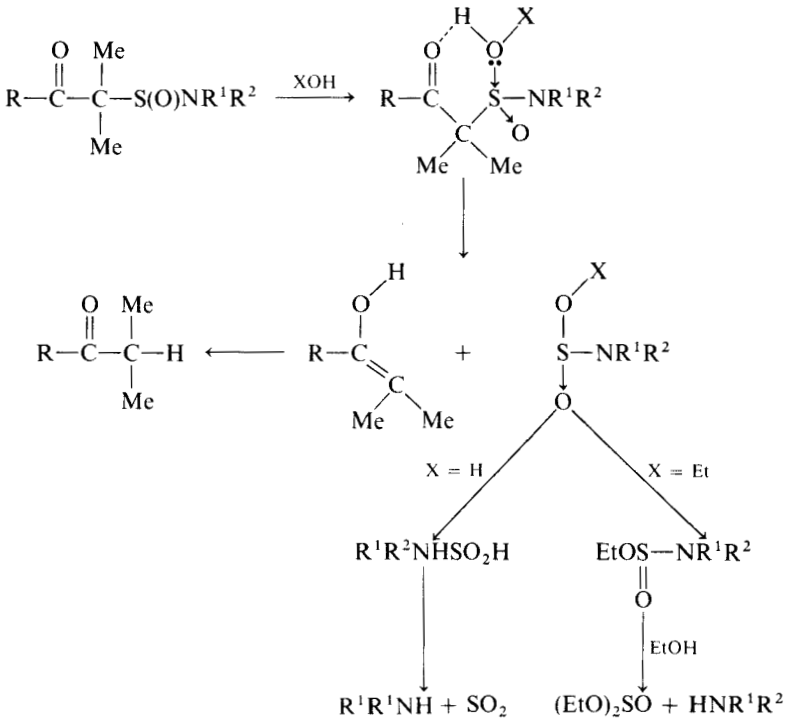
Two different schemes may be proposed for the above reactions, i.e. the initial attack of the nucleophile could occur at either of the two electron-deficient sites in the molecule, the sulphoxide or carbonyl centres. The first scheme, which is an extension of that proposed by Corey[2] for the oxidation of β-hydroxysulphinamides by manganese dioxide to ketones, involves attack of the sulphoxide group by the nucleophile forming a six-membered ring as shown in Scheme 1.

However attack could also occur at the carbonyl group giving a reaction path as shown in Scheme 2.

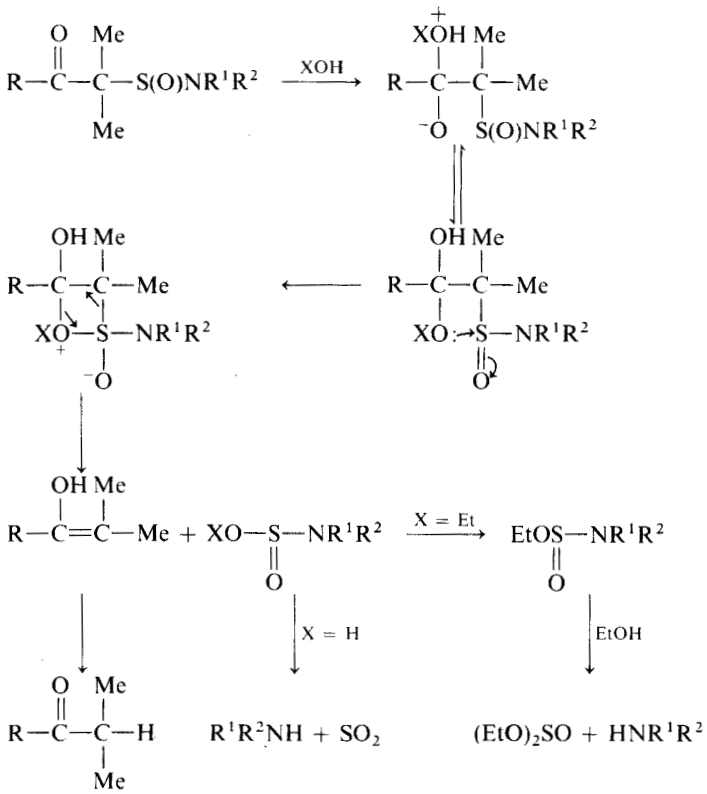
The second scheme involving attack at the carbonyl group is also in agreement with a reaction pathway proposed by us for the rearrangement of β-ketosulphinamides in the presence of diethylamine. The hydrolysis of β-ketosulphinamides by water occurs very readily, generally at room temperature, to give high yields of the ketone and the amine. However in the case of 2-methyl-3-oxo-5-phenylpentane-2-sulphanilide (**7**) the solid compound did not go into solution at room temperature and hydrolysis was effected by treating with water at 60° for 18 hours.

b) Reaction with Diethylamine

We anticipated that treatment of the β-ketosulphinamide with a secondary base such as diethylamine could well give us the original ketone plus a sulphurous amide by a pathway analogous to that shown in Scheme 2.



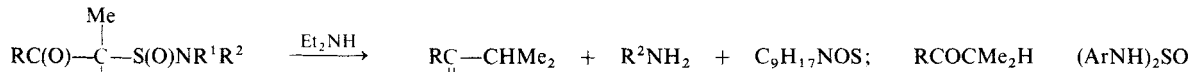
SCHEME 1



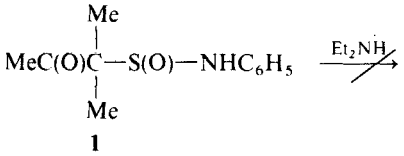
SCHEME 2

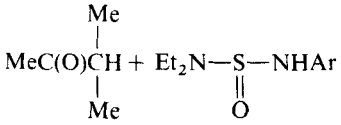
TABLE II

The reactions of certain β-ketosulphinamides with diethylamine are summarised in Table II

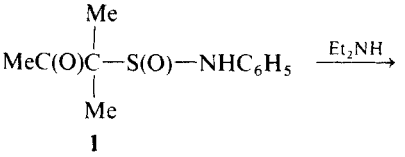


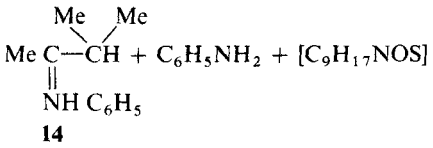
No.	R	R¹	R²	R R²	R²		RCOCHMe₂ R	
1	Me	H	C_6H_5	+	+	+	−	−
2	Me	H	$H_6H_4CH_3m$	+[9]	+	+	−	−
3	Me	H	Et	+[9]	−?	+	−	−
4	Me_2CH	H	C_6H_5	−	−	−	+,65%	+,32%
5	C_6H_5	H	C_6H_5	−	−	−	+,68%	+,34%
6	C_6H_{11}	H	C_6H_5	+[9]	−	−	−	−
8	Me	Et	Et			no reaction		
9	Me	Me	C_6H_5			no reaction		
	Adamantane-1-sulphinanilide					no reaction		





However instead of the expected products we obtained an azomethine, the amine derived from the sulphinamide, and an unidentified product $C_9H_{17}NOS$.





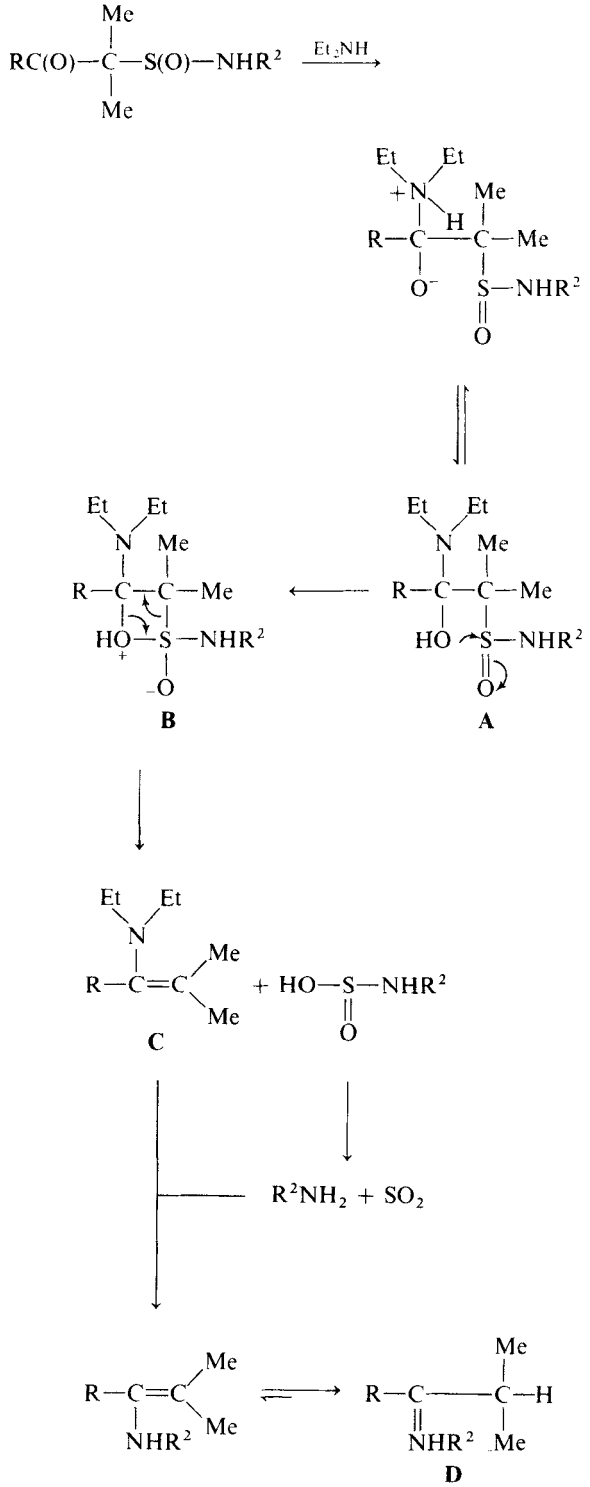
The following Scheme 3 is suggested for the reaction pathway

We envisage an initial attack by the amine on the carbonyl group of the β-ketosulphinamide, cf Scheme 2. In cases where there is high steric hindrance to attack, e.g. where R = Me_2CH (**4**), or where there is charge delocalisation around the ring, R = C_6H_5 (**5**), attack at the carbonyl group does not occur and the reaction follows Scheme 1 to give the parent ketone and dianilinosulphoxide (**15**). The formation of dianilinosulphoxide may be explained by decomposition of the initial product $Et_2N—SO—NHC_6H_5$ to give aniline followed by further attack of the formed aniline on the initial product.

We found that the results obtained when we treated a number of ketones with aniline to form an azomethine substantiated our views on the reactivity of the carbonyl group in this reaction. Thus neither di-isopropyl ketone nor phenyl isopropyl ketone reacted with aniline whereas cyclohexyl isopropyl ketone gave an azomethine under similar conditions. It should be noted that the tertiary sulphinamides (**8** and **9**) did not react with diethylamine, i.e. they did not rearrange nor did they undergo the "normal" cleavage reaction.

The β-hydroxysulphinamide (**A**) may then eliminate sulphur dioxide and an amine via the cyclic four-membered ring (**B**) to give the enamine (**C**) by a preferred[6] *cis*-elimination. Treatment of isopropyl ketones with diethylamine did not give rise to an enamine. Hence we suggest that enamine formation depends on the presence of both the carbonyl and sulphoxide groups in an 1,3-position within the molecule enabling ready elimination to take place. The enamine (**C**) relieves strain by the reaction with aniline and then tautomerises to the more stable imino-form (**D**).

Treatment of 2 - methyl - 3 - oxobutane - 2 - sulphinanilide (**1**) with diethylamine in the presence

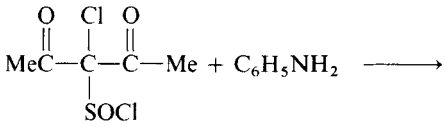


SCHEME 3

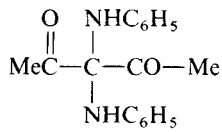
of a base of comparable strength to aniline, e.g. *m*-toluidine, resulted in the formation, in equal amounts, of *N*-2(3-methylbutylidene)aniline and *N*-2(3-methylbutylidene)*m*-toluidine. The use of *p*-anisidine, a much stronger base than aniline, resulted in the formation of *N*-2(3-methylbutylidene)*p*-anisidine only. These experiments suggest the reaction to be intermolecular in accordance with Scheme 3. However rather surprisingly we found that *N*-2(3-methylbutylidene)aniline readily underwent an exchange reaction with *m*-toluidine to give *N*-2(3-methylbutylidene)*m*-toluidine. This is contrary to the reported exchanges of primary aromatic amines with azomethines which were found to be difficult and to require the reaction to be effected in a sealed tube at 120–130° for two to three hours.[7] We are continuing our research into the mechanism of this rearrangement.

c) Reaction with Aniline

A weak carbon sulphur bond may also be seen in the reaction between 3-chloro-2,4-dioxopentane-3-sulphinyl chloride (**12**) and aniline. Thus the carbon-sulphur bond is cleaved to give an anilino-compound rather than the sulphur-chlorine bond to give the sulphanilide. 3-Chloro-2,4-dioxopentane-3-sulphinyl chloride (**12**) was prepared by cleaving bis(diacetylmethyl) disulphide (**11**) with chlorine in the presence of acetic anhydride. The method is an adaptation of that of Douglass.[8]

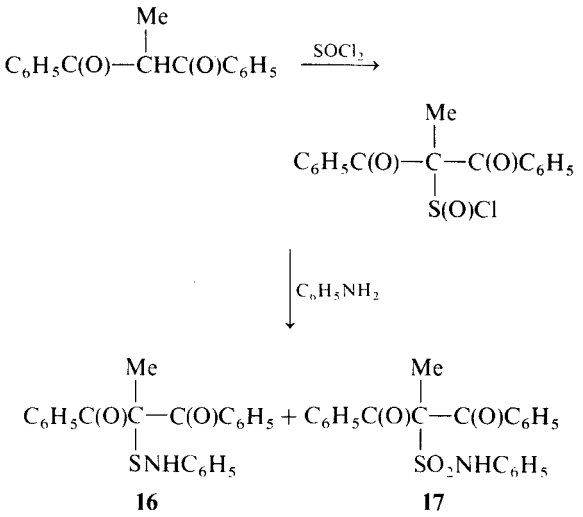


12



13

However treatment of the sulphinyl chloride derived from 1,1-dibenzoylethane with aniline gave a mixture of the disproportionation products, i.e. the sulphenanilide and the sulphonanilide.



Treatment of 1,1-dibenzoylethane with thionyl chloride under reflux resulted in the formation of an oil which was impossible to purify. Investigation of the structure of the oil showed, however, that it contained mainly the sulphinyl chloride. The oil was then dissolved in dry ether and aniline was added in an effort to characterise the sulphinyl chloride as the sulphinalide. However the sulphinanilide was not obtained and only the disproportionation products (**16** and **17**) could be isolated.

EXPERIMENTAL

2-Methyl-3-oxobutane-2-sulphinanilide (**1**) Aniline (0.2 mole) in dry diethyl ether was added slowly to 2-methyl-3-oxobutane-2-sulphinyl chloride[1] (0.1 mole) in dry diethyl ether (100 ml.). The reaction flask was surrounded by ice to minimise decomposition of the sulphinanilide. The reaction mixture was stirred for a further thirty minutes after the addition of aniline. The precipitated anilinium hydrochloride was then filtered off and the ether removed using a rotary evaporator. The sulphinanilide was obtained as a yellowish-white solid, m.p. 52–53°, yield 85%. NMR (CCl_4) τ 3.00 (m,5H), 3.30 (s,1H), 7.80 (s,3H), 8.48 (s,3H), 8.62 (s,3H). IR (KBr disc) δ_{max} 1700 (C=O), 1068 (S=O) cm^{-1}. MS: 225 (M+), 139, 86, 77, 71, 64, 43.

2 - Methyl - 3 - oxobutane - 2 - sulphin - m - toluidide (**2**) 2 - Methyl - 3 - oxobutane - 2 - sulphinyl chloride[1] (0.1 mole) was treated with *m*-toluidine (0.2 mole) using the procedure given above for **1**. The *m*-toluidide was obtained in an 85% yield, m.p. 61°. NMR (CCl_4) τ 2.35–3.35 (m,5H), 7.75 (s,6H) 8.45 (s,3H), 8.60 (s,3H). R (KBr disc) γ_{max} 1696 (C=O), 1060 (S=O) cm^{-1}. MS: 239 (M^+), 153, 91, 86, 71, 64, 43.

N - Ethyl - 2 - methyl - 3 - oxobutane - 2 - sulphinamide (**3**) 2 - Methyl-3-oxobutane-2-sulphinyl chloride[1] (0.1 mole) was treated with ethylamine (0.2 mole) using the procedure described for **1**. The sulphinamide was obtained in a 72% yield, distillation resulted in decomposition. NMR ($CDCl_3$) τ 6.90 (q,2H), 8.30 (s,3H), 8.90 (m,6H), 9.10 (s,3H). IR (thin film) γ_{max} 1660 (C=O), 1100 (S=O) cm^{-1}. (Calc. for $C_7H_{15}NO_2S$: C, 47.73; H, 8.47; N, 7.95; S, 18.20. Found: C, 47.9; H, 8.8; N, 8.2; S, 18.1%).

2,4 - Dimethyl - 3 - oxopentane - 2 - sulphinanilide (**4**) 2,4 - Dimethyl - 3 - oxopentane - 2 - sulphinyl chloride[1] (0.1 mole) was treated with aniline (0.2 mole) using the procedure described for **1**. The sulphinanilide was obtained in a 90% yield, m.p. 69°. NMR ($CDCl_3$) τ 2.60–3.50 (m,5H), 5.20 (s,IH), 7.00 (sp IH), 8.45 (s,6H), 9.00 (d,6H). IR (KBr disc) γ_{max} 1690 (C=O), 1062 (S=O) cm^{-1}. (Calc. for $C_{13}H_{19}NO_2S$: C, 61.66; H, 7.51; N, 5.53; S, 12.64. Found: C, 62.1; H, 7.8; N, 5.8; S, 12.4%).

2 - Methyl - 1 - oxo - 1 - phenylpropane - 2 - sulphinanilide (**5**) 2 - Methyl - 1 - oxo - 1 - phenylpropane - 2 - sulphinyl chloride[1] (0.1 mole) was treated with aniline (0.2 mole) using the procedure described for **1**. The sulphinanilide was obtained in a 73% yield, m.p. 66°. NMR ($CDCl_3$) τ 3.30 (m,1OH), 3.60 (s,IH), 8.20 (s,6H). IR (KBr disc) γ_{max} 1710 (C=O), 1060 (S=O) cm^{-1}. (Calc. for $C_{16}H_{17}NO_2S$: C, 66.90; H, 5.92; N, 4.90; S, 11.15. Found: C, 66.9; H, 6.1; N, 4.7; S, 11.0%).

1 - Cyclohexyl - 2 - methyl - 1 - oxopropane - 2 - sulphinanilide (**6**) 1 - Cyclohexyl - 2 - methyl - 1 - oxopropane - 2 - sulphinyl chloride[9] (0.1 mole) was treated with aniline (0.2 mole) using the procedure described for **1**. The sulphinanilide was obtained in an 88% yield, m.p. 69–70°. NMR ($CDCl_3$) τ 2.70–3.30 (m,5H), 3.70 (s,IH), 7.70–9.00 (m,11H), 8.42 (s,3H), 8.50 (s,H). IR (KBr disc) γ_{max} 1680 (C=O), 1060 (S=O) cm^{-1}. (Calc. for $C_{16}H_{23}NO_2S$: C, 65.53; H, 7.84; N, 4.78; S, 10.90. Found: C, 65.2; H, 7.6; N, 4.6; S, 10.7%).

2 - Methyl - 3 - oxo - 5 - phenylpentane - 2 - sulphinanilide (**7**) 2 - Methyl - 3 - oxo - 5 - phenylpentane - 2 - sulphinyl chloride[9] (0.1 mole) was treated with aniline (0.2 mole) using the procedure described for **1**. The sulphinanilide was obtained in an 82% yield, recrystallised from hot ethanol to give white plates, m.p. 86°. NMR ($CDCl_3$) τ 2.65 (m,1OH), 3.22 (s,IH), 7.12 (s,4H), 8.42 (s,3H), 8.60 (s,3H). IR (KBr disc) γ_{max} 1710 (C=O), 1060 (S=O) cm^{-1}. (Calc. for $C_{18}H_{21}NO_2S$: C, 68.57; H, 6.67; N, 4.45; S, 10.16. Found: C, 68.4; H, 6.9; N, 4.4; S, 9.9%).

NN - Diethyl - 2 - methyl - 3 - oxobutane - 2 - sulphinamide (**8**) 2 - Methyl - 3 - oxobutane - 2 - sulphinyl chloride[1] (0.1 mole) was treated with diethylamine (0.2 mole) using the procedure described for **1**. The sulphinamide was obtained as a liquid in an 87% yield, distillation resulted in decomposition. NMR (CCl_4) τ 6.90 (q,4H), 7.15 (s,3H), 8.60 (s,3H), 8.72 (s,3H) 8.88 (t,6H). IR (thin film) γ_{max} 1690 (C=O), 1070 (S=O) cm^{-1}. (Calc. for $C_9H_{19}NO_2S$: C, 52.68; H, 9.26; N, 6.83; S, 15.61. Found: C, 52.3; H, 9.2; N, 6.7; S, 15.4%).

N,2 - Dimethyl - 3 - oxobutane - 2 - sulphinanilide (**9**) 2 - Methyl - 3 - oxobutane - 2 - sulphinyl chloride[1] (0.1 mole) was treated with *N*-methylaniline using the procedure described for **1**. The sulphinanilide was obtained as a liquid in an 84% yield, distillation resulted in decomposition. NMR (CCl_4) τ 2.95 (m,5H), 7.15 (s,6H), 8.65 (s,3H), 8.75 (s,3H). IR (thin film) ν_{max} 1700 (C=O), 1055 (S=O) cm^{-1}. (Calc. for $C_{12}H_{17}NO_2S$: C, 60.30; H, 7.13; N, 6.47; S, 13.30. Found: C, 60.4; H, 7.4; N, 6.3; S, 13.0%).

2-Methyl-3-oxobutane-2-sulphinpiperidide (**10**) 2-Methyl-3-oxobutane-2-sulphinyl chloride[7] (0.03 mole) was treated with piperidine (0.6 mole) using the procedure described for **1**. The sulphinpiperidide was obtained in an 84% yield, b.p. 60–65° (0.2 mm). NMR ($CDCl_3$) τ 6.95 (m,4H), 7.7 (s,3H), 8.4m, 8.55s, 8.62s (12H). IR (thin film) ν_{max} 1700 (C=O), 1083 (S=O) cm^{-1}. MS: 217 (M^+), 133, 132, 85, 84.

bis(Diacetylmethyl) disulphide (**11**) Disulphur dichloride (0.1 mole) was slowly added to a stirred solution of acetylacetone (0.4 mole) in dry petroleum ether (60–80°, 150 ml) maintained at 0°. Hydrogen chloride was evolved and the powdery crystals which precipitated within ten minutes were filtered off, washed with petroleum ether (60–80°) and recrystallised from ethanol. The disulphide was obtained in a 61% yield, m.p. 88–89°. NMR ($CDCl_3$) τ − 7.20 (s,2H), 7.63 (s,12H). IR (KBr disc) 1550 (C=C—OH), 650 (C—S), 470 (S—S) cm^{-1}. (Calc. for $C_{10}H_{14}O_4S_2$: S, 24.42. Found: S, 25.1%).

3-Chloro-2,4-dioxopentane-3-sulphinyl chloride (**12**) bis (Diacetylmethyl) disulphide (**11**, 0.1 mole), acetic anhydride (0.2 mole) and carbon tetrachloride (20 ml) 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) was passed into the reaction mixture over ninety minutes. The temperature was slowly allowed to rise to 25° over a further ninety minutes and finally the reaction mixture was warmed to 40° for fifteen minutes. The mixture was then fractionally distilled under reduced pressure to give the sulphinyl chloride in a 43% yield, b.p. 66–70° (0.7 mm). NMR (CCl_4) τ 7.55 (s). IR (thin film) 1750, 1715, 1150 (S=O) cm^{-1}. (Calc. for $C_5H_6Cl_2O_3S$: Cl, 32.72; S, 14.75. Found: Cl, 32.2; S, 14.0%).

3,3-Dianilopentane-2,4-dione (**13**) Aniline (0.05 mole) was slowly added to a cooled solution of the sulphinyl chloride (**12**, 0.01 mole) in dry benzene (50 ml). The precipitate of anilinium hydrochloride which appeared immediately was filtered off and the reaction mixture was kept at room temperature for eighteen hours. The solvent was then removed and the red oil was dissolved in aqueous ethanol (30 ml, 8% v/v). Crystals of the dione (**13**) precipitated within twenty-four hours, m.p. 115°. NMR ($CDCl_3$) τ 2.9–3.3 (m,10H), 4.03 (s,2H), 7.95 (s,6H). IR ν_{max} 3370, 1716 (C=O) cm^{-1}. MS: 282 (M^+), 264, 239, 221, 195, 146, 118, 104, 94, 93, 77.

Treatment of 2-methyl-3-oxobutane-2-sulphinanilide (**1**) *with water* The sulphinanilide (**1**, 0.1 mole) was treated with water (0.3 mole) and the reaction mixture was stirred overnight at room temperature. The mixture was then extracted several times with ether and the combined extracts were dried over anhydrous sodium sulphate. Excess ether was then removed and the residual liquid on distillation at normal pressure afforded a colourless liquid in 74% yield, b.p. 94–96°, identified as 3-methylbutan-2-one by GLC, NMR, and IR.

The residual liquid was then distilled under reduced pressure to give a colourless liquid in 71% yield, b.p. 44–46° (1.0 mm), identified as aniline by GLC, NMR and IR.

Treatment of **1** *with ethanol* The sulphinanilide (**1**, 0.1 mole) was treated with ethanol (0.3 mole) and the reaction mixture was stirred overnight at room temperature. Excess ethanol was then distilled off at normal pressure using a fractionating column. The resulting liquid was further distilled at normal pressure to give a 68% yield of 3-methylbutan-2-one, identified by GLC, NMR, and IR.

The residual liquid, on distillation under reduced pressure, gave two fractions; *i* diethyl sulphite, b.p. 34–40° (0.8 mm), yield 62%, identified by GLC, NMR, and IR, and ii aniline, b.p. 46–48° (0.8 mm), yield 64%, identified by GLC, NMR, and IR.

Treatment of **1** *with diethylamine* The sulphinanilide (**1**,0.1 mole) was treated with diethylamine (0.3 mole) and the reaction mixture was stirred overnight at room temperature. The excess diethylamine was removed using a rotary evaporator and the residual oil was distilled under pressure to give three fractions; i aniline, b.p. 44–46° (1.0 mm), 26% yield by GLC, identified by GLC, NMR, and IR, ii *N*-2(3-methylbutylidene)aniline (**14**), b.p. 58–60° (1.0 mm), 40% yield by GLC, NMR (CCl_4) τ 2.80–3.50 (m,5H), 7.50 (sp,IH), 8.40 (s,3H), 8.80 (d,6H). IR (thin film) ν_{max} 1662, 1600, 1385, 1370 cm^{-1}. MS; 161.120039, given for $C_{11}H_{15}N$: 161.120444, and iii, yield 34%, b.p. 92–94° (0.8 mm), MS: 187.103475, given for $C_9H_{17}NOS$: 187.103080. (Calc. for $C_9H_{17}NOS$: C, 57.80; H, 9.09; N, 7.50; S, 17.10. Found: C, 58.1; H, 8.8; N, 7.2; S, 16.8%).

N-2(3-Methylbutylidene)aniline (**14**) Aniline (0.1 mole) and 3-methylbutan-2-one (0.1 mole) were mixed with benzene (50 ml) at room temperature and then refluxed for four hours. Water was collected using a water separator and excess benzene was then removed using a rotary evaporator. The resultant brown liquid was then distilled under reduced pressure to give (**14**) as a colourless liquid, 75% yield, b.p. 54–56 (0.3 mm). NMR (CCl_4) τ 2.8–3.5 (m,5H), 7.50 (sp,1H), 8.40 (s,3H), 8.88 (d,6H). (Calc. for: $C_{11}H_{15}N$: C, 81.88; H, 9.31; N, 8.71. Found: C, 81.7; H, 9.1; N, 8.6%).

Treatment of 2-methyl-1-oxo-1-phenylpropane-2-sulphinanilide (**5**) *with diethylamine* The sulphinanilide (**5**,0.1 mole) was treated with diethylamine (0.3 mole) and the reaction mixture was stirred overnight at room temperature. Excess diethylamine was then removed using a rotary evaporator and the residual brown oil was then distilled under reduced pressure to give two fractions; i dianilinosulphoxide (**15**), b.p. 28–30° (0.5 mm), yield 34%. NMR (CCl_4) τ 2.0–3.6 (m,10H), 6.30 (s,2H). IR (thin film) ν_{max} 3460, 3380, 1280, 1160 cm^{-1}. (Calc. for $C_{12}H_{12}N_2OS$: C, 61.50; H, 5.83; N, 12.08; S, 15.58. Found: C, 61.1; H, 5.5; N, 11.9; S, 15.3%), and ii isopropyl phenyl ketone, identified by GLC, NMR, and IR. Fractions *i* and *ii* were obtained in an 1:2 molar ratio.

Treatment of 1,1-dibenzoylethane-1-sulphinyl chloride with aniline The oil (2g), obtained by refluxing 1,1-dibenzoylethane (0.01 mole) with thionyl chloride (0.1 mole),[10] was dissolved in dry ether (50 ml) and excess aniline (6g) was added slowly whilst the reaction mixture was stirred and cooled in ice. The anilinium hydrochloride was then filtered off, excess solvent was removed from the filtrate and the material obtained was dissolved in aqueous ethanol (50 ml, 1.5% v/v). On standing for twenty-four hours yellow crystals of *1,1-dibenzoylethane-1-sulphenanilide* (**16**) were precipitated, 21%, yield, m.p. 160° on recrystallisation from hot ethanol. NMR ($CDCl_3$) τ 2.15–2.80 (m,15H), 5.28 (s,IH), 8.12 (s,3H). IR (KBr disc) 3340, 1678 (C=O) cm^{-1}. (Calc. for $C_{22}H_{19}NO_2S$: S, 8.86. Found: S, 9.0%).

The aqueous ethanolic solution which produced **16** gave a second crop of crystalals on standing at room temperature for a further forty-eight hours, m.p. 130°. They were identified as a

two-component mixture containing **16** as well as 1,1-dibenzoylethane-1-sulphonanilide (**17**). NMR ($CDCl_3$) τ 2.80 (m,15H), 5.48 (s,2H), 8.74 (s,3H). IR (KBr disc) 3415 (NH), 1668 (C=O), 1320, 1155 cm^{-1}.

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