65. *The Preparation and Oxidation of Sulphides formed from o-Nitrobenzenesulphenyl Chloride and Ketones.*

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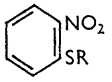
o-Nitrobenzenesulphenyl chloride reacts with acetone, acetophenone, acetylacetone, benzoylacetone, and dibenzoylmethane to form sulphides (I—V). Oxidation with hydrogen peroxide at 80° converts both sulphides (I) and (III) into sulphone (VI), and both (II) and (IV) into sulphone (VII). Oxidation at room temperature again produces (VI) from both (I) and (III), but (IV) and (V) give the corresponding sulphoxides (VIII) and (IX). Some properties of the sulphoxides have been examined and reductions have been carried out on the sulphides.

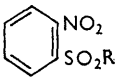
o-Nitrobenzenesulphenyl chloride reacts with acetone,[1] acetophenone,[2] acetylacetone, benzoylacetone, and dibenzoylmethane to form respectively the sulphides (I—V). The sulphides (III, IV, and V) were also prepared by reaction of the sulphenyl chloride with the copper complex of the corresponding diketone. When these sulphides were oxidised with hydrogen peroxide in acetic acid–acetic anhydride [3] at 80°, the acetyl compound (I) and (III) gave the sulphone (VI), the sulphides (II) and (IV) gave the sulphone (VII), and the dibenzoyl compound (V) gave benzoic acid. When the oxidation was carried out at 20°, (I) and (III) again gave the sulphone (VI), but (IV) now gave the sulphoxide (VIII), and (V) gave the sulphoxide (IX). The sulphoxides (VIII and IX) were unstable to heat and easily hydrolysed by dilute acid in ethanol to benzoylacetone and dibenzoylmethane, respectively. The sulphoxide (VIII), when refluxed with aqueous ammonia or dilute

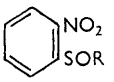
[1] Zincke and Farr, *Annalen*, 1912, **391**, 57.
[2] Kharasch, Wehrmeister, and Zigermann, *J. Amer. Chem. Soc.*, 1947, **69**, 1613.
[3] Truitt, Stead, and Long, *J. Amer. Chem. Soc.*, 1949, **71**, 3511.

aqueous ethanol, gave the simpler sulphoxide (X). Sulphoxides (VIII) and (X) were oxidised to the same sulphone (VII) by hydrogen peroxide.

Reduction of the sulphides (III, IV, and V) with stannous chloride in acetic acid containing hydrogen chloride (cf. Zincke and Baeumer [4]) produced 2-methylbenzothiazole





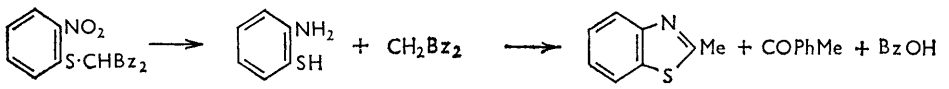


(I) R = CH_2Ac
(II) R = CH_2Bz
(III) R = $CHAc_2$
(IV) R = CHBzAc
(V) R = $CHBz_2$

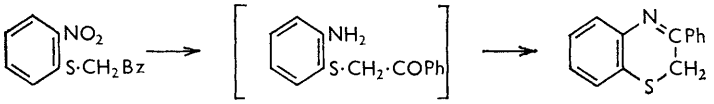
(VI) R = CH_2Ac
(VII) R = CH_2Bz

(VIII) R = CHBzAc
(IX) R = $CHBz_2$
(X) R = CH_2Bz

as one of the products. This reaction probably proceeds by scission of the S–C bond, resulting in the intermediate formation of the diketone and thiophenol, the latter then reacting with the solvent (acetic acid) to form 2-methylbenzothiazole, *e.g.*, with (V):



This is supported by the fact that dibenzoylmethane, when treated under the same conditions with the stannous chloride solution, gave acetophenone and benzoic acid.



On the other hand, reduction of the sulphide (II) produced 3-phenyl-1,4-benzothiazine [5] by ring closure of the intermediate amino-sulphide.

Experimental

Reaction of o-*Nitrobenzenesulphenyl Chloride with Ketones and Diketones.*—(*a*) A solution of *o*-nitrobenzenesulphenyl chloride (7·6 g., 0·04 mole) and acetophenone (6 g., 0·05 mole) in ethylene chloride (100 c.c.) was refluxed until hydrogen chloride was no longer evolved (4 hr.). The solution was stored for 2—3 hr., and the solid which separated was collected, dried, and recrystallised from chloroform–hexane to give yellow plates of ω-(*o*-nitrophenylthio)acetophenone (II), m. p. 145—146° (80%) (Kharasch *et al.*[2] give m. p. 141°). Reaction of the sulphenyl chloride with acetylacetone, benzoylacetone, and dibenzoylmethane was carried out as above (see Table). With acetone, only 1·5 hours' heating was necessary, and the excess of acetone was distilled off.

Sulphide	M. p.*	Yield (%)	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
(I)	81—82° [a]	75									
(II)	145—146 [b]	60									
(III)	141·5—142·5 [a]	70	52·3	4·3	5·5	12·4	$C_{11}H_{11}NO_4S$	52·2	4·35	5·5	12·65
(IV)	116·5—117·5 [c]	65	61·0	4·15	4·1	9·9	$C_{16}H_{13}NO_4S$	60·95	4·1	4·4	10·2
(V)	149—149·5 [c]	55	67·0	3·9	3·4	8·4	$C_{21}H_{15}NO_4S$	66·8	4·0	3·7	8·5

* Solvents for recrystallisation: (*a*) aqueous ethanol, (*b*) chloroform–hexane, (*c*) aqueous acetic acid.

(*b*) A solution of the sulphenyl chloride (0·02 mole) and the copper complex (0·01 mole) of acetylacetone, benzoylacetone, or dibenzoylmethane in dry chloroform was refluxed for 15 min.,

[4] Zincke and Baeumer, *Annalen*, 1918, **416**, 108.
[5] Unger, *Ber.*, 1897, **30**, 609.

filtered, and washed with dilute sulphuric acid, then water, and dried (Na_2SO_4). The chloroform was distilled off, and the residue recrystallised to give the required sulphides. The yields in these cases were 62—70%.

Oxidation of Sulphides.[3]—(a) The sulphide (4 g.) was suspended in glacial acetic acid (40 c.c.) and acetic anhydride (10 c.c.), and the mixture heated to 80°. Hydrogen peroxide (30%; 10 c.c.) was then added dropwise at such a rate that the temperature remained at 70—80° during the addition. The solution was then heated on a steam-bath for 15 min. and allowed to cool. For isolation of sulphone (VI) the solution was diluted with water and extracted with ether, the ether washed and evaporated, and the residue crystallised from aqueous ethanol. Sulphone (VII) was precipitated when the solution was set aside, and was also recrystallised from aqueous ethanol. Sulphide (I) gave *acetonyl o-nitrophenyl sulphone* (VI) (45%), m. p. 84—85° (Found: S, 12·9. $C_9H_9NO_5S$ requires S, 13·2%); (II) gave *phenacyl o-nitrophenyl sulphone* (VII) (80%), m. p. 136·5—137·5° (Found: S, 10·2. $C_{14}H_{11}NO_5S$ requires S, 10·5%); (III) gave (VI; 25%); (IV) gave (VII; 30%); only benzoic acid (60%) was isolated from (V).

(b) *Oxidations at* 20°. A mixture of the sulphide (4 g.), acetic acid (40 c.c.), acetic anhydride (10 c.c.), and 30% hydrogen peroxide (10 c.c.) was stored for 5 days at 15—20°. Sulphides (I) and (III) each gave sulphone (VI) (35%), extracted with ether after dilution with water (as above); (II) gave sulphone (VII) (80%) as a precipitate; (IV) gave *α-acetylphenacyl o-nitrophenyl sulphoxide* (VIII) (70%) as a precipitate which when washed with water and dried had m. p. 107—108° (decomp.) (Found: C, 57·7; H, 3·7; N, 4·5; S, 10·0. $C_{16}H_{13}NO_5S$ requires C, 58·0; H, 3·9; N, 4·2; S, 9·7%); (V) gave *dibenzoylmethyl o-nitrophenyl sulphoxide* (IX) (96%) as a precipitate which when washed with water, ethanol, and ether, had m. p. 103·5—104° (Found: C, 63·9; H, 3·6; N, 3·5; S, 7·9. $C_{21}H_{15}NO_5S$ requires C, 64·1; H, 3·8; N, 3·6; S, 8·1%).

Hydrolysis of Diketo-sulphoxides (VIII) *and* (IX).—The sulphoxide (3 g.) was suspended in 95% ethanol (50 c.c.), dilute hydrochloric acid (15 c.c.) added, and the mixture heated on a steam-bath until a clear solution resulted (1·5 hr.). The solution was cooled and diluted with water, and the precipitate collected, dried, and recrystallised; (VIII) gave benzoylacetone (77%), and (IX) gave dibenzoylmethane (70%).

Preparation of o-*Nitrophenyl Phenacyl Sulphoxide* (X).—The sulphoxide (VIII) (2 g.) was heated on a steam-bath with dilute aqueous ammonia for 20 min., and the mixture allowed to cool and then filtered. The residue was washed with dilute sulphuric acid and recrystallised from ethanol to give *o-nitrophenyl phenacyl sulphoxide* (X), m. p. 148—149° (decomp.) (Found: S, 11·0. $C_{14}H_{11}NO_4S$ requires S, 11·1%). A further crop was obtained by acidification of the mother-liquor, the total yield being 97%.

Oxidation of Sulphoxides.—A solution of sulphoxide (X) (2·9 g.) in acetic acid (40 c.c.) and 30% hydrogen peroxide (5 c.c.) was heated on the steam-bath for 30 min., allowed to cool, and diluted with water, and the precipitate recrystallised from aqueous ethanol to give the sulphone (VII) (60%).

A suspension of sulphoxide (VIII) (3 g.) in acetic acid (30 c.c.) and acetic anhydride (7·5 c.c.) was heated to 80°, and 30% hydrogen peroxide (7·5 c.c.) added dropwise. The solution was cooled and diluted with water, and the precipitate recrystallised from aqueous ethanol to give the sulphone (VII) (50%).

Reduction of the Nitro-sulphides.—Stannous chloride solution [4] was prepared by bubbling dry hydrogen chloride through a suspension of stannous chloride (200 g.) in acetic acid (380 c.c.) until a clear solution was obtained. A mixture of nitro-sulphide (5 g.) and stannous chloride solution (50 c.c.) was refluxed for 4—6 hr., cooled, and made just alkaline with 10% aqueous sodium hydroxide.

(a) *Sulphide* (II). The alkaline solution was extracted with nitrobenzene (3 × 100 c.c.), the extract steam-distilled, and the residue recrystallised from nitrobenzene–ethanol to give 3-phenyl-1,4-benzothiazine (40%), m. p. 230—232° (Unger [5] gives m. p. 233°).

(b) *Sulphide* (III). The alkaline solution was steam-distilled, the distillate extracted with ether (3 × 80 c.c.), and the ether washed, dried (Na_2SO_4), and evaporated. The residual oil, b. p. 238—241°, was identified as 2-methylbenzothiazole (50%) by preparation of its picrate, m. p. 156°.[6]

(c) *Sulphide* (IV). The ether extract [obtained as in (b)] was washed with dilute hydrochloric acid, then water, and dried. Evaporation of the ether left acetophenone (68%)

[6] Finar and Montgomery, *J.*, 1960, 483; contrast Clark, *J.*, 1928, 2319.

(identified as its semicarbazone). The acid extract was neutralised with 10% aqueous sodium hydroxide, and extracted with ether, etc. [as in (b)], to give 2-methylbenzothiazole (40%).

(d) *Sulphide* (V). The ether extract [obtained as in (b)] was washed successively with dilute sodium hydroxide, water, dilute hydrochloric acid, and water, and dried. Distillation of the ether left acetophenone (40%). The alkaline extract was acidified with hydrochloric acid, the solution extracted with ether, and the ether extract washed, dried, and evaporated to give, on recrystallisation from water, benzoic acid (40%), m. p. 120—121°. The acid extract was neutralised with dilute sodium hydroxide, and extracted with ether, which was dried and distilled off to leave 2-methylbenzothiazole (35%).

Fission of Dibenzoylmethane.—Dibenzoylmethane (5 g.) in the stannous chloride solution (50 c.c.) was refluxed for 4—6 hr. The cooled solution was neutralised and steam-distilled. The distillate was extracted with ether (3 × 50 c.c.), and the ether extracted with dilute sodium hydroxide solution, then water, and dried. Evaporation of the ether left acetophenone (50%). The alkaline extract was acidified and extracted with ether (3 × 50 c.c.), and the ether dried and distilled to leave, on recrystallisation from water, benzoic acid (40%).

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