536. o-*Arylsulphinylbenzaldehydes.*

By J. D. LOUDON and D. M. SMITH.

Normal oxidation to the corresponding sulphone (III), effected by the action of chlorine on 5-nitro-2-(*p*-tolylthio)benzaldehyde (I) or 5-nitro-2-toluene-*p*-sulphinylbenzaldehyde (II), is diverted to give 5-nitro-2-toluene-*p*-sulphonylbenzylidene dichloride (IV) in the presence of hydrogen chloride. The latter reaction appears to be restricted to benzaldehydes which have an *ortho* thio- or sulphinyl substitutent. Some comments are offered on the course of this reaction.

o-SULPHINYLBENZALDEHYDES have not been studied hitherto, but seemed likely to provide fresh examples of interaction[1] between *ortho*-substituents. Accordingly, 5-nitro-2-toluene-*p*-sulphinylbenzaldehyde (II) was chosen as an accessible representative of the class, and, as its study developed, some closely allied compounds were prepared for reference and comparison. This preparative work is described first, the compounds being named for brevity according to the functions associated with (a) the sulphur atom and (b) the carbon atom in the side-chain.

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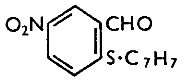
[1] Cf. Loudon and Wellings, *J.*, 1960, 3470.

The sulphide-aldehyde (I), in the form of its diacetate, was successively oxidised to the sulphoxide- and the sulphone-diacetate, from which, by acidic hydrolysis, the sulphoxide-aldehyde (II) and the sulphone-aldehyde (III) were, respectively, prepared. All three aldehydes reacted with phosphorus pentachloride, but whereas (I) and (III) gave the corresponding benzylidene dichlorides *e.g.*, (III) ⟶ (IV), the sulphoxide-aldehyde (II)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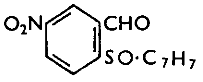
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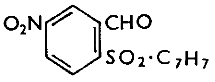
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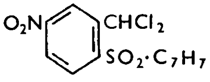
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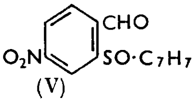
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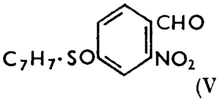
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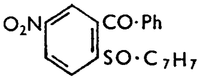
(VII)

gave, together with a trace of the sulphone-dichloride, the sulphide-dichloride instead of the sulphoxide-dichloride. However, the latter dichloride was readily obtained from the former by controlled oxidation. The sulphoxide-aldehyde (II) was also exceptional in resisting conversion into the sulphoxide-diacetate; thus, it was wholly recovered from treatment with various proportions of acetic anhydride and sulphuric acid, reagents which rapidly converted the aldehydes (I) and (III) into their diacetates. The aldehyde (II), however, readily formed the dimethyl acetal in normal acid-catalysed reaction with methanol. Three additional sulphoxides, (V), (VI), and (VII), were similarly prepared by controlled oxidation of the corresponding sulphides, with the aldehyde function, when present, protected as the diacetate.

The sulphoxide-aldehyde (II) reacted with hydrogen chloride in dimethylformamide at room temperature to give a mixture of the sulphone-dichloride (IV) and the sulphide-aldehyde (I), the latter crystallising as the reaction proceeded. The purified products were obtained in nearly equal amounts and together accounted for 80% of the reacting sulphoxide. They show that the reaction combines oxidation-reduction with a remarkably easy conversion of an aldehyde function into a dichloromethyl group.

Under the same conditions, neither the sulphide-aldehyde nor the sulphone-aldehyde was appreciably affected by hydrogen chloride, but the sulphoxide-dichloride was reduced almost quantitatively to sulphide-dichloride. Sulphuric acid in place of hydrogen chloride was without permanent effect on the sulphoxide-aldehyde or the sulphoxide-dichloride or on a mixture of these, and it is therefore improbable that mutual oxidation-reduction by sulphoxides can explain the reaction in question. A known relationship[2] between sulphides and sulphoxides is given by the equilibrium series:

$$R_2SO + 2HCl \rightleftharpoons R_2\overset{+}{S}(OH),Cl^- + HCl \rightleftharpoons R_2\overset{+}{S}Cl,Cl^- + H_2O \rightleftharpoons R_2S + Cl_2 + H_2O$$

which would account for the sulphide-aldehyde produced, whilst providing, in chlorine or its equivalent, a necessary oxidant. The relevance of this relation was confirmed by the reaction of chlorine with the sulphide-aldehyde, whereby the sulphone-dichloride was again formed, accompanied in this case by the sulphone-aldehyde. Formation of these two sulphones thus represents departure from the equilibrium series and it is striking that the sulphone-dichloride is the only chlorinated product found, despite many experiments and the proved efficiency of chromatoplate control to detect sulphide- or sulphoxide-dichloride. The results of exploratory experiments 1—9 (see Table) indicate in a qualitative way that, whilst oxidation by chlorine usually leads to the sulphone-aldehyde-(expts. 5 and 7), intervention by hydrogen chloride causes formation of the sulphone-dichloride (expts. 1 and 5; 6, 7, and 9), and for this chlorine also is necessary (expts. 1

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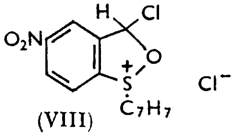
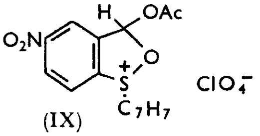
[2] Cf. Fries and Vogt, *Annalen*, 1913, **396**, 75.

and 2). However, unless given time to make its intervention effective, hydrogen chloride does not restrict oxidation of the sulphoxide- to the sulphone-aldehyde (expts. 1 and 4). Formation of the sulphone-dichloride thus appears to depend upon nicely balanced contributions from chlorine and hydrogen chloride.

Comparison of pertinent behaviour in the isomeric sulphoxide-aldehydes (V) and (VI) suggests that juxtaposition of the aldehyde and sulphoxide groups is necessary for conversion into a sulphone-dichloride in the manner described. Thus, the sulphide- and sulphoxide-aldehydes of the 4-nitro-series, cf. (V), matched their 5-nitro-analogues in yielding the 4-nitro-sulphone-dichloride, with corresponding co-products. On the other hand, the sulphoxide-aldehyde (VI) was unchanged by hydrogen chloride, and the sulphoxide-ketone (VII), despite favourably placed substituents, was merely reduced to the appropriate sulphide-ketone.


(VIII)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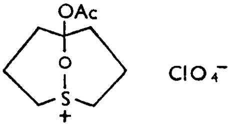
(X)

As a tentative explanation of the course by which the sulphone-dichloride (II) is formed, we suggest that the departure caused by hydrogen chloride from the equilibrium series leads reversibly to a cyclic intermediate (VIII), and that oxidation of this intermediate is concerted with ring-opening to form the dichloride. In the complex circumstances of the reaction, experimental verification of this view is difficult, but there is some evidence that reversible formation of a similar intermediate (IX) may account for the failure of the sulphoxide-aldehyde (II), in contrast with the ability of its isomer (VI), to form a diacetate under normal conditions. When the aldehyde (II) was treated with acetic anhydride in the presence of perchloric acid, the addition of ether to the solution caused precipitation of a colourless perchlorate which was, unfortunately, very unstable. It exploded when heated, quickly became yellow in presence of moisture, regenerating the sulphoxide-aldehyde, and released two equivalents of acid to the aqueous phase when suspended in water. Its infrared spectrum, taken in a rapidly prepared Nujol mull, shows a peak at 1780 cm.$^{-1}$. This is attributed to the acetate group, and closely corresponds to that (1777 cm.$^{-1}$) reported by Leonard and Johnson[3] for the acetate (X) prepared from the monocyclic 1-thiacyclo-octan-5-one 1-oxide.

EXPERIMENTAL

Light petroleum had b. p. 60—80°.

5-*Nitro*-2-p-*tolylthiobenzylidene diacetate* (88%), m. p. 117° (from acetic acid), was obtained by adding concentrated sulphuric acid (0·5 ml.) to a suspension of 5-nitro-2-(*p*-tolylthio)-benzaldehyde[4] (20 g.) in acetic anhydride (150 ml.), and, after 2 hr. at ambient temperature, pouring into water (1·5 l.) (Found: C, 57·7; H, 4·3; N, 3·9. $C_{18}H_{17}NO_6S$ requires C, 57·6; H, 4·6; N, 3·7%).

5-*Nitro*-2-*toluene*-p-*sulphinylbenzaldehyde* (II).—A cold solution of the sulphide-diacetate (30 g.) in acetic acid (900 ml.) was gradually treated with 30% hydrogen peroxide (120 ml.), and after 24 hr. the whole was added to iced water (3 l.) affording 5-*nitro*-2-*toluene*-p-*sulphinylbenzylidene diacetate* (80%), m. p. 114° (from methanol) (Found: C, 55·1; H, 4·5; N, 3·5. $C_{18}H_{17}NO_7S$ requires C, 55·2; H, 4·4; N, 3·6%), *benzene solvate*, m. p. 93—95° (from benzene–light petroleum) (Found: C, 58·4; H, 5·0; N, 3·6. $C_{18}H_{17}NO_7S,\frac{1}{2}C_6H_6$ requires C, 58·6; H, 4·7; N, 3·3%). Hydrolysis, as described for the sulphone-diacetate, cf. (III), gave the

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[3] Leonard and Johnson, *J. Amer. Chem. Soc.*, 1962, **84**, 3701.

[4] Campbell, Dick, Ferguson, and Loudon, *J.*, 1941, 747.

sulphoxide-aldehyde (II), m. p. 178° (from benzene), $\nu_{max.}$ 1680 (CHO); 1525, 1340 (NO_2); 1075, 1050, 1030, 1010 cm.$^{-1}$ (SO?) (Found: C, 58·2; H, 4·1; N, 4·8. $C_{14}H_{11}NO_4S$ requires C, 58·1; H, 3·8; N, 4·8%). It formed an *oxime*, m. p. 156°, having previously melted at *ca.* 80° and resolidified (from ethanol) (Found: C, 55·2; H, 4·0; N, 9·0. $C_{14}H_{12}N_2O_4S$ requires C, 55·25; H, 4·0; N, 9·2%). The 2,4-*dinitrophenylhydrazone*, m. p. 280° (from dimethylformamide–ethanol), retained solvent of crystallisation (Found: C, 51·1; H, 3·9; N, 16·1. $C_{20}H_{15}N_5O_7S,C_3H_7NO$ requires C, 50·9; H, 4·1; N, 15·5%). A suspension of the sulphoxide-aldehyde (1 g.) in methanol (3 ml.) containing concentrated sulphuric acid (0·2 ml.) became homogeneous when gently warmed; then the *dimethyl acetal* gradually crystallised, m. p. 97° (from methanol) (Found: C, 57·5; H, 4·8; N, 4·4. $C_{16}H_{17}NO_5S$ requires C, 57·3; H, 5·1; N, 4·2%).

A suspension of the sulphoxide-aldehyde (2·4 g.) in acetic anhydride (2·5 ml.) was slowly treated with a solution of perchloric acid (AnalaR, 72%; 0·75 ml.) in acetic acid (2 ml.). The aldehyde dissolved and a colourless salt was precipitated. Precipitation was completed by the addition of dry ether, and the salt, thoroughly washed with ether by repeated decantation, was dried to constant weight *in vacuo.* This salt (1·5408 g.) reacted with water, forming the sulphoxide-aldehyde and affording 50 ml. of 0·1415N-acid solution, whence the equivalent of the salt is 212·3 (Calc. for $C_{16}H_{14}ClNO_9S$: 215·9).

5-*Nitro*-2-*toluene*-p-*sulphonylbenzaldehyde* (III).—To a solution of the sulphide-diacetate (7 g.) in acetic acid (80 ml.) at 100°, 30% hydrogen peroxide (60 ml.) was added slowly, and after 45 min. the mixture was cooled and poured into water, affording 5-*nitro*-2-*toluene*-p-*sulphonylbenzylidene diacetate* (5·3 g.), m. p. 150° (from acetic acid) (Found: C, 53·0; H, 4·35; N, 3·6. $C_{18}H_{17}NO_8S$ requires C, 53·1; H, 4·2; N, 3·4%). This (5 g.) was heated for 30 min. under reflux with 6N-sulphuric acid (100 ml.) and acetic acid (80 ml.) and cooled, to give the *sulphone-aldehyde* (90%), m. p. 144° (from acetic acid), $\nu_{max.}$ 1680 (CHO); 1530, 1345 (NO_2); 1315, 1155 cm.$^{-1}$ (SO_2) (Found: C, 55·1; H, 3·8; N, 4·7. $C_{14}H_{11}NO_5S$ requires C, 55·1; H, 3·6; N, 4·6%).

5-*Nitro*-2-p-*tolylthiobenzylidene Dichloride.*—The melt obtained by heating 5-nitro-2-(*p*-tolylthio)benzaldehyde (10 g.) with phosphorus pentachloride (20 g.) for 5 min. was cooled and added to crushed ice. The resultant oil was extracted with benzene and the extract was washed with aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$), and the recovered oil purified by passage in benzene through alumina. The *dichloride* (65%) had m. p. 75° (from light petroleum) (Found: C, 51·1; H, 3·3; N, 4·4. $C_{14}H_{11}Cl_2NO_2S$ requires C, 51·2; H, 3·4; N, 4·3%). It was hydrolysed to the aldehyde (I) when heated for 3 hr. with aqueous sulphuric–acetic acid but with concentrated sulphuric acid formed a red solution which, by addition to water, gave a mixture of 2-methyl-7-nitrothio-xanthen and -xanthone; these were separated by fractional crystallisation and identified by comparison with authentic specimens.[4]

5-*Nitro*-2-*toluene*-p-*sulphonylbenzylidene dichloride* (IV), m. p. 142° (from ethanol), was obtained (*a*) in 82% yield from the sulphone-aldehyde and phosphorus pentachloride, and (*b*) in 70% yield by oxidising the sulphide-dichloride with hydrogen peroxide in acetic acid at 100° for 1 hr. (Found: C, 46·6; H, 3·15; N, 4·1. $C_{14}H_{11}Cl_2NO_4S$ requires C, 46·7; H, 3·1; N, 3·9%). It resisted hydrolysis by mineral acids (cf. following Paper).

5-*Nitro*-2-*toluene*-p-*sulphinylbenzylidene dichloride* (60%), m. p. 163—166° (from light petroleum), was obtained when 30% hydrogen peroxide (16 ml.) was added to a solution of the sulphide-dichloride (4 g.) in acetic acid (80 ml.) at 100°, and after 3 min. the whole was cooled and poured on to crushed ice (Found: C, 48·6; H, 3·1; N, 4·2. $C_{14}H_{11}Cl_2NO_3S$ requires C, 48·85; H, 3·2; N, 4·1%). In cold dimethylformamide it reacted (*a*) with hydrogen chloride, giving sulphide-dichloride (96%), and (*b*) with chlorine, giving sulphone-dichloride (70%).

A vigorous reaction occurred when the sulphoxide-aldehyde (II) (0·5 g.) and phosphorus pentachloride (1 g.) were mixed. The resultant melt was briefly heated (5 min.), cooled, added to crushed ice, and the oil recovered in benzene. Trituration with methanol gave the sulphide-dichloride (0·34 g.). Evaporation of the methanol filtrate, and chromatography in benzene–light petroleum (3 : 1) on alumina, gave a further crop of this dichloride (0·1 g.; total yield, 79%); benzene then eluted the sulphone-dichloride (IV) (0·02 g., 3%).

Experiments 1—9 (cf. Table).—The reaction mixtures were saturated at ambient temperature with the (dry) gaseous reagent(s), sealed, and set aside for 18 hr. Products were separated, if necessary by chromatography, recrystallised, and identified by mixed m. p.s and infrared spectra. In experiment 1 the sulphoxide-aldehyde gave a deposit of sulphide-aldehyde (0·13 g.).

Addition of the mixture to water afforded a solid which, by fractional crystallisation from benzene–light petroleum, gave more sulphide-aldehyde (0·31 g.), sulphoxide-aldehyde (0·04 g.), and a residue. Chromatography of the residue in benzene on alumina gave sulphone-dichloride (0·41 g.) eluted in benzene, and sulphoxide-aldehyde (0·1 g.) eluted in benzene–methanol.

Conversions of the sulphoxide-aldehyde (II) and the sulphide-aldehyde (I).

Expt.	Starting material (mg.)	Gaseous reagent	Additive	Solvent (ml.)	Products (%)			
					(I)	(II)	(III)	(IV)
1	(II) (1160)	HCl	—	DMF (18)	40	12	—	29
2	(II) (145)	,,	PhOH (47 mg.)	DMF (2)	88	—	—	—
3	(II) (145)	,,	—	C_6H_6 (8)	80 *	—	—	—
4	(II) (500)	$HCl + Cl_2$ †	—	DMF (8)	—	Trace ‡	83	2
5	(II) (1000)	Cl_2	—	DMF (15)	—	—	80	8
6	(I) (1000)	,,	—	,,	—	—	44	41
7	,,	,,	K_2CO_3 (2 g.)	,,	—	—	71	Trace ‡
8	,,	,,	C_5H_5N (2 ml.)	,,	—	—	60 *	Trace ‡
9	,,	$HCl + Cl_2$ †	—	,,	—	—	12 *	60

* Second crop of inferior quality. † Chlorine and hydrogen pre-mixed in approximately equal volumes. ‡ Detected by plate chromatography but not isolated.

With chloroform in place of dimethylformamide (D.M.F.) as solvent, the yield of sulphide-aldehyde was 48%, and of sulphone-dichloride 10% (minimal); a gummy fraction was not resolved into its components.

In experiment 6 the product from the interaction of the sulphide-aldehyde and chlorine was precipitated by water and chromatographed in benzene on alumina; the sulphone-dichloride was eluted with 10% ether–benzene and the sulphone-aldehyde with pure ether.

4-*Nitro*-2-p-*tolylthio- and* 2-*Nitro*-4-p-*tolylthio-benzylidene Diacetate*.—A mixture (1·36 g.) of the two nitro-*p*-tolylthiobenzaldehydes, obtained by the action of *p*-methyl(thiophenol) and sodium hydroxide on a solution of 2,4-dinitrobenzaldehyde in aqueous ethanol,[4] was suspended in acetic anhydride (10 ml.), concentrated sulphuric acid (0·3 ml.) was added, and the whole shaken to form a light-red solution. After 3 hr., during which some crystallisation occurred, water (100 ml.) was added and 4-*nitro*-2-p-*tolylthiobenzylidene diacetate* was collected, yellow prisms (1·11 g.), m. p. 129° (from acetic acid) (Found: C, 57·55; H, 4·7%). Further dilution of the filtrate gave 2-*nitro*-4-p-*tolylthiobenzylidene diacetate*, cream-coloured needles, m. p. 104° (from ethanol) (Found: C, 57·4; H, 4·6; N, 3·9%). These diacetates were identified by their alternative preparations from the individual aldehydes[4] and are more easily separated than the mixed aldehydes.

4-*Nitro*-2-*toluene*-p-*sulphinylbenzaldehyde* (V).—The corresponding *benzylidene diacetate*, obtained by controlled oxidation of 4-nitro-2-*p*-tolylthiobenzylidene diacetate, crystallised from hot methanol, on slow cooling, as needles, m. p. 144—148°, or on rapid cooling as hard tiny prisms, m. p. 140° (Found: C, 55·1; H, 4·5; N, 3·75%). On hydrolysis it gave the *aldehyde* (V), m. p. 211° (from benzene–light petroleum) (Found: C, 58·4; H, 3·9; N, 5·0%). The semi-solid mass resulting from the interaction (18 hr.) of this aldehyde (0·5 g.) and hydrogen chloride in dimethylformamide (10 ml.) was added to iced water, and the total solid was fractionally crystallised from acetic acid, affording 4-nitro-2-(*p*-tolylthio)benzaldehyde, m. p. and mixed m. p. 147° (0·16 g., 34%), and 4-nitro-2-toluene-*p*-sulphonylbenzylidene dichloride, m. p. and mixed m. p. 144—145° (see below) (0·14 g., 23%).

4-*Nitro*-2-*toluene*-p-*sulphonylbenzaldehyde*, m. p. 181° (from acetic acid) (Found: C, 55·1; H, 3·8%), prepared by way of the *benzylidene diacetate*, m. p. 165° (from acetic acid) (Found: C, 53·1; H, 4·25%), reacted with phosphorus pentachloride to form the *benzylidene dichloride*, m. p. 145° (from ethanol) (Found: C, 46·9; H, 3·25; N, 4·1%), also obtained in admixture with 4-nitro-2-toluene-*p*-sulphonylbenzaldehyde when 4-nitro-2-(*p*-tolylthio)benzaldehyde was treated with chlorine in dimethylformamide.

2-*Nitro*-4-*toluene*-p-*sulphinylbenzaldehyde* (VI), m. p. 137° (from benzene–light petroleum) (Found: C, 57·8; H, 3·8; N, 5·0%), was prepared by hydrolysis of the *benzylidene diacetate*, m. p. 143° (from methanol) (Found: C, 55·0; H, 4·6; N, 3·7%), obtained by controlled oxidation of 2-nitro-4-*p*-tolylthiobenzylidene diacetate. It was re-converted into the diacetate when warmed with acetic anhydride containing a little concentrated sulphuric acid.

5-*Nitro-2-toluene-*p-*sulphinylbenzophenone* (VII).—To a solution of 5-nitro-2-(*p*-tolylthio)-benzophenone (4 g.) in acetic acid (80 ml.) at 100°, hydrogen peroxide (16 ml.) was added and, after 4 min., the whole was poured on to crushed ice. The *sulphoxide* (VII) (3·7 g.) had m. p. 154° (from ethanol) (Found: C, 65·9; H, 4·3; N, 4·0. $C_{20}H_{15}NO_4S$ requires C, 65·7; H, 4·1; N, 3·8%).

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