44. *The Action of Sulphinates on* 1 : 5-*Dichloro*-2 : 4-*dinitrobenzene.*

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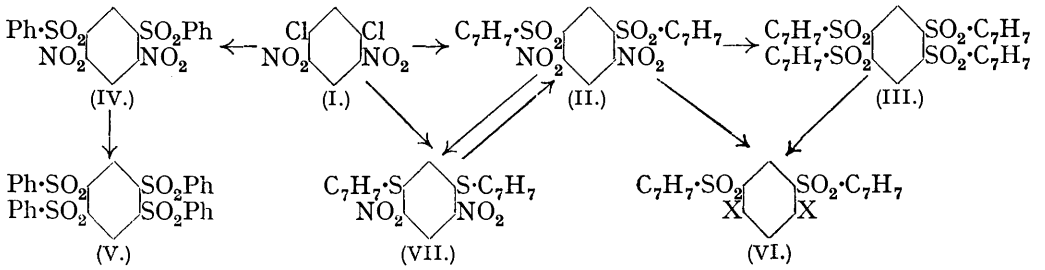
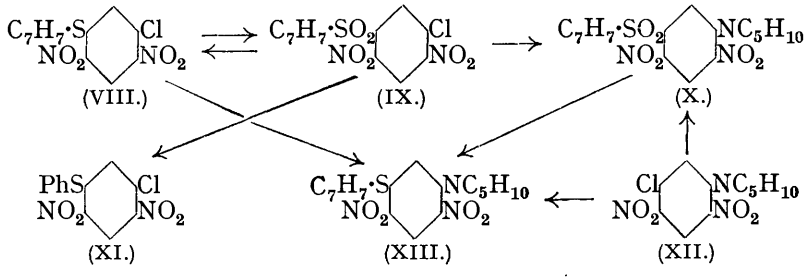
One interesting feature attending the use of sulphinates in displacing suitably activated substituents from a benzene nucleus consists in the fact that the sulphonyl groups so introduced may in turn activate new centres in the molecule and thus lead to further reaction. For instance, treatment of 2 : 4-dinitrochlorobenzene with sodium benzenesulphinate yields first 2 : 4-dinitrodiphenylsulphone and then 2 : 5-diphenylsulphonylnitrobenzene (Loudon, J., 1936, 218). Moreover, although the activating power of a single sulphonyl group may be slight (in comparison with nitro), yet by analogy with similar cases established by Schöpff and his co-workers (*Ber.*, 1891, **24**, 3771, 3785) it is to be anticipated that the combined effects of two such groups situated *meta* to each other will be considerable. From these points of view the action of sodium *p*-toluenesulphinate on 1 : 5-dichloro-2 : 4-dinitrobenzene (I) provides a case of particular interest, since here the arrangement of groups is such that ultimate production of tetra-*p*-tolylsulphonylbenzene may be expected. Experiment, in fact, showed that even under relatively mild conditions reaction proceeds beyond stage (II), yielding a mixture of sulphones from which the *tetrasulphone* (III) was isolated. The most interesting of the intermediate products, the *disulphonyl* compound (II), was obtained by employing in the reaction the free sulphinic acid instead of its salt—a modification which was unnecessary in the phenyl series (I $\longrightarrow$ IV $\longrightarrow$ V), since here under similar conditions the weaker replacing power of the benzenesulphinate (cf. J., 1935, 896) permitted isolation of (IV), the *tetrasulphone* (V) being formed only at higher temperatures.

The reactions of (II) with ammonia and piperidine also show the mobility of both nitro-groups. With the former reagent (II) and (III) each gave the *diamine* (VI, X = NH_2), also prepared from (II) by reduction, and similarly the *dipiperidino*-derivatives produced from (II) and (III) were identical (VI, X = NC_5H_{10}). On the other hand the sodium salt of *p*-thiocresol reacted with (II) to give the *dinitro-dithioether* (VII), directly obtained with this reagent from (I), thus providing another instance of the preferential replacement of

sulphonyl by mercaptide groups (cf. preceding paper). A similar selective action was also observed in the reactions of the *chlorodinitro-sulphone* (IX), which was obtained by oxidation of the *monothioether* (VIII) produced together with (VII) from (I). With theoretical



amounts of the reagents the chlorine atom was replaced by piperidine (IX ⟶ X), whereas alkaline *p*-thiocresol replaced the toluenesulphonyl group (IX ⟶ VIII). Since in reactions of the latter type the products might result from some unusual reduction of the sulphone group, we examined also the action of alkaline thiophenol on (IX) and, in harmony with the replacement view, obtained the *phenyl thioether* (XI), also directly prepared from (I). The other replacements depicted in the following scheme confirm the nature of the products referred to.



The results recorded here lend further support to the criticisms already advanced (Le Fèvre and Turner, J., 1927, 1114, and refs. given) against the conclusions of Borsche and Bahr (*Annalen*, 1913, **402**, 81), *viz.*, that there exists a fundamental difference in the mobilities of the two chlorine atoms in (I) [and correspondingly, in those of the nitro-groups in (II)]. Indeed, the ease with which both chlorine atoms are replaced renders difficult any qualitative assessment of the effect of the first replacement on the reactivity of the residual halogen. For this purpose, however, advantage was taken of the low replacing power of free *p*-toluenesulphinic acid as reagent and it was found that, of the compounds (IX) and (VIII or XII)—respectively derived from (I) by replacing one chlorine atom by a *m*-directing group on the one hand, and by a more powerful *op*-directing group (relative to Cl) on the other—the chlorine of (IX) alone underwent replacement. This result may be compared with the reappearance of suppressed halogen mobility following acetylation of certain chloronitroanilines (Lindemann and Pabst, *Annalen*, 1928, **462**, 24), and also with the fact that in the formation of (X) from (IX) by the action of piperidine the sulphonyl group has survived reaction conditions which occasion its replacement in the corresponding dinitrodiphenylsulphones (X; NC_5H_{10} replaced by H) (J., 1935, 537).

Experimental.

2 : 4-*Dinitro*-1 : 5-*di*-p-*tolylthiobenzene* (VII).—*p*-Thiocresol (2 mols.) and 1 : 5-dichloro-2 : 4-dinitrobenzene (1 mol.), dissolved in alcohol, were treated with a 10% solution of sodium hydroxide (2 mols.). The solid *product*, after crystallisation from acetic acid, formed yellow plates, m. p. 233° (Found : N, 7·0. $C_{20}H_{16}O_4N_2S_2$ requires N, 6·8%).

5-*Chloro*-2 : 4-*dinitro*-4′-*methyldiphenyl sulphide* (VIII) was obtained, after removal of (VII), as the more soluble product of a similar experiment in which molecular proportions of the

reagents were used and the temperature was maintained below 10°. It formed yellow needles, m. p. 147—148° (from alcohol) (Found : N, 8·75. $C_{13}H_9O_4N_2ClS$ requires N, 8·6%).

2 : 4-*Dinitro*-1 : 5-*diphenylthiobenzene*, needles, m. p. 253° (Found : N, 7·4. $C_{18}H_{12}O_4N_2S_2$ requires N, 7·3%), and 5-*chloro*-2 : 4-*dinitrodiphenyl sulphide*, needles, m. p. 108° (Found : N, 9·0. $C_{12}H_7O_4N_2ClS$ requires N, 9·0%), were similarly prepared by means of thiophenol.

2 : 4-*Dinitro*-1 : 5-*di*-p-*tolylsulphonylbenzene* (II).—(A) The dithioether (VII) was oxidised by heating with excess of hydrogen peroxide in acetic acid solution for 2 hours at 100°. (B) *p*-Toluenesulphinic acid (2 g.) and 1 : 5-dichloro-2 : 4-dinitrobenzene (1·5 g.) were refluxed in alcohol (30 c.c.) for 30 minutes. In each case the *product*, after crystallisation from acetic acid, melted at 228° (Found : S, 13·3. $C_{20}H_{16}O_8N_2S_2$ requires S, 13·45%). Treatment of its alcoholic dioxan solution as described under (VII, above) gave the dithioether (VII), m. p. and mixed m. p. 233°.

2 : 4-*Dinitro*-1 : 5-*diphenylsulphonylbenzene* (IV), m. p. 251°, was obtained by similar methods (Found : S, 14·5. $C_{18}H_{12}O_8N_2S_2$ requires S, 14·3%).

1 : 2 : 4 : 5-*Tetra*-p-*tolylsulphonylbenzene* (III).—1 : 5-Dichloro-2 : 4-dinitrobenzene (2 g.) in warm alcohol (30 c.c.) and sodium *p*-toluenesulphinate (6 g.) in hot water (18 c.c.) were mixed and refluxed for 1 hour. The precipitate which rapidly formed melted indefinitely at 279° and was similar to that produced when (II) was heated (1 hour) with the sulphinate in acetic acid. Each product was partially purified (m. p. 306°) by crystallisation from methyl ethyl ketone, but residual nitro-compounds were best removed by reduction with stannous chloride and concentrated hydrochloric acid (9 g. and 100 c.c. respectively per 1·5 g. of material) in acetone (300 c.c.), followed by treatment with 20% sodium hydroxide solution (150 c.c.) and extraction of the solid with acetone. After crystallisation from methyl ethyl ketone the *product*, m. p. 315°, was free from nitrogen (micro-Dumas) (Found : S, 18·1. $C_{34}H_{30}O_8S_4$ requires S, 18·4%).

1 : 2 : 4 : 5-*Tetraphenylsulphonylbenzene* (V) was prepared by refluxing (IV) in acetic acid–ethylene glycol (1 : 1) with sodium benzenesulphinate (5 mols.) for a few minutes, heating being stopped when colour began to be developed. On cooling, the *product* separated; it crystallised from methyl ethyl ketone in colourless needles (nitrogen-free), m. p. 305° (Found : S, 19·8. $C_{30}H_{22}O_8S_4$ requires S, 20·0%).

2 : 4-*Diamino*-1 : 5-*di*-p-*tolylsulphonylbenzene* (VI, X = NH_2).—(A) Either (II) or (III) in methyl alcohol (20 c.c. per 2 g.) was heated in a sealed tube at 150° with concentrated aqueous ammonia (3 c.c., *d* 0·88) for 3 hours; cream-coloured needles were deposited on cooling. These were washed with boiling acetone and were obtained colourless by crystallisation from ethylene glycol; m. p. 293°. (B) The same *compound* was obtained by reduction of (II) (2 g.) with stannous chloride (18 g.) and hydrochloric acid (20 c.c.) in alcohol (20 c.c.), followed by treatment with 20% sodium hydroxide solution (300 c.c.) and extraction of the solid with acetic acid (Found : N, 6·8. $C_{20}H_{20}O_4N_2S_2$ requires N, 6·7%).

2 : 4-*Dipiperidino*-1 : 5-*di*-p-*tolylsulphonylbenzene* (VI, X = NC_5H_{10}) was prepared by heating (II) or (III) with excess of piperidine for 2 minutes. The solution was cooled, water added, and the precipitated solid extracted with concentrated hydrochloric acid, from which the compound was reprecipitated by addition of water. The product formed yellow plates, m. p. 228° (from alcohol) (Found : N, 4·95. $C_{30}H_{36}O_4N_2S_2$ requires N, 5·0%).

2 : 4-*Dipiperidino*-1 : 5-*diphenylsulphonylbenzene*, m. p. 221°, was prepared from (IV) in the same way (Found : N, 5·45. $C_{28}H_{32}O_4N_2S_2$ requires N, 5·3%).

5-*Chloro*-2 : 4-*dinitro*-4′-*methyldiphenylsulphone* (IX) was prepared by oxidation of the sulphide with hydrogen peroxide in acetic acid; m. p. 198° (from acetic acid) (Found : N, 8·0. $C_{13}H_9O_6N_2ClS$ requires N, 7·9%). Treatment of an alcoholic dioxan solution of the compound with *p*-thiocresol (1 mol.) and 10% sodium hydroxide solution gave a mixture of mono- and di-thioethers (VIII and VII, separated as under VIII), whilst with thiophenol the corresponding phenyl derivatives were produced.

5-*Chloro*-2 : 4-*dinitrodiphenylsulphone*, m. p. 187°, was similarly prepared (Found : S, 9·4. $C_{12}H_7O_6N_2ClS$ requires S, 9·4%).

2 : 4-*Dinitro*-5-*piperidino*-4′-*methyldiphenylsulphone* (X) was obtained in felted orange-yellow needles, m. p. 180° (from alcohol), by refluxing an aqueous alcoholic solution of 5-chloro-2 : 4-dinitropiperidinobenzene (Le Fèvre and Turner, *loc. cit.*) and sodium *p*-toluenesulphinate. The same compound was formed by heating (IX) with excess of piperidine (Found : N, 10·3. $C_{18}H_{19}O_6N_3S$ requires N, 10·4%).

2 : 4-*Dinitro*-5-*piperidino*-4′-*methyldiphenyl sulphide* (XIII) was prepared by refluxing (VIII) in piperidine (1 hour) and also by treating (X) or (XII) in alcohol with *p*-thiocresol and sodium hydroxide in the usual way; it formed yellow plates, m. p. 192°, from alcoholic dioxan (Found : N, 11·2. $C_{18}H_{19}O_4N_3S$ requires N, 11·3%).

Compounds (IX), (VIII), and (XII) were each heated in acetic acid solution with *p*-toluene-

sulphinic acid (1 mol.). (IX) yielded 2 : 4-dinitro-1 : 5-di-*p*-tolylsulphonylbenzene (m. p. and mixed m. p.) and (VIII) and (XII) were recovered unchanged.

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