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48. *The Action of Sulphinates on 2 : 4-Dinitrodiphenylsulphones.*

By James D. Loudon.

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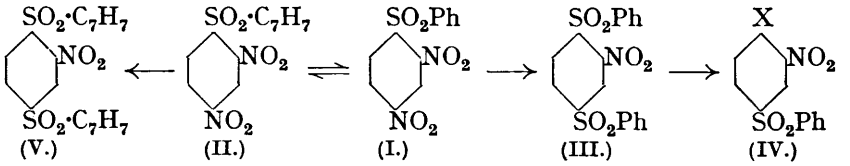
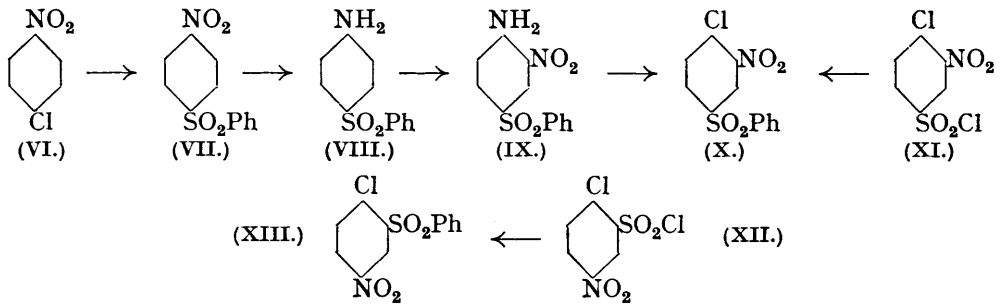
It has previously been shown (Loudon, J., 1935, 537) that the action of sodium *p*-toluenesulphinate on 2 : 4-dinitrodiphenylsulphone results in a rapid and reversible exchange of sulphonyl groups (I $\rightleftharpoons$ II), accompanied by slower secondary reactions of unknown nature, apparently incurred by the continued action upon (I) and (II) of sulphinate present in excess or produced during the exchange. To avoid unnecessary complications in investigating this second phase, the action of sodium benzenesulphinate on 2 : 4-dinitrodiphenylsulphone (I) was first examined. Analysis of the isolated product indicated a nitrobis(phenylsulphonyl)benzene structure (*e.g.*, III), and its reactions showed the presence of one mobile phenylsulphonyl group. For instance, with alcoholic alkali a mixture of a *phenol* (IV; X = OH) and its *ethyl* ether (X = OEt) was readily produced, and alcoholic ammonia and piperidine gave an *amine* (X = NH_2) and a *piperidino*-derivative (X = NC_5H_{10}) respectively.



Since the mobility of this phenylsulphonyl group is comparable with that in (I), the inference may be drawn that it arises from the combined activating influences of both the residual nitro- and the second phenylsulphonyl group (for the activating effect of analogous combinations upon halogens, cf. *inter alia* Le Fèvre and Turner, J., 1927, 1113), and hence that the formation of the disulphonyl compound from (I) probably consists in replacement of one or other nitro-group by phenylsulphonyl (contrast the action of potassium cyanide on 2 : 4-dinitrochlorobenzene, where CN enters position 3; Van Heteren, *Rec. trav. chim.*, 1901, **20**, 107; Blanksma, *ibid.*, 1902, **21**, 424).

The selection of the *p*-nitro-group in (I) as the group actually concerned in the replacement follows from synthetic evidence, *viz.*, the mononitro-derivative (IX) of *p*-aminodiphenylsulphone was identical with the amine obtained from (III) with alcoholic ammonia, and was converted into the *chloronitro*-compound (X), from which (III) and its reaction products (IV) were produced by treatment with the appropriate reagents. Further, (X) was also obtained from the Friedel–Crafts condensation between 4-chloro-3-nitrobenzenesulphonyl chloride (XI) and benzene, whereas the isomeric *compound* (XIII), obtained in a similar way from (XII), yielded a *piperidino*-derivative quite distinct from (IV) (X = NC_5H_{10}).



A parallel series of reactions and synthesis similarly identified the product of the action of sodium *p*-toluenesulphinate on (II) as 1-*nitro*-2 : 5-*di*-p-*tolylsulphonylbenzene* (V), but in this series the condensation between (XI) and toluene gave unworkable products. In both series the projected formation of the chloronitro-compounds by mononitration of

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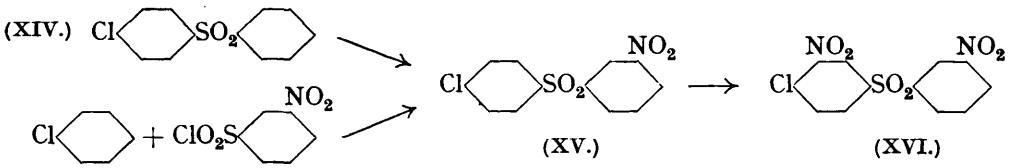
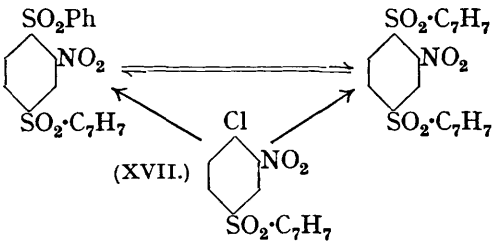
p-chlorodiphenylsulphone (XIV) and *p*-chlorophenyl-*p*-tolylsulphone was frustrated by entrance of the nitro-group into the non-halogenated nucleus, as shown by the absence of halogen mobility in the product (XV) (piperidine test) and by an independent preparation.



This result is analogous to the heteronuclear nitration of monohalogenated diphenyl derivatives, but the more closely related case of the benzophenone class does not appear to have been investigated. Dinitration of (XIV) yielded the active *chloro*-compound (XVI), from which a *piperidino*-derivative and the corresponding *amine* were readily obtainable. The disulphonyl derivatives obtained from (X), from its *p*-tolyl analogue (XVII), and from (XVI), all displayed the capacity to exchange sulphonyl groups adjacent to the nitro-group, but this capacity was less marked than in the case of the 2 : 4-dinitrodiphenylsulphones.



These results sufficiently indicate one aspect of the changes involved in the action of sulphinates on 2 : 4-dinitrodiphenylsulphones—others, which probably originate in the reducing powers of the sulphinates, have not been investigated. Whilst, as might be expected, replacement of the mobile nitro-group by arylsulphonyl was found to occur in both *o*- and *p*-dinitrobenzenes under the conditions employed for reaction with the corresponding chloronitro-compounds, the replacement of the *p*-nitro-groups in (I) and (II) involves some special features requiring further investigation. In this connexion, however, two points deserve mention: (1) in general, sulphinates may be expected to differ from the usual reagents (amines, hydroxides, etc.) employed to detect mobility in nitro-compounds, in that the latter, by introducing NH_2, OH, etc., tend to neutralise the effect of the nitro-group in facilitating further attack by anions, and (2) in particular, neither the nitro-group in (VII) nor that in the *o*-isomeride is replaced under the conditions sufficient to effect the replacements (I ⟶ III), (II ⟶ V).

Experimental.

1-Nitro-2 : 5-diphenylsulphonylbenzene (III).—A solution of 2 : 4-dinitrodiphenylsulphone (5 g.) and sodium benzenesulphinate (10 g.) in hot aqueous dioxan was refluxed for 3—4 hours. The semi-solid mass which separated on cooling or on addition of water was washed with alcohol, then with water, and crystallised from acetic acid, forming colourless felted needles, m. p. 157—158°, soluble without decomposition in warm concentrated sulphuric acid and only very slowly attacked by aqueous alkali. The same *compound* was obtained by boiling the reagents for a few minutes in ethylene glycol solution (Found: C, 53·5; H, 3·5; N, 3·8; S, 16·1. $C_{18}H_{13}O_6NS_2$ requires C, 53·6; H, 3·3; N, 3·5; S, 15·9%).

3-Nitro-4-piperidinodiphenylsulphone (IV, X = NC_5H_{10}) was prepared by dissolving (III) in boiling piperidine, followed by dilution with water, extraction of the precipitate with hot concentrated hydrochloric acid, and reprecipitation with water. It formed salmon-coloured plates, m. p. 133°, from alcohol (Found: N, 7·9. $C_{17}H_{18}O_4N_2S$ requires N, 8·1%).

Action of Aqueous-alcoholic Alkali on (III).—A suspension of (III) (0·4 g.) in alcohol (15 c.c.)

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and 3% aqueous caustic soda (4 c.c.) was refluxed till complete dissolution was effected. After partial removal of the alcohol, addition of water yielded an oil, which slowly solidified and was found to be 3-*nitro*-4-*ethoxydiphenylsulphone*; it formed needles, m. p. 147°, from alcohol (Found: N, 4·65. $C_{14}H_{13}O_5NS$ requires N, 4·8%). The filtrate from this substance gave on acidification with acetic acid 3-*nitro*-4-*hydroxydiphenylsulphone*, which crystallised from alcohol in almost colourless plates, m. p. 137° (Found: N, 5·1. $C_{12}H_9O_5NS$ requires N, 5·0%).

1-*Nitro*-2 : 5-*di*-p-*tolylsulphonylbenzene* (V), prepared in the same manner as (III), had similar appearance and properties. M. p. 220—221° (Found: C, 56·1; H, 4·3; N, 3·4; S, 15·0. $C_{20}H_{17}O_6NS_2$ requires C, 55·7; H, 3·9; N, 3·3; S, 14·85%).

3-*Nitro*-4-*piperidino*-4′-*methyldiphenylsulphone* was obtained in two forms—rapid crystallisation of the crude product [preparation similar to (IV) above] from hot alcohol yielding one form, m. p. 96—97°, which, kept in contact with the solvent, changed to the second form, m. p. 107—108°, also obtained directly by slower crystallisation (Found: N, 7·95. $C_{18}H_{20}O_4N_2S$ requires N, 7·8%).

3-*Nitro*-4-*hydroxy*-4′-*methyldiphenylsulphone*, m. p. 157—158° (Found: N, 4·9. $C_{13}H_{11}O_5NS$ requires N, 4·8%), and its *ethyl* ether, m. p. 143—144° (Found: N, 4·2. $C_{15}H_{15}O_5NS$ requires N, 4·4%), were prepared as in the cases of their lower homologues.

Mononitrodiphenylsulphones.—The following procedure dispenses with the sealed tubes employed in two instances by Ullmann and Pasdermadjian (*Ber.*, 1901, **34**, 1150). The requisite chloronitrobenzene and sodium sulphinate in molecular proportion were boiled in ethylene glycol for 3—4 hours. The product which separated on cooling (or on addition of water) was washed with alcohol and water and crystallised (charcoal) from alcohol or acetic acid. *o*-Nitrodiphenylsulphone had m. p. 147° (Found: N, 5·3. Calc.: N, 5·3%). *p*-Nitrodiphenylsulphone had m. p. 143° (Found: N, 5·4%). 2-Nitro-4′-methyldiphenylsulphone had m. p. 156° (*Chem. Abs.*, 1933, 998, patent, gives m. p. 156—157°) (Found: N, 5·2%).

4-*Nitro*-4′-*methyldiphenylsulphone* had m. p. 170° (Found: N, 5·2. $C_{13}H_{11}O_4NS$ requires N, 5·05). *o*- and *p*-Dinitrobenzenes (0·5 g.), treated in the same way for 30—40 minutes, gave the corresponding sulphones (m. p. and mixed m. p.).

4-*Amino*-4′-*methyldiphenylsulphone* (for indirect preparation, cf. Halberkmann, *Ber.*, 1922, **55**, 3074).—The nitro-sulphone (6 g.) was added in small quantities at a time to a boiling solution of stannous chloride (15 g.) in alcohol (15 c.c.) and the resulting solution after addition of concentrated hydrochloric acid (15 c.c.) was cooled and slowly stirred into 300 c.c. of 20% caustic soda solution. The precipitated amine was repeatedly extracted with alcohol and was crystallised from the same solvent; m. p. 181° (Found: N, 5·6. Calc.: N, 5·7%). 2-Amino-4′-methyldiphenylsulphone, similarly prepared, had m. p. 120—121° (Halberkmann, *loc. cit.*, gives m. p. 120—121°) (Found: N, 5·7%).

3-*Nitro*-4-*aminodiphenylsulphone* (IX).—(*A*) *p*-Aminodiphenylsulphone (Ullmann and Pasdermadjian, *loc. cit.*) was converted into the p-*toluenesulphonamide*, m. p. 190° (from acetic acid), by treatment with *p*-toluenesulphonyl chloride and pyridine (Found: N, 4·0. $C_{19}H_{17}O_4NS_2$ requires N, 3·6%). The sulphonamide (6 g.) was heated with nitric acid (6 c.c.; *d* 1·4) in acetic acid solution (60 c.c.) for 1 hour; on cooling, 3-*nitro*-4-p-*toluenesulphonamidodiphenylsulphone* crystallised, m. p. 171° (from acetic acid) (Found: N, 6·8. $C_{19}H_{16}O_6N_2S_2$ requires N, 6·5%). Hydrolysis by warm concentrated sulphuric acid yielded the required *amine*, m. p. 169—170° from acetic acid (Found: N, 9·9. $C_{12}H_{10}O_4N_2S$ requires N, 10·1%).

(*B*) 1-Nitro-2 : 5-diphenylsulphonylbenzene (0·5 g.), methyl alcohol (5 c.c.), and concentrated ammonia solution (0·6 c.c.) were heated in a sealed tube at 130° for 5 hours. The yellow crystalline product had m. p. 168—169° (from acetic acid), undepressed by admixture with the amine from (*A*).

3-*Nitro*-4-*amino*-4′-*methyldiphenylsulphone*.—(*A*) 4-Amino-4′-methyldiphenylsulphone yielded the p-*toluenesulphonamide*, m. p. 213—214° (from acetic acid) (Found: N, 3·8. $C_{20}H_{19}O_4NS_2$ requires N, 3·5%). From the nitration solution [the amide (8 g.), acetic acid (80 c.c.), and nitric acid (6 c.c.; *d* 1·4) after 1 hour's refluxing] there separated 3 : 5-*dinitro*-4-p-*toluenesulphonamido*-4′-*methyldiphenylsulphone* in colourless felted needles, m. p. 221° (Found: N, 8·25. $C_{20}H_{17}O_8N_3S_2$ requires N, 8·5%), which was hydrolysed to 3 : 5-*dinitro*-4-*amino*-4′-*methyldiphenylsulphone*, yellow needles (from acetic acid), m. p. 216° with previous softening at 205° (Found: N, 12·4. $C_{13}H_{11}O_6N_3S$ requires N, 12·5%). The constitution of this compound follows from its non-identity with 3 : 3′-dinitro-4-amino-4′-methyldiphenylsulphone (cf. below). The mother-liquor of the nitration solution after removal of the dinitro-compound gave on dilution with water 3-*nitro*-4-p-*toluenesulphonamido*-4′-*methyldiphenylsulphone*, m. p. 129—130° after repeated crystallisation from alcoholic dioxan (Found: N, 6·4. $C_{20}H_{18}O_6N_2S_2$

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requires N, 6·3%). Hydrolysis of this product with concentrated sulphuric acid yielded the required *amine* (yellow needles, m. p. 184°, from acetic acid).

(*B*) The same amine (m. p. and mixed m. p. 184—185°) was obtained from (V) and alcoholic ammonia in the way already described for the phenyl homologue (Found : N, 9·7. $C_{13}H_{12}O_4N_2S$ requires N, 9·6%).

4-*Chloro*-3-*nitrodiphenylsulphone* (X).—(*A*) 3-Nitro-4-aminodiphenylsulphone was subjected to Hodgson and Walker's modification of the Sandmeyer reaction (J., 1933, 1620). The product formed pale yellow needles, m. p. 127°, from alcoholic dioxan. (*B*) 4-Chloro-3-nitrobenzenesulphonyl chloride, prepared by nitration of *p*-chlorobenzenesulphonyl chloride as described by Davies and Wood (J., 1928, 1125) but with the use of nitric acid (*d* 1·53), melted at 61—62° (from light petroleum) instead of 39—40° (*loc. cit.*). Fischer (*Ber.*, 1891, **24**, 3188) gives m. p. 40—41°, whereas Pollak and Katscher (*Monatsh.*, 1930, **55**, 371) find the value 59—60° (Found : N, 5·4. Calc. : N, 5·5%). The sulphonyl chloride (6 g.), aluminium chloride (6 g.), and benzene (10 c.c.) were heated on the water-bath for 1 hour. The semi-solid mass obtained on cooling and addition to water was extracted with hot acetic acid, from which the required product separated, m. p. and mixed m. p. with (*A*) 125—126° after purification (Found : N, 4·8. $C_{12}H_8O_4NClS$ requires N, 4·7%). Treatment with piperidine in the usual way gave the piperidino-derivative (IV; X = NC_5H_{10}), m. p. and mixed m. p. with the piperidino-compound prepared from (II) 132—133°. Digestion with aqueous alkali yielded the phenol, m. p. and mixed m. p. 137°, and with alcoholic sodium ethoxide, the ethyl ether, m. p. and mixed m. p. 147—148°.

4-*Chloro*-3-*nitro*-4′-*methyldiphenylsulphone* was prepared as described for (X, *A*) and gave corresponding halogen replacements; m. p. 120° (from alcohol) (Found : N, 4·6. $C_{13}H_{10}O_4NClS$ requires N, 4·5%).

2-*Chloro*-5-*nitrodiphenylsulphone* (XIII) was prepared from the sulphonyl chloride (XII) in the usual way (cf. X, *B*) and crystallised from dioxan in long silky needles, m. p. 174° (Found : N, 4·9. $C_{12}H_8O_4NClS$ requires N, 4·7%). Treatment with piperidine gave 5-*nitro*-2-*piperidinodiphenylsulphone* in yellow plates, m. p. 178° (Found : N, 8·1. $C_{17}H_{18}O_4N_2S$ requires N, 8·1%).

4-*Chloro*-3′-*nitrodiphenylsulphone* (XV).—(*A*) Solutions of 4-chlorodiphenylsulphone (2·5 g.) and potassium nitrate (1 g.) in concentrated sulphuric acid (5 c.c. each) were mixed at 10° and, after 12 hours, poured into water. The solid was crystallised repeatedly from acetic acid. (*B*) *m*-Nitrobenzenesulphonyl chloride (2 g.), chlorobenzene (3 c.c.), and aluminium chloride (2 g.), treated in the usual way, gave the same *product* in colourless needles, m. p. 139—140° (Found : N, 4·9. $C_{12}H_8O_4NClS$ requires N, 4·7%).

4-*Chloro*-3 : 3′-*dinitrodiphenylsulphone* (XVI) was prepared in similar fashion from the mononitro-sulphone (XV) (3 g.), sulphuric acid (9 c.c.), and potassium nitrate (1 g.) or by direct dinitration; m. p. 146° (from acetic acid) (Found : N, 8·3. $C_{12}H_7O_6N_2ClS$ requires N, 8·2%). The *piperidino*-derivative was obtained in salmon-coloured leaflets, m. p. 151—152° (Found : N, 10·7. $C_{17}H_{17}O_6N_3S$ requires N, 10·7%).

3 : 3′-*Dinitro*-4-*aminodiphenylsulphone*, prepared from (XVI) and methyl-alcoholic ammonia (cf. IX, *B*), had m. p. 238° (from ethylene glycol) (Found : N, 13·2. $C_{12}H_9O_6N_3S$ requires N, 13·0%).

The following compounds were prepared in a similar way from 4-chloro-4′-methyldiphenylsulphone : 4-*chloro*-3′-*nitro*-4′-*methyldiphenylsulphone*, m. p. 103° (Found : N, 4·6. $C_{13}H_{10}O_4NClS$ requires N, 4·5%); 4-*chloro*-3 : 3′-*dinitro*-4′-*methyldiphenylsulphone*, m. p. 152° (Found : N, 7·9. $C_{13}H_9O_6N_2ClS$ requires N, 7·85%); 3 : 3′-*dinitro*-4-*piperidino*-4′-*methyldiphenylsulphone*, m. p. 149—150° (Found : N, 10·4. $C_{18}H_{19}O_6N_3S$ requires N, 10·4%); and 3 : 3′-*dinitro*-4-*amino*-4′-*methyldiphenylsulphone*, m. p. 231° (Found : N, 12·5. $C_{13}H_{11}O_6N_3S$ requires N, 12·5%).

By heating equimolecular proportions of sodium benzene- or *p*-toluene-sulphinate in aqueous alcohol (or dioxan) with the requisite chloronitro-compound (X, XVI, XVII) for 30—60 minutes, the following disulphones were prepared; they were purified by crystallisation from acetic acid : 1-nitro-2 : 5-diphenylsulphonyl- and -2 : 5-di-*p*-tolylsulphonyl-benzene; 1-*nitro*-5-*phenylsulphonyl*-2-p-*tolylsulphonylbenzene*, m. p. 180° (Found : N, 3·6. $C_{19}H_{15}O_6NS_2$ requires N, 3·4%); 1-*nitro*-2-*phenylsulphonyl*-5-p-*tolylsulphonylbenzene*, m. p. 212° (Found : N, 3·5. $C_{19}H_{15}O_6NS_2$ requires N, 3·4%); 1-*nitro*-2-*phenylsulphonyl*-5-m-*nitrophenylsulphonylbenzene*, m. p. 233° (from *cyclo*hexanone) (Found : N, 6·4. $C_{18}H_{12}O_8N_2S_2$ requires N, 6·25%); and 1-*nitro*-5-m-*nitrophenylsulphonyl*-2-p-*tolylsulphonylbenzene*, m. p. 232° (Found : N, 6·0. $C_{19}H_{14}O_8N_2S_2$ requires N, 6·1%).

Exchanges between the 2-arylsulphonyl groups were effected in dioxan solution as previously described (J., 1935, 537), the reactions here requiring 30 minutes' heating to attain equilibrium.

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