Photochemical Transformations. Part XXII.† Some Reactions of 2,4-Dinitrobenzenesulphenyl Derivatives

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Aromatic sulphides were prepared by the photolysis of 2,4-dinitrobenzenesulphenyl acetate with aromatic compounds. The reaction is general and is shown to proceed *via* electrophilic attack by the 2,4-dinitrobenzenesulphenium ion, or its precursor. Transfer of oxygen from the *ortho*-nitro-group to the sulphur atom for 2,4-dinitrobenzenesulphenyl derivatives is demonstrated under photolytic conditions. Evidence is accumulated for the formation of a nitrene type of intermediate in certain of these redox reactions.

PHOTOLYSIS of 2,4-dinitrobenzenesulphenyl derivatives of carboxylic acids (I; R = acyl) in benzene solutions was previously shown to liberate the carboxylic acid and simultaneously to form 2,4-dinitrodiphenyl sulphide (III; Ar = Ph) in good yield.[1] Evidence was also obtained that the aromatic sulphide is formed by electrophilic attack on the solvent benzene by the 2,4-dinitrobenzenesulphenium cation (II). In the present Paper it is demonstrated that such substitutions are general; the results are tabulated.

The reaction follows the known ease of attack onto substituted benzenes.[2] Thus anisole is substituted with greater ease than benzene; similarly, chlorobenzene is attacked only with difficulty. Since, in most cases, no reaction occurred in the absence of light, the reaction is equivalent to a photocatalysed Friedel–Crafts reaction. With highly activated aromatic substrates, such as *NN*-dimethylaniline and *NN*-dimethyl-*p*-toluidine, a slow dark reaction occurred with the sulphenyl acetate in refluxing benzene solution to give the corresponding sulphides (III; R = p-$Me_2N{\cdot}C_6H_4$) and (IV; R^1 = NMe_2, R^2 = Me), respectively. However, photolysis greatly increased the rate of these reactions, all the sulphenyl acetate being consumed within fifteen minutes. The use of the aromatic hydrocarbons, naphthalene, anthracene, and phenanthrene as substrates showed that, in all cases, the normal position for electrophilic substitution was attacked. Reaction of the sulphenyl acetate with either furan or thiophen gave substitution in the 2-position, as anticipated for electrophilic attack. Indole and skatole proved too reactive giving rapid reactions even in the dark. The indole reaction product was shown to be the 3-substituted indole by comparison with an authentic sample prepared from 3-thiocyanoindole.[5]

A few experiments were carried out using 2-nitrobenzenesulphenyl acetate. Irradiation of this compound in benzene gave mainly the disulphide, 2,2′-di-

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† Part XXI, D. H. R. Barton, G. S. Ramsay and D. Wage, *J. Chem. Soc.* (*C*), 1967, 1915.

[1] D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, *J. Chem. Soc.*, 1965, 3571.

[2] F. G. Bordwell, ‘ Organic Chemistry,’ The Macmillan Co., New York, 1963, p. 517.

nitrodiphenyl disulphide; with anisole as solvent the expected substitution product (V), formed, again with large amounts of the corresponding disulphide. It appears that the 2-nitrobenzenesulphenyl acetate is less reactive than the dinitro-compound as an electrophilic reagent. This indicates the desirability for the second nitro-function. Since this would be expected to inhibit the formation of the sulphenium ion, the possibility cannot be ruled out that a free sulphenium ion is not involved but that, upon photolysis of 2,4-dinitrobenzenesulphenyl acetate, an excited state forms, which is activated for electrophilic attack. This is followed by loss of acetate. Thus, for benzene substitution, one could write:

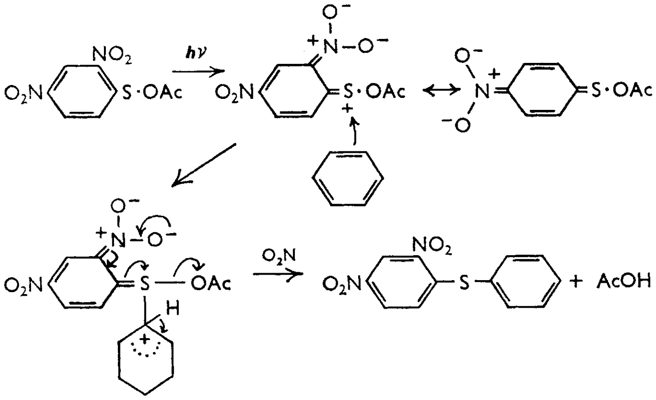

Photo-Friedel–Crafts reactions with 2,4-dinitrobenzenesulphenyl acetate [a]

Acetate (mmole)	Substrate	(mmole)	Solvent	(ml.)	Time (min.)	Product	Yield (%)
1·0	Benzene	6	Benzene	125	60	(III; R = Ph) [1]	73 [c]
1·0	Anisole	1·0	Benzene	125	60	(III; R = *p*-$MeOC_6H_4$) [1]	74 [c]
0·5	Anisole	6	Anisole	25	60	(III; R = *p*-$MeOC_6H_4$) [1]	80
2·0	Anisole	2·0	Chlorobenzene	100	60	(III; R = *p*-MeC_6H_4) [1]	66 [d]
2·0	Chlorobenzene	6	Chlorobenzene	100	60	(III; R = *p*-ClC_6H_4) [3]	14 [d]
1·9	1,4-Dimethoxybenzene	1·9	Benzene	100	20	(IV; $R^1 = R^2$ = OMe)	55
2·0	*NN*-Dimethylaniline	4·0	Benzene	150	70	(III; R = *p*-$Me_2N{\cdot}C_6H_4$) [3]	27
2·0	*NN*-Dimethyl-*p*-toluidine	3·3	Benzene	150	40	(IV; $R^1 = Me^2N$, $R_2 = Me_3$)	23
2·0	Naphthalene	2·0	Chlorobenzene	100	15	(III; R = 1-naphthyl) [3]	41 [d]
1·0	Anthracene	1·0	Chlorobenzene	15	15	(III; R = 9-anthryl)	74 [d]
1·0	Phenanthrene	1·0	Chlorobenzene	15	10	(III; R = 9-phenanthryl) [3]	82 [d]
2·0	Thiophen	*b*	Thiophen	9	45	(III; R = 2-thienyl) [4]	13
2·0	Furan	*b*	Furan–Benzene (1 : 10)	110	60	(III; R = 2-furyl)	28

[a] See Experimental section for method. [b] Excess, as solvent. [c] From ref. 1. [d] Kept below 100° by a water-bath.

Other 2,4-dinitrobenzenesulphenyl derivatives were also photolysed. It is well known that light can induce homolysis of disulphides.[6] The photolysis of 2,4-dinitrodiphenyl disulphide (VI) was investigated to determine whether homolytic or heterolytic cleavage occurs. Irradiation of (VI) in benzene gave disproportionation to diphenyl disulphide and 2,2′,4,4′-tetranitrodiphenyl disulphide. The benzene derivative (III; R = Ph) was not observed. Using anisole as solvent had little effect on the course of the reaction although traces of the anisole derivative (III; R = *p*-$MeOC_6H_4$) were detected by thin-layer chromatography. It is known that polar solvents can induce heterolytic cleavage of disulphides.[7] It is clear, however, that the mechanism (radical) of photolysis of (VI) is entirely different to the mechanism pertinent to the acyl derivatives discussed above.

Since diaryl disulphides are photolysed homolytically, it was considered likely that the sulphenyl esters of phenols should also cleave homolytically, upon irradiation, to give the corresponding phenoxy-radicals of interest in the study of phenolic coupling.[8] Photolysis of *p*-tolyl 2,4-dinitrobenzenesulphenate (I; R = *p*-MeC_6H_4) in benzene rapidly gave a red solution with formation of a dark precipitate. The precipitate proved to be mainly 2,2′,4,4′-tetranitrodiphenyl disulphide and 2-amino-4-nitrobenzenesulphonic acid (VII; R = OH). The red filtrate was phenolic. Its thin-layer chromatographic analysis showed traces of material identical to Pummerer's ketone (VIII),[9] presumably formed by coupling of phenolic radicals produced by photolysis, and a large amount of *p*-cresol. Irradiation of the phenyl ester (I; R = Ph) gave a similar result. In an attempted trapping reaction the phenyl ester (I; R = Ph) was photolysed with diphenyl disulphide when 2,4-dinitrodiphenyl disulphide was isolated. The lack of ionic cleavage of the sulphur–oxygen bond during photolysis was also demonstrated by the absence of any 4′-hydroxy-2,4-dinitrodiphenyl sulphide among the reaction products. This would be expected from heterolytic cleavage by recombination of the 2,4-dinitrobenzenesulphenium cation with the liberated phenolate anion.

Careful chromatography of the reaction liquid from the photolysis of the tolyl ester (I; R = *p*-MeC_6H_4) afforded small amounts of two further photoproducts.

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[3] C. M. Buess and N. Kharasch, *J. Amer. Chem. Soc.*, 1950, **72**, 3529.

[4] R. D. Schulz and W. C. Fredericks, *J. Org. Chem.*, 1962, **27**, 1302.

[5] M. S. Grant and H. R. Snyder, *J. Amer. Chem. Soc.*, 1960, **82**, 2742.

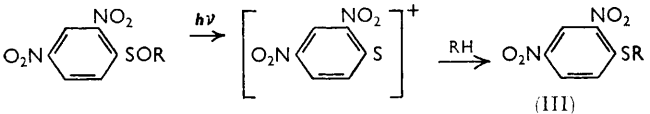
[6] W. E. Lyons, *Nature*, 1948, **162**, 1004; W. H. C. Rueggeberg, J. Chernak, I. M. Rose, and E. E. Reid, *J. Amer. Chem. Soc.*, 1948, **70**, 2292; W. H. C. Rueggeberg, J. Cook, and E. E. Reid, *J. Org. Chem.*, 1948, **13**, 110; G. Leandri and A. Tundo, *Ann. Chim.* (*Italy*), 1954, **44**, 63.

[7] S. Archer and M. Suter, *J. Amer. Chem. Soc.*, 1952, **74**, 4298.

[8] A. I. Scott, *Quart. Rev.*, 1965, **10**, 1.

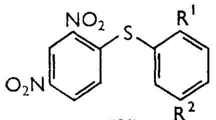
[9] D. H. R. Barton, A. M. Deflorin, and O. E. Edwards, *J. Chem. Soc.*, 1956, 530.

The major component showed, in its mass spectrum, a parent ion at *m*/*e* 306 and a major fragmentation, with loss of 64 mass units, corresponding to loss of sulphur dioxide. Its infrared spectrum had absorptions due to secondary amine and sulphonate groups. It has been assigned the structure (IX; R = Me). The minor yellow photoproduct was the amino-sulphonate (VII; R = *p*-MeC_6H_4O). These products must arise by transfer of oxygen from the *ortho*-nitro-group to the sulphur atom. The incorporation of nitrogen into the tolyl ring must be due to an electrophilic species and possibly involves a nitrene type of intermediate.[10] Such insertion of nitrogen into aromatic systems has analogy with the proposed route for the reaction of triethyl phosite with nitro-groups.[11] The phenyl ester (I; R = Ph) gave similar products.

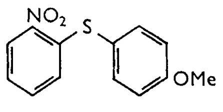


(I) (II) (III)

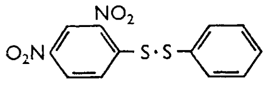
R = aromatic substrate



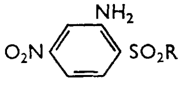
(IV)



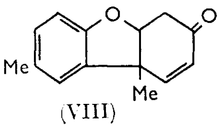
(V)



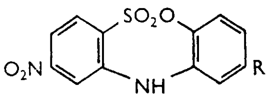
(VI)



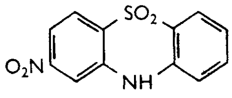
(VII)



(VIII)



(IX)



(X)

As an extension of these reactions benzyl 2,4-dinitrobenzenesulphenate (I; R = $PhCH_2$) was irradiated in benzene solution. It was anticipated that, if the nitrene intermediate formed, it would readily abstract hydrogen atoms from the benzylic carbon atom to give, eventually, benzaldehyde or benzoic acid. A rapid photoreaction of the ester was observed but neither benzaldehyde nor benzoic acid was detected. The principal products were the amino-sulphonic acid (VII; R = OH) and diphenylmethane. The reaction must proceed *via* formation of the benzyl sulphonate (VII; R = $PhCH_2O$), or its precursor, followed by solvent attack and cleavage of the sulphur to substrate bond. To confirm that solvent was participating the photolysis was repeated using anisole as solvent. In this case a mixture of 2- and 4-methoxydiphenylmethanes formed. The case of photolysis of the benzyl ester (I; R = $PhCH_2$) is in contrast with that of simpler alkyl esters which were much more stable towards photolysis.

Since the phenyl esters (I; R = aryl) gave small amounts of cyclised products, it would be expected that similar cyclisation products should form from any aryl sulphide containing an *ortho*-nitro-group. 2,4-Dinitrodiphenyl sulphide proved reasonably stable to irradiation in benzene solution. After 33 hr. over 70% of the starting material was recovered. The remaining products included a small amount of a yellow solid which showed a parent ion at *m*/*e* 276 in its mass spectrum, as well as a single band at 3420 cm.$^{-1}$ in its infrared spectrum, indicative of a diaryl amine; it must therefore be the expected cyclisation product (X).[12]

The photolysis of some anilide derivatives of 2,4-dinitrobenzenesulphenic acid was next briefly investigated. When either the *N*-methyl-*p*-toluidide or *N*-methylanilide was photolysed in benzene solution a slow reaction occurred but no hydrogen abstraction from the *N*-alkyl group took place. Instead the principal photoproducts were the corresponding sulphanilides (VII; R = *p*-$MeC_6H_4NMe_2$) and (VII; R = C_6H_4NMe) in which intramolecular oxygen transfer has occurred. Hydrolysis of the *N*-methylanilide (VII; R = C_6H_4NMe) with sulphuric acid gave the amino-sulphonic acid (VII; R = OH).

In contrast, when the aniline derivative (III; Ar = PhNH) was photolysed, a complex mixture of products rapidly formed from which *cis*- and *trans*-azobenzene were isolated, together with the amino-sulphonic acid (VII; R = OH).

The constant occurrence of the amino-sulphonic acid (VII; R = OH) in the above photoreaction products deserves comment. Its formation requires cleavage of the sulphur to substituent bond accompanied by abstraction of one hydrogen atom, presumably from the solvent, and addition of one molecule of water, either during the reaction or during working up. That the sulphonic acid was liberated, and not the sulphinic acid, was confirmed by mass spectroscopy. Examination of a typical precipitate, isolated by direct filtration, from the photolysis of 2,4-dinitrobenzenesulphenylacetate in benzene, showed a parent ion at *m*/*e* 218, corresponding to the amino-sulphonic acid (VII; R = OH) but no peak at *m*/*e* 202, as expected for the sulphinic acid.

EXPERIMENTAL

Infrared spectra were recorded on a Unicam SP 200 spectrometer as Nujol mulls, unless otherwise specified.

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[10] P. A. Smith, J. M. Clegg, and J. H. Hall, *J. Org. Chem.*, 1958, **23**, 524.

[11] J. I. G. Cadogan and M. Cameron-Wood, *Proc. Chem. Soc.*, 1962, 361; J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831; J. I. G. Cadogan and M. J. Todd, *Chem. Comm.*, 1967, 178; G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, 1966, **31**, 3882.

[12] M. F. Grundon and B. T. Johnson, *J. Chem. Soc.* (*B*), 1966, 255.

Ultraviolet spectra were measured on a Unicam SP 800 instrument in ethanol solution. Mass spectra were determined on an A.E.I. MS9 machine. ^{1}H n.m.r. spectra were taken on a Varian A60 spectrometer (on permanent loan from the Wellcome Trust) using tetramethylsilane as internal reference in deuteriochloroform solution. Thin-layer chromatography was carried out using Merck silica gel GF$_{254}$, with acetone–benzene mixtures as solvent. Light petroleum refers to the fraction of boiling range 40—60°.

General Procedure for Irradiation.—The nitro-compound to be photolysed (usually 250—500 mg.) in an anhydrous solvent (freshly dried) containing the aromatic substrates (if any) was placed in a 250 ml. Pyrex flask equipped with a stirrer, nitrogen inlet, and a condenser. Irradiation was from beneath using a 125 w high pressure mercury arc lamp. With benzene as solvent the reaction mixture was allowed to heat to reflux; with higher boiling solvents the temperature was controlled to below 100° with water cooling. At intervals during the photolysis samples were withdrawn in order to follow the course of reaction, using either infrared or ultraviolet spectroscopy, or by following the formation of products by thin-layer chromatography. Control reactions were run by heating the compounds in the same solvent in the dark and to the appropriate temperature for similar periods as in the photolytic runs.

Irradiation with Anisole.—The sulphenyl acetate (I; R = Ac) (126 mg.) in anisole (25 ml.) was irradiated for 1 hr. The reaction mixture was chromatographed over alumina (grade III; 50 g.). Elution with benzene gave 4-methoxy-2′,4′-dinitrodiphenyl sulphide (III; R = p-MeO·C$_6$H$_4$) (120 mg., 80%), m. p. 115° (lit.,[1] m. p. 115°).

Irradiation with Chlorobenzene.—The sulphenyl acetate (I; R = Ac) (506 mg.) in chlorobenzene (100 ml.) was photolysed, with water cooling, for 1 hr. Chromatographic separation of the reaction mixture afforded, by benzene elution, 4′-chloro-2,4-dinitrodiphenyl sulphide (III; Ar = p-Cl·C$_6$H$_4$) (30 mg., 14%), m. p. 120—123° (from benzene).[3]

Irradiation with 1,4-*Dimethoxybenzene*.—The sulphenyl acetate (I; R = Ac) (500 mg.) and 1,4-dimethoxybenzene (267 mg.) in benzene (100 ml.) were photolysed for 20 min. to give, after isolation in the usual manner, 2,5-*dimethoxy*-2′,4′-*dinitrodiphenyl sulphide* (IV; R^1 = R^2 = OMe) (360 mg., 55%), m. p. 179—181° (from benzene–light petroleum), $\nu_{\text{max.}}$ 1530, 1370 (NO$_2$), and 1235 cm.$^{-1}$ (C–O); $\lambda_{\text{max.}}$ 208·5 (ε 35,600) 228 mμ (ε 24,000), 264 (shoulder, ε 10,100), mμ (ε 14,500); ^{1}H n.m.r. bands at τ 6·21 (3H, singlet), 6·28 (3H, singlet), and aromatic protons in the region 3·07 to 1·03 (6H) (Found: C, 50·0; H, 3·5; N, 8·5. $C_{14}H_{12}N_2O_6S$ requires C, 50·0; H, 3·6; N, 8·35%).

Photolysis with NN-*Dimethylaniline*.—The acetate (I; R = Ac) (512 mg.) and dimethylaniline (0·5 ml.) in benzene (150 ml.) were photolysed for 70 min. After washing the reaction mixture with N-hydrochloric acid (3 × 100 ml.) the organic layer was dried (MgSO$_4$), before filtering and evaporating to small bulk. The residue was chromatographed to give, with 1 : 1 benzene–light petroleum, red crystals of the sulphide (III; R = p-Me$_2$NC$_6$H$_4$) (170 mg., 27%). Crystallised from benzene these had m. p. 177° (lit.,[3] 175—176°); $\nu_{\text{max.}}$ 1520 and 1340 cm.$^{-1}$ (NO$_2$); ^{1}H n.m.r. bands at τ 7·02 (6H, singlet), and 3·4—1·00 (7H) (Found: N, 13·6; S, 10·1. Calc. for $C_{14}H_{13}N_3O_4S$: N, 13·25; S, 10·0%).

A thermal reaction of the sulphenyl chloride (III; R = Cl) (1·7 g.) with dimethylaniline (1·8 ml.) in benzene (20 ml.) under reflux, gave after 10 min. reaction and working up, the sulphide (III; Ar = p-Me$_2$NC$_6$H$_4$) (1·3 g., 56%), m. p. 177°.

2,4-*Dinitrophenyl* 2-(NN-*Dimethyl*)*amino*-5-*methylphenyl Sulphide* (IV; R^1 = Me$_2$·N, R^2 = Me).—*NN*-Dimethyl-p-toluidine (450 mg.) and the sulphenyl acetate (252 mg.) were irradiated in benzene (150 ml.) for 40 min. to give, after working up, the *sulphide* (84 mg., 23%). From benzene this formed red needles, m. p. 145—148°, $\nu_{\text{max.}}$ 1530 and 1345 cm.$^{-1}$ (NO$_2$); $\lambda_{\text{max.}}$ 210 (34,500), 246 (19,000), 266 (16,000), and 338 (14,200); ^{1}H n.m.r. bands at τ 7·27 (6H, singlet), 7·67 (3H, singlet), 2·72—2·67 (3H, multiplet) 3·06 (1H, doublet; J = 9·0 c./sec.), 1·92 (1H, quartet; J = 2·5, 9·0 c./sec.), 0·86 (1H, doublet; J = 2·5 c./sec.). The mass spectrum showed a parent ion at m/e 333 (Found: C, 54·1; H, 4·2; N, 12·3; S, 9·4. $C_{15}H_{15}N_3O_4S$ requires C, 54·05; H, 4·5; N, 12·6; S, 9·6%).

A thermal reaction between *NN*-dimethyl-p-toluidine (2 g.) and the sulphenyl chloride (III; R = Cl) (1·0 g.) in methylene dichloride (15 ml.) with aluminium chloride (1·0 g.) as catalyst gave, after 30 min. at reflux, the same sulphide (IV; R^1 = Me$_2$N, R^2 = Me) (1·16 g., 59%), m. p. 150°.

Irradiation with Naphthalene.—The sulphenyl acetate (I; R = Ac) (526 mg.) and naphthalene (272 mg.) in chlorobenzene (100 ml.) were irradiated for 15 min. Chromatography of the concentrated reaction product gave, after recrystallisation from benzene, pale yellow needles of 2,4-dinitrophenyl 1-naphthyl sulphide (III; R = 1-naphthyl) (272 mg., 41%), m. p. 174—176° (lit.,[3] m. p. 176°) (Found: C, 58·9; H, 3·2; N, 8·5; S, 9·5. Calc. for $C_{16}H_{10}N_2O_4S$: C, 58·9; H, 3·3; N, 8·8; S, 9·8%. The ^{1}H n.m.r. spectrum showed a broad aromatic proton region of τ 3·39—0·9 (all protons).

Irradiation with Phenanthrene.—The acetate (I; R = Ac) (257 mg.) and phenanthrene (188 mg.) in chlorobenzene (15 ml.) were irradiated for 10 min. After chromatography the yellow sulphide (III; R = 9-phenanthryl) was eluted (325 mg., 82%), m. p. 250° (from benzene) (lit.,[3] m. p. 251°). Its ^{1}H n.m.r. spectrum showed aromatic protons as a complex pattern at τ 3·21—0·82.

Irradiation with Anthracene.—In the usual manner anthracene (179 mg.) and the acetate (I; R = Ac) (257 mg.) were irradiated for 15 min. in chlorobenzene (15 ml.). After chromatography the reaction product yielded 2,4-*dinitrophenyl* 9-*anthryl sulphide* (III; R = 9-anthryl) (276 mg., 74%), m. p. 264° (from benzene), $\nu_{\text{max.}}$ 1595 (aromatic), 1525, and 1350 cm.$^{-1}$ (NO$_2$); $\lambda_{\text{max.}}$ 218 (37,600), 246 (sh) (100,000), 256 (158,400), 324 (14,700), 334 (15,500), 362 (15,500), and 374 (15,500); ^{1}H n.m.r. bands at τ 3·20—0·82 (Found: C, 63·9; H, 3·4; N, 7·15; S, 8·6. $C_{20}H_{12}N_2O_4S$ requires C, 63·8; H, 3·2; N, 7·15; S, 8·5%).

Irradiation with Furan.—The sulphenyl acetate (518 mg.) and furan (10 ml.) in benzene (100 ml.) were irradiated for 1 hr. After filtering and evaporating to small bulk the reaction product was chromatographed through alumina (25 g.), using benzene as solvent, to give pale yellow needles of the *sulphide* (III; R = 2-furyl) (109 mg., 28%), m. p. 110—114° (from benzene–light petroleum), $\nu_{\text{max.}}$ 1530, 1350 (NO$_2$), 1010, and 840 cm.$^{-1}$ (ether); $\lambda_{\text{max.}}$ 223 (ε 19,500) and 310 (ε 10,100); ^{1}H n.m.r. bands at τ 3·34 (1H, quartet; J = 2·0, 3·2 c./sec.), 3·04 (1H, doublet; J = 9·0 c./sec.), 2·98 (1H, quartet; J = 0·6, 3·2 c./sec.), 2·21 (1H, quartet; J = 0·6, 2·0 c./sec.), 1·75 (1H, quartet; J = 9·0, 2·5 c./sec.), and 0·90 (1H, doublet; J = 2·5 c./sec.) (Found: C, 45·3; H, 2·5; N, 10·4; S, 12·2. $C_{10}H_6N_2O_5S$ requires C, 45·15; H, 2·3; N, 10·5; S, 12·0%).

Irradiation with Thiophen.—The acetate (I; R = Ac) (502 mg.) and thiophen (9 ml.) in benzene (140 ml.) were irradiated for 45 min. The reaction mixture was worked up in the usual way to give, after chromatography, the sulphide (III; R = 2-thienyl) as a pale yellow solid (70 mg., 13%), m. p. 117—119° (from benzene) (lit.,[4] m. p. 119—120°), ^{1}H n.m.r. bands at τ 2·86 (1H, doublet; J = 9 c./sec.), 2·72 (1H, quartet; J = 3·5, 5 c./sec.), 2·52 (1H, quartet; J = 1·5, 3·5 c./sec.), 2·22 (1H, quartet; J = 1·5, 5 c./sec.), 1·75 (1H, quartet J = 2·5, 9 c./sec.), and 0·89 (1H, doublet; J = 2·5 c./sec.).

The same sulphide was also prepared by a normal Friedel–Crafts reaction between thiophen (5 ml.) and the sulphenyl chloride (III; R = Cl) (1·0 g.), with boron trifluoride etherate (0·6 ml.) as catalyst. After heating to a gentle reflux, with stirring under nitrogen for 90 min. the reaction mixture was concentrated under reduced pressure, and then chromatographed. Yellow crystals of the sulphide (III; R = 2-thienyl) formed (1·1 g., 91%), m. p. 117—119° undepressed on mixed m. p. with the photoproduct.

2-(2,4-*Dinitrobenzenesulphenyl*)-3-*methylindole*.—The sulphenyl acetate (509 mg.) and skatole (260 mg.) in benzene (100 ml.) were heated to reflux, in the dark, for 90 min. The mixture was evaporated to small bulk before chromatographing through alumina (grade III) to give the *sulphide* (III; R = 3-methylindolyl) (380 mg., 58%). M. p. 199—203° (from ethyl acetate–benzene), $\nu_{max.}$ 3450 (NH), 1535, and 1345 cm.$^{-1}$ (NO_2); $\lambda_{max.}$ 220 (ε 35,000), 279 (ε 13,800), 298 (ε 14,900), and 335 mμ (shoulder, ε 10,600); ^{1}H n.m.r. bands at τ 7·62 (3H, singlet) and 3·2—0·9 (7H) (Found: C, 54·7; H, 3·8; N, 12·8; S, 9·4. $C_{15}H_{11}N_3O_4S$ requires C, 54·7; H, 3·6; N, 12·8; S, 9·7%).

3-(2,4-*Dinitrobenzenesulphenyl*)*indole*.—Indole (116 mg.) and the sulphenyl acetate (I; R = Ac) (250 mg.) in benzene (100 ml.) were heated to reflux in the dark for 1 hr. The solvent was then evaporated off and the residue was chromatographed to give light yellow crystals of the sulphide (III; R = 3-indolyl) (253 mg., 80%), m. p. and mixed m. p. 175° (lit.,[5] m. p. 175°).

Irradiations with 2-*Nitrobenzenesulphenyl Acetate*.[13]—These were carried out in a similar manner to that described above for the 2,4-dinitro-series. (a) *In benzene*. 2-Nitrobenzenesulphenyl acetate (200 mg.) in benzene (100 ml.) was photolysed for 1 hr. The reaction was followed by thin-layer chromatography. No 2-nitrodiphenyl sulphide was detected by comparison with authentic material.[13] A large amount of a dark precipitate formed (120 mg.) which, from its infrared spectrum, was 2,2′-dinitrodiphenyl disulphide, m. p. 195—199°.[14]

(b) *In anisole*. 2-Nitrobenzenesulphenyl acetate (368 mg.) in anisole (20 ml.) was irradiated in the usual way for 10 min. Chromatographic separation of the products afforded, initially, 4-methoxy-2′-nitrodiphenyl sulphide (244 mg., 55%), m. p. and mixed m. p. 92—94° (lit.,[15] m. p. 94°). Further elution of the alumina column with benzene gave 2,2′-dinitrodiphenyl disulphide (80 mg., 30%).

Irradiation of 2,4-*Dinitrodiphenyl Disulphide* (VI).[16]—The disulphide (400 mg.) in benzene (100 ml.) was irradiated for 150 min. After filtration the reaction mixture was chromatographed on alumina (25 g.). Elution with light petroleum gave diphenyl disulphide (120 mg., 41%), m. p. 60—61°.[17] Further elution gave back starting disulphide (63 mg., 16%). The precipitate (195 mg.) was mainly 2,2′,4,4′-tetranitrodiphenyl disulphide, m. p. 189—193°. When this reaction was repeated, using anisole as solvent, essentially the same result as above was obtained except that, by thin-layer chromatography a very small amount of 4-methoxy-2′,4′-dinitrodiphenyl sulphide was detected.

Preparation and Photolysis of p-*Tolyl* 2,4-*Dinitrobenzenesulphenate* (I; R = p-MeC_6H_4).—A solution of 2,4-dinitrobenzenesulphenyl chloride (1·35 g.), *p*-cresol (4·7 g.), and pyridine (1 ml.) in dry methylene dichloride (50 ml.) was stirred whilst heating to a gentle reflux for 30 min. The reaction mixture was cooled and washed with N-hydrochloric acid (2 × 100 ml.) and finally water (6 × 100 ml.). The organic layer was dried (Na_2SO_4), filtered, and evaporated to give an oil. Addition of benzene (5 ml.) and ether (10 ml.) afforded yellow needles of the *ester* (1·38 g., 84%), m. p. 122° (from benzene–ethanol), $\nu_{max.}$ 1530 and 1350 cm.$^{-1}$ (NO_2); $\lambda_{max.}$ 211 (ε 28,500), 255 (ε 17,900), and 323 mμ (ε 13,100); ^{1}H n.m.r. bands at τ 7·71 (3H, singlet), 2·91 (4H, singlet), 2·17 (1H, doublet; J = 9 c./sec.), 1·60 (1H, quartet; J = 2·5, 9 c./sec.), and 0·90 (1H, doublet; J = 2·5 c./sec.) (Found: C, 50·7; H, 3·4; N, 9·0. $C_{13}H_{10}N_2O_5S$ requires C, 51·0; H, 3·3; N, 9·2%).

After irradiation of this ester (252 mg.) in benzene (100 ml.) for 30 min., the product was filtered and chromatographed. Elution with benzene–light petroleum gave back starting material (19 mg.) whilst benzene elution afforded an *amine* (1·7 mg.), m. p. 137—142°; $\nu_{max.}$ 3500, 3400 (NH_2), 1360, and 1180 cm.$^{-1}$ (SO_2). The mass spectrum of this compound showed a parent ion at *m/e* 308, as well as strong peaks at *m/e* 201 (loss of OC_6H_4Me) and 137 (loss of $SO_2OC_6H_4Me$) (Found: C, 51·1; H, 4·0; N, 8·9. $C_{13}H_{12}N_2O_5S$ requires C, 50·7; H, 3·9; N, 9·1%). This compound has been assigned the structure of the *amine* (VII; R = *p*-MeC_6H_4O).

Further elution of the chromatography column, with 1 : 1 benzene–acetone gave the *imine* (IX; R = Me) (57 mg., 23%), m. p. 285—289° (from benzene–light petroleum), $\nu_{max.}$ 3375 (NH), 1540, 1350 (NO_2), 1365, and 1175 cm.$^{-1}$ (SO_2); $\lambda_{max.}$ 208 (ε 18,800), 288 (ε 22,000), and 400 (ε 1150). The mass spectrum had a parent ion at *m/e* 306 as well as peaks at *m/e* 242 (loss of SO_2) and 196 (loss of SO_2 and NO_2). It had ^{1}H n.m.r. bands at τ 4·9 (1H), and 7·39 (3H) (in pyridine) (Found: C, 51·0; H, 3·3; N, 8·9. $C_{13}H_{10}N_2O_5S$ requires C, 51·0; H, 3·3; N, 9·15%).

When a freshly irradiated solution of the tolyl ester was filtered, evaporated, and chromatographed on alumina with chloroform elution a complex phenolic fraction was obtained. The infrared spectrum of this fraction showed a weak band at 1660 cm.$^{-1}$, similar to that of Pummerer's ketone (VIII). This compound was also detected, but not isolated, by comparison with an authentic sample on thin-layer chromatography. The main constituent of the phenolic fraction was *p*-cresol, shown by thin-layer chromatography, and by its infrared and ultraviolet absorption patterns.

Irradiation of Phenyl 2,4-*Dinitrobenzenesulphenate* (I; R = Ph).[18]—The ester (241 mg.) in benzene (100 ml.) was

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[15] R. H. B. Galt and J. D. Loudon, *J. Chem. Soc.*, 1959, 885.

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irradiated as above for 30 min. Isolation, by the procedure used for the tolyl ester, gave the *sulphonate* (IX; R = H) (48 mg., 20%), m. p. 129°, $\nu_{max.}$ 3375 (N–H), 1370, and 1170 cm.$^{-1}$ (SO_2) (Found: C, 49·4; H, 2·9; N, 9·6. $C_{12}H_8N_2O_5S$ requires C, 49·3; H, 2·8; N, 9·4%). Similarly, the corresponding *amine* (VII; R = OPh) was also obtained (20 mg., 8%), m. p. 119—122°; $\nu_{max.}$ 3500, 3400 (NH_2), and 1370, 1170 cm.$^{-1}$ (SO_2); $\lambda_{max.}$ 202 (29,400), 236 (35,600), and 378 mμ (3900) (Found: C, 49·4; H, 3·8; N, 9·5; S, 10·9. $C_{12}H_{10}N_2O_5S$ requires C, 49·1; H, 3·4; N, 9·5; S, 10·9%).

A repeated photolysis of the ester (I; R = Ph) (400 mg.) was carried out. Examination of the precipitate (276 mg.) showed it was mainly 2,2′,4,4′-tetranitrodiphenyl disulphide. Evaporation of the mother-liquor gave a red gum which had a strong phenolic odour and which showed a broad absorption at 3350 cm.$^{-1}$. Neither the phenyl sulphide (III; R = Ph) nor 2,4-dinitrophenyl 4-hydroxyphenyl sulphide could be detected amongst the reaction products by thin-layer chromatography.

Finally, photolysis of the ester (292 mg.) with diphenyl disulphide (439 mg.) in benzene for 20 min. gave, after chromatography, diphenyl disulphide (395 mg.), followed by 2,4-dinitrodiphenyl disulphide (22mg.), m. p. and mixed m. p. 83—85°. No exchange took place in a control dark reaction.

Irradiation of the Benzyl Ester (I; R = $PhCH_2$).—The benzyl ester (453 mg.) in benzene (100 ml.) was irradiated in the usual way for 12 hr. Filtration removed the dark precipitate (267 mg.). Chromatography through alumina (25 g.), using light petroleum as eluant, gave diphenylmethane (138 mg., 56%), identical in its mass spectrum and ^1H n.m.r. spectrum to authentic material. Examination of the precipitate showed it to be mainly 2-amino-4-nitrobenzenesulphonic acid (VII; R = OH).

With anisole as solvent the benzene ester (502 mg.) gave a mixture of 2- and 4-methoxydiphenylmethane (280 mg., 93%). A quantitative analysis of this mixture, using a Pye-Argon gas-liquid chromatography on 10% Apiezon M, showed this to be in the ratio 23 : 77, respectively.

Photolysis of 2,4-*Dinitrodiphenyl Sulphide*.—The sulphide (300 mg.) in benzene (100 ml.) was photolysed as usual for 48 hr. Chromatography gave, with light petroleum–benzene elution, starting material (227 mg., 72%). Further elution gave a small quantity of a yellow crystalline solid (3 mg.) which showed $\nu_{max.}$ (chloroform) 3420 cm.$^{-1}$ (NH), and in its mass spectrum a parent ion at *m/e* 276, as required for 2-nitrophenothiazine-5,5-dioxide (X). That the sulphonyl group was present was also indicated by smooth loss of 110 mass units (loss of NO_2 and SO_2) to give a strong peak at *m/e* 166.

Preparation and Photolysis of 2,4-*Dinitrobenzenesulphenyl*-N-*methylanilide* (III; Ar = MeNPh).—A mixture of 2,4-dinitrobenzenesulphenyl chloride (308 mg.) and *N*-methylaniline (300 mg.) in benzene (50 ml.) was shaken at room temperature for 1 hr. The solution was filtered and the filtrate was evaporated to small bulk to give, eventually, orange prisms of the *anilide* (400 mg.), m. p. 92—96° (from benzene); $\nu_{max.}$ 1525 and 1345 (NO_2) cm.$^{-1}$; $\lambda_{max.}$ 206 (ε 36,100), 244 (ε 24,000), and 326 mμ (ε 10,600); ^1H n.m.r. bands at τ 6·5 (3H, singlet), and 3·1—1·6 (8H) (Found: S, 9·9. $C_{13}H_{11}N_3O_4S$ requires S, 9·8%).

A solution of the *N*-methylanilide (626 mg.) in benzene (150 ml.) was irradiated in the usual manner for 45 min. Chromatographic separation of the products afforded, as the major component, 2-*amino*-4-*nitrobenzenesulphonyl*-N-*methylanilide* (VII; R = MeNPh) (82 mg.) as an orange solid, m. p. 146° (from ethanol), $\nu_{max.}$ 3680, 3380 (NH_2), 1340, 1150 (SO_2), 1540, and 1350 cm.$^{-1}$ (NO_2); $\lambda_{max.}$ 205 (ε 29,100), 237 (ε 28,300), and 380 mμ (ε 3300); ^1H n.m.r. bands at τ 6·7 (3H, singlet), 4·80 (2H, broad singlet), and 3·30—2·70 (8H). The mass spectrum showed a parent ion at *m/e* 307 and a strong peak at 139 (loss of $SO_2N(Me)Ph$) (Found: C, 51·1; H, 4·4; N, 13·6; S, 10·6. $C_{13}H_{13}N_3O_4S$ requires C, 50·8; H, 4·3; N, 13·7; S, 10·4%).

Preparation and Photolysis of 2,4-*Dinitrobenzenesulphenyl*-N-*methyl*-p-*toluidide*.—In a similar manner to the above, 2,4-dinitrobenzenesulphenyl chloride (1·17 g.) and *N*-methyl-*p*-toluidine (1·21 g.) gave the corresponding N-*methyl*-p-*toluidide* (1·56 g.), m. p. 150—152° (from benzene) $\nu_{max.}$ 1530 and 1350 (NO_2) cm.$^{-1}$; $\lambda_{max.}$ 206 (ε 36,100), 245 (ε 25,500), and 313 mμ (ε 10,900); and ^1H n.m.r. bands at τ 7·7 (3H, singlet), 6·50 (3H, singlet), 2·92 (4H, singlet), 2·49 (1H, doublet; *J* = 9 c./sec.), 1·68 (1H, quartet; *J* = 2·5, 9 c./sec.), and 0·85 (1H, doublet; *J* = 2·5 c./sec.) (Found: C, 52·8; H, 4·2; N, 13·3; S, 10·2. $C_{14}H_{13}N_3O_4S$ requires C, 52·7; H, 4·1; N, 13·2; S, 10·0%).

Irradiation of the anilide (500 mg.) for 3 hr. in benzene (100 ml.) gave, as the major product, 2-*amino*-4-*nitrobenzenesulphonyl* N-*methyl*-p-*toluidide* (VII; R = *p*-$MeNC_6H_4Me$) (13%), m. p. 167—170°, $\nu_{max.}$ 3500, 3400 (NH_2), 1540, 1355 (NO_2), 1360, and 1170 (SO_2) cm.$^{-1}$; $\lambda_{max.}$ 207 (ε 22,300), 236 (ε 24,500), and 375 mμ (ε 2850); ^1H n.m.r. bands at τ 7·66 (3H), 6·70 (3H), 4·81 (2H, broad singlet), and a multiplet about 2·5 (7H) (Found: C, 52·3; H, 4·8; N, 13·0. $C_{14}H_{15}N_3O_4S$ requires C, 52·2; H, 4·7; N, 13·1%).

Photolysis of 2,4-*Dinitrobenzenesulphenylanilide* (III; R = NHPh).[19]—The anilide (500 mg.) in benzene (100 ml.) was irradiated in the usual manner for 1 hr. The reaction mixture was evaporated to small bulk and filtered through alumina. Elution with 1 : 1 benzene–light petroleum gave azobenzene (55 mg., 34%) as mixture of *cis*- and *trans*-isomers. The *trans*-isomer isolated by preparative layer chromatography, had m. p. 65—68°. A mixed m. p. with an authentic sample was undepressed; $\nu_{max.}$ 1496, 1070, 782, and 700 cm.$^{-1}$; $\lambda_{max.}$ 316 mμ (ε 20,000).

Hydrolysis of 2-*Amino*-4-*nitrobenzenesulphonyl*-N-*methylanilide* (VII; R = MeNPh.—The sulphanilide (10 mg.) was dissolved in 80% sulphuric acid (0·5 ml.) and was heated to 165° for 5 min. The solution was cooled to room temperature and the solution was poured into water (1 ml.). The solid precipitate was filtered off and the filtrate was neutralised with sodium hydroxide to pH 7. A few drops of a 15% (w/v) aqueous solution of *S*-benzylisothiouronium chloride were added to give a crystalline precipitate. This was collected by centrifugation before drying. The precipitate (6·7 mg.) had m. p. 95—96°. A mixed m. p. with an authentic sample of the *S*-benzylisothiouronium salt of 2-amino-4-nitrobenzene sulphonic acid (VII; R = OH) was undepressed and the two samples had superimposable infrared spectra.

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