408. *Reactions of Polynitro-aromatic Compounds with Alkaline Sulphides. Part I. Aryl Monosulphide Formation by Interaction of Sodium Thioaryloxides with Polynitro-aromatic Compounds containing Labile Nitro-groups.*

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From a study of twenty-three reactions between nitro-thioaryloxides and polynitro-derivatives of benzene, toluene, and naphthalene, it is concluded that aromatic monosulphides are formed *via* the process :

$$R(NO_2)_{x-1}\cdot SNa + R(NO_2)_x = [R(NO_2)_{x-1}]_2S + NaNO_2$$

Only polynitro-compounds with labile nitro-groups react, and, in a few cases involving *p*-dinitro-compounds, the reaction is more complex; *e.g.* a 40% yield of *pp'*-dinitroazobenzene has been obtained from the interaction of *p*-dinitrobenzene with sodium *p*-nitrothiophenoxide, in addition to what is apparently a mixture of monosulphides.

It is tentatively suggested that two distinct reactions are involved in the interactions of polynitro-aromatic compounds with alkaline sulphides, *viz.*, (1) whole or partial reduction of a nitro-group (or groups), and (2) replacement of a nitro-group (or groups) by a sulphur-containing radical, *e.g.* –SNa with sodium sulphides. Aromatic monosulphides then arise by the further reaction cited above. The relative extent of each reaction appears to be largely determined by the positivity of the carbon atom to which the reactive nitro-group is attached.

THE great variety of products which arise during the reduction of nitro-aromatic compounds by alkaline sulphides includes those formed by whole or part reduction of the nitro-group(s), and those formed by replacement of the nitro-group(s) by the anionoid sulphide reagent such as thiols and mono- and di-sulphides; *e.g.*, *o*-dinitrobenzene can give *o*-nitroaniline, *o*-nitrothiophenol, and 2 : 2'-dinitrodiphenyl mono- and di-sulphides [the production of polysulphides (Blanksma, *Rec. Trav. chim.*, 1901, **20**, 144) is regarded by the present authors as doubtful]. 2 : 3 : 5-Trinitro-1 : 4-dimethylbenzene gives 5-nitro-3-amino-1 : 4-dimethylbenzene-2-sulphonic acid with either sodium sulphide or sodium hydrogen sulphide in ethanol (Blanksma, *ibid.*, 1905, **24**, 49).

Reduction of nitro-groups and also their replacement by anionoid reagents are facilitated by the presence of kationoid substituents, particularly when in *op*-positions (Cohen and McCandlish, *J.*, 1905, **87**, 1257; Loudon and Shulman, *J.*, 1941, 722). Hence the positivity of the carbon atom to which the reacting nitro-group is attached is a determining factor of the reactivity, *viz.*, with increase of positivity replacement by –SNa (or other sulphur-containing radicals as in disulphide formation) progressively competes with reduction until it becomes exclusive.

Accumulating experimental evidence (Hodgson and Ward, unpublished work) indicates that monosulphides arise generally *via* a two-stage mechanism, *viz.*, (1) formation of thioaryl oxide and (2) its reaction with unchanged nitro-compound. Since previous work on such reactions between thioaryloxides and nitro-compounds has been almost confined to the anthraquinone series (D.R-PP. 116,951, 224,589, 254,561; cf. also Decker and Würsch, *Annalen*, 1906, **348**, 239; Gattermann, *Annalen*, 1912, **393**, 113) with a few isolated examples in the benzene series, it was thought desirable to investigate reactions of this type with a variety of benzene and naphthalene compounds.

In the present paper, the second stage of this mechanism has been demonstrated for reactions between *o*- and *p*-dinitrobenzene, 3 : 4-dinitrotoluene, 3 : 4 : 5-trinitrotoluene, 1 : 2- and 1 : 4-dinitronaphthalenes, and 1 : 4 : 5-trinitronaphthalene with sodium *o*- and *p*-nitro-, 2 : 4-dinitro-, and 2-nitro-4-methyl-thiophenoxide and 2- and 4-nitro- and 2 : 4-dinitro-1-thionaphthoxide. The reaction occurs only with compounds which possess labile nitro-groups.

Whereas no precise quantitative measurements were made, it appeared that sodium 2-nitro-4-methylthiophenoxide was the most reactive reagent, and that sodium *p*-nitro- was more reactive than sodium *o*-nitro-thiophenoxide, though both were more reactive than the corresponding 2 : 4-dinitro-compound. Similarly sodium 2- and 4-nitro-1-thionaphthoxides were more reactive than 2 : 4-dinitro-1-thionaphthoxide, which appears to be the least reactive of all the reagents tried. The above data are in accord with the work of Evans and Smiles (*J.*, 1935, 181), who pointed out that the negative character of the thiol group was weakened by nitro-groups in *op*-positions. Sodium *o*-aminothiophenoxide gave unsatisfactory results in preliminary trials and was not further investigated. The following did not react: nitrobenzene and 1 : 8-dinitronaphthalene with sodium *p*-nitrothiophenoxide, *m*-dinitrobenzene and 1 : 3 : 5-trinitrobenzene with sodium 4-nitro-1-thionaphthoxide, and 1-nitronaphthalene, 1 : 5-dinitronaphthalene, and 2 : 6-dinitronaphthalene with sodium *o*-nitrothiophenoxide. Whilst the reaction between sodium 4-nitro-1-thionaphthoxide and *p*-dinitrobenzene afforded the expected 4-nitrophenyl 4-nitro-1-naphthyl sulphide, the corresponding reaction between sodium *p*-nitrothiophenoxide and 1 : 4-dinitronaphthalene gave a pure dinitrophenyl naphthyl sulphide which has not yet been identified but differs from the above, and also from 4-nitrophenyl 1-nitro-2-naphthyl sulphide which was a possible reaction product (Hodgson and Leigh, *J.*, 1938, 1031).

The following reactions involving *p*-dinitrobenzene were complex *viz.*, with sodium *o*-nitro- and *p*-nitro-thiophenoxides, and with 2-nitro-1-thionaphthoxide. The product obtained with sodium *o*-nitrothiophenoxide appears to be a mixture of difficultly separable monosulphides, possibly 2 : 4′-dinitro- and 2 : 2′-dinitro-diphenyl sulphides; the latter would be an anomalous result (cf. Hodgson and Leigh, *loc. cit.*). Sodium *p*-nitrothiophenoxide gave a similar mixed product but in addition *ca.* 40% of *pp*′-dinitroazobenzene was obtained, which must have been due to the reduction of *p*-dinitrobenzene by the thiophenoxide although no oxidation products of the latter were isolated (cf. Gattermann, *loc. cit.*, who reported that thio-alkyl and -benzyl-oxides in reaction with nitro-derivatives of anthraquinone were oxidised to disulphides with reduction of the nitro- to the amino-group; cf. also Richardson, *J.*, 1926, 522; Loudon and Holmes, *J.*, 1940, 1521; Simons and Ratner, *J.*, 1944, 421). From sodium 2-nitro-1-thionaphthoxide only a very small amount of a complex dark-coloured product could be isolated.

It would appear that dinitro- and trinitro-aromatic compounds are much more reactive towards sodium thioaryloxides than the corresponding chloronitro- or chlorodinitro-compounds. The reactions involving 3 : 4 : 5-trinitrotoluene and 1 : 4 : 5-trinitronaphthalene were completed almost as soon as the reactants were mixed, while 1 : 2- and 1 : 4-dinitronaphthalenes appear to be more reactive than *o*- and *p*-dinitrobenzenes; 3 : 4-dinitrotoluene is the least reactive as would be expected from the neutralising effect of the electron-repelling methyl on the electron-attracting nitro-group, which then has a diminished effect on the neighbouring 3-nitro-group. *o*-Dinitrobenzene is less reactive than *p*-dinitrobenzene, and in this respect resembles the lower reactivity of *o*-chloronitro- compared with *p*-chloronitro-benzene (cf. Hodgson and Wilson, *J.*, 1925, **127**, 440).

3 : 4 : 5-Trinitrotoluene by reaction with a large excess of sodium *p*-nitrothiophenoxide gave the same product and yield as when equimolecular quantities were used, so that the other nitro-groups were rendered inactive by the replacement of the 3-nitro-group on monosulphide formation.

The monosulphides arising from the interaction of thioaryloxides and nitro-aromatic compounds were identified where possible with authentic specimens of known compounds, or with specimens prepared by interaction of the thioaryloxide with the corresponding chloronitro-aromatic compounds. The following new monosulphides were prepared in this way: 2 : 4-*dinitrophenyl* 4-*nitro*-1-*naphthyl* (from sodium 4-nitro-1-thionaphthoxide and 1-chloro-2 : 4-dinitrobenzene); 2- and 4-*nitrophenyl* 2 : 4-*dinitro*-1-*naphthyl* and 2 : 4 : 4′-*trinitro*-1 : 1′-*dinaphthyl* (from sodium *o*- and *p*-nitrothiophenoxide and 4-nitro-1-thionaphthoxide with

1-chloro-2 : 4-dinitronaphthalene); 2 : 6 : 2′-*trinitro*-4-*methyldiphenyl* (from sodium *p*-nitrothiophenoxide and 4-chloro-3 : 5-dinitrotoluene) and 4-*nitrophenyl* 4 : 5-*dinitro*-1-*naphthyl sulphide* (from sodium *p*-nitrophenoxide and 1-bromo-4 : 5-dinitronaphthalene).

The product from sodium *o*-nitrothiophenoxide and 3 : 4-dinitrotoluene was not identical with 2 : 2′-dinitro-4-methyldiphenyl sulphide (from sodium 2-nitro-4-methylthiophenoxide and *o*-dinitrobenzene) and hence must be 2 : 6′-*dinitro*-3′-*methyldiphenyl sulphide.* Similarly that from sodium 2-nitro-4-methylthiophenoxide and 3 : 4-dinitrotoluene must be 2 : 6′-*dinitro*-4 : 3′-*dimethyldiphenyl sulphide*, the 3-nitro-group being labile as above. The product from sodium *p*-nitrothiophenoxide and 3 : 4 : 5-trinitrotoluene was not identical with that obtained from 4-chloro-3 : 5-dinitrotoluene and the same thioaryloxide, and hence must be 2 : 3 : 4′-*trinitro*-5-*methyldiphenyl sulphide.* The product from sodium *p*-nitrothiophenoxide and 1 : 4 : 5-trinitronaphthalene was not identical with 4-nitrophenyl 4 : 5-dinitro-1-naphthyl sulphide (from sodium *p*-nitrothiophenoxide and 1-bromo-4 : 5-dinitronaphthalene) and hence must be 4-nitrophenyl 4 : 8-dinitro-1-naphthyl sulphide.

The work of Zincke and Röse (*Annalen*, 1914, **406**, 108) on the interaction of sodium disulphide with 4-chloro-3-nitrotoluene has been repeated and confirmed; similarly that of Talen (*Rec. Trav. chim.*, 1928, **47**, 782) on the interaction of sodium mono- and di-sulphides with 1-chloro-2 : 4-dinitronaphthalene. Sodium 2-nitro-4-methylthiophenoxide and 2 : 4-dinitro-1-thionaphthoxide have been prepared by reduction of the corresponding disulphides.

1-Chloro-2 : 4-dinitronaphthalene can be satisfactorily prepared directly from 2 : 4-dinitrotoluene-*p*-sulphon-1-naphthalide, utilising the combined hydrolysis-diazotisation procedure of Hodgson and Birtwell (*J.*, 1943, 433), and carrying out the Sandmeyer reaction with the solution obtained in this manner.

EXPERIMENTAL.

(M. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.)

Preparation of Initial Materials.—1-*Chloro*-2 : 4-*dinitronaphthalene.* This was prepared directly in 65% yield from 2 : 4-dinitrotoluene-*p*-sulphon-1-naphthalide by combined hydrolysis, diazotisation, and Sandmeyer reaction (cf. Hodgson and Walker, *J.*, 1933, 1620; Hodgson and Birtwell, *loc. cit.*)

Sodium thioaryloxides. The corresponding aryl disulphide was reduced either in aqueous alcohol with sodium monosulphide–sodium hydroxide, or in ethanol with glucose–sodium hydroxide; after reduction the solution was diluted and the thiol precipitated with hydrochloric acid, filtered off, washed with water, and redissolved in hot ethanol containing *ca.* 1·5 equivs. of sodium hydroxide.

2 : 2′-*Dinitro*-4 : 4′-*dimethyl*-1 : 1′-*diphenyl disulphide.* A solution of 4-chloro-3-nitrotoluene (5 g.) in ethanol (20 c.c.) was refluxed for 90 minutes with one of crystallised sodium sulphide (3·5 g.) and sulphur (0·45 g.) in ethanol (10 c.c.) and water (5 c.c.); the initial intense red colour had then almost disappeared; the mixture was then cooled and the yellow crystalline disulphide (1·8 g.) removed, washed with cold ethanol and water, and dried; m. p. 176°, which was unchanged after one crystallisation from glacial acetic acid (Zincke and Röse, *Annalen*, 1914, **406**, 108, give m. p. 176°).

2-*Nitro*-4-*methylphenylthiol.* A suspension of the above disulphide (1 g.) in boiling ethanol (20 c.c.) and water (5 c.c.) containing glucose (0·55 g.) and sodium hydroxide (0·4 g.) was refluxed for 10 minutes; the mixture was then diluted with water (5 vols.) and the thiol precipitated by addition of hydrochloric acid and then removed, washed with water, and redissolved in ethanol (25 c.c.) and water (5 c.c.) containing sodium hydroxide (0·2 g.).

2 : 4 : 2′ : 4′-*Tetranitro*-1 : 1′-*dinaphthyl mono- and di-sulphides.* (*a*) A solution of 1-chloro-2 : 4-dinitronaphthalene (2 g.) in acetone (80 c.c.) was treated gradually with a hot solution of sodium sulphide (1 g.) in ethanol (10 c.c.) and water (2 c.c.); the initial red colour, which tended to disappear in a few seconds, became permanent when all the sulphide had been added, and the pure 2 : 4 : 2′ : 4′-tetranitro-1 : 1′-dinaphthyl sulphide (1·4 g.; 75% yield) separated. This, when crystallised from glacial acetic acid, had m. p. 283—284° (Talen, *loc. cit.*, gives m. p. 283°). The filtrate on oxidation with potassium ferricyanide afforded 2 : 4 : 2′ : 4′-tetranitro-1 : 1′-dinaphthyl disulphide (0·35 g.; *ca.* 20% yield).

(*b*) When the chlorodinitronaphthalene [see (*a*) above] (2 g.) was treated with a hot solution of sodium sulphide (0·95 g.) and sulphur (0·15 g.) (corresponding to 0·5 mol. sodium disulphide) in ethanol (10 c.c.) and water (4 c.c.), a precipitate of monosulphide (1·6 g.; m. p. 275—280°) resulted; the disulphide (0·35 g.) was obtained by oxidation of the filtrate as under (*a*).

(*c*) When 1 mol. of sodium sulphide was used, the reaction product remained in solution, and on oxidation with potassium ferricyanide, afforded the disulphide (1·95 g.; *ca.* 100% yield), which when recrystallised from glacial acetic acid had m. p. 216—220° (decomp.) [Talen, *loc. cit.*, gives 230° (decomp.)].

Preparation of Aryl Monosulphides by the Reaction of Sodium Thioaryloxides with Halogenonitroaromatic Compounds.—*General procedure.* A solution of the halogeno-compound (*ca.* 30—50% excess) in hot ethanol was treated with a hot solution of the thioaryloxide in aqueous ethanol; in some cases reaction was immediate and the monosulphide separated from the hot solution, but otherwise the separation only occurred after refluxing the mixture, and an indication of the completion of the reaction was then given by the depth of colour of the solution. The monosulphide was removed, washed with water and ethanol, dried, and crystallised from a suitable solvent (usually aqueous or glacial acetic acid).

2 : 4′-*Dinitrodiphenyl sulphide.* *p*-Chloronitrobenzene (2·5 g.) in ethanol (20 c.c.) and sodium *o*-nitrothiophenoxide (*ca.* 2·3 g.) were heated together under reflux for 4 hours (yield 1·8 g.). When crystallised from glacial acetic acid the sulphide had m. p. 162°, and mixed melt with the product from the interaction of *o*-dinitrobenzene with sodium *p*-nitrothiophenoxide, 163—164° (Evans and Smiles, *J.*, 1935, 185,

TABLE OF RESULTS.

No.	Thioaryloxide.	Polynitro-aromatic compound.	Reaction period (mins.).	Yield (%). Crude.	Yield (%). Pure.	Product.	Remarks.
1	*o*-Nitrothiophenoxide	*o*-Dinitrobenzene	45	—	56	2 : 2-Dinitrodiphenyl sulphide, m. p. 122° (ethanol).	—
2	*o*-Nitrothiophenoxide	3 : 4-Dinitrotoluene	45	—	—	2 : 6′-*Dinitro*-3′-*methyldiphenyl sulphide*, m.p. 98° (50% aqueous acetic acid) (Found : S, 10·67. $C_{13}H_{10}O_4N_2S$ requires S, 11·07%).	Product separates as an oil, readily soluble in hot ethanol.
3	*o*-Nitrothiophenoxide	1 : 2-Dinitronaphthalene	30	71	—	2-Nitrophenyl 2-nitro-1-naphthyl sulphide m. p. 195—197° (glacial acetic acid) (Hodgson and Leigh, *J.*, 1938, 1031, give 196—197°).	—
4	*o*-Nitrothiophenoxide	1 : 4-Dinitronaphthalene	30	69	—	2-Nitrophenyl 4-nitro-1-naphthyl sulphide m. p. 159—160° (glacial acetic acid) (*idem, ibid.*, give 157—158°).	—
5	*p*-Nitrothiophenoxide	*o*-Dinitrobenzene	30	—	73	2 : 4′-Dinitrophenyl sulphide (glacial acetic acid), m. p. 163—164°.	
6	*p*-Nitrothiophenoxide	3 : 4 : 5-Trinitrotoluene	10	—	95	2 : 3 : 4′-*Trinitro*-5-*methyldiphenyl sulphide*, m. p. 155—156° (alcohol) (Found : S, 9·22. $C_{13}H_9O_6N_3S$ requires S, 9·5%).	Cream-coloured needles.
7	*p*-Nitrothiophenoxide	1 : 2-Dinitronaphthalene	30	79	—	4-Nitrophenyl 2-nitro-1-naphthyl sulphide, m. p. 121—122° (50% aqueous acetic acid) (Hodgson and Leigh, *J.*, 1938, 1031, give 121—122°).	—
8	*p*-Nitrothiophenoxide	1 : 4 : 5-Trinitronaphthalene	10	—	—	4-*Nitrophenyl* 4 : 8-*dinitro*-1-*naphthyl sulphide* (glacial acetic acid), m. p. 216—217° (Found : S, 8·9. $C_{16}H_9O_6N_3S$ requires S, 8·6%).	Sand-coloured parallelepipeds.
9	2-Nitro-4-methylthiophenoxide	*o*-Dinitrobenzene	5	—	80	2 : 2′-*Dinitro*-4-*methyldiphenyl sulphide*, m. p. 127—128° (50% aqueous acetic acid) Found : S, 11·1. $C_{13}H_{10}O_4N_2S$ requires S, 11·1%).	Lemon-yellow needles.
10	2-Nitro-4-methylthiophenoxide	3 : 4-Dinitrotoluene	90	—	75	2 : 6′-*Dinitro*-4 : 3′-*dimethyldiphenyl sulphide*, m. p. 131—132° (50% aqueous acetic acid) (Found : S, 10·35. $C_{14}H_{12}O_4N_2S$ requires S, 10·56%).	Pale yellow elongated plates.
11	2 : 4-Dinitrothiophenoxide	*o*-Dinitrobenzene	90	—	20	2 : 4 : 2′-Trinitrodiphenyl sulphide, m. p. 107° (50% aqueous acetic acid).	—
12	2 : 4-Dinitrothiophenoxide	*p*-Dinitrobenzene	90	—	30	2 : 4 : 4′-Trinitrodiphenyl sulphide, m. p. 168° (50% aqueous acetic acid).	—

13	2 : 4-Dinitrothiophenoxide	1 : 4-Dinitronaphthalene	90	—	45	2 : 4-Dinitrophenyl 4-nitro-1-naphthyl sulphide, m. p. 185—190° (75% aqueous acetic acid).	—
14	2-Nitro-1-thionaphthoxide	*o*-Dinitrobenzene	30	—	63	2-Nitrophenyl 2-nitro-1-naphthyl sulphide, m. p. 193—196° (glacial acetic acid) (Hodgson and Leigh, *J.*, 1938, 1031 give 196—197°).	— —
15	2-Nitro-1-thionaphthoxide	1 : 2-Dinitronaphthalene	30	50	—	2 : 2′-Dinitro-1 : 1′-dinaphthyl sulphide, m. p. 204° (glacial acetic acid) (Hodgson and Leigh, *J.*, 1937, 1352, give 204—205°).	—
16	2-Nitro-1-thionaphthoxide	1 : 4-Dinitronaphthalene	30	41	—	2 : 4′-Dinitro-1 : 1′-dinaphthyl sulphide, m. p. 162—163° (glacial acetic acid) (Hodgson and Leigh, *J.*, 1937, 1352, give 162—163°).	—
17	4-Nitro-1-thionaphthoxide	*o*-Dinitrobenzene	30	54	—	2-Nitrophenyl 4-nitro-1-naphthyl sulphide, m. p. 157—158° (glacial acetic acid) (Hodgson and Leigh, *J.*, 1938, 1031, give 157—158°).	—
18	4-Nitro-1-thionaphthoxide	*p*-Dinitrobenzene	30	36	—	4-Nitrophenyl 4-nitro-1-naphthyl sulphide, m. p. 232—236° (glacial acetic acid) (Hodgson and Leigh, *J.*, 1938, 1031, give 236—238°).	—
19	4-Nitro-1-thionaphthoxide	1 : 2-Dinitronaphthalene	30	—	55	2 : 4′-Dinitro-1 : 1′-dinaphthyl sulphide, m. p. 163—164° (glacial acetic acid, twice) (Hodgson and Leigh, *J.*, 1938, 1032, give 162—163°).	
20	4-Nitro-1-thionaphthoxide	1 : 4-Dinitronaphthalene	30	64	—	4 : 4′-Dinitro-1 : 1′-dinaphthyl sulphide, m. p. 237—240° (glacial acetic acid) (Hodgson and Leigh, *J.*, 1937, 1352, give 239—240°).	—
21	2 : 4-Dinitrothionaphthoxide	*o*-Dinitrobenzene	90	—	Very small	2-Nitrophenyl 2 : 4-dinitro-1-naphthyl sulphide, m. p. 220—228° (glacial acetic acid).	—
22	2 : 4-Dinitrothionaphthoxide	*p*-Dinitrobenzene	90	*ca.* 5	—	4-Nitrophenyl 2 : 4-dinitro-1-naphthyl sulphide, m. p. 180—200°.	Product somewhat impure even after two crystallisations.
23	2 : 4-Dinitrothionaphthoxide	1 : 4-Dinitronaphthalene	180	*ca.* 10	—	2 : 4 : 4′-Trinitro-1 : 1′-dinaphthyl sulphide, m.p. 208—210° (glacial acetic acid) (Found: S, 7·7. $C_{20}H_{11}O_6N_3S$ requires S, 7·63%).	—

give m. p. 158—159°) (Found : S, 11·72. Calc. for $C_{12}H_8O_4N_2S$: S, 11·6%). In contrast, the reaction between *o*-chloronitrobenzene and sodium *p*-nitrothiophenoxide was much slower than the above; 45% of unchanged *o*-chloronitrobenzene was recovered by steam distillation after 6 hours' heating under reflux, and the reaction product itself was difficult to purify (Found : S, 10·95%).

2 : 4 : 4'-*Trinitrodiphenyl sulphide.* This compound was prepared from 1-chloro-2 : 4-dinitrobenzene (5 g.), ethanol (50 c.c.), and sodium *p*-nitrothiophenoxide (2·5 g.). The reaction was immediate, and the yield of monosulphide almost quantitative; it separated from 80% aqueous acetic acid in lemon-yellow plates, m. p. 164° and mixed m. p. 165° with the same product from the reaction of *p*-dinitrobenzene with sodium 2 : 4-dinitrothiophenoxide (Blanksma, *Rec. Trav. chim.*, 1901, **20**, 405, gives m. p. 155°) (Found : S, 10·1. Calc. for $C_{12}H_7O_6N_3S$: S, 10·0%).

2 : 4 : 2'-*Trinitrodiphenyl sulphide.* When this compound was prepared from sodium *o*-nitrothiophenoxide, 2 hours' heating under the reflux was required for the completion of the reaction. The yield was almost quantitative. The sulphide was crystallised from 80% aqueous acetic acid from which it separated in lemon-yellow plates, m. p. 116° which could not be raised by further crystallisation (Blanksma, *loc. cit.*, gives m. p. 131°) (Found : S, 9·62. Calc. for $C_{12}H_7O_6N_3S$: S, 10·0%).

2 : 4-*Dinitrophenyl* 4-*nitro*-1-*naphthyl sulphide.* This separated at once when 1-chloro-2 : 4-dinitrobenzene reacted with sodium 4-nitro-1-thionaphthoxide. The *sulphide* crystallised from 80% aqueous acetic acid in cream micro-needles, m. p. 193° (Found : S, 8·31. $C_{16}H_9O_6N_3S$ requires S, 8·63%).

4-*Nitrophenyl* 2 : 4-*dinitro*-1-*naphthyl sulphide.* The *sulphide* (2·5 g.) separated immediately when 1-chloro-2 : 4-dinitronaphthalene (2·5 g.) reacted with sodium *p*-nitrothiophenoxide (1·5 g.); it crystallised from hot 80% aqueous acetic acid in sand-coloured rhombs, m. p. 197—198° (Found : S, 8·16. $C_{16}H_9O_6N_3S$ requires S, 8·63%).

2-*Nitrophenyl* 2 : 4-*dinitro*-1-*naphthyl sulphide.* This was prepared as above from the *o*-nitro-compound. After 10 minutes' heating under reflux separation was complete. The *sulphide* (2·5 g.) crystallised from 80% aqueous acetic acid in ochre hexagonal plates, m. p. 225—226° (Found : S, 8·67. $C_{16}H_9O_6N_3S$ requires S, 8·63%).

2 : 4 : 4'-*Trinitro*-1 : 1'-*dinaphthyl sulphide.* 4-Nitro-1-thionaphthoxide similarly gave the *dinaphthyl sulphide* which crystallised from glacial acetic acid in cream micro-needles, m. p. 216° (Found : S, 7·9. $C_{20}H_{11}O_6N_3S$ requires S, 7·63%).

Reactions with 4-*chloro*-3-*nitrotoluene.* The yields of monosulphide were negligible when 4-chloro-3-nitrotoluene reacted with sodium 2-nitro- and 2-nitro-4-methyl-thiophenoxide and 4-nitro-1-thionaphthoxide, even if reaction was allowed to proceed for 8 hours under reflux and although the thioaryloxide had disappeared.

2 : 6 : 2'-*Trinitro*-4-*methyldiphenyl sulphide.* When a mixture of 4-chloro-3 : 5-dinitrotoluene (2 g.) in ethanol (30 c.c.) was refluxed for 5½ hours with sodium *p*-nitrothiophenoxide (1·75 g.) the *diphenyl sulphide* was formed; it separated (1·5 g.) from 80% aqueous acetic acid in lemon-yellow needles, m. p. 100° (Found : S, 9·52. $C_{13}H_9O_6N_3S$ requires S, 9·52%), which were readily soluble in cold acetic acid.

4-*Nitrophenyl* 4 : 5-*dinitro*-1-*naphthyl sulphide.* This was prepared by refluxing 1-bromo-4 : 5-naphthalene (0·75 g.) in acetone (60 c.c.) with sodium *p*-nitrothiophenoxide (0·5 g.) for 10 minutes; it separated from the hot solution in almost quantitative yield and crystallised from glacial acetic acid in lemon-yellow crystals of the *sulphide*, m. p. 221° (Found : S, 8·59. $C_{16}H_9O_6N_3S$ requires S, 8·6%).

Preparation of Aryl Monosulphides by the Reaction of Sodium Thioaryloxides with Dinitro-aromatic Compounds.—General procedure. A hot solution of the dinitro-aromatic compound (0·0075 mol.) in the minimum amount of ethanol was treated with a hot solution of the thioaryloxide (0·005 mol.) in 80—90% aqueous ethanol containing *ca.* 1·5 equivs. of sodium hydroxide. In several cases reaction was completed almost at once, but, generally, heating under reflux was necessary until the red colour due to the sodium thioaryloxide had disappeared. The monosulphide usually separated from the hot solution. After removal, it was washed with cold alcohol and water, and dried before recrystallisation. Some of the reaction products were dark owing to the presence of impurities. These dark products were often accompanied by some sulphur. A few of the nitro-compounds were relatively insoluble in hot alcohol (*e.g.* 1 : 4 : 5-trinitronaphthalene, 2 : 6-dinitronaphthalene), and a suspension in this medium was used.

Some Abnormal Reactions involving p-*Dinitro-aromatic Compounds.*—(*a*) Sodium *o*-nitrothiophenoxide (1·75 g.) and *p*-dinitrobenzene (2 g.) were treated as above and, after refluxing for 30 minutes, the cooled mixture was filtered. The yellow crystalline product (1 g.; *ca.* 40% yield calculated as monosulphide) was treated with steam to remove any unchanged *p*-dinitrobenzene; the crude product had m. p. 138—140° which was raised to 142—145° by repeated crystallisation from glacial acetic acid (Found : N, 11·7; S, 11·0. Calc. for $C_{12}H_8O_4N_2S$: N, 10·0; S, 11·6%).

(*b*) Sodium *p*-nitrothiophenoxide (4·0 g.) and *p*-dinitrobenzene (4·0 g.) were treated as above, and the reddish-orange product (3·1 g.) dissolved in the minimum amount of boiling glacial acetic acid, from which *pp'*-dinitroazobenzene (1·3 g.) separated on cooling and was filtered off; m. p. 223° (Found : N, 20·4. Calc. for $C_{12}H_8O_4N_4$: N, 20·6%). From the filtrate, on concentration, an orange-yellow product (1·1 g.) separated, m. p. 147—148° after extraction with a little boiling glacial acetic acid (Found : S, 10·5. Calc. for $C_{12}H_8O_4N_2S$: S, 11·5%). The m. p. was not raised by treatment with a hot aqueous alcoholic solution of sodium hydroxide and glucose, although some thioaryloxide was produced as indicated by oxidation of the intense blue liquor with hot potassium ferricyanide solution. The original filtrate, after removal of the reaction product, contained some unchanged starting materials. *p*-Dinitrobenzene was removed by steam distillation; a substance of low m. p. remained which was soluble in hot ethanol but not in alkali hydroxides. The steam distillate, after removal of *p*-dinitrobenzene, gave no precipitate on addition of barium chloride, indicating the absence of sodium *p*-nitrobenzenesulphonate.

(*c*) Sodium 2-nitro-1-thionaphthoxide (1·0 g.) and *p*-dinitrobenzene (1·0 g.), after refluxing for 30 minutes as above, afforded only a black product (0·2 g.) which on crystallisation from glacial acetic acid had m. p. 223—227°; the solution in acetic acid was purple and changed through the colour sequence blue-green, green, and lilac on dilution with water, these colours being reversed on addition of increasing amounts of glacial acetic acid to the lilac solution.

(*d*) Sodium *p*-nitrothiophenoxide (1·25 g.) and 1 : 4-dinitronaphthalene (1·5 g.), after refluxing for 30 minutes as above, afforded a crystalline product (1·75 g.; 76% yield calculated as monosulphide) which was removed from the hot solution and separated from hot glacial acetic acid in lemon-yellow crystals, m. p. 152—153° (Found: S, 9·91. Calc. for $C_{16}H_{10}O_4N_2S$: S, 9·8%).

The authors thank Imperial Chemical Industries Ltd., Dyestuffs Division, for gifts of chemicals, the Department of Scientific and Industrial Research for a Senior Research Award to one of them (E. R. W.), and Mr. G. Walker for the preparation of several initial materials.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, January 26th*, 1948.]