403. *The Prevention of Diazo-oxide Formation in the Replacement of the Diazonium Group by Bromine or Iodine.*

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Methods are described for replacing the diazonium group by bromine or iodine in diazonium salts, such as those derived from 3-bromo-1-nitro-2- or 2,4-dinitro-1-naphthylamine, whereby the diazo-oxide formation that occurs with the conventional Sandmeyer reagents is suppressed or eliminated. These new methods still yield diazo-oxides with trinitronaphthylamines, such as 2,4,5-trinitro-1-naphthylamine, apparently because here diazotisation by the methods of Hodgson and Turner or Piercey and Ward directly yields the diazo-oxide and not the diazonium salt.

Improved preparations of 2,4-dinitro- and 2,4,5-trinitro-*N*-toluene-*p*-sulphonyl-1-naphthylamine and similar compounds are described.

The unusual 3-bromination of 1,6-dinitro-*N*-toluene-*p*-sulphonyl-2-naphthylamine in pyridine is now proved by conversion of the product into 3-bromo-1,6-dinitronaphthalene.

2,4-DINITRO-1-NAPHTHYLAMINE can be readily diazotised by the method of Hodgson and Turner [1] and addition of the diazonium solution to the normal Sandmeyer reagents gives good yields of 1-bromo- and 1-chloro-2,4-dinitronaphthalene.[2-4] Reaction with aqueous potassium iodide, however, yields mainly 1-diazo-4-nitro-2-naphthol with some 1-iodo-2,4-dinitronaphthalene (cf. Hodgson and Walker,[2] and Elias and Parker [4]), which is to be expected since addition of the diazonium solution to water gives the diazo-oxide immediately. We find that 1,6-dinitro-2-naphthylamine behaves similarly. Hardy and Ward,[5] however, found that diazotising 2,4,x-trinitro-1-naphthylamines (where $x = 3$, 5, 6, 7, or 8) by the Hodgson and Turner method,[1] and adding the solution to the normal Sandmeyer reagents for introduction of chlorine, bromine, or iodine, gave, in all cases, only the corresponding diazo-oxide. They also found that these amines could not be deaminated by Hodgson and Turner's [6] or Hodgson and Birtwell's method,[7] which gave excellent yields of dinitronaphthalenes from 2,4-dinitro-1- and 1,6-dinitro-2-naphthylamine. Thus, whilst these types of decomposition are normally favoured by the presence of electron-withdrawing groups (especially in *ortho*- or *para*-position to the diazonium group), progressive activation ultimately favours reactions involving nucleophilic displacement of substituent groups adjacent to the diazonium group: The obvious mechanism of diazo-oxide formation is by nucleophilic attack of water on the diazonium salt. Hence, in decomposition of diazonium compounds which are exceptionally prone to diazo-oxide formation it is desirable to eliminate water from the reaction system so far as possible. The need to do this will be greater (*a*) with naphthalene than with the corresponding benzene derivatives, since diazo-oxide formation is more favoured with the former, and (*b*) in replacement by iodine which involves a neutral aqueous medium rather than the acidic media (militating against diazo-oxide formation) employed for introducing bromine or chlorine.

Recently we required substituted 2,3-dihalogenonaphthalenes for the synthesis of substituted dibenzobiphenylenes by Ward and Pearson's method [8] and we found that attempts to introduce bromine or iodine into amines such as 3-bromo-1-nitro- and 3-bromo-1,6-dinitro-2-naphthylamine by diazotisation by Hodgson and Turner's method, followed

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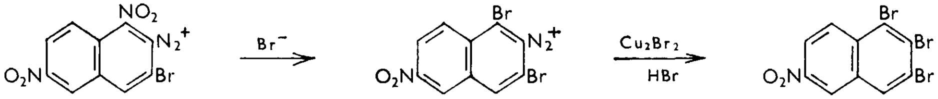
[1] Hodgson and Turner, *J.*, 1943, 86.
[2] Hodgson and Walker, *J.*, 1933, 1620.
[3] Hodgson and Ward, *J.*, 1948, 2017.
[4] Elias and Parker, *J.*, 1962, 2616.
[5] Hardy and Ward, *J.*, 1957, 2634.
[6] Hodgson and Turner, *J.*, 1942, 748.
[7] Hodgson and Birtwell, *J.*, 1943, 433.
[8] Ward and Pearson, *J.*, 1961, 515.

by normal decomposition, gave only the corresponding 2-diazo-1-naphthol. However, replacement of the diazonium group by bromine, by means of a suspension of cuprous bromide in 45% w/v hydrogen bromide–acetic acid, and by iodine by means of a suspension of finely ground potassium iodide in acetic acid, gave in moderate yield 3-bromo-2-iodo- and 2,3-dibromo-1-nitronaphthalene from 3-bromo-1-nitro-2-naphthylamine, and 3-bromo-2-iodo-1,6-dinitronaphthalene from 3-bromo-1,6-dinitro-2-naphthylamine, reactions being carried out in the cold for 12—24 hr. An attempted preparation of 2,3-dibromo-1,6-dinitronaphthalene gave a tribromonitronaphthalene, presumably 1,2,3-tribromo-6-nitronaphthalene, by the sequence:



These dihalogeno-compounds appeared to decompose in hot solvents and were thus hard to purify.

In one experiment addition of diazotised 3-bromo-1-nitro-2-naphthylamine to potassium iodide in acetic acid slowly produced a bright yellow solid. This proved to be readily soluble in water, giving a red orange solution which subsequently precipitated 3-bromo-2-diazo-1-naphthol, suggesting that the yellow solid was 3-bromo-1-nitronaphthalene-2-diazonium tri-iodide. Hantzsch[9] obtained a red explosive compound, thought to be a diazonium tri-iodide, on mixing 2,4-di-iodobenzenediazonium chloride and potassium iodide. More recently Carey *et al.*[10] isolated and authenticated several compounds of this type. Unfortunately we were unable to repeat this experiment and authenticate our own specimen.

Attempts to introduce chlorine into these diazonium salts by the conventional reagent or by a suspension of cuprous chloride in acetic acid saturated with hydrogen chloride yielded mixed products from which nothing could be characterised.

Our new methods were also satisfactory for introduction of bromine or iodine into diazotised 2,4-dinitro-1- and 1,6-dinitro-2-naphthylamine. We also found that 2-chloro-1,6-dinitronaphthalene was obtained in good yield by using cuprous chloride in hydrochloric–acetic acid. However, if 2,4,x-trinitro-1-naphthylamines (where $x = 5$, 7, or 8) were diazotised by the method of Hodgson and Turner,[1] or of Piercey and Ward[11] and then treated with our new reagents, in all cases (chlorine, bromine, or iodine) the product was the corresponding 1-diazo-2-naphthol, even when we diazotised the bases in the presence of sufficient oleum to take up the water formed by the diazotisation itself. Moreover, we were unable to couple any of these " diazonium solutions " with 2-naphthol in aqueous sodium hydroxide or 2-naphthylamine in acetic acid. This suggests that the product of " diazotisation " is the diazonaphthol itself and not the diazonium salt. Little is known, as yet, about the detailed mechanism of diazotisation by nitrosylsulphuric acid in sulphuric–acetic acid, but the diazonaphthol could be formed directly from the trinitronaphthylamine rather than through the diazonium salt. Further, the formation of these diazonaphthols, even in very strongly acid media, may be related to the formation of diazonium compounds and diazo-oxides in nitration[12] or to the so-called self-diazotisation studied by Sihlbom.[13]

3-Bromo-1,6-dinitro-2-naphthylamine was prepared by Consden and Kenyon[14] by

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[9] Hantzsch, *Ber.*, 1895, **28**, 683.

[10] Carey, Jones, and Millar, *Chem. and Ind.*, 1959, 1018; Carey and Millar, *Chem. and Ind.*, 1960, 97.

[11] Piercey and Ward, *J.*, 1962, 3841.

[12] Vesely and Dvorak, *Chem. Listy*, 1923, **17**, 163; Ward, Coulson, and Wells, unpublished work; Coulson, Thesis, London, 1955; Wells, Thesis, London, 1958; Smith, Brown, Martin-Smith, Reid, Scott, and Sim, *Chem. and Ind.*, 1962, 982.

[13] Zollinger, " Diazo and Azo Chemistry," Interscience Publ., Inc., New York, 1961, p. 20.

[14] Consden and Kenyon, *J.*, 1935, 1591.

bromination of 1,6-dinitro-*N*-toluene-*p*-sulphonyl-2-naphthylamine in pyridine as long ago as 1935. It has never been authentically orientated, although Ward and Wells [15] suggested a mechanism for this unusual 3-substitution. Its constitution has now been proved. Deamination gives a bromodinitronaphthalene, which must be 3-bromo-1,6-dinitronaphthalene, since it is also obtained by deamination of 2-bromo-4,7-dinitro-1-naphthylamine.[5]

Bunnett and Conner [16] obtained 1-iodo-2,4-dinitrobenzene in 87% yield from 1-chloro-2,4-dinitrobenzene by halogen exchange, using sodium iodide in refluxing dimethylformamide. We have prepared 1-iodo-2,4-dinitronaphthalene, in 30—50% yield, in a similar manner. Although it is difficult to get reproducible results owing to formation of tarry by-products, this route is probably the most convenient since 1-chloro-2,4-dinitronaphthalene can be easily prepared on the large scale from the readily available 2,4-dinitro-1-naphthol. We were unable to convert 1-chloro-2,4,5-trinitronaphthalene into the iodo-compound in this way.

2,4-Dinitro-*N*-toluene-*p*-sulphonyl-1-naphthylamine is usually prepared by a two-stage process: 1-naphthylamine is treated with toluene-*p*-sulphonyl chloride in pyridine and the purified derivative is nitrated in acetic acid.[17] We find that the two stages can be combined by acylation in refluxing acetic acid, followed by nitration in the same solution. 2,4,5-Trinitro-*N*-toluene-*p*-sulphonyl-1-naphthylamine was similarly obtained in 60% overall yield from 5-nitro-1-naphthylamine (cf. ref. 18).

EXPERIMENTAL

General Procedure for Diazotisation and Subsequent Replacement of the Diazonium Group by Bromine or Iodine.—In all cases starting materials were substituted *N*-toluene-*p*-sulphonylnaphthylamines. These were hydrolysed by dissolution in the minimum amount of sulphuric acid (*d* 1·84), heating at 40° for 5 min.; then cooled to 20°, and diazotised by Hodgson and Turner's method.[1] The diazonium solution was then added, with stirring, to a suspension of cuprous bromide (freshly prepared) (*ca.* 1 g. per g. of amide) in a 45% w/v solution (25 ml. per g. of Cu_2Br_2) of hydrogen bromide in acetic acid or to a suspension of finely ground potassium iodide (*ca.* 1 g. per g. of amide) in acetic acid (*ca.* 20 ml. per g. of potassium iodide). Stirring was continued at room temperature for 12—24 hr. and the mixture then poured on ice. The solids were collected, washed with water (also with aqueous sodium thiosulphate when iodide was used), and dried. 1-Bromo-2,4-dinitronaphthalene was obtained in 25% yield by extraction with ethanol (charcoal) and had m. p. 159° (from ethanol) (Hodgson and Walker [2] give m. p. 160°). 1-*Iodo*-2,4-*dinitronaphthalene* was extracted by hot benzene (charcoal), the cooled extract being filtered through alumina and concentrated; the yield was *ca.* 25%; the product, crystallised from ethanol, had m. p. 181° (Found: C, 35·0; H, 1·4; I, 35·05. $C_{10}H_5IN_2O_4$ requires C, 34·9; H, 1·5; I, 36·9%) (Elias and Parker [4] give m. p. 182—183°). 2-*Bromo*-, m. p. 174—176° (from ethanol) (Found: C, 40·5; H, 1·7; Br, 27·1. $C_{10}H_5BrN_2O_4$ requires C, 40·0; H, 1·7; Br, 27·0%), and 2-*iodo*-1,6-*dinitronaphthalene*, m. p. 217° (from ethanol) (Found: C, 35·0; H, 1·4; I, 35·7%), were obtained similarly (25%). 3-*Bromo*-2-*iodo*-1-*nitronaphthalene* was obtained in the same way as 1-iodo-2,4-dinitronaphthalene; crystallised from acetic acid, it had m. p. 163° (yield 30—80%) (Found: C, 31·7; H, 1·2; N, 3·4; Halogen, 1 equiv. in 192 g. $C_{10}H_5BrINO_2$ requires C, 31·8; H, 1·3; N, 3·7%; Halogen, 1 equiv. in 189 g.). 2,3-*Dibromo*-1-*nitronaphthalene* was extracted by hot ethanol in *ca.* 15% yield and had m. p. 178° (from ethanol) (Found: C, 36·35; H, 1·5; N, 3·6; Br, 47·5. $C_{10}H_5Br_2NO_2$ requires C, 36·3; H, 1·5; N, 4·2; Br, 48·3%). 3-*Bromo*-2-*iodo*-1,6-*dinitronaphthalene* was extracted by hot alcohol, then filtered through alumina; the extract, when concentrated, gave the product (50%), m. p. 195—215° (from ethanol) (Found: C, 28·3; H, 0·9; Halogen, 1 equiv. in 210 g. $C_{10}H_4BrIN_2O_4$ requires C, 28·4; H, 0·95%; Halogen, 1 equiv. in 211·5 g.). 1,2,3-*Tribromo*-6-*nitronaphthalene*, extracted

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[15] Ward and Wells, *J.*, 1961, 4866.

[16] Bunnett and Conner, *J. Org. Chem.*, 1958, **23**, 305.

[17] Hodgson and Smith, *J.*, 1935, 1854.

[18] Hodgson and Turner, *J.*, 1942, 723.

by hot ethanol (charcoal), had m. p. 207° (from ethanol) (Found: C, 29·6; H, 0·95; Br, 55·2. $C_{10}H_4Br_3NO_2$ requires C, 29·3; H, 1·0; Br, 58·5%).

1,3-*Dibromo*-2-*iodonaphthalene*.—1,3-Dibromo-2-naphthylamine was diazotised and added to aqueous potassium iodide. The *iodide* (70%) had m. p. 108·5—109·5° (from alcohol) (Found: C, 29·0; H, 0·8; Br + I, 70·1. $C_{10}H_5Br_2I$ requires C, 29·2; H, 1·2; Br, 38·8; I, 30·8%).

2-*Chloro*-1,6-*dinitronaphthalene*.—1,6-Dinitro-2-naphthylamine was diazotised and added to cuprous chloride in hydrochloric acid (*d* 1·2). The product (30%) had m. p. 175° (from ethanol) (Ceillier and Wahl [19] give 179°). Alternatively the diazonium solution obtained from 1,6-dinitro-*N*-toluene-*p*-sulphonyl-2-naphthylamine (2·5 g.) by hydrolysis in sulphuric acid (*d* 1·84) followed by diazotisation by Hodgson and Turner's method was added dropwise to a suspension of cuprous chloride (2·5 g.) in acetic acid (50 ml.) previously saturated with hydrogen chloride, whilst hydrogen chloride was passed into the mixture; the mixture was kept overnight, then poured on ice, and the product obtained by extracting the dried solids with hot benzene (200 ml.; charcoal) and concentration of the extract to 10 ml. This gave material (1·0 g., 60%) of m. p. 175° (from ethanol).

3-*Bromo*-2-*nitronaphthalene*.—Obtained in 55% yield by a conventional Sandmeyer reaction from 3-nitro-2-naphthylamine, this compound had m. p. 84° (from ethanol). McLeish and Campbell [20] obtained an 8% yield (m. p. 84°) from 3-bromo-2-naphthylamine by diazotisation and replacement of the diazonium- by the nitro-group.

1-*Iodo*-2,4-*dinitronaphthalene by Halogen Exchange* [with B. LILLEY].—1-Chloro-2,4-dinitronaphthalene was refluxed with sodium iodide (15 g.) in dimethylformamide (25 ml.) for 15 min., the hot mixture was poured on ice, and the solids were collected, washed with much water, and dried; the product, m. p. 175—185° (60—80%), when crystallised from acetic acid (charcoal) and chromatographed on alumina, had m. p. 181° (yield 30—50%).

3-*Bromo*-1,6-*dinitro*-2-*naphthylamine*.—When prepared by the method of Consden and Kenyon, chromatographed on alumina, and crystallised from ethanol, this base had m. p. 243—245° (Consden and Kenyon give 238—241°) (Found: C, 38·8; H, 1·9; N, 13·4; Br, 26·0. Calc. for $C_{10}H_6BrN_3O_2$: C, 38·5; H, 1·9; N, 13·5; Br, 25·6%). The amine was diazotised by Hodgson and Turner's method and addition to ice gave 3-*bromo*-2-*diazo*-6-*nitro*-1-*naphthol*; after chromatography in benzene on alumina, this had m. p. 179—182° (Found: C, 40·7; H, 1·8; Br, 27·1. $C_{10}H_4BrN_3O_3$ requires C, 40·8; H, 1·4; Br, 27·2%) (yield *ca.* 80%). Addition of this compound to methanol and cuprous oxide,[6] followed by addition of the mixture to ice-water, gave a solid which by extraction with ethanol (charcoal) afforded 3-*bromo*-1,6-*dinitronaphthalene*, m. p. 156° (from ethanol) (Found: C, 41·0; H, 1·7; Br, 29·5. $C_{10}H_5BrN_2O_4$ requires C, 40·4; H, 1·7; Br, 29·9%); this was also obtained from 2-bromo-4,7-dinitro-1-naphthylamine by a similar procedure, the products being proved identical by mixed m. p. and infrared spectroscopy.

2,4-*Dinitro- and* 2,4,5-*Trinitro*-N-*toluene*-p-*sulphonyl*-1-*naphthylamine* [with J. JOHL and B. LILLEY].—1-Naphthylamine (14 g.) and toluene-*p*-sulphonyl chloride (21 g.) were refluxed in acetic acid (70 ml.) for 3 hr. and, after cooling to 60°, a crystal of sodium nitrite was added, followed portionwise by nitric acid (*d* 1·42; 19 ml.), the temperature being allowed to rise to 65°. After 15 min. the mixture was set aside overnight, and the crystals were collected and washed with ether; this gave 2,4-dinitro-*N*-toluene-*p*-sulphonyl-1-naphthylamine (50%), m. p. 165° (from ethanol) (Hodgson and Smith [17] give 165°). The trinitro-compound was obtained similarly, by refluxing together 5-nitro-1-naphthylamine (5 g.) and toluene-*p*-sulphonyl chloride (5·3 g.) in acetic acid (25 ml.), and then adding nitric acid (*d* 1·42; 3·5 ml.) as above; the yield was 60%, and the m. p. 206° (from ethanol) (Hodgson and Turner [18] give 206°).

The authors thank Dr. K. Morgan (University of Birmingham) for infrared spectra measurements and Dr. J. Hyman (Fundamental Research Company, Berkeley, California) for gifts of chemicals.

LEICESTER COLLEGE OF TECHNOLOGY, LEICESTER. [*Received, October* 15*th*, 1962.]

[19] Ceillier and Wahl, *Compt. rend.*, 1949, **228**, 1299.
[20] McLeish and Campbell, *J.*, 1937, 1103.