The Migration of Aromatic Nitro-groups.

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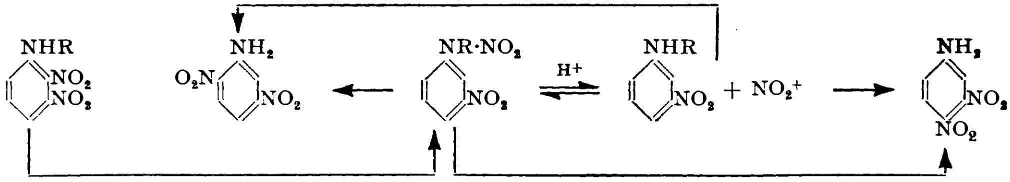
2 : 3-Dinitroacetanilide, 2 : 3-dinitroaniline, and 2 : 3-dinitrophenol undergo rearrangement when heated with concentrated sulphuric acid, but the corresponding 2 : 5- and 3 : 4-disubstituted compounds do not. A mechanism is suggested for the reaction.

Welsh (*J. Amer. Chem. Soc.*, 1941, **63**, 3276) reported that 2 : 3-dinitroacetanilide is hydrolysed to 2 : 3-dinitroaniline in 60% yield when heated with concentrated sulphuric acid at 110° for 5 min. Surprisingly, it has now been found that, when the mixture is heated for 20 min., 2 : 5-dinitroaniline (12%) is also formed in addition to the expected 2 : 3-dinitroaniline (57%). Furthermore, after 8 hours' heating of the mixture 2 : 3-dinitroaniline is not isolated and only 2 : 5-dinitroaniline (47%) and 3 : 4-dinitroaniline (24%) are obtained. An intermediate time of heating yields a mixture of the three dinitroanilines. Under the same conditions, 2 : 3-dinitroaniline is similarly rearranged. Thus, when 2 : 3-dinitroaniline is heated with sulphuric acid for 8 hr., almost the same yields as before of 2 : 5-dinitroaniline (42%) and 3 : 4-dinitroaniline (23%) are isolated. However, this rearrangement is apparently slower than that observed with 2 : 3-dinitroacetanilide, as lower conversions are obtained with shorter times of heating (see Experimental section). Both 2 : 5- and 3 : 4-dinitroaniline can be recovered quantitatively after heating with sulphuric acid.

When 2 : 3-dinitroaniline is heated with sulphuric acid in the presence of an excess of anisole for 4 hr., 2 : 5-dinitroaniline (26%), *N*-methyl-2 : 5-dinitroaniline (5%), 3 : 4-dinitroaniline (12%), 2 : 3-dinitroaniline (16%), and *m*-nitroaniline (13%) are formed. The formation of *N*-methyl-2 : 5-dinitroaniline is of interest, as it involves a transmethylation which is effected by demethylation of the anisole and subsequent methylation of 2 : 5-dinitroaniline. Nitrophenols or nitroanisoles were not isolated, presumably owing to sulphonation and oxidation under the conditions used.

The following mechanism is proposed for the rearrangement :



R = H or Ac

All reactants are considered to be protonated in the sulphuric acid medium (cf. Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40). The first stage is the conversion of the 2 : 3-dinitro-compounds into the corresponding 3 : *N*-dinitro-compounds *. This reaction, which is a reversal of the normal conversion of *N*-nitro-compounds into *C*-nitro-compounds, is assumed to be brought about by steric crowding of the 2-nitro-group, and is expected to proceed *via* a reversal of the mechanism proposed by Hughes (see Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 628) for the nitramine rearrangement. The formation of the *N*-nitro-compound is assumed to take place more readily with 2 : 3-dinitroacetanilide than with 2 : 3-dinitroaniline. The steric factor is of obvious importance, as neither 2 : 5- nor 3 : 4-dinitroaniline rearranges under the conditions used. In addition, a highly acidic medium is necessary, since alcoholic hydrochloric acid converts 2 : 3-dinitroacetanilide into 2 : 3-dinitroaniline quantitatively.

The *N*-nitro-compound formed may, in part, rearrange intramolecularly to 2 : 5-dinitroaniline (cf. Hughes and Jones, *J.*, 1950, 2678; Hughes, *op. cit.*), and it is also possible that some 3 : 4-dinitroaniline may be formed thus. However, this cannot be

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settled until more is known about the mechanism of the rearrangement of *N*-nitro-compounds to the corresponding *p*-nitro-compounds.

In addition, part of the *N*-nitro-compound must undergo acidolysis to *m*-nitroaniline (or *m*-nitroacetanilide) and a nitrating agent (assumed to be the nitronium ion). This is shown by the fact that *m*-nitroaniline is isolated from the reaction mixture when anisole is added. Hughes and Jones (*loc. cit.*) have established that *N*-methyl-2 : 4 : *N*-trinitroaniline undergoes acidolysis in either pure or aqueous (80%) sulphuric acid.

The nitrating agent produced is then assumed to react with the *m*-nitroaniline (or *m*-nitroacetanilide), finally forming 2 : 5- and 3 : 4-dinitroaniline. The formation of 2 : 5-dinitroaniline in this way is not regarded as appreciable, since the yield of 2 : 5-dinitroaniline (partly as the *N*-methyl derivative) is almost unchanged in the presence of anisole. However, this reaction appears important in the formation of 3 : 4-dinitroaniline, as a greatly reduced yield of this compound is obtained in the presence of anisole.

It has also been found that 2 : 3-dinitrophenol is partly converted into 2 : 5-dinitrophenol when heated with concentrated sulphuric acid, whereas 2 : 5- and 3 : 4-dinitrophenol are not rearranged. Again, only the sterically-hindered nitro-group is capable of migration.

Since the completion of this work, Dr. W. L. Mosby has kindly drawn our attention to a paper by Frisch, Silverman, and Bogert (*J. Amer. Chem. Soc.*, **1943**, **65**, 2432), who have shown that 4-amino-3-nitroveratrole is partly rearranged to 4-amino-5-nitroveratrole when heated with acetic acid–phosphoric acid. Although no investigation of the mechanism was made, this rearrangement further supports the concept that the lability of the *o*-nitro-group is dependent on both a high acidity and steric hindrance.

EXPERIMENTAL

M. p.s are corrected. Analyses are by Dr. W. Zimmermann.

Nitration of m-*Nitroacetanilide*.—*m*-Nitroacetanilide (85 g.), dissolved in small portions in fuming nitric acid (300 ml.; *d* 1·50), was slowly added to stirred concentrated sulphuric acid (300 ml.), the temperature being maintained at 0—5° by the addition of solid CO_2. The mixture was then poured on ice (1 kg.) and the product filtered off, washed, and dried. Crystallisation of the crude product from ethanol (1·5 l.) gave 2 : 3-dinitroacetanilide (34 g.; m. p. 188°). The filtrate was refluxed (4 hr.) with concentrated hydrochloric acid (200 ml.) and, after evaporation, the residue was dissolved in benzene and chromatographed on alumina, benzene being used as eluant. 2 : 5-Dinitroaniline (7·8 g.; m. p. 136°), 2 : 3-dinitroaniline (7·6 g.; m. p. 126°), and 3 : 4-dinitroaniline (4·3 g.; m. p. 153°) were eluted in that order. This method avoids the tedious fractional crystallisation recommended by Welsh (*loc. cit.*).

Action of Sulphuric Acid on 2 : 3-*Dinitroacetanilide, and on* 2 : 3-, 2 : 5-, *and* 3 : 4-*Dinitroaniline*.—The appropriate compound (5·0 g.) was heated with concentrated sulphuric acid (11 ml.; 98%) in a toluene-vapour bath. After the requisite time, the mixture was poured on to ice and the precipitate was filtered off and washed. The dried solid was dissolved in benzene and chromatographed on alumina. Table 1 summarises the results.

TABLE 1.

Compound	Time (hr.)	Yield of dinitroaniline (%)			Compound	Time (hr.)	Yield of dinitroaniline (%)		
		2 : 3-	2 : 5-	3 : 4-			2 : 3-	2 : 5-	3 : 4-
2 : 3-Dinitroacetanilide	0·33	57	12	0	2 : 3-Dinitroaniline	0·33	96	4	0
	4·25	5	46	23		4·25	20	34	18
	8·00	0	47	24		8·00	0	42	23
					2 : 5-Dinitroaniline	7·5	0	100	0
					3 : 4-Dinitroaniline	7·5	0	0	100

Rearrangement in the Presence of Anisole.—2 : 3-Dinitroaniline (17·2 g.) was heated (4·25 hr.) at 110° with concentrated sulphuric acid (40 ml.) and anisole (53 ml.). The mixture was poured on ice, and the solution extracted with ether (extract *A*). The aqueous solution was neutralised with sodium hydroxide and again extracted with ether (extract *B*). Both extracts were dried (Na_2SO_4) and evaporated, and the residues were dissolved in benzene and chromatographed on alumina. Elution with benzene gave the following :

Extract A. (i) A pale yellow substance (0·75 g.) which was not satisfactorily purified, (ii) *N*-methyl-2 : 5-dinitroaniline (0·95 g., 5%), which crystallised from ethanol or *cyclo*hexane as red needles, m. p. and mixed m. p. 168·5—169° (lit., 163°) (Found : C, 43·0; H, 3·7; N, 21·6. Calc. for $C_7H_7O_4N_3$: C, 42·7; H, 3·6; N, 21·3%), (iii) 2 : 5-dinitroaniline (4·45 g., 26%), m. p. and mixed m. p. 137°, (iv) 2 : 3-dinitroaniline (2·70 g., 16%), m. p. and mixed m. p. 126°, and (v) 3 : 4-dinitroaniline (2·04 g., 12%), m. p. and mixed m. p. 153°.

Extract B. (i) The unidentified substance above (0·17 g.) and (ii) *m*-nitroaniline (1·75 g., 13·5%), m. p. and mixed m. p. 113°.

Hydrolysis of 2 : 3-*Dinitroacetanilide.*—2 : 3-Dinitroacetanilide (5·0 g.) was refluxed (3 hr.) with ethanol (100 ml.) and concentrated hydrochloric acid (20 ml.). After dilution with water, the mixture gave 2 : 3-dinitroaniline (94%), m. p. and mixed m. p. 127°.

Nitration of m-*Nitrophenol.*—*m*-Nitrophenol (80 g.) was nitrated by Sidgwick and Aldous's method (*J.*, 1921, **119**, 1002). The first crops of 2 : 5-dinitrophenol (14 g.; m. p. 105°) and 3 : 4-dinitrophenol (18 g.; m. p. 137°) were separated as suggested by these authors. The residue was chromatographed on silica, with benzene as eluant, and 2 : 5-dinitrophenol (8·0 g.), 2 : 3-dinitrophenol (7·1 g.; m. p. 145°), *m*-nitrophenol (9·0 g.), and 3 : 4-dinitrophenol (16·0 g.) were obtained in that order. Chromatography is more satisfactory than the fractional crystallisation procedure used by Sidgwick and Aldous.

Action of Sulphuric Acid on 2 : 3-, 2 : 5-, *and* 3 : 4-*Dinitrophenol.*—The appropriate compound (3·0 g.) was heated with concentrated sulphuric acid in an ethanol, toluene, or chlorobenzene vapour bath. After the requisite time, the mixture was poured on ice, and the product was filtered off, washed and dried. The filtrate was extracted with ether, the solid obtained on evaporation was combined with the above product, and the mixture was chromatographed on silica in benzene. Table 2 summarises the results.

TABLE 2.

	H_2SO_4	Time		Yield of dinitrophenol (%)		
Compound	(ml.)	(hr.)	Temp.	2 : 3-	2 : 5-	3 : 4-
2 : 3-Dinitrophenol	50	7·5	78°	93	0	0
	30	7·0	112	25	7·5	0
	20	3·0	128	8	6	0
2 : 5-Dinitrophenol	10	5·0	78	0	97	0
	10	4·0	128	0	23	0
3 : 4-Dinitrophenol	10	6·5	78	0	0	100
	10	4·0	128	0	0	87

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