XCV.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part II. The Dinitrotoluenes.*

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A REVIEW of the results obtained by previous workers on the reactivity of substituents in the benzene nucleus, as determined by the presence of nitro-groups in the ortho- or para-position led one of us (Kenner, T., 1914, **105**, 2717) to associate this influence with the meta-directive properties of this group, and it was suggested that ortho-para-directive groupings or atoms might confer mobility on substituents in the meta-position. Further, it was concluded that the displacement of such mobile substituents depended primarily on the formation of a molecular compound, which underwent rearrangement and decomposition, leading to the products actually isolated. In this way, the failure of the nitro-group to exert its usual steric effects was accounted for, but the action of such influences, for example, on the part of methyl groups, in inhibiting the formation of the necessary additive compound furnished a simple explanation of some exceptional cases which previously seemed inexplicable.

With the object of testing the validity of these conclusions, a qualitative study of the action of ammonia and sodium methoxide on 2:3-, 3:4-, and 2:5-dinitrotoluenes has been made.

Of the two nitro-groups in 2:3-dinitrotoluene, it is clear from the foregoing that the effect of the methyl group would be expected to make that in the 3-position the more mobile. A necessary preliminary of its displacement, however, is the formation of an additive compound with the 2-nitro-group, but this is sterically inhibited by the methyl and the 3-nitro-groups. As a result, the 3-nitro-group must take part in the preliminary reaction, and the 2-nitro-group be displaced. Experiment fully confirmed this inference, the respective products of the action of sodium methoxide

and of methyl-alcoholic ammonia being easily identified as pure 6-nitro-*o*-tolyl methyl ether and 3-nitro-*o*-toluidine.

The case of 3:4-dinitrotoluene is simpler, since the two nitro-groups are equally accessible for the purpose of the formation of the preliminary molecular compound. The influence of the methyl group again favours the displacement of the 3-nitro-group, and, indeed, the product of the action of methyl-alcoholic ammonia at 150° was found to consist to the extent of 93·5 per cent. of 4-nitro-*m*-toluidine, the remainder being in all likelihood 3-nitro-*p*-toluidine. The main product of the action of sodium methoxide was an insoluble compound, evidently of high molecular weight, and very probably a stilbene derivative of the type prepared by Green (T., 1908, **93**, 1721) from *p*-nitrotoluene. A small amount of 6-nitro-*m*-tolyl methyl ether was obtained; the oily portion of this product, which did not crystallise, may possibly have contained 2-nitro-*p*-tolyl methyl ether, since this compound is described as melting at 8·5° (de Vries, *Rec. trav. chim.*, 1909, **28**, 2), but the quantity available was too small for identification.

The results obtained with 2:5-dinitrotoluene show that in this case both the possible isomerides are produced. Whilst the 5-nitro-group may be expected to be the more mobile, it is not surprising that the steric influence of the methyl group above referred to asserts itself and sufficiently reduces the velocity of formation of the additive compound with the 2-nitro-group to permit of the 5-nitro-group taking an appreciable part in the preliminary reaction. When, therefore, 2:5-dinitrotoluene was heated with methyl-alcoholic ammonia at 160° for six hours, a period which sufficed for the completion of the reaction in the case of the 3:4-isomeride, about 45 per cent. of the dinitro-compound remained unchanged. By prolonging the reaction, a mixture of amines was produced, consisting of about 88 per cent. of 5-nitro-*o*-toluidine with 12 per cent. of 6-nitro-*m*-toluidine. On the other hand, the relatively small quantity of crystals which separated from the oily product of the action of sodium methoxide on the dinitrotoluene consisted of 4-nitro-*m*-tolyl methyl ether. Apparently, therefore, the influence of the methyl group is not sufficiently great completely to prevent the formation of the alternatively possible products.

The colour changes, indicative of the formation of an additive compound, which take place on adding ammonia to the three dinitrotoluenes are in accord with the explanations given above. 3:4-Dinitrotoluene at once gives a red coloration in the cold, the 2:5-compound gives a red colour only on warming, and the 2:3-compound gives only a yellow colour, even when the mixture is heated.

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The experimental results are therefore easily explained in terms of the hypothesis previously advanced. This is also very largely true of the interesting data communicated by Holleman and his collaborators (*Rec. trav. chim.*, 1915, **35**, 1), and summarised below in regard to the dichloronitrobenzenes and the chlorodinitrobenzenes. In the table, the figures in clarendon type indicate the substituents which suffer displacement under the influence of sodium methoxide, diethylamine, or ammonia:

	Reaction constants at 85° (time in hours).			Reaction constants at 25° (time in hours).	
	CH ₃ ONa.	(C ₂ H ₅) ₂ NH.		CH ₃ ONa.	NH ₃ .
NO ₂ : Cl: Cl.			Cl: NO ₂ : NO ₂ .		
1: 2: 4	19.41	0.027	1: 2: 4	90.6	0.0206
1: 3: 4	17.42	0.0044	1: 2: 5	33.5	0.00512
1: 2: 5	3.93	0.0067	1: 3: 4	26.22	0.00807
1: 2: 3	1.74	0.0016	1: 2: 3	6.0	0.0137
1: 2: 6	0.135	0.00024	1: 2: 6	2.76	0.0121

Considering first the results from the dichloronitrobenzenes, the displacement of the chlorine atom in the ortho-position with respect to the nitro-group in the 1:2:4-compound in preference to that in the para-position is particularly interesting. It is in accordance with the views now represented, but the fact that the reaction constant of *p*-chloronitrobenzene is greater than that of the ortho-compound led Holleman to expect that the para-atom would be displaced. It will be observed that the order of the constants observed with diethylamine differs slightly from those obtained with sodium methoxide, showing that the nature of the reagent cannot be neglected in considering the relative activities of such compounds. The order of the values obtained with sodium methoxide corresponds with that to be anticipated as a result of applying the considerations already discussed. Both the nitro-group and the second chlorine atom co-operate in rendering one of the chlorine atoms of the 1:2:4-isomeride mobile; in the 1:3:4-derivative, the influence of the 3-chlorine atom is contrary to that of the nitro-group, but there is no steric hindrance to the formation of the additive compound such as may very possibly occur in the case of the otherwise similar 1:2:5-derivative; in the 1:2:3-compound there is the added complication of steric hindrance by the chlorine atom in the 3-position to the later stages of the reaction, whilst the relative stability of the 1:2:6-isomeride is accounted for by the powerful steric hindrance to the formation of the initial compound.

The chlorodinitrobenzenes are more interesting, since all three substituents are capable of displacement. Apparently, only one product is obtained in each case, and the result of displacement is

in every case in accord with anticipation, except that in the case of the 1:2:5-compound it is not possible to foresee which of the opposing influences discussed in connexion with 2:5-dinitrotoluene will be the stronger. The great divergence between the order of the values of the two sets of reaction constants suggests that in one or both series the nature of the nitro-derivative is not the chief determining factor in determining their relative activities, and little value can attach to their discussion from this point of view. Of the two series, the values obtained with sodium methoxide correspond the better with the views expressed above. A prominent feature of the quantitative results is the great increase in the magnitude of the constants over those of the corresponding dichloronitrobenzenes. Holleman illustrates this by a comparison of 2:4-dichloronitrobenzene with 4-chloro-*o*-dinitrobenzene (1:3:4), of 3:4-dichloronitrobenzene with 2-chloro-*p*-dinitrobenzene (1:2:5), and of 2:3-dichloronitrobenzene with 3-chloro-*o*-dinitrobenzene (1:2:3). Of each pair, the first suffers displacement of a chlorine atom, the second of a nitro-group in molecules otherwise identical, but the ratios of the respective constants at 25° are 800, 1000, and 2000. Similarly, the chlorodinitrobenzenes react with methylalcoholic ammonia at 100°, but the dinitrotoluenes were recovered practically unchanged after treatment under such conditions.

As regards the constitution of the intermediate compounds postulated in these reactions, arguments were advanced in the previous paper against the quinonoid formula (I), proposed by several workers, and preference was given to Werner's (II) or, alternatively, to Pfeiffer's formula (III):

(I.)

(II.)

(III.)

The results since obtained would appear to strengthen the case against the quinonoid formula, which can offer no satisfactory explanation of the formation of one of the possible isomerides, either alone or in an overwhelmingly predominating amount. For example, in order to explain on this basis the formation of 3-nitro-*o*-toluidine from 2:3-dinitrotoluene, it appears necessary to assume that the methyl group exerts some directive influence, resulting in the formation of the compound (IV). In the case of 3:4-dinitrotoluene, however, such an influence would be expected to involve the formation of the product (V), from which 3-nitro-*p*-toluidine should be obtained.

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Considerations of this kind appear to lead inevitably to the choice of some formula of the type (II) or (III).

(IV.)

(V.)

EXPERIMENTAL.

The dinitrotoluenes were prepared according to the directions of Meisenheimer and Hesse (*Ber.*, 1919, **52**, 1161), whilst the strengths of sodium methoxide and ammonia solutions were those employed by Holleman (*loc. cit.*), in order that the results obtained in the two series of experiments might be comparable.

Action of Sodium Methoxide on 2:3-Dinitrotoluene.—2:3-Dinitrotoluene (1.5 grams) was heated for nine hours on the water-bath with a solution of sodium (0.2 gram) in methyl alcohol (5 c.c.). The product consisted of a dark oil, which distilled almost entirely at 140°/24 mm., leaving a small, tarry residue. There can be no doubt that the product was 6-nitro-*o*-tolyl methyl ether, since this compound, which is referred to by Hofmann and Miller (*Ber.*, 1881, **14**, 568) as a yellow liquid, was obtained as a golden-yellow oil (b. p. 134°/21 mm.) by the action of sodium methoxide on 2-chloro-3-nitrotoluene (Found: N=8.53. Calc.: N=8.38 per cent.).

2 : 2' - Dimethoxy - 3 : 3' - azoxytoluene,

which was also produced in small amount in the above preparation, separated from alcohol in diamond-shaped prisms melting at 144° (Found: N=9.86. $C_{16}H_{18}O_3N_2$ requires N=9.79 per cent.).

Action of Ammonia on 2:3-Dinitrotoluene.—The dinitro-compound was quite unaffected by treatment on the water-bath with 2.5*N*-methyl-alcoholic ammonia (20 c.c.). The mixture was therefore heated under pressure for fifteen hours at 150—160°. The resulting solution, on evaporation, left a residue (m. p. 97°), which did not depress the melting point of 3-nitro-*o*-toluidine.

Reduction of 2:3-Dinitrotoluene.—2-Nitro-*m*-toluidine was obtained by Limpricht (*Ber.*, 1885, **18**, 1452) by reducing 2:3-dinitrotoluene with hydrogen sulphide in boiling alcoholic ammonia solution. As it was a possible product of the above reaction, it was decided to attempt its preparation.

(1) In an experiment by Mr. H. Burton, hydrogen sulphide was passed for three hours through a boiling solution of the dinitro-compound (3.6 grams) in alcohol (25 c.c.) to which ammonia solution (10 c.c.: D 0.880) had been added. The product obtained after filtration and evaporation was fractionally crystallised from alcohol. The main product, after recrystallisation from benzene, consisted of yellow prisms melting at 150° . Analysis showed it to be *dinitroditolyl sulphide*, $(C_6H_3Me \cdot NO_2)_2S$, most probably the 2:2':6:6'-isomeride (Found: N=8.92. $C_{14}H_{12}O_4N_2S$ requires N=9.2 per cent.). The more readily soluble product, after recrystallisation from benzene, melted at 54° . Although Limpricht's base melted at 55° , it is uncertain whether our compound was 2-nitro-*m*-toluidine, since it was not acetylated under ordinary conditions. The quantity available was too small for analysis, and the course of the present work did not necessitate closer investigation.

(2) A solution of stannous chloride (11.4 grams) and hydrogen chloride (16 grams) in absolute alcohol (50 c.c.) was added drop by drop to a cold solution of 2:3-dinitrotoluene (3.64 grams) in alcohol (50 c.c.). After half an hour, the solution was diluted and extracted with ether. The residue, after evaporation of the ether, was resolved into its components by treatment with light petroleum. The more readily soluble consisted of unchanged dinitro-compound, whilst the sparingly soluble product (1.2 grams) separated from a mixture of ether and light petroleum in long, stout, deep red prisms melting at 106° (Found: N=18.45. $C_{14}H_{12}O_4N_4$ requires N=18.66 per cent.). The compound was therefore a *dinitroazotoluene*, probably the 2:2':3:3'- rather than the 6:6':2:2'-isomeride.

Action of Sodium Methoxide on 3:4-Dinitrotoluene.—The products obtained from 3:4-dinitrotoluene (3 grams) consisted of a black, insoluble product (0.8 gram), probably a stilbene derivative (see p. 853), a dark red, resinous product (0.5 gram) soluble in alkali, and an oil. From the latter, a few crystals separated after some weeks. These, after purification by draining on a porous tile and solution in light petroleum, were obtained as colourless plates melting at 53 – 57° . A mixture with an equal quantity of the original dinitrotoluene (m. p. 59 – 60°) softened at 40° and melted completely at 50° . The quantity available was too small for analysis, but there can be little doubt that the substance was 6-nitro-*m*-tolyl methyl ether, the description of which corresponds with our product, and of which the melting point is variously given as 51 – 52° (Reissert and Scherk, *Ber.*, 1898, **31**, 398), 60° (Fischer and Rigaud, *Ber.*, 1902, **35**, 1259), and 62° (Khotinsky

and Jacopson-Jacopmann, *Ber.*, 1909, **42**, 3099). 2-Nitro-*p*-tolyl methyl ether forms pale yellow crystals melting at 8.5° (de Vries, *loc. cit.*), and it is therefore possible that some of this was present in the portion of the oil which did not solidify.

Action of Ammonia on 3:4-Dinitrotoluene.—From the product obtained by heating 3:4-dinitrotoluene (1.82 grams) with 2.5*N*-methyl-alcoholic ammonia (32 c.c.) for six hours at 150° were obtained pure 4-nitro-*m*-toluidine (m. p. 109° ; 1.1 grams), and a further quantity (0.15 gram) of impure product (m. p. 82°). By the application of Holleman's freezing-point method, it was shown that this corresponded with mixtures containing 4-nitro-*m*-toluidine with either 32 or 61 per cent. of 3-nitro-*p*-toluidine. Since the addition of the latter base to our product caused a rise in the temperature of solidification in agreement with the calculated, it contained 61 per cent. of this base.

4-Nitro-o-tolyl Methyl Ether.—The product of the interaction of 2-chloro-5-nitrotoluene and sodium methoxide, after isolation in the usual manner, crystallised from light petroleum in long, radiate needles melting at 63° (Found: $N=8.35$. $C_8H_9O_3N$ requires $N=8.38$ per cent.).

Action of Sodium Methoxide on 2:5-Dinitrotoluene.—By the action of sodium methoxide on 2:5-dinitrotoluene (3 grams), an oil (2 grams) was obtained, from which a quantity of crystals separated overnight; a further quantity separated when the oil was stirred with light petroleum. These, when collected and purified by crystallisation from light petroleum, melted at 55° , the melting point of 4-nitro-*m*-tolyl methyl ether (Reissert and Scherk, *loc. cit.*). A mixture with the original dinitro-derivative liquefied at the ordinary temperature, whilst that with 4-nitro-*o*-tolyl methyl ether melted at 28° . It is therefore clear that one of the products of the reaction was 4-nitro-*m*-tolyl methyl ether, but the other possible isomeride may also have been present, since the oil did not solidify completely even after some months.

6-Nitro-m-toluidine.—This compound was prepared according to the directions of Noelting and Stoecklin (*Ber.*, 1891, **24**, 564), who recommend steam-distillation of the products of nitrating *m*-toluidine until the distillate is no longer yellow. It was, however, found that 6-nitro-*m*-toluidine is slightly volatile in steam, and therefore the yellow colour does not completely disappear. When 16 litres of distillate, containing 11.7 grams of base, had been collected from the product of nitrating 32 grams of *m*-toluidine, the melting point of the crystals deposited, which had gradually risen during the distillation from 63° to 87° , suddenly rose to 133° , which was also the melting point of the residue in the distillation

flask. Although the authors named give 138° as the melting point, this could not be attained in the present case, either by repeated crystallisation or by purification of the base through its acetyl derivative, which was easily obtained by the addition of a drop of sulphuric acid to a mixture of the base with acetic anhydride. It separated from dilute alcohol in small prisms (m. p. 104°), and was easily hydrolysed by treatment with concentrated hydrochloric acid (Found: N=14.20. Calc.: N=14.4 per cent.).

2-Nitro-5-nitrosotoluene.—6-Nitro-*m*-toluidine (10 grams) was shaken for sixteen hours with Caro's acid (400 c.c.) from potassium persulphate (70 grams) and sulphuric acid (77 grams). The product (7 grams), after crystallisation from alcohol, melted at 113° (Found: C=50.37; H=3.59. $C_7H_6O_3N_2$ requires C=50.60; H=3.61 per cent.).

By oxidation with fuming nitric acid (10 parts), it was easily converted into 2:5-dinitrotoluene.

Action of Ammonia on 2:5-Dinitrotoluene.—The dinitro-compound (1 gram) was heated with alcoholic ammonia (32 c.c.) at 150° for fifteen hours. The residue obtained by evaporating the resulting solution was stirred with cold concentrated hydrochloric acid. The base precipitated from the acid solution by ammonia melted at 115 – 120° , but after crystallisation from dilute alcohol it melted at 127° , as did also its mixture with 5-nitro-*o*-toluidine. Since, on the other hand, its mixture with 6-nitro-*m*-toluidine melted at 114 – 115° , it is clear that the product in question was 5-nitro-*o*-toluidine. The low yield was due to the formation of a tarry product, which was insoluble in hydrochloric acid, and was not further investigated. According to measurements of the solidification points of mixtures of 5-nitro-*o*-toluidine with 6-nitro-*m*-toluidine, the crude base precipitated from acid solution contained about 88 per cent. of the former.

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