obtained. The mother liquor was concentrated and the products separated by chromatography. The yield of N^2-benzyl-N^1-butyl-N^2-methyl-N^1-phenyl-1,2-propanediamine, n_D^{25} 1.5497, was 420 mg. The infrared absorption spectrum had a more intense alkyl band than the analogous N^1-ethyl compound and lacked a CO or NH band.

Anal. Calcd. for $C_{21}H_{30}N_2$: C, 81.2; H, 9.7; N, 9.0. Found: C, 80.3; H, 9.8; N, 9.0.

The dipicrate was prepared and recrystallized from ethanol, m.p. 99–100°.

Anal. Calcd. for $C_{33}H_{36}N_8O_{14}$: C, 51.4; H, 4.7; N, 14.6. Found: C, 51.5; H, 5.2; N, 14.4.

N-(2-Benzylmethylaminopropyl)acetanilide (V). This compound was prepared by the reaction of N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine with acetic anhydride. The yield of *N*-(2-benzylmethylaminopropyl)acetanilide, b.p. 150–156°/0.1 mm. and n_D^{25} 1.5552, was 86%.

Anal. Calcd. for $C_{19}H_{24}N_2O$: C, 77.0; H, 8.2; N, 9.4. Found: C, 76.7; H, 8.2; N, 9.3.

N-(2-Benzylmethylaminopropyl)butyranilide (VII). This compound, b.p. 165–167°/0.2 mm. and n_D^{25} 1.5446, was obtained in 80% yield by the reaction of N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine with butyric anhydride.

Anal. Calcd. for $C_{21}H_{28}N_2O$: C, 77.7; H, 8.7; N, 8.6. Found: C, 77.6; H, 9.0; N, 8.6.

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The Nitration of 4-Nitro-*o*-iodotoluene

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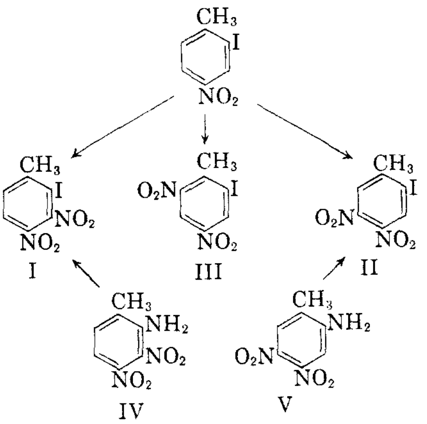
Dinitroiodo compounds have received little attention, as only a few of them are described in the literature. During a program of research on nitration of some iodo[2,3] compounds in this laboratory, nitration of 4-nitro-*o*-iodotoluene was undertaken for detailed investigation. The reaction can be expected to give three dinitro isomers, *viz.*, 3,4-(I); 4, 5-(II) and 4,6-(III) dinitro-*o*-iodotoluenes.

Only two isomers, *i.e.*, 4,5-dinitro-(II) and 4,6-dinitro-*o*-iodotoluene (III), were isolated from the reaction mixture. The identity of 4,5-dinitro-*o*-iodotoluene (II) was confirmed by an unequivocal synthesis from 4,5-dinitro-*o*-toluidine[4] (V) by Sandmeyer's reaction. Attempts to prepare 4,6-dinitro-*o*-iodotoluene (III) from 4,6-dinitro-*o*-toluidine[5] failed. 3,4-Dinitro-*o*-iodotoluene (I) has also been synthesized from 3,4-dinitro-*o*-toluidine[4] (IV). 4,5-Dinitro-*o*-iodotoluene (II) behaves normally with hydrazine hydrate giving 2-nitro-5-iodo-*p*-tolylhydrazine as the main product. The structure is assigned by analogy with other hydrazine preparations.[2]



The various dinitroiodo isomers prepared above can be distinguished readily, by taking advantage of their color reactions in acetone solution with aqueous sodium hydroxide, in which colors ranging from light red to intense green are produced.

EXPERIMENTAL[6]

Nitration of 4-nitro-o-iodotoluene. To a suspension of 4-nitro-*o*-iodotoluene (10 g.) in concd. sulfuric acid (42 ml., d. 1.8), fuming nitric acid (14 ml., d. 1.5) was added dropwise with vigorous shaking. It was then heated on a water bath for about 2 hr. and poured on crushed ice. The yellow crystalline material which separated was repeatedly crystallized successively from ethanol and methanol to give 4,5-dinitro-*o*-iodotoluene (5.2 g.) as yellow flakes, m.p. 97°.

Anal. Calcd. for $C_7H_5O_4N_2I$: I, 41.2. Found: I, 41.0.

The mother-liquor on standing deposited crystals of 4,6-dinitro-*o*-iodotoluene (1 g.) which crystallized from ethanol as pale yellow needles, m.p. 178°.

Anal. Calcd. for $C_7H_5O_4N_2I$: I, 41.2. Found: I, 40.8.

There remained an oil (1.5 g.) which could not be induced to crystallize.

3,4- and 4,5-Dinitro-o-toluidines[4] were prepared according to the method described previously.

4,5-Dinitro-o-iodotoluene. 4,5-Dinitro-*o*-toluidine (0.5 g.) dissolved in concd. sulfuric acid (5 g.) containing a little water was diazotized at 0° with sodium nitrite (0.4 g.). After 0.5 hr. the mixture was treated with a solution of potassium iodide (5 g.) in water. The 4,5-dinitro-*o*-iodotoluene formed was isolated in the usual manner and recrystallized from ethanol as yellow flakes (0.4 g.), m.p. 96°; mixed melting point with a sample of 4,5-dinitro-*o*-iodotoluene obtained by nitration of 4-nitro-*o*-iodotoluene remained undepressed.

3,4-Dinitro-o-iodotoluene was prepared by adopting a procedure, similar to that described above, from 3,4-dinitro-*o*-toluidine as pale yellow needles, m.p. 117°.

Anal. Calcd. for $C_7H_5O_4N_2I$: I, 41.2. Found: I, 40.7.

2-Nitro-5-iodo-p-tolylhydrazine. To a solution of 4,5-dinitro-*o*-iodotoluene (5 g.) in ethanol twice the equivalent

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(1) Present address: Central Drug Research Institute, Lucknow (India).

(2) R. S. Kapil, *J. Chem. Soc.*, **24,** 4127 (1959).

(3) R. S. Kapil, *J. Org. Chem.*, in press.

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(6) All melting points are uncorrected.

quantity of hydrazine hydrate was added dropwise with vigorous shaking. It was kept for about an hour, when the 2-nitro-5-iodo-*p*-tolylhydrazine which precipitated was filtered, washed well with water, dried, and recrystallized from ethanol–ethyl acetate mixture as orange red needles (2.8 g.) m.p. 163°.

Anal. Calcd. for $C_7H_8O_2N_3I$: I, 43.3. Found: I, 42.8.

The *acetyl* derivative was crystallized from ethanol as lemon yellow needles, m.p. 217°.

Anal. Calcd. for $C_9H_{10}O_3N_3I$: I, 37.9. Found: I, 37.7.

The *benzoyl* derivative was crystallized from ethanol as pale yellow needles, m.p. 199°.

Anal. Calcd. for $C_{14}H_{12}O_3N_3I$: I, 31.9. Found: I, 31.6.

Color reactions in acetone solution with aqueous sodium hydroxide were performed as described earlier.[7]

The various characteristic colors produced are recorded below:

o-Iodotoluenes	Colors Produced
3,4-Dinitro-	Intense green
4,5-Dinitro-	Light red
4,6-Dinitro-	Violet

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Nitration of 1,3,5-Trihalobenzenes

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The nitration of 1,3,5-tribromobenzene by mixed acid has previously been hindered by decomposition and the migration of the bromine atoms to other positions on the ring under the conditions of nitration employed.[1] We have reinvestigated the nitration of symmetrical trihalobenzenes and have developed a procedure for the nitration of 1,3,5-tribromobenzene which has greatly reduced bromine migration and decomposition of the starting material and extended it to 1,3,5-trichlorobenzene and other sterically hindered compounds. By nitrating 1,3,5-tribromo-2,4-dinitro- or 1,3,5-trichlorobenzene in a solution of potassium nitrate in fuming sulfuric acid good yields of the corresponding trinitro compounds were obtained, compared with 20–30% over-all yields by previous methods.[1] The method was found to be useful for nitrating other aromatic compounds such as 2,4,2′,4′-tetranitrobibenzyl which previously had been converted to the hexanitro compound in low yield.[2]

The nitration of tribromobenzene was carried out in two steps. Because the singular position of the bromine atoms *ortho, ortho, para* to the three open positions on the ring should enhance ring reactivity only mild conditions were used for the dinitration of 1,3,5-tribromobenzene in contrast to prolonged reaction periods at reflux temperature in earlier work.[3] This compound was easily nitrated in nearly quantitative yield at 25–60° by mixed fuming nitric acid and commercial concentrated sulfuric acid in less than an hour. However if the nitration mixture were held at this temperature after nitration was complete bromine evolution occurred.

The nitration of the sixth position required more drastic conditions because of the intense deactivation effect of the nitro groups and steric hindrance of the bromine atoms *ortho* to the open position. Because of the low yields and extensive decomposition encountered by previous workers in nitrating with mixed acids this method of nitration was not further investigated. Instead nitration of 1,3,5-tribromo-2,4-dinitrobenzene by a solution of potassium nitrate dissolved in fuming sulfuric acid gave yields up to 74% without excessive bromine migration or decomposition.[4] Some 1,2,3,5-tetrabromo-4,6-dinitrobenzene was found in the reaction products, as well as some unidentified low melting by-products which were not separable by the usual means. An investigation of reaction conditions showed that the optimum rate of nitration was obtained at a ratio of four moles of nitrate to one of dinitrotribromobenzene. The rate of nitration was also sharply affected by the reaction temperature. At temperatures below 120° long reaction periods were necessary, but at 130° and above, extensive decomposition began to occur and the formation of the side reaction product, 1,2,3,5-tetrabromo-4,6-dinitrobenzene, was favored. Optimum reaction was obtained at 125–127° for a reaction period of eight to nine hours. The optimum concentration of potassium nitrate relative to fuming sulfuric acid was not determined other than to assume complete utilization of the nitrate to give NO_2^+ ions. Millen and others[5] have given evidence that twelve weight per cent nitric acid in 35% fuming sulfuric acid produces $(NO_2^+)(HS_2O_7^-)$ as the only solute, a concentration of nitrating agent nearly equivalent to that used in this study.

Although the two step nitration procedure produced *sym*-trinitrotrichlorobenzene in good yield, it was found that 1,3,5-trichlorobenzene could be trinitrated in 73% yield in one step by the fuming sulfuric acid–potassium nitrate solution. Optimum reaction was obtained by using a molar ratio of

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