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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[7] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **117**, 784 (1920).

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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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[1] (a) C. L. Jackson and J. F. Wing, *Am. Chem. J.*, **10**, 283 (1888). (b) C. L. Jackson and J. F. Wing, *Am. Chem. J.*, **12**, 7, 167 (1890).

[2] K. G. Shipp, Private Communication.

[3] H. J. Backer and S. J. Van der Baan, *Rec. trav. chim.*, **56**, 1175 (1937).

[4] C. Weygand, *Organic Preparation*, Interscience Publishers, Inc., New York, N. Y., 1945, p. 279.

[5] D. J. Millen, *J. Chem. Soc.*, 2589 (1950).

trichlorobenzene to potassium nitrate and sulfur trioxide of one to eight to twenty for eighteen hours at 135°.

### EXPERIMENTAL

*1,3,5-Tribromo-2,4-dinitrobenzene.* 1,3,5-Tribromobenzene (31.5 g., 0.1 mole) was added portionwise to a solution of 155 g. of commercial white fuming nitric acid, assay 95%, in 62 g. of concd. sulfuric acid at room temperature, allowing the autogenous temperature to rise no higher than 60°. Within 10 min. after the addition was complete the reaction mixture was cooled and the solid collected, washed, and dried. 1,3,5-Tribromo-2,4-dinitrobenzene was obtained in 98% yield, m.p. 191°; recrystallized, m.p. 192°.

*Anal.*[6] Calcd. for $C_6H\ Br_3N_2O_4$: C, 17.80; H, 0.25; Br, 59.22. Found: C, 17.91; H, 0.22; Br, 59.08.

*1,3,5-Trichloro-2,4,6-trinitrobenzene.* Potassium nitrate (40.4 g., 0.4 mole) was added to 266.5 ml. (1.0 mole) of 30% oleum at 65° with external cooling to maintain this temperature. The resulting mixture of potassium salts and nitration solution was then heated to 110°, becoming clear at 95°. 1,3,5-Trichlorobenzene (9.0 g., 0.005 mole) was added with stirring. The temperature was raised to 130–135° and held for 18 hr. After cooling to room temperature the viscous mixture was slowly poured onto three times its volume of flaked ice. The solid which separated was collected, washed free of acid, dried, and recrystallized from chloroform. 1,3,5-Trichloro-2,4,6-trinitrobenzene was obtained in 73% yield, m.p. 190°.

*Anal.* Calcd. for $C_6Cl_3N_3O_6$: C, 22.75; Cl, 33.65; N, 13.27. Found: C, 22.72; Cl, 33.62; N, 12.81.

*1,3,5-Tribromo-2,4,6-trinitrobenzene.* The above procedure was also used for nitration of 0.12 mole (48.5 g.) of 1,3,5-tribromo-2,4-dinitrobenzene employing instead 0.54 mole (54.5 g.) of potassium nitrate dissolved in 320 g. of 30% fuming sulfuric acid (1.2 moles of sulfur trioxide), heated at 125 ±1° for 9 hr. There was obtained after recrystallization from chloroform a 74% yield of 1,3,5-tribromo-2,4,6-trinitrobenzene, m.p. 297°, and 6% of 1,2,3,5-tetrabromo-4,6-dinitrobenzene, m.p. 232°.

*Anal.* Calcd. for $C_6Br_3N_3O_6$: C, 16.02; Br, 53.30; N, 9.34. Found: C, 16.30; Br, 53.45; N 9.16. Calcd. for $C_6Br_4N_2O_4$: C, 14.90; Br, 66.09; N, 5.79. Found: C, 15.02; Br, 65.81; N, 5.87.

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[6] Analyses by Oakwold Laboratories, Alexandria, Va.

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## Reactions of Dinitrogen Tetroxide with Alicyclic Sulfides

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The reactions of dinitrogen tetroxide with 1,4-dithiane and 1,3,5-trithiane have been investigated in connection with a general study of addition compounds of dinitrogen tetroxide with organic sulfides. Bell and Bennett[1] made a slight reference to the oxidation of 1,4-dithiane in ether solution by nitrous fumes to give predominantly 1,4-dithiane α-disulfoxide [*trans* isomer] and a little 1,4-dithiane β-disulfoxide [*cis* isomer], but they gave few experimental details. The results reported here shed some light on the intermediates formed in the course of the reaction. More especially, we would like to call attention to an unexpected isomerization of 1,4-dithiane α-disulfoxide to 1,4-dithiane monosulfone.

Dinitrogen tetroxide is known to oxidize alkyl sulfides to the corresponding sulfoxides.[2] Methyl phenyl sulfide has also been oxidized to methyl phenyl sulfoxide by means of dinitrogen tetroxide.[3] Addison and Sheldon[2] have shown also that dinitrogen tetroxide forms molecular addition compounds with alkyl sulfoxides. They suggested that the formation of such addition compounds may inhibit further oxidation of the sulfur by dinitrogen tetroxide and explain why the sulfoxides rather than sulfones are produced.

### EXPERIMENTAL

1,4-Dithiane was prepared by the method of Masson,[4] which involves the reaction between potassium sulfide and ethylene dibromide in ethanol solution. The product which we obtained by this procedure melted at 111–112°[5] (lit.[4] 111°). Commercial nitrogen dioxide was dried by passing it through a glass tube filled with phosphorus (V) oxide and sand. Solid dinitrogen tetroxide (m.p. −11.5°, lit.,[6] m.p. −11.2°) was then collected in a trap cooled with Dry Ice and stored in a refrigerator until needed. Eastman White Label 1,3,5-trithiane (m.p. 216–218°, lit.[7] m.p. 216°) was used without further purification.

About 1 g. of 1,4-dithiane was dissolved in a few ml. of chloroform. A large excess of dinitrogen tetroxide was distilled into this solution and the entire mixture held at 0° for about 12 hr. At the end of this time, the system was composed of a deep blue solution with a white precipitate on the bottom of the container. The excess oxides of nitrogen were removed with an aspirator, at room temperature, and the white solid residue were collected and stored over Drierite in a desiccator. After this treatment, the white solid was odorless and decomposed at 225–230°. This same product was obtained by mixing 1,4-dithiane and dinitrogen tetroxide in the absence of a solvent. When this white, solid product (prepared by either method) was recrystallized from 95% ethanol, it produced a mixture of 1,4-dithiane α-disulfoxide (m.p. 263–265° dec., lit.[1] m.p. 263°) and 1,4-dithiane β-disulfoxide (m.p. 242–243° dec., lit.,[1] m.p. 235–250°). The isomers were separated by the fractional crystallization method described by Bell and Bennett.[1] The mixture was composed of 93–94% of the α-disulfoxide and 6–7% of the β-disulfoxide. The yield of the combined α- and β-disulfoxides was quantitative based upon the amount of 1,4-dithiane used.

*Anal.* Calcd. for $C_4H_8S_2O_2$ (α- or β-form): C, 31.6%; H, 5.3%. Found: for the α-isomer, C, 31.7%; H, 5.5%; for the β-isomer, C, 31.6%; H, 5.3%.[8]

Decomposition points of mixtures of these products with

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[1] E. Bell and G. Bennett, *J. Chem. Soc.*, 1798 (1927).

[2] C. Addison and C. Sheldon, *J. Chem. Soc.*, 2705 (1956).

[3] Von L. Horner and F. Hubenett, *Ann.*, **597**, 193 (1953).

[4] O. Masson, *J. Chem. Soc.*, **49**, 233 (1886).

[5] All melting and decomposition points are uncorrected.

[6] W. Giauque and J. Kemp, *J. Chem. Phys.*, **6**, 40 (1938).

[7] A. Hofmann, *Ber.*, **3**, 584 (1870).

[8] Analyses performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.