[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

The Nitro Substitution for the Aromatic Mercuric Group. The Preparation of *o*-Dinitrobenzene

YOSHIRO OGATA AND MASARU TSUCHIDA

Received March 15, 1956

o-Nitrophenylmercuric chloride was converted into *o*-dinitrobenzene by treatment with concentrated nitric acid in 91% yield. The preparation of *o*-dinitrobenzene in 26% yield was also accomplished *via* the mercuric ion-catalyzed nitration of nitrobenzene and recrystallization from nitric acid to remove the *meta* isomer which was produced simultaneously in *ca.* 24% yield.

In a previous paper,[1] the mercuration of nitrobenzene in nitric acid as the solvent has been shown to produce *o*- and *m*-mercurated nitrobenzene in 37 and 57% yield, respectively. Since *o*-dinitrobenzene is usually prepared by the reaction of diazonium fluoborate and sodium nitrite in the presence of copper powder,[2] it seemed desirable to determine whether or not *o*-dinitrobenzene could be synthesized *via* the mercuric ion-catalyzed nitration of nitrobenzene.

The conversion of arylmercuric halides into their nitro derivatives has been studied to only a small extent. The only example in the literature is that of the preparation of *o*- and *p*-chloronitrobenzenes from the corresponding chlorophenylmercuric chlorides.[3]

We have found that *o*-dinitrophenylmercuric chloride is effectively converted into *o*-dinitrobenzene by the action of concentrated nitric acid (*sp. gr.* 1.386) at 95° for 10 minutes. Since the yield is high (91%), it is improbable that the *ortho* compound is formed *via* the elimination of the *o*-chloromercuric group followed by the nitration of the nitrobenzene produced. In addition, an attempt at the preparation of *o*-dinitrobenzene by the nitration of nitrobenzene with concentrated nitric acid containing a mercuric salt as a catalyst was also successful. The *meta* isomer, which was produced simultaneously in an amount comparable to the *ortho* isomer, was effectively removed on crystallization from conc'd nitric acid. The nitration of nitrobenzene is difficult without the mercuric salt under these conditions.

An attempted extension of this mercuric ion-catalyzed procedure to the preparation of some other nitro aromatic compounds with abnormal orientation was unsuccessful (*e.g.*, 9-fluorenone, α-nitronaphthalene, α-naphthalenesulfonic acid, benzenesulfonic acid, benzophenone, diphenyl sulfone, pyridine, benzoic acid, methyl benzoate, *m*-dinitrobenzene, and *p*-chloronitrobenzene).

EXPERIMENTAL

o-Dinitrobenzene from o-nitrophenylmercuric chloride. A mixture of isomeric nitrophenylmercuric chlorides was prepared by Dimroth's method.[4] The crude solid product was finely powdered and extracted with a small amount of cold acetone or benzene. The extract upon evaporation gave sufficiently pure *o*-nitrophenylmercuric chloride for the next step. To 30 ml. of conc'd nitric acid (*sp. gr.* 1.386) was added 1 g. of this material. The mixture was warmed with vigorous stirring to 95° and kept for 10 minutes at that temperature, whereupon the solid gradually dissolved and the liquid became reddish-brown. The mixture was poured into a large quantity of water, and the precipitate was collected and washed with water. Crystallization from aqueous methanol gave 0.43 g. (91.7%) of *o*-dinitrobenzene, in light yellow needles, m.p. 117°, and mixture m.p. with the authentic material prepared by the nitration of nitrobenzene, 117°. Furthermore, on reduction and acetylation of the *o*-dinitrobenzene, there was obtained *o*-diacetaminobenzene (m.p. and mixture m.p. 186°). A small amount of *m*-nitrophenylmercuric chloride was usually obtained as a residue on the filter paper.

The displacement of a *m*-chloromercuric group by a nitro group was rather difficult and necessitated more prolonged heating or more concentrated nitric acid.

Mercuric ion-catalyzed nitration of nitrobenzene. A mixture of nitrobenzene (2.5 g.), conc'd nitric acid (40 ml.), and mercuric oxide (5 g.) was heated with stirring at 95° for 10 hours. The mixture was diluted with water, and the precipitate was filtered and submitted to steam-distillation. After a small amount of unreacted nitrobenzene had been distilled off, the residue soon solidified on cooling. After washing with water and drying, the crude product weighed 2.8 g. The product was dissolved in hot conc'd nitric acid and after cooling the deposited crystals were filtered, washed with a small amount of conc'd nitric acid, then thoroughly with water, and dried, to give light-yellow needles. The yield was 0.62 g. of the substance with m.p. 115°. The filtrate was poured into a large volume of water, and the precipitate was filtered, dried, and crystallized from dry methanol. As a first crop, *m*-dinitrobenzene (0.81 g., 23.7%) was separated, which on further recrystallization from aqueous methanol, gave 0.61 g. of pure material melting at 91°. The dry methanolic mother liquor was again diluted with water, and the precipitate was crystallized from conc'd nitric acid as described above to afford another crop (0.27 g.) of *o*-dinitrobenzene. The total yield of the collected crops was 0.89 g. (26.1%). On recrystallization from aqueous methanol the melting point was raised to 117.5°.

The use of a higher concentration of nitric acid gave a *meta*-nitro product according to the normal orientation rule, and the use of lower concentration resulted in the preferential production of the intermediate nitrophenylmercuric nitrates. Longer reaction times did not raise the yield.

---

(1) Ogata and Tsuchida, *J. Org. Chem.*, **20**, 1637 (1956).

(2) Starkey, *Org. Syntheses*, Coll. Vol. **2**, 225 (1943).

(3) Hanke, *J. Am. Chem. Soc.*, **45**, 1321 (1923).

(4) Dimroth, *Ber.*, **35**, 2032 (1902).

An experiment with a smaller amount of nitrobenzene, in order to omit the steam-distillation process, gave the high yield based on nitrobenzene, but the mercuric salt was less effectively used. The use of the larger quantity of nitrobenzene is recommended.

Nitration of nitrobenzene without a mercuric salt. Nitration did not take place under the same conditions unless the mercuric salt was added. Even if more conc'd nitric acid was employed, there was obtained only a poor yield (2.8%) of *o*-dinitrobenzene, although the *meta* isomer was obtained in a considerable amount (67%).

Other attempts to convert some aromatic mercuric salts into the corresponding nitro derivatives. The nitration of the mercuric salts of 9-fluorenone or α-nitronaphthalene gave a mixture of isomeric mono- and poly-nitro compounds, no predominant formation of *ortho* substitution being observed. With pyridine and *m*-dinitrobenzene, no appreciable amount of nitro compound was obtained. Benzoic acid and methyl benzoate afforded considerable amounts of oxynitro compounds as well as the *meta*-nitro compounds. Benzophenone and diphenyl sulfone produced a large amount of unidentifiable resinous material and no isolable amount of *ortho*-nitro compound was obtained. With benzenesulfonic acid, α-naphthalenesulfonic acid, and *p*-chloronitrobenzene, the abnormal orienting effect of mercuric salt could not be observed.

Acknowledgments. The authors are indebted to Mr. Y. Takagi for his assistance in performing some of the experiments.

KYOTO, JAPAN