*3, 4-Benzotropolone and Related Compounds. III*1). *Nitration of 3, 4-Benzotropolone**

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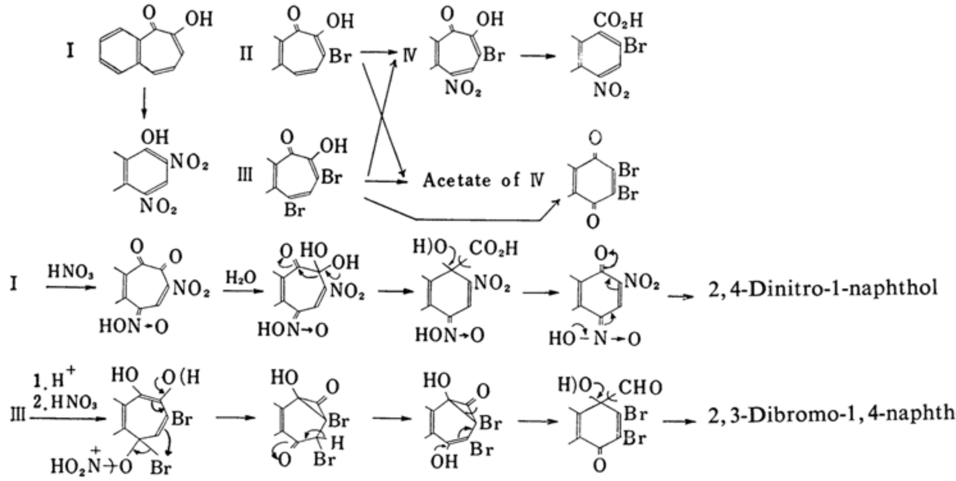
It has been reported that 3, 4-benzotropolone (I) can be nitrated to produce dinitro-3, 4-benzotropolone2). This nitration will now be re-examined.

Nitration of I with nitric acid in an acetic acid solution unexpectedly produced 2, 4-dinitro-1-naphthol, which was identified by mixed melting point determination and further by infrared-spectral agreement with an authentic sample3). No nitro derivative of I was isolated from the nitration product. I gave the same product in a lower yield even when one molar equivalent of nitric acid was employed. This transformation may be represented by the scheme described below. A similar type of ring contraction has been observed in the iodination of tropolone with sodium hypoiodite to produce 2, 4, 6-triiodophenol4).

7-Bromo-3, 4-benzotropolone (II) was nitrated in an acetic acid solution to yield 5-nitro-7-bromo-3, 4-benzotropolone (IV). Since IV was highly susceptible to resinification during nitration, it was collected by filtration as soon as the reaction was completed. The yield of IV was somewhat improved when the reaction mixture was poured into a sodium bicarbonate solution before the filtration of the product. IV showed a brown coloration with ferric chloride, gave methyl ether and underwent rearrangement with alkali into 2-bromo-4-nitro-1-naphthoic acid. This behavior is characteristic of nitrotropolones. Nitration of II in acetic anhydride afforded the acetate of IV, which was hydrolyzed and then methylated to give the same methyl ether of IV as was obtained above. It has been known that monocyclic tropolones resist nitration in a concentrated sulfuric acid solution owing to the formation of a tropolonium (dihydroxytropylium) cation5). Nevertheless, II was successfully nitrated in concentrated sulfuric acid to afford IV. This fact indicates that II is less basic than monocyclic tropolones presumably because the condensed benzene ring restricts the resonance of the tropolone ring. III, although its tropolone ring is blocked by



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1) Part II: This Bulletin, **35**, 117 (1962).

2) T. Nozoe, Y. Kitahara and T. Ando, *Proc. Japan Acad.*, **27**, 107 (1951).

3) F. Bender, *Ber.*, **22**, 996 (1889).

4) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **73**, 828 (1951); J. W. Cook, A. R. Gibb and R. A. Raphael, *J. Chem. Soc.*, **1951**, 2244. Formation of 6-quinolinol derivative by bromination of 8-isopropylpyrido(3,2-d)-tropolone has been reportrd by K. Yamane, 13th Annual Meeting of Chem. Soc. Japan, 1960.

5) T. Nozoe, *Proc. Japan Acad.*, **26** (9), 32 (1950); J. W. Cook, J. D. Loudon and D. K. V. Steel, *J. Chem. Soc.*, **1954**, 530.

bromo substituents, reacted with nitric acid in an acetic acid solution in such a manner that one of its two bromine atoms was replaced by a nitro group to yield IV. Similarly, nitration of III in acetic anhydride gave the acetate of IV. The nitration of III in concentrated sulfuric acid did not take place at room temperature, but was effected at 100°C, resulting in the unexpected formation of 2, 3-dibromo-1, 4-naphthoquinone, which showed no melting point depression on admixture with an authentic sample⁶⁾. Under the same conditions, 5, 7-dichloro-3, 4-benzotropolone was also transformed into 2, 3-dichloro-1, 4-naphthoquinone which was identical with an authentic sample⁷⁾. This reaction may include oxidation with nitric acid followed by migration of bromine atom, as described above. Treatment of II and III with nitric acid under more drastic conditions gave phthalic acid. In all nitrations mentioned above, the condensed benzene ring remained not nitrated.

Experimental

2, 4-Dinitro-1-naphthol from 3, 4-Benzotropolone (I).—To an ice-cooled solution of 200 mg. of I in 0.5 ml. of acetic acid was added 0.18 ml. (2 mol. equiv.) of concentrated nitric acid diluted with an equal volume of acetic acid. After standing for 10 min. with ice-cooling, the solution was diluted with 1 ml. of water to produce a precipitate. This was collected, washed with a small amount of cold methanol in order to remove a resinous material and then recrystallized from methanol to give 70 mg. (26%) of greenish yellow prisms of the dinitronaphthol, m. p. 137.5∼138°C (decomposed at 140°C with effervescence), the melting point of which was undepressed on admixture with an authentic sample³⁾ prepared by the nitration of α-naphthol. (Found: C, 51.34; H, 2.60; N, 11.83. Calcd. for $C_{10}H_6O_5N_2$: C, 51.29; H, 2.58; N, 11.96%.)

5-Nitro-7-bromo-3, 4-benzotropolone (IV). —*a) Nitration of 7-Bromo-3,4-benzotropolone (II).—In Acetic Acid:* To a mixture of 0.085 ml. (0.95 mol. equiv.) of concentrated nitric acid and 0.9 ml. of acetic acid was added 300 mg. of II. On stirring at room temperature, the suspension went into solution in a few minutes and then in an additional several minutes there separated out a crystalline powder (140 mg.), which was collected by filtration. On dilution with water, the filtrate gave a further crop of the product (10 mg.) which was also collected. The combined products were washed with a small amount of methanol to remove a resinous material and recrystallized from methanol to afford 110 mg. (30%) of IV as yellow scales decomposing at 161°C with effervescence. On rapid heating, the decomposition point was raised to 167°C. The mother liquor gave 30 mg. of unchanged material.

In another experiment, soon after the nitration had been completed, the reaction mixture was poured into a saturated sodium bicarbonate solution; the product was then collected and recrystallized from methanol to give 140 mg. (40%) of IV. λ(MeOH), mμ(log ε): 215(4.19), 268(3.92), 485 (4.20).

Found: C, 44.63; H, 2.33; N, 4.88. Calcd. for $C_{11}H_6O_4NBr$: C, 44.62; H, 2.04; N, 4.73%.

In Concentrated Sulfuric Acid: A mixture of 0.085 ml. (0.95 mol. equiv.) of concentrated nitric acid and an equal volume of concentrated sulfuric acid was added to 300 mg. of II dissolved in 1.5 ml. of concentrated sulfuric acid, and the solution was left aside for 10 min. at room temperature. On pouring it on crushed ice, a resinous product separated, which was collected and washed with 2 ml. of methanol, leaving a crystalline mass. Recrystallization from methanol afforded 105 mg. (29%) of IV decomposing at 160°C, as well as 65 mg. of unchanged material.

The nitration in concentrated sulfuric acid at 100°C resulted in resinification of a greater part of II besides the recovery of a minute amount of unchanged material.

b) Nitration of 5,7-Dibromo-3,4-benzotropolone (III).—A 300-mg. sample of III was treated with a mixture of 0.068 ml. (1 mol. equiv.) of concentrated nitric acid and 0.6 ml. of acetic acid in the same manner as above, affording IV in a lower yield (45 mg., 16%).

Attempted nitration of III in concentrated sulfuric acid at room temperature resulted in the recovery of unchanged material.

The nitration products of II and III obtained above proved to be the same from mixed melting point determination of their methyl ethers.

The Methyl Ether of IV.—Yellow prisms from dilute methanol, m. p. 146.5°C.

Found: C, 46.47; H, 2.81; N, 4.85. Calcd. for $C_{12}H_8O_4NBr$: C, 46.48; H, 2.60; N, 4.52%.

The p-Toluidine Salt of IV.—A red crystalline powder which darkened at 124°C and decomposed at 161°C with effervescence.

Found: C, 53.98; H, 3.98; N, 7.27. Calcd. for $C_{11}H_6O_4NBr\cdot C_7H_9N$: C, 53.62; H, 3.75; N, 6.95%.

The Acetate of IV.—*Nitration of II in Acetic Anhydride.*—A mixture of 0.085 ml. (0.95 mol. equiv.) of concentrated nitric acid and 0.34 ml. of acetic anhydride was added to 300 mg. of II suspended in 1.5 ml. of acetic anhydride. The suspension was warmed for a while until it went into solution. The acetic anhydride was decomposed with ice, and the product was then collected, washed with a small amount of methanol and recrystallized from methanol to afford 110 mg. (27%) of the acetate of IV as yellow prisms decomposing at 164°C with effervescence.

Found: C, 46.40; H, 2.22; N, 3.92. Calcd. for $C_{13}H_8O_5NBr$: C, 46.18; H, 2.39; N, 4.14%.

Nitration of III in Acetic Anhydride.—A suspension of 200 mg. of III in acetic anhydride was treated with a mixture of 0.046 ml. of concentrated nitric acid and 0.18 ml. of acetic anhydride in the same manner as above, affording 35 mg. (18%) of the acetate of IV.

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6) C. Liebermann and S. Schlossberg, *Ber.*, **32**, 2097 (1899).

7) J. B. Conant and L. F. Fieser, *J. Am. Chem. Soc.*, **46**, 1873 (1924).

The acetate of IV obtained above was hydrolyzed by refluxing its methanolic solution in the presence of a few drops of concentrated hydrochloric acid, the product was treated with ethereal diazomethane to yield the methyl ether of IV.

2-Bromo-4-nitro-1-naphthoic Acid from IV.—A 100-mg. sample of IV was dissolved in 5 ml. of 2 N potassium hydroxide, and the solution was allowed to stand for 10 min. at room temperature. Acidification of the solution with hydrochloric acid and recrystallization of the product from methanol gave 80 mg. (80%) of yellow, granular crystals, m. p. 190°C. λ(MeOH), mμ(log ε): 220(4.76), 255(4.24), 285(3.67), 320(3.68), 340(3.80).

Found: C, 44.77; H, 2.01; N, 4.79. Calcd. for $C_{11}H_6O_4NBr$: C, 44.62; H, 2.04; N, 4.73%.

Formation of 2, 3-Dibromo-1, 4-naphthoquinone from 5, 7-Dibromo-3, 4-benzotropolone (III).—To a solution of 200 mg. of III in 1 ml. of concentrated sulfuric acid was added a mixture of 0.046 ml. (1 mol. equiv.) of concentrated nitric acid and 0.4 ml. of concentrated sulfuric acid. The solution was heated at 100°C for 10 min. and then poured on ice, producing a resinous product. Recrystallization of the product from methanol afforded 55 mg. (29%) of deep yellow needles of the dibromonaphthoquinone, m. p. 218°C, the melting point of which was undepressed on admixture with an authentic sample⁶⁾. (Found: C, 37.77; H, 1.56%. Calcd. for $C_{10}H_4O_2Br_2$: C, 38.01; H, 1.28%.) Unchanged material (65 mg.) was also recovered.

2, 3-Dichloro-1, 4-naphthoquinone from 5, 7-Dichloro-3, 4-benzotropolone.—A similar treatment of 100 mg. of 5, 7-dichloro-3, 4-benzotropolone with 0.032 ml. (1 mol. equiv.) of concentrated nitric acid in concentrated sulfuric acid gave 15 mg. (16%) of yellow needles of the dichloronaphthoquinone, m. p. 195~196°C, identified by mixed melting point determination with an authentic sample⁷⁾, besides 25 mg. of unchanged material.

Oxidation of III with Nitric Acid.—A 200-mg. sample of III was heated with 0.5 ml. of concentrated nitric acid at 100°C for 10 hr. The product which separated on cooling was collected and recrystallized from water to yield 40 mg. of phthalic acid, m. p. and mixed m. p. 200~201°C (decomp.).

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