rotation and analysis was dried *in vacuo* over phosphorus pentoxide at 100°. This salt melted at 170–180°.

Rotation. 0.5000 g. made up to 5 cc. in methyl alcohol gave α_D, 2.86°; $l = 2$; $[\alpha]^{25}_D$ 14.3°.

Anal. Calcd. for $C_{24}H_{30}O_4N_2Br_2S$: N, 4.65; Br, 26.54; S, 5.32. Found: N, 4.54; Br, 26.18; S, 5.11.

Fraction 4 was the impure salt of the *l*-amine and was not purified further.

Impure salt of *l*-amine: *Rotation.* 0.1804 g. made up to 5 cc. in methanol at 20° gave α_D −1.12; $l = 2$; $[\alpha]^{25}_D$ −15.5°. On standing for fifty hrs., $[\alpha]^{25}_D$ −6.5°.

***d*-2,6-Dibromo-3,3′-diamino-4,4′-ditolyl.**—The pure salt was dissolved in the minimum amount of cold methyl alcohol and immediately poured into ice water containing an excess of aqueous ammonia. The precipitate was filtered and dried in a vacuum desiccator at room temperature. It melted at the same temperature as the racemic base, due, probably, to racemization before melting.

The mutarotation of the *d*-amine salt and the racemization of the free amine are given in Table II.

Summary

A 2,6-disubstituted diphenyl, 2,6-dibromo-3,3′-diamino-4,4′-ditolyl has been prepared and resolved.

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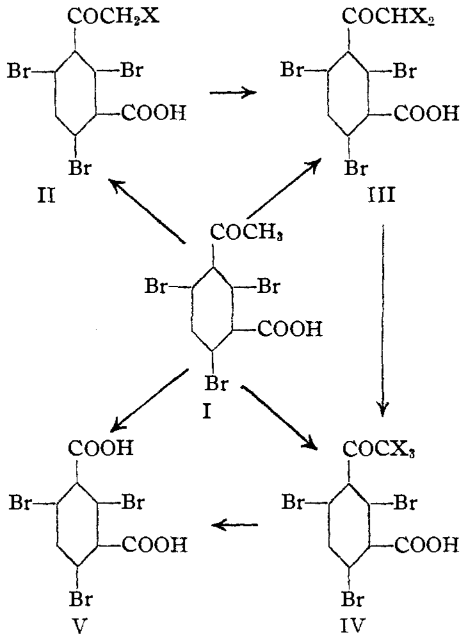
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Haloform Reaction. XV. Stepwise Halogenation

BY BENTON A. BULL, WM. E. ROSS AND REYNOLD C. FUSON

The mechanism of the haloform reaction has long been assumed to involve stepwise halogenation followed by chain cleavage of the trihalomethyl derivatives to a haloform and a salt. Because of the rapidity with which the reaction takes place it is extremely difficult to demonstrate the formation of intermediate derivatives. We have found that the introduction of steric hindrance diminishes the rate of the process and, by this means, it has been possible in a number of cases to interrupt the reaction at the last stage,[1] *i. e.*, to isolate the trihalomethyl ketones. In a single instance—one in which the hindrance was due to the presence of halogen atoms ortho to the ketone group—we were able to isolate a monohalomethyl derivative.[2] Subsequently, we have found that ketones which are soluble in alkali react in a manner better adapted for a study of the mechanism.[1] By incorporating both of these desirable features in a single molecule we have been able, in the present work, to interrupt the haloform reaction at each of the stages postulated above.

The compound in question is 2,4,6-tribromo-3-acetylbenzoic acid (I). It was prepared from the corresponding nitrile.[3] When treated for fifteen minutes with cold sodium hypobromite solution this acid was converted into 2,4,6-tribromo-3-monobromoacetylbenzoic acid (II, X = Br). Treatment of one hour's duration converted this compound as well as the original acid (I) into 2,4,6-tribromo-3-dibromoacetylbenzoic acid (III, X = Br). Each of these three compounds could, in turn, be converted into 2,4,6-tribromo-3-tribromoacetylbenzoic acid (IV, X = Br) by extending the time of treatment to twenty-four hours.



The keto-acid (I) was treated in a similar manner with cold sodium hypochlorite solution, but the monochloroacetyl derivative could not be isolated; in five minutes the dichloroacetyl derivative (III, X = Cl) had formed. Both this compound and I were converted into the corre-

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[1] See Johnson and Fuson, THIS JOURNAL, **56**, 1417 (1934), and preceding papers of this series.

[2] Fuson, Bertetti and Ross, *ibid.*, **54**, 4380 (1932).

[3] Fuson, Lewis and DuPuis, *ibid.*, **54**, 1119 (1932).

sponding trichloroacetyl derivative (IV, X = Cl) by treatment for one hour.

The trihalomethyl ketones (IV) are sufficiently stable to be recovered unchanged from cold solutions of alkali, but, at higher temperatures, are rapidly converted to 2,4,6-tribromoisophthalic acid (V). The monobromoacetyl (II, X = Br) and the dihaloacetyl (III) derivatives were also converted into the dibasic acid by treatment with warm solutions of hypohalites.

Experimental

2,4,6 - Tribromo - 3 - acetylbenzonitrile.—This compound was prepared in yields of 35% of the theoretical amount by a slight modification of the original procedure of Fuson, Lewis and DuPuis.[3] The amine was more satisfactorily diazotized in glacial acetic acid, according to the method of Montagne.[4] It was then poured into a great excess of cuprous cyanide.

2,4,6-Tribromo-3-acetylbenzoic Acid (I).—Five grams of the nitrile was refluxed for three hours with a mixture of two parts concentrated sulfuric acid, one part water, and one part glacial acetic acid—all by volume. The reaction mixture was then cooled to 10° and the calculated amount of sodium nitrite, dissolved in the minimum amount of water, was run in, with stirring, beneath the surface of the liquid. The mixture was warmed until all the nitrogen was evolved, and was then poured into water and filtered. Light tan crystals were obtained by recrystallizing from methyl alcohol or chloroform–petroleum ether; m. p. 192–193° (decomp.).

Anal. Calcd. for $C_9H_5O_3Br_3$: Br, 60.0. Found: Br, 60.0.

2,4,6-Tribromo-3-monobromoacetylbenzoic Acid (II, X = Br).—One-half gram of I was dissolved in ice-cold 10% sodium hydroxide solution and treated for fifteen minutes with ice-cold 10% sodium hypobromite solution. The mixture was then treated with cold sodium bisulfite, acidified, and the product extracted with ether, from which it was precipitated with low-boiling petroleum ether. The white crystalline compound melted at 178–179° (decomp.).

Anal. Calcd. for $C_9H_4O_3Br_4$: Br, 66.6. Found: Br, 66.5, 66.6.

2,4,6-Tribromo-3-dibromoacetylbenzoic Acid (III, X = Br).—One-half gram of I was treated as above for one hour at 0°. The white crystalline product obtained from chloroform and low-boiling petroleum ether melted at 187–188° (decomp.).

Anal. Calcd. for $C_9H_3O_3Br_5$: Br, 71.6. Found: Br, 71.7.

The dibromoacetyl compound was also obtained from the monobromoacetyl compound (II, X = Br) by treating the latter with ice-cold hypobromite for one hour. The dibromoacetyl compound was recovered unchanged after standing overnight in 10% alkali.

2,4,6-Tribromo-3-tribromoacetylbenzoic Acid (IV, X = Br).—Twenty-five hundredths gram of I was stirred for twenty-five hours with ice-cold hypobromite solution. The product obtained upon acidification was recrystallized from an ether–petroleum ether mixture; m. p. 196° (decomp.).

Anal. Calcd. for $C_9H_2O_3Br_6$: Br, 75.2. *Found:* Br, 75.3.

The tribromoacetyl compound was also obtained from both the monobromoacetyl (II, X = Br) and the dibromoacetyl (II, X = Br) compounds by treatment with cold hypobromite solutions for twenty-four hours.

The tribromoacetyl compound was recovered unchanged after standing for five minutes in ice-cold dilute alkali.

2,4,6-Tribromo-3-dichloroacetylbenzoic Acid (III, X = Cl).—Twenty-five hundredths gram of I was treated with cold 20% hypochlorite solution for five minutes. The product obtained upon acidification was recrystallized from ether–petroleum ether; m. p. 180–181° (decomp.).

Anal. Calcd. for $C_9H_3O_3Br_3Cl_2$: mg. AgX per mg. subs., 1.81. Found: 1.78.

2,4,6-Tribromo-3-trichloroacetylbenzoic Acid (IV, X = Cl).—Twenty-five hundredths gram of I was treated with 10% cold hypochlorite solution for one hour. The compound was recrystallized from chloroform–petroleum ether mixture; m. p. 182–183° (decomp.).

Anal. Calcd. for $C_9H_2O_3Br_3Cl_3$: mg. AgX per mg. subs., 1.98. Found: 1.96.

The trichloroacetyl compound was recovered unchanged after standing for five minutes in ice-cold dilute alkali.

2,4,6-Tribromo-isophthalic Acid (V).—One-half gram of I was warmed for one-half hour with alkaline hypobromite solution. Acidification precipitated the dibasic acid which was recrystallized from chloroform–petroleum ether mixture; m. p. 275–277°.

Anal. Calcd. for $C_8H_3O_4Br_3$: Br, 59.6. Found: Br, 59.6.

The monohaloacetyl (II), and the dihaloacetyl (III) compounds also gave the dibasic acid when warmed with hypohalites. The trihaloacetyl compounds (IV) gave the dibasic acid when warmed with alkali.

Summary

An example of the haloform reaction has been discovered in which it has been possible to isolate successively the mono-, di- and trihalomethyl ketones ordinarily postulated as intermediates.

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[4] Montagne, *Rec. trav. chim.*, **21**, 384 (1902).