The intermediate compound, α-nitrosoanisyl chloride, was treated with hot sodium carbonate solution. The material liquefied and then partially solidified. Upon separating the product and recrystallizing it from alcohol it was identified as the di-(*p*-methoxyphenyl)-furazane oxide by mixed melting point. Anisohydroxamyl chloride when treated in a similar way gave identical results.

Summary

Stereoisomeric anisohydroxamyl chlorides were not obtained by chlorinating the anisaldoximes either with chlorine gas or with nitrosyl chloride. In the latter reaction an unstable nitroso intermediate was isolated and studied. By chlorinating with an excess of chlorine, *m*-chloro and *m,m'*-dichloroanisohydroxamyl chlorides were prepared.

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The Cleavage of Carbonyl Compounds by Alkalies. X. Trihalomethylketonic Acids[1]

BY BENTON A. BULL AND REYNOLD C. FUSON

In the preparation and cleavage of the hindered trihalomethyl ketones previously reported, the question has arisen as to whether the insolubility of these compounds in the aqueous solutions used might not have an important influence on the rates at which the reactions proceed. The use of alcohol and pyridine as solvents has disclosed some evidence which supports this point of view.[2] In order to subject this idea to a crucial test, 3,5-dimethyl-4-acetylbenzoic acid (V) has been synthesized and studied. Since this compound and the trihalomethylketonic acids derived from it are soluble in aqueous alkalies, the insolubility factor is eliminated.

As the starting point for the synthesis of the ketonic acid, dimethylterephthalic acid (I)[3] was used. Esterification with methanol gave the half ester (II), which was then converted into the corresponding acid chloride (III) by the action of thionyl chloride. Treatment with methylzinc iodide, followed by hydrolysis, transformed the acid chloride into the desired keto acid (V).

3,5-Dimethyl-4-acetylbenzoic acid when dissolved in solutions of sodium hypochlorite and sodium hypobromite gave, respectively, 3,5-dimethyl-4-trichloroacetylbenzoic acid (VI) and 3,5-dimethyl-4-tribromoacetylbenzoic acid (VII). This synthesis of these trihalomethylketonic acids *in alkaline solution* demonstrates that they are moderately stable toward alkalies. Moreover, when dissolved in sodium hydroxide solutions at 0° they could

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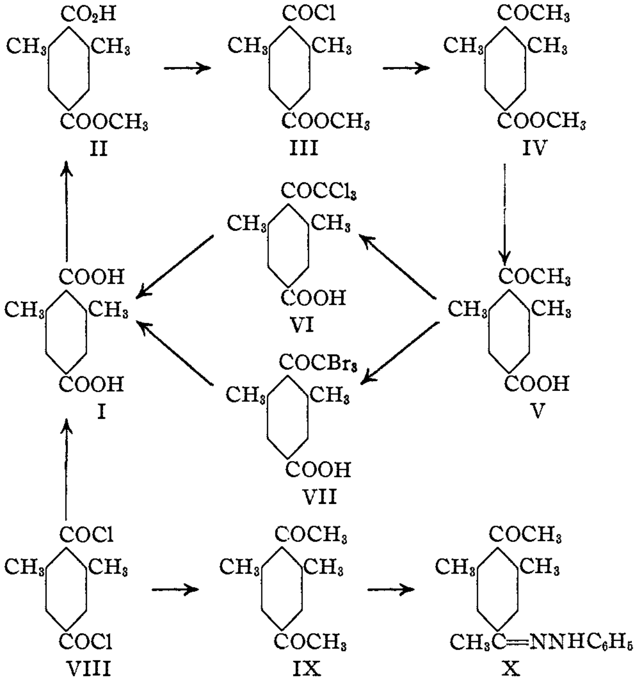
(1) Eighth paper on the haloform reaction. For references to previous articles see Fuson, Bertetti and Ross, THIS JOURNAL, **54**, 4380 (1932).

(2) Fuson, Lewis and Du Puis, *ibid.*, **54**, 1114 (1932).

(3) Noyes, *Am. Chem. J.*, **20**, 809 (1898); Hufferd and Noyes, THIS JOURNAL, **43**, 928 (1921).

be recovered undecomposed. However, if these solutions were allowed to stand or were heated the trihalomethylketonic acids underwent cleavage to give dimethylterephthalic acid.

An attempt was also made to prepare the tribromo compound (VII) by the action of sodium hypobromite on 2,6-dimethyl-*p*-diacetylbenzene (IX). The diketone was obtained from the acid chloride (VIII) of dimethylterephthalic acid by treatment with methylzinc iodide. The identity of the diketone was confirmed by the preparation of the phenylhydrazone (X). This method of preparing the trihalomethylketonic acid gave a very impure product, and was abandoned in favor of the one first described.



The foregoing results make it certain that the stability of hindered trihalomethyl ketones toward aqueous alkali can be due at most only in part to the insolubility of these compounds in water. Obviously, the principal factor responsible for the unusual stability of these compounds is the hindrance offered by the ortho substituents.

Experimental

2,6-Dimethyl-4-carbomethoxybenzoic Acid (II).—The method of Noyes[3] gave the acid ester in nearly the theoretical amounts. The crude ester, melting at 168–175°, was used without further purification.[4]

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[4] Noyes gives the melting point of the pure compound as 189–190°. The yields were, however, not improved by the use of the purified ester.

2,6-Dimethyl-4-carbomethoxybenzoyl Chloride (III).—Seventy grams of the acid ester (II) was placed in a 500-cc. flask and 500 g. of thionyl chloride was added slowly through a dropping funnel. The resulting mixture was heated under reflux for an hour and was then allowed to stand overnight at room temperature. The excess thionyl chloride was removed by distillation at atmospheric pressure and the residual oil was distilled under diminished pressure. The pure chloride boiled at 147–150° at 8 mm.; the yield was 59 g., or 78% of the theoretical amount.

Anal. Calcd. for $C_{11}H_{11}O_3Cl$: Cl, 15.7. Found: Cl, 15.6.

3,5-Dimethyl-4-acetylbenzoic Acid (V).—Ten grams of the acid chloride (III) in 50 cc. of dry toluene was added dropwise to 40 cc. of an approximately 4 molal methylzinc iodide solution contained in a 200-cc. three-necked flask surrounded by an ice-bath. The ice-bath was then removed and the reaction mixture was allowed to stand for two weeks. A few cubic centimeters of water was then added cautiously to decompose the excess methylzinc iodide. The resulting basic zinc salts were dissolved by the addition of 50 cc. of dilute sulfuric acid. The toluene layer was separated, shaken with ammonium hydroxide solution and then with a solution of sodium bicarbonate containing some sodium thiosulfate. The toluene layer was dried over sodium sulfate and the toluene was removed by distillation. The residue was heated under reflux for two hours with 50 cc. of a 10% solution of sodium hydroxide. The cold alkaline solution was shaken twice with ether and then acidified with dilute sulfuric acid. The product was decolorized by treatment with norite and was then freed from the dimethylterephthalic acid by repeated recrystallization from alcohol. A final recrystallization from water gave the keto acid in the form of colorless needles melting at 160–161°. The yield was 2 g., or 24% of the theoretical amount.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.7; H, 6.3. Found: C, 68.5; H, 6.3.

3,5-Dimethyl-4-trichloroacetylbenzoic Acid (VI).—One-half gram of 2,6-dimethyl-4-acetylbenzoic acid was dissolved in a few cubic centimeters of 10% sodium hydroxide solution at 0° and an excess of cold 10% sodium hypochlorite solution was added. Within ten minutes a precipitate formed. This was removed by filtration and treated with dilute sulfuric acid. The product obtained in this way was recrystallized several times from methanol; it then separated in the form of colorless needles melting at 165–166°.

Anal. Calcd. for $C_{11}H_9O_3Cl_3$: C, 44.70; H, 3.1; Cl, 36.02. Found: C, 44.76; H, 3.4; Cl, 36.25.

The trichloromethylketonic acid was dissolved in a 5% solution of sodium hydroxide at 0° and the mixture was allowed to stand at this temperature for five minutes. It was then filtered and the filtrate was immediately acidified with dilute sulfuric acid. The finely divided precipitate which separated was collected on a filter, washed with water and dried on a clay plate. It gave a positive Beilstein test and melted at 156–160°. A mixture of this material with the original trichloro compound melted at 157–161°.

A similar treatment of the trichloro compound with alkali was carried out at room temperature. At the end of ten minutes it was found that none of the halogen-containing compound could be recovered. The entire product in this case was 2,6-dimethylterephthalic acid melting at 293–295°. It was identified by means of a mixed melting point.

3,5-Dimethyl-4-tribromoacetylbenzoic Acid (VII).—One-half gram of 3,5-dimethyl-4-acetylbenzoic acid was dissolved in 5 cc. of a 10% solution of sodium hydroxide solution at 0° and an excess of cold 10% sodium hypobromite solution was added. Within ten minutes the mixture became colored and a colorless precipitate separated from the solution which had now a mauve color. The precipitate was collected on a filter, washed with a solution of sodium bisulfite and then treated with dilute sulfuric acid. The product after several recrystallizations from methanol was obtained in the form of colorless crystals melting at 161–162°.

Anal. Calcd. for $C_{11}H_9O_3Br_3$: C, 30.8; H, 2.1; Br, 55.93. Found: C, 30.7; H, 2.3; Br, 56.19.

The tribromomethylketonic acid was dissolved in an excess of 5% sodium hydroxide solution at 0°. The solution was allowed to stand for five minutes at this temperature. It was then filtered and the filtrate was acidified with dilute sulfuric acid. The precipitate obtained in this way melted with decomposition at 154–156°. A mixture of this product and the starting material melted at 155–158°.

A similar experiment carried out at room temperature showed that after ten hours the cleavage was incomplete. In this case the recovered material melted at 197–205°. Pure dimethylphthalic acid was obtained by recrystallization of this sample from water.

2,6-Dimethyl-1,4-diacetylbenzene (IX).—The method of preparation of this diketone was similar to that used by Berend and Herms[5] for *p*-diacetylbenzene. To 26 g. of 2,6-dimethylterephthalic acid were added 60 g. of phosphorus oxychloride and 90 g. of phosphorus pentachloride. After the spontaneous reaction had moderated the mixture was heated on a steam-bath overnight. It was then filtered by means of a glass wool plug and the phosphorus oxychloride was distilled at atmospheric pressure. The residue was distilled under diminished pressure; the fraction coming over at 124–138° at 20 mm. was collected. The acid chloride was obtained in a yield of 75% of the theoretical amount. It was used without further purification.

A solution of 30 g. of the acid chloride in 50 cc. of dry toluene was added dropwise to an excess of methylzinc iodide. The mixture was stirred for twenty-four hours. The toluene layer was then treated successively with solutions of sulfuric acid, ammonium hydroxide, sodium bicarbonate and sodium thiosulfate. It was dried and distilled; the fraction collected at 165–175° solidified and was recrystallized from low-boiling petroleum ether. The pure diketone was colorless and melted at 61.5–62°. The yield was 5.5 g.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.37. Found: C, 75.7; H, 7.52.

Phenylhydrazone.—This derivative after recrystallization from aqueous alcohol melted at 154–156°.

Anal. Calcd. for $C_{18}H_{20}ON_2$: N, 10.0. Found: N, 10.3.

The diketone reacted with sodium hypobromite to give dimethylterephthalic acid and carbon tetrabromide but the desired 3,5-dimethyl-4-tribromoacetylbenzoic acid was not obtained in pure form by this method.

Summary

3,5-Dimethyl-4-acetylbenzoic acid has been synthesized and treated with solutions of hypochlorite and hypobromite. In this way the corresponding trichloromethyl- and tribromomethylketonic acids have been prepared.

The trihalomethylketonic acids have been shown to be moderately stable to solutions of alkali at 0°. At higher temperatures they undergo cleavage to form 2,6-dimethylterephthalic acid.

These results have been interpreted to mean that the unusual stability of hindered trihalomethyl ketones to aqueous alkalies is due primarily to the

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(5) Berend and Herms, *J. prakt. Chem.*, [2] **74**, 123 (1906).

hindrance involved and only in part to the insolubility of the ketones in the aqueous solutions used.

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The Dehydration of Capryl Alcohol

BY FRANK C. WHITMORE AND JOHN M. HERNDON[1]

In a recent paper[2] it is reported that octanol-2 was "transformed by elimination of water into octene." Following the same procedure octanol-1 was dehydrated and in describing the product it is stated that "it is to be expected that this is octene-1." The results showed "that the two octene preparations notwithstanding the great difference between the starting materials had practically the same characteristics. Further, the unsaturation of both preparations approaches the theoretical value." Because of the present interest in molecular rearrangements in this Laboratory[3] and in view of some related work on the dehydration of capryl alcohol, this paper is presented. Highly purified capryl alcohol (octanol-2) has been dehydrated and the resulting products have been ozonized with the conclusion that they consist of octene-2 and octene-1, the former predominating. Octene-1 has been prepared and purified. From the constants of octene-1 and octene-2[4] it appears that the material obtained by Waterman and teNuyl from octanol-1 was a mixture of octene-2 and octene-1 rather than pure octene-1.

Experimental

Purification of Capryl Alcohol.—This alcohol was purified by careful distillation through an adiabatic packed column,[5] 8.3 meters high and 7.6 cm. in diameter.

Physical constants of pure octanol-2: b. p. 177.3° (731 mm.) (Cottrell): n_D^{20} 1.4260; d_4^{20} 0.817. This material gave no precipitate with sodium bisulfite solution even on long standing.

Dehydration of Capryl Alcohol.—In a 3-liter flask, provided with a 25 × 2 cm. packed column[6] of the total condensation, adjustable take-off type, was placed 250 cc. of phosphoric acid (sp. gr. 1.7). The flask was heated in an oil-bath to 235°. Five moles (650 g.) of the pure capryl alcohol was added dropwise. The water and olefin were distilled through the column and collected during four hours. The oily layer, carefully separated from the aqueous portion of the distillate, was fractionated through

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[1] Presented in partial fulfilment of the requirements for the Ph.D. degree.

[2] Waterman and teNuyl, *Rec. trav. chim.*, **51**, 533 (1932).

[3] See THIS JOURNAL, **54**, 3279 (1932).

[4] Constants for octene-2 kindly given by C. E. Boord.

[5] The construction and operation of this column have been described in detail by Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932). The capryl alcohol was supplied by the Rohm and Haas Co. of Philadelphia, Pa.

[6] See THIS JOURNAL, **54**, 3451 (1932).