nitrile with the exception of the *o*-nitro derivative, which gave considerable nitrile even at 0°. At 97–100°, the yields of nitrile were higher than those obtained at 30°, and in several cases even greater than those of oxime. As with the acetyl derivatives, the elimination reaction appears to have a higher temperature coefficient than the hydrolysis.

It should be pointed out that the yields of nitrile obtained from these carbethoxy derivatives are higher, and those of oxime correspondingly lower, than those obtained from the analogous acetyl-α-aldoximes under the same conditions.[1] Evidently, a carbethoxy-α-aldoxime eliminates the elements of acid to form nitrile more readily, and/or undergoes hydrolysis less rapidly, than the corresponding acetyl-α-derivatives.

In Table II are given the yields of products obtained from the reactions of potassium amide in liquid ammonia with certain carbethoxy-α-derivatives. It can be seen that high yields of nitrile and low yields of oxime were produced.

Summary

1. The relative yields of nitriles and oximes formed in the reactions of carbethoxy-α-benzaldoximes with sodium hydroxide are a function of the temperature.

2. Contrary to the previously accepted view, that certain carbethoxy derivatives of α-benzaldoximes have β-configurations, it has been shown that they are all of the α-type.

3. The carbethoxy-α-benzaldoximes with sodium hydroxide give higher yields of nitrile, and lower yields of oxime, than the corresponding acetyl-α-benzaldoximes.

DURHAM, N. C. RECEIVED SEPTEMBER 11, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Dehalogenation of β-Bromo Acids. IV. β-Bromophenylpyruvic Acid

BY BEN SOBIN AND G. BRYANT BACHMAN

In the present work an effort has been made to extend the β-bromo acid synthesis of olefin derivatives to the preparation of ketenes. It seemed probable from previous studies[1] that α-keto-β-bromo acids ought to dehalogenate predominantly as follows

$$\mathrm{RCHBrCOCOOH} \longrightarrow \mathrm{RCH{=}C{=}O + HBr + CO_2} \qquad (1)$$

in view of the strongly electronegative character of the α-carbonyl group. In order to test this hypothesis, β-bromophenylpyruvic acid was prepared and its dehalogenation studied under a variety of conditions.

The difficulty of selecting a suitable solvent and a suitable dehalogenating agent for the proposed study was immediately apparent, for no substance could be present at any time which would react with the ketene formed. This of course eliminated a good many common solvents and bases from consideration. At first sight, tertiary amines seemed ideally suited for the purpose both as solvents and as dehalogenating agents. When the reaction was tried, however, with pyridine and dimethylaniline the results were unsatisfactory. Carbon dioxide was evolved as expected but the products were tars which were apparently complex in nature and which contained no ketene.

An endeavor was next made to adapt the method to the synthesis of ketene derivatives. It was hoped that primary or secondary amines either in the presence or absence of other solvents would react to form substituted amides of phenylacetic acid. Here again, however, in addition to carbon dioxide only tars were obtained, and no evidence was found of the presence of simple ketene derivatives. Fortunately, we were able to secure decomposition in the desired manner by simply boiling the bromo acid with water. Carbon dioxide was evolved and phenylacetic acid in 77% yield was recovered from the solution. Furthermore, when an aqueous solution of the acid was shaken with silver oxide the same product was obtained in 94% yields. It is difficult to account for the product formed other than by assuming the intermediate formation of phenylketene which then reacted further with water to form phenylacetic acid.

$$\mathrm{C_6H_5CHBrCOCOOH} \longrightarrow \mathrm{C_6H_5CH{=}C{=}O + HBr + CO_2} \qquad (2)$$

$$\mathrm{C_6H_5CH{=}C{=}O + H_2O} \longrightarrow \mathrm{C_6H_5CH_2COOH} \qquad (3)$$

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(1) Bachman, THIS JOURNAL, **55**, 4279 (1933); Farrell and Bachman, *ibid.*, **57**, 1281 (1935); Alberts and Bachman, *ibid.*, **57**, 1284 (1935).

The above reactions are remarkably sensitive to increases in the hydroxyl-ion content of the solution. With sodium carbonate solution no phenylacetic acid was formed and the principal product consisted of benzoylcarbinol.

$$C_6H_5CHBrCOCOOH \xrightarrow{Na_2CO_3} C_6H_5CHOHCHO + CO_2 + HBr \quad (4)$$

$$C_6H_5CHOHCHO \longrightarrow C_6H_5COCH_2OH \quad (5)$$

The spontaneous rearrangement of mandelic aldehyde to benzoylcarbinol (5) has been previously pointed out by Nef[2] and by others. Evans[3] has shown that benzoylcarbinol undergoes further decomposition in the presence of alkalies to form benzoic acid. This substance was also identified in the reaction product and increased in amount at the expense of the benzoylcarbinol upon prolonged boiling of the reaction mixture.

With sodium bicarbonate which is intermediate in basicity between water and sodium carbonate a 40% yield each of phenylacetic acid and benzoylcarbinol was obtained and a new product as yet unidentified made its appearance in small amounts. It was a bright yellow solid, m. p. 218–219°, which qualitative tests showed to be an alpha hydroxy acid of high molecular weight. It was but slightly soluble in most organic solvents.

In view of the reaction of bromophenylpyruvic acid with water it was decided to attempt the preparation of the ethyl ester of phenylacetic acid by reaction with alcohol. Accordingly a solution of the bromo acid in ethyl alcohol was boiled until no more carbon dioxide was evolved. The product after distillation and saponification yielded a little benzoic acid but no phenylacetic acid. Better success was obtained when an alcoholic solution of the bromo acid was treated with a half molal portion of silver oxide. From the filtrate a 36% yield of ethyl phenylacetate was obtained by distillation.

Further efforts to adapt the dehalogenation of α-keto-β-bromoacids to the synthesis of ketenes and their derivatives are being made.

Experimental

Preparation of β-Bromophenylpyruvic Acid.—To 55 g. of phenylpyruvic acid[4] suspended in 750 cc. of carbon tetrachloride was added slowly with stirring 54 g. of bromine. The solid product was filtered and allowed to stand for two days at the end of which time no more hydrogen bromide was being evolved. The yield was practically quantitative and the product melted at 103–104°. Recrystallization from benzene gave fine yellow needles with the same melting point.

Anal. Calcd. for $C_9H_7O_3Br$: Br, 32.84. Found: Br, 32.84, 32.86.

Conversion of β-Bromophenylpyruvic Acid to Phenylacetic Acid.—Four grams ($^1/_{60}$ mole) of the bromo acid in 50 cc. of water was refluxed one-half hour and the filtered solution extracted with ether several times. The extract yielded 1.3 g. of a product which, after recrystallization from petroleum ether, melted at 76° and was confirmed as phenylacetic acid by a mixed melting point with an authentic sample; yield 77%.

In a similar experiment 2.0 g. of bromo acid dissolved in 50 cc. of water was shaken with 0.9 g. of silver oxide and finally warmed on the steam-bath. After removal of the silver bromide a 94% yield of phenylacetic acid was recovered from the filtrate.

Conversion of β-Bromophenylpyruvic Acid to Ethyl Phenylacetate.—To 24 g. of the bromo acid in 200 cc. of absolute alcohol was added portionwise 11.5 g. of silver oxide. At the end of the initial reaction the mixture was filtered and the filtrate distilled. There was obtained 6 g. (36% yield) of a product (b. p. 120–130° at 20 mm.) which upon saponification yielded phenylacetic acid.

Reaction of β-Bromophenylpyruvic Acid with Other Reagents.—With Aqueous Sodium Carbonate.—A solution of 24 g. of the bromo acid in 40 cc. of 25% sodium carbonate was refluxed for one-half hour. Upon cooling and extracting with ether 5.0 g. of benzoylcarbinol, m. p. 85°, was obtained. The identity of this substance was confirmed by oxidizing it to mandelic acid, m. p. 118°, with cupric acetate by the method of Evans.[3]

The alkaline solution from which the benzoylcarbinol had been extracted was then acidified with dilute hydrochloric acid, extracted with ether, and the ether evaporated. The thick oil which remained was extracted with petroleum ether. Evaporation of the petroleum ether left 3 g. of benzoic acid, m. p. 121°. The amide was also prepared for confirmation and melted at 128°.

With Aqueous Sodium Bicarbonate.—Four grams of the bromo acid was gradually added to 3.5 g. of sodium bicarbonate dissolved in 41 cc. of water, and allowed to stand overnight. Extraction of the alkaline solution with ether, and subsequent evaporation of the ether left 0.5 g. (40% theoretical) of benzoylcarbinol. The solution was then acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the ether left a yellow gummy solid. The solid was extracted with boiling petroleum ether for an hour, and yielded in this way 0.9 g. (40% theoretical) of phenylacetic acid. The yellow residue from the extraction was difficultly soluble in hot benzene, from which on cooling it crystallized as very fine yellow needles. When dry, the powder was found to be highly electrophoric, and to have a melting point of 218–219°. Qualitative tests showed it to be an acid. It gave a yellow color with ferric chloride indicating the presence of an hydroxyl group alpha to a carbonyl. An alcoholic solution decolorized bromine water and potassium permanganate solution. It did not give a phenylhydrazine test. However, it reacted with acetyl chloride to give a derivative melting at 162–163°. The neutralization equivalent was

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(2) Nef, *Ann.*, **355**, 247 (1907).

(3) Evans, THIS JOURNAL, **35**, 125 (1906).

(4) Hemmerlé, *Ann. chim.*, [9] **7**, 229 (1917).

found to be 181 and the molecular weight as determined by the melting point depression of naphthalene as 373. Evidently there were two carboxyl groups in the molecule. The compound was analyzed for carbon and hydrogen. *Anal.* C, 73.1, 73.3; H, 4.4, 4.4. From the carbon and hydrogen analysis and the molecular weight determination the molecular formula of the yellow compound was calculated to be most probably $C_{23}H_{16}O_5$.

With Nitrogen Bases.—Portions of the bromo acid were treated in turn with anhydrous pyridine, aniline, dimethylaniline and diethylamine. In all cases an evolution of carbon dioxide resulted, and considerable heat was evolved. All three amines gave tarry and gummy masses from which the reaction products could not be isolated. With aqueous ammonium hydroxide a dark brown solution was obtained which yielded a little benzoylcarbinol by extraction with ether. Upon acidification a tar precipitated which was almost insoluble in most organic solvents.

Summary

1. The dehalogenation of β-bromophenylpyruvic acid has been studied under a variety of conditions. Evidence has been obtained for the intermediate formation of phenylketene under certain of the above conditions.

2. The possibilities and some of the difficulties of utilizing the dehalogenation of α-keto-β-bromo acids as a new method of synthesis of ketene derivatives have been pointed out.

COLUMBUS, OHIO RECEIVED SEPTEMBER 19, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Reactions between Organomercury Compounds and Nitrosyl Compounds[1,2]

BY LEE IRVIN SMITH AND F. LOWELL TAYLOR

The reactions between nitrosyl compounds and organomercury compounds were discovered by Baeyer,[3] who first prepared nitrosobenzene by the action of nitrosyl bromide upon diphenylmercury.[4]

Bamberger[5] studied the reactions between nitrogen oxides and bis-arylmercury compounds. Apparently, he concluded that the action of nitrogen sesquioxide upon organomercury compounds was entirely different from that of nitrogen dioxide. He represented the reaction between nitrogen dioxide and diphenylmercury by equation (1).

$$(C_6H_5)_2Hg + N_2O_4 \longrightarrow C_6H_5HgNO_3 + C_6H_5NO \quad (1)$$

Despite the fact that he also obtained a small quantity of nitrosobenzene by the action of nitrogen sesquioxide, Bamberger represented the reaction between the sesquioxide and diphenylmercury by equation (2).

$$(C_6H_5)_2Hg + 2N_2O_3 \longrightarrow C_6H_5HgNO_3 + C_6H_5N_2NO_3 \quad (2)$$

He ascribed the formation of the nitrosobenzene to the action of nitrogen dioxide formed by dissociation of the sesquioxide. Moreover, nitric oxide did not act upon diphenylmercury, but did act upon nitrosobenzene, *o*-nitrosotoluene, and *p*-bromonitrosobenzene. The corresponding diazonium nitrates were formed (equation 3).

$$C_6H_5NO + 2(NO) \longrightarrow C_6H_5N_2NO_3 \quad (3)$$

In the present work it was found that nitrogen sesquioxide, nitrogen dioxide, and nitrosyl chloride formed nitroso compounds by their action upon organomercury derivatives of polymethylbenzenes. The nitroso group replaced the mercury, which was removed as an inorganic salt. Equations (4) and (5) express the reactions in general forms, where NOX denotes the nitrosyl compounds.[6]

$$R_2Hg + NOX \longrightarrow RHgX + RNO \quad (4)$$
$$RHgX + NOX \longrightarrow HgX_2 + RNO \quad (5)$$

A diazonium nitrate was formed only when a mixture of nitrogen sesquioxide and excess nitric oxide was allowed to act upon a mercury compound. It seemed, then, that the primary reaction (5) between nitrogen sesquioxide and the arylmercury compound was accompanied by a

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[1] Polymethylbenzenes. XIV. Paper XIII, THIS JOURNAL, **57**, 2370 (1935).

[2] Abstracted from the thesis of F. L. Taylor, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, March, 1935.

[3] Baeyer, *Ber.*, **7**, 1638 (1874).

[4] Gilman and Wright [THIS JOURNAL, **55**, 3302 (1933); **56**, 1415 (1934)] treated 2-chloromercurifuran with nitrosyl chloride, but did not isolate a product from the reaction.

[5] E. Bamberger, *Ber.*, **30**, 506 (1897); **32**, 3546 (1899); Kunz, *ibid.*, **31**, 1528 (1898).

[6] If conclusions as to the structures of nitrogen oxides are valid when based upon their reaction products, nitrogen sesquioxide is nitrosyl nitrite and the dioxide is nitrosyl nitrate. See, Wieland, *Ann.*, **328**, 154; **329**, 225 (1903); **340**, 63 (1905); **424**, 71 (1921); *Ber.*, **53**, 210, 1343 (1920); **54**, 1776 (1921); Battegay *et al.*, *Bull soc. chim.*, **41**, 1336 (1927); **43**, 109 (1928); Reihlen and Hake, *Ann.*, **452**, 47 (1927); Schaarschmidt *et al.*, *Ber.*, **57**, 32, 2065 (1924).