tion of sedoheptulose, have made it almost certain that β-sedoheptitol is L-gulo-D-*talo*-heptitol, the enantiomorph of D-gulo-L-*talo*-heptitol. The older record of absence of rotation for both substances is not compatible with the view that they are enantiomorphs unless it be inferred that their rotations are so very low as to have escaped detection in the past. Since it must be assumed on theoretical grounds that optical activity of enantiomorphs should always be detectable by some method of observation, the two alcohols have been prepared again and carefully purified. The pure substances show the following properties: β-sedoheptitol, m.p. 128–129°, $[\alpha]^{20}D$ −0.75° (water), +4.3° (borax solution), +49.6° (molybdate solution); D-gulo-L-*talo*-heptitol, m.p. 128–129°, $[\alpha]^{20}D$ +0.95° (water), −4.6° (borax solution), −49.7° (molybdate solution). They have the same melting point and under comparable conditions they exhibit rotations which are equal in magnitude within the limits of measurement and are opposite in sign, as is to be expected for enantiomorphs. β-Sedoheptitol is L-gulo-D-*talo*-heptitol.

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[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

o-Chlorophenylbenzoylacetylene

BY CHARLES L. BICKEL

A recent paper from this Laboratory described the preparation of *o*-chlorodibenzoylmethane by the reaction of alcoholic potassium hydroxide with the dibromide of *o*-chlorobenzalacetophenone.[1] The action of bases on α,β-dibromo ketones gives a variety of products and has been carefully studied by a number of investigators.[2] In no case, however, has an acetylenic ketone been obtained as a product of these reactions. In 1904, Watson[3] attempted without success to prepare phenylbenzoylacetylene from benzalacetophenone dibromide and also from α-bromobenzalacetophenone. From the dibromide he obtained β-ethoxybenzalacetophenone (a product one would expect) and from α-bromobenzalacetophenone he reported products which were presumably formed by the cleavage of the acetylenic ketone.

When the present author prepared *o*-chlorodibenzoylmethane for the first time, the residual oil, obtained by treating *o*-chlorobenzalacetophenone dibromide with alcoholic potassium hydroxide and by removing β-methoxy-*o*-chlorobenzalacetophenone, deposited a small amount of a substance which was not further investigated at the time. Subsequent analyses indicated that the substance was *o*-chlorophenylbenzoylacetylene, I. The reactions of the compound confirm this structure.

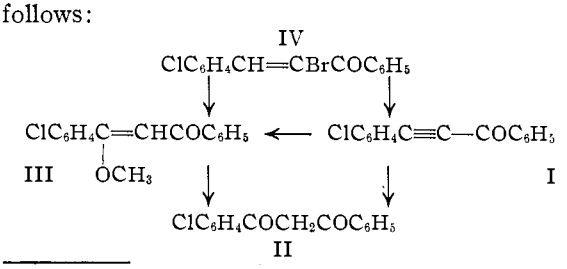
Compound I is converted quantitatively into *o*-chlorodibenzoylmethane II by the action of concentrated sulfuric acid followed by treatment with iced water, a method used by Nef,[4] Moureu[5] and Fuson[6] to confirm the structure of acetylenic ketones. Compound I adds methyl alcohol in an alcoholic solution of potassium hydroxide to give β-methoxy-*o*-chlorobenzalacetophenone III as the only product. The addition of alcohols to acetylenic ketones had previously been reported by Moureu and Brachin,[7] who found that phenylbutyrylacetylene and phenylpropionylacetylene gave addition products with ethyl alcohol in the presence of sodium ethylate.

Preparation of the acetylenic ketone I from a known substance was finally achieved by the removal of the elements of hydrogen bromide from α-bromo-*o*-chlorobenzalacetophenone IV, using potassium hydroxide in a mixture of acetone and water. The acetylenic ketone is the only product so far isolated from this reaction; there is no evidence of cleavage.

Moureu and Delange[8] found that phenylbenzoylacetylene is cleaved by alcoholic potassium hydroxide, giving acetophenone and potassium benzoate as products. *o*-Chlorophenylbenzoylacetylene reacts with alcoholic potassium hydroxide, but the reaction is one of addition rather than cleavage.

Watson[3] found that α-bromobenzalacetophenone reacted with solid potassium hydroxide, giving cleavage products. The *o*-chloro analog behaves similarly at the temperature of the water-bath, but is apparently unaffected when an ether solution of the compound is left in contact with solid potassium hydroxide for twenty-four hours.

The above transformations are summarized as follows:



(1) Bickel, THIS JOURNAL, **68**, 865 (1946).

(2) Kohler and Addinall, *ibid.*, **52**, 3728 (1930). This paper summarizes the action of bases on α,β-dibromo ketones and cites the most important references.

(3) Watson, *J. Chem. Soc.*, **85**, 1319 (1904).

(4) Nef, *Ann.*, **308**, 275 (1899).

(5) Moureu and Delange, *Bull. soc. chim.*, **25**, 303 (1901).

(6) Fuson, Ullyot and Hickson, THIS JOURNAL, **61**, 410 (1939).

(7) Moureu and Brachin, *Bull. soc. chim.*, **33**, 131 (1905).

(8) Moureu and Delange, *Compt. rend.*, **130**, 1259 (1900).

The ease with which *o*-chlorophenylbenzoylacetylene reacts with methyl alcohol in the presence of bases explains the fact that acetylenic ketones are not among the products obtained when α,β-dibromo ketones are treated with alcoholic solutions of bases.

Experimental

α-Bromo-*o*-chlorobenzalacetophenone, IV.—In the earlier paper[1] IV was prepared by the action of an alcoholic solution of anhydrous potassium acetate on the dibromide. Two other methods of preparation are herein described. Method A is particularly significant since α,β-dibromo ketones are not generally pyrolyzed to give α-bromo unsaturated ketones as the chief product.

A. By the Pyrolysis of the Dibromide.—Five grams of *o*-chlorobenzalacetophenone dibromide was heated for one and one-half hours at 170°, the evolution of hydrogen bromide practically ceasing after one hour. The liquid was allowed to cool and then taken up in ether. The washed and dried ether solution gave 2.7 g. of α-bromo-*o*-chlorobenzalacetophenone melting at 59°, a yield of 75%. The residual material consisted of about 0.5 g. of unchanged dibromide and an oil which has not as yet given solid products.

B. By the Action of Pyridine on the Dibromide.—A solution of 15.5 g. of the dibromide in 25 cc. of pyridine was refluxed for thirty minutes. By the usual manipulations, 6.2 g. of IV was obtained, a yield of 50%. The residual oil has not crystallized.

***o*-Chlorophenylbenzoylacetylene, I.**—A solution of 5 g. of α-bromo-*o*-chlorobenzalacetophenone in 15 cc. of acetone (free of methyl alcohol) and a solution of 1.3 g. of potassium hydroxide in 15 cc. of water were mixed and the mixture was refluxed for one hour. The cooled solution was diluted with 200 cc. of water and extracted with ether. The ether solution, red in color, gave 2.8 g. of the acetylenic ketone. Separation of the acetylenic ketone and the residual, viscous oil is extremely difficult since there is little difference in solubility. The yield of acetylenic ketone is therefore higher than is indicated by the above description.

o-Chlorophenylbenzoylacetylene is very soluble in ether but only sparingly soluble in petroleum ether. It crystallizes as long colorless needles and melts at 94°.

Anal. Calcd. for $C_{15}H_9OCl$: C, 74.8; H, 3.77. Found: C, 74.9, 74.6, 74.7; H, 3.81, 3.78, 3.74.

Conversion of I into *o*-Chlorodibenzoylmethane, II.—A solution of one gram of the acetylenic ketone in 15 cc. of concentrated sulfuric acid was left at room temperature for forty-eight hours and then poured into iced water. The ether extract gave a quantitative yield of the copper salt of the diketone when shaken with saturated cupric acetate solution. The diketone was recovered from the copper salt and identified by comparison with a known sample.

Conversion of I into β-Methoxy-*o*-chlorobenzalacetophenone, III.—One gram of the acetylenic ketone was dissolved in a solution of one gram of potassium hydroxide in 30 cc. of methyl alcohol. After standing for five hours at room temperature, β-methoxy-*o*-chlorobenzalacetophenone had crystallized from the solution. All of the material was poured into iced water. The ether extract gave 1.1 g. of β-methoxy-*o*-chlorobenzalacetophenone melting at 114°, practically a quantitative yield.

The Action of Potassium Hydroxide on I.—An absolute ether solution of 0.5 g. of the acetylenic ketone was left in contact with 2 g. of potassium hydroxide pellets for twelve hours. The acetylenic ketone was recovered.

The Action of Bases on IV. A. Solid Potassium Hydroxide.—A mixture of 3.35 g. of the bromo ketone and 1.4 g. of potassium hydroxide pellets reacted vigorously when heated on the water-bath for a few minutes. The resulting solid cake was cooled and then treated with water and ether. Acidification of the water layer gave the calculated quantity of benzoic acid, assuming complete cleavage.

B. Solid Sodium Carbonate.—Procedure A was followed, substituting 4 g. of anhydrous sodium carbonate for the potassium hydroxide. The bromo ketone was recovered.

C. Aqueous Potassium Hydroxide.—Three grams of the bromo ketone was added to a solution of 15 g. of potassium hydroxide in 100 cc. of water and the mixture was refluxed for two and one-half hours. The bromo ketone was unchanged.

D. Solid Potassium Hydroxide and Ether.—An absolute ether solution of 5 g. of the bromo ketone was left in contact with 5 g. of potassium hydroxide pellets for twenty-four hours. The bromo ketone did not react.

Summary

The preparation of *o*-chlorophenylbenzoylacetylene from α-bromo-*o*-chlorobenzalacetophenone is reported.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Extension of the Modified Stobbe Condensation. Acid-Catalyzed Decomposition of the Products and a Lacto–Enoic Tautomerism[1]

BY WILLIAM S. JOHNSON, JACK W. PETERSEN[2] AND WILLIAM P. SCHNEIDER[3]

In previous work[4,5,6] it was demonstrated that in the Stobbe condensation of ketones with diethyl succinate the use of potassium *t*-butoxide in *t*-butyl alcohol generally gave higher yields and purer products during shorter reaction periods than were obtained by the classical procedure with sodium ethoxide. Applications of the modified procedure to three additional ketones, benzophenone, acetophenone and propiophenone are reported herewith as well as an account of the acid-catalyzed decarbethoxylation of the products.

Benzophenone is an especially suitable ketone for the study of the Stobbe condensation because the resulting half-ester (I), in contrast to that derived from a ketone like acetophenone, has neither stereo nor structural isomers, and is a homogeneous crystalline material lending itself

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(4) Johnson, Goldman and Schneider, THIS JOURNAL, **67**, 1357 (1945).

(5) W. S. Johnson, H. C. E. Johnson and Petersen, *ibid.*, **67**, 1360 (1945).

(6) Johnson and Petersen, *ibid.*, **67**, 1366 (1945).