there was deposited 0.5 g. of an **anil**; colorless crystals from alcohol, m. p. 219–222°.

Anal. Calcd. for $C_{21}H_{21}NO_3$: C, 75.2; H, 6.3. Found: C, 74.9; H, 6.4.

Ethyl α-(β-Cyanoethyl)-α-phenylacetoacetate, XII.—Ethyl α-phenylacetoacetate (20.6 g.) was dissolved in 25 ml. of *t*-butyl alcohol which had been saturated with potassium hydroxide. Then 5.3 g. of acrylonitrile was added, and the mixture was stirred for one hour. Water and a little acetic acid were added; the product was removed with ether and fractionally distilled, giving 7 g., b. p. 180–220° at 0.003 mm.

Anal. Calcd. for $C_{15}H_{17}NO_3$: C, 69.5; H, 6.6. Found: C, 69.2; H, 6.5.

The material reacted with 75% sulfuric acid, and carbon dioxide was evolved, but careful search revealed no phenylcyclohexanedione in the products.

Ethyl α-(β-Cyanoethyl)-α-methylacetoacetate, XIII.—From 25 g. of ethyl α-methylacetoacetate and 9.2 g. of acrylonitrile with potassium hydroxide in *t*-butyl alcohol, there was obtained 20 g. of product, b. p. 118–118.5° at 4 mm., n^{25}_{D} 1.445.

Anal. Calcd. for $C_{10}H_{15}NO_3$: C, 60.9; H, 7.7. Found: C, 61.0; H, 7.7.

Carbon dioxide was evolved when the substance was treated with 75% sulfuric acid, but no methylcyclohexanedione could be isolated.

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Summary

Treatment of γ-substituted-γ-acetylpimelonitriles with hot 40–80% sulfuric acid leads to the formation of 4a-substituted-Δ^8-octahydro-2,7-quinolinediones. The structures of two such products have been established, and a mechanism for the reaction is suggested. An apparently similar reaction takes place when γ-acetyl-γ-phenylpimelic acid is treated with sulfuric acid.

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

The Debromination of α,β-Dibromo Ketones by Bases

BY CHARLES L. BICKEL*

The reaction of α,β-dibromo ketones with alcoholic solutions of bases has been carefully studied[1] and has been used extensively for the preparation of both β-diketones and α-diketones. The first step in the reaction is assumed to be the elimination of the beta bromine atom as hydrogen bromide, an unsaturated α-bromo ketone being formed.

$$\mathrm{R{-}CHBr{-}CHBr{-}CO{-}R \longrightarrow R{-}CH{=}CBr{-}CO{-}R}$$

This assumption has been verified in many instances by the isolation of the monobromide. The subsequent action of bases on the monobromide leads to a variety of derivatives, the product or products in a particular case depending on the nature of the base, the solvent and the terminal groups.

Recent communications from this Laboratory[2] described the preparation of acetylenic ketones from unsaturated α-bromoketones, using acetone instead of an alcohol as the solvent.

$$\mathrm{R{-}CH{=}CBr{-}CO{-}R \longrightarrow R{-}C{\equiv}C{-}CO{-}R}$$

In the light of the above, it seemed reasonable to predict that the intermediate preparation and isolation of the monobromides might be unnecessary and that the acetylenic ketones might therefore be prepared directly from the dibromides by the elimination of two molecules of hydrogen bromide, using acetone as the solvent.

$$\mathrm{R{-}CHBr{-}CHBr{-}CO{-}R \not\longrightarrow R{-}C{\equiv}C{-}CO{-}R}$$

This is, however, not the case.

The action of potassium hydroxide on an acetone solution of the dibromides results in debromination and in the formation of the chalcones from which the dibromides were derived.

$$\mathrm{R{-}CHBr{-}CHBr{-}CO{-}R \longrightarrow R{-}CH{=}CH{-}CO{-}R}$$

Six dibromides have been debrominated in this way, indicating that the reaction may be expected in the case of other dibromides not herein studied. The reaction appears to be clean-cut. The yields of the chalcones are high and there is no evidence of the formation of either the α-bromo ketones or the acetylenic ketones. The absence of acetylenic ketones among the reaction products necessarily means that the α-bromo ketones were not formed as intermediates.[2] Thus, in the absence of alcohols, the action of potassium hydroxide resembles that of zinc, iron and acetic acid, or potassium iodide, agents which convert chalcone dibromides into the parent chalcones.

Basic agents other than potassium hydroxide can be used for the debromination reaction but are not as effective. Sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate were so used and gave the corresponding chalcone as a product. On the other hand, the action of potassium acetate in acetone gave the α-bromo ketone, the same product that is obtained in alcohol solution.

Comparable experiments with 2-chlorochalcone dibromide and α-bromo-2-chlorochalcone indicate that the debromination of the dibromide is a faster process than is the elimination of hydrogen bromide from the α-bromo compound.

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

[2] Bickel, *ibid.*, **69**, 73, 2134 (1947).

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Experimental

The dibromides of chalcone, 2-chlorochalcone, 4-methoxychalcone, 4'-methoxychalcone and 4'-bromochalcone were prepared by the bromination of the corresponding chalcones; their properties have been reported elsewhere. The preparation and properties of 4'-chlorochalcone dibromide have apparently not been recorded in the literature. The present author has used this dibromide in the preparation of *p*-chlorodibenzoylmethane[3] but neglected to characterize the substance. 4'-Chlorochalcone dibromide, obtained in excellent yield by the bromination of 4'-chlorochalcone in chloroform solution, crystallizes as tiny, colorless needles and melts at 190–191°.

Anal. Calcd. for $C_{15}H_{11}OClBr_2$: C, 44.7; H, 2.76. Found: C, 44.5, 44.6; H, 2.90, 2.90.

Debromination of the Dibromides

A. By Potassium Hydroxide and Acetone.—Since the procedure was essentially the same for all the dibromides, the general method is outlined and the individual results are then listed.

A mixture of 10 g. of the dibromide, 100 ml. of alcohol-free acetone and 2.1 equivalents of potassium hydroxide (pellets) was stirred for two hours at 25–30° by means of a magnetic stirrer.[4] The resulting mixture was poured into about 200 ml. of water, enough dilute hydrochloric acid was added to reduce the orange-red color to a pale yellow, and the organic product was ether extracted. The chalcone was isolated from the ether solution in the usual way and then identified by a mixed melting point with an authentic sample. Duplicate runs were carried out in the case of each dibromide.

The yields of chalcone, 2-chlorochalcone, 4-methoxychalcone, 4'-methoxychalcone, 4'-bromochalcone and 4'-chlorochalcone were 75, 65, 75, 90, 95 and 85%, respectively. The yields parallel the solubilities of the chalcones in ether; the most insoluble chalcones were isolated in the highest yields while the most soluble chalcones, chalcone and 2-chlorochalcone, were the most difficult to separate from the residual oils. It is probable, therefore, that the yields of these latter chalcones are higher than indicated above.

In those cases in which an appreciable quantity of the material was not accounted for as the chalcone, the residual oil was tested for both the α-bromo ketone and the acetylenic ketone. For example, the residual oil remaining after the isolation of 2-chlorochalcone was treated with a methanol solution of potassium hydroxide. β-Methoxy-2-chlorochalcone,[5] the product from either the α-bromo ketone or the acetylenic ketone, is quite insoluble in cold methanol and is easily isolated. None of this substance was detected. Further evidence of the absence of the α-bromo ketone and the acetylenic ketone was obtained by acidifying the product of the alcoholic base reaction and then testing for *o*-chlorodibenzoylmethane[5] with cupric acetate. None of the copper salt of the diketone was formed.

B. By Potassium Hydroxide, Acetone and Water.—The only significant difference between this procedure and that of method A is that a solution of the potassium hydroxide in about 25 ml. of water was added drop by drop to a stirred mixture of the dibromide and acetone. The mixture was then stirred for about one hour and finally treated as in method A. The yields of chalcones ranged from 45 to 75%; as in method A, there was no evidence of the formation of α-bromo ketones or acetylenic ketones.

C. By Other Bases.—Neither method A nor method B effected the debromination of the dibromides when sodium carbonate, sodium bicarbonate, potassium carbonate or potassium bicarbonate was substituted for potassium hydroxide. In each case the dibromide was recovered. When method B was modified by refluxing the mixture for several hours, the chalcones were formed. The highest yield of chalcone, however, was about 60%, unidentified oils accounting for the remainder of the product.

Other Experiments

2-Chlorochalcone Dibromide and Potassium Acetate.—A mixture of 10 g. of the dibromide, 10 g. of potassium acetate and 100 ml. of alcohol-free acetone was refluxed for two hours. By the usual manipulations, **α-bromo-2-chlorochalcone**[5] was isolated in good yield. The dibromide was recovered when the mixture was stirred at 25–30° for the same time.

α-Bromo-2-chlorochalcone and Potassium Hydroxide.—A mixture of 15 g. of the monobromide, 100 ml. of alcohol-free acetone and 2.7 g. of potassium hydroxide pellets was stirred for four hours at 25–30°. The products included 7.4 g. of *o*-chlorophenylbenzoylacetylene,[2] 4 g. of unchanged monobromide, and a small quantity of an unidentified oil.

Summary

The debromination of chalcone dibromides by the action of bases in the presence of alcohol-free acetone is described.

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[3] Bickel, THIS JOURNAL, **67**, 2205 (1945).

[4] Bickel, *ibid.*, **71**, 1451 (1949).

[5] Bickel, *ibid.*, **68**, 866 (1946).