Anal. Calcd. for $C_{12}H_{13}O_3Br$: C, 50.52; H, 4.60; Br, 28.04. Found: C, 50.63; H, 4.87; Br, 27.83.

1-Bromo-1,4-dibenzoylbutane.—Twenty grams of δ-bromo-δ-benzoylvaleric acid and 14 cc. of thionyl chloride were warmed gently on the steam-bath for one hour; then the excess thionyl chloride was removed by heating the reaction mixture to 60° under diminished pressure. The δ-benzoyl-δ-bromovaleryl chloride thus obtained was added dropwise to an ice-cold suspension of 18 g. of aluminum chloride in 100 cc. of benzene. After the addition of the acid chloride the reaction mixture was allowed to stand overnight at room temperature. Decomposition of the complex gave 13 g. of 1-bromo-1,4-dibenzoylbutane which melted at 62–63°.

Anal. Calcd. for $C_{18}H_{17}O_2Br$: Br, 23.16. Found: Br, 23.31.

The Benzoate of 1-Hydroxy-1,4-dibenzoylbutane.—Five grams of 1-bromo-1,4-dibenzoylbutane was dissolved in a solution of 1.2 g. of sodium benzoate in 75 cc. of ethyl alcohol and 10 cc. of water. The reaction mixture was heated under reflux for three hours. The alcohol was then removed from the solution and the residue was taken up in ethyl acetate. Addition of petroleum ether (b. p. 25–45°) to the solution precipitated crystals which melted at 110–111°. Three grams of the keto ester was obtained.

Anal. Calcd. for $C_{25}H_{22}O_4$: C, 77.75; H, 5.78. Found: C, 77.67; H, 5.89.

2-Phenyl-3-benzoylcyclopentanone.—A solution of 5 g. of the benzoate of 1-hydroxy-1,4-dibenzoylbutane in 60 cc. of alcohol was added to 200 cc. of 85% phosphoric acid and the mixture heated under reflux for twelve hours. At the end of this time, the reaction mixture was poured into 200 cc. of ice water and allowed to stand about thirty minutes. The precipitate was decolorized with norite and recrystallized from ethyl alcohol. There was obtained 3 g. of fine, colorless needles, melting at 156–158°. A mixed melting point with an authentic sample of 2-phenyl-3-benzoylcyclopentanone showed no depression.

Summary

Hot phosphoric acid converts 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran (II) to a cyclopentanone derivative. A mechanism is postulated which involves the formation of 1-hydroxy-1,4-dibenzoylbutane as an intermediate. The benzoate of this compound has been prepared and treated with phosphoric acid; the product is the cyclopentanone in question. This result lends support to the proposed mechanism.

URBANA, ILLINOIS RECEIVED OCTOBER 26, 1936

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

Dihydro-1,4-pyrans. V. The Structure of the 3-Cyano Derivatives

BY H. H. HULLY, F. H. BROCK AND REYNOLD C. FUSON

In a previous paper[1] the cyano compounds resulting from the action of sodium cyanide on certain 1,4-dibromo-1,4-diaroylbutanes were assigned tentatively a dihydro-1,4-pyran structure. Strong support for this structure was obtained by degradation of the cyano compound obtained from 1,4-dibromo-1,4-dibenzoylbutane. Use of the Beckmann rearrangement led to a series of derivatives whose properties were in accord with predictions based on the structure originally assigned (I).[2] The end-product of this degradation has subsequently been definitely identified as α-hydroxy-δ-benzoylvaleric acid (II).[3] In view of these results, it seems certain that the original cyano compound has the dihydro-1,4-pyran structure.

In the search for confirmatory evidence, we have studied the effects of certain oxidizing and reducing agents on this dihydro-1,4-pyran.

Concentrated nitric acid attacks the ethylenic bond and produces the nitric ester of a nitro alcohol. By analogy with similar cases[4] we have assigned structure III to this compound. Its formation was the first definite proof of the presence of the ethylenic bond in the parent substance.

Catalytic hydrogenation, however, did not affect the ethylenic bond. On the contrary, the carbonyl group was attacked preferentially. The resulting alcohol (IV) was found to yield a urethan when treated with phenyl isocyanate. Treatment with chromic acid oxidized the alcohol to the original ketone. Concentrated nitric acid converted the carbinol (IV) into the same derivative (III) which was obtained from the original cyano pyran (I).

Ozone attacked the ethylenic linkage and produced an ozonide which led to ring opening in the expected manner. The cleavage product (V), when treated with alkali, gave benzoic acid (one

---

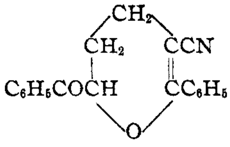
(1) Fuson, Kuykendall and Wilhelm, THIS JOURNAL, **53**, 4187 (1931).

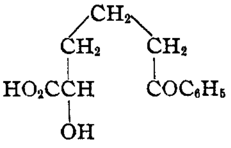
(2) Kao and Fuson, *ibid.*, **54**, 313 (1932).

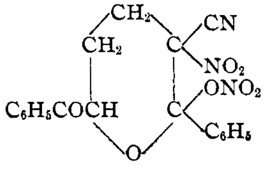
(3) Fuson, Wojicik and Turck, *ibid.*, **56**, 235 (1934).

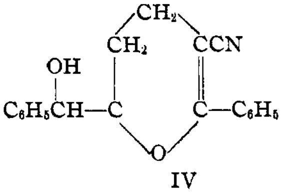
(4) See, for example, Van Der Lee, *Rec. trav. chim.*, **47**, 920 (1928).

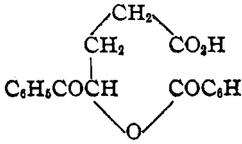
mole), and a mixture of compounds from which succinic acid was isolated.

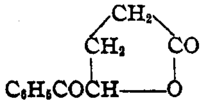

I


II


III


IV


V


VI

Attempts to synthesize this open-chain derivative were, however, unsuccessful.[3] To this end γ-bromo-γ-benzoylbutyric acid was prepared and treated with silver benzoate. The only product which could be obtained was the γ-benzoylbutyrolactone (VI).

Experimental

The Action of Nitric Acid on 2-Phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran.—One gram of 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran was dissolved in 5 cc. of glacial acetic acid and a solution of 1 cc. of concentrated nitric acid (sp. gr., 1.42) in 3 cc. of glacial acetic acid was added slowly. The reaction mixture was heated at 100° for one hour. Oxides of nitrogen were evolved during this time. The solution was then poured into 200 cc. of ice water, the precipitate collected on a filter and crystallized from ethyl alcohol. There was obtained 1 g. of a product melting at 139.5–140°, with evolution of oxides of nitrogen.

Anal. Calcd. for $C_{16}H_{15}O_7N_3$: C, 57.43; H, 3.81. Found: C, 57.31, 57.29; H, 4.04, 3.93.

This compound, to which was assigned formula III, was also made by the action at 0° of fuming nitric acid on the carbinol (IV).

Reduction of 2-Phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran.—Seven and eighteen-hundredths grams of 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran was dissolved in 300 cc. of ethyl acetate and treated with hydrogen under a pressure of three atmospheres for fourteen hours in the presence of a platinum oxide catalyst. The platinum was removed from the solution, and the ethyl acetate removed by distillation. The residue, after several recrystallizations from dilute alcohol, melted at 110–113°.

The carbinol could not be purified satisfactorily, since deposition of an oil always accompanied crystallization. Treatment of the carbinol with phenyl isocyanate, however, gave the corresponding urethan, which could be satisfactorily purified by crystallization from ethyl alcohol. The melting point is 137–138°.

Anal. Calcd. for $C_{26}H_{22}O_3N_2$: N, 6.83. Found: N, 6.92.

Oxidation of the Carbinol.—One gram of the carbinol was dissolved in 10 cc. of glacial acetic acid, and to this was added 0.2 g. of chromic anhydride in 40 cc. of acetic acid. The solution was warmed on the steam cone for ten minutes. The solution was then diluted with 200 cc. of water, neutralized with aqueous sodium hydroxide and extracted with ether. Evaporation of the ether left a residue which melted at 105–106° after recrystallization from ethyl acetate. A mixed melting point with 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran gave no depression. The yield was practically quantitative.

Ozonolysis of 2-Phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran.—Two grams of 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran was dissolved in 40 cc. of glacial acetic acid and a moderate stream of ozone was bubbled through the solution for seven hours. The ozonide was decomposed by the addition of water. After several hours crystals were deposited; these were dissolved in ethyl acetate and reprecipitated by the addition of petroleum ether (b. p. 25–45°). After several recrystallizations, the acid melted at 113°; yield 0.5 g.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.14; neut. equiv., 312. Found: C, 69.39; H, 5.27; neut. equiv., 316.

The semicarbazone melted (from an alcohol–water mixture) at 190–195°, with decomposition.

Anal. Calcd. for $C_{19}H_{19}O_5N_3$: C, 61.8; H, 5.15. Found: C, 62.2; H, 5.4.

Hydrolysis of the Benzoate of γ-Hydroxy-γ-benzoylbutyric Acid (V).—Sixteen-hundredths of a gram of the benzoate of γ-hydroxy-γ-benzoylbutyric acid, which was produced by the ozonolysis just described, was treated with an excess of sodium hydroxide solution and allowed to stand overnight. The solution was then acidified and concentrated to a volume of 5 cc.; it was then extracted with ether. Evaporation of the ether left crystals which melted at 182–184°. A mixed melting point with succinic acid showed no depression.

Summary

Further evidence has been obtained in confirmation of the dihydro-1,4-pyran structure previously assigned to the cyano compound derived from 1,4-dibromo-1,4-dibenzoylbutane by the action of sodium cyanide.

URBANA, ILLINOIS RECEIVED OCTOBER 30, 1936