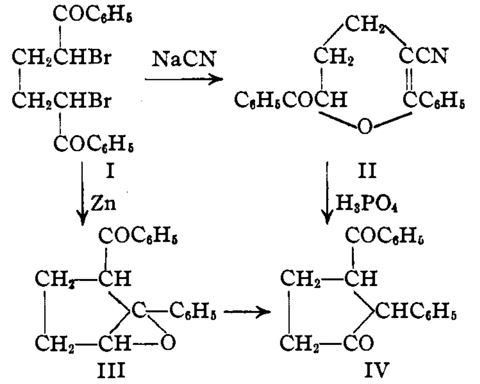
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

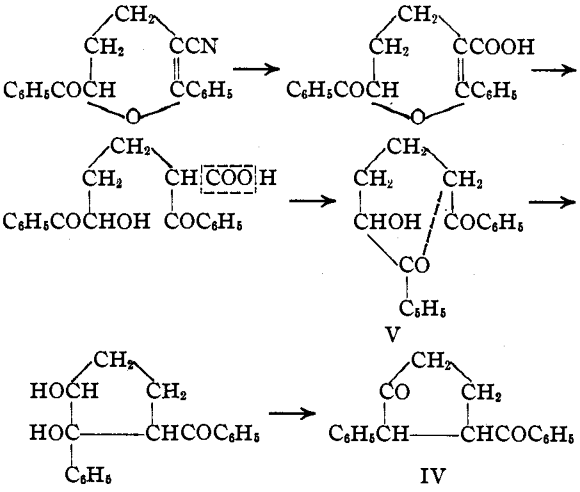
A Cyclopentane Derivative from 1,4-Dibromo-1,4-dibenzoylbutane

BY REYNOLD C. FUSON, ARNOLD LIPPERT, R. V. YOUNG AND H. H. HULLY

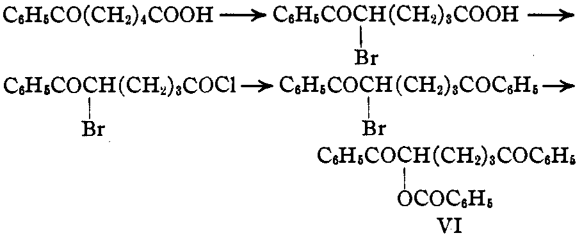
A cyclopentane derivative (IV) was obtained by rearrangement of the oxide (III), which is formed when 1,4-dibromo-1,4-dibenzoylbutane (I) is treated with zinc.[1] It has now been found that this transformation of the diketone (I) into the cyclopentanone can be effected in another way. The first step involves the action of sodium cyanide on the dibromo diketone, and gives a cyano dihydro-1,4-pyran (II).[2] When this nitrile is heated with sirupy phosphoric acid, it is converted to the cyclopentanone (IV).



This curious change of II into IV involves hydrolysis of the cyano group, opening of the dihydro-1,4-pyran ring, decarboxylation of the resulting acid and finally closure to the cyclopentanone. It seems probable that these reactions take place in the following sequence



In an effort to gain some insight into this complex change, we have prepared the benzoate of the hydroxy diketone (V) and subjected it to the action of phosphoric acid. The synthesis of the benzoate (VI) was accomplished by the following series of transformations



$$C_6H_5CO(CH_2)_4COOH \longrightarrow C_6H_5CO\underset{Br}{CH}(CH_2)_3COOH \longrightarrow C_6H_5CO\underset{Br}{CH}(CH_2)_3COCl \longrightarrow C_6H_5CO\underset{Br}{CH}(CH_2)_3COC_6H_5 \longrightarrow C_6H_5CO\underset{OCOC_6H_5}{CH}(CH_2)_3COC_6H_5$$

VI

This benzoate should be hydrolyzed by the hot 85% phosphoric acid to the hydroxy diketone (V), and the latter, if really an intermediate in the process, should yield the cyclopentanone. The result of the test was an 80% yield of the expected compound (IV). This lends support to the proposed mechanism.

Experimental

The transformation of the cyano compound (II) into the cyclopentanone (IV) can be effected by use of sulfuric acid or phosphoric acid. The best yields were obtained by use of the following procedure. Ten grams of the cyano compound was dissolved in 300 cc. of 85% phosphoric acid and 25 cc. of 95% ethyl alcohol. The mixture was stirred for eighteen hours and then heated under reflux on a hot-plate for eight hours. When the reaction mixture had cooled, it was placed in a 2-liter beaker and diluted to a volume of 1800 cc. by addition of water. The yellow solid which separated over a period of several hours was removed by filtration and recrystallized from ethyl alcohol. The melting point was 159–159.5° (corr.) and was not depressed by admixture with 2-phenyl-3-benzoylcyclopentanone. The yield was 40% of the theoretical amount.

The benzoate of 1-hydroxy-1,4-dibenzoylbutane was synthesized by the following series of reactions.

δ-Bromo-δ-benzoylvaleric Acid.—Thirty grams of δ-benzoylvaleric acid, prepared according to Hill,[3] was dissolved in 300 cc. of hot carbon tetrachloride. To this solution was added 25 g. of bromine through a capillary tube extending beneath the surface of the liquid. The reaction was complete in about ten minutes. Air was then drawn through the warm solution until the volume was about 150 cc. When cooled, the solution deposited crystals which were purified by precipitation from a cold ethyl acetate solution by the addition of petroleum ether (25–45°). The yield is 30 g. of product which melts at 109–110°.

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[1] Fuson and Farlow, THIS JOURNAL, **56**, 1593 (1934); Babcock and Fuson, *ibid.*, **58**, 2325 (1936).

[2] Fuson, Kuykendall and Wilhelm, *ibid.*, **53**, 4187 (1931).

[3] Hill, *ibid.*, **54**, 4105 (1932).

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

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[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).