cator over concentrated sulfuric acid. It weighed 7.1 g.; a yield of 27.8% on the basis of the bromo-ester. The product melted at 108°, the recorded melting point of 3-hydroxy-crotonic acid.

**Preparation of *dl*-Threonic Acid (Step 5).**—To 10.2 g. (0.1 mole) of 3-hydroxy-crotonic acid in 500 cc. of water and 2.5 cc. of a 1% aqueous solution of osmic acid was added 6.4 g. (0.033 mole) of silver chlorate in two portions separated by an interval of twenty-four hours. After forty-eight hours the silver chloride was removed by filtration, and the filtrate reduced in volume as completely as possible in vacuum at 60° and 15 mm. The sirupy residue was dissolved in 30 cc. of acetone, the solution filtered from a small amount of dark material, and most of the acetone evaporated from a crystallizing dish on the steam-bath. The material was then stored in a vacuum desiccator over concentrated sulfuric acid until bubbling ceased. The partly crystalline mass was then dissolved in 10 cc. of ethyl acetate and the solution chilled in an ice-salt bath. The crystals were separated and washed with a mimimum of ethyl acetate. The product, which melted at 97°, weighed 6.5 g.; a yield of 48% based on the hydroxy acid. A small portion of the product was recrystallized from the same solvent. This material melted at 99°. It showed no depression of the melting point when mixed with a sample of *dl*-threonic acid which had been prepared by Braun.

## Summary

The work of Kirrman and Rambaud on the preparation of 3-hydroxy-crotonic acid was successfully repeated. The yield, however, was very low.

Their procedure has been modified so that 3-hydroxy-crotonic acid can now be obtained in four steps from acrolein in 8.6% yield.

3-Hydroxy-crotonic acid has been oxidized to *dl*-threonic acid with silver chlorate and osmic acid in 48% yield. The over-all yield of threonic acid, from acrolein in five steps, (4.1%) compares favorably with that obtained by Braun (2.5%) in six steps from glycerol-1,3-dichlorohydrin.

CHICAGO, ILLINOIS RECEIVED OCTOBER 16, 1939

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NATIONAL CENTRAL UNIVERSITY, CHINA]

# Keto-cyclol Tautomerism of 1,6-Diketones. 1,4-Dibromo-1,4-dibenzoylbutane*

BY TSI-YU KAO

In seeking for a direct method for the preparation of 1,2-dibenzoylcyclobutane (IV) the action of molecular silver on 1,4-dibromo-1,4-dibenzoylbutane was tried. Since silver is a monovalent element it appeared altogether unlikely that it would lead to a Reformatsky condensation such as that reported by Fuson and Farlow.[1] These authors treated 1,4-dibromo-1,4-dibenzoylbutane with zinc and obtained besides 1,4-dibenzoylbutane (III) three other compounds: 2-phenyl-3-benzoylcyclopentanone, 1-phenyl-5-benzoyl-1-cyclopentene (IX), and its oxide (VIII).

Molecular silver actually gave a small yield of the desired cyclobutane derivative, but the chief product was 1-phenyl-5-benzoyl-1-cyclopentene oxide (VIII). The formation of this substance is explained adequately by the keto-cyclol tautomerism of 1,6-diketones. This mechanism explains equally well the formation of the cyclopentene derivatives from the dibromo compound (I) by the action of zinc dust.

While the cyclol forms of simple 1,6-diketones have not been isolated, there is considerable evidence that their existence is possible. For example, Baeyer and Liebig[2] obtained 1-cyclopentenealdehyde as well as adipaldehyde by oxidation of $\alpha,\alpha'$-dihydroxysuberic acid. Marshall and Perkin[3] showed that 1,4-diacetylbutane when distilled or boiled with alcoholic potash gave 1-acetyl-2-methyl-1-cyclopentene. By the action of sodamide on 1,4-dibenzoylbutane Bauer[4] obtained two isomeric cyclopentene derivatives: 2-phenyl-3-benzoyl-1-cyclopentene and 1-phenyl-2-benzoyl-1-cyclopentene. The latter was prepared by Skraup and Guggenheimer[5] by heating 1,4-dibenzoylbutane at 300–310°. Similarly, 2,4,5-triphenyl-1-benzoyl-1-cyclopentene results when 1,4-dibenzoyl-2,3-diphenylbutane is treated with sodium ethylate.[6] All of these transformations can be explained as due to the elimination of water from the cyclol form of the diketone or diacid.

Still more striking evidence for the existence of the cyclol forms has been furnished by Vogel,[7] who showed that 2,2,3,3-tetramethyl-1,4-diacetylbutane exists only in the cyclol form.

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(*) Original manuscript received January 16, 1939.

(1) Fuson and Farlow, THIS JOURNAL, **56**, 1593 (1934).

(2) Baeyer and Liebig, *Ber.*, **31**, 2107 (1898).

(3) Marshall and Perkin, *J. Chem. Soc.*, **57**, 241 (1890).

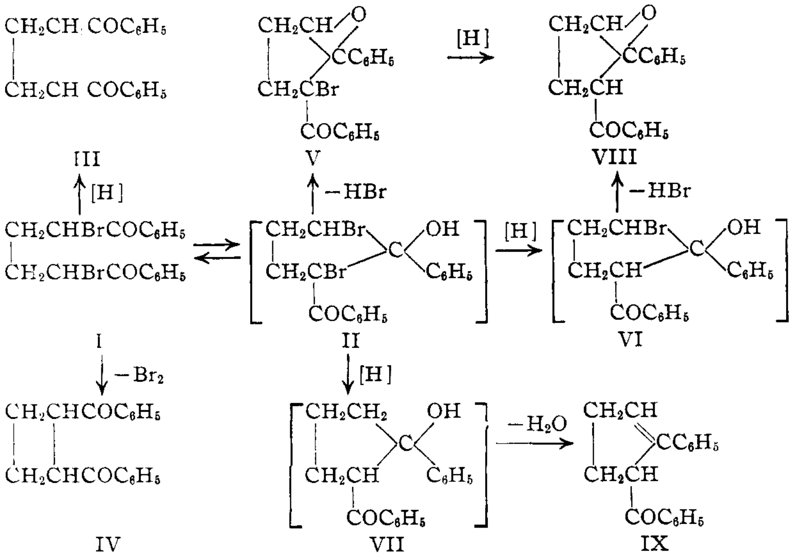
(4) Bauer, *Compt. rend.*, **155**, 288 (1912).

(5) Skraup and Guggenheimer, *Ber.*, **58B**, 2495 (1925).

(6) Conant and Cutter, THIS JOURNAL, **48**, 1026 (1926).

(7) Vogel, *J. Chem. Soc.*, **128**, 594 (1927).

The results presently reported can be explained similarly by assuming 1,4-dibromo-1,4-dibenzoylbutane to exist in both the keto (I) and the cyclol (II) forms. Removal of bromine from the keto form by the action of molecular silver yields 1,2-dibenzoylcyclobutane, and elimination of hydrogen bromide and one bromine atom from the cyclo form gives rise to the cyclopentene oxide (VIII). The probable course of these reactions is represented bv the diagram



Debromination of I and II yields, respectively, 1,4-dibenzoylbutane and the cyclopentene (IX), presumably formed from the cyclol, VII. The oxide (VIII) could be formed either by elimination of hydrogen bromide from the cyclol, VI, or by debromination of the bromo oxide (V).

The latter method of formation has been shown to be possible. The bromo oxide (V) is formed when the dibromide (I) is treated with sodium cyanide,[8] diethylamine or sodium acetate. The sodium derivative of ethyl malonate produces the same change. When the bromo compound (V) is treated with zinc dust and sodium iodide in acetone it gives the oxide (VIII). This reaction serves also to establish the structure of the bromo oxide (V).

## Experimental

**Action of Molecular Silver on 1,4-Dibromo-1,4-dibenzoylbutane.**—A mixture of 15 g. of the dibromide, 32 g. of sodium iodide and 15 g. of molecular silver (prepared by the method of Gomberg and Cone[9]) was covered with acetone and heated for eight hours under reflux. The mixture was filtered while hot and the filtrate allowed to run into a large volume of water. The residue was washed two or three times with hot acetone and finally extracted with acetone in a Soxhlet apparatus. The acetone solution obtained in this way was also poured into water. It usually contained very little organic material.

The water–acetone mixture was heated to remove the acetone and the product separated by filtration and dried. The filtrate, which was always turbid, was extracted twice with benzene to make sure that no material was lost; very little was recovered, however. The yellow product was first extracted with petroleum ether (b. p. 40–60°) in a Soxhlet apparatus for four hours and then with ethyl alcohol (in portions) until all of the organic compounds were removed. This usually required about twenty-four hours.

From the petroleum ether was obtained a solid melting at 115–140°. Fractional crystallization from alcohol gave *cis*-1,2-dibenzoylcyclobutane (m. p. 121–122°) and 1-phenyl-5-benzoyl-1-cyclopentene oxide (m. p. 169.5–170.5°) in yields of 13 and 37%, respectively. Both compounds were identified by the method of mixed melting points. The former was the more soluble and was contained in the mother liquors from which the latter had crystallized. A small amount of 1,4-dibenzoylbutane also was isolated.

**1 - Phenyl - 5-bromo - 5-benzoyl-1-cyclopentene Oxide.**—A mixture of 4.2 g. of 1,4-dibromo-1,4-dibenzoylbutane, 17 g. of diethylamine and 30 cc. of dry benzene was refluxed for about thirty minutes. The bromo compound dissolved to give a wine-red solution. The mixture was filtered to remove the crystals of diethylamine hydrobromide which were then washed with benzene. The washings were added to the filtrate and the solvent was distilled under diminished pressure. The clear, viscous oily residue was dissolved in ether and the solution washed successively with hydrochloric acid and water. After the solution was dried the solvent was removed and the residue crystallized from alcohol: yield, 2 g. (59%); m. p. 138–139°.

The same compound was obtained by using sodium cyanide or sodium acetate instead of diethylamine but yields were low.

**Action of the Sodium Derivative of Ethyl Malonate on 1,4-Dibromo-1,4-dibenzoylbutane.**—This experiment was originally carried out with the intention of making ethyl 2,5-dibenzoyl-1,1-cyclopentanedicarboxylate. The product, however, was identical with the bromo compound of Kao and Fuson and proved to be 1-phenyl-5-benzoyl-5-bromo-1-cyclopentene oxide (V).

To a solution of 1.2 g. of metallic sodium in 50 cc. of absolute ethyl alcohol was added first 4.2 g. of ethyl malonate and then a solution of 10 g. of the dibromide in 100 cc. of dry benzene. The stopper of the reaction flask was secured with a wire and the vessel was placed in a water-

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[8] Kao and Fuson, THIS JOURNAL, **54**, 313 (1932).

[9] Gomberg and Cone, *Ber.*, **39**, 3286 (1906).

bath which was heated to boiling and kept at that temperature for five hours. The contents were evaporated nearly to dryness and the residue crystallized from ethyl acetate. The bromo compound melted at 138–139°; yield, 64% of the theoretical amount.

**Debromination of 1-Phenyl-5-bromo-5-benzoyl-1-cyclopentene Oxide.**—A mixture of 7 g. of the bromo oxide, 7 g. of zinc dust, 10 g. of sodium iodide and 100 cc. of dry acetone was refluxed for eight hours. The mixture was filtered and the residue washed several times with hot acetone. The acetone solution was poured into a large volume of water and the precipitated oxide purified by recrystallization. It melted at 169–170° and was identified by the mixed melting point method as 1-phenyl-5-benzoyl-1-cyclopentene oxide. The yield was 0.7 g.

## Summary

Treatment with molecular silver converts 1,4-dibromo-1,4-dibenzoylbutane into a mixture of 1,4-dibenzoylbutane, 1,2-dibenzoylcyclobutane and 1-phenyl-5-benzoyl-1-cyclopentene oxide. With the sodium derivative of ethyl malonate the dibromide yields 1-phenyl-5-benzoyl-5-bromo-1-cyclopentene oxide. The latter is also formed from the dibromide by the action of diethylamine Treatment of the oxide with zinc dust and sodium iodide in acetone converts it to the bromine-free cyclopentene oxide.

These transformations are interpreted on the assumption that the dibromide exists in tautomeric keto and cyclol forms.

CHUNKING, SZECHUAN, CHINA
RECEIVED DECEMBER 4, 1939

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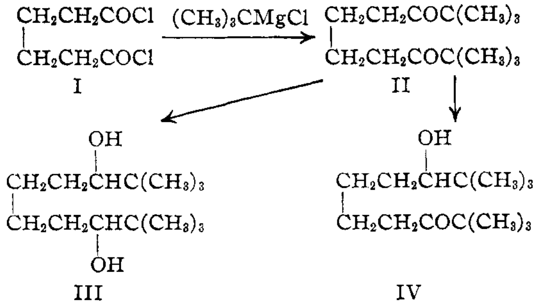
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

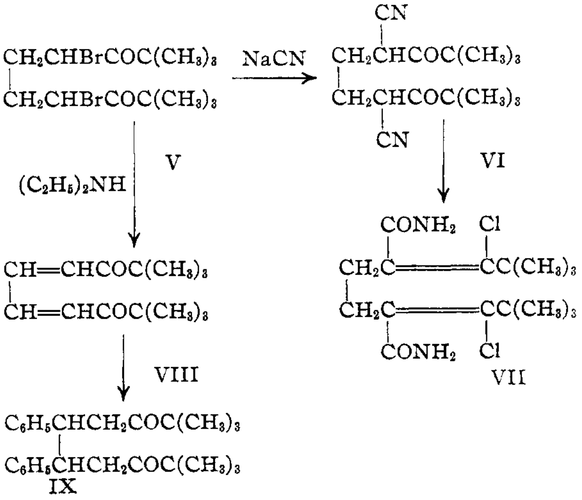
# 1,4-Dibromo-1,4-dipivalylbutane

BY REYNOLD C. FUSON AND JOHN W. ROBINSON, JR.

1,4-Dibromo-1,4-dipivalylbutane (V) has been synthesized for use in connection with a general study of ring closures of 1,4-dihalogen compounds. The primary problem from the synthetic point of view was that of making the parent diketone, 1,4-dipivalylbutane (II). This compound was obtained in yields of 25% by treatment of adipyl chloride with *t*-butylmagnesium chloride. An excess of the Grignard reagent must be avoided at all times to minimize reduction of the diketone. Incomplete reaction gave δ-pivalylvaleric acid [$(CH_3)_3CCO(CH_2)_4CO_2H$]. It was impossible to eliminate completely the formation of this by-product; the average yield of this substance was about 20%.



The use of an excess of *t*-butylmagnesium chloride gave an oil which evidently contained the diol (III) or the hydroxy ketone (IV) or both. An attempt was made to obtain the desired diketone by oxidation of the oil with chromic acid but only low yields resulted.



**The dibromide** (V) was formed without difficulty but only one of the two possible stereoisomeric forms was isolated. Its structure was proved by cleavage to pivalic acid by the action of alkali on the pyridinium salt.

Treatment of the dibromide with sodium cyanide was found to give the corresponding dinitrile (VI) together with a liquid which had the composition of the cyanocyclobutane derivative which might be expected by analogy with the behavior of