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

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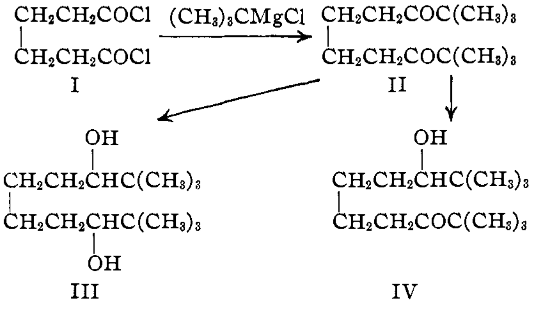
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

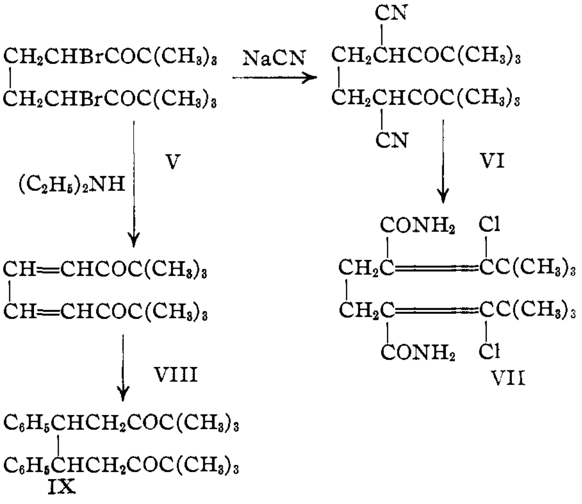
1,4-Dibromo-1,4-dipivalylbutane

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 dibromoadipic esters.[1] On the other hand, the conversion of 1,4-dibromo-1,4-diaroylbutanes to dihydro-1,4-pyrans under these conditions[2] suggests that the liquid might be the dihydro-1,4-pyran, isomeric with the cyclobutane derivative. The data at hand do not permit a decision between these two possibilities.

Treatment with diethylamine dehydrohalogenated the dibromide (V) giving 1,4-dipivalyl-1,3-butadiene (VIII). This compound failed to condense with maleic anhydride, but reacted with phenylmagnesium bromide to yield 1,4-dipivalyl-2,3-diphenylbutane (IX). Catalytic hydrogenation converted the diene to the saturated diketone (II).

The dicyano diketone (VI) gave two moles of gas in the Grignard machine,[3] but attempts to alkylate it and to effect ring closure through the disodium derivative were fruitless. The cyano groups showed extraordinary resistance to the action of hydrolytic agents. Long heating with aqueous sodium hydroxide, for example, did not alter the compound. However, heating with concentrated hydrochloric acid in a closed tube produced a remarkable transformation. The product proved to be a chloro amide which probably has the structure VII. This is a novel type of reaction for β-keto nitriles; presumably its realization in this instance is to be ascribed to the steric hindrance afforded by the *t*-butyl radical.

Experimental

Synthesis of 1,4-Dipivalylbutane

A. By Condensation of Adipyl Chloride with *t*-Butylmagnesium Chloride.—To an ice cold solution of 0.136 mole of adipyl chloride in 400 cc. of absolute ether was added gradually over a two-hour period 0.30 mole of *t*-butylmagnesium chloride in 500 cc. of absolute ether. Vigorous stirring was used during the addition and the temperature of the reaction mixture maintained at 0°. Stirring was continued for three hours after the addition was complete.

The mixture was decomposed at 0° with ammonium chloride and worked up in the usual way. The ether solution was washed with aqueous sodium carbonate solution and dried. Evaporation of the ether left an oil which could be crystallized from low-boiling petroleum ether. In this way 6.5 to 8.5 g. of 1,4-dipivalylbutane was obtained melting at 52–52.5°.

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.19; H, 11.40.

The di-2,4-dinitrophenylhydrazone when purified by repeated crystallization from chloroform melted at 251–252° (uncor.).

Anal. Calcd. for $C_{26}H_{34}N_8O_8$: C, 53.23; H, 5.84; N 19.09. Found: C, 52.87; H, 5.97; N, 18.81.

Distillation of the filtrate from the crystallization of 1,4-dipivalylbutane gave 5 g. of a neutral oil boiling at 119–124° (3.5 mm.). It appeared to be impure 2,2,9,9-tetramethyl-3,8-decanediol (III).

Anal. Calcd. for $C_{14}H_{30}O_2$: C, 72.98; H, 13.12. Found: C, 71.56; H, 11.12.

The sodium carbonate solution was acidified with hydrochloric acid and extracted with ether. In this way there was obtained 5 g. of δ-pivalylvaleric acid boiling at 151–153° (2 mm.) and melting at 45–47°.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.48; H, 9.74. Found: C, 64.53; H, 9.61.

B. By Oxidation of the Neutral Oil.—One gram of the neutral oil boiling at 119–124° (3.5 mm.) was treated with 1 g. of chromic acid in glacial acetic acid solution. Only a small amount of the diketone could be isolated.

1,4-Dibromo-1,4-dipivalylbutane.—The bromination of 1,4-dipivalylbutane in warm carbon tetrachloride proceeded rapidly to give a 90% yield of the dibromide. The product crystallized from an ether–petroleum ether mixture, m. p. 119.5–120°.

Anal. Calcd. for $C_{14}H_{24}O_2Br_2$: C, 43.77; H, 6.30. Found: C, 43.67; H, 6.29.

Cleavage to pivalic acid was effected by the following procedure. One gram of the dibromide was dissolved in 10 cc. of ethyl acetate, 5 g. of pyridine was added and the mixture allowed to stand for twenty-four hours. The solid which formed was removed by filtration and the filtrate heated nearly to boiling; an additional quantity of the solid resulted. The solid was dissolved in 10 cc. of water and treated with cold 5% sodium hydroxide solution. An intense red color developed. The solution was acidified with dilute sulfuric acid and extracted five times with ether. In this way pivalic acid was isolated, m. p. 34–35°.

1,4-Dipivalyl-1,3-butadiene.—A solution of 4 g. of 1,4-dibromo-1,4-dipivalylbutane and 20 g. of diethylamine in 100 cc. of dry benzene was boiled under reflux for fourteen hours. The diethylamine hydrobromide was removed by filtration and the filtrate concentrated to about 15 cc. under reduced pressure. Cooling the benzene solution to 0° caused the butadiene to separate in white cotton-like crystals. These were recrystallized from methanol, m. p. 145–146°. The yield was 21% of the theoretical.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.90; H, 10.22.

The di-2,4-dinitrophenylhydrazone melted at 280–282°.

Anal. Calcd. for $C_{26}H_{30}N_8O_8$: C, 53.60; H, 5.19. Found: C, 53.32; H, 5.19.

Reduction was carried out in two ways.

A. With Sodium Hydrosulfite.—This method gave a solid melting at 70–72° which decolorized solutions of permanganate in acetone and discharged the color of carbon tetrachloride solutions of bromine without evolution of hydrogen bromide. The compound was not studied further.

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(1) Fuson and Kao, This Journal, **51**, 1536 (1929); Fuson, Kreimeier and Nimmo, *ibid.*, **52**, 4074 (1930).

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

(3) Kohler, Fuson and Stone, *ibid.*, **49**, 3181 (1927).

B. With Hydrogen.—Raney nickel was used as the catalyst. The product had a melting point of 52–53° which was not depressed by the addition of 1,4-dipivalylbutane.

Reaction of the Butadiene with Phenylmagnesium Bromide.—This reaction was carried out in the usual manner. A solid was isolated melting at 206–207° which is the melting point given for 2,3-diphenyl-1,4-dipivalylbutane.[4]

1,4-Dicyano-1,4-dipivalylbutane.—A mixture of 8 g. of 1,4-dibromo-1,4-dipivalylbutane, 4 g. of powdered sodium cyanide, 120 cc. of absolute alcohol and 120 cc. of dry ethyl acetate was refluxed for forty hours. Removal of the solvents left a dark brown residue to which was added 150 cc. of water. The aqueous solution was extracted with four 50-cc. portions of ether. The resulting solution was evaporated to dryness and the residue crystallized from alcohol. The dinitrile was obtained in yields of 1.4 to 1.7 g., m. p. 92–93°.

Anal. Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.53; H, 8.75; N, 10.13. Found: C, 69.75; H, 8.72; N, 10.17.

Reaction of the Dinitrile with Hydrochloric Acid.—A mixture of 0.5 g. of the dinitrile and 10 cc. of concentrated hydrochloric acid was heated in a closed tube (capacity about 30 cc.) for two hours at 140–150°. A solid was obtained which after recrystallization from benzene melted at 198–200°. The yield was 0.33 g.

Anal. Calcd. for $C_{15}H_{26}Cl_2N_2O_2$: C, 55.02; H, 7.50; N, 8.02; Cl, 20.30; mol. wt., 349. Found: C, 55.18; H, 7.43; N, 7.46; Cl, 20.70; mol. wt., 330.

The alcoholic filtrate left after the separation of the dicyano compound was found to contain a neutral oil boiling at 163–168° (6 mm.); n^{20}_{D} 1.4722.

The 2,4-dinitrophenylhydrazone was crystallized from alcohol, m. p. 225–227°.

Anal. Calcd. for $C_{21}H_{27}N_5O_5$: C, 58.76; H, 6.34; N, 16.30. Found: C, 58.30; H, 6.49; N, 16.45.

An **oxime** was formed by heating a mixture of 1 g. of the oil, 1.5 g. of hydroxylamine hydrochloride, 3 g. of potassium acetate and 10 cc. of water. It was crystallized from alcohol, m. p. 183–185°.

Anal. Calcd. for $C_{15}H_{24}N_2O_2$: C, 68.15; H, 9.15. Found: C, 68.28; H, 8.96.

Repetition of the foregoing test using sodium hydroxide in place of potassium acetate gave an **isomeric oxime** melting at 146–148°.

Anal. Calcd. for $C_{16}H_{24}N_2O_2$: C, 68.15; H, 9.15; N, 10.59. Found: C, 68.23; H, 9.14; N, 10.47.

Summary

1,4-Dipivalylbutane (II) has been prepared by the action of *t*-butylmagnesium chloride on adipyl chloride.

1,4-Dibromo-1,4-dipivalylbutane (V) has been converted to the corresponding dicyano compound (VI) and to 1,4-dipivalyl-1,3-butadiene (VIII).

URBANA, ILLINOIS RECEIVED DECEMBER 4, 1939

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[4] Hill and Susselman, THIS JOURNAL, 53, 4424 (1931).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The 1,2,4-Trimesityl 1,4-Diketones and Related Compounds, Including the Stereoisomeric Mono and Dienols[1]

BY ROBERT E. LUTZ AND CHARLES J. KIBLER

The preparation of this series of compounds was undertaken in order to extend the study of the hindering effect of mesityl groups. It was expected that here the damping of the keto–enol shift and the consequent increase in the persistence of enolic forms would make it possible to prepare some of the stereoisomeric mono and dienols or, at least, to obtain evidence of their existence. Furthermore, it was hoped that new information might be obtained concerning the properties of highly hindered enolic groups and the mechanism of certain reactions which supposedly proceed through enolic intermediates, particularly furan ring closure.[2] This report deals with a preliminary investigation in which these objectives were in a degree accomplished.

The Saturated 1,4-Diketone (III).—The starting point in the synthesis of these compounds was di-(trimethylbenzoyl)-ethylene (I). Addition of mesitylmagnesium bromide at 20° gave the monoenolate II by 1,4-addition, the reaction proceeding quickly but stopping at this point. When the reaction mixture was hydrolyzed by means of dilute hydrochloric or acetic acid, the saturated diketone III was produced in good yield; the free monoenol could not be isolated and was quite mobile, ketonizing quickly to the saturated diketone even when dilute acetic acid under mild conditions was used.

That the reaction between mesitylmagnesium bromide and di-(trimethylbenzoyl)-ethylene actually stopped at the stage of the monoenolate, II, was demonstrated (a) by conversion of the product with alcoholic iodine or bromine into the

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[1] This paper was presented at the Boston meeting of the American Chemical Society, September 14, 1939.

[2] Lutz and Reveley, THIS JOURNAL, 61, 1854 (1939).