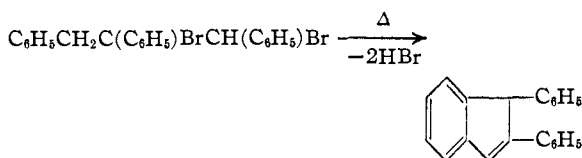


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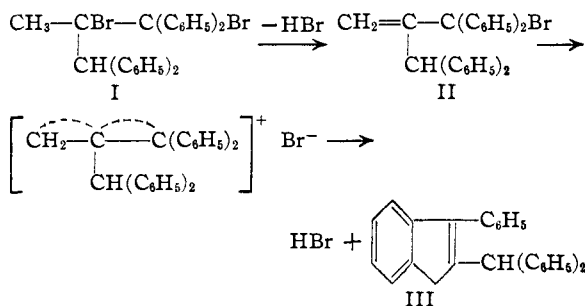
## The Thermal Decomposition of the Dibromide of $\beta$ -Methyl- $\alpha,\alpha,\gamma,\gamma$ -tetraphenylpropene

BY C. F. KOELSCH AND R. V. WHITE

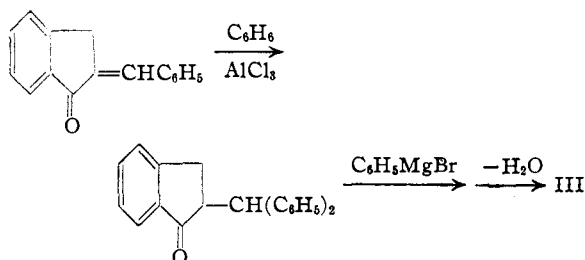
In connection with an investigation of the properties of certain indenenes<sup>1</sup> a synthesis of 2-methyl-1,1,3-triphenylindene was reported. Before this synthesis was developed, an attempt was made to prepare the hydrocarbon by a reaction analogous to that used by Orechhoff<sup>2</sup> for the synthesis of 1,2-diphenylindene



The dibromide of  $\beta$ -methyl- $\alpha,\alpha,\gamma,\gamma$ -tetraphenylpropene (I) was prepared by standard methods. When it was heated in acetic acid, a hydrocarbon  $\text{C}_{28}\text{H}_{22}$  was formed. But this hydrocarbon was not the expected 2-methyl-1,1,3-triphenylindene, since on oxidation it yielded benzophenone and an acid  $\text{C}_{15}\text{H}_{12}\text{O}_3$ , probably benzophenone-*o*-acetic acid, together with some oily material that could not be characterized. The results indicated that the hydrocarbon  $\text{C}_{28}\text{H}_{22}$  was 2-benzohydryl-3-phenylindene (III) formed by the reactions



The structure of the product was then substantiated by synthesis, according to the scheme



It is remarkable that the dibromide (I) loses a proton from the unsubstituted methyl group to form II,<sup>3</sup> but in no other simple way can the formation of III from I be accounted for. An analogy may exist in the observation made in a not yet completed investigation that when  $\alpha,\beta$ -dibromo- $\beta$ -phenylpropane is heated in acetic acid, hydrogen bromide is lost and a monobromo compound is formed. This substance boils at 140–145° at 23 mm., is an extremely potent lachrymator, and reacts vigorously with alcoholic potash to form a bromine-free substance. However, when  $\alpha,\beta$ -dibromo- $\beta$ -phenylpropane is treated with alcoholic potash,  $\alpha$ -bromo- $\beta$ -phenylpropene is formed, and this vinyl bromide boils at 225–228° (105–106° at 9 mm.), is not a lachrymator, and is inert toward alcoholic alkali.

### Experimental

**$\beta$ -Methyl- $\alpha,\alpha,\gamma,\gamma$ -tetraphenylpropene.**— $\alpha$ -Methyl- $\beta,\beta$ -diphenylpropionic acid, m. p. 161°, was prepared (yield 61%) and converted into the methyl ester, m. p. 85–86° (yield 75%) according to the methods of Eijkmann.<sup>4</sup>

A solution of the methyl ester (25 g.) in ether was added to 125 ml. of 2 molar phenylmagnesium bromide. The mixture was boiled for three hours and then decomposed with iced hydrochloric acid. The product, freed of solvents and biphenyl by steam distillation, was boiled for fifteen minutes with acetic acid containing a few drops of sulfuric acid. Cooling gave 15 g. of the propene (43%), which melted at 132–133°.

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{24}$ : C, 93.3; H, 6.7. Found: C, 93.0; H, 6.9.

Oxidation of the hydrocarbon (3 g.) in hot acetic acid with chromic anhydride (2 g.) gave a colorless neutral product (1.8 g.) which melted at 118–119°. This oxidation product, probably 3,3,4,4-tetraphenylbutanone-2, formed by a pinacol rearrangement,<sup>5</sup> was not affected by boiling with formic acid or with acetic-sulfuric acid.

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{24}\text{O}$ : C, 89.3; H, 6.4. Found: C, 89.1; H, 6.5.

**2-Benzohydryl-3-phenylindene (III).**—A solution of  $\beta$ -methyl- $\alpha,\alpha,\gamma,\gamma$ -tetraphenylpropene (2 g.) in acetic acid (140 ml.) was treated with bromine (1 g.) and allowed to stand at room temperature for forty hours. The solution was then distilled to a small volume and cooled, giving 1.43 g. (72%) of colorless needles that melted at 162–163.5°.

(3) Cf. Church, Whitmore and McGrew, *THIS JOURNAL*, **56**, 184 (1934); Whitmore and Mosher, *ibid.*, **63**, 1120 (1941).

(4) Eijkmann, *Chem. Weekblad*, **5**, 655 (1909).

(5) Cf. Meerwein, *Ann.*, **396**, 207 (1913).

(1) Koelsch and White, *J. Org. Chem.*, **6**, 602 (1941).

(2) Orechhoff, *Ber.*, **47**, 94 (1914); Ruggli, *Ann.*, **414**, 125 (1917).

*Anal.* Calcd. for  $C_{28}H_{22}$ : C, 93.8; H, 6.2. Found: C, 93.6; H, 6.5.

The hydrocarbon was not affected when it was boiled with alcoholic sodium hydroxide.

**Oxidation of III.**—A mixture of 1 g. of III in 40 ml. of acetic acid with 1 g. of chromic anhydride in a little water was heated on a steam-bath for fifteen minutes. The neutral oxidation products consisted of benzophenone (steam distilled) and a non-volatile oil (0.5 g.) which had an orange-pink color. The acidic fraction (0.13 g.) formed colorless needles that melted at 130–131° after crystallization from ligroin. Analysis indicated that this substance was **benzophenone-*o*-acetic acid**.

*Anal.* Calcd. for  $C_{15}H_{12}O_3$ : C, 75.0; H, 5.0. Found: C, 74.9; H, 5.1.

**2-Benzohydrilindanone.**—2-Benzalindanone, m. p. 109° (yield 95%), was prepared according to the method of Kipping.<sup>6</sup>

A mixture of 4 g. of this ketone with 25 ml. of benzene and 4.6 g. of aluminum chloride was boiled until the original bright yellow complex had become dark red-brown (thirty minutes). Decomposition with iced hydrochloric acid and crystallization from ether-ligroin gave 4 g. (74%) of a colorless product that melted at 109–111°.

*Anal.* Calcd. for  $C_{22}H_{18}O$ : C, 88.6; H, 6.1. Found: C, 88.2; H, 6.2.

2-Benzohydril-3-phenylindene, m. p. 161–163°, alone or mixed with the hydrocarbon obtained from the propene dibromide, was obtained from this ketone in a yield of

(6) Kipping, *J. Chem. Soc.*, **65**, 498 (1894).

30% by treatment with an excess of phenylmagnesium bromide followed by dehydration of the resulting oily carbinol with acetic acid containing 2% of sulfuric acid.

**Addendum.**—**Synthesis of 3-Methyl-2-Phenylindone.**—The substance named was required for an attempted synthesis of 3'-methyl-2'-phenylspiro[fluorene-9,1'-indene]. A solution of 2-phenylindandione-1,3 in benzene was added to two equivalents of ethereal methylmagnesium iodide. The mixture was boiled for two hours and then decomposed with iced hydrochloric acid. The organic layer was washed with dilute sodium hydroxide to remove unchanged diketone, the solvents were removed, and the neutral product (17.5 g.) was distilled under reduced pressure. Crystallization from alcohol gave orange crystals (10 g., 45%) that melted at 69–71°.

*Anal.* Calcd. for  $C_{16}H_{12}O$ : C, 87.2; H, 5.5. Found: C, 86.7; H, 5.6.

With *o*-xenylmagnesium iodide the ketone gave an oily product, and no crystalline material could be obtained from this when it was treated with dehydrating agents.

### Summary

Heating the dibromide of  $\beta$ -methyl- $\alpha,\alpha,\gamma,\gamma$ -tetraphenylpropene in acetic acid yields 2-benzohydril-3-phenylindene. The elimination of hydrogen bromide must involve an unsubstituted methyl rather than a benzohydril group. An independent synthesis of the product is described.

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 22, 1943

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## The Reactions and Enolization of Cyclic Diketones. VII. 3-*t*-Butyl-1,2-diketohydrindene

BY C. F. KOELSCH

It has been pointed out previously<sup>1</sup> that the nature of the group present on carbon-3 of a substituted 1,2-diketohydrindene is an important factor in determining whether the derivative will exist in the solid state in its ketonic or in its enolic modification. A 3-phenyl group favors enolization, for 1,2-diketo-3-phenylhydrindene is enolic whereas 1,2-diketohydrindene is ketonic. Likewise a 3-methyl group favors the existence of the enolic form, for 1,2-diketo-6-nitrohydrindene is yellow<sup>2</sup> and therefore ketonic, but 1,2-diketo-3-methyl-6-nitrohydrindene is red and therefore enolic. Unfortunately, a direct comparison of 1,2-diketohydrindene with its 3-methyl derivative cannot be made, since the latter

substance has been obtained only as a red glass.<sup>3</sup>

One is inclined to generalize from these examples that any hydrocarbon residue substituted for hydrogen on carbon-3 will favor enolization. But this generalization is unwarranted, for as is shown in the present paper 3-*t*-butyl-1,2-diketohydrindene is ketonic. Suppression of enolization by the *t*-butyl group was expected, and can be ascribed to the so-called electron repelling property of this group. The effect is probably identical with the one noted by Whitmore and Rohrmann,<sup>4</sup> who found that dehydration of neopentyl carbinols involves the methylene hydrogens of the neopentyl group only to a minor extent.

3-*t*-Butyl-1,2-diketohydrindene is a crystalline

(1) Koelsch and Geissman, *J. Org. Chem.*, **3**, 480 (1938).

(2) v. Braun and Heider, *Ber.*, **49**, 1268 (1916).

(3) v. Braun and Kirschbaum, *ibid.*, **46**, 3041 (1913).

(4) Whitmore and Rohrmann, *This Journal*, **63**, 2033 (1941).