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-Benzohydrylindanone.—2-Benzalindanone, m. p 109° (yield 95%), was prepared according to the method of Kipping.[6]

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-Benzohydryl-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 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′-phenyl*spiro*[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 β-methyl-α,α,γ,γ-tetraphenylpropene in acetic acid yields 2-benzohydryl-3-phenylindene. The elimination of hydrogen bromide must involve an unsubstituted methyl rather than a benzohydryl group. An independent synthesis of the product is described.

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 22, 1943

(6) Kipping, *J. Chem. Soc.*, **65**, 198 (1894).

[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[1] 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[2] 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.[3]

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,[4] 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

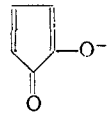
(1) Koelsch and Geissman, *J. Org. Chem.*, **3**, 480 (1938).

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

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

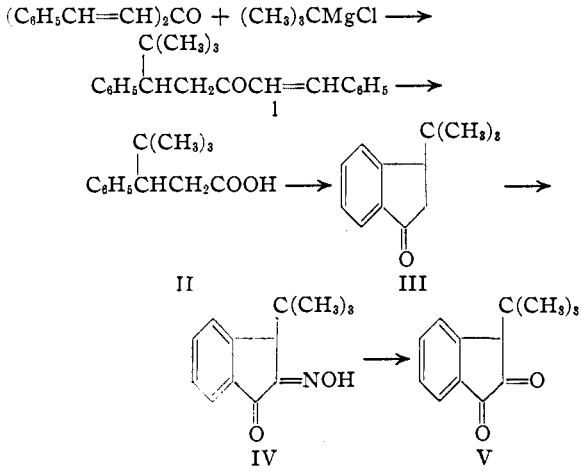
(4) Whitmore and Rohrmann, THIS JOURNAL, **63**, 2033 (1941).

solid whose orange-yellow color is almost indistinguishable from that of 3,3-dimethyl-[5] 3,3-diphenyl-,[5] or 3-methyl-3-phenyl-1,2-diketohydrindene[6]; this color is markedly different from that of the enolic 1,2-diketo-3-phenylhydrindene[7] and its analogs. Solutions of 3-*t*-butyl-1,2-diketohydrindene in organic solvents show only an orange-pink diketone color, but solutions in aqueous alkalies are deep blue like those of other substances containing the chromophore

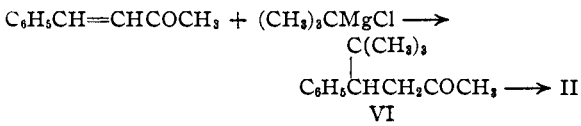


A solution of the diketone in carbon tetrachloride does not decolorize bromine in the cold, and although the diketone is attacked immediately by aqueous sodium peroxide, it is remarkably stable to air. A sample which had stood for four years in a corked vial was partly oxidized to *t*-butylhomophthalic acid and partly converted to a reddish oil, but it still contained about 20% of the diketone unchanged. Samples of crystalline 1,2-diketo-3-phenylhydrindene became completely resinous after storage for six months under the same conditions.

The diketone was synthesized through the series of reactions indicated below.



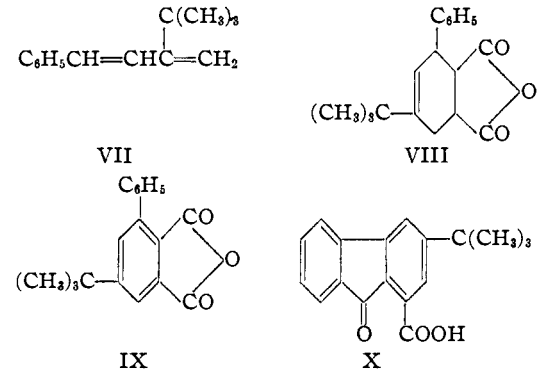
Before these reactions were developed, the synthesis of β-*t*-butylhydrocinnamic acid (II) was carried out in the following way.



This method was later abandoned in favor of the one previously outlined because the oxidation of VI with hypohalites gave unsatisfactory yields; conversion of VI to II was best accomplished by condensing VI with benzaldehyde and then oxidizing the resulting benzal compound (I).

The use of the second method led to the interesting discovery that a considerable proportion of the reaction product from benzalacetone and *t*-butylmagnesium chloride was formed through 1,2-addition. This result was quite unexpected, for phenylmagnesium bromide,[8] ethylmagnesium bromide,[8] and *i*-amylmagnesium iodide[9] add 1,4 to benzalacetone to the extent of 12, 60 and 52%, respectively, and the results of Stevens[10] indicate that *t*-butylmagnesium chloride adds 1,4 to crotonaldehyde and to ethylideneacetone to a much greater extent than do phenyl- and ethylmagnesium bromides.

The present 1,2-addition product could not be separated as such from the 1,4 product. Distillation caused it to lose water, and the resulting γ-*t*-butyl-α-phenylbutadiene-α,γ (VII) could not be freed of VI by repeated fractionation. The mixture of VI and VII was therefore treated with maleic anhydride; the crystalline adduct (VIII) was then easily separated from the ligroin-soluble ketone (VI). The anhydride (VIII) was characterized as that of a dibasic acid by hydrolysis, as a hydroaromatic substance by dehydrogenation to IX, and as containing a phenyl group *ortho* to a carboxyl group by conversion into the fluorenone X.



Experimental

ζ,ζ-Dimethyl-α,ε-diphenylhepten-α-one-γ (I).—A solution of dibenzalacetone (200 g.) in warm benzene was added to a cooled solution of *t*-butylmagnesium chloride prepared

(5) Koelsch and Le Claire, *J. Org. Chem.*, **6**, 516 (1941).
(6) Koelsch and Hochmann, *ibid.*, **3**, 503 (1938).
(7) Koelsch, THIS JOURNAL, **58**, 1321 (1936).
(8) Kohler, *Am. Chem. J.*, **38**, 511 (1908).
(9) Ponomarev, *Khim. Referat. Zhur.*, No. 9, 31 (1939) (*Chem. Abs.*, **34**, 5830 (1940)).
(10) Stevens, THIS JOURNAL, **57**, 1112 (1935).

from 48 g. of magnesium. The mixture was boiled for fifteen minutes and then decomposed with iced sulfuric acid. Part of the product (130 g.) crystallized immediately; the remainder (60 g.) was obtained by concentrating the mother liquors. Recrystallized from acetic acid, the product formed white plates, m. p. 146–148°.

Anal.[11] Calcd. for $C_{21}H_{24}O$: C, 86.2; H, 8.2. Found: C, 86.5; H, 8.1.

β-*t*-Butylhydrocinnamic Acid (II).—A solution of 33 g. of I in one liter of acetone was stirred while powdered potassium permanganate was added as long as it was decolorized (used, 58 g.; calcd., 59.5 g.). The mixture was filtered, concentrated, and treated with water and dilute sulfuric acid. The precipitated acid was crystallized from dilute acetic acid, giving 12.7 g. of fine colorless needles that melted at 114–116°.

The same product was obtained but in poorer yields by oxidizing I with chromic anhydride in acetic acid.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.7. Found: C, 75.7; H, 8.7.

The **anilide**, cotton-like needles that melted at 123–125° after recrystallization from alcohol, was obtained by treating a benzene solution of the acid chloride (see below) with aniline.

Anal. Calcd. for $C_{19}H_{23}NO$: C, 81.2; H, 8.2. Found: C, 81.2; H, 8.4.

3-*t*-Butylhydrindone-1 (III).—A mixture of II (28 g.) and thionyl chloride (30 ml.) was warmed for thirty minutes, the excess thionyl chloride was distilled under reduced pressure, and the residue was taken up in benzene (100 ml.). Aluminum chloride (20 g., calcd. 18 g.) was added in portions, and when the rapid reaction was complete, the mixture was decomposed with iced hydrochloric acid. The product was distilled, giving 21.5 g. of a colorless oil b. p. 150–153° at 20 mm. The ketone crystallized when cooled in ice but melted below room temperature.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.9; H, 8.5. Found: C, 82.9; H, 8.5.

The **oxime** separated from alcohol in the form of needles, m. p. 135–137°.

Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.8; H, 8.4. Found: C, 76.7; H, 8.3.

3-*t*-Butyl-2-oximinohydrindone-1 (IV).—A solution of III (21.5 g.) and butyl nitrite (20 ml.) in 50 ml. of ethanol was treated at 22° with 2 ml. of concd. hydrochloric acid. The temperature was allowed to rise to 65° and kept at this point for one hour. The mixture was then poured into dilute sodium hydroxide and unchanged III was removed with ether. Acidification followed by crystallization from alcohol gave a small amount of an oily acidic product and 13 g. of IV; the latter formed faintly yellow flat needles, m. p. 182–185°.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 72.1; H, 6.8. Found: C, 71.9; H, 6.9.

3-*t*-Butyl-1,2-diketohydrindene (V).—A mixture of IV (0.5 g.), formalin (1 ml.), acetic acid (1 ml.), and concd. hydrochloric acid (1 ml.) was boiled for thirty minutes. The orange oil resulting was taken up in ether, washed with water, and shaken with 5 ml. of a saturated sodium bisulfite solution. The bisulfite compound (pearly white plates easily soluble in water) was removed and warmed with dilute hydrochloric acid. The solid diketone so obtained crystallized from dilute acetic acid in the form of orange-yellow needles or from benzene–ligroin in the form of orange-yellow plates; both modifications melted at 76–78°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.2; H, 6.9. Found: C, 77.5; H, 6.8.

With alcoholic *o*-phenylenediamine, the diketone yielded **11-*t*-butyl-11-indeno[1,2-b]quinoxaline** (*Ring Index* 2517), which crystallized from alcohol in the form of faintly yellow needles that melted at 131–132°.

Anal. Calcd. for $C_{19}H_{18}N_2$: C, 83.2; H, 6.6. Found: C, 83.4; H, 6.4.

The blue solution of the diketone in aqueous sodium hydroxide was stable on boiling, but it became colorless on standing in air for eight hours. It was immediately decolorized by the calculated amount of hydrogen peroxide, and acidification then yielded **α-*t*-butylhomophthalic acid.** The acid was nearly insoluble in benzene, but it crystallized from dilute acetic acid in the form of colorless prisms that melted at 176–178° with gas evolution.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8. Found: C, 66.0; H, 6.9.

α-*t*-Butylhomophthalic anhydride, prepared by boiling the acid for one minute with acetic anhydride, formed colorless plates from benzene, m. p. 106–107°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.6; H, 6.4. Found: C, 71.7; H, 6.5.

Reaction of *t*-Butylmagnesium Chloride with Benzalacetone.—A solution of 35 g. of benzalacetone in 25 ml. of ether was added to ethereal *t*-butylmagnesium chloride prepared from 12 g. of magnesium; gas was evolved during the addition. The mixture was decomposed with water and then iced sulfuric acid, and the product was distilled. There were obtained 28 g. of an oil, b. p. 140–155° at 20 mm., a small fore-run, and about 10 g. of a nonvolatile residue.

A mixture of 24 g. of the 140–155° fraction with 11 g. of maleic anhydride was warmed to 100° for thirty minutes, then cooled and mixed with petroleum ether. The solid (18.6 g.) was removed, and the oil remaining was distilled.

The oil was **ε,ε-dimethyl-δ-phenylhexanone-β** (VI).—It boiled at 145–150° at 20 mm. and solidified on cooling. Recrystallized from ligroin it formed white needles (*ca.* 8 g.), m. p. 61–62°. Its conversion into I and II has been noted in the first part of this paper.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.4; H, 9.8. Found: C, 82.4; H, 9.9.

The solid was **5-*t*-butyl-3-phenyl-Δ⁴-tetrahydrophthalic anhydride** (VIII). It was purified by solution in boiling dilute sodium hydroxide, and the resulting **5-*t*-butyl-3-phenyl-Δ⁴-tetrahydrophthalic acid** was crystallized from dilute acetic acid. It formed fine white needles that sintered at 170° and melted at 190–192° with gas evolution.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.5; H, 7.3; neut. equiv., 151. Found: C, 71.3; H, 7.4; neut. equiv., 148.

(11) The author is indebted to Mr. S. T. Rolfson for the micro analyses reported in this paper.

The silver salt was insoluble in water but decomposed by dilute nitric acid.

Anal. Calcd. for $C_{18}H_{20}Ag_2O_4$: Ag, 41.8. Found: Ag, 41.8.

Boiled with acetic anhydride for one minute, the acid was reconverted into the **anhydride** VIII, which formed colorless needles after crystallization from benzene, m. p. 177–178°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.1; H, 7.0. Found: C, 75.8; H, 6.8.

5-*t*-Butyl-3-phenylphthalic Acid.—A mixture of 0.5 g. of 5-*t*-butyl-3-phenyltetrahydrophthalic acid with 0.15 g. of sulfur was heated at 250° for five minutes. The pale yellow melt was dissolved in boiling dilute sodium hydroxide; acidification gave a yellow precipitate which was dissolved in warm dilute sodium carbonate (charcoal) and reprecipitated by pouring into hot 1:1 hydrochloric acid. The product separated from dilute acetic acid in the form of colorless prisms that sintered at 170° and melted at 190–192° with gas evolution.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.0. Found: C, 73.2; H, 6.1.

The acid was soluble in warm dilute sodium carbonate, but to isolate it from such a solution it was necessary to precipitate it by pouring the salt solution into an excess of hot mineral acid. If the usual procedure of acidification was followed, there was precipitated an **acid sodium salt**, apparently completely insoluble in water. This acid salt crystallized from dilute acetic acid in the form of very fine matted white needles that did not melt at 270°.

Anal. Calcd. for $C_{18}H_{17}O_4Na + C_{18}H_{18}O_4$: Na, 3.7. Found: Na, 3.9.

The **phthalic anhydride** (**IX**) was obtained by boiling the acid with acetic anhydride for a short time. Recrystallized from benzene–ligroin it melted at 142–143°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.2; H, 5.7. Found: C, 77.2; H, 5.7.

3-*t*-Butylfluorenone-1-carboxylic Acid (**X**).—A solution of 0.4 g. of 5-*t*-butyl-3-phenylphthalic acid in 4 ml. of concd. sulfuric acid was heated for five minutes at 100°. The resulting dark red solution was poured on ice, giving 0.4 g. of a bright yellow solid. Recrystallized from dilute acetic acid, the product formed plates that melted at 184–186°. It had a pure yellow color with no trace of the orange tint characteristic of fluorenone-1-carboxylic acid; its solution in aqueous sodium carbonate was pale yellow.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.2; H, 5.7. Found: C, 77.3; H, 6.0.

Summary

3-*t*-Butyl-1,2-diketohydrindene is entirely ketonic, the enolization usual in 3-substituted diketohydrindenes being suppressed by the *t*-butyl group.

t-Butylmagnesium chloride adds 1,4 to benzalacetone, but also and to an unexpectedly large extent 1,2.

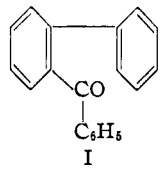
MINNEAPOLIS, MINNESOTA RECEIVED MARCH 22, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

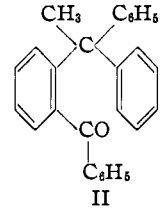
Aromatic Cyclodehydration. XII.[1] The Mechanism of the Cyclization of *o*-Benzylphenones. II

BY CHARLES K. BRADSHER[2] AND E. STUDLEY SMITH[3]

In the preceding communication of this series[1] we presented evidence that the cyclization of *o*-benzylphenones does *not* proceed through an enolic intermediate. This conclusion was based upon the behavior of *o*-phenylbenzophenone (I) and the imine of *o*-benzoyl-1,1,1-triphenylethane (II) in boiling 48% hydrobromic acid. It is believed that cyclization was effected in both cases,



I



II

but in only the first of these were we able to demonstrate that fact by synthesis. In the second, and theoretically more important, case involving the formation of a 9,10-dihydroanthracene derivative, our attempt to confirm the identity of the product by synthesis was unsuccessful.[4] We felt that by choosing a suitable ketone or, more exactly, ketimine, it would be possible to obtain upon cyclization, a 9,10-dihydroanthracene derivative whose structure could be demonstrated by an alternative method of synthesis. This has now been accomplished.

The ketimine chosen was the imine (VII) of *o*-benzoyl-2,2-diphenylpropane, prepared by the series of reactions illustrated. First, methyl *o*-

(1) For the preceding communication of this series see THIS JOURNAL, **65**, 854 (1943).

(2) National Research Fellow (participating basis 1941–1942).

(3) Eastman Kodak Scholar 1941–1942.

(4) There are alternative methods which would be expected to lead to the synthesis of 9,10-diphenyl-9-methyl-10-alkoxy-9,10-dihydroanthracenes, but the possibility of stereoisomerism in this series made a continuation of this approach appear unprofitable.