18.7 g. (32%). After washing with petroleum ether, recrystallization from hot water gave plates, m. p. 118.7–120.5°, and a further recrystallization from ethyl acetate gave clusters of glistening colorless plates, m. p. 119.4–120.5°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.40; H, 9.57. Found: C, 71.28; H, 9.55.

Microtitration with 0.01 *N* sodium hydroxide (phenolphthalein) gave equivalent weight: 167.9, 168.3. Calcd. 168.2.

Determination of the absorption spectrum in ethanol solution gave $\lambda_{max.}$ 255 mμ, log ϵ = 4.12.

The Ferric Chloride Test.—As a result of the insolubility of the dione in cold water (the solid is waxy, and is not wetted under these conditions), no color appeared on addition of aqueous ferric chloride to a suspension of the substance. If, however, the hot aqueous solution of the dione was cooled and filtered, the filtrate gave a strong red-violet color with one drop of 1% aqueous ferric chloride solution.[15]

Summary

The condensation of acyloin enolates with ethyl acetate leads to the formation of 1,3-cyclopentanediones.

[15] *Cf.* Blaise and Maire, *Bull. soc. chim.*, [4] **3**, 427 (1908).

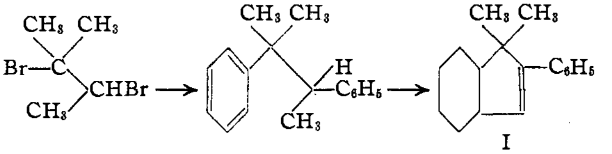
CAMBRIDGE, MASS. RECEIVED DECEMBER 15, 1942

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

The Action of Methylmagnesium Iodide on Methyl α-Phenylcinnamate and a Synthesis of 1,1-Dimethyl-2-phenylindene

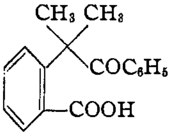
BY C. F. KOELSCH AND PAUL R. JOHNSON

In connection with an investigation on the pyrolysis of indene derivatives[1] a sample of 1,1-dimethyl-2-phenylindene was required. It had been reported that this hydrocarbon was formed[2] by the action of trimethylethylene bromide on benzene in the presence of aluminum bromide.



The hydrocarbon so obtained melted at 50–51°, gave an acidic oxidation product that melted at 198° (formulated as II), and gave a nitro derivative that melted at 140°. But these properties are in exact agreement with those of 1,1-dimethyl-3-phenylindene,[1] and it was therefore believed that the Friedel–Crafts reaction involved a rearrangement and that the product was really the isomer (III) of I.

This belief was confirmed by the results of the work described in the present paper, in which it is shown that I has properties different from those previously ascribed to it. The 198° acidic oxidation product is therefore IV, and the 142° nitro derivative is 1,1-dimethyl-2(?)-nitro-3-phenylindene.



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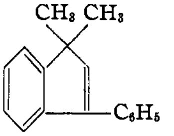
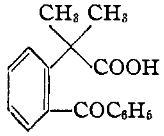
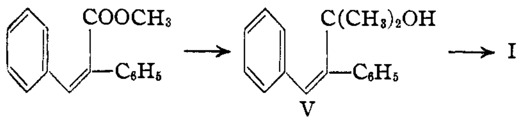


III



IV

The synthesis of I first attempted involved the reactions



But no solid product could be obtained by the action of acids on V. Oxidation of the oils produced by dehydrating agents gave only benzoic acid, indicating that no indene had been formed.

If the product of the reaction between methylmagnesium iodide and methyl α-phenylcinnamate were a ketone, formed by 1,2- and 1,4-additions, it would not yield an indene. The Grignard product had been studied previously[3] and its structure had been based on the formation of benzoic and acetic acids from it by oxidation. Since these acids might also result from the oxidation of a 1,4-addition product, it became necessary to secure new evidence regarding the structure.

Reduction with sodium and alcohol gave a carbinol, and this carbinol was identical with the product (VI) obtained from methylmagnesium

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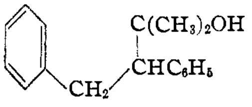
[1] Koelsch and Johnson, THIS JOURNAL, **65**, 567 (1943).

[2] Earl and Smythe, *J. Proc. Roy. Soc. N. S. Wales*, **44**, 90 (1930), *Brit. Chem. Abstracts*, A, 340 (1931).

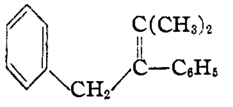
[3] Kohler and Heritage, *Am. Chem. J.*, **33**, 153 (1905).

iodide and methyl α,β-diphenylpropionate. Accordingly, the structure V assigned by Kohler and Heritage is correct, and the failure of the compound to yield an indene must be a real although unexpected property of the carbinol itself. Perhaps the phenyl and the carbinol groups are on opposite sides of the double bond (the ester used in the Grignard reaction has this configuration),[4] but it is difficult to believe that such a configuration is maintained in the resonating cation formed from V and acids.

The indene I was finally prepared by a modification of Orechoff's synthesis.[5]



VI



VII

The carbinol VI was dehydrated, giving VII, and the dibromide of this olefin was boiled in acetic acid, yielding I. The indene melted at 61–62°, and on oxidation was converted into an acid (II) isomeric with IV.

Experimental

2-Methyl-3,4-diphenyl-3-butene-2-ol (V).—α-Phenylcinnamic acid was obtained in nearly quantitative yield by boiling a mixture of 108 g. of phenylacetic acid, 100 g. of benzaldehyde, 100 g. of anhydrous sodium acetate, and 250 ml. of acetic anhydride for ten hours. A solution of 52 g. of the acid in 250 ml. of methanol containing 4 ml. of concd. sulfuric acid, boiled for nine hours, gave 32 g. (62%) of the methyl ester, m. p. 75–76°. The ester (42 g.) in 200 ml. of ether, added to ethereal methylmagnesium iodide prepared from 12.7 g. of magnesium, gave a clear solution, and no color changes were noted during the addition. The mixture was hydrolyzed with iced ammonium chloride (hydrolysis with dilute hydrochloric acid gave oily products), and the product was isolated in the usual way; yield, 21 g. (50%), m. p. 69–70° (reported,[3] 68°).

The carbinol absorbed bromine in chloroform, contrary to the statement of Kohler. It gave no iodoform test, and it could be distilled at atmospheric pressure without decomposition. In one experiment, dehydration with sulfuric acid in acetic acid gave a small amount of oily material that boiled at 160–180° at 10 mm., and there was isolated from this a few mg. of I, but in most dehydrations (sulfuric or hydrochloric acid in methanol or acetic acid) only oily products were obtained.

2-Methyl-3,4-diphenylbutanol-2 (VI).—(a) One gram of V in 10 ml. of dry alcohol was treated with 1 g. of sodium. After the metal had dissolved, water and ether were added. Removal of the ether left an oil which crystallized on rubbing with cold petroleum ether; yield, 0.1 g.; m. p. 68–69°.

(b) α,β-Diphenylpropionic acid, obtained in 85% yield by electrolytic reduction of α-phenylcinnamic acid, gave methyl α,β-diphenylpropionate (b. p. 168° at 8 mm.) in a yield of 94%. This ester (17.5 g.) in ether was added to methylmagnesium iodide prepared from 5.25 g. of magnesium. The mixture was hydrolyzed with iced ammonium chloride, and the product was crystallized from ligroin. It formed colorless crystals (15–15.5 g., 86–88%) that melted at 68–69°.

Anal. Calcd. for $C_{17}H_{20}O$: C, 85.0; H, 8.4. Found: C, 84.9; H, 8.6.

2-Methyl-3,4-diphenylbutene-2 (VII).—A solution of 15 g. of VI in 50 ml. of acetic acid containing 0.5 ml. of concd. sulfuric acid was kept at 100° for two hours and then poured into water. The product was taken up in ether and then distilled. It was obtained in nearly quantitative yield, boiled at 150° at 10 mm. or 176–178° at 26 mm., and had a refractive index ($n^{24}\text{D}$) of 1.5632.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.8; H, 8.2. Found: C, 90.7, 90.7; H, 8.1, 8.3.

Since an entirely satisfactory analysis could not be obtained, the olefin (0.5 g.) was further characterized by oxidation with chromic anhydride (0.3 g.) in acetic acid at room temperature (one hour). This treatment yielded desoxybenzoin (m. p. 54–55°, oxime, m. p. 97°) together with a small amount of benzoic acid.

1,1-Dimethyl-2-phenylindene (I).—Bromine (8 g.) was added to a solution of 11 g. of VII in 75 ml. of chloroform. The solvent was distilled and replaced by 100 ml. of acetic acid, and the resulting solution was boiled for thirty minutes. Water was added, and the product was taken up in ether and distilled, giving 9 g. of a yellow oil that boiled at 160–162° at 8 mm. and crystallized on rubbing with cold methanol. Recrystallization gave 5 g. (45%) of a colorless product that melted at 61–62°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.5; H, 7.5.

α,α-Dimethyldesoxybenzoin-*o*-carboxylic Acid (II).—A solution of 0.5 g. of I and 1.8 g. of chromic anhydride (calcd. for oxidation to *phthalic* acid) in 15 ml. of acetic acid was kept at 100° for five hours, then cooled and poured into water and ether. The ether solution was shaken out with dilute sodium carbonate. This extract was acidified, giving 0.1 g. of a water insoluble acid, m. p. 175–185° (crude); a very small amount of benzoic acid was present in the aqueous mother liquor. Evaporation of the ether containing the supposedly neutral oxidation products left a colorless solid (0.25 g.), m. p. 185–195° (crude). This solid was soluble in boiling dilute sodium carbonate, and on purification was found to be identical with the acidic oxidation product. This peculiar behavior of the acid was noted in several confirmatory oxidations; the compound can be extracted from ether with sodium carbonate completely only on prolonged shaking. The pure product, crystallized from acetic acid, melted at 210–211°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 75.8; H, 5.9.

The acid was extremely stable to further oxidation. A solution of it (0.1 g.) in dilute sodium carbonate was boiled for seven hours with 0.07 g. of potassium permanganate. Very little manganese dioxide was formed, and acidification gave 0.09 g. of unaltered starting material.

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(4) Bakunin, *Gazz. chim. ital.*, **27**, II, 49 (1897).

(5) Orechoff, *Ber.*, **47**, 94 (1914).

Summary

A synthesis of 1,1-dimethyl-2-phenylindene is described, and it is shown that a hydrocarbon previously believed to have this structure is actually 1,1-dimethyl-3-phenylindene. The finding of Kohler and Heritage that the reaction between methylmagnesium iodide and methyl α-phenylcinnamate involves 1,2-addition is confirmed.

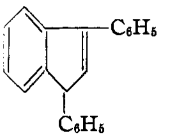
MINNEAPOLIS, MINN. RECEIVED DECEMBER 21, 1942

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

The Thermal Isomerization of Some Indene Derivatives

BY C. F. KOELSCH AND PAUL R. JOHNSON

In a previous paper[1] it was shown that the pyrolysis of α,α,γ-triphenylpropylene yielded, among other products, 1,3-diphenylindene (I), 1,2-diphenylindene (II), and 2,3-diphenylindene (III). The 1,3-compound obviously resulted from dehydrogenation of the propylene with accompanying cyclization. Data were presented which rendered it likely that the formation of 1,2- and 2,3-diphenylindenes was not a result of isomerization followed by cyclization, but was instead a result of these processes in the reverse order.



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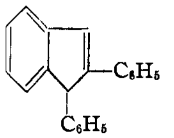

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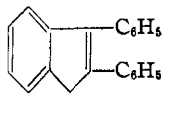


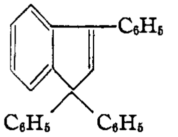
III

In the present paper it is shown that I is transformed into a mixture of II and III at 450°, and that therefore the mechanism previously outlined is at least possible. Of considerably greater interest is the discovery that the isomerization is reversible. Any of the three compounds mentioned yielded the same mixture of products on pyrolysis; in a large number of runs on each of the indenes, the products were I (8–20%), II (4–6%), and III (47–65%). An indene mixture containing the three substances in approximately the ratios indicated, passed through the pyrolysis tube five times without any change in composition.

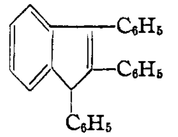
Reversibility in the present example indicates that the failure of v. Braun and Manz[2] to detect any 1(or 3)-phenylindene in the pyrolysis product of 2-phenylindene was caused by an unfavorable equilibrium, the reverse rearrangement having been demonstrated.

Since II and III are interconvertible under conditions much milder than those involved in pyrolysis, it was not possible to tell whether the phenyl from position 3 or that from position 1 was involved in the isomerization of I. In order to gain some insight into this question, the pyrolysis of more highly substituted indenes was studied. That migration from position 1 was possible was shown in three examples.

1,1,3-Triphenylindene (IV) gave 1,2,3-triphenylindene (V) at 490° in an 86% yield; the remainder of the product was a red gummy substance. 3′-Phenyl-*spiro*-[fluorene-9,1′-indene](VI) gave 13-phenyl-(13)-dibenzo[ac]fluorene (VII) in an 80% yield, and 17% of the starting material was recovered. The question of reversibility in these two cases is of particular interest. The results are best interpreted as showing that the point of equilibrium, assuming reversibility in the reaction, is far toward the side of the products V and VII, for in the case of IV, no starting material was found in the products, and in the case of VI, the presence of starting material in the product was probably a result of the special conditions necessary for carrying out the pyrolysis. Under the usual conditions VI was largely



IV



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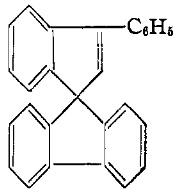
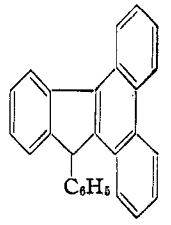


VI



VII

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[1] Koelsch and Johnson, *J. Org. Chem.*, **6**, 534 (1941).

[2] v. Braun and Manz, *Ber.*, **62**, 1059 (1929).