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.

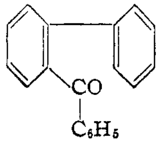
MINNEAPOLIS, MINNESOTA RECEIVED MARCH 22, 1943

[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, 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.



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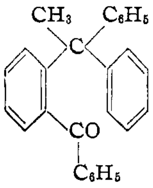

II

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

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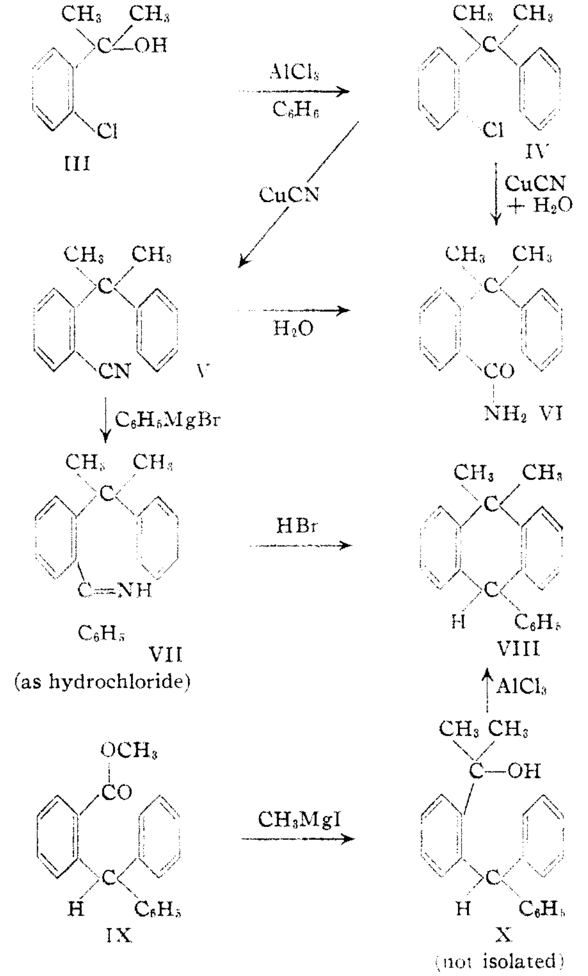
(1) For the preceding communication of this series see THIS JOURNAL, **65**, 854 (1943).

(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.

chlorobenzoate was converted to *o*-chlorophenyldimethylcarbinol (III) by the action of methylmagnesium iodide. This carbinol, in the presence of aluminum chloride, condensed with benzene to give *o*-chloro-2,2-diphenylpropane (IV). The nitrile (V) was prepared by the action of cuprous cyanide on the halide (IV) and was converted to the ketimine (VII) of *o*-benzoyl-2,2-diphenylpropane by the action of phenylmagnesium bromide. Refluxing the salt of this imine (VII) with 48% hydrobromic acid, gave, instead of the expected bromide,[5] a hydrocarbon having the composition of 9,9-dimethyl-10-phenyl-9,10-dihydroanthracene (VIII).



The structure of the new hydrocarbon (VIII) has been demonstrated very simply. Methyl *o*-benzohydrylbenzoate[6] was treated with methylmagnesium iodide, and the crude carbinol (X) was cyclized by the action of aluminum chloride. The resulting product was identical with the new hydrocarbon (VIII) which is, therefore, 9,9-dimethyl-10-phenyl-9,10-dihydroanthracene.

Thus, it may be regarded as demonstrated that cyclization in the presence of boiling hydrobromic acid may take place with the formation of a six-membered ring, even in a case in which enolization of a ketonic intermediate[7] cannot be involved.

One other observation worthy of note is that *o*-(α,α-dimethylbenzyl)-benzamide (VI), which may be prepared either from the halide (IV) or the nitrile (V) by the action of cuprous cyanide and water, is very resistant to hydrolysis. This is probably a result of steric hindrance.

Experimental

***o*-Chlorophenyl-dimethylcarbinol** (III).—A solution of 170 g. of methyl *o*-chlorobenzoate in ether was added to a solution of methylmagnesium iodide prepared from 355 g. of methyl iodide and 62 g. of magnesium and the mixture refluxed for two hours. The reaction product was decomposed with ice and ammonium chloride and the ethereal layer separated, dried and concentrated. The residue was distilled *in vacuo* yielding 140 g. (82.5%) of a colorless oil, b. p. 108–111° (12 mm.). A sample was redistilled for analysis, b. p. 94° (8 mm.).

Anal. Calcd. for $C_9H_{11}OCl$: C, 63.35; H, 6.50. Found: C, 63.72; H, 6.46.

***o*-Chloro-2,2-diphenylpropane** (IV).—A solution of 140 g. of the above carbinol in 350 cc. of dry benzene was added dropwise to a suspension of 55.2 g. of aluminum chloride in benzene cooled in an ice-bath. The addition was at such a rate that the temperature did not rise above 10°. Stirring was continued overnight during which time the reaction was allowed to reach room temperature. The mixture was decomposed with ice and dilute hydrochloric acid and the benzene layer washed, concentrated and the residue vacuum-distilled through a Widmer column. After a small forerun, 114.5 g. (61%) of *o*-chloro-2,2-diphenylpropane was obtained, b. p. 143–147° (7 mm.). An analytical sample was obtained by redistillation, b. p. 146° (7 mm.).

Anal. Calcd. for $C_{15}H_{15}Cl$: Cl, 15.37. Found: Cl, 15.29.

***o*-Cyano-2,2-diphenylpropane** (V).—A mixture of 11.6 g. of the halide (IV) prepared above, 4.66 g. of cuprous cyanide, 1 cc. of phenylacetonitrile and 13 cc. of pyridine was heated in a sealed tube for forty-eight hours at 250°

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[5] In previous cyclization experiments (ref. 1) with compounds analogous to this ketimine, the crude cyclization product was a bromide which was not isolated as such, but converted to the more convenient alkoxyl derivative. In this case, the expected bromide was 9,9-dimethyl-10-phenyl-10-bromo-9,10-dihydroanthracene. If this compound was formed, indeed, it probably underwent reduction in the presence of the boiling hydrobromic acid.

[6] Haller and Guyot, *Compt. rend.*, **139**, 9 (1904).

[7] On the basis of present information, we cannot discount the possibility that cyclization of these hindered imines proceeds directly, *i. e.*, without hydrolysis to an intermediate ketone. A possible mechanism for such a cyclization could be formulated in much the same terms employed in the case of the *o*-benzylphenones (note 1).

Worked up in the usual way, the product was obtained as colorless prisms from alcohol, m. p. 62–64°; yield 7.55 g. (68%). An analytical sample was obtained by repeated recrystallization from alcohol, m. p. 62–63.5°.

Anal. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83. Found: C, 86.38; H, 6.39.

The nitrile was unaffected after refluxing for forty-nine hours with 10% alcoholic potassium hydroxide.

o-(α,α-Dimethylbenzyl)-benzamide (VI). (a) From the Halide (IV).—A mixture of 11.6 g. of the halide, 9.5 g. of cuprous cyanide, 30 cc. of pyridine and 4 cc. of water was heated for four days at 250°. Worked up in the usual way and recrystallized from alcohol, 2.4 g. (20%) of the amide (VI) was obtained, m. p. 132–134°.

(b) From the Nitrile (V).—A mixture of 4 g. of the nitrile, 10 cc. of pyridine, 1.4 cc. of water and 1 g. of cuprous cyanide was heated in a sealed tube for four days at 250°. Worked up as usual and crystallized from benzene-petroleum ether, 1.33 g. (31%) of the amide m. p. 132–135°, was obtained. The yield was not increased if heating was continued for ten days, and in each case some of the nitrile was recovered. A sample, prepared for analysis by repeated crystallization from alcohol, was obtained as white prisms, m. p. 136.5–137.5°.

Anal. Calcd. for $C_{16}H_{17}ON$: C, 80.30; H, 7.16. Found: C, 80.30; H, 7.33.

The amide was not affected when refluxed for forty-nine hours with a mixture of concentrated hydrochloric acid and acetic acid. Likewise, heating with concentrated hydrochloric acid alone for forty-eight hours at 200° in a sealed tube was without effect.

The Hydrochloride of the Imine of o-Benzoyl-2,2-diphenylpropane (VII).—A solution of 5 g. of the nitrile (V) in 50 cc. of benzene was added to the Grignard reagent prepared from 14.2 g. of bromobenzene and 2.2 g. of magnesium and the mixture refluxed overnight. Upon addition of ice and hydrochloric acid, the imine hydrochloride precipitated and was collected and air-dried; yield 4.55 g. (60%). A sample was prepared for analysis by repeated reprecipitation from benzene by hydrochloric acid.

Anal. Calcd. for $C_{22}H_{22}NCl$: N, 4.17; Cl, 10.56 Found: N, 4.15; Cl, 10.42.

The imine hydrochloride was quite resistant to hydrolysis. After twenty-nine hours of refluxing with 10% hydrochloric acid, the hydrochloride was recovered and no ketone was obtained.

Action of Boiling Hydrobromic Acid on the Imine Hydrochloride (VII).—A suspension of 0.5 g. of the imine hydrochloride in 25 cc. of 48% hydrobromic acid was refluxed for forty-eight hours. At the conclusion of this period, the product was extracted with benzene and the purified benzene extract concentrated. The residue was purified by vacuum sublimation giving 0.2 g. (47.5%) of **9,9-dimethyl-10-phenyl-9,10-dihydroanthracene** (VIII), m. p. 144–145°. A sample purified for analysis by recrystallization from alcohol was obtained as white prisms, m. p. 145–146°.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.75; H, 7.23.

Synthesis of 9,9-Dimethyl-10-phenyl-9,10-dihydroanthracene (VIII).—A solution of 5 g. of methyl *o*-benzhydrylbenzoate[6] was added to a Grignard reagent prepared from 5.9 g. of methyl iodide and 1.1 g. of magnesium and the mixture refluxed for two hours. The reaction product was decomposed with ice and ammonium chloride and the solvent layer washed, dried and concentrated. Since preliminary attempts at crystallization or distillation at 10–15 mm. pressure[8] showed little promise, the intermediate carbinol (X) was not isolated, but used directly in the cyclization. A solution of the above carbinol in 50 cc. of carbon disulfide was added dropwise to a mechanically stirred suspension of 2.5 g. of aluminum chloride in 50 cc. of carbon disulfide. The temperature was kept below 10° by means of an ice-bath for the first two or three hours and was then allowed to rise slowly to room temperature. The product was decomposed with ice and hydrochloric acid, the washed extract was concentrated and the residue purified by vacuum sublimation followed by crystallization from ethyl alcohol. The product was obtained as white needles, m. p. 139–141°; yield 0.75 g. (16%, based on the ester). Recrystallized, it melted at 144–146° and gave no depression of melting point when mixed with a sample of the hydrocarbon prepared from the imine (VII).

Summary

It has been demonstrated that the action of hydrobromic acid on a suitable imine may bring about cyclization to form a six-membered ring even though the ketone expected as an intermediate could not undergo enolization.

DURHAM, N. C.

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[8] Apparently decomposition took place when distillation was attempted at this pressure.