3. Interaction of germanium tetrachloride and *p*-tolylmagnesium bromide yielded principally tri-*p*-tolylgermanium bromide, indicating the probable cause of low yields of tetraarylgermanes hitherto obtained by this method.

4. Controlled action of hydrogen bromide on tetraphenyl- and tetra-*p*-tolylgermanium yielded the corresponding triarylgermanium bromide and aromatic hydrocarbon.

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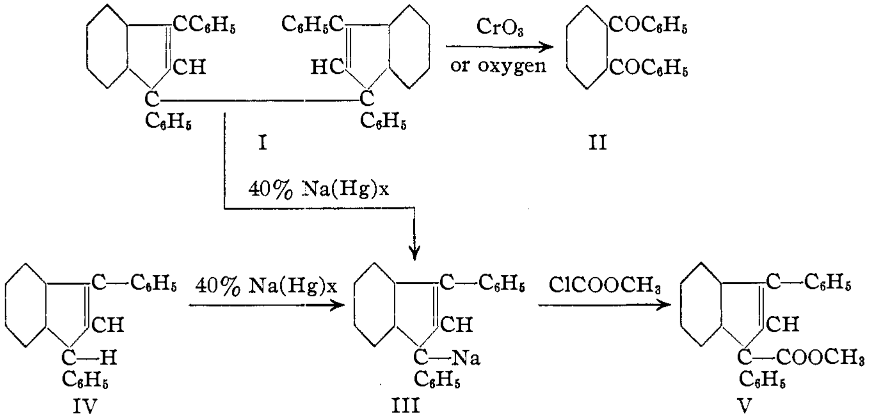
Rearrangements of the Polyines. V. Reactions of Bis-1,1'-(1,3-diphenylindenyl)

BY M. T. GOEBEL AND C. S. MARVEL

Bis-1,1'-(1,3-diphenylindenyl) (I) has recently been prepared[1] for the purpose of comparing it with the isomeric hydrocarbon $C_{42}H_{30}$, which is formed by the rearrangement of tetraphenyldiphenylethinylethane.[2] A comparison of the physical properties of these two hydrocarbons showed that they were not identical. The present study of the chemical reactions of bis-1,1'-(1,3-diphenylindenyl) has shown that it resembles the hexaarylethanes rather than the hydrocarbons produced when tetraaryldiethinylethanes undergo rearrangement.



Bis-1,1'-(1,3-diphenylindenyl) (I) was oxidized readily by chromic acid to give almost quantitative yields of *o*-dibenzoylbenzene (II) and no *o*-benzoylbenzoic acid was obtained. Under the same conditions Moureu's hydrocarbon[2] yielded no *o*-dibenzoylbenzene but did give *o*-benzoylbenzoic

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(1) Halley and Marvel, THIS JOURNAL, **54**, 4450 (1932).

(2) Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927); Wieland and Kloss, *Ann.*, **470**, 217 (1929); Munro and Marvel, THIS JOURNAL, **54**, 4445 (1932).

acid. The bisindenyl was rapidly oxidized to *o*-dibenzoylbenzene by oxygen at the temperature of boiling xylene. Some oxygen was absorbed by a cold solution of the bisindenyl but no definite oxidation products were isolated.

The bisindenyl gave a faintly yellow colored solution in xylene at room temperature. Heating this solution out of contact with air caused the color to deepen and subsequent cooling caused this color to fade. However, the color change was not strictly reversible and continued heating and cooling changed the bisindenyl into a gummy solid.

The bisindenyl was slowly cleaved by 1% sodium amalgam but readily by 40% amalgam or sodium–potassium alloy to give a metal derivative (III) which was identical with the one prepared from 1,3-diphenylindene (IV). The identity of the two metal derivatives was shown by converting them to the same methyl ester of 1,3-diphenylindene-1-carboxylic acid (V).

These reactions of bis-1,1′-(1,3-diphenylindenyl) show that it contains a weak central carbon–carbon linkage and apparently dissociates to an unstable free radical at elevated temperatures. It is related in structure to the diarylvinyldiarylmethyl radicals of Ziegler[3] and to the triphenylindenyl of Kohler.[4]

Experimental

Bis-1,1′-(1,3-diphenylindenyl).—The procedure of Halley and Marvel[2] was followed but somewhat larger runs were made. The product was obtained in yields of 65% of the theoretical amount, m. p. 195–196°. It was also readily prepared by treating 1,3-diphenylindene with 40% sodium amalgam and treating the resulting metal alkyl with tetramethylethylene bromide.

Oxidation. 1. With Potassium Dichromate.—A solution of 1 g. of the hydrocarbon and 5 g. of potassium dichromate in 50 cc. of glacial acetic acid was boiled under a reflux condenser for about ten hours. The solution was poured into water, the precipitate was collected on a suction filter and then recrystallized from alcohol. The yield was 0.8 g. of *o*-dibenzoylbenzene, m. p. 145–146°. The identification was made by taking a mixed melting point of this material with *o*-dibenzoylbenzene prepared according to the method of Guyot and Catel.[5]

2. With Oxygen.—A solution of the bisindenyl in xylene did not absorb a measurable amount of oxygen at 30°. However, at the temperature of boiling xylene, the solution did absorb oxygen and the bisindenyl was oxidized to *o*-dibenzoylbenzene.

A solution of 0.5 g. of the bisindenyl in 30 cc. of xylene was placed in a flask attached to a gas buret filled with oxygen. The solution was heated to boiling and shaken vigorously for about thirty minutes. The solution was maintained at the boiling point of xylene by heating the flask occasionally with a small flame. The mixture was cooled, and the oxygen absorption (92 cc., 0°, 760 mm.) measured. The treatment was repeated but no further oxygen was absorbed. During the first treatment with oxygen there was a series of color changes which seemed of interest since they occurred in every trial. The solution was pale yellow at the beginning. During the first three minutes of the reaction, this color faded until the solution was entirely colorless. Then during the next five minutes a deep red color developed. At the end of thirty minutes this

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(3) Ziegler, *Ann.*, **434**, 34 (1923).

(4) Kohler, *Am. Chem. J.*, **40**, 217 (1908).

(5) Guyot and Catel, *Bull. soc. chim.*, [3] **35**, 1135 (1906).

color had faded and the solution was again yellow in color. From the reaction mixture 0.3 g. of *o*-dibenzoylbenzene was obtained.

A solution of 1 g. of the bisindenyl in 200 cc. of chloroform was shaken in an atmosphere of dry oxygen for three days. A deep red color developed in the solution and about 20 cc. of oxygen (0°, 760 mm.) was absorbed. Evaporation of the solution gave a red gum from which no crystalline material could be separated.

Effect of Heat.—A solution of the bisindenyl in xylene became deeper yellow in color on heating and the color faded on cooling. After two or three times the deeper color no longer faded. Evaporation of the solution gave a very impure sample of the bisindenyl. Prolonged heating in xylene changed the bisindenyl to gummy products which could not be identified.

Reduction.—Reduction of the bisindenyl by boiling 1 g. with 1.5 g. of phosphorus in 5 cc. of constant boiling hydriodic acid and 50 cc. of glacial acetic acid gave 0.8 g. of 1,3-diphenylhydrindene (m. p. 156–157°) which was identical with a sample of this material which was prepared by the method of Ziegler, Grabbe and Ulrich.[6]

Cleavage with Alkali Metals. With 1% Sodium Amalgam.—A solution of 1 g. of the bisindenyl in 250 cc. of dry ether gave a distinctly yellow colored solution when shaken with 10 cc. of 1% sodium amalgam for thirty minutes.

With 40% Sodium Amalgam.—A solution of 1.5 g. of the bisindenyl in 250 cc. of dry ether was shaken with 10 cc. of 40% sodium amalgam. The characteristic yellow color developed in ten minutes. The mixture was shaken overnight, the sodium derivative was treated with methyl chloroformate and a 20% yield of 1-carbomethoxy-1,3-diphenylindene was obtained. The ester was characterized by comparing it with the material described below.

With Liquid Sodium–Potassium Alloy.—A solution of 1 g. of the bisindenyl in 250 cc. of ether was shaken with 5 g. of liquid sodium–potassium alloy. A yellow color developed at once. After about thirty minutes the metal derivative was converted to the carbomethoxy derivative. The yield was 0.6 g. If the alloy was allowed to react for a longer period a secondary reaction occurred and no ester could be obtained.

1-Carbomethoxyl-1,3-diphenylindene.—A solution of 2 g. of 1,3-diphenylindene in 250 cc. of dry ether was shaken with 10 cc. of 40% sodium amalgam. The reaction seemed to be complete in about an hour, as little hydrogen was evolved after that time. At the end of about twenty-four hours, the excess amalgam was frozen and the yellow solution of the sodium derivative was decanted. An atmosphere of dry nitrogen was maintained over the solution during these operations. A slight excess of methyl chloroformate was added to the solution and then the solution was washed with water, dried over magnesium sulfate and the solvent evaporated. The residue was recrystallized from a mixture of ethyl acetate and methanol. The yield was 1.5 g. of a product melting at 99–100°.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.62; H, 5.56; mol. wt., 326. Found: C, 84.66, 84.58; H, 5.62, 5.51; mol. wt. (Rast), 334, 317.

The corresponding acid could not be obtained by treating the metallic derivative with dry carbon dioxide. When these experiments were performed the carbon dioxide discharged the color of the metal alkyl solution but on working up the reaction mixture only the original 1,3-diphenylindene was recovered. Attempts to hydrolyze the methyl ester with alcoholic potassium hydroxide and subsequent liberation of the acid by addition of mineral acid gave a gum which could not be purified.

Summary

Bis-1,1′-(1,3-diphenylindenyl) has been found to have many properties

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(6) Ziegler, Grabbe and Ulrich, *Ber.*, **57**, 1983 (1924).

which are characteristic of hexaarylethanes and must therefore be classed as a new type of hydrocarbon which contains an active carbon–carbon single bond.

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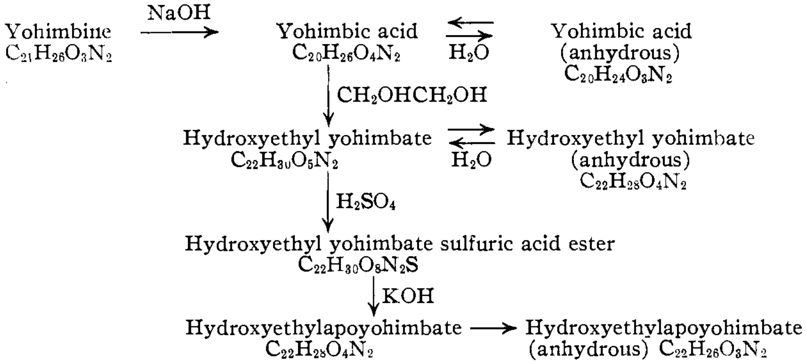
Some Hydroxy and Amino Esters of Yohimbic Acid

BY DAVID E. WORRALL

Yohimbine is an optically active alkaloid occurring in the bark of the African yohimbus tree. The present investigation is concerned with an attempt to increase the anesthetic action by the introduction of certain groups. Yohimbic acid exists in two forms differing one from the other by a molecule of water. Yohimbine is the methyl ester of anhydrous yohimbic acid and results whether one starts with hydrated or anhydrous yohimbic acid. Similarly ethyl alcohol forms an ester with yohimbic acid corresponding to the anhydrous form. On the contrary, propyl and butyl alcohols form esters that retain the additional molecule of water.[1]

It has been found in the present investigation that yohimbic acid forms esters with the polyhydric alcohols, ethylene glycol, trimethyleneglycol and glycerol, as well as with ethylene chlorohydrin, reacting with one equivalent of each. The resulting esters are derivatives of the hydrated form of yohimbic acid. The additional molecule of water is easily eliminated by drying in a vacuum over phosphorus pentoxide, a process that is reversed by exposing the product to air. The new esters turn yellow on exposure to light, form water-soluble salts with acids, etc. Esters are formed with sulfuric acid that on hydrolysis with alkali regenerate sulfuric acid, thereby producing an unsaturated group in the alkaloid. This reaction results in a base containing one molecule less of water than the



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(1) Barger and Field, *J. Chem. Soc.*, **123**, 3003 (1923).