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

The Action of Lithium on α,α,γ,γ,γ-Pentaphenylpropylene[1]

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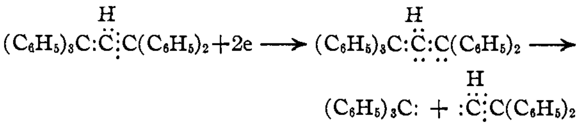
The action of sodium on 1,1,3-triphenylindene results in the replacement of hydrogen and the migration of a phenyl group, and yields the sodium derivative of 1,2,3-triphenylindene.[2] If a similar rearrangement were brought about by the action of sodium on the indene's analog, α,α,γ,γ,γ-pentaphenylpropylene,[3] the product would be the sodium derivative of α,α,β,γ,γ-pentaphenylpropylene, a compound the synthesis of which has been attempted vainly by other methods.[4]

$$(C_6H_5)_2C{=}CH{-}C(C_6H_5)_3 \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)C(C_6H_5)_2Na$$

The action of 40% sodium amalgam on the propylene is extremely slow; after shaking these reagents in ether for seven days, a red solution is obtained which contains only an insignificant amount of organo-alkali compound. The propylene reacts more rapidly with lithium, but although lithium rearranges 1-biphenylene-3-phenylindene normally, the action of this metal on the propylene leads to products which are formed through cleavage rather than through rearrangement. On hydrolysis of the products there is obtained triphenylmethane and α,α,δ,δ-tetraphenylbutene-β, while carbonation yields triphenylacetic acid and α,α,δ,δ-tetraphenyl-Δ^{β}-butene-α,δ-dicarboxylic acid. Dimerization of the primarily formed diphenylvinyl-lithium leading to tetraphenylbutenedilithium is to be expected from the results of Schlenk and Bergmann.[5]

The cleavage of pentaphenylpropylene by lithium is closely related to the cleavage of γ,γ,γ-triphenylpropyl iodide by sodium, and constitutes, by analogy, additional evidence that the latter reaction does not involve positive fragments, but rather negative ions as suggested by Wooster and Morse.[6] These authors point out that the removal of a halogen with its complete octet to leave a positive fragment is extremely improbable; in the present case the formation of a positive fragment by such a process is impossible since no halogen is present to be removed. The primary reaction is probably best represented as



$$(C_6H_5)_3C{:}\overset{H}{\ddot{C}}\vdots C(C_6H_5)_2 + 2e \longrightarrow (C_6H_5)_3C{:}\underset{\cdot\cdot}{\overset{H}{\ddot{C}}}{:}\underset{\cdot\cdot}{C}(C_6H_5)_2 \longrightarrow (C_6H_5)_3C{:} + {:}\overset{H}{\ddot{C}}\vdots C(C_6H_5)_2$$

Experimental

α,α,γ,γ,γ-Pentaphenylpropanol.—Treatment of the product obtained by the action of phenylmagnesium bromide on methyl β,β,β-triphenylpropionate with water regenerates the ester nearly quantitatively. The use of lithium, however, leads to the desired synthesis.

The mixture obtained by the addition of 34 g. of methyl β,β,β-triphenylpropionate to a phenyl-lithium solution containing 2.1 g. of the metal is boiled for thirty minutes and then treated with water. Evaporation of the ethereal solution leaves a solid which, after crystallization from ligroin and then from butyl alcohol weighs 34 g. and melts at 139–140°.

Anal. Calcd. for $C_{33}H_{28}O$ (440): C, 89.96; H, 6.41. Found: C, 90.24, 90.21; H, 6.46, 6.39; mol. wt. (Rast), 440.

The carbinol is converted into a mixture of 1,1,3,3-tetraphenylhydrindene with a little pentaphenylpropylene by boiling for one hour with a 4% solution of sulfuric acid in acetic acid, but the complete separation of this mixture is difficult and wasteful.

α,α,γ,γ,γ-Pentaphenylpropylene.—Pentaphenylpropanol (9.5 g.) is warmed with thionyl chloride for thirty minutes, and the excess of the latter then removed by warming under reduced pressure. The resulting oil is boiled with dilute alcoholic potassium hydroxide for thirty minutes, the alcohol distilled, and the mixture extracted with ether. The solid remaining after evaporating the ether is crystallized twice from acetic acid, yielding 3.8 g. of pentaphenylpropylene which forms white crystals that melt at 132–133°.

Anal. Calcd. for $C_{33}H_{26}$: C, 93.79; H, 6.21. Found: C, 93.42; H, 6.02.

Boiling the propylene (0.5 g.) for three hours with 10 ml. of 4% sulfuric acid in acetic acid converts it into 1,1,3,3-tetraphenylhydrindene which melts at 191–192°. This hydrindene is colorless and is recovered quantitatively after boiling for six hours with an excess of aqueous potassium permanganate.

Anal. Calcd. for $C_{33}H_{26}$: C, 93.79; H, 6.21. Found: C, 93.46; H, 5.71.

On heating its acetic acid solution with chromic acid at 60°, pentaphenylpropylene yields benzophenone and triphenylcarbinol; these substances are separated easily by extracting a solution of a mixture of them in petroleum ether with 80% sulfuric acid.

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(1) Abstracted from the thesis of R. H. Rosenwald, submitted to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, December, 1936.

(2) Ziegler and Crossmann, *Ber.*, **62**, 1768 (1929).

(3) An unsuccessful attempt to obtain this hydrocarbon has been reported by Schlenk, Bergmann and Rodloff, *Ann.*, **487**, 153 (1931).

(4) Koelsch, THIS JOURNAL, **54**, 3384 (1932).

(5) Schlenk and Bergmann, *Ann.*, **463**, 106 (1928).

(6) Wooster and Morse, THIS JOURNAL, **56**, 1735 (1934).

Pentaphenylpropylene (0.5 g.) is reduced when its solution in butyl alcohol (40 ml.) is treated with sodium (1.8 g.). The resulting **$\alpha,\alpha,\gamma,\gamma,\gamma$-pentaphenylpropane** (0.4 g.) crystallizes from acetic acid in the form of small needles that melt at 158–159°.

Anal. Calcd. for $C_{33}H_{28}$: C, 93.34; H, 6.66. Found: C, 93.22; H, 6.97.

Action of Sodium Amalgam on the Propylene.—The red solution obtained by shaking pentaphenylpropylene in ether with 40% sodium amalgam for seven days is decolorized by the addition of alcohol. After washing the solution with water and evaporating the ether, there is obtained 0.8 g. of a crystalline product which melts at 131–133° alone or mixed with the starting material.

Action of Lithium on the Propylene.—A solution of the propylene (1 g.) in ether (50 ml.) usually becomes red after shaking for twenty-four hours with finely-cut lithium (0.4 g.). To ensure complete reaction, shaking should be continued for seven days.

Such a solution treated with alcohol yields an oil after removal of the lithium hydroxide and the ether. This oil when dissolved in acetic acid deposits 0.2 g. of $\alpha,\alpha,\delta,\delta$-tetraphenylbutene-$\beta$ (m. p. 139–140°, literature,[7] 140.5), while from the acetic acid mother liquor is obtained a small amount of triphenylmethane (m. p. 92° from petroleum ether). There are no indications of the presence of a third product, but the difficulty of separating these two hydrocarbons prevents their quantitative isolation.

A solution of the lithium compounds from pentaphenylpropylene (1 g.) is decolorized when carbon dioxide is passed into it. From the resulting mixture there is obtained a solid (1 g.) soluble in dilute sodium carbonate. By fractional crystallization from ethyl alcohol this solid may be separated into the less soluble triphenylacetic acid (0.3 g.), which melts at 264–266° alone or mixed with an authentic sample, and tetraphenylbutenedicarboxylic acid (0.22 g.). The latter product gives benzophenone on oxidation with aqueous potassium permanganate and melts at 255–257° alone or mixed with a sample prepared according to the method of Schlenk and Bergmann[7] (p. 102).

Action of Lithium on 1-Biphenylene-3-phenylindene.—An ethereal solution of 1-biphenylene-3-phenylindene (0.5 g.) is shaken for three days with an excess of lithium and then treated with alcohol. Crystallization of the product from acetic acid yields 0.4 g. of 1,2,3,4-dibenzo-9-phenylfluorene which melts at 209° alone or mixed with a known sample.[8]

Summary

$\alpha,\alpha,\gamma,\gamma,\gamma$-Pentaphenylpropylene is cleaved by lithium, yielding triphenylmethyl-lithium and, through dimerization of the other product, $\alpha,\alpha,\delta,\delta$-tetraphenylbutenedilithium.

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(7) Schlenk and Bergmann, *Ann.*, **463**, 106 (1928).

(8) Koelsch, This Journal, **56**, 480 (1934).

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[A COMMUNICATION FROM THE LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Use of Polarographs in Determining Ketones

BY GERALD T. BORCHERDT, VILLIERS W. MELOCHE AND HOMER ADKINS

The solution of a number of problems in organic chemistry depends upon obtaining a method of analysis for small amounts of ketones and aldehydes in mixtures containing two or more such compounds. The present paper is concerned with the development of procedures for the use of the polarograph for the accurate determination of acetophenone and *p*-chlorobenzophenone separately and in mixtures with each other. A subsequent paper illustrates the value of the procedures in following a tautomeric change.

Two different polarographs have been used in this study, the one a Heyrovsky instrument and the other a product of Leeds and Northrup. The former makes its record on photographic paper which must be developed, while the latter instrument draws a line in ink similar to that made by the well-known Leeds and Northrup potentiometer temperature recorder.[1,2]

A polarograph is an instrument which continuously increases the potential across a cell, at the same time making a record of the amount of current passing through the cell. The cell is a small glass vessel containing 0.01 to 5.00 ml. of a solution to be analyzed. A stream of fine drops of mercury flows from a capillary (cathode) through the solution to the floor of the cell, which is covered with mercury (anode).

Current flows through the cell after the potential across it has reached a value characteristic of the most readily reducible compound in the cell. The amount of current flowing then increases rapidly with a small increase in potential across the cell. During this time is drawn the "A" portion of the curve, as indicated in Fig. 1. This

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(1) For references on Heyrovsky polarograph see review paper by Winkel and Proske, *Angew. Chem.*, **50**, 18 (1937). See also "Chemische Analysen mit dem Polarographen," by Dr. Hans Hohn, Verlag von Julius Springer, Berlin, 1937.

(2) Funds for the purchase of the instruments used in this investigation were provided by the Graduate Research Committee of the University of Wisconsin.