

pressure, this material melted at 90–93°. The melting point was not changed by further treatment. The material was evidently not a single product but analysis indicated a formula $C_{42}H_{30}(COOCH_3)_2$.

Anal. Calcd. for $C_{42}H_{30}O_4$: C, 84.7; H, 5.52. Found: C, 85.4; H, 5.68.

This product requires further study but it is of interest because it shows that the true ethane and its rearrangement product give distinctly different compounds when treated with sodium amalgam.

Summary

Tetraphenyldiphenylethinyethane has been prepared in solution. This hydrocarbon is oxidized by oxygen, is cleaved by 40% sodium amalgam, and readily rearranges to an isomeric hydrocarbon, $C_{42}H_{30}$, which is identical with the hydrocarbon which has previously been prepared by the action of metals on diphenylphenylethynylchloromethane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

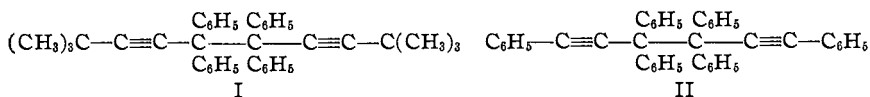
REARRANGEMENTS OF POLYINES. III. THE SYNTHESIS OF BIS-1,1'-(1,3-DIPHENYLINDYL)

BY L. F. HALLEY AND C. S. MARVEL

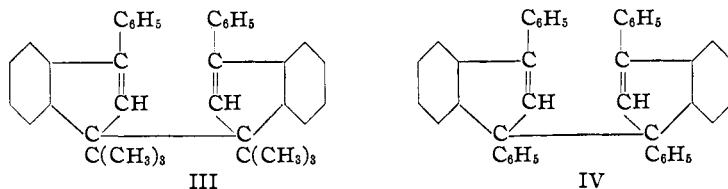
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Recent investigations¹ have shown that certain tetraaryl-diethynylethanes readily undergo rearrangement and yield isomeric hydrocarbons of unknown structures. The two compounds which have been studied thus far are *sym.*-tetraphenyldi-*tert.*-butylethinyethane (I) and *sym.*-tetraphenyldiphenylethinyethane (II). While these ethanes exhibit a reactivity which resembles that of the hexa-arylethanes, the isomeric



hydrocarbons obtained by their rearrangement are much more stable compounds. A study of the reactions of the hydrocarbon, $C_{38}H_{38}$, obtained by the rearrangement of tetraphenyldi-*tert.*-butylethinyethane (I) led to the suggestion that it might have a diindene structure (III).

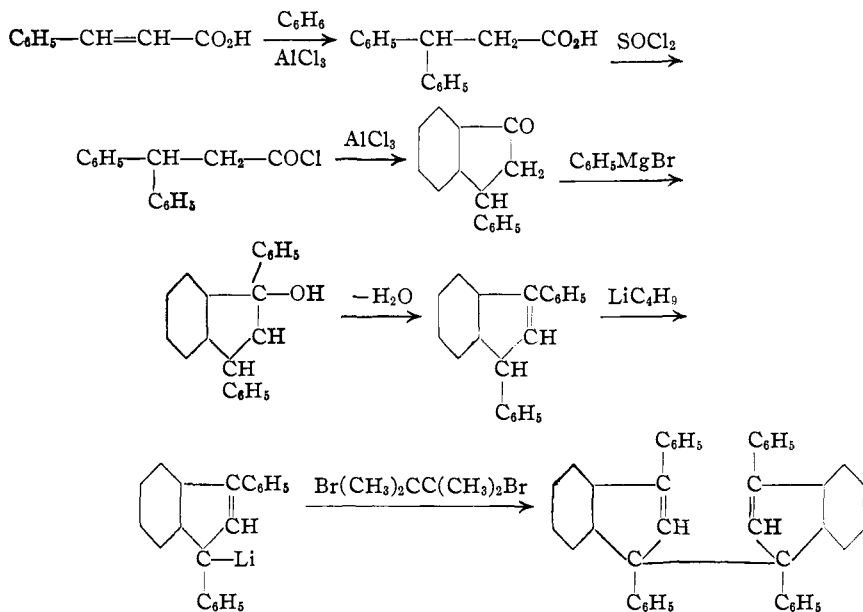


¹ (a) Stampfli and Marvel, *THIS JOURNAL*, **53**, 4057 (1931); (b) Althausen and Marvel, *ibid.*, **54**, 1174 (1932); (c) Munro and Marvel, *ibid.*, **54**, 4445 (1932).

If tetraphenyldiphenylethynylethane (II) rearranges in an analogous manner it might be expected to produce bis-1,1'-(1,3-diphenylindyl) (IV). That the two hydrocarbons, $C_{38}H_{38}$ and $C_{42}H_{30}$, obtained by the respective rearrangements of the ethanes (I and II), do have similar structures is indicated by the work which has been reported previously.^{1b,1c} A further indication of the resemblance in structure has been found in the oxidation of $C_{42}H_{30}$ to *o*-benzoylbenzoic acid, a product which had previously been obtained by the oxidation of the hydrocarbon, $C_{38}H_{38}$.

The preparation of bis-1,1'-(1,3-diphenylindyl) seemed to offer the most satisfactory method of checking up on the suggestion that diindenes are produced when the polyines undergo spontaneous rearrangement.

The synthesis has been accomplished by the following reactions



β,β -Diphenylpropionic acid was prepared by the method of Vorländer and Czensny² from cinnamic acid, benzene and anhydrous aluminum chloride. β,β -Diphenylpropionyl chloride has been mentioned in the literature³ but details for its preparation have not been given. It was obtained readily by the action of thionyl chloride on the acid. The ring closure to give 3-phenylindanone was accomplished by the method of Kohler.³ 1,3-Diphenylindene was prepared according to the procedure of Ziegler, Grabbe and Ulrich⁴ and converted to the lithium derivative by the method

² Vorländer and Czensny, *Ber.*, **56**, 1131 footnote (1923).

³ Kohler, *Am. Chem. J.* **31**, 649 (1904).

⁴ Ziegler, Grabbe and Ulrich, *Ber.*, **57**, 1983 (1924).

recently used by Blum-Bergmann.⁵ This lithium derivative was coupled to give the diindene.⁶

The bis-1,1'-(1,3-diphenylindyl) thus obtained does not agree in its properties with the hydrocarbon, $C_{42}H_{30}$, obtained by the rearrangement of tetraphenyldiphenylethynylethane.^{1c} The diindene has a higher melting point ($190-191^\circ$) and the melting point is greatly depressed ($158-163^\circ$) when this compound is mixed with the hydrocarbon, $C_{42}H_{30}$ (m. p. $172-173^\circ$).

Two stereochemical forms (meso and racemic) of the diindene are theoretically possible. In the work^{1b} on the hydrocarbon, $C_{38}H_{38}$, obtained by spontaneous rearrangement of tetraphenyl-di-*tert.*-butylethynylethane, it was found possible to produce a further isomerization to a higher melting compound by the prolonged action of heat on a solution of the hydrocarbon in glacial acetic acid in the presence of dry hydrogen chloride. The hydrocarbon, $C_{42}H_{30}$, was also found to yield a higher melting product when it was heated with hydrogen chloride in acetic acid but this compound melted at about 261° and was not identical with the diindene which had been synthesized.

Thus it seems doubtful that molecules of the diindene type are produced by the spontaneous rearrangement of tetra-aryldiethynylethanes and further work is needed before definite structures can be assigned to these rearrangement products.

Experimental

Bis-1,1'-(1,3-diphenylindyl).—Lithium *n*-butyl was prepared according to the procedure of Ziegler and Colonius⁷ from 9.3 g. (0.1 mole) of *n*-butyl chloride and about 3.5 g. (0.5 mole) of lithium shavings in 100 cc. of dry benzene. The benzene solution was decanted into a second flask while an atmosphere of dry nitrogen was maintained over the solution. Then a solution of 7 g. (0.026 mole) of 1,3-diphenylindene was added slowly. A yellow precipitate formed almost at once but the flask was stoppered tightly and shaken for about thirty-six hours. At the end of this period the solution was filtered through an alundum filter plate and to the precipitate was added a solution of 5 g. (0.02 mole) of tetramethylethylene bromide in 100 cc. of dry benzene. An atmosphere of dry nitrogen was maintained over the solutions during all of these operations. A reaction between the lithium derivative of the indene and the bromide was indicated by the liberation of some heat and a change in the nature of the insoluble material. After about one-half hour the solution was again filtered through an alundum plate, washed with a little water, dried over sodium sulfate and the solvent was evaporated by drawing a current of air through the solution under reduced pressure. The crystalline residue was purified by dissolving in alcohol and ether and concentrating this solution under reduced pressure until crystals began to appear. The solution was then cooled in an ice-bath and filtered. The crystals were washed with three small portions of low

⁵ Blum-Bergmann, *Ann.*, **484**, 36 (1930); see also Schlenk and Bergmann., *ibid.*, **463**, 192 (1928).

⁶ Ziegler and Schnell, *ibid.*, **437**, 244 (1924).

⁷ Ziegler and Colonius, *ibid.*, **479**, 135 (1930).

boiling petroleum ether to remove any excess tetramethylethylene bromide. The product thus obtained weighed 3.5 g. (50% of the theoretical amount) and melted at 185–186°. Three further crystallizations from alcohol raised the melting point to 190–191° where it remained unchanged by further purification.

Anal. Subs., 0.2216, 0.1883; CO₂, 0.7590, 0.6517; H₂O, 0.1140, 0.0930. Calcd. for C₄₂H₃₀: C, 94.38; H, 5.62. Found: C, 93.41, 94.39; H, 5.76, 5.53. *Mol. wt.* (Rast). Subs., 0.0051; camphor, 0.52; Δ^t, 8°. Calcd. for C₄₂H₃₀: mol. wt., 534. Found: mol. wt., 486.

The Hydrocarbon, C₄₂H₃₀.—The hydrocarbon was prepared by the action of silver on diphenylphenylethynylchloromethane⁸ and also by the two methods more recently described,⁹ namely, the reduction of diphenylphenylethynylcarbinol with titanium trichloride and the oxidation of the 1,1,3-triphenylpropine with potassium permanganate solution. The product from the first reaction was not readily purified. The best product melted at 172–173°.

Oxidation of the Hydrocarbon, C₄₂H₃₀.¹⁰—To a solution of 0.55 g. of the hydrocarbon in 15 cc. of glacial acetic acid was added 1.1 g. of chromium trioxide. The solution was boiled under a reflux condenser for about eight hours, allowed to stand for forty hours and then poured into 75 cc. of water. The aqueous solution was extracted twice with ether. The ether extracts were combined and extracted with 5% sodium hydroxide solution. The first extract removed most of the acetic acid, and when it was evaporated and acidified no insoluble acids precipitated. A second extraction with 5% sodium hydroxide was then made and on concentration and acidification, 0.1785 g. of air-dried water-insoluble acid was obtained. This material melted at 70–112°. On drying in an Abderhalden dryer at 76° at 40 mm., some crystals sublimed and collected in the cooled portion of the dryer. This sublimate weighed 0.085 g. and proved to be benzoic acid, m. p. 120–121°. The residual material in the dryer was recrystallized from carbon tetrachloride and again dried in an Abderhalden dryer at 100° (3 mm.) for about twenty hours. It then melted at 127.5–128.5° and did not depress the melting point of an authentic specimen of anhydrous *o*-benzoylbenzoic acid.

Rearrangement of the Hydrocarbon, C₄₂H₃₀.—A solution of 5 g. of the hydrocarbon, C₄₂H₃₀, in 100 cc. of glacial acetic acid was heated to boiling and a current of dry hydrogen chloride was passed through the boiling solution for about four hours. A precipitate separated and after filtering and recrystallizing from glacial acetic acid this product melted at 261–262°. The yield was about 1 g. This material was not thoroughly investigated but a molecular weight determination (Rast method) showed the material was not polymerized (mol. wt. 503). A smaller fraction of material melting at 290° was obtained.

Summary

1. Oxidation of the hydrocarbon, C₄₂H₃₀, obtained by the action of metals on diphenylphenylethynylchloromethane or by the rearrangement of tetraphenyldiphenylethynylethane has yielded *o*-benzoylbenzoic acid.

2. Bis-1,1'-(1,3-diphenylindyl) has been synthesized and it is not identical with the hydrocarbon, C₄₂H₃₀, obtained by the methods mentioned above.

3. These results make it seem unlikely that the compound obtained

⁸ Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] 41, 56 (1927).

⁹ Wieland and Kloss, *Ann.*, 470, 217 (1928).

¹⁰ We are indebted to Mr. J. Harmon for this portion of the experimental work.

by the spontaneous rearrangement of tetraphenyl-di-*tert.*-butylethynyl-ethane has the diindene structure which was recently suggested for it.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

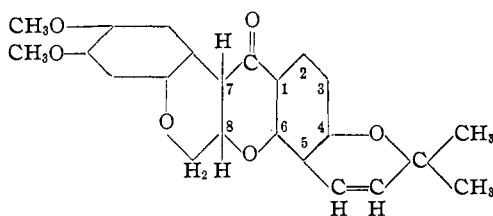
TEPHROSIN. II. ISOTEPHROSIN

BY E. P. CLARK AND H. V. CLABORN

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In a recent communication¹ formula I was proposed as representing the structure of deguelin, and it was also indicated that tephrosin is an hydroxydeguelin in which the hydroxyl group replaces one of the hydrogen atoms attached to either carbon atom 7 or 8.



I. Deguelin

In the course of the preparation of tephrosin from a recent shipment of Peruvian cubé root a white crystalline material separated which after purification melted at 252°. The substance was an isomer of tephrosin, as shown by its molecular composition, its methoxyl content, and the ease with which it was converted to dehydrodeguelin by the loss of a molecule of water. The material has been designated as isotephrosin.

Isotephrosin is a colorless crystalline material which like tephrosin is optically inactive. It is considerably less soluble in ordinary solvents than is tephrosin, and it is oxidized by potassium permanganate to a dicarboxylic acid isomeric with tephrosindicarboxylic acid.

While the ready conversion of isotephrosin into dehydrodeguelin, through the loss of a molecule of water, leaves no doubt that the difference between tephrosin and isotephrosin consists in the orientation of the hydrogen and hydroxyl groups on carbon atoms 7 and 8, no definite information is available as to the exact configurations existing at these carbon atoms. The most plausible assumption is that if in tephrosin the hydroxyl group is on carbon 7, then in isotephrosin the hydroxyl group would be on carbon atom 8 or *vice versa*.

Although there appears to be no immediate prospect of reaching a definite decision concerning these configurations, it is, nevertheless, an interesting fact that the two isomeric forms of this compound exist.

¹ Clark, *THIS JOURNAL*, **54**, 3000 (1932).