The specific gravities of the esters at 20/4° were determined by means of a calibrated 25-cc. pycnometer. Surface tension was measured by means of the du Noüy tensiometer. The parachors were calculated by the formula $M\gamma^{1/4}/d$, in which M is the molecular weight, γ is the surface tension in dynes per centimeter and d is specific gravity. The theoretical values are based on the constants of Mumford and Phillips,[11] namely, C = 9.2, H = 15.4, O = 20, double bond = 19, branched chain = −3 and carbonyl in ester = −3. Indices of refraction were measured by means of the Zeiss immersion refractometer. The molecular refraction for each ester was calculated from the Lorenz–Lorentz atomic values.

Summary

1. The yield of levulinic esters from cane sugar has been improved by esterification of *crude* levulinic acid and purification of the resulting esters.
2. Four new alkyl esters of levulinic acid have been prepared.
3. Observations have been made of corrected boiling point, specific gravity, surface tension and index of refraction of twelve alkyl esters of levulinic acid.

---

[11] Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929).

PITTSBURGH, PENNSYLVANIA

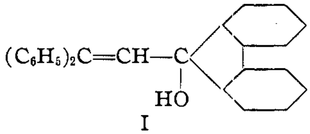
RECEIVED MARCH 29, 1933
PUBLISHED AUGUST 5, 1933

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

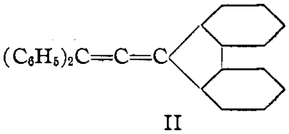
1-Diphenylene-3-phenylindene

BY C. FREDERICK KOELSCH

In a recent paper by E. Bergmann and others[1] α-diphenylene-γ,γ-diphenylallyl alcohol (I) is described as a solid melting at 118–121° with gas evolution. In the same paper it is noted that when this alcohol is warmed with acetic acid or with acetyl chloride there is formed a hydrocarbon melting at 139–140°, and this compound is formulated as α-diphenylene-γ,γ-diphenylallene (II).



I



II

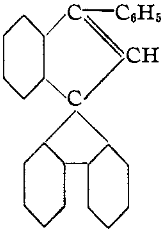
Experiments carried out in this Laboratory, which are the subject of the present communication, have led to somewhat different results and conclusions. α-Diphenylene-γ,γ-diphenylallyl alcohol obtained by the reaction of fluorenone with β,β-diphenylvinylmagnesium bromide, the same method as that used by the German investigators, melts at 98–99°; its dehydration by warming with acids results in the formation of a colorless

---

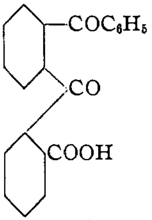
[1] Bergmann, Hoffmann and Meyer, *J. prakt. Chem.*, [2] **135**, 253 (1932).

hydrocarbon melting at 140–141°, apparently identical with the allene of Bergmann and co-workers. Thermal dehydration of the allyl alcohol, the usual method of converting a tetraarylallyl alcohol into an allene,[2] takes place at a surprisingly high temperature and gives a colorless hydrocarbon which melts at 308–311°. Neither of these dehydration products is the allene, for since the allene in question contains a fulvene grouping, it should be colored.[3] The structure of the thermal dehydration product is still under investigation.

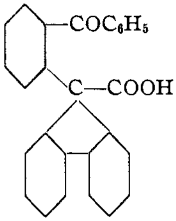
The product obtained by acidic dehydration is definitely shown by the reactions described below to be 1-diphenylene-3-phenylindene (III). When this hydrocarbon is cautiously oxidized with chromic acid, four products are obtained. Two of these are neutral substances whose structures are not yet proved, and two are acidic. The acidic substances are *o*-benzoylbenzophenone-*o*-carboxylic acid (IV) and 9-(*o*-benzoylphenyl)-fluorene-9-carboxylic acid (V). The latter acid may be decarboxylated to give *o*-9-fluorylbenzophenone (VI). No oxime could be obtained from this ketone, but it reacts with phenylmagnesium bromide to form *o*-9-fluoryltriphenylcarbinol (VII).



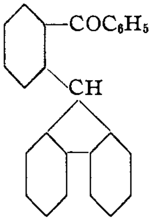
III



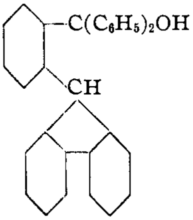
IV



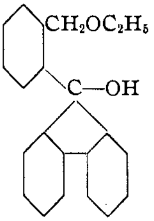
V



VI



VII



VIII

This same carbinol is obtained by a separate synthesis which leaves no doubt as to its structure. The Grignard reagent from *o*-bromobenzyl ethyl ether[4] and fluorenone give 9-(*o*-α-ethoxytolyl)-fluorenol-9 (VIII). On oxidation with chromic acid this carbinol gives in good yield diphenylenephthalide (IX).[5]

---

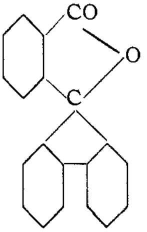
(2) Ziegler, *Ann.*, **434**, 57, 74 (1923).

(3) *Cf.* Staudinger, *Ber.*, **39**, 3067 (1906).

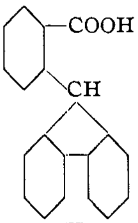
(4) Blicke and Weinkauff, THIS JOURNAL, **54**, 1450 (1932).

(5) This substance has recently been prepared [Weiss and Knapp, *Monatsh.*, **61**, 65 (1932)] in an extremely poor yield by a reaction which I was unable to carry out successfully [Koelsch, THIS JOURNAL, **54**, 3389, note 9 (1932)].

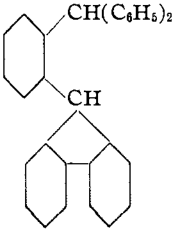
Reduction of this phthalide with sodium amalgam yields *o*-9-fluorylbenzoic acid (X), and this acid with an excess of phenylmagnesium bromide gives *o*-9-fluoryltriphenylcarbinol (VII). The identity of this carbinol with the one obtained from the indene is shown by a mixed melting point; on reduction each gives 9-*o*-fluoryltriphenylmethane (XI); and on warming the halochromic sulfates in acetic acid each gives a hydrocarbon, presumably 9,10-dihydro-10,10-diphenyl-1,9-phenyleneanthracene (XII).



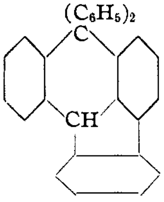
IX



X



XI



XII

Some further reactions of 1-diphenylene-3-phenylindene may be noted here. Nitration and bromination of the substance take place with ease. The nitro compound formed, 1-diphenylene-2(?)-nitro-3-phenylindene, is remarkably resistant to reduction, being unaffected by tin and alcoholic hydrochloric acid and even by sodium in hot amyl alcohol. It has not been possible to obtain a Grignard reagent from the bromination product, 1-diphenylene-2(?)-bromo-3-phenylindene, but by heating with cuprous cyanide the bromo compound is converted into the corresponding cyano compound. This nitrile has resisted all attempts at hydrolysis.

The indene is reduced by sodium in amyl alcohol to a dihydro compound. However, with 40% sodium amalgam in dry ether a yellow-orange monosodium compound is formed, the hydrolysis of which gives a new hydrocarbon isomeric with the original indene. This rearranged hydrocarbon is being investigated.

α-Diphenylene-γ,γ-diphenylallyl alcohol has been converted through its methyl ether and the corresponding sodium compound into a radical. These substances will be described in a subsequent paper.

Experimental

α-Diphenylene-γ,γ-diphenylallyl Alcohol (I).—To the Grignard reagent from 50 g. of β,β-diphenylvinyl bromide and 3.8 g. of magnesium is added slowly and with stirring a saturated benzene solution of 26 g. of fluorenone. On the following day the solid magnesium compound is filtered off, washed with dry ether and decomposed with iced ammonium chloride. The colorless product is crystallized from alcohol containing a little ammonia; seeding is very advantageous. There is obtained 34.5 g. (67%) of colorless needles that melt at 98–99°.

Anal. Calcd. for $C_{27}H_{20}O$: C, 90.0; H, 5.5. Found: C, 89.8; H, 5.4.

Heated in a capillary tube, the substance darkens at around 200°; gas bubbles are first noticeable at 210°. When the alcohol (1 g.) is heated at 225–230° it melts, evolves water, darkens and then resolidifies. The product, crystallized from benzene and petroleum ether, forms a fine white powder that melts at 308–311°.

Anal. Calcd. for $C_{27}H_{18}$: C, 94.7; H; 5.3. Found: C, 94.5; H, 5.4.

1-Diphenylene-3-phenylindene (III).—The allyl alcohol is dissolved in hot acetic acid, a few drops of sulfuric acid are added, and the solution is boiled until it is nearly colorless. On cooling, the solution deposits the indene nearly quantitatively; recrystallization from acetic acid gives colorless prisms that melt at 140–141°.

Anal. Calcd. for $C_{27}H_{18}$: C, 94.7; H, 5.3. Found: C, 94.9; H, 5.2.

Oxidation of 1-Diphenylene-3-phenylindene.—A solution of 10 g. of the indene in 400 ml. of acetic acid is cooled to 20° and 9 g. of chromic acid dissolved in a little water and 50 ml. of acetic acid is added. After four days the solution is poured into water and extracted three times with ether. The combined extracts are washed with cold dilute potassium hydroxide.

Acidification of a small portion of the alkaline extract precipitates 9-(*o*-benzoylphenyl)-fluorene-9-carboxylic acid, which after crystallization from ether–petroleum ether melts at 160–163° with gas evolution.

Anal. Calcd. for $C_{27}H_{18}O_3$: C, 83.1; H, 4.6. Found: C, 83.2; H, 5.0.

The acid is decarboxylated to 9-*o*-benzoylphenylfluorene by melting or by warming its solution in dilute potassium carbonate.

The remainder of the alkaline extract is boiled; the 9-*o*-benzoylphenylfluorene is filtered off and crystallized from acetic acid. It forms colorless prisms that melt at 168–169°; yield 3.6 g.

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.1; H, 5.2. Found: C, 89.8; H, 5.5.

The filtrate from the 9-*o*-benzoylphenylfluorene is acidified and the precipitate is recrystallized from toluene and then from acetic acid, giving 0.25 g. of *o*-benzoylbenzophenone-*o*-carboxylic acid melting at 224–225°, identified by mixed melting point and by conversion into the lactone of 9-*o*-carboxyphenyl-9-oxyanthrone-10.[6]

Two unidentified neutral compounds $C_{27}H_{18}O_2$ and $C_{26}H_{18}O_2$ separable from each other by crystallization from alcohol are contained in the ether from which the acidic oxidation products have been removed. These substances, a knowledge of whose structures is not indispensable to the present proof of the structure of 1-diphenylene-3-phenylindene, will be discussed in a future paper.

Nitration of 1-Diphenylene-3-phenylindene.—To a solution of 2 g. of the indene in 30 ml. of acetic acid is added 1.5 g. of nitric acid (d. 1.42). After heating at 90–95° for thirty minutes, the solution is cooled and the product is recrystallized from acetic acid, giving 1.6 g. of yellow needles that melt at 197–198°.

Anal. Calcd. for $C_{27}H_{17}O_2N$: C, 83.7; H, 4.4. Found: C, 83.6; H, 4.9.

Bromination of the Indene.—To a cold solution of 2 g. of the indene in 10 ml. of carbon tetrachloride is added 1 g. of bromine. The solvent is evaporated and the residue is crystallized from acetic acid, giving a quantitative yield of the bromo compound, colorless needles that melt at 157–158°.

Anal. Calcd. for $C_{27}H_{17}Br$: C, 76.8; H, 4.0. Found: C, 76.7; H, 4.3.

1-Diphenylene-2(?)-cyano-3-phenylindene.—The bromo compound (3 g.) is heated at 250–260° for five hours with 1 g. of cuprous cyanide. The cooled melt is pulverized and extracted with hot benzene. The product can be obtained colorless only by distillation at 20 mm.; it is then crystallized from acetic acid, giving 1.5 g. of colorless prisms that melt at 210–212°.

Anal. Calcd. for $C_{28}H_{17}N$: C, 91.5; H, 4.7. Found: C, 91.2; H, 4.9.

---

[6] Cook, *J. Chem. Soc.*, 62 (1928).

Reduction of the Indene.—To 1 g. of the indene in 30 ml. of boiling amyl alcohol is added 1 g. of sodium. After the metal has dissolved, the solvent is steam distilled and the residue is crystallized from acetic acid, giving 0.7 g. of colorless prisms that melt at 125–127°.

Anal. Calcd. for $C_{27}H_{20}$: C, 94.2; H, 5.8. Found: C, 94.1; H, 5.8.

Reaction of the Indene with Sodium Amalgam.—A solution of 1 g. of the indene in 25 ml. of ether is shaken under nitrogen with an excess of 40% sodium amalgam for two days. To the resulting deep yellow-brown solution, which often deposits orange crystals, is added alcohol. The amalgam is frozen, and the ether together with the suspended solid is decanted and washed with water. The product, which is nearly insoluble in ether, is filtered off and recrystallized from xylene. It forms fine white needles that melt at 213–215°.

Anal. Calcd. for $C_{27}H_{18}$: C, 94.7; H, 5.3. Found: C, 94.5; H, 5.2.

Into a solution of the sodium compound prepared as described above is bubbled dry carbon dioxide as long as the color persists. The excess amalgam is removed, and water and dilute sulfuric acid are added. A small amount of insoluble substance, the rearranged indene, is filtered off, and the ether is separated and evaporated. The product is crystallized from ethyl acetate and petroleum ether. The acid forms white crystals that melt at 187–190° with the evolution of carbon dioxide, resolidify and melt again at 203–206°.

Anal. Calcd. for $C_{28}H_{18}O_2$: C, 86.9; H, 4.7. Found: C, 86.7; H, 4.8.

Recrystallization of the decarboxylated acid gives the pure rearranged indene melting at 213–215°.

9-(*o*-α-Ethoxytolyl)-fluorenol-9.—To a solution of *o*-α-ethoxyltolylmagnesium bromide containing 3 g. of magnesium is added 10 g. of fluorenone in benzene. The solid magnesium compound is filtered off, washed with dry ether and decomposed with iced ammonium chloride. The product is crystallized from carbon tetrachloride and petroleum ether. There is obtained 11 g. of white prisms that melt at 102–103°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.6; H, 6.3. Found: C, 83.4; H, 6.4.

9-Chloro-9-(*o*-α-ethoxyltolyl)-fluorene, prepared from the carbinol with thionyl chloride in ether and recrystallized from ether–petroleum ether, forms large colorless prisms that melt at 113–114°.

Anal. Calcd. for $C_{22}H_{19}OCl$: Cl, 10.6. Found: Cl, 10.8.

Diphenylene Phthalide.—To a solution of 9 g. of 9-(*o*-α-ethoxytolyl)-fluorenol-9 in 100 ml. of acetic acid is added 13.5 g. of sodium dichromate, and the mixture is boiled for three hours. The solution is then poured into water, the product filtered off and crystallized from acetic acid and then from toluene, when it forms white prisms that melt at 219–220°; yield, 4.6 g.; with hot concd. sulfuric acid a faint orange color reaction is obtained.

Anal. Calcd. for $C_{20}H_{12}O_2$: C, 84.5; H, 4.2. Found: C, 84.5; H, 4.5.

***o*-9-Fluorylbenzoic Acid.**—A solution of 4 g. of diphenylene phthalide in hot absolute alcohol is boiled for one hour with 30 g. of 8% sodium amalgam. The mercury is removed, most of the alcohol is distilled and dilute hydrochloric acid is added. The solid is filtered off and boiled for two hours with an excess of 5% sodium carbonate; the insoluble part (2.5 g.) is unchanged phthalide. The alkaline solution is acidified and the precipitated *o*-fluorylbenzoic acid is crystallized from acetic acid. The product forms white plates that melt at 237–238° and give a blue-violet color with hot concd. sulfuric acid; yield, 1 g.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.8; H, 4.9. Found: C, 83.5; H, 4.9.

o-**9-Fluoryltriphenylcarbinol.** (a) **From 9-*o*-Benzoylphenylfluorene.**—To a solution of phenylmagnesium bromide containing 0.5 g. of magnesium is added 1 g. of the ketone. After it has been refluxed for thirty minutes, the mixture is decomposed with dilute sulfuric acid. The product, crystallized from ether–petroleum ether, forms colorless prisms that melt at 214°.

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.5; H, 5.7. Found: C, 90.2; H, 5.7.

(b) **From *o*-9-Fluorylbenzoic Acid.**—To a solution of phenylmagnesium bromide containing 0.5 g. of magnesium is added 0.5 g. of the acid. After refluxing for one hour, the mixture is decomposed with dilute sulfuric acid. The product (0.6 g.) is crystallized from acetic acid and then from ether–petroleum ether, when it melts at 213–214° (mixed melting point).

o-**9-Fluoryltriphenylchloromethane.**—To a solution of the carbinol in the minimum amount of dry ether is added an excess of thionyl chloride. On standing the solution deposits colorless crystals which become brown at 220° and melt with decomposition at 242–248°.

Anal. Calcd. for $C_{32}H_{23}Cl$: C, 86.8; H, 5.3. Found: C, 86.6; H, 5.3.

o-**9-Fluoryltriphenylmethane.**—An acetic acid solution of the carbinol is refluxed with an excess of granulated zinc until a portion cooled and added to sulfuric acid gives no color. After crystallization from acetic acid and then from xylene–petroleum ether, the product forms colorless crystals that melt at 258–260°.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.1; H, 5.9. Found: C, 94.0; H, 6.2.

9,10-Dihydro-10,10-diphenyl-1,9-phenyleneanthracene.—To a solution of *o*-9-fluoryltriphenylcarbinol in acetic acid is added a drop of sulfuric acid. The red-brown solution is boiled for a few minutes or until it is nearly colorless. The product, which crystallizes out on cooling, is recrystallized from acetic acid, when it forms fine white needles that melt at 215–220° with blackening.

Anal. Calcd. for $C_{32}H_{22}$: C, 94.6; H, 5.4. Found: C, 94.2; H, 5.4.

Summary

The hydrocarbon obtained by the acidic dehydration of α-diphenylene-γ,γ-diphenylallyl alcohol is shown to be 1-diphenylene-3-phenylindene and not an allene.

MINNEAPOLIS, MINNESOTA

RECEIVED APRIL 3, 1933
PUBLISHED AUGUST 5, 1933