

Summary

Isatin has been condensed with acetophenone to yield 3-hydroxy-3-phenacyloxindole. Some chemical properties and derivatives of this compound are described.

3-Phenacylideneoxindole and 3-phenacyloxindole failed to rearrange to give quinoline derivatives under the experimental conditions employed. This suggested that 3-phenacylideneoxindole is not an intermediate in the Pfitzinger synthesis of cinchophen from isatin and acetophenone.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

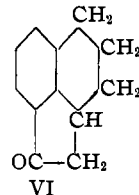
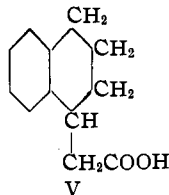
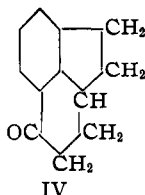
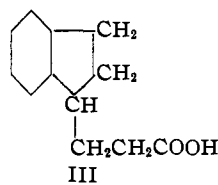
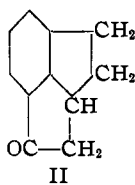
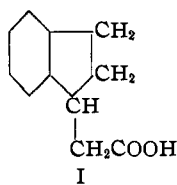
THE INDENE FROM ALPHA, GAMMA-BISDIPHENYLENE-BETA-PHENYLALLYL ALCOHOL

By C. FREDERICK KOELSCH¹

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A molecule whose structure involves two fused five membered rings adjacent to each other on a benzene nucleus is, as mechanical models show, so highly strained that it is generally regarded as being incapable of existence. Several unsuccessful attempts to obtain such a molecule have been recorded. V. Braun and Reutter² were unable to convert hydrindene-1-acetic acid (I) into the tricyclic ketone (II), while the homologous hydrindene-1- β -propionic acid (III) and tetralin-1-acetic acid (V) were readily cyclized to the ketones (IV) and (VI).

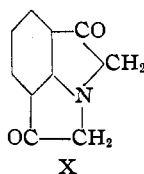
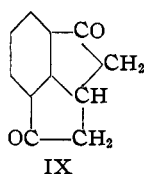
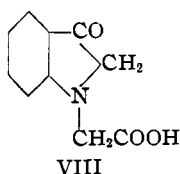
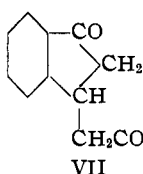


Similarly Jackson and Kenner³ were unable to convert 1-ketohydrindene-3-acetic acid (VII) or indoxylacetic acid (VIII) into the tricyclic compounds (IX) and (X).

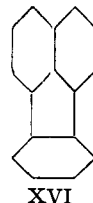
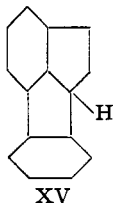
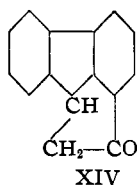
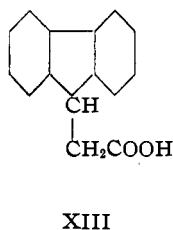
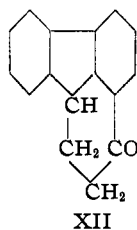
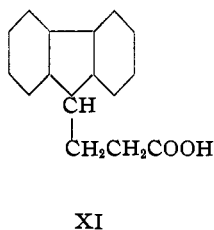
¹ National Research Fellow in Chemistry.

² V. Braun and Reutter, *Ber.*, **59**, 1922 (1926).

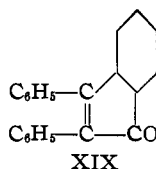
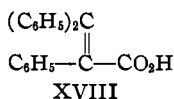
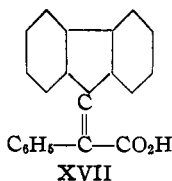
³ Jackson and Kenner, *J. Chem. Soc.*, 573 (1928).



V. Braun and Anton⁴ showed that while fluorene-9-propionic acid (XI) could be cyclized to (XII), fluorene-9-acetic acid (XIII) could not be converted into (XIV). They also showed that fluoranthene did not have the previously accepted formula $C_{15}H_{10}$ and the structure (XV), but had the formula $C_{16}H_{10}$ and the structure (XVI).



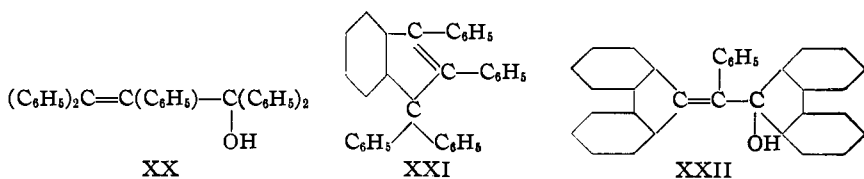
It has recently been shown⁵ that α -phenyl- β -diphenyleneacrylic acid (XVII) was not cyclized under conditions which led to the formation of 2,3-diphenylindone (XIX) from α,β,β -triphenylacrylic acid (XVIII). And although pentaphenylallyl alcohol (XX) was converted into tetraphenylindene (XXI) by even a trace of acid, α,γ -bisdiphenylene- β -phenylallyl alcohol (XXII) gave a fairly stable chloride when treated with hydrogen chloride.⁶



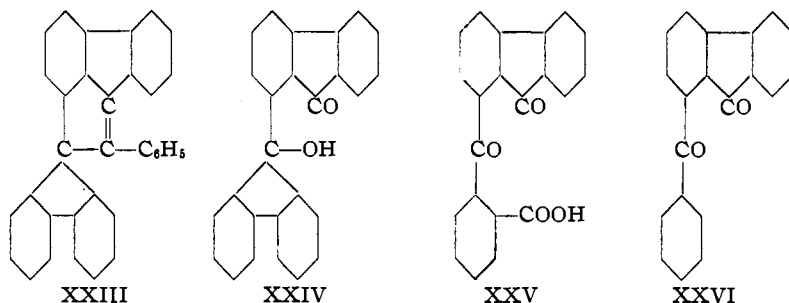
⁴ V. Braun and Anton, *Ber.*, **62**, 145 (1929).

⁵ Koelsch, *THIS JOURNAL*, **54**, 3384 (1932).

⁶ Data to be published soon.



The acetic acid solution of the halochromic sulfate of α,γ -bisdiphenylene- β -phenylallyl alcohol slowly loses its color, and a yellow hydrocarbon $\text{C}_{33}\text{H}_{20}$ is formed. In the present paper it is shown that this hydrocarbon contains the structure hitherto considered impossible and is 1-diphenylene-2-phenyl-3,4-phenyleneindene (XXIII).



On oxidation it gives benzoic acid and 1-diphenyleneoxymethylfluorenone (XXIV) whose functional groups are shown to be carbonyl and hydroxyl by its reaction with phenylmagnesium bromide to form 1-diphenyleneoxy-methyl-9-oxy-9-phenylfluorene and its reaction with thionyl chloride to form 1-diphenylenechloromethylfluorenone.

Further oxidation of the oxy-oxo compound gives *o*-(fluorenone-1-carbonyl)-benzoic acid (XXV). This acid exists in two interconvertible forms, one yellow and the other orange. It is believed that the more deeply colored form is an inner oxonium salt as Hantzsch⁷ showed to be the case with fluorenone-1-carboxylic acid, which is orange in the solid state or in highly polar solvents and yellow, as are its salts, chloride and esters, in other solvents.

Decarboxylation of *o*-(fluorenone-1-carbonyl)-benzoic acid gives 1-benzoylfluorenone (XXVI), which is identical with the compound prepared from the chloride of fluorenone-1-carboxylic acid, benzene and aluminum chloride.

A new synthesis of *o,m'*-ditolyl, from which fluorenone-1-carboxylic acid is obtained by oxidation to *iso*-diphenic acid and subsequent cyclization of this, is described.

Experimental

α,γ -Bisdiphenylene- β -phenylallyl Alcohol.—A mixture of 70 g. of α -phenyl- β -diphenylenevinyl bromide,⁵ 5 g. of magnesium, a small crystal of iodine and 500 ml. of

⁷ Hantzsch, *Ber.*, **49**, 226 (1916).

ether is refluxed with stirring. Heating is stopped after the reaction starts and is resumed when necessary and continued until the magnesium is completely dissolved. A saturated solution of fluorenone (35 g.) in toluene is added slowly. Stirring and refluxing are continued for one hour, and the mixture is then allowed to stand for ten hours. The magnesium compound is filtered off, washed well with ether and decomposed with iced ammonium chloride. The adhering ether is removed by gentle warming, and the solid residue is washed with water, dried and crystallized from toluene (150 ml.). The first crop of crystals weighs 23.5 g. and from the mother liquor by adding an equal volume of petroleum ether is obtained an additional 15 g.

The product crystallizes in yellow prisms that melt at 192–193.5°. With concd. sulfuric acid it gives a deep violet color; its solution in acetic acid is colored violet by sulfuric acid and red-brown by hydrochloric acid.

Anal. Calcd. for $C_{33}H_{22}O$: C, 91.3; H, 5.1. Found: C, 91.4; H, 5.4.

A solution of 0.6 g. of the alcohol in 35 ml. of acetic acid treated with 0.6 g. of chromic acid in a little water and boiled for a short time gives 0.15 g. of crude benzoic acid and 0.25 g. of steam distilled fluorenone.

1-Diphenylene-2-phenyl-3,4-phenyleneindene (XXIII).—A solution of 14.5 g. of α, γ -bisdiphenylene- β -phenylallyl alcohol in 250 ml. of hot acetic acid is cooled and before crystallization starts, 5 ml. of sulfuric acid in 10 ml. of acetic acid is added. The deep violet solution is allowed to stand for thirty minutes or until it has become light brown. The product is filtered off and crystallized from toluene and petroleum ether. There is obtained 12.2 g. of yellow prisms that melt at 196–197°.

Anal. Calcd. for $C_{33}H_{22}$: C, 95.2; H, 4.8. Found: C, 95.1; H, 5.0.

The hydrocarbon reacts readily with 40% sodium amalgam in dry ether to form a black sodium compound whose hydrolysis gives an amorphous substance. An amorphous product is also obtained by reduction with sodium in boiling amyl alcohol.

When the indene (1 g.) is warmed with an excess of undiluted bromine, hydrogen bromide is evolved and a heptabromo derivative is formed (2.3 g.). Crystallized from benzene and petroleum ether, the compound forms yellow needles that melt at 328–331°. It is quite resistant to chromic acid in acetic acid and when attacked is apparently completely oxidized.

Anal. Calcd. for $C_{33}H_{13}Br_7$: C, 40.9; H, 1.3. Found: C, 41.1; H, 1.5.

1-Diphenyleneoxymethylfluorenone (XXIV).—To a suspension of 6 g. of $C_{33}H_{20}$ in 50 ml. of hot acetic acid is added slowly a solution of 6 g. of chromic acid in a little water and 30 ml. of acetic acid. When the reaction is over, the solution is boiled for a few minutes, cooled and poured into water. The products are taken up in ether, from which solution sodium carbonate removes benzoic acid (0.5 g. after recrystallization). The ether is evaporated to a small volume, and the product which separates is recrystallized from benzene and petroleum ether; yield, 2.3 g. of yellow prisms that melt at 222–224°.

Anal. Calcd. for $C_{26}H_{16}O_2$: C, 86.6; H, 4.4. Found: C, 86.4; H, 4.6.

Reaction with Thionyl Chloride.—A solution of 0.7 g. of 1-diphenyleneoxymethylfluorenone and 1 g. of thionyl chloride in a little benzene is refluxed for fifteen minutes. The solvent is distilled under reduced pressure and the residue is crystallized from ether and petroleum ether; yield, 0.6 g. 1-Diphenylenechloromethylfluorenone forms yellow crystals that melt to a red liquid at 200–203°.

Anal. Calcd. for $C_{25}H_{15}OCl$: C, 82.3; H, 4.0; Cl, 9.4. Found: C, 81.9; H, 4.4; Cl, 9.2.

Reaction with Phenylmagnesium Bromide.—A solution of 1.2 g. of 1-diphenyleneoxymethylfluorenone in 25 ml. of toluene is added to the Grignard reagent from 3 g. of

phenyl bromide. After refluxing for thirty minutes, the solution is hydrolyzed with iced ammonium chloride. The ether, diphenyl, etc., are steam distilled, and the residue is crystallized from hot ethanol (250 ml.). The product, 1-diphenyleneoxymethyl-9-oxy-9-phenylfluorene, forms white plates that melt at 260–262° and contain one molecule of alcohol which is not lost at 100°. With concd. sulfuric acid it gives a brown-orange color.

Anal. Calcd. for $C_{33}H_{22}O_2 + C_2H_6O$: C, 84.4; H, 5.8. Found: C, 84.8; H, 5.8.

The alcohol of crystallization is driven off when the substance is heated at 140° under reduced pressure for one hour.

Anal. Calcd. for $C_{33}H_{22}O_2 + C_2H_6O$: C_2H_6O , 9.5. Found: loss in weight, 9.1. Calcd. for $C_{33}H_{22}O_2$: C, 87.6; H, 5.0. Found: C, 87.6; H, 5.1.

o-(Fluorenone-1-carboyl)-benzoic Acid (XXV).—When 1-diphenyleneoxymethylfluorenone (0.2 g.) is oxidized in acetic acid with 0.6 g. of chromic acid, it gives 0.1 g. of *o*-(fluorenone-1-carboyl)-benzoic acid as the sole product.

This acid is best obtained, however, by oxidizing the mixture of substances remaining in the ether mother liquor from which 1-diphenyleneoxymethylfluorenone has been crystallized. This yellow glassy substance (1.4 g. from 3 g. of $C_{23}H_{20}$) is completely freed of ether, dissolved in acetic acid and boiled while a concd. aqueous solution of chromic acid (3 g.) is added. The solution is then poured into water and the product is taken up in ether, from which it is removed with sodium carbonate solution. The crude acid is dissolved in hot acetic acid. If this solution is cooled rapidly, or if it is disturbed while cooling, the product (0.3 g.) separates in the form of bright yellow needles that melt at 208–209°.

Anal. Calcd. for $C_{21}H_{12}O_4$: C, 76.7; H, 3.7. Found: C, 76.5; H, 3.7.

If the acetic acid solution is cooled very slowly and kept free from disturbance and from seed of the yellow form, the product separates as deep orange prisms that melt at 210–212°.

Anal. Found: C, 76.6; H, 3.8.

A mixture of the two forms of the acid melts at 205–209°. The two forms are stable in the solid state, but either may be converted into the other by proper crystallization from acetic acid.

Decarboxylation of *o*-(Fluorenone-1-carboyl)-benzoic Acid.—A mixture of 0.303 g. of the orange acid with 0.02 g. of cupric carbonate is heated at 250° as long as gas is evolved (twenty minutes; loss in weight, 0.049 g.). The dark melt is boiled with acetic acid, poured into water and taken up in ether. This solution is washed with dilute sulfuric acid and with sodium carbonate and then dried with sodium sulfate. Petroleum ether is added to precipitate tarry impurities which are discarded. The mother liquor is distilled under reduced pressure, and the residue is crystallized twice from ethanol. The product, 1-benzoylfluorenone, forms yellow needles that melt at 114–116° alone or mixed with a sample synthesized as described below; yield, 0.09 g.

Anal. Calcd. for $C_{26}H_{12}O_2$: C, 83.8; H, 4.2. Found: C, 83.8; H, 4.2.

o,m'-Ditolyl.—To the Grignard reagent from 13 g. of *o*-tolyl bromide is added dropwise an ether solution of 5.8 g. of 1-methylcyclohexene-1-one-3,⁸ and the mixture is refluxed for thirty minutes with stirring. Hydrolysis with dilute sulfuric acid and distillation of the product gives 6 g. of 1-methyl-3-*o*-tolylcyclohexadiene-1,3 which boils at 145–148° (21 mm.).

Anal. Calcd. for $C_{14}H_{16}$: C, 91.3; H, 8.7. Found: C, 89.9; H, 8.6.

⁸ Rabe and Pollock, *Ber.*, 40, 2926 (1912).

The unsaturated hydrocarbon (5.9 g.) is heated with sulfur (2 g.) at 250° until no more hydrogen sulfide is evolved (one hour) and then distilled. There is obtained 4.5 g. of *o,m'*-ditolyl boiling at 265–267°.

1-Benzoylfluorenone.—The *o,m'*-ditolyl (4 g.) on oxidation with potassium permanganate gives 2.3 g. of *iso*-diphenic acid (m. p. 215–216°) and this is converted into fluorenone-1-carboxylic acid (m. p. 191–193°) by treatment with sulfuric acid.⁹

Fluorenone-1-carboxylic acid (0.35 g.) is refluxed with an excess of thionyl chloride for one hour and then warmed under reduced pressure. The crystalline acid chloride remaining is dissolved in 10 ml. of benzene, and 0.5 g. of aluminum chloride is added. After it has been warmed on a water-bath for ten minutes, the mixture is hydrolyzed with ice and hydrochloric acid. The benzene solution is separated and the solvent is distilled under reduced pressure. The residue is crystallized from alcohol, when there is obtained 0.2 g. of 1-benzoylfluorenone in the form of yellow needles that melt at 114–116°. The compound gives a red-brown color with sulfuric acid.

Anal. Calcd. for C₂₀H₁₂O₂: C, 83.8; H, 4.2. Found: C, 84.2; H, 4.3.

Summary

The halochromic sulfate of α,γ -bisdiphenylene- β -phenylallyl alcohol decomposes in acetic acid solution to give 1-diphenylene-2-phenyl-3,4-phenyleneindene, a hydrocarbon which contains a ring system hitherto considered impossible.

The structure of this hydrocarbon is proved by its degradation through 1-diphenyleneoxymethylfluorenone and *o*-(fluorenone-1-carbonyl)-benzoic acid to 1-benzoylfluorenone.

An independent synthesis of 1-benzoylfluorenone is described.

⁹ Mayer and Freitag, *Ber.*, **54**, 354 (1921).

CAMBRIDGE, MASSACHUSETTS

COMMUNICATIONS TO THE EDITOR

THE PREPARATION OF *l*-ARABINOSE AND *l*-RIBOSE BY THE OXIDATION OF *l*-ARABINAL WITH BENZOIC PERACID

Sir:

By the reactions *l*-arabinose \longrightarrow acetobromo-*l*-arabinose \longrightarrow diacetyl-*l*-arabinal \longrightarrow *l*-arabinal, employed by Gehrke and Aicher [*Ber.*, **60**, 918 (1927)] and by Meisenheimer and Jung [*ibid.*, **60**, 1462 (1927)] we have prepared 75 g. of crystalline *l*-arabinal, with melting point 78–81° and $[\alpha]_D^{20-25} -192^\circ$, in chloroform. An aqueous solution of 68 g. of this *l*-arabinal was stirred with a solution of benzoic peracid in ethyl acetate according to the general procedure of Levene and Tipson [*J. Biol. Chem.*, **93**, 631 (1931)]. The titration with iodine by the directions of Goebel [*ibid.*, **72**, 801 (1927)] was then equivalent to the oxidation of 78% of the *l*-arabinal to aldopentose. The observed rotation of the solution gave, on the basis of the above yield of aldopentose, the value $[\alpha]_D^{20-25} +49.77^\circ$. This rotation has now been shown to be due largely to the presence of both *l*-arabinose and *l*-ribose in the reaction product.