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

The Attempted Synthesis of Some Compounds Containing the *Iso*-indene Nucleus

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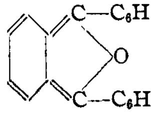
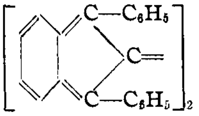
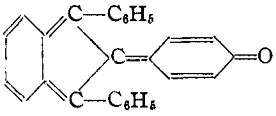
α,α-Diphenyl-β,β-benzofuran (I) is the only compound known definitely to contain an *o*-quinoid structure similar to that formerly postulated for rubrene (II).[1] That this type of structure is formed with difficulty or once formed is not stable is indicated by the relative ease of oxidation of anthracene as compared with phenanthrene, the radical nature of 2,3,6,7-dibenzanthracene, the immediate rearrangement of *o*-quinone-bisdiphenylmethide and other similar phenomena.


I


II

The present investigation was undertaken with the object of throwing some light on the structure and possible tautomeric nature of rubrene through a study of the reactions of the compounds (III) and (IV).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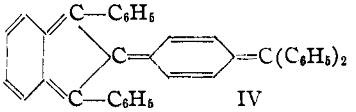
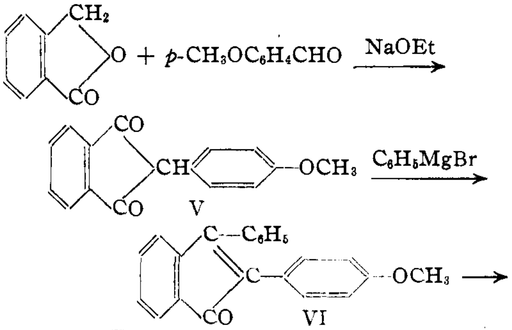

IV

Although these substances could not be prepared, it is believed that the syntheses themselves and what few conclusions may be drawn from such negative results warrant publication.

2-(*p*-Quino-)-1,3-diphenyl*iso*indene (III).—The synthesis of this compound was attempted through the following reactions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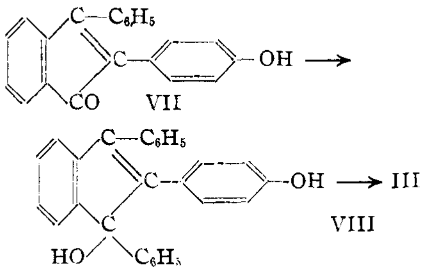
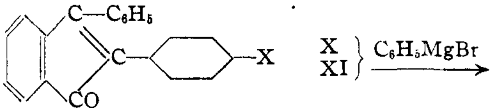
VI


VII

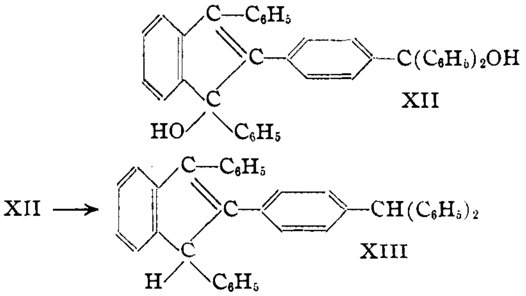
VIII

The substance (VIII) could not be dehydrated either by heat alone or by hot acetic acid; when boiled with acetic acid containing a trace of sulfuric acid, it was converted into a white amorphous substance, the reaction being apparently similar to the condensation undergone by 1,2,3-triphenylindenol and 9-phenylfluorenol under like conditions. Similar to Gomberg's easily dehydrated hydroxytriaryl carbinols in that a completely conjugated system connects the phenolic and the alcoholic hydroxyl groups, the compound (VIII) probably owes its resistance to dehydration to the difficulty of forming the necessary *o*-quinoid structure.

2-(*p*-Diphenylmethylenequino)-1,3-diphenyl*iso*indene (IV).—The synthesis of this substance was attempted by the reactions



IX (X = COOH)
X (X = COOR)
XI (X = COC_6H_5)


XII

XIII

Neither the glycol (XII), its dimethyl ether, nor its dichloride could be obtained crystalline. The action of metals on the crude dichloride gave intractable orange gums whose solutions were not affected by air.

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[1] Since this work was completed Dufraisse and Velluz [*Compt. rend.*, **201**, 1394 (1935)] have suggested and proved that rubrene has an entirely different structure.

Experimental

2-*p*-Anisylindandione-1,3 (V).—A mixture of 110 g. of phthalide and 110 g. of anisaldehyde is added to a solution of 20.5 g. of sodium in 400 ml. of absolute ethanol. After boiling for fifteen minutes, the deep red solution is poured into water, the alcohol is distilled and the product is precipitated with hydrochloric acid. After crystallization from acetic acid the diketone forms colorless needles that melt at 152–154°; yield 68 g. The remainder of the anisaldehyde is converted into anisyl alcohol and anisic acid.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 75.52; H, 4.70.

2-*p*-Anisyl-3-phenylindone (VI).—A solution of 65 g. of anisylindandione in hot toluene is added to phenylmagnesium bromide containing 15 g. of magnesium. The mixture is boiled for one hour and decomposed with iced sulfuric acid. After the unchanged diketone (7 g.) has been extracted with sodium carbonate, the product is distilled at 15 mm. and crystallized from acetic acid. There is obtained 43 g. of red needles that melt at 117–118°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.6; H, 5.1. Found: C, 85.01; H, 5.21.

2-*p*-Hydroxyphenyl-3-phenylindone (VII).—The methoxy ketone (VI) (30 g.) is hydrolyzed by boiling for six hours with a mixture of 120 ml. of acetic acid and 30 ml. of 40% hydrobromic acid. The product, purified by solution in sodium hydroxide and reprecipitation, separates from acetic acid in red plates that contain acetic acid; m. p. 163–165°.

Anal. Calcd. for $C_{21}H_{14}O_2\cdot 0.5C_2H_4O_2$: C, 80.4; H, 4.9. Found: C, 80.3; H, 4.9.

Dilute aqueous sodium hydroxide dissolves the phenol, giving a purple solution.

The benzoate, prepared with aqueous alkali and benzoyl chloride, forms red prisms that melt at 145°.

Anal. Calcd. for $C_{28}H_{18}O_3$: C, 83.5; H, 4.5. Found: C, 83.5; H, 4.4.

1,3-Diphenyl-2-*p*-hydroxyphenylindenol (VIII).—A benzene solution of the hydroxydiphenylindone is added to an excess of phenylmagnesium bromide. The mixture is worked up in the usual way, and the product, which like all triarylated indenols shows a tendency to supercool, is purified by recrystallization of its sodium salt. The pure phenol-alcohol crystallizes from ether–ligroin as a colorless powder that melts at 196–197°.

Anal. Calcd. for $C_{27}H_{20}O_2$: C, 86.1; H, 5.3. Found: C, 85.9; H, 5.3.

It is readily soluble in acetic acid and can be recovered unchanged after boiling with this solvent. The acetic acid solution becomes red on the addition of a trace of sulfuric acid and now, on boiling, a white amorphous substance is deposited, which is insoluble in the common solvents.

Hydrolysis of Cyanodiphenylindone.—The cyano compound (0.5 g.)[2] is boiled with a mixture of 5 ml. of sulfuric acid and 5 ml. of water until the originally melted substance has resolidified. The mixture is poured into water; the solid is powdered and extracted with hot sodium carbonate solution. The neutral product, **2-*p*-carbamidophenyl-3-phenylindone,** crystallizes from acetic acid in orange needles (0.15 g.) that melt at 248–254° with decomposition.

Anal. Calcd. for $C_{22}H_{15}O_2N$: C, 81.2; H, 4.6. Found: C, 80.5; H, 4.6.

The acidic product (IX) is precipitated with hydrochloric acid and crystallized from acetic acid, when it forms orange plates (0.35 g.) that melt at 212–214° and can be distilled without decomposition at 15 mm. The acid may also be obtained by boiling the amide with 1:1 sulfuric acid and water.

Anal. Calcd. for $C_{22}H_{14}O_3$: C, 80.8; H, 4.3. Found: C, 80.31; H, 4.3.

On boiling with the appropriate alcohol containing a little sulfuric acid, 2-*p*-carboxyphenyl-3-phenylindone is esterified. The esters (X), obtained in yields of about 80%, are best purified by distillation at 15 mm. followed by crystallization.

The methyl ester, from toluene, forms orange plates that melt at 167–168°.

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.2; H, 4.7. Found: C, 81.3; H, 4.8.

The ethyl ester, from ethanol, forms orange needles that melt at 120–121°.

Anal. Calcd. for $C_{24}H_{18}O_3$: C, 81.4; H, 5.1. Found: C, 81.4; H, 5.3.

2-*p*-Benzoylphenyl-3-phenylindone (XI).—The acid (IX) dissolved in benzene is treated with a slight excess of phosphorus pentachloride, and after short boiling, with 2.2 equivalents of aluminum chloride. The solution is boiled for fifteen minutes, decomposed with iced acid and washed with sodium carbonate. The product crystallizes from acetic acid in red-orange prisms that melt at 169–171°. This diketone may be distilled at 15 mm. without decomposition.

Anal. Calcd. for $C_{28}H_{18}O_2$: C, 87.0; H, 4.69. Found: C, 86.6; H, 4.55.

2-(*p*-α-Oxybenzohydrylphenyl)-1,3-diphenylindenol-1 (XII).—The methyl ester, the ethyl ester or the phenyl ketone derived from 2-*p*-carboxyphenyl-3-phenylindone dissolve easily in an excess of phenylmagnesium bromide. Decomposition of these solutions with iced acid followed by steam distillation gives in each case a pale orange glassy substance, easily soluble in acetic acid or in methanol. The solution in acetic acid becomes deep green with a trace of sulfuric acid. The methanol solution, on the addition of a little sulfuric acid, deposits an orange gum easily soluble in ether and nearly insoluble in methanol, but this dimethyl ether (?) cannot be crystallized. The chloride (?) obtained from the glycol with hydrogen chloride in benzene or with acetyl chloride also forms an uncrystallizable oil.

2-*p*-Benzohydrylphenyl-1,3-diphenylindene (XIII).—This hydrocarbon can be obtained from the glycol, the dimethyl ether or the chloride as follows. One gram of granulated zinc is added to a solution of one gram of any of the substances mentioned in 20 ml. of acetic acid. The solution is boiled and a drop of concd. hydrochloric acid is added; boiling is continued until the deep green solution is colorless, when more hydrochloric acid is added.

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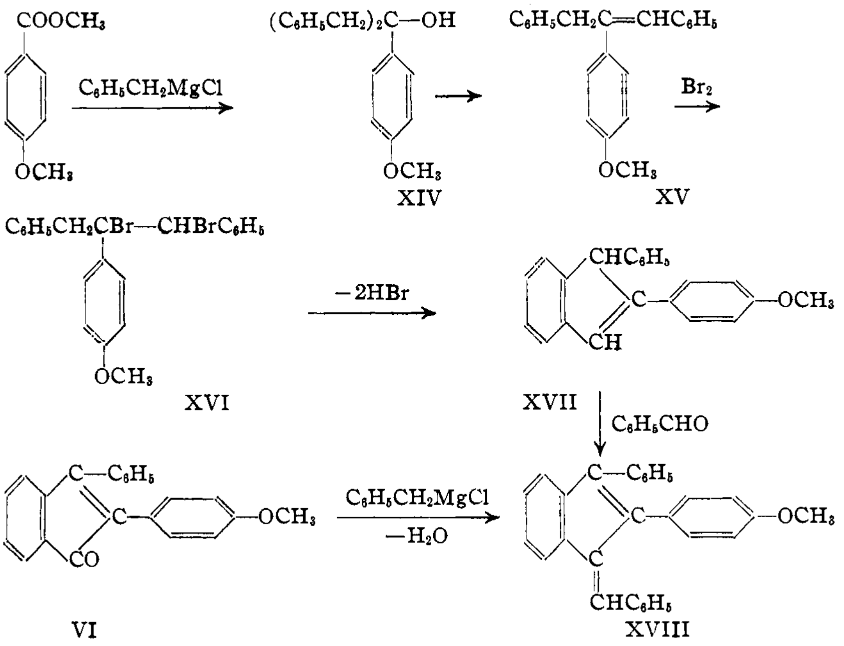
(2) Koelsch, This Journal, **58**, 1328 (1936).

This treatment is continued until the green color is no longer restored by hydrochloric acid. Water and ether are added, the ether solution is freed of acetic acid, dried and evaporated. The product is crystallized from ether-petroleum ether and then from acetic acid, when it forms small colorless flat needles that melt at 173–175°. It may be distilled without decomposition at 15 mm., and this is the most convenient way to purify large quantities (15 g.) of the substance.

Anal. Calcd. for $C_{40}H_{30}$: C, 94.1; H, 5.9. Found: C, 94.4; H, 6.3.

On treating the hydrocarbon in acetic acid with chromic acid, it is oxidized to *o*-dibenzoylbenzene and *p*-carboxytriphenylcarbinol, identified in each case by comparison with an authentic sample.

A Check on the Structure of 2-*p*-Anisyl-3-phenylindone.—In order to make certain of the structure of this compound, the following reactions were carried out



Two products are obtained from the dibromide (XVI), but only the indene (XVII) has been isolated in a pure state.

α,γ-Diphenyl-β-*p*-anisyl-propanol-β (XIV).—This carbinol, obtained in a yield of about 75%, is crystallized from ether-petroleum ether and then from ethanol. It forms white plates that melt at 93–94°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 83.0; H, 6.9. Found: C, 83.4; H, 7.0.

α,γ-Diphenyl-β-*p*-anisylpropene (XV).—This substance is obtained in a quantitative yield by boiling the above carbinol in acetic acid containing a little sulfuric acid.

It forms white plates that melt at 82–83° from ethanol.

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.0; H, 6.7. Found: C, 87.7; H, 6.7.

2-*p*-Anisyl-1-phenylindene (XVII).—The propene dissolved in 2.5 times its weight of acetic acid is treated with the calculated amount of bromine, and the solution is boiled for twenty minutes.

The product is distilled under reduced pressure (decomposition of the bromopropene) and crystallized from acetic acid and then from ligroin, when it forms pale orange plates that melt at 120–122°; yield about 35%.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.5; H, 6.0. Found: C, 87.8; H, 6.0.

1-Benzal-2-*p*-anisyl-3-phenylindene (XVIII).—(a) To a solution of 0.5 ml. of benzaldehyde and 1 g. of the indene (XVII) in 10 ml. of hot *n*-propyl alcohol is added a solution of 0.1 g. of sodium in 2 ml. of ethanol. The benzal compound is rapidly deposited, and on recrystallization from acetic acid forms yellow needles that melt at 188–190° (1.2 g.).

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.1; H, 5.7. Found: C, 90.0; H, 5.6.

(b) A benzene solution of the indone (VI) is added to an excess of benzylmagnesium chloride. Since the resulting carbinol is an oil, it is dehydrated by boiling in acetic acid with a trace of sulfuric acid. The product is identical with that obtained in (a).

Summary

Some unsuccessful attempts to obtain compounds containing the *iso*-indene nucleus are recorded. These failures lend support to the supposition that this nucleus is unstable.

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