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THE REDUCTION OF CERTAIN POLYARYLATED INDENONES

C. F. H. ALLEN AND J. A. VANALLAN

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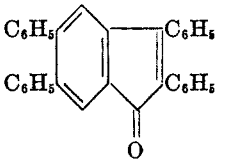
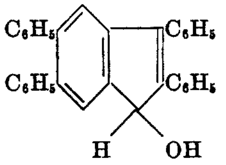
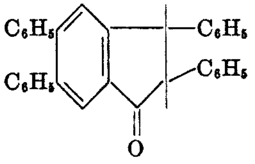
Polyarylated ind*e*nones having phenyl groups in the 2- and 3-positions offer several points of attack by reducing agents, *e.g.*, 1,2-reduction of the carbonyl group, 1,4-reduction of the α,β-unsaturated ketone linkage. When treated with zinc and acetic acid, a carbinol (I) is formed from 2,3,5,6-tetraphenylind*e*none, whereas reduction in a neutral medium, using the Adams platinum oxide catalyst, results in the ind*a*none (II). The evidence follows.

The carbinol (I) shows one active hydrogen and no addition when treated quantitatively with methylmagnesium iodide. It gives a chloride (III) when treated with thionyl chloride. The infrared absorption curve shows that there is a strong hydroxyl region, but none in the carbonyl range, and the ultraviolet absorption is practically identical with that of 2-*p*-bromophenyl-1-hydroxy-3,5,6-triphenylindene, as well as closely resembling that of 1,2,3,5,6-pentaphenylindene (1), indicating similarity of structure (Fig. 1).





I



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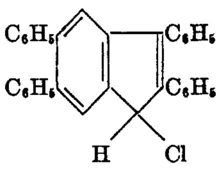

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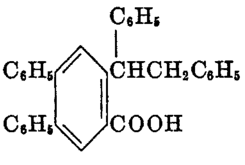

IV

The ind*a*none (II) is colorless; its infrared curve shows a band in the carbonyl region, while the ultraviolet absorption closely resembles that of 3,3,5,6-tetraphenylindanone (Fig. 2). Because the ind*a*none (II) was obtained by a catalytic reduction, it undoubtedly has the *cis*-configuration (2). An attempt to epimerize it to the *trans*-form by alkali resulted in the formation of an acid

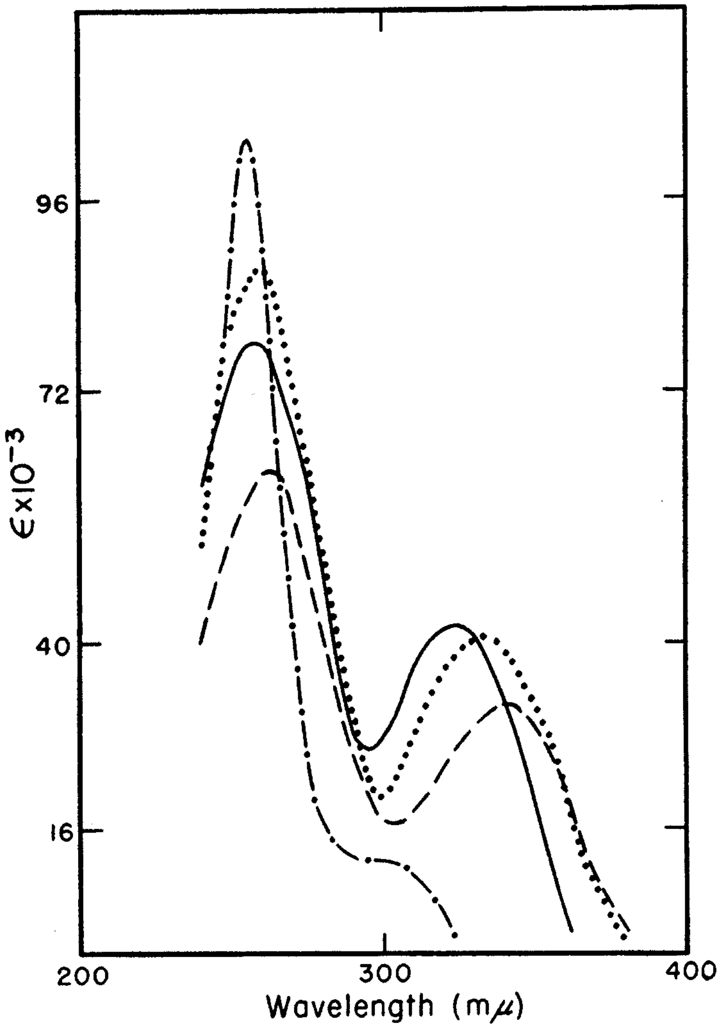

FIG. 1. ULTRAVIOLET ABSORPTIONS. ——— 1,2,3,5,6-Pentaphenylindene; — — — — 2-(4-Bromophenyl)-3,4,5-triphenylinden-1-ol; •••••••• 1,2,3,4-Tetraphenylinden-1-ol; —•—•—•—• 1,1,3,5,6-Pentaphenylindene; (solvent, dioxane).

(probably IV) by ring cleavage. These reductions have their counterpart in the reduction of 2,3-diphenylind*a*none (3–5).

2-Bromo-3,4,5,6-tetraphenylind*e*none (V) is reduced, first to a bromoind*a*none (VI) and then to the bromine-free ketone (VII) by zinc and acetic acid; the stepwise reduction and debromination indicate an *alpha*-bromo-ketone. The ultraviolet absorptions of these compounds are similar to the absorption of 3,3,5,6-tetraphenylind*a*none (Fig. 2). The bromine-free ketone shows one addition but no active hydrogen when treated quantitatively with methylmagnesium iodide.

The brominated ind*e*none (V) results when an excess of bromine reacts with

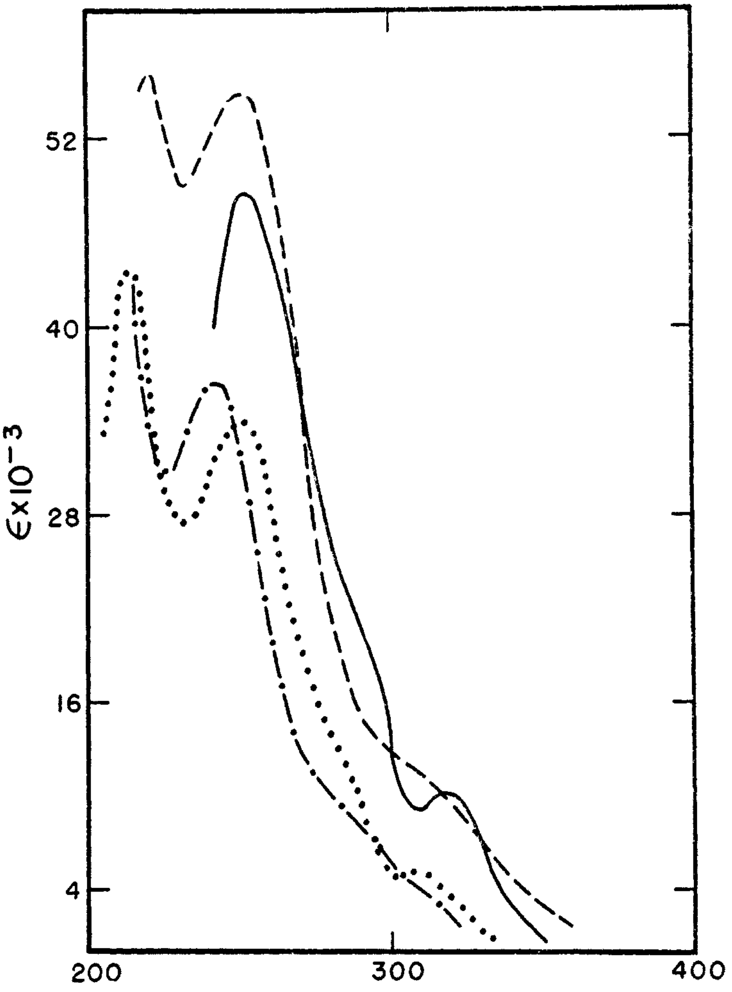

FIG. 2. ULTRAVIOLET ABSORPTIONS. ——— 3,4,5,6-Tetraphenylindanone (in isooctane); — — — — 2-Bromo-3,4,5,6-tetraphenylindanone (in acetonitrile); —•—•—•—• *cis*-2,3,5,6-Tetraphenylindanone (in chloroform); •••••••• 3,3,5,6-Tetraphenylindanone (in isoöctane).

3,3a,5,6-tetraphenyl-3a,4-dihydroindenone (VIII) (6); it was tentatively assigned another structure [XII in reference (6)] in the absence of experimental evidence which has now been accumulated. The brominated compound gives a bromocarbinol (IX); the latter not only gives the blue halochromism with concentrated sulfuric acid, characteristic of phenylated indenols, but also gives an acetate (X) when treated with acetic anhydride. Oxidation of the carbinol (IX) gives a substance, the analytical values for which correspond to those for 1,2-dibenzoyl-3,4,5-triphenylbenzene (XI); the ultraviolet absorption of the latter is similar to that of 1,2-dibenzoyl-4,5-diphenylbenzene (1 in Fig. 3). In addi-

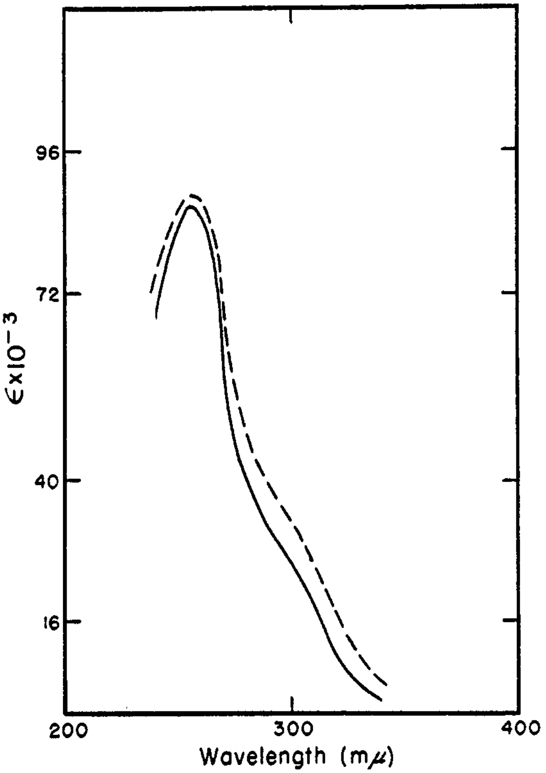

FIG. 3. ULTRAVIOLET ABSORPTIONS. ———— 1,2-Dibenzoyl-4,5-diphenylbenzene (in dioxane);— — — — 1,2-Dibenzoyl-3,4,5-triphenylbenzene (in dioxane).

tion to the foregoing, the bromoindenone (V) was oxidized by permanganate in pyridine or chromium trioxide, resulting in 2-benzoyl-3,4,5-triphenylbenzoic acid (XII), the ultraviolet absorption of which is like that of 2-benzoyl-4,5-diphenylbenzoic acid (Fig. 4). Both these acids appear to exist in the tautomeric pseudoacidic form (XIIa) since they show one active hydrogen and two additions when treated quantitatively with methylmagnesium iodide (7, 8); they did not give an anthraquinone on attempted cyclization with sulfuric acid. Treatment of the acid with hydrazine yields a substance, presumably an hydroxyphthalazine (XIII). These reactions, which, taken together with the absorption spectra (Fig. 4), support the 2-bromoindenone structure (V) and are summarized in Chart 1.

The formation of the bromoindenone (V) from the dihydroindenone (VIII) was quite unexpected, and can be accounted for only by a complicated mechanism; the latter, however, involved no new assumptions.[1] The initial reaction (Chart 2) is the addition of bromine to the indene double bond, followed by a loss of hydrogen bromide (A, B). The enolate (C), formed by the addition of a

[1] We are indebted to Dr. J. F. Tinker, of these Laboratories, for valuable discussions regarding this mechanism.

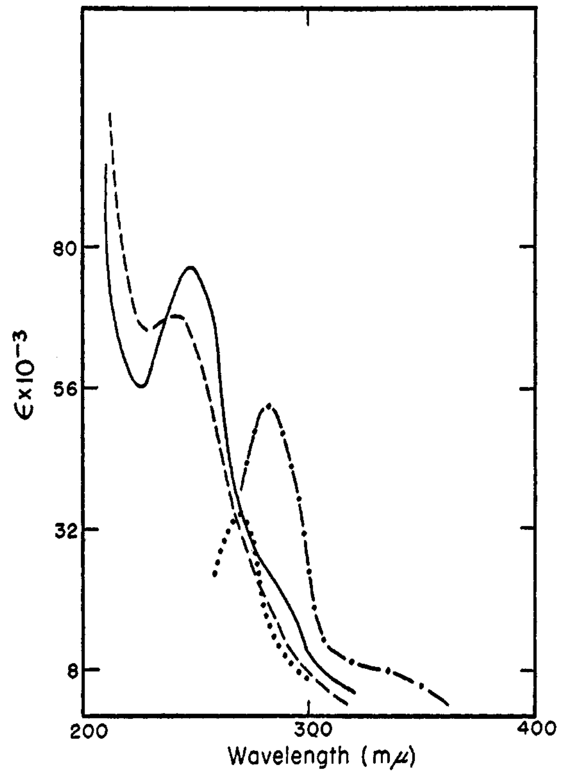

FIG. 4. ULTRAVIOLET ABSORPTIONS. ——— 2-Benzoyl-4,5-diphenylbenzoic acid (in methanol); — — — — 2-Benzoyl-3,4,5-triphenylbenzoic acid (in methanol); —•—•—•—• 2,3,5,6-Tetraphenylindenone (in dioxane); •••••••• 2-Bromo-3,4,5,6-tetraphenylindenone (in dioxane).

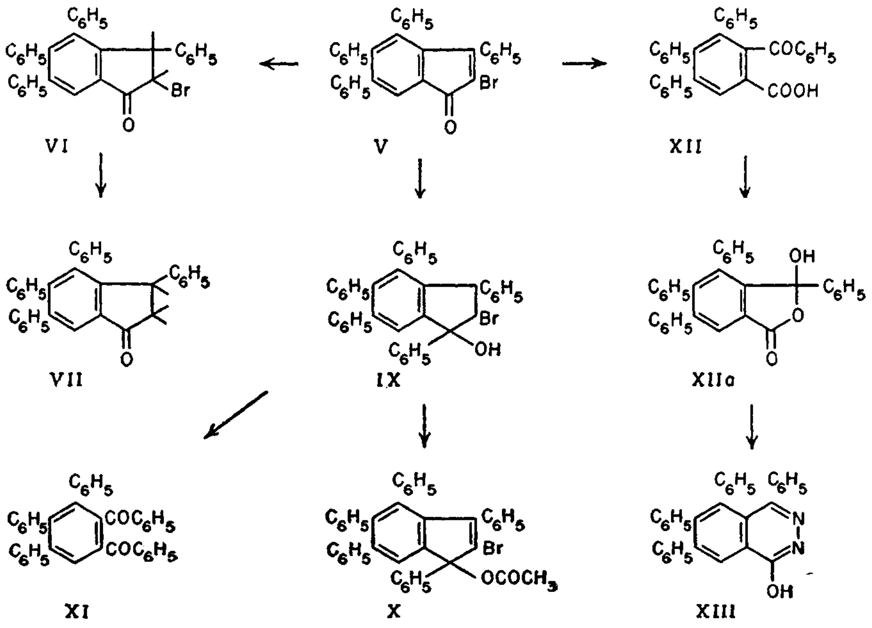

CHART 1

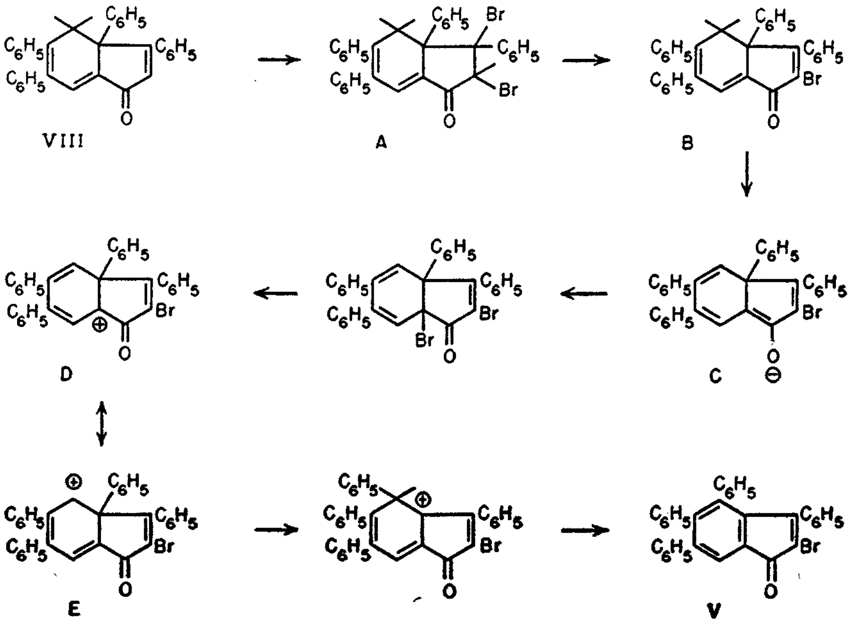

Chart 2

proton, is further attacked by the excess bromine, the intermediate bromo compound losing a bromide ion to give a carbonium ion that is tertiary, allylic, and benzylic (C, D). The ion (D, E) attains the aromatic condition by shift of the angular phenyl group and loss of a proton (E-5).

EXPERIMENTAL

2,3,5,6-Tetraphenyl-1-indenol (I). A mixture of 7 g. of 2,3,5,6-tetraphenylindenone, 60 ml. of acetic acid, and 7 g. of zinc dust was refluxed for 5 minutes; the color disappeared and a white precipitate formed. The residue, after filtration, was extracted with boiling dioxane, the solution was filtered, and the solvent evaporated; after a similar procedure, using acetic acid with the latter residue, the indenol was obtained. It was finally crystallized from xylene; m.p., 247–248°.

Anal. Calc'd for $C_{33}H_{24}O$: C, 90.9; H, 5.5.

Found: C, 90.9; H, 5.6; 1.2 active H, no addition.

1-Chloro-2,3,5,6-tetraphenylindene (III) resulted from one hour's heating on the steam-bath of 1 g. of the above carbinol and 7 ml. of thionyl chloride; the residue, after removal of the excess reagent, was recrystallized from toluene-ligroin—0.9 g.; m.p. 229–230°.

Anal. Calc'd for $C_{33}H_{23}Cl$: C, 87.0; H, 5.0; Cl, 7.8.

Found: C, 86.5; H, 5.3; Cl, 7.8.

cis-2,3,5,6-Tetraphenylindanone (II). A solution of 5 g. of 2,3,5,6-tetraphenylindenone in 100 ml. of ethyl acetate containing 0.1 g. of the Adams platinum oxide catalyst was reduced at 25–30° and an initial pressure of 46 lbs.; it was decolorized after 4 minutes. It was filtered through Filter-Cel, the solvent was removed, and the white residue was slurried with alcohol; the solid (2.7 g.) then was recrystallized from toluene, whereupon it melted at 198°.

Anal. Calc'd for $C_{33}H_{24}O$: C, 90.9; H, 5.5.

Found: C, 91.2, 91.2; H, 5.6, 5.4; one addition, no active H.

4,5-Diphenyl-2-(α,β-diphenylethyl)benzoic acid (IV). A mixture of 1 g. of the *cis*-ketone and 20 ml. of 20% methanolic potassium hydroxide was heated on the steam-bath; 20 ml.

of methanol was added after 5 minutes, and refluxing maintained for one hour, when the solid had entirely dissolved. The alkaline solution was poured into dilute acetic acid, the precipitate was collected and dried. It was recrystallized from toluene, from which it separated in fine needles; m.p. 269–270°.

Anal. Calc'd for $C_{33}H_{26}O_2$: C, 87.2; H, 5.7.
Found: C, 87.2; H, 5.4.

2-Bromo-3,4,5,6-tetraphenylindenone (V) is best obtained by the following procedure: A solution of 20 g. of the dienone (VIII) (6) in 75 ml. of chloroform was treated with 5 ml. of bromine in 15 ml. of the same solvent; hydrogen bromide was copiously evolved on warming. After 20 minutes, the solvent was evaporated, and the residue was heated with 50 ml. of acetic acid for 20 minutes, cooled, and the residual red solid (21 g., 88%) was collected. It was recrystallized from acetic anhydride (18.5 g., 78%), xylene, and anhydride again, without changing the melting point, 229–230° uncorr.

Anal. Calc'd for $C_{33}H_{21}BrO$: C, 77.2; H, 4.1.
Found: C, 77.4; H, 4.4.

Reduction of the bromoindenone (V). A mixture of 9 g. of the bromo ketone, an equal weight of zinc dust, and 100 ml. of acetic acid was refluxed for ¾ hour, and the solution was filtered and poured into water; the solid was separated and air-dried (weight, 8.3 g.). It was extracted with alcohol; the insoluble portion (4.3 g.) was recrystallized from xylene, giving the bromine-free indanone (VII); m.p. 218–219°.

Anal. Calc'd for $C_{33}H_{24}O$: C, 90.9; H, 5.5.
Found: C, 90.5; H, 5.6; 1 addition, no active H.

After several days' standing, the alcoholic extract deposited 4 g. of crystals (VI), which were recrystallized once from benzene-ligroin and once from toluene; m.p. 216–217°.

Anal. Calc'd for $C_{33}H_{23}BrO$: C, 77.0; H, 3.1.
Found: C, 76.9; H, 4.1.

The last substance was treated by a similar reductive procedure, and gave the bromine-free indanone (VII).

2-Bromo-1,3,4,5,6-pentaphenyl-1-indenol (IX). This substance was obtained by treating 5 g. of the bromoindenone (V) in 25 ml. of benzene with the phenylmagnesium bromide made from 11 g. of bromobenzene and 2.4 g. of magnesium in 100 ml. of ether. After one-half hour, the reaction product was decomposed by iced-acetic acid, and the solid carbinol was recrystallized from xylene; 4.5 g., m.p. 240°, resulted. The carbinol gave a deep purple color with concentrated sulfuric acid.

Anal. Calc'd for $C_{39}H_{27}O$: C, 79.0; H, 4.6.
Found: C, 79.2; H, 4.9.

The *acetate* formed with acetic anhydride and a trace of sulfuric acid, m.p. 209–210°, after crystallizing from *n*-butyl alcohol or ligroin.

Anal. Calc'd for $C_{41}H_{30}O_2$: C, 77.8; H, 4.7.
Found: C, 77.8; H, 4.9.

2-Benzoyl-3,4,5-triphenylbenzoic acid (XII). A mixture of 2 g. of the bromo ketone (V), 2 g. of potassium permanganate, and 20 ml. of pyridine was allowed to stand for 2 hours, and then warmed for 10 minutes on the steam-bath. It then was made strongly acid with hydrochloric acid, and enough sodium bisulfite was added to dissolve the oxides of manganese. The organic acid was separated by filtration, dried, and recrystallized from acetic acid, giving 1 g.; m.p. 267–268°. Less satisfactorily, a mixture of 5 g. of the bromo ketone (V), 4 g. of chromium trioxide, and 50 ml. of acetic acid was refluxed for 15 minutes; the initial reaction was very vigorous. It gave a rather intractable mixture on dilution, which was worked up as seemed appropriate, using solvents, sodium hydroxide, and hydrogen peroxide; the same acid was ultimately obtained in a poor yield. It gave a blue color with concentrated sulfuric acid.

Anal. Calc'd for $C_{32}H_{22}O_3$: C, 84.6; H, 4.8.
Found: C, 84.8; H, 4.6; 1 active H, 2 additions.

The methyl ester was prepared by treating 1 g. of the acid with 5 ml. of thionyl chloride, removing the excess reagent, and adding a solution of 3 ml. of pyridine and 15 ml. of methanol to the residue. After warming on the steam-bath for one-half hour, the solution was poured into water, and the ester recrystallized from benzene-methanol; m.p. 177–178°.

Anal. Calc'd for $C_{33}H_{24}O_3$: C, 84.5; H, 5.1.

Found: C, 84.6; H, 5.3.

1-Hydroxy-4,5,6,7-tetraphenyl-2,3-diazanaphthalene (XIII). A solution of 0.8 g. of the acid, 0.3 ml. of hydrazine hydrate, and a little methanol was refluxed for 3 hours, and evaporated to dryness. Xylene was added, and the whole was boiled to remove water, the product then being recrystallized from acetic acid; it melted above 290°.

Anal. Calc'd for $C_{32}H_{22}N_2O$: C, 85.2; H, 4.9; N, 6.2.

Found: C, 85.0; H, 4.7; N, 6.1.

SUMMARY

Polyaryl indenones are reduced both catalytically and by zinc and acetic acid; the latter gives a carbinol (1,2-reduction) while a 1,4-reduction product results when a catalyst is employed. Related reaction products are also described.

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