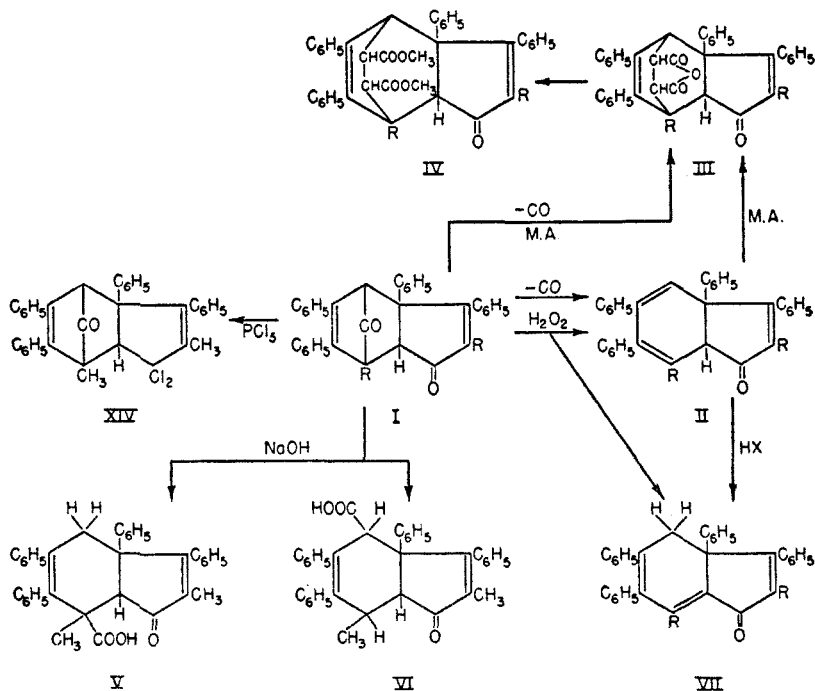


DIHYDROINDENONES AND RELATED COMPOUNDS FROM
 α -ALKYLANHYDROACETONEBENZILS

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The bimolecular products formed from α -alkylanhydroacetonebenzils (1, 2) behave differently from their homologs, when treated with organometallic compounds (3). Consequently, it was of interest to determine their behavior with other reagents to see whether there are differences, and, if so, whether they are of kind or degree. It has previously been shown (1, 2) that the action of alkaline reagents on all the anhydroacetonebenzils examined is the same. Most of the work described in this paper was done with the dimeric product from α -methylanhydroacetonebenzil, but the *n*-amyl homolog was employed to check certain observations.



The bimolecular products (I) are easily decarbonylated by heating for a short time to dihydroindenones (II), and the latter add maleic anhydride readily; this behavior serves to locate the double bonds. The bridged anhydrides (III) are easily transformed into the corresponding methyl esters (IV). It has been previously shown that the same monoanhydrides (III), along with dianhydrides derived from the monomeric cyclopentadienone, are also formed when the bimolecular products are heated with maleic anhydride at 200° (1).

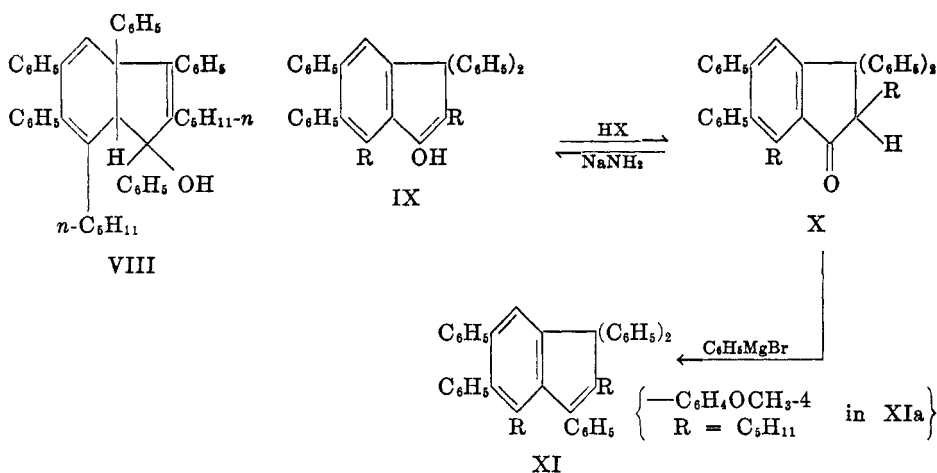
The dihydroindenone (II; R = CH₃) was also obtained when the acid (V) was degraded by oxidation (1). When the bimolecular product itself is treated with alkaline hydrogen peroxide, the same dihydroindenone (II) results, but there is, in addition, about an equal amount of an isomer. The new isomer is no longer capable of adding maleic anhydride. Since it is also formed by the action of hydrogen ion on II, it resembles the unalkylated homolog (4), and is assigned the structure VII. It is assumed that the alkali cleaves the carbonyl bridge to a mixture of acids (V, VI), which are then degraded in the usual manner (1).

When the bimolecular product (I; R = CH₃) is decarbonylated by being heated for a long time, alone or in quinoline, a new isomer (m.p. 168°) of II results. This same substance can also be obtained by similarly heating the isomers (II, VII; R = CH₃); it is, therefore, the end-product of a series of intermediate isomers. The new substance does not add maleic anhydride. When treated quantitatively with methylmagnesium iodide, the new isomer evolves one equivalent of methane but shows no addition; the starting material is recovered upon acidification. It does not give an acetyl derivative with acetic anhydride. When treated with mineral acid or thionyl chloride, it gives an isomer, m.p. 229°, which is a ketone; when the latter is treated with sodium amide, it regenerates the first substance. These two isomers are, thus, related as ketonic and enolic forms.

These observations at once recall similar instances (5, 6) in which a keto-enol transformation was noted, the formation of the substances involving the shift of a phenyl group. When such a shift is considered in the case at hand, the apparent discrepancies disappear. Structure IX is assigned to the enol and X to the ketone. There is no evidence that enables one to decide whether, in proceeding from II or VII to IX, there is a single 1,2-shift or two 1,3-shifts of the phenyl group, in the latter case proceeding through an intermediate carbinol (VII). There are analogies for both possibilities, that for the second being perhaps a little better. The driving force is probably the tendency to form an aromatic system.

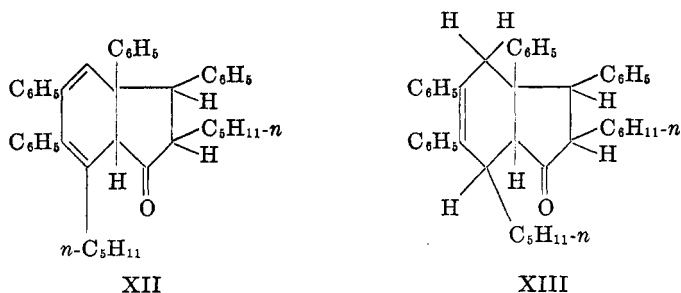
The behavior of the three isomeric ketones (II, VII, X) with phenylmagnesium bromide is interesting in that the same hydrocarbon results; in no case (when R = CH₃) could an intermediate carbinol be isolated. The hydrocarbon is colorless and does not add maleic anhydride. Obviously there has again been a rearrangement of a phenyl group. By analogy with unalkylated indenones (7) in which it was shown that the tendency was always to give a *gem*-diphenylindene, the structure of the new hydrocarbon is written as shown in XI.

With the amyl homolog (II; R = *n*-C₅H₁₁), a carbinol (VIII) results. Upon dehydration this gave a hydrocarbon, which was also obtained from the isomer (VII; R = *n*-C₅H₁₁) without isolation of a carbinol. When the indenone (II; R = *n*-C₅H₁₁) was treated with *p*-methoxyphenylmagnesium bromide, an ether corresponding to the hydrocarbon was formed, again without evidence of an intermediate carbinol. All these hydrocarbons (and the ether) undoubtedly have the same type of structure (XI).



The fact that only 1,2-addition of the Grignard reagents has occurred, rather than both 1,2- and 1,4-additions involving the benzene ring, as was found to take place with the unalkylated homolog (4), is attributed to substitution on the β -carbon of the double bond which forms part of the conjugated system involving the carbonyl group, for it is well known (8) that when several possible positions for addition are available, the one utilized will be the one in which there is the least substitution.

The indenone (II; $R = n\text{-C}_5\text{H}_{11}$) was catalytically reduced by hydrogen in the presence of Raney nickel. It gave a dihydro and a tetrahydro derivative; both of these still retained the carbonyl group, for they show one addition but no active hydrogen with methylmagnesium iodide. The dihydro derivative is assigned the structure XII because it was expected that the conjugated system terminating in oxygen would be most easily reduced; in confirmation, it was found to add maleic anhydride. The tetrahydro derivative is represented by XIII, on the assumption that 1,4-addition of hydrogen to the conjugated system in the six-membered ring has taken place. Up to the present, it has not been found possible to add hydrogen to the double bond in this ring bearing phenyl groups (2).



The bimolecular product (I; $R = \text{CH}_3$) has other reactions. When it is treated with phosphorus pentachloride, one oxygen atom is replaced by two chlorine

atoms. The resulting dichloride (XIV) can be decarbonylated, which shows that the carbonyl bridge is still present. It is concluded, therefore, that it was the indenone oxygen atom that was replaced.

EXPERIMENTAL

The bimolecular products (I) have been previously described (1), as have the maleic anhydride addition products (III). At the time it was thought that a molecule of benzene had been lost in the latter; the calculated analytical values for the various possibilities were so nearly the same that it was impossible to distinguish between them. The molecular-weight determinations were satisfactory if carried out in benzene, but low in carbon tetrachloride (2). From the data which have gradually been collected it is now evident that the previous assumption of the loss of benzene was incorrect.

The bridged esters (IV) were formed by esterifying the anhydrides. A suspension of the latter (5 g.) in 250 ml. of methanol and 15 ml. of concentrated sulfuric acid was refluxed for 20 hours, at which point complete solution was attained. After the addition of 400 ml. of water and after standing in the ice chest, the separated ester was collected and recrystallized from benzene-methanol. The yield of pure ester (IV; R = CH₃) was 3.3 g., m.p. 124°; it contains one molecule of benzene of crystallization. The *amyl* homolog, m.p. 129°, crystallized without solvent.

Anal. Calc'd for C₄₁H₃₆O₅·C₆H₆ (IV; R = CH₃): C, 81.9; H, 6.3.

Found: C, 81.9; H, 6.1.

Calc'd for C₄₉H₃₂O₅ (IV; R = *n*-C₅H₁₁): C, 81.7; H, 7.2.

Found: C, 81.8; H, 6.9.

Oxidation of the bimolecular product by alkaline hydrogen peroxide. A mixture of 5 g. of the bridged compound (I; R = CH₃), 100 ml. of alcohol, 1 ml. of 40% sodium hydroxide, and 10 ml. of 30% hydrogen peroxide was stirred and refluxed for ten hours, cooled, and filtered. The solid (4.5 g.) was fractionally crystallized from acetic acid; the isomer (VII; R = CH₃), m.p. 202°, separated first, while the previously described isomer, 3,3a,5,6-tetraphenyl-2,7-dimethyl-3a,7a-dihydroindenone, m.p. 164°, was isolated from the filtrate. The new isomer, 3,3a,5,6-tetraphenyl-2,7-dimethyl-3a,4-dihydroindenone (VII; R = CH₃), also resulted in a 92% yield when 18.5 g. of the isomer, m.p. 164°, in 85 ml. of hot acetic acid containing 1 ml. of concentrated sulfuric acid was warmed on the steam-bath for two hours. Both isomers show the same red halochromism with concentrated sulfuric acid.

Anal. Calc'd for C₃₅H₂₈O: C, 90.5; H, 6.0; mol. wt., 464.

Found: C, 90.7; H, 6.2; mol. wt. (in C₆H₆), 448.

When treated quantitatively with methylmagnesium iodide, it evolved no gas but showed one addition.

The *amyl* homologs (II, VII; R = *n*-C₅H₁₁) were similarly obtained, and had melting points of 125° (from isopropyl alcohol) and 99-100°, respectively.

Anal. Calc'd for C₄₈H₄₄O (II, R = *n*-C₅H₁₁): C, 89.5; H, 7.6; mol. wght., 576.

Found: C, 89.3; H, 7.5; mol. wt. (in C₆H₆), 583, 586; one addn.; no act. H.

Action of heat on the bimolecular products (I) 1,1,5,6-tetraphenyl-2,4-dimethyl-3-hydroxyindene (IX) and 3,3a,5,6-tetraphenyl-2,7-dimethyl-3a,7a-dihydroindenone (II; R = CH₃). When 10 g. of the methylated bimolecular product (I; R = CH₃) was heated for three hours at 240°, and the hot liquid poured into 55 ml. of isopropyl alcohol and allowed to stand, 7.8 g. of IX crystallized. After two recrystallizations from acetic acid, the product had the melting point 168°; it gave a pale lemon-yellow color with concentrated sulfuric acid.

Anal. Calc'd for C₃₅H₂₈O: C, 90.5; H, 6.0.

Found: C, 90.4; H, 5.8; 1 act. H, no addn.

This enol is regenerated from the magnesium complex upon acidification. It does not add maleic anhydride.

If the heating was interrupted when the evolution of gas ceased (not over ten minutes), the isomer (VII; R = CH₃) crystallized, under similar treatment, in a yield of 85%; it melted at 164°, and was identical with the previously prepared material (1). It gives a bright red color with concentrated sulfuric acid.

The 168° isomer was also obtained by refluxing substance II or the bimolecular product I (R = CH₃) in quinoline for 70 minutes, or in trichlorobenzene for seven hours, and adding to it 50 ml. of methanol; and by heating substance VII, m.p. 202°, for one-half hour at 240–250°, until the red halochromism changed to yellow.

3,3,5,6-Tetraphenyl-2,7-dimethylindanone (X) was obtained by refluxing for three and one-half hours, a mixture of 6 g. of the enol (IX) and 10 ml. of thionyl chloride, evaporating, and refluxing the residue with methanol. The alcohol was decanted and the insoluble material taken up in chloroform, treated with Norit, filtered, and diluted by an equal volume of methanol. The ketone slowly separated in a yield of 3.2 g.; it was twice recrystallized from *n*-butyl alcohol, then from toluene; m.p. 229°.

Anal. Calc'd for C₃₅H₂₃O: C, 90.5; H, 6.0.

Found: C, 90.9; H, 5.7; no act. H; 1 addn.

When a mixture of 0.8 g. of X and 0.5 g. of sodium amide in 10 ml. of cymene was refluxed one-half hour and worked up, 0.4 g. of the enolic isomer (IX) was obtained.

2-Bromo-3,3,5,6-tetraphenyl-2,7-dimethylindanone resulted upon bromination of 1 g. of X in 10 ml. of chloroform; hydrogen bromide was evolved. Methanol was added, and the combined solvents were allowed to evaporate. The residue was then recrystallized from butyl alcohol. The bromoindanone melts at 218° with dec.

Anal. Calc'd for C₃₅H₂₇BrO: C, 77.2; H, 5.0.

Found: C, 77.5; H, 5.2.

1,1,3,5,6-Pentaphenyl-2,4-dimethylindene (XI; R = CH₃). To the Grignard reagent prepared from 15.7 g. of bromobenzene and 60 ml. of ether there was added 1.7 g. of the indanone (X) in 30 ml. of benzene, and the ether removed by the usual forcing conditions. After two hours, the reaction mixture was decomposed in the usual manner, and the hydrocarbon recrystallized from acetic acid. It forms nearly colorless crystals, m.p. 218°, that give no color with concentrated sulfuric acid.

Anal. Calc'd for C₄₁H₃₂: C, 94.0; H, 6.1; mol. wt., 524.

Found: C, 94.0; H, 6.0; mol. wt. (in C₆H₆), 495.

The same hydrocarbon was likewise obtained by a similar Grignard reaction from the dihydroindenones (II, VII). It does not add maleic anhydride. Efforts to isolate a carbinol by decomposing the reaction products with ammonium chloride were unsuccessful; the hydrocarbon was obtained in each instance. A carbinol was isolated in the amyl series, however.

1,3,3a,5,6-Pentaphenyl-2,7-di-n-amyl-3a,7a-dihydroindenol-1 (VIII) was prepared by a similar procedure; 10 g. of the ketone (II; R = *n*-C₅H₁₁) gave 9 g. of the carbinol (80% yield), m.p. 109°, from alcohol.

Anal. Calc'd for C₄₉H₅₀O: C, 90.0; H, 7.6; mol. wt., 654.

Found: C, 89.7; H, 7.7; mol. wt. (in C₆H₆), 629.

When the carbinol was warmed in acetic acid containing a drop of sulfuric acid and cooled again, a 72% yield of the hydrocarbon, *1,1,3,5,6-pentaphenyl-2,4-di-n-amylindene* (XI; R = *n*-C₅H₁₁), m.p. 170°, was obtained after recrystallizing from acetic acid.

Anal. Calc'd for C₄₉H₄₈: C, 92.5; H, 7.5.

Found: C, 92.1; H, 7.8.

The same hydrocarbon was also obtained from a similar Grignard treatment of the dihydroindenone (VII; R = *n*-C₅H₁₁).

When the dihydroindenone (II; R = *n*-C₅H₁₁) was similarly treated with *p*-methoxyphenylmagnesium bromide, the ether (corresponding to the hydrocarbon) (XIa) resulted; the yield was 74%. After recrystallization from isopropyl alcohol, it melted at 150°.

Anal. Calc'd for C₅₀H₅₀O: C, 90.0; H, 7.5.

Found: C, 90.1; H, 7.4.

3,3a,5,6-Tetraphenyl-2,7-di-n-amyI-3a,7a-dihydroindanone (XII) and the corresponding *3a,4,7,7a-tetrahydro* compound (XIII) were obtained by reducing the dihydroindenone (II; R = *n*-C₈H₁₁) at 4 atmospheres and 70–80°. A mixture of 2 g. of the substance, 0.4 g. of Raney nickel, and 40 ml. of isopropyl alcohol was treated with hydrogen for 15 hours; the gauge dropped 9.5 units. The catalyst was removed by filtration; on chilling, 1.1 g. of the dihydro derivative separated. The filtrate was evaporated to dryness, and the residue crystallized from alcohol; the *tetrahydro* derivative had a melting point of 140°. The *dihydro* compound was recrystallized from acetic acid, after which it had a melting point of 213°.

Anal. Calc'd for C₄₃H₄₆O (A; dihydro): C, 89.3; H, 8.0. For C₄₃H₄₈O (B; tetrahydro): C, 89.0; H, 8.3.

Found: (A) C, 89.4; H, 7.8; no act. H, one addn. (B) C, 88.9; H, 8.3; no act. H; one addn.

SUMMARY

Two homologous series of dihydroindenones have been obtained from the corresponding carbonyl bridge compounds, and their behavior with various reagents has been determined. The reactions parallel those of the lower unalkylated homolog in most respects.

However, the type of indanone having two phenyl groups on one carbon atom, previously obtained only from the bimolecular product, in these series was formed from the bimolecular products *and* from the dihydroindenones. In its behavior it is parallel to a series that was examined earlier. The same hydrocarbon was obtained from all three series.

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