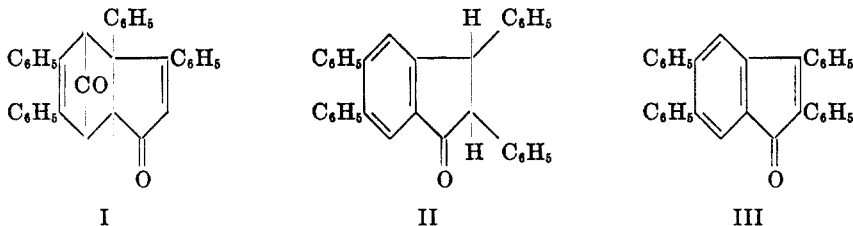


THE STRUCTURE OF JAPP'S INDANONE

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Nearly seventy years ago, Japp (1) treated 3,4-diphenyl-2-cyclopenten-4-olone, "anhydroacetonebenzil," with acidic dehydrating agents and obtained a "bimolecular product," $C_{34}H_{24}O_2$; when the latter was heated, it lost carbon monoxide and gave a ketone, $C_{33}H_{24}O$. The structures of both of these were developed twenty years ago (2, 3); we concluded that the first substance had the structure (I), which is a representative of the now numerous class of carbonyl bridge compounds (4). To the second was assigned (3) the structure of an indanone (II), because it was dehydrogenated by sulfur to the tetraphenylindenone (III). The structure of the latter was deduced by a stepwise degradation using unambiguous reactions. The indenone and all the key degradation products were subsequently synthesized by well-established reactions, so their structures are certain (4).



The dimer (I) gave oxygen-containing products when treated with oxidizing agents (5, 6), from which it is regenerated with evolution of oxygen; the identity of the regenerated substance with the original dimer was not recognized at the time, and it was thought that an isomer was obtained. When the infrared spectra of the dimer and supposed isomer were found to be identical, it became necessary to re-examine the substances involved.

The basis of the supposed isomerization was the production of the indanone (IV) on decarbonylation of the regenerated substance. The structure of IV (Fig. 1) is, therefore, very important; the previous evidence has been checked, confirmed, and extended. The facts follow: A 1,2-diketone (V) results from the action of selenium dioxide (5); the diketone not only gives a quinoxaline derivative, but it is degraded stepwise to products that have been synthesized in an unambiguous manner (6). Two hydrogen atoms in IV are replaced by chlorine or bromine (5) to give mono- and di-halides (VI, VIa); the halogen can be replaced, stepwise, by reducing agents, with regeneration of the starting material (IV) (6). The presence of a methylene group adjacent to the carbonyl is shown by condensation with anisaldehyde, resulting in the usual type of arylidene derivative (VII). These results establish the relation of the groups in the five-membered ring of IV. But the infrared and ultraviolet spectra (Figs. 1a, b) of

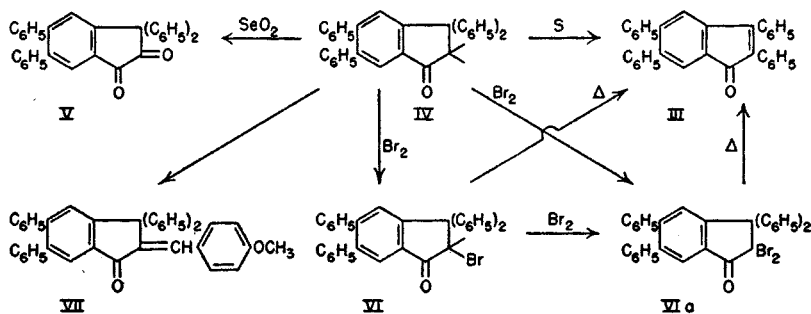
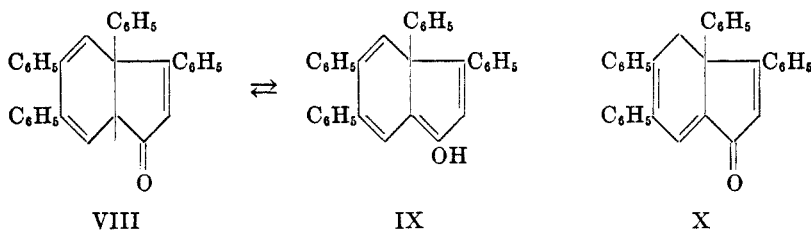


FIG. 1

IV and of Japp's indanone are identical, as are all other physical and chemical properties. Therefore, Japp's compound must have structure IV.¹ We have confirmed the fact that the indanone (IV) is dehydrogenated by sulfur to the indenone (III). We have, furthermore, obtained the same indenone (III) by heating the mono- and di-bromindanones, reactions which were paralleled many years ago by Moureu, Dufraisse and Baylocq (7) with the simple 3,3-diphenylindanone; the over-all change is equivalent to a dehydrogenation.

In view of all the foregoing, new interpretations are needed to account for the formation of IV from the dimer (I) and for the formation of III by the paths shown.

It has previously been established that the product (3) formed on decarbonylation is the dihydroindenone (VIII), which isomerizes in acidic media, to X, which may then be thermally rearranged to IV. The paths of transformation are clear. The diene (VIII) formed initially, treated with any catalyst that promotes enolization, comes into equilibrium with the enol (IX) and with the isomeric ketone (X); the latter is favored, since both double bonds are now conjugated with the carbonyl, and one is part of a stilbene system.



The subsequent rearrangement, which is brought about by heating the substance X alone or in solution in a high-boiling solvent, can be explained in terms of the carbonium-ion theory. One of the resonance hybrids of X is IXa (Fig. 2), which carries a positive charge in a position favorable to rearrangement. The adjacent atom carries a (phenyl) group of fair migratory aptitude, and forms, by

¹ Since the indanone has the structure IV, the monobromo and dibromo derivatives described in Reference 8, are identical with VI and VIa of this paper, and the indenone V (10) is IV above.

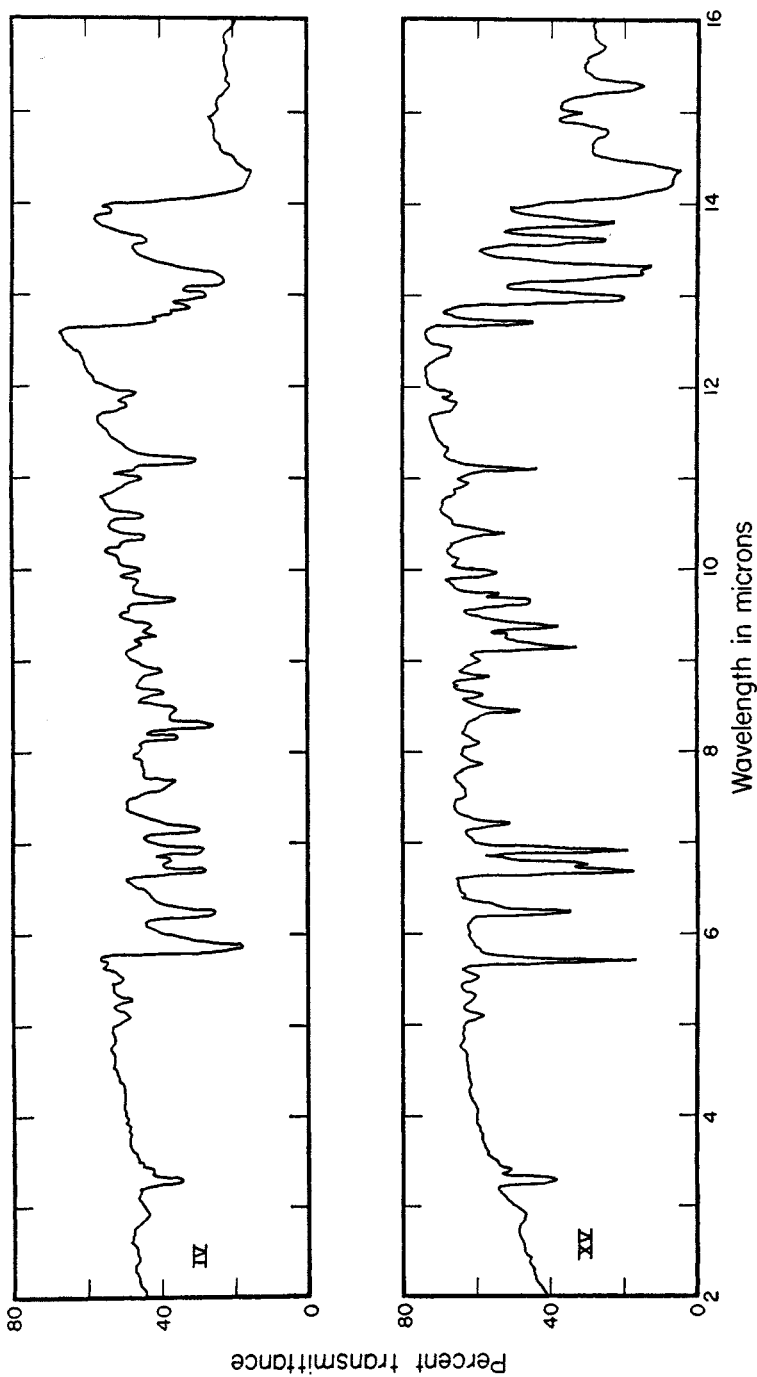


FIG. 1a. INFRARED ABSORPTION OF JAPP'S INDANONE, IV, AND THE BICYCLIC KETONE, XV.

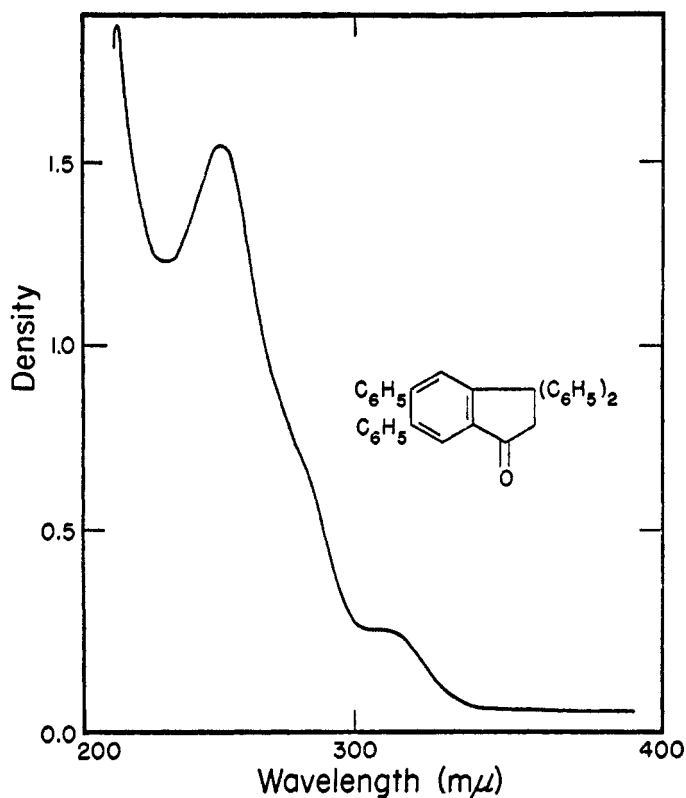


FIG. 1b. ULTRAVIOLET ABSORPTION OF JAPP'S INDANONE.

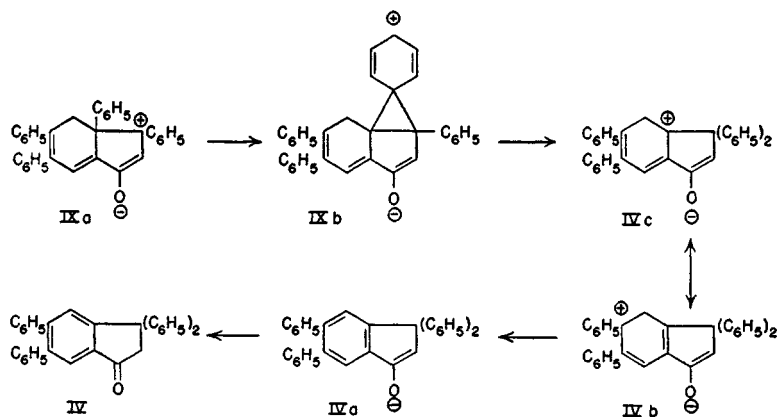


FIG. 2

loss of this group, a stabilized carbonium ion. The migration can be visualized as proceeding through a transition state (IXb), which contains a phenonium ion, to the more stable IVc, having a double-vinylous benzyl carbonium ion (IVb). The latter loses a proton, forming IVa, the enolate of IV; subsequent gain

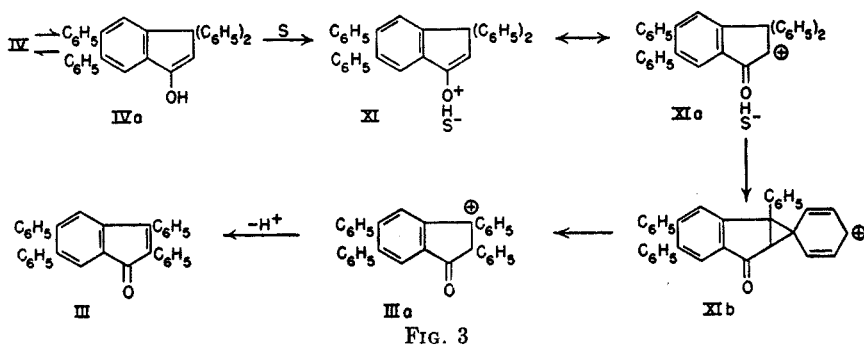


FIG. 3

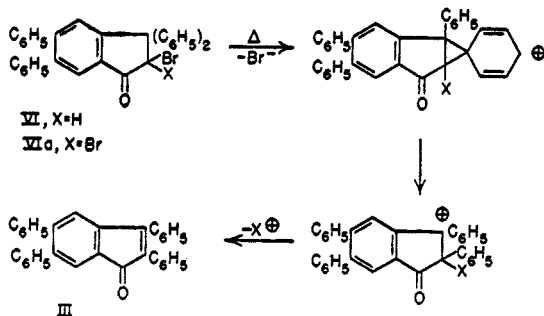


FIG. 4

of a proton leads to IV. This rearrangement is not as easy as that of benzpinacol, but the positive charge is more diffuse.²

The dehydrogenation of IV to the indenone (III) by sulfur, with migration of a phenyl group, is likewise explicable. Sulfur reacts with the enol (IV_a, Fig. 3) to form a coordination compound, then abstracts a pair of electrons, leaving the oxygen with a sextet; this deficient oxonium ion (XII) is isoelectric with a carbonium ion. The arrangement of the carbonium ion contributor (XII_a) is optimum for rearrangement, since it contains a migrant group, the shift of which (XII_b → III_a) results in a more stable diphenylmethylcarbonium ion; loss of the proton yields the rearrangement product (III).

Strong heating of the halides (VI, VI_a) causes loss of a bromide ion, leading to the transition intermediate shown; final *beta*-elimination of bromonium or hydrogen ions yields III (Fig. 4). When the dihydroindenone (X) and the indanone (IV) are treated with phenylmagnesium bromide and the organometallic derivatives are decomposed by ammonium chloride, the same carbinol results.³ The reaction products have identical infrared spectra and mixture melt-

² An analogous instance is the rearrangement of α,β -dibenzoylstyrene to triphenylcrotonolactone. See Japp and Klingemann, *J. Chem. Soc.*, 57, 662 (1890), and compare Vaillant's work [Vaillant, *Ann. chim.*, 10, 333 (1945)] on the rearrangement of diarylindanones; his mechanism, while similar, is much more cumbersome.

³ The identity was not recognized at the time; the carbinols VII and VIII of Reference 11 should be stricken from the literature. In Reference 9 the hydrocarbon IX is nonexistent; the formation of the lactone X by oxidation of the hydrocarbon VII (XIII in the current paper) is accounted for as proceeding through the oxanol XII.

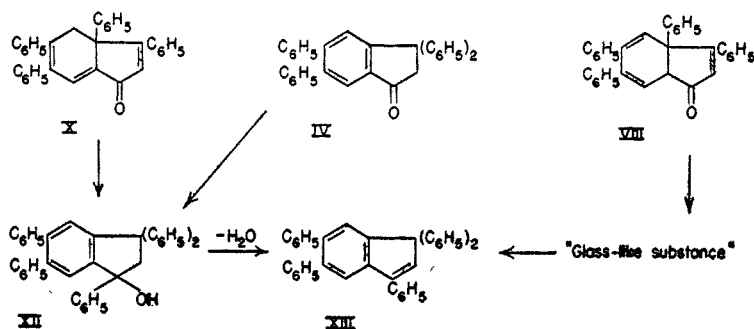
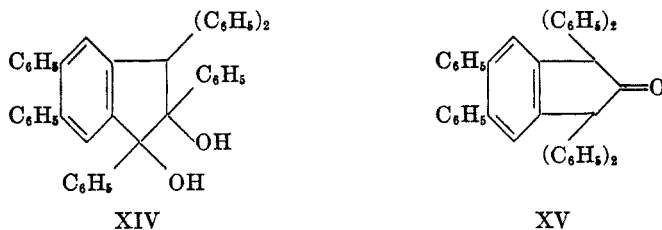


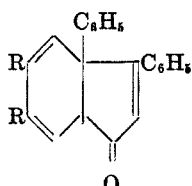
Fig. 5

ing points are not depressed. The structure of the hydrocarbon formed by dehydration of the carbinol has been previously (9) proved to be XIII (Fig. 5); since this also corresponds to V, it is reasonable to assign the structure XII to the carbinol. The dihydroindenone (VIII) gave a glasslike carbinol, which was dehydrated to the same hydrocarbon.

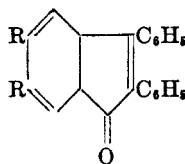
The glycol (XIV) that results (6) from the action of excess phenylmagnesium bromide upon the diketone (V) undergoes a pinacol-type rearrangement when treated with mineral acid in acetic acid solution, and gives the bicyclic ketone, XV. The evidence for this structure is based largely on absorption spectra, since it is a hindered ketone and fails to react with methylmagnesium iodide. The observed infrared carbonyl absorption is at $5.70\text{ m}\mu$ (Fig. 1a), characteristic for a cyclopentanone; the alternatively possible 1-indanone would have shown a carbonyl band at $5.8\text{--}5.9\text{ m}\mu$, since it would have been part of a conjugated system involving a double bond of the ring. One analogous instance involving 3-methyl-1,2-diphenyl-1,2-indanediol has been described (10).



With the revision of the structure of Japp's indanone, it becomes necessary to revert to the first-used structures of all the dihydroindenones, which had the angular phenyl group. The presence of this group in the 3a- position was convincingly proved in one instance (12) and there was no doubt at all except in the few substances which were derived from anhydroacetonebenzil. In these instances, the angular phenyl group was considered to have been shifted to the 2- position, since at that time it was believed that Japp's indanone was a 2,3-diphenyl derivative. Since this is now shown to be incorrect, there is no longer any support for this particular phenyl migration, and structures based on the assumption (4) should be replaced by those originally proposed.



(correct)



(incorrect)

The ultraviolet curves were obtained with a Cary double-beam recording spectrophotometer, Model 11. The solutions were run against the same thickness of pure solvent (methanol). The infrared spectra were obtained on a Baird double-beam recording spectrophotometer using rock-salt optics. Samples were prepared as Nujol mulls or as pressed plates in potassium bromide.

EXPERIMENTAL

Most of the substances were on hand from previous work.

2-(4-Methoxybenzal)-3,3,5,6-tetraphenyl-1-indanone (VII). A mixture of 5 g. of Japp's indanone (IV), 2 ml. of anisaldehyde, 0.5 g. of sodium acetate, and 100 ml. of absolute alcohol was refluxed for 4 hours; the product (4.2 g.) separated on standing overnight and was recrystallized from acetic acid (it separated very slowly). The bright yellow crystals (2.3 g.) melted at 218–219°.

Anal. Calc'd for $C_{41}H_{30}O_2$: C, 88.3; H, 5.4.

Found: C, 88.0; H, 5.3.

2-Oxo-1,1,3,3,5,6-hexaphenylindene (XV). A solution of 0.5 g. of the glycol (XIV) in 15 ml. of acetic acid, containing 3 drops of concentrated sulfuric acid, was refluxed for 4 hours; the product began to separate after 30 minutes. It (0.32 g.) was recrystallized from benzene-petroleum ether; m.p. 285°.

Anal. Calc'd for $C_{45}H_{32}O$: C, 91.8; H, 5.5.

Found: C, 91.6; H, 5.4.

The rearrangement was also brought about by a mixture of red phosphorus and iodine (13).

Acknowledgment. We are indebted to Dr. D. W. Stewart and Miss T. J. Davis for the absorption curves, and to Dr. J. F. Tinker for valuable suggestions.

SUMMARY

The structure of this substance, first obtained sixty-six years ago, has been shown to be 3,3,5,6-tetraphenylindanone. The structure attributed to it twenty years ago, 2,3,5,6-tetraphenylindanone, is, thus, corrected, as are those of related substances. A hexaphenyl-2-indanone is also described. Mechanisms to account for the various rearrangements have been proposed.

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