# Polyarylated Indenes

BY C. F. H. ALLEN AND J. W. GATES, JR.

During the course of our work on polyarylated substances in the indene series, several isomeric hydrocarbons to which no structures were assigned were described. It was obvious that there had been rearrangements in some instances. In this paper, structures are assigned and supporting evidence is discussed.

When 2,3,5,6-tetraphenylindenone I[1,2] is treated with phenylmagnesium bromide, it gives a carbinol II that cannot be dehydrated since there is no available hydrogen. It is converted to a bromoindene III by the action of hydrogen bromide in acetic acid. This bromoindene is similar in all respects to the known 1-bromo-1,2,3-triphenylindene.[3] Thus, it is pale yellow; it gives an ethoxyindene with boiling alcohol; it gives a deep red solution when treated with phenylmagnesium bromide which, after three days, become colorless, and deposits a hydrocarbon, 1,1,2,3,5,6-hexaphenylindene IV; upon reduction with zinc and acetic acid, it gives a pentaphenylindene, m. p. 280°.

The structure of this hydrocarbon appears clear from its method of preparation, and is confirmed by the production of the known 4,5-diphenyl-*o*-dibenzoylbenzene V[4] and benzoic acid upon oxidation with chromium trioxide. It is, thus, 1,2,3,5,6-pentaphenylindene VI.

I   II

III   IV
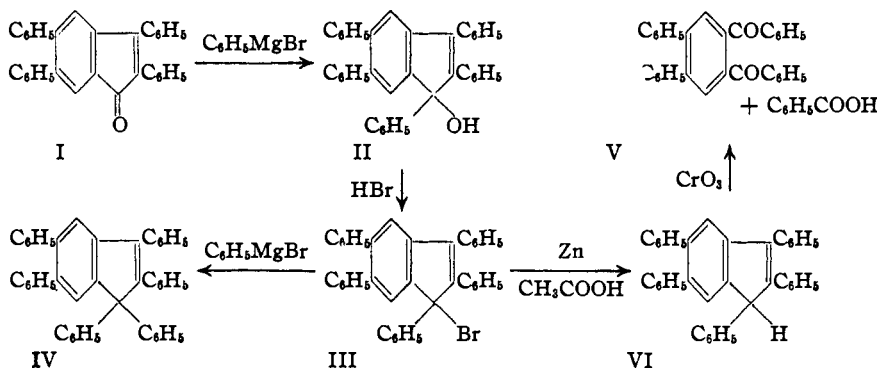
The same hydrocarbon is obtained by heating the carbinol secured by the action of phenylmagnesium bromide upon the bimolecular product that results by treating anhydracetonebenzil with acidic dehydrating agents at 300°.[5]

An isomeric hydrocarbon VII, m. p. 227°, the structure of which appears clear from its method of synthesis, is obtainable from 3,3,5,6-tetraphenylindanone VIII.[6] The structure was con-

firmed by an oxidation procedure using chromium trioxide, which gave only the diketone V, a reaction completely in line with that of the simpler indene.[3]

VIII

VII   V
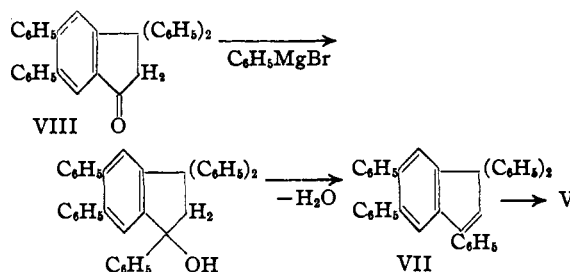
It had been planned originally to interrelate these two series by converting the diketone corresponding to VIII into the hexaphenylindene IV, through the glycol resulting from the action of excess phenylmagnesium bromide.[6] Unfortunately, the glycol could not be reduced to the hydrocarbon.

A third isomeric hydrocarbon, m. p. 222°, has been described[7] which was secured by the dehydration of several carbinols, formed by the interaction of phenylmagnesium bromide and 2,3,5,6-tetraphenylindanone or dienones isomeric with this substance; at the time it was stated that

V

"there must have been a rearrangement in two of the dehydrations." Since, from the method of preparation, it would be expected to have the structure VI, it now appears that there has been a rearrangement in all three instances.

This third hydrocarbon is colorless and does not add maleic anhydride; it does not give benzil upon oxidation. These facts exclude any of the possible structures having an *o*-quinonoid bond system and so leaves IX (R = C_6H_5) as the only possibility. When it is treated with chromium trioxide in acetic acid, it gives a lactone X (R = C_6H_5); on fusion with sodium amide, the new substance gives a derivative of 9,10-diphenylanthracene. The new hydrocarbon shows a violet fluorescence, and was identical with a synthetic specimen, secured by reducing the known 2,3,9,10-tetraphenyl-9,10-dihydroxy-9,10-dihydroanthracene[8] with potassium iodide in acetic acid. It is,

(1) Allen and Spanagel, THIS JOURNAL, **55**, 3773 (1933).

(2) Allen and Gates, *ibid.*, **65**, 419 (1943).

(3) Kohler, *Am. Chem. J.*, **40**, 217 (1908).

(4) Allen and Gates, THIS JOURNAL, **65**, 1283 (1943).

(5) Allen and Gates, *ibid.*, **64**, 2123 (1942).

(6) Allen and Gates, *ibid.*, **64**, 2441 (1942).

(7) Allen and Gates, *ibid.*, **64**, 2120 (1942).

(8) Allen and Bell, *ibid.*, **62**, 2408 (1940).

therefore, 2,3,9,10-tetraphenylanthracene XI (R = C₆H₅).

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A few years ago an analogous reaction was recorded by Koelsch.[9] He obtained 9,10-diphenylanthracene from 2,3,3-triphenylindanone by an essentially similar series of reactions. It is thus possible to assign the structure 2,3,3,5,6-pentaphenylindene IX (R = C$_6$H$_5$) to the third hydrocarbon (m. p. 222°).

Our interpretation of the mechanism of the reactions resulting in the formation of the anthracene derivative necessarily differs from that proposed by Koelsch, for the similar but not identical series of reactions, because of the isolation of a lactone from the chromic acid treatment. The first step is presumably oxidation of the indene to an enol A (hydrogen atoms attached to an indene ring are known to be readily oxidized to hydroxyl[3]) to the double bond of which an oxygen atom is then added. Since the oxanol B is an unstable type,[9] it isomerizes to XII which forms the lactone X by the mechanism suggested in our recent paper on oxidoketones in the indene series.[10] Sodium amide then reacts with lactone, first opening the ring to a hydroxycarboxylic acid D, which loses carbon dioxide in known manner[3]; the triphenylmethane derivative E then cyclizes to a dihydroanthracene, and is dehydrogenated to the tetraphenylanthracene XI (R = C$_6$H$_5$).
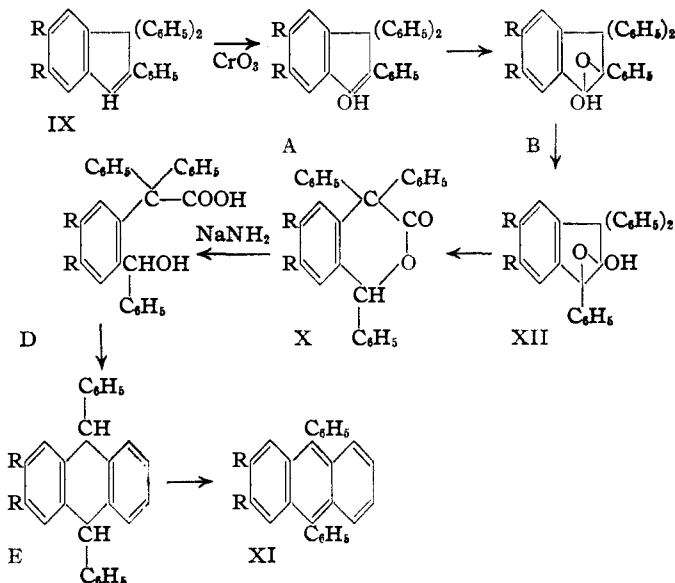
In order to be sure there was no difference in the type of reaction due to the presence of the extra phenyl groups, the enol benzoate of 2,3,3-triphenylindanone[9] was treated with chromium trioxide; the resulting oxidobenzoate was hydrolyzed by aqueous alkali to the ketol, m. p. 156°. Both these substances with sodium amide gave 9,10-diphenylanthracene. The two series are thus parallel.

(9) Koelsch, J. Org. Chem., 8, 456 (1938).
(10) Allen and Gates, THIS JOURNAL, 65, 1230 (1943).

If all three hydrocarbons are heated at 400°, the one of m. p. 280° is unchanged, but both of the others are isomerized into it, VI. That is, pyrolysis has resulted in the shift of a phenyl group in the last two instances. This is in line with Koelsch's conclusion that triphenylindenes having two phenyl groups attached to the same carbon atom are rearranged at 450° into the more symmetrical 1,2,3-isomer.[11] The isomerization of 2,3,3,5,6-pentaphenylindene IX to 1,2,3,5,6-pentaphenylindene VI involves a 1,3-shift of a phenyl group—another example of such a rearrangement.[12] Incidentally, it is a type not included in Koelsch's work.

Every ketone in the indene series with phenylmagnesium bromide gave a carbinol corresponding to it[4,5,6]; care was taken in each instance to decompose the magnesium complex with ammonium chloride. Dehydration of the carbinol was accomplished by the use of mineral acids in acetic acid, from 60° to the boiling point of the solution; thus, it appears that in those instances in which a rearrangement was observed, it was brought about by the mineral acid. This is different from the pyrolysis results—otherwise, but one hydrocarbon, the heat-stable 280° isomer, VI, would be found. An example which illustrates this conclusion is the carbinol from the bimolecular product,[5] which loses carbon monoxide and water at 300°, to give VI. All these carbinols, which differ only in the location of hydrogen atoms and double bonds, have the phenyl group on the indene ring in the 1,2- and 3-positions. Since the dehydration of them all results in the indene IX, having the 2,3,3 arrangement, it is apparent that the 1-phenyl group has undergone a 1,3-shift.

From these results it may be concluded that in partially reduced indene derivatives, in which α,γ-rearrangements are possible, mineral acids will tend to favor the formation of those isomers having gem-diphenyl groups.

Experimental

The pentaphenylindenes have all been described previously. The pyrolysis of these hydrocarbons was carried out for one and a half hours at 420°. The yields were 70–85%. 1,3,3,5,6-Pentaphenylindene, m. p. 227°, and 2,3,3,5,6-pentaphenylindene, m. p. 222°, were converted into 1,2,3,5,6-pentaphenylindene, m. p. 280°.

1,1,2,3,5,6-Hexaphenylindene IV was prepared by adding a benzene solution of 1-bromo-1,2,3-triphenylindene[5] to a two-fold excess of phenylmagnesium bromide. After three days of stirring at room temperature, the deep red solution had become colorless. The new hydrocarbon was then isolated by appropriate manipulation, using benzene as a solvent; it melts at 269–270°.

Anal. Calcd. for C$_{46}$H$_{32}$: C, 94.4; H, 5.6. Found: C, 94.2; H, 5.8.

(11) Koelsch and Johnson, ibid., 65, 567 (1943).
(12) Allen and VanAllan, ibid., 65, 1384 (1943); all the earlier references are given in this paper.

1-Ethoxy-1,2,3,5,6-pentaphenylindene was secured by refluxing a 10% solution of the bromoindene in ethanol for one-half hour, and recrystallizing from benzene–petroleum ether; it melts at 175–176°.

Anal. Calcd. for $C_{41}H_{32}O$: C, 91.1; H, 5.9. Found: C, 91.2; H, 6.2.

Oxidation.—A mixture of 4 g. of the indene, m. p. 280°, 5 g. of chromium trioxide and 40 cc. of acetic acid was refluxed for one-half hour, and worked up by appropriate manipulation. It gave 2 g. of 4,5-diphenyl-*o*-dibenzoylbenzene V, and 0.4 g. of benzoic acid.

In a similar manner 2 g. of the hydrocarbon, m. p. 227°, was oxidized; it gave 1 g. of the diketone V and only sufficient benzoic acid for a melting point determination.

When 5 g. of the hydrocarbon, m. p. 222°, was treated by the same procedure, it gave 3 g. of the lactone X (R = C_6H_5), m. p. 184–185°.

Anal. Calcd. for $C_{39}H_{28}O_2$: C, 88.6; H, 5.3; mol. wt., 528. Found: C, 88.4; H, 6.1; mol. wt. (in benzene), 560.

The lactone is insoluble in sodium carbonate, but dissolves in alcoholic sodium hydroxide and is reprecipitated by mineral acid. It shows no activity in the Grignard machine; this failure to show addition is attributed to the *gem*-diphenyl group.

2,3,9,10-Tetraphenylanthracene XI (R = C_6H_5).—From the lactone: a suspension of 1 g. each of sodium amide and the above lactone in 10 cc. of *p*-cymene was refluxed for four hours, water added and the cymene distilled with steam. The solid product was filtered and crystallized from acetic acid, it melts at 324–325°, and shows a bluish-violet fluorescence.

Anal. Calcd. for $C_{38}H_{26}$: C, 94.6; H, 5.4; mol. wt., 482. Found: C, 94.4; H, 5.6; mol. wt. (in benzene) 486.

Employing the previously described procedure,[8] the same hydrocarbon resulted when the known 9,10-diol was reduced by potassium iodide in acetic acid.

The Triphenyl Indene Series.—Following the procedures in the literature,[9] 2,3,3-triphenylindanone, its enol-benzoate, oxido enol-benzoate, and ketol, m. p. 156° were prepared. In the case of the oxido enol-benzoate, a 1 : 1-addition product containing acetic acid, and melting at 125° crystallized from the reaction mixture.

Anal. Calcd. for $C_{36}H_{28}O_5$: C, 80.0; H, 5.2. Found: C, 79.9; H, 5.4.

On recrystallizing from benzene–petroleum ether, it at once gave the solvent-free product, m. p. 196°. Our analytical figures on the ketol were in exact agreement with those published. In the Grignard machine it showed one active hydrogen and one addition.

When either the oxido enol-benzoate, or the ketol was treated with sodium amide in cymene, by the procedure described above, the known 9,10-diphenylanthracene resulted. It was identical with an authentic specimen.[13]

Summary

The structures of three polyarylated indenes which were prepared by dehydration under acidic conditions of certain carbinols have been determined.

Two are rearranged to the third on being heated to 420°.

One of the hydrocarbons is converted into a lactone by the action of chromium trioxide; the lactone gives a derivative of 9,10-diphenylanthracene on heating with sodium amide. The nature of these and of other rearrangements encountered is discussed.

(13) Simonis and Remmert, *Ber.*, **48**, 208 (1915).

The Reaction between Quinones and Metallic Enolates. XVIII. Mechanisms[1]

BY LEE IRVIN SMITH, R. T. ARNOLD AND JOSEPH NICHOLS

Four halogenated alkylquinones have now been studied with which there is opportunity for the two reactions with sodiomalonic ester, replacement and formation of a coumarin derivative, to occur simultaneously. From bromotrimethylquinone, only a coumarin was obtained, and of the three possible coumarins, only one, I, resulted.[2] Of the three dibromodimethyl-parabenzoquinones, the meta compound[3] gave only a coumarin, whereas the ortho-[4] and para-isomers[1] reacted only by replacement. In these last two compounds one or both halogen atoms could be replaced by malonic ester residues; the first quite readily, but the second only with difficulty and in poor yield. Smith and Austin[4] concluded that the important factor in determining the course of the reaction of the dibromoquinones was the relative position of the bromine atoms; they did not develop this thesis, which was, in fact, an outgrowth of the speculations of Smith

and Johnson[2] as to why only one coumarin was formed from bromotrimethylquinone.
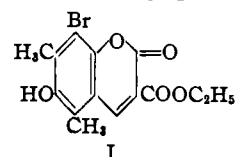
It is obvious that the controlling factor is the lability of the bromine atoms concerned; when these are highly active, replacement becomes rapid, and when the bromine atoms are unreactive, time becomes available for a pentad-enolization of the quinone[5] with resultant addition of malonic ester to form a coumarin. By application of the concept of resonance to these quinones, it is possible to explain and to correlate all the facts so far known with regard to the course of these reactions. Some of the contributing resonance forms of dibromo-*p*-xyloquinone II may be represented as follows

(1) XVII, Smith and Nichols, THIS JOURNAL, **65**, 1739 (1943).
(2) Smith and Johnson, *ibid.*, **59**, 673 (1937).
(3) Smith and Byers, *ibid.*, **63**, 612 (1941).
(4) Smith and Austin, *ibid.*, **64**, 528 (1942).

(5) (a) Fuson, *Chem. Rev.*, **16**, 1 (1935); (b) Smith and Horner, THIS JOURNAL, **60**, 676 (1938).