

[COMMUNICATION NO. 908 FROM THE EASTMAN KODAK RESEARCH LABORATORIES]

## The Thermal Decomposition of Certain Polyarylated Carbinols

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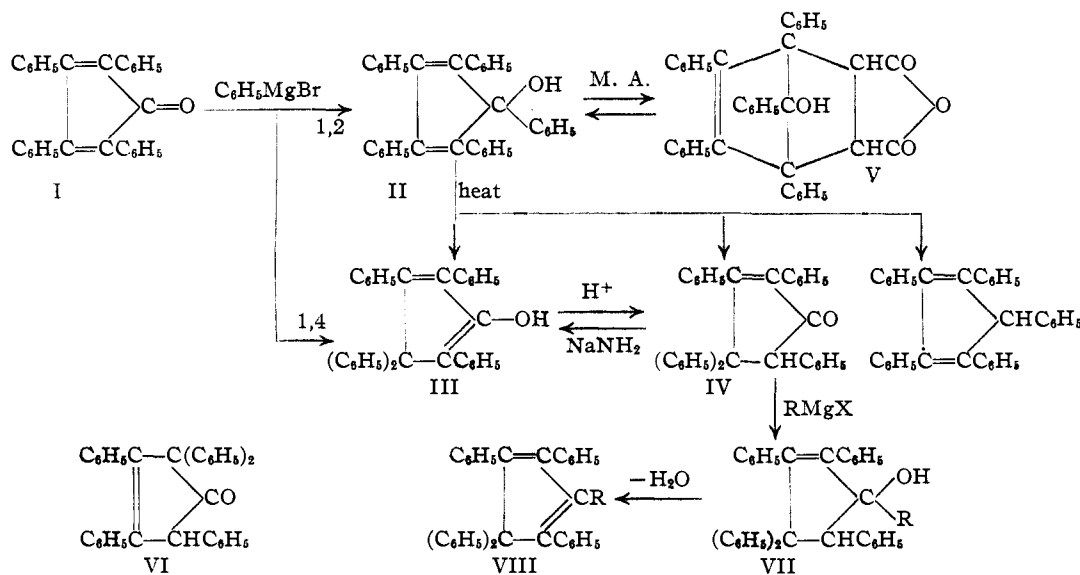
When tetraphenylcyclopentadienone I is treated with phenylmagnesium bromide in ether in the usual manner, it forms a carbinol II by 1,2-addition to the carbonyl group. The structure of the latter was proved conclusively by Ziegler<sup>1</sup>; in further confirmation we have found that it adds maleic anhydride to give an endocarbinol V, showing its diene nature. When the carbinol II is heated or distilled, small amounts of water, benzaldehyde and pentaphenylcyclopentadiene are formed, but the main product is a mixture of two mutually interconvertible substances III, IV, isomeric with the carbinol and with each other. The same two substances and maleic anhydride result when V is distilled, *i. e.*, the diene synthesis is reversed and the carbinol is rearranged.

The higher melting of the new isomers shows one active hydrogen and no addition in the Grignard machine, whereas the lower-melting one shows the reverse. The higher-melting form is converted to its isomer by acidic reagents, while the lower-melting form is transformed to the higher-melting form by means of sodium amide. These properties suggest that the substances are related to each other as keto-enol forms, having the structures indicated, III being the enol.

ketone IV was shown by the formation of a carbinol VII with phenylmagnesium bromide, followed by dehydration to an unsaturated hydrocarbon VIII.

When tetraphenylcyclopentadienone I is treated with phenylmagnesium bromide in ethyl ether or in benzene, the carbinol II is formed, but in isoamyl ether at its boiling point (*i. e.*, "forced" conditions), the enol III results; this is readily understandable as 1,4-addition to the conjugated system. It is *not* a case of rearrangement of the magnesium derivative of II, formed by 1,2-addition, for if this salt is made from the carbinol, it is found to be unaffected by heating in isoamyl ether. It is well known<sup>2</sup> that stable enols can be obtained with highly arylated  $\alpha,\beta$ -unsaturated ketones.

Further evidence confirming the structures of III and IV is afforded by chromic acid oxidation when the sole products are benzophenone and benzoic acid. The production of the ketone proves that the two phenyl groups are attached to one carbon atom. The alternatively possible isomeric ketone VI is excluded because (1) it could not be formed in the Grignard reaction by any conceivable mechanism except 1,6-addition—



The presence of the grouping  $-\text{CHCO}-$  in the

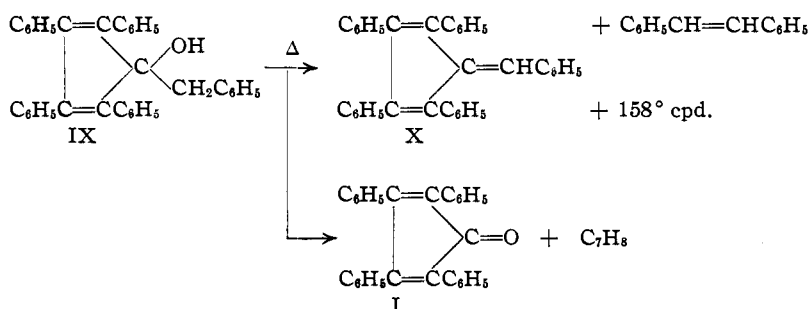
(1) Ziegler and Schnell, *Ann.*, **445**, 277 (1925).

(2) Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943, 2d ed., Chap. 7, p. 673.

not seriously considered because there have hitherto been no known instances except in polynuclear compounds—and (2) one of the oxidation products would be benzil, no trace of which was found. So far, unfortunately, no suitable synthesis has been devised, the components usually being degraded themselves rather than reacting in the desired way.

The formation of the isomers by heating Ziegler's carbinol II seems to be an instance of 1,3-shift of a phenyl group.<sup>3</sup> Were it the hydroxyl group that underwent a rearrangement, there would be no visible change, for the product would be the same as the starting material. The use of a homologous Grignard reagent might afford useful evidence on this point. However, 4-methoxyphenylmagnesium bromide gave only a carbinol, formed by 1,2-addition, even under forced conditions.

With the expectancy of securing additional information on the pyrolysis of the above type of carbinols, 1-benzyl-2,3,4,5-tetraphenylcyclopentadienol-1 IX was heated in the same manner. The results showed little similarity. The main product was the fulvene X formed by dehydration of the carbinol; smaller amounts of tetraphenylcyclopentadienone I, stilbene, toluene, and a trace of a substance, m. p. 158° (if the reaction mixture was worked up with acetic acid), were also secured. There was no evidence of any rearrangement product. The tetraphenylcyclopentadienone could have resulted by a loss of toluene, or benzal radicals and hydrogen (source of the stilbene?).

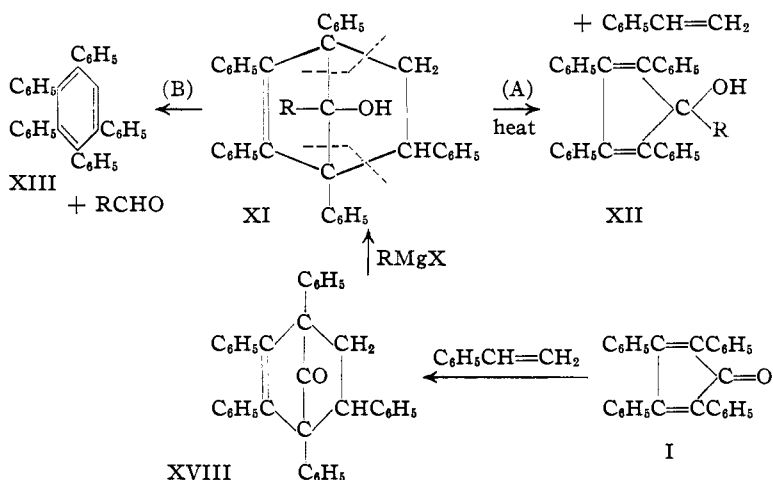


It was not possible to interpret the results obtained from a study of the substances next consid-

(3) Allen and Gates, *THIS JOURNAL*, **64**, 2123 (1942).

ered until the experimental work, described up to this point, had been done. As will become evident, the products are, in some measure, the same.

It is now known<sup>4</sup> that a carbonyl bridge in cyclic compounds has the usual reactivity of such a group, and that the apparent exceptions in the cyclohexene ring systems, in which it is eliminated as carbon monoxide, are readily correlated with the principle that a carbon-carbon bond which is beta to a double bond is favorably situated for cleavage<sup>5</sup> (double bond rule<sup>6</sup>). The carbinols XI that result from the interaction of the bridge carbonyl group of XVIII and Grignard reagents are also decomposed by heat, but there is no evolution of carbon monoxide. If these substances followed Schmidt's rule, two modes of cleavage would be expected; in one (A) the prod-



ucts would be styrene and a carbinol XII (a cyclopentadienol), and in the other (B), pentaphenylbenzene XIII (or a reduced form of the hydrocarbon) and a divalent radical R-C-OH,

which might very likely rearrange to an aldehyde.

When this reaction was first carried out, the mixture of products secured, except for styrene, which was formed in considerable amount, and benzaldehyde, did not contain any recognizable substances. Accordingly, the anticipated carbinol II (XII, R = C<sub>6</sub>H<sub>5</sub>)

(4) Allen and VanAllan, *ibid.*, **64**, 1260 (1942).

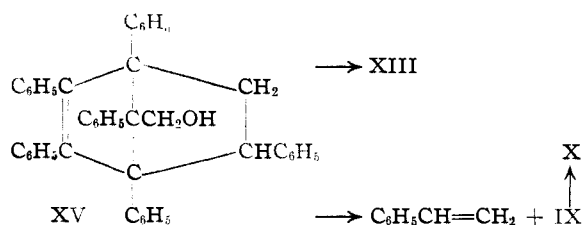
(5) Hurd, "Pyrolysis of Carbon Compounds," Reinhold Publishing Corporation, New York, N. Y., 1929, p. 76.

(6) Schmidt, *Chem. Rev.*, **17**, 140 (1935).

was examined under similar conditions, with the results described above. The isomers III and IV were then identified among the products of the pyrolysis of the bridged compound. The substance most easily isolated, however, is of an entirely different nature. It contains an inactive oxygen atom which disappears when the substance is treated with perchloric acid (but not hydrogen iodide or bromide), and pentaphenylbenzene XIII is formed. This observation implies that the type of cleavage involving the loss of the bridge has occurred.

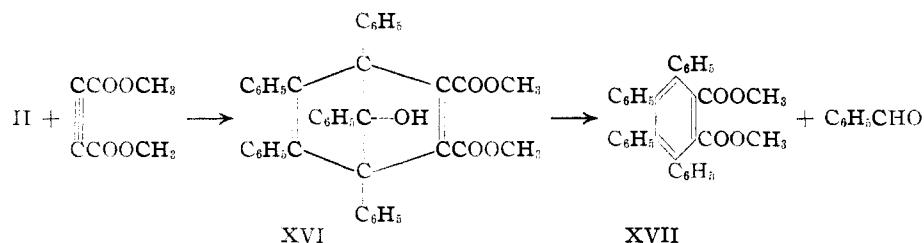
The fate of the bridge in this instance is not entirely clear. A portion turns up as benzaldehyde, but, obviously, the oxygen in the oxygen-containing substance must have come from the carbinol oxygen. The nature of the oxygen-containing substance XIV is in doubt. The oxygen is not present as a hydroxyl group, for the substance is unaffected by methylmagnesium iodide or by acetic anhydride; it is removed only by perchloric acid.<sup>7</sup> This suggests that the oxygen is linked in some way so that it could form an oxonium salt (*i. e.*, ethereal or highly hindered ketonic linkage). However, there is no evidence

proof that the formation of pentaphenylbenzene does not involve the bridge carbon or groups attached thereto.



By analogy with the previous instance, the bridge would be expected to turn up as phenylacetaldehyde. When the oil was treated with 2,4-dinitrophenylhydrazine, however, only the known 2,4-dinitrophenylhydrazone of tetracyclopentadienone was found. The fate of the bridge is thus uncertain in this instance.

In order to have a more favorable example in which but one mole of decomposition is possible, acetylenedicarboxylic ester was added to Ziegler's carbinol II. The addition product XVI decomposed smoothly, on being heated, to give benzaldehyde and the known tetraphenylphthalic ester XVII.<sup>9</sup>



to warrant writing tentative structures that might be suggested by analogy with some compounds described by Dilthey.<sup>8</sup>

A similar pyrolysis was carried out with the benzyl carbinol XV (XI, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>). The products identified were pentaphenylbenzene, styrene, the carbinol IX, and the corresponding fulvene X; that is, both modes of cleavage are also found. In this instance, the expected carbinol IX is stable enough, at the high temperature used, so that it can be isolated, even though a portion undergoes dehydration to the corresponding unsaturated hydrocarbon. There was no intermediate oxygen-containing substance, however, only the pentaphenylbenzene being produced. The use of the benzyl compound affords

In an addition product of this new type XVI, it would be anticipated that the bridge would be eliminated relatively easily, because it is now attached to carbon atoms which are located *beta* to two sets of double bonds, both of which favor cleavage of the same single bonds. That this is so appears from the clean reaction, leading to but two products. It should also be pointed out that this is the first instance known in which an addition product, derived from an acetylenic addend, has been isolated.

It is thus evident that, when a carbinol bridge is cleaved from substances of these types described, it rearranges to an aldehyde or secondary product derived from it.

In an excellent summary of the diene synthesis, Norton<sup>10</sup> has collected the facts regarding the be-

(7) The substance is insoluble in cold concentrated sulfuric acid, but destroyed when brought into solution by heating.

(8) Dilthey and Putter, *J. prakt. Chem.*, **149**, 192 (1937).

(9) Allen and Sheps, *Can. J. Research*, **11**, 171 (1934).

(10) Norton, *Chem. Rev.*, **31**, 319 (1942), esp. pp. 387, 469.

havior of bridged molecules on being heated. Although not pointed out, it should be noted that their behavior is in accord with and explicable in the light of the double bond rule. *The behavior of the bridge is dependent upon its relation to the double bond, and not on the nature of the atoms forming the bridge.* It is also to be emphasized "that the bridge, as such, does not confer special properties on the atoms included in the bridge, although the natural human tendency appears to be that one will tend to place the more reactive portion of the molecule in the bridge on drawing the structure of such a bridged compound."<sup>9</sup>

A few other carbonyl and carbinol bridge compounds in which there is an unsaturated linkage are known:<sup>11</sup> these are stable to heat, being readily distillable unchanged. In these, however, the double bond is not in the essential relation to the bridge just mentioned. Their stability thus confirms the conclusions drawn.

## Experimental

### I. The Carbinols and Related Compounds

**A. Pentaphenylcyclopentadienol II** was prepared following the directions of Ziegler,<sup>1</sup> but using benzene as a solvent. The yield was practically quantitative. 1-*p*-Methoxyphenyltetraphenylcyclopentadienol-1 was secured from tetracyclopentadienone I and *p*-methoxyphenylmagnesium bromide, regardless of variations in solvent. It crystallizes from benzene-methanol in prisms, m. p. 203°.

*Anal.* Calcd. for C<sub>36</sub>H<sub>28</sub>O<sub>2</sub>: C, 87.8; H, 5.7. Found: C, 87.6; H, 5.7.

**B. (1) Addition of Maleic Anhydride to the Carbinol II: 7-hydroxy-1,4,5,6,7-pentaphenylbicyclo[2.2.1]-5-hepten-2,3-dicarboxylic Anhydride, V.**—One gram each of the carbinol and maleic anhydride were melted and heated until the mixture suddenly solidified. After extraction with boiling benzene, the residue was crystallized from xylene, from which it separates in prisms, m. p. 220°.

*Anal.* Calcd. for C<sub>39</sub>H<sub>28</sub>O<sub>4</sub>: C, 83.6; H, 5.0. Found: C, 83.2; H, 4.9.

**B. (2) Addition of Methyl Acetylenedicarboxylate to the Carbinol II; the Addition Product XVI.**—A solution of 4.6 g. of the carbinol, 4 g. of ester and 50 cc. of benzene was refluxed for eighteen hours, cooled and the solid filtered. An additional amount was obtained by concentration of the filtrate. The combined solid was warmed at 213–215° for ten minutes and recrystallized twice from acetic acid. The addition product separates in needles, m. p. 209°; it gives a dark brown color with concentrated sulfuric acid. This and the remaining analyses are collected in Table I.

**C. (1) The requisite 1,2,4,5,6-pentaphenylbicyclo[2.2.1]-5-hepten-7-one, XVIII,** was prepared by warming together styrene and tetraphenylcyclopentadienone I in

benzene. It crystallizes from benzene-methanol in prisms, m. p. 191°.

**C. (2) The bridged phenyl carbinol XI** (R = C<sub>6</sub>H<sub>5</sub>) (1,2,4,5,6,7-hexaphenylbicyclo[2.2.1]-5-hepten-7-ol) was made by the usual Grignard procedure, from phenylmagnesium bromide acting upon the carbonyl-bridged ketone,<sup>3</sup> using benzene as a solvent. The yield was 89%. The benzyl carbinol (XI, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) was also prepared in benzene. The methyl carbinol (XI, R = CH<sub>3</sub>) was made in isoamyl ether. The ketone XVIII was not attacked by  $\alpha$ -naphthylmagnesium bromide.

**D. 2,3,3,4,5-Pentaphenyl-1,4-cyclopentadien-1-ol, III** resulted when the ethyl ether from the preparation of phenylmagnesium bromide was replaced by isoamyl ether, and the mixture refluxed for eight hours. After suitable manipulations, the product was recrystallized from benzene, from which it separates in needles that melt at 189°, and gives a magenta color in concentrated sulfuric acid. The yield was 73%. The magnesium enolate does not absorb oxygen.

### II. Heat Treatments

Since the heat treatment was the same for all the substances, one procedure will suffice. The substance was placed in a 250-cc. distilling flask connected with two receivers in series (traps cooled by dry-ice and acetone), heated by a metal-bath, and a vacuum of at least 15 mm. maintained. As heat was applied, the substance melted; liquid products distilled and were condensed in the traps, the effervescence being very vigorous. After one-half hour, at 290–300°, the quiescent melt was cooled to room temperature and worked up by appropriate means. Styrene was identified and estimated after conversion to its dibromide, and benzaldehyde as the 2,4-dinitrophenylhydrazone. The solid products were weighed directly.

**A. (1) Pentaphenylcyclopentadienol II** (40 g.) gave 33.8 g. of 2,3,4,4,5-pentaphenyl-2-cyclopentadien-1-one, IV, m. p. 164°; 2 g. of 1,2,3,4,5-pentaphenylcyclopentadiene, m. p. 250°; and benzaldehyde. The solid, after heating, was poured while hot into *n*-butyl alcohol, and the solid that separated was recrystallized from acetic acid. The material insoluble in this reagent was the hydrocarbon, which is most easily purified by use of *o*-dichlorobenzene.

(2) When the carbinol was distilled, after evolution of volatile products had ceased, the enolic isomer III, m. p. 189°, resulted.

**B.** When the anhydride V was heated, the residue in the flask was a mixture (m. p. 173–175°) of the ketonic and enolic isomers IV and III; instead of attempting the tedious separation, it was all converted to the ketonic form by hydrogen bromide, as described below. The yield was 79%.

**C. 1-Benzyl-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol-1 IX<sup>12</sup>** was heated for ten minutes at 290–300°, followed by distillation of volatile products *in vacuo*. There were obtained the known fulvene, benzaltetraphenylcyclopentadiene X, as the main product (47% yield), and lesser amounts of tetraphenylcyclopentadienone, stilbene, toluene and a substance (1% yield), m. p. 158° (when acetic acid was used as a solvent; this is not XXII—a mixed melting point is depressed 20°).

(11) Allen and Sallans, *Can. J. Research*, **9**, 574 (1933).

(12) Löwenbein and Ulich, *Ber.*, **58**, 2666 (1925).

D. (1) When 40 g. of the carbinol XI ( $R = C_6H_5$ ) was heated, the products were 2.6 g. of styrene, 1.6 g. of benzaldehyde, 15.4 g. of the ketone IV, and 11.2 g. of the oxygen-containing compound XIV. The loss was 4 g.

(2) When the carbinol XI ( $R = C_6H_5CH_2$ ) was heated, the products were styrene, pentaphenylbenzene, stilbene, tetraphenylcyclopentadienone and the 158° compound.

E. The bridged ester XVI decomposed rapidly at 250°, and benzaldehyde was collected in the receiver. The glassy residue was recrystallized several times from methanol, after which it had the correct melting point, and there was no depression on admixture with an authentic specimen.<sup>7</sup> The yield of aromatic ester was 75%.

### III. Proof of Structures of III and IV. A. Oxidation.

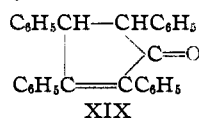
Both ketonic and enolic forms gave only benzophenone and benzoic acid, in the same amounts, upon chromic acid oxidation, using acetic anhydride as a solvent. As the reaction was vigorous, the chromium trioxide was added in three portions. The organic products were extracted from the diluted oxidation mixture by means of chloroform, from which the benzoic acid was removed by aqueous sodium carbonate. The benzophenone was then steam-distilled; the yield was 60%. It was identified by comparison of its melting point and that of its 2,4-dinitrophenylhydrazone with authentic specimens. It has been pointed out previously<sup>13</sup> that certain structures may be eliminated from consideration by the non-production of benzil.

**B. Interconversion.**—**Enol to ketone:** a solution of 3 g. of the enol, 5 cc. of 48% hydrobromic acid, and 20 cc. of acetic acid was refluxed for five hours, poured into water, and worked up in the usual way. The conversion was practically quantitative.

**Ketone to enol:** a mixture of 3 g. of ketone, 0.7 g. of sodium amide, and 15 cc. of xylene was refluxed for four and one-half hours; alcohol was then added and the xylene steam-distilled. The organic material was extracted with chloroform and the extract then appropriately manipulated.

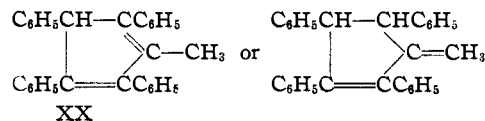
**C. Presence of Ketone Group and Adjacent  $\alpha$  Hydrogen.**—To the phenylmagnesium bromide prepared from 2.4 g. of magnesium was added 10 g. of the ketone IV; after ten minutes of heating, it was allowed to stand overnight and then worked up in the usual manner. The carbinol (VII  $R = C_6H_5$ ) was obtained in a yield of 8 g. It crystallizes from benzene-methanol in prisms, m. p. 248°. When methylmagnesium iodide was used, the carbinol was not isolated, for it lost water and gave the hydrocarbon VIII or its isomer, having a  $=CH_2$  group. The hydrocarbon rapidly decolorizes bromine and evolves hydrogen bromide. The phenyl carbinol VII ( $R = C_6H_5$ ) was dehydrated to the hydrocarbon (VIII  $R = C_6H_5$ ) by acetic anhydride or acetyl chloride. It recrystallizes from ligroin or benzene-ethanol in rods, m. p. 172°.

D. For comparison with IV, the tetraphenyl ketone XIX<sup>14</sup> was prepared and treated with methylmagnesium iodide, yielding a hydrocarbon XX.



(13) Kohler and Mydans, *THIS JOURNAL*, **54**, 4673 (1932).

(14) Diltthey, *J. prakt. Chem.*, **128**, 149 (1930).



The color reactions of the ketones IV and XIX and behavior with bromine were the same.

Both the ketones IV and XIX failed to react when treated with anhydrous aluminum chloride in benzene, a procedure that frequently results in the addition of the elements of benzene to the double bond of  $\alpha,\beta$ -unsaturated ketones.<sup>15,16</sup> Tetraphenylcyclopentadienone and the bimolecular product from  $\alpha,\beta$ -dimethylanhydracetonebenzil, which reacts in its monomeric form,<sup>4</sup> both give completely reduced cyclopentanones when treated with anhydrous aluminum chloride in benzene. The dimethyldiphenylcyclopentanone is a known substance<sup>17</sup>; it was identical with ours.

2,3,4,5-Tetraphenylcyclopentanone is new; it melts at 328°.

*Anal.* Calcd. for  $C_{35}H_{30}O$ : C, 89.7; H, 6.2. Found: C, 89.4; H, 5.6.

It is the only ketone in the series of reduction products of tetraphenylcyclopentadienone not described by Diltthey.<sup>18</sup> It gave a phenylcarbinol with phenylmagnesium bromide; m. p. 254°.

*Anal.* Calcd. for  $C_{35}H_{30}O$ : C, 90.3; H, 6.4; mol. wt., 466. Found: C, 90.3; H, 5.9; mol. wt. (in benzene), 473, 463.

The formation of reduction products when  $\alpha,\beta$ -unsaturated ketones are treated with anhydrous aluminum chloride in benzene has been reported previously.<sup>19</sup>

**E. Unsuccessful Attempts to Synthesize IV.**—Phenylbenzoin and dibenzyl ketone did not give crystalline condensation products when treated with alcoholic alkali, piperidine, or hydrogen chloride. The latter gave oils. Strong alkaline solutions cleaved the phenylbenzoin to benzhydrol and benzoic acid, but weak solutions were without action.

IV. The oxygen-containing compound formed pentaphenylbenzene, when to 1 g., dissolved in 3 cc. of hot acetic anhydride, was added, dropwise, 0.5 cc. of 72% perchloric acid; after boiling for three minutes, the solution was cooled, ether added, and the whole left in the ice box for several days. The hydrocarbon that separated was recrystallized from *n*-propyl alcohol; a mixed melting point with an authentic specimen showed no depression.

**V. Acetates of the Carbinols.**—In an attempt to dehydrate the benzyl carbinol IX with acetyl chloride or acetic anhydride, an acetate XXI was always formed instead of the expected fulvene X. It crystallizes from acetic acid in rods, m. p. 195°. This behavior seemed unusual, for tertiary alcohols seldom form acetates as readily. However, it was found that Ziegler's carbinol II also forms an acetate (XXII, m. p. 158°) with acetic anhydride under the same conditions, so it appears that the behavior of cyclic

(15) Eaton, Black and Fuson, *THIS JOURNAL*, **56**, 687 (1934).

(16) Koelsch, *J. Org. Chem.*, **3**, 456 (1938).

(17) Japp and Maitland, *J. Chem. Soc.*, **85**, 1473 (1904).

(18) Diltthey, *J. prakt. Chem.*, **139**, 1 (1934).

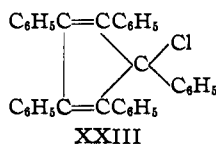
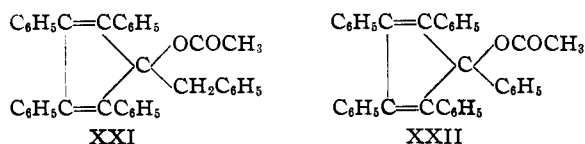
(19) Alexander, Jacoby and Fuson, *THIS JOURNAL*, **57**, 2208 (1935).

TABLE I  
 PROPERTIES OF NEW SUBSTANCES

No.	Emp. formula	M. p., °C.	Grignard Active H	machine Addition	Analyses					
					C	Calcd. H	Mol. wt.	C	Found H	Mol. wt.
III	C <sub>35</sub> H <sub>26</sub> O	189 <sup>a</sup>	1	0	90.9	5.6		90.6	5.6	
IV	C <sub>35</sub> H <sub>26</sub> O	164 <sup>b</sup>	0	1	90.9	5.6		90.8	5.6	
VII, R = C <sub>6</sub> H <sub>5</sub>	C <sub>41</sub> H <sub>32</sub> O	248	1	0	91.0	5.9	540	90.6	6.1	534, 540
VIII, R = CH <sub>3</sub>	C <sub>36</sub> H <sub>28</sub>	159 <sup>c</sup>			93.7	6.1	460	93.4	6.1	479, 478
VIII, R = C <sub>6</sub> H <sub>5</sub>	C <sub>41</sub> H <sub>30</sub>	172 <sup>c</sup>			94.3	5.8	522	94.3	5.7	494, 489
XX	C <sub>30</sub> H <sub>24</sub>	163			93.7	6.2		93.8	6.2	
<sup>d</sup>	C <sub>28</sub> H <sub>36</sub>	250 <sup>b</sup>			94.1	5.9	466	94.1	5.8	443
XIV	C <sub>36</sub> H <sub>28</sub> O	172 <sup>c</sup>	0	0	90.7	5.9	476	90.9	5.9	470
XVIII	C <sub>37</sub> H <sub>28</sub> O	191 <sup>c</sup>	0	1	91.0	5.7		90.9	5.5	
XI, R = C <sub>6</sub> H <sub>5</sub>	C <sub>43</sub> H <sub>34</sub> O	258 <sup>c</sup>			91.2	6.0		91.6	5.8	
XI, R = CH <sub>3</sub>	C <sub>38</sub> H <sub>32</sub> O	209 <sup>c</sup>	1	0	90.5	6.3		90.5	6.2	
XI, R = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	C <sub>44</sub> H <sub>36</sub> O	212 <sup>b</sup>			90.9	6.2		90.8	6.1	
XXI	C <sub>38</sub> H <sub>30</sub> O <sub>2</sub>	195 <sup>b</sup>			87.9	5.8	518	87.8	5.9	523, 532
XXII	C <sub>37</sub> H <sub>28</sub> O <sub>2</sub>	158 <sup>c</sup>			88.1	5.6		88.2	5.7	
XVI	C <sub>41</sub> H <sub>27</sub> O <sub>5</sub>	209 <sup>b</sup>			81.5	5.3		81.2	5.7	

<sup>a</sup> Needles. <sup>b</sup> Rods. <sup>c</sup> Prisms. <sup>d</sup> Pentaphenylcyclopentadiene.

carbinols cannot be predicted from what is known about open-chain aliphatic tertiary alcohols. The second acetate XXII, on treatment with hydrogen chloride in acetic acid, was converted into the known chloride XXIII,<sup>1</sup> which showed that there had been no rearrangements.



### Summary

The action of phenylmagnesium bromide upon tetraphenylcyclopentadienone is to form a car-

binol by 1,2-addition, or an enolate by 1,4-addition under forced conditions.

Upon being heated, the carbinol is rearranged to a mixture, composed of the enolate obtained by 1,4-addition and its isomeric ketonic modification. Both forms are interconvertible. The rearrangement appears to be another instance of a 1,3-shift of a phenyl group.

Several carbinol bridge compounds have been prepared.

On being heated, they decompose in at least two ways, both of which are in accordance with the double bond rule.

By one mode of decomposition, the anticipated carbinol can be isolated unless it is itself rearranged by the heat. By the other, the bridge is eliminated and found as an aldehyde.

ROCHESTER, NEW YORK

RECEIVED JANUARY 22, 1943