

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]
**SYNTHESES WITH TRIARYLVINYLMAGNESIUM BROMIDES.
 PENTAARYLALLYL ALCOHOLS**

BY C. FREDERICK KOELSCH¹

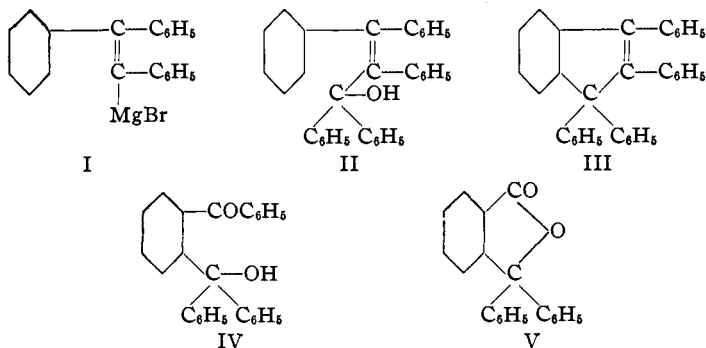
RECEIVED APRIL 27, 1932

PUBLISHED AUGUST 5, 1932

The interest attaching to compounds of trivalent carbon in which the methane carbon atom bears two aryl groups and one unsaturated aliphatic group has led to the investigation described in this paper. The object of this research has been to synthesize a pentaarylallyl radical, $R_2C=CR-CR_2-$, and to compare the behavior of this substance with that of the less highly phenylated tetraarylallyl radicals, $R_2C=CH-CR_2-$, of Ziegler. Although this object has not yet been attained, the present results are presented for their inherent interest.

It was reported previously² that triphenylvinylmagnesium bromide (I) reacted with benzophenone to form an addition product whose hydrolysis gave back the ketone and triphenylethylene. When, however, the reaction is carried out at an elevated temperature in toluene solution, it follows the normal course, yielding an $-OMgBr$ compound whose hydrolysis gives pentaphenylallyl alcohol (II).

In order to prepare a radical from pentaphenylallyl alcohol it is necessary to convert it first into a halide or an ether, but no means have yet been found for carrying out either of these reactions. When this alcohol is treated with any acidic reagent, even cold 1% alcoholic sulfuric acid, it loses water, forming a hydrocarbon $C_{33}H_{24}$. Since the oxidation of this hydrocarbon gives *o*-benzoyltriphenylcarbinol (IV) and benzoic acid, and further diphenylphthalide (V), it must be 1,1,2,3-tetraphenylindene (III).



The ease with which indene ring closure takes place in pentaphenylallyl alcohol results, at least in part, from the spatial arrangement of the atoms in the molecule. In Fig. 1 is shown a diagrammatic representation of the

¹ National Research Fellow in Chemistry.

² Koelsch, *THIS JOURNAL*, 54, 2045 (1932).

arrangement of the part of the molecule involved in the reaction. In this diagram the assumptions are made that (1) all joined carbon atoms are at an equal distance a from each other; (2) the valence of the phenyl group extends radially; and (3) the valences of the aliphatic carbon atoms are inclined to the double bond at an angle of 109° . None of these assumptions is more than approximately true, but together they allow the calculation of the distance d between the o -position of the γ -phenyl group and the hydroxyl-bearing carbon atom. This distance is found to be $1.14a$.

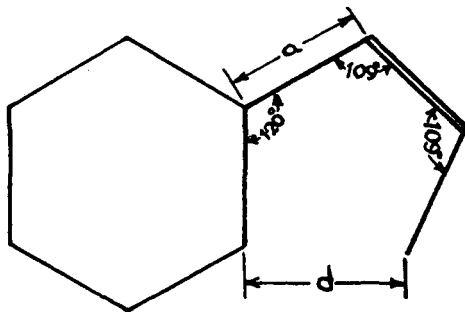


Fig. 1.—The spatial arrangement of pentaarylallyl alcohol.

These steric considerations suggest a basis for synthesizing a pentaarylallyl alcohol unable to undergo indene ring closure. If the two phenyl

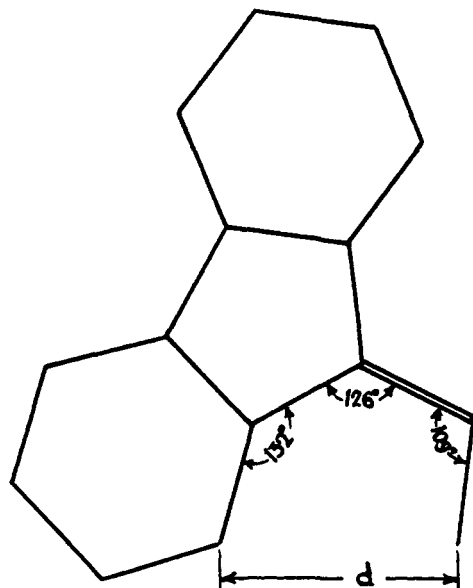


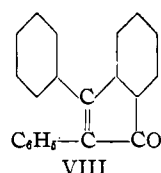
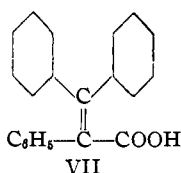
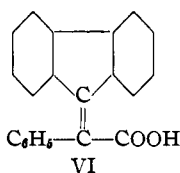
Fig. 2.—The spatial arrangement of α, α, β -triphenyl- γ -diphenyleneallyl alcohol.

groups on the γ -carbon atom are tied together, the conditions existing may be represented as in Fig. 2. Again, all joined carbon atoms are assumed to be at equal distances, and the pentagon involved in the structure is assumed to be regular. Here the distance d between the o -position of the γ -phenyl (ene) group and the hydroxyl-bearing carbon atom is calculated to be $1.86a$. Indene ring closure, since it involves the joining of these positions, should thus be impossible.

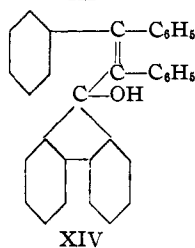
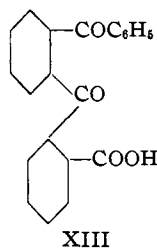
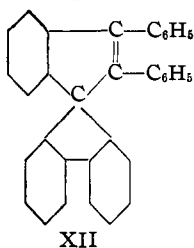
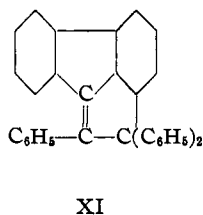
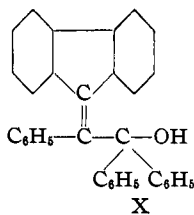
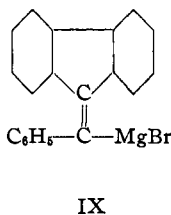
These calculations were experimentally verified using α -phenyl- β -diphenyleneacrylic acid (VI). This acid and its chloride are stable under conditions³ which lead to the formation of diphenylindone (VIII) or substituted diphenylindones from α, β, β -triphenylacrylic acid (VII) or its derivatives.

α -Phenyl- β -diphenylenevinylmagnesium bromide (IX) reacts with benzophenone to produce the expected α, α, β -triphenyl- γ -diphenyleneallyl

³ Koelsch, THIS JOURNAL, 54, 2487 (1932).



alcohol (X). Surprisingly, it was found that here, too, as in the case of pentaphenylallyl alcohol, even the mildest acidic reagents cause the elimination of water with the formation of a hydrocarbon $\text{C}_{33}\text{H}_{22}$. The oxidation of this hydrocarbon gives *o*-benzoylbenzophenone-*o*-carboxylic acid (XIII) and benzoic acid, showing that the "impossible" indene ring closure does not take place with the formation of (XI), but that an allylic rearrangement accompanies the dehydration, and that the hydrocarbon $\text{C}_{33}\text{H}_{22}$ is 1-diphenylene-2,3-diphenylindene (XII).



Finally, α -diphenylene- β,γ,γ -triphenylallyl alcohol (XIV), obtained from triphenylvinylmagnesium bromide and fluorenone, is distinctly different from its isomer (X), but treatment with an acidic reagent causes it to lose water with the formation of the same 1-diphenylene-2,3-diphenylindene (XII).

A subsequent paper will describe α,γ -bisdiphenylene- β -phenylallyl alcohol and its conversion into a radical.

Experimental

Benzalfluorene Dibromide.—A hot solution of 85 g. of benzalfluorene in 85 ml. of acetic acid is cooled rapidly to form a fine crystalline suspension, and at 20–35° (cooling) is added a solution of 55 g. of bromine in 55 ml. of acetic acid. On scratching and further cooling the dibromide separates. It is filtered off and washed with dilute acetic acid and with water; yield, 126 g. or 91%. The product melts at 116° with decomposition (literature⁴ 112°). Recrystallization is unnecessary and causes some decomposition.

⁴ Thiele and Henle, *Ann.*, **347**, 298 (1906).

α -Phenyl- β -diphenylenevinyl Bromide.—This compound can be prepared by the thermal decomposition of benzalfluorene dibromide, either in acetic acid or without a solvent, but the product thus obtained in a yield of 25–30% is difficult to purify. The decomposition in acetic acid in the presence of sodium acetate is likewise very unsatisfactory.

The following method gives a yield of 85–89%. A solution of 30 g. of potassium hydroxide in 15 ml. of water and 100 ml. of alcohol is added to a solution of 125 g. of benzalfluorene dibromide in 300 ml. of alcohol. The mixture is stirred vigorously and refluxed for twenty-five minutes on a water-bath. The solid product is filtered off after cooling, washed well with water and recrystallized from acetic acid (600–625 ml.). There is obtained 86 g. of pure bromide, and from the mother liquor by distilling to 50 ml. an additional 2.5 g. The product crystallizes in yellow prisms that melt at 127°.

Anal. Calcd. for $C_{20}H_{13}Br$: C, 72.0; H, 3.9. Found: C, 71.8; H, 3.9.

α -Phenyl- β -diphenylenevinylmagnesium Bromide (IX).—The Grignard reagent is prepared according to the usual procedure³ for triarylvinylmagnesium bromides. It separates as a green oil difficultly soluble in ether, or as yellow crystals.

Reaction with Benzoyl Chloride.—To the Grignard reagent from 5 g. of the bromide is added an ether solution of 2 ml. of benzoyl chloride. The product, α -phenyl- β -diphenyleneacrylophenone, is isolated in the usual way and crystallized from ethyl acetate. It forms small yellow plates that melt at 300–303°.

Anal. Calcd. for $C_{27}H_{18}O$: C, 90.5; H, 5.0. Found: C, 90.5; H, 5.1.

α -Phenyl- β -diphenyleneacrylic Acid (VI).—The Grignard reagent from 6.5 g. of α -phenyl- β -diphenylenevinyl bromide is carbonated in the usual way,⁸ and the product is crystallized from acetic acid. It forms fine needles that melt at 182–183°. It is soluble in cold concd. sulfuric acid, giving a pale green solution that becomes colorless on dilution with water.

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.5; H, 4.7; neut. equiv., 298. Found: C, 84.0; H, 4.6; neut. equiv., 298.

Reaction with Thionyl Chloride.—Equal weights (0.5 g.) of α -phenyl- β -diphenyleneacrylic acid and thionyl chloride are refluxed together in 2 ml. of carbon tetrachloride for four hours. No red color appears. The solution is stirred into cold aqueous ammonia, the carbon tetrachloride is evaporated and the remaining solid is crystallized from alcohol. The yellow product, α -phenyl- β -diphenyleneacrylamide, melts at 128–129° and gives a test for nitrogen.

Anal. Calcd. for $C_{21}H_{16}ON$: C, 84.8; H, 5.0. Found: C, 85.0; H, 5.3.

Pentaphenylallyl Alcohol (II).—To the Grignard reagent from 10 g. of triphenylvinyl bromide is added 5 g. of benzophenone. Toluene is added and the mixture is distilled to 85°. It is refluxed until the bright red color has changed to light yellow (about four hours) and then it is allowed to stand for ten hours. The crystalline magnesium compound is filtered off, washed with dry ether and decomposed with iced ammonium chloride containing some ammonia. The oil is taken up in ether. This solution is dried with potassium hydroxide, distilled to a small volume under reduced pressure and mixed with petroleum ether. The product crystallizes very slowly; yield, 3.1 g.

The combined mother liquors from this preparation give 2.25 g. of tetraphenylindene on treatment with acid.

Pentaphenylallyl alcohol forms small white crystals that melt at 108–109°; its solution in acetic acid gives a green color with acetyl chloride or sulfuric acid that disappears immediately.

Anal. Calcd. for $C_{33}H_{26}O$: C, 90.4; H, 5.9. Found: C, 90.1; H, 6.0.

$\alpha,\alpha,\beta,\gamma,\beta,\beta$ -Hexaphenylbutadiene.—This hydrocarbon (0.4 g.) was isolated from the mother liquors of a preparation of pentaphenylallyl alcohol involving 20 g. of triphenylvinyl bromide. It can be prepared from triphenylvinylmagnesium bromide and cupric chloride⁵ in a 55% yield. It crystallizes from benzene and petroleum ether in faintly yellow needles that melt at 213–214°.

Anal. Calcd. for $C_{40}H_{30}$: C, 94.2; H, 5.8. Found: C, 93.9; H, 5.8.

α,α,β -Triphenyl- γ -diphenyleneallyl Alcohol (X).—To the Grignard reagent from 5 g. of α -phenyl- β -diphenylenevinyl bromide is added 2 g. of benzophenone. The mixture is refluxed for three hours and allowed to stand for twenty-four hours or until the original red-brown color has faded to a light tan. The solid magnesium compound is removed, washed with ether and decomposed with iced ammonium chloride. The crude solid is washed with alcohol containing a little ammonia, dried and crystallized from benzene and petroleum ether; yield, 1.75 g. The alcohol forms yellow prisms that melt at 217–219°; its solution in acetic acid gives no color with sulfuric acid; with hot concd. sulfuric acid the alcohol gives a green color which is permanent on dilution with water.

Anal. Calcd. for $C_{33}H_{24}O$: C, 90.9; H, 5.5. Found: C, 90.9; H, 5.6.

α -Diphenylene- β,γ,γ -triphenylallyl Alcohol (XIV).—Fluorenone (2 g.) is added to the Grignard reagent from 5 g. of triphenylvinyl bromide. The solution is treated and the product is isolated as described under α,α,β -triphenyl- γ -diphenyleneallyl alcohol. The product is crystallized from alcohol containing a little ammonia, and then from carbon tetrachloride and petroleum ether; yield, 1.35 g. α -Diphenylene- β,γ,γ -triphenylallyl alcohol forms colorless crystals that melt at 150–151°.

Anal. Calcd. for $C_{33}H_{24}O$: C, 90.9; H, 5.5. Found: C, 91.0; H, 5.5.

Dehydration of the Pentaarylallyl Alcohols.—All of the alcohols described above lose water to form colorless indenenes when cold dilute alcoholic sulfuric acid is added to their solutions in methyl or ethyl alcohol. The indenenes are best prepared by warming an acetic acid solution of an allyl alcohol with a few drops of sulfuric acid, hydrochloric acid, or acetyl chloride. They can also be prepared by boiling the alcohols with undiluted acetyl chloride. The data concerning the indenenes recrystallized from acetic acid are summarized in Table I.

TABLE I
THE INDENENES (III) AND (XII)

()-indene	M. p., °C.	Formula	Analysis			
			Calcd.		Found	
			C	H	C	H
1,1,2,3-Tetraphenyl-	149–150	$C_{33}H_{24}$	94.2	5.8	94.0	5.8
1-Diphenylene-2,3-diphenyl-	^a 174–175	$C_{33}H_{22}$	94.7	5.3	94.5	5.3
	^b 174–175				94.5	5.3

^a From α,α,β -triphenyl- γ -diphenyleneallyl alcohol.

^b From α -diphenylene- β,γ,γ -triphenylallyl alcohol.

Oxidation of 1,1,2,3-Tetraphenylindene

(a) To *o*-Benzoyltriphenylcarbinol (IV).—To a solution of 1.85 g. of the hydrocarbon in acetic acid is added 5 g. of chromic acid in acetic acid and water. After refluxing for one hour the mixture is poured into water and extracted with ether. Sodium carbonate removes benzoic acid from the ether extract, and steam distillation gives 0.13 g. of benzophenone. Since the residue crystallizes with great difficulty, it is con-

⁵ Cf. Sakellarios and Kyrimis, *Ber.*, 57, 322 (1924).

verted into 9,9-diphenylanthrone by distillation.⁶ There is obtained 0.55 g. of the crude anthrone (m. p. 180–190°) which after crystallization from toluene and ligroin melts at 191–193° alone or mixed with a known sample of diphenylanthrone.⁷

(b) **To Diphenylphthalide (V).**—The oxidation is carried out as in (a) using 1.7 g. of tetraphenylindene and 9 g. of chromic acid. From the ether extract of the oxidation products is obtained 0.1 g. of benzoic acid. The oily residue left after the removal of the ether from the neutral part becomes crystalline on rubbing with alcohol, and after recrystallization from this solvent the product, diphenylphthalide, melts at 114–115° (mixed m. p.) and weighs 0.5 g.

Oxidation of 1-Diphenylene-2,3-diphenylindene.—The hydrocarbon (3.9 g.) in acetic acid is oxidized with 12 g. of chromic acid by refluxing for two hours. The solution is poured into water and extracted with ether. Sodium carbonate removes benzoic acid and *o*-benzoylbenzophenone-*o'*-carboxylic acid; the former (0.25 g.) is dissolved out with warm water, leaving 0.6 g. of the crude keto acid. This melts at 224–225° (literature⁸ 228°) and weighs 0.4 g. after recrystallization from acetic acid.

Anal. Calcd. for C₂₁H₁₄O₄: C, 76.3; H, 4.2. Found: C, 76.2; H, 4.3.

On treatment with ethereal diazomethane the acid gives the methyl ester, which melts at 162–163° (literature⁸ 165°); on heating with sulfuric acid, it gives the lactone of 9-*o*-carboxyphenyl-9-oxyanthrone-10 which melts at 235–237° (literature⁸ 239°).

The neutral substance not removed from the ether solution of the oxidation products by sodium carbonate is crystallized from acetic acid, distilled at 15 mm. and recrystallized. There is obtained 0.1 g. of a white compound⁹ crystallizing in needles that melt at 204–206°.

Anal. Calcd. for C₂₃H₁₈O₃: C, 83.6; H, 4.5. Found: C, 83.4; H, 4.5.

Summary

Triphenylvinylmagnesium bromide reacts with benzophenone and with fluorenone to give pentaarylallyl alcohols. On treatment with acids these alcohols lose water forming tetraarylindenes.

α -Phenyl- β -diphenylenevinylmagnesium bromide and carbon dioxide give α -phenyl- β -diphenyleneacrylic acid, which because of its steric arrangement cannot form an indone.

α,α,β -Triphenyl- γ -diphenyleneallyl alcohol, obtained from α -phenyl- β -diphenylenevinylmagnesium bromide and benzophenone, is prevented from forming an indene by its steric arrangement. However, acids cause it to undergo an allylic rearrangement, the resulting alcohol then losing water to form a tetraarylindene.

CAMBRIDGE, MASSACHUSETTS

⁶ Barnett, Cook and Nixon, *J. Chem. Soc.*, 510 (1927).

⁷ Howell, *THIS JOURNAL*, 42, 2335 (1920).

⁸ Cook, *J. Chem. Soc.*, 62 (1928).

⁹ It was thought that this compound might be diphenylenephthalide, and that it might be prepared by the oxidation of 9-*o*-tolyl-9-oxyfluorene, but it has not been possible to isolate a lactone from the oxidation products of this carbinol. 9-*o*-Tolyl-9-oxyfluorene was obtained in good yield from *o*-tolylmagnesium iodide and fluorenone. After crystallization from acetic acid it melted at 118–119° and gave a deep red color with concd. sulfuric acid.

Anal. Calcd. for C₂₀H₁₆O: C, 88.2; H, 5.9. Found: C, 87.8; H, 5.9.