[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

ATTEMPTED SYNTHESIS OF 1,2,3-TRIPHENYL-1,3-BUTADIENE. SYNTHESIS AND PROPERTIES OF 1,2,3-TRIPHENYLALLYL ALCOHOL

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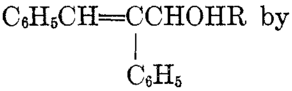
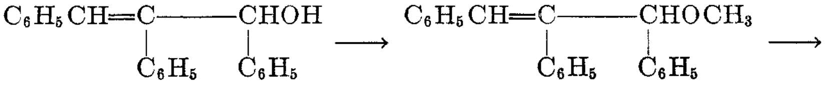
Among the already known phenyl-substituted 1,3-butadienes the following have been shown to give addition compounds with philodienic components: 1-phenylbutadiene (1), 2-phenylbutadiene (2), 1,2-diphenylbutadiene (3), 2,3-diphenylbutadiene (4), 1,4-diphenylbutadiene (1), and 1,2,4-triphenylbutadiene (3). The only exception in this series appears to be the 1,2,3,4-tetraphenyl-substituted product (5, 6), and by comparison with phenyl-substituted 9-vinylphenanthrenes we submitted the hypothesis (3), that 1,2,3-triphenylbutadiene (V) also should be inert in the Diels-Alder reaction, because it contains three neighboring carbon atoms, each of which is linked to an aromatic group. In these open-chain dienes the phenyl groups must be arranged in a way which does not favor the approaching of philodienic molecules, in contrast to the behavior of polyphenyl cyclopentadienones (7). So far, the synthesis of the diene V has failed, but some of the observations we made on the intermediary stages may be of general interest and are therefore dealt with in this paper.

Kohler and co-workers (8) have shown that α-phenylbenzalacetophenone reacts with Grignard reagents mainly in the 1,4-position to give substituted benzyldesoxybenzoins, $C_6H_5\underset{R}{C}H\underset{C_6H_5}{C}HCOC_6H_5$. On the other hand, α-phenylcinnamic aldehyde behaves "normally" (9) and yields the carbinols $C_6H_5CH{=}\underset{C_6H_5}{C}CHOHR$ by 1,2-addition. By interaction of this aldehyde with phenylmagnesium bromide, we prepared 1,2,3-triphenylallyl alcohol (I), identical with the reduction product obtained from benzaldesoxybenzoin with aluminum isopropoxide. We then intended to proceed along the following scheme:

$$C_6H_5\underset{R}{C}H\underset{C_6H_5}{C}HCOC_6H_5$$



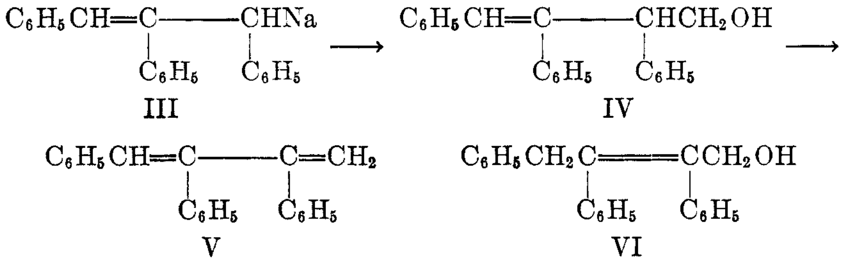
$$C_6H_5CH{=}\underset{C_6H_5}{C}CHOHR$$



$$\underset{\text{I}}{C_6H_5CH{=}\underset{C_6H_5}{C}{-\!\!-\!\!-}\underset{C_6H_5}{CHOH}} \longrightarrow \underset{\text{II}}{C_6H_5CH{=}\underset{C_6H_5}{C}{-\!\!-\!\!-}\underset{C_6H_5}{CHOCH_3}} \longrightarrow$$

I

II



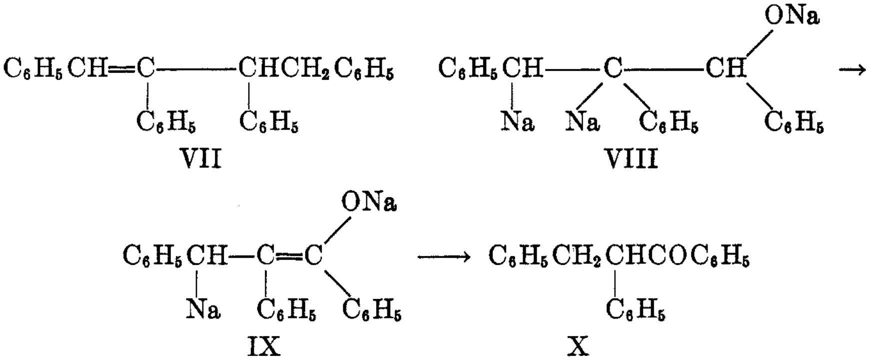
$$\underset{\text{III}}{C_6H_5CH{=}\underset{C_6H_5}{\underset{|}{C}}{-}\underset{C_6H_5}{\underset{|}{C}}HNa} \longrightarrow \underset{\text{IV}}{C_6H_5CH{=}\underset{C_6H_5}{\underset{|}{C}}{-}\underset{C_6H_5}{\underset{|}{C}}HCH_2OH} \longrightarrow$$

$$\underset{\text{V}}{C_6H_5CH{=}\underset{C_6H_5}{\underset{|}{C}}{-}\underset{C_6H_5}{\underset{|}{C}}{=}CH_2} \qquad \underset{\text{VI}}{C_6H_5CH_2\underset{C_6H_5}{\underset{|}{C}}{=}\underset{C_6H_5}{\underset{|}{C}}CH_2OH}$$

Compound I was easily methylated in cold methanol with a few drops of concentrated sulfuric acid. After a few minutes the methyl ether (II) began to crystallize out. II reacts smoothly with sodium powder in ether, and the product III, when decomposed with paraformaldehyde, is converted into 2,3,4-triphenyl-3-buten-1-ol. However, it proved impossible to dehydrate IV to the desired butadiene (V). Acetyl chloride, *e.g.*, formed the acetate of IV, which was stable even on heating to 350°. Tschugaeff's method yielded a yellow oil, which was sensitive to air and did not give satisfactory analytical figures. It may be that this oil consisted partly of the required diene, because it decolorized bromine, whereas I and IV did not. Anyhow, condensation of this impure material with maleic anhydride was unsuccessful. The failure to dehydrate IV satisfactorily, raised the question whether this carbinol had really the structure ascribed to it, or was the product (VI) of an allylic rearrangement. To decide this point, the sodium compound III was brought into reaction with benzyl chloride, because all the possible reaction products are known (6). A hydrocarbon of m.p. 147–148° was obtained, which most probably represents 1,2,3,4-tetraphenyl-1-butene (VII), although direct comparison with an authentic sample could not be carried out. The synthesis of VII proves that no rearrangement has occurred. Therefore the conclusion seems justified that also in the reaction product with formaldehyde the double bond remains in its original position.

With triphenylallyl alcohol we observed a very curious reaction. In ethereal solution, it reacts with sodium, not in the usual way to form an alcoholate, but to establish apparently a metal-to-carbon bond, since the solution acquired a deep wine-red color. After decomposition with ethanol, two substances could be isolated from the reaction mixture: benzyldesoxybenzoin, m.p. 120° (X), and a dihydro product of m.p. 92°, which was identified with the α form of 1,2,3-triphenylpropanol (10). The preparation of an authentic sample of this compound is described below.

The formation of benzyldesoxybenzoin, which resembles an intramolecular oxidation-reduction process, may be explained in various ways: Sodium metal may add to the ethylenic linkage and at the same time form an alcoholate, so that the trisodium compound (VIII) becomes the intermediate.



$C_6H_5CH{=}\underset{C_6H_5}{C}-\underset{C_6H_5}{CH}CH_2C_6H_5$

VII

$C_6H_5\underset{Na}{CH}-\underset{Na\quad C_6H_5}{C}-\overset{ONa}{\underset{C_6H_5}{CH}} \rightarrow$

VIII

$C_6H_5\underset{Na}{CH}-\underset{C_6H_5}{C}{=}C\begin{smallmatrix}ONa\\ C_6H_5\end{smallmatrix} \longrightarrow C_6H_5CH_2\underset{C_6H_5}{CH}COC_6H_5$

IX X

When NaH is split off from VIII, the enolate is obtained which, when sodium is replaced by hydrogen, is tautomerized to benzyldesoxybenzoin.

TABLE I

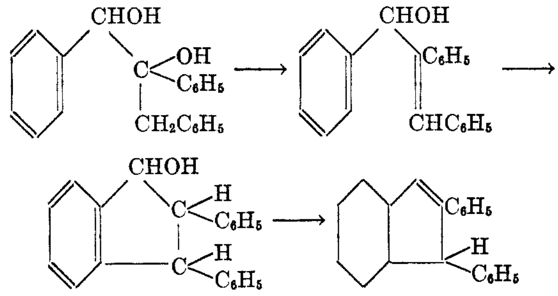
	TRIPHENYLALLYL ALCOHOL	α-TRIPHENYLPROPANOL
Triphenylallyl alcohol (93°)	93°	97–98°
α-Triphenylpropanol (92°)	97–98°	92°
β-Triphenylpropanol (87°)	87–89°	76–85°

VIII may give the triphenylpropanol directly by replacement of sodium by hydrogen. It is also possible that sodium effects an allylic rearrangement into the enol form of X. In this case, triphenylpropanol owes its formation to a special addition reaction. Experiments are now under way to clear up the mechanism of this reaction.

For the synthesis of α-triphenylpropanol, required for comparison with the above product, we reduced I catalytically, whereby a mixture of the α and β forms was obtained. As only the β form is produced by reduction of benzyldesoxybenzoin with sodium amalgam (11), the result of the various reduction processes apparently depends on the sequence in which the two unsaturated linkages are hydrogenated. The accompanying table shows the mixed melting points of I and the stereoisomeric triphenylpropanols: A mixture of the α form and I (which melt at about the same temperature) shows an elevation of the melting point.

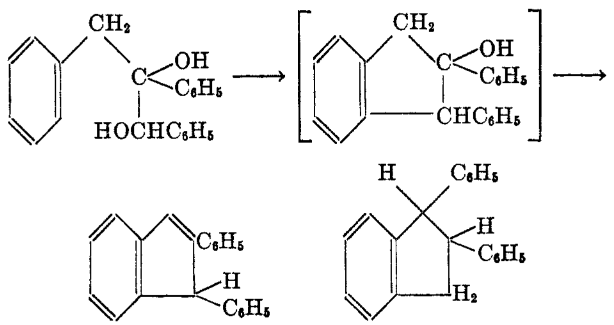
In the Grignard synthesis of I we observed that on working up the reaction mixture with dilute acid, 1,2-diphenylindene (XI) is formed in place of triphenylallyl alcohol. The compound I was already assumed (12) to be the intermediary stage in the cyclization of α-benzylhydrobenzoin according to the scheme A, in preference to the alternative scheme B (13).

A.



XI

B.



XII

Our experience with triphenylallyl alcohol supports the first reaction mechanism; namely, (a) heating the methyl ether II with concentrated sulfuric acid to 90° immediately produces XI by splitting off methanol; (b) when acetylation of I is attempted with acetyl chloride, the liberated hydrochloric acid also causes simultaneous cyclization and deacetylation; (c) the acetate of I can be isolated by the use of acetic anhydride and is readily converted into XI by sulfuric acid at 100°; (d) when hydriodic acid is used, all the above mentioned substances yield directly the higher-melting form of 1,2-diphenylhydrindene (XII) (14), which is best prepared in this way.

It is obvious that cyclization always occurs by way of the intermediary indanol derivatives. These easily split off a molecule of ROH (R = H, CH_3, $COCH_3$) and yield the indene system. Indanol derivatives have already been shown to be very unstable (15). On the other hand, it is not understandable, how the acetate of I or its methyl ether could suffer direct "cyclodehydration" with elimination of ROH. It may be noted also, that triphenylallyl alcohol is thermally stable and can be distilled *in vacuo* without cycloisomerization.

EXPERIMENTAL

1,2,3-Triphenylallyl alcohol (I). To a Grignard solution, produced from bromobenzene (10 g.) and magnesium (1.6 g.), α-phenylcinnamic aldehyde (4.5 g.) was added. When decomposed with ammonium chloride, the reaction mixture yielded directly a crystalline product, which was recrystallized from ligroin; prisms, m.p. 93°, yield 3.5 g.

Anal. Calc'd for $C_{21}H_{18}O$: C, 88.1; H, 6.3.
Found: C, 87.8; H, 6.2.

With hot conc'd sulfuric acid, the substance gives an olive-green solution. Bromine is not decolorized.

When the above reaction mixture is treated with dilute sulfuric acid and the residue distilled *in vacuo* at 125° and 0.2 mm., a thick, yellow syrup is obtained, which is induced to crystallize upon trituration with petroleum ether. Recrystallization from high-boiling petroleum ether yielded needles of m.p. 177°, which did not depress the melting point of an authentic sample of 1,2-diphenylindene.

Anal. Calc'd for $C_{21}H_{16}$: C, 94.0; H, 6.0.
Found: C, 93.85; H, 6.3.

1,2,3-Triphenylallyl alcohol was also obtained from benzaldesoxybenzoin (27.5 g.) and aluminum isoproproxide (41 g.) in isopropanol (200 cc.). On decomposing the solution with potassium hydroxide, an oil separated, which crystallized after a few hours. It was identical with the product from the Grignard reaction; yield, 25 g.

Triphenylallyl acetate. Triphenylallyl alcohol (0.5 g.) was boiled in acetic anhydride (5 cc.). The solution was poured into ice-water and the precipitate recrystallized from butanol (tetragonal plates) or high-boiling petroleum ether (rods); m.p. 129°.

Anal. Calc'd for $C_{23}H_{20}O_2$: C, 84.1; H, 6.1.
Found: C, 84.35; H, 6.1.

In contact with conc'd sulfuric acid, the crystals stain first red-brown, but immediately change to green, the reaction becoming exothermic. After heating the mixture on a steam-bath for two minutes, water was added, and the white precipitate was identified as 2,3-diphenylindene.

When triphenylallyl alcohol, its acetate, or its methyl ether were boiled for one hour with hydriodic acid, and the solution poured into water, a brown syrup was obtained. It was dissolved in carbon tetrachloride, washed with soda and thiosulfate solution and distilled, b.p. 180–200° at 5 mm. The bright yellow distillate was triturated with petroleum ether. Recrystallization from isopropanol yielded long, glistening rods, m.p. 126°, which did not depress the melting point of 1,2-diphenylhydrindene.

Reaction with sodium. I (5.7 g.) was shaken with sodium powder (2 g.) in ether for 48 hours. The residue obtained after decomposition with ethanol and evaporation of the solvent, crystallized on trituration with petroleum ether. It was twice recrystallized from ligroin, whereby a mixture of prisms and needles settled down. These were separated mechanically. (a) Needles, from alcohol, m.p. 119°; mixed melting point with benzyldesoxybenzoin, 120°. (b) Prisms, from ligroin, m.p. 92°; mixed melting point with the α form of 1,2,3-triphenylpropanol, 92°.

Anal. Calc'd for $C_{21}H_{20}O$: C, 87.5; H, 7.0.
Found: C, 87.0; H, 7.3.

Catalytic reduction. A solution of I (11 g.) in glacial acetic acid (50 cc.) was hydrogenated in the presence of 1 g. of catalyst (palladium on barium sulfate). In one hour, 950 cc. (754 mm., 26°) was absorbed; calc'd, 950 cc. After evaporation of the solvent, the residue was triturated with petroleum ether and recrystallized from methanol. The mixture of needles and prisms so obtained was separated mechanically. The needles had the m.p. 92°, after recrystallization from ethanol. They proved to be the α form of 1,2,3-triphenylpropanol. The β form was obtained from ligroin as prisms, m.p. 86–87°. A mixture of the two stereoisomers melted between 76° and 85°.

2,3,4-Triphenyl-3-buten-1-ol (IV). I (5.7 g.) was dissolved in methanol (50 cc.), and 5 drops of conc'd sulfuric acid added. After a few minutes at room temperature, the methyl ether (II) began to separate; it was recrystallized from ligroin, m.p. 96°, mixed melting point with I, 80–85°.

Anal. Calc'd for $C_{22}H_{20}O$: C, 88.0; H, 6.7; OCH_3, 10.3.
Found: C, 87.85; H, 6.7; OCH_3, 10.3.

An ethereal solution of the methyl ether (10 g.) was shaken with sodium (8 g.) for 48 hours, whereby the solution acquired a deep red color. The sodium compound (III) was then decomposed with paraformaldehyde (1.5 g.). The residue from the ethereal solution was distilled *in vacuo*, b.p. 205° at 2.0 mm., and then triturated with petroleum ether. The product crystallized from dilute ethanol in long lancets, m.p. 106°, which became green in contact with conc'd sulfuric acid, and dissolved in it with red-brown color when heated. This substance (IV) did not decolorize bromine.

Anal. Calc'd for $C_{22}H_{20}O$: C, 88.0; H, 6.7.
Found: C, 88.1; H, 6.7.

When 1.5 g. of the carbinol (IV) was refluxed for two hours with acetyl chloride (5 cc.), a crystalline acetate was obtained, which formed rods from ethanol, m.p. 94°. After heating this substance to 350° under normal pressure, or after distillation *in vacuo* (b.p. 280° at 0.03 mm.), it was recovered unchanged.

Anal. Calc'd for $C_{24}H_{22}O_2$: C, 84.2; H, 6.4.
Found: C, 83.9; H, 6.4.

With conc'd sulfuric acid the acetate of IV gives a deep violet color.

The alcohol (IV) (2.5 g.) was boiled with 1 g. of sodium powder in xylene for 6 hours, the solution filtered, and treated first with carbon disulfide (5 cc.), then boiled for two hours with methyl iodide (5 cc.). After filtering off the sodium iodide, the solution was shaken with silver powder and then distilled, b.p. 155° at 0.2 mm. A thick, yellow syrup was obtained, which decolorized bromine strongly. No picrate could be isolated from the alcoholic solution of this substance, nor any addition product with maleic anhydride.

Anal. Calc'd for $C_{22}H_{18}$: C, 93.6; H, 6.4.
Found: C, 88.9; H, 6.2.

The addition compound III, prepared from II (2 g.) and sodium powder (1 g.) in ether, was decolorized with benzyl chloride (1 g.), and the residue which remained after evaporation of the solvent was recrystallized first from methanol, then twice from acetic acid; m.p. 147–148°.

Anal. Calc'd for $C_{28}H_{24}$: C, 93.3; H, 6.7.
Found: C, 93.0; H, 6.7.

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SUMMARY

1. 1,2,3-Triphenylallyl alcohol and its derivatives are easily cyclized to 1,2-diphenylindene.

2. The synthesis of 1,2,3-triphenylbutadiene by dehydration of 2,3,4-triphenyl-3-buten-1-ol failed.

3. The abnormal reaction of 1,2,3-triphenylallyl alcohol with sodium is described.

4. Catalytic reduction of this alcohol yields a mixture of the stereoisomeric triphenylpropanols.

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