

THE CONDENSATION OF SOME OF THE DIPHENYL ALKYL
CARBINOLS WITH PHENOL IN THE PRESENCE OF
ANHYDROUS ALUMINUM CHLORIDE

by

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I Introduction

In 1916, Huston and Friedeman (1) condensed benzyl alcohol with benzene in the presence of anhydrous aluminum chloride. This work was followed, in 1924, by the condensation of benzyl alcohol with phenol by Huston (2).

In 1927, Huston, Lewis and Grotemut (3) condensed benzohydrol, methyl phenyl carbinol, and ethyl phenyl carbinol with phenol.

Attempts to condense diphenyl ethyl carbinol, didiphenyl n-propyl carbinol, and diphenyl iso-propyl carbinol with benzene were carried out in 1933 and 1934 by Huston and Wilsey (4) and Huston and Hradel (5). No condensation resulted, but the carbinols underwent dehydration.

The condensation of diphenyl methyl carbinol with phenol in the presence of anhydrous aluminum chloride was reported by Welsh and Drake (6) in 1938.

To investigate further the use of anhydrous aluminum chloride as a condensing agent, the author has condensed the following diphenyl alkyl carbinols with phenol: diphenyl ethyl carbinol, diphenyl n-propyl carbinol, diphenyl iso-propyl carbinol, diphenyl n-butyl carbinol, diphenyl iso-butyl carbinol, diphenyl sec-butyl carbinol, diphenyl tert-butyl carbinol, and diphenyl n-amyl carbinol.

II Historical

The condensation of alcohols with phenol has been accomplished by the use of numerous condensing agents, a few of which are anhydrous aluminum chloride, zinc chloride, magnesium chloride, alkali bisulfites, sulfuric acid, phosphoric acid, and perchloric acid.

The first condensation of alcohols with phenol was reported by Liebmann (7) with the use of zinc chloride as condensing agent. The first use of anhydrous aluminum chloride as a condensing agent for alcohols and aromatic compounds was in 1897 when Nef (8) mentioned the formation of diphenyl methane from benzyl alcohol and benzene. Huston and Friedeman (1) repeated this work and reported a 30% yield of diphenyl methane. Huston and Friedeman (9) later condensed aromatic secondary alcohols and mixed aliphatic-aromatic secondary alcohols with benzene, and Huston (2) condensed benzyl alcohol with phenol, anisole, and phenetole.

In 1926, Huston and Sager (10) attempted to condense the following primary alcohols with benzene: methyl, ethyl, n-propyl, n-butyl, iso-butyl, iso-amyl, phenyl ethyl, phenyl propyl, and allyl. With the exception of allyl alcohol, which gave a 16% yield of allyl benzene, no condensation resulted. Allyl alcohol was condensed with phenol by Huston and Newmann (11).

Triphenyl methane was the only product isolated

from the attempted condensation of triphenyl carbinol with benzene by Huston and Davis (12) in 1927.

In 1924, Huston and Goodemoot (13) condensed cyclo-butyl, cyclo-pentyl, and cyclo-hexyl carbinols with benzene. As expected, cyclo-butyl carbinol showed the greatest reactivity.

Only dehydration of the carbinols resulted when Huston and Wilsey (4) and Huston and Hradel (5) and Huston and Macomber (14) attempted to condense diaryl alkyl carbinols and dialkyl aryl carbinols with benzene.

Up to this time, the investigations in this field had indicated that, if an alcohol is to be successfully condensed with benzene or phenol in the presence of anhydrous aluminum chloride, its alpha carbon must be unsaturated, that is, double bonded or a member of a benzene ring or strained alicyclic ring.

The formation of cumene from iso-propyl alcohol and benzene by Huston and Hsieh (15) in 1936 was the first successful condensation involving a saturated aliphatic alcohol. Huston, Hsieh, and Fox (15), (16) later condensed the tertiary butyl, amyl, and hexyl alcohols with benzene and phenol. Subsequently, some of the tertiary heptyl and octyl alcohols were condensed with benzene and phenol by Huston and co-workers (17).

Results similar to those of Huston, Hsieh, and Fox were obtained by Tzukervanik and co-workers (18) in

their condensations of some of the simple secondary and tertiary aliphatic alcohols with benzene and toluene.

In 1938, Welsh and Drake (6) reported the condensation of diphenyl methyl carbinol with phenol. However, none of the diphenyl alkyl carbinols used in this investigation have been condensed with phenol.

III Discussion

(1) Preparation of the Diphenyl Alkyl Carbinols

Diphenyl ethyl carbinol has been prepared from ethyl magnesium iodide and benzophenone by Klages (19), Hell and Bauer (20), Sabatier and Murat (21), from diethyl mercury, benzophenone and sodium by Schorigen (22), from ethyl propionate and phenyl magnesium bromide by Masson (23), and from propionyl chloride and phenyl magnesium bromide by Gilman, Fothergill, and Parker (24).

Diphenyl n-propyl carbinol has been prepared from ethyl butyrate and phenyl magnesium bromide by Masson (23), Sabatier and Murat (21), Scaup and Freundlich (25), and Schlenk and Bergmann (26). Klages and Heilmann (27) claim to have prepared it from n-propyl magnesium iodide and benzophenone. However, Scaup and Freundlich (25) and Schlenk and Bergmann (28) claimed that his product was benzohydrol resulting from the reduction of the benzophenone by the Grignard reagent. Sabatier and Murat (21) reported a very small yield of the carbinol from n-propyl magnesium chloride and benzophenone; the principal product was benzohydrol.

Diphenyl iso-propyl carbinol has been prepared from ethyl iso-butyrate and phenyl magnesium bromide by Sabatier and Murat (21), Levy (29), Ramart-Lucas and Salmon-Legagneur (30), Schlenk and Bergmann (28), and from iso-propyl magnesium iodide and benzophenone by

Sabatier and Murat (21). In this laboratory (31) an attempt to prepare it from iso-propyl magnesium bromide and benzophenone gave benzohydrol as the principal product.

Diphenyl n-butyl carbinol has been prepared from ethyl n-valerate and phenyl magnesium bromide by Schlenk and Bergmann (26).

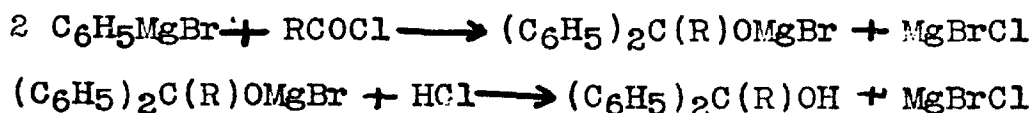
Diphenyl iso-butyl carbinol has been prepared from methyl iso-valerate and phenyl magnesium bromide by Sabatier and Murat (21) and von Auwers (32).

Diphenyl sec-butyl carbinol has not been prepared as far as the author has been able to determine.

Diphenyl tert-butyl carbinol has been prepared from trimethyl acetophenone and phenyl magnesium bromide (33) by Ramart-Lucas (34), and from the ethyl ester of trimethyl acetic acid and phenyl magnesium bromide by Schlenk and Racky (35) and by Bateman and Marvel (36).

Diphenyl n-amyl carbinol has been prepared from ethyl caproate and phenyl magnesium bromide by Masson (23) and Schlenk and Bergmann (26).

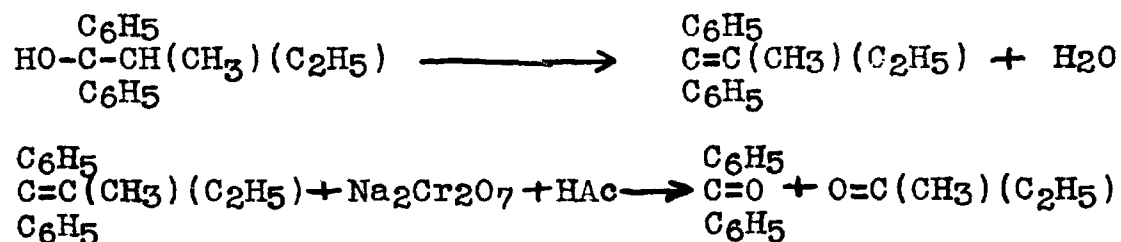
For this investigation, the diphenyl alkyl carbinols, with the exception of diphenyl ethyl carbinol, were prepared from phenyl magnesium bromide and the corresponding acid chlorides, the method of Gilman, Fothergill, and Parker (24).



Diphenyl ethyl carbinol was prepared from ethyl propionate and phenyl magnesium bromide.

In addition, diphenyl n-propyl carbinol, diphenyl iso-propyl carbinol, and diphenyl n-amyl carbinol were prepared from the corresponding esters and diphenyl n-propyl carbinol was prepared from butyrophenone. The yields of the carbinols from the acid chlorides and esters were 65% to 80%.

Diphenyl sec-butyl carbinol was prepared from methyl ethyl acetyl chloride and phenyl magnesium bromide in 65% yield. It is a light yellow, viscous liquid. Its structure was proved by dehydration and oxidation of the resulting hydrocarbon with chromic acid. Benzophenone and methyl ethyl ketone were isolated, the latter as its semicarbazone, M.P. 143° (37).



Physical Constants of the Diphenyl Alkyl Carbinols

Compound	M.P.	B.P.
diphenyl ethyl carbinol	94-5°	128-30° / 2 mm.
diphenyl n-propyl carbinol		128-9° / 1 mm.
diphenyl iso-propyl carbinol	52-3°	125-6° / 1 mm.
diphenyl n-butyl carbinol		133-4° / 1 mm.
diphenyl iso-butyl carbinol		129-30° / 1 mm.
diphenyl sec-butyl carbinol		126-7° / 1 mm.
diphenyl tert-butyl carbinol		124-5° / 1 mm.
diphenyl n-amyl carbinol	46-7°	142-3° / 1 mm.

Physical Constants of the Dehydration Products of

Compound	M.P.	B.P.
1,1 diphenyl 1-propene	51-2°	94-5° / 1 mm.
1,1 diphenyl 1-butene		115-6° / 2 mm.
1,1 diphenyl 2 methyl 1-propene		101-2° / 1 mm.
1,1 diphenyl 1-pentene		112-3° / 1 mm.
1,1 diphenyl 3 methyl 1-butene		110-2° / 1 mm.
1,1 diphenyl 2 methyl 1-butene		108-9° / 1 mm.
2,2 diphenyl 3 methyl 3-butene		102-3° / 1 mm.
1,1 diphenyl 1-hexene		130-1° / 1 mm.

B.P.	Sp. G.	Index of Refraction	
177-8°/ 16 mm.			
178-9°/ 15 mm.	$\frac{25^\circ}{25^\circ} 1.0428$	$n_D^{25^\circ}$	1.5727
178-9°/ 15 mm.			
191-2°/ 15 mm.	$\frac{25^\circ}{25^\circ} 1.0478$	$n_D^{25^\circ}$	1.5658
184-5°/ 15 mm.	$\frac{25^\circ}{25^\circ} 1.0430$	$n_D^{25^\circ}$	1.5682
185-6°/ 15 mm.	$\frac{25^\circ}{25^\circ} 1.0445$	$n_D^{25^\circ}$	1.5664
185-6°/ 14 mm.	$\frac{25^\circ}{25^\circ} 1.0546$	$n_D^{25^\circ}$	1.5731
204-5°/ 15 mm.			
the Diphenyl Alkyl Carbinols			
B.P.	B.P.	Sp. G.	Index of Refraction
151-2°/ 16mm.	281-2°/ 743mm.		
164-5°/ 15mm.	288-9°/ 743mm.	$\frac{25^\circ}{25^\circ} 1.0096$	$n_D^{25^\circ} 1.5950$
155-6°/ 15mm.	285-6°/ 743mm.	$\frac{25^\circ}{25^\circ} 1.0004$	$n_D^{25^\circ} 1.5962$
180-1°/ 19mm.	300-1°/ 743mm.	$\frac{25^\circ}{25^\circ} 1.0022$	$n_D^{25^\circ} 1.5942$
169-70°/ 18mm.	292-3°/ 743mm.	$\frac{25^\circ}{25^\circ} 0.9813$	$n_D^{25^\circ} 1.5816$
165-6°/ 18mm.		$\frac{25^\circ}{25^\circ} 0.9944$	$n_D^{25^\circ} 1.5822$
156-7°/ 15mm.		$\frac{25^\circ}{25^\circ} 0.9790$	$n_D^{25^\circ} 1.5759$
180-1°/ 17mm.	305-7°/ 738mm.	$\frac{25^\circ}{25^\circ} 0.9987$	$n_D^{25^\circ} 1.5968$

(2) Condensation of the Diphenyl Alkyl Carbinols with Phenol in the Presence of Anhydrous Aluminum Chloride

The eight diphenyl alkyl carbinols were condensed with phenol by the following procedure:

Anhydrous aluminum chloride is added, with stirring to a mixture of phenol and diphenyl alkyl carbinol dissolved in petroleum ether. After standing three to four days, the mixture is decomposed with ice and HCl, extracted with diethyl ether, and the ether removed. The phenols of this mixture are separated from the non-phenolic compounds by the use of alcoholic KOH and petroleum ether. The phenolic and non-phenolic fractions are separately fractionally distilled.

For the discussion of the products, the condensations of the eight diphenyl alkyl carbinols with phenol are divided into three groups involving the condensations of (1) the diphenyl primary-alkyl carbinols, (2) diphenyl secondary-alkyl carbinols, and (3) a diphenyl tert-alkyl carbinol.

(1) Products from the Condensations with Phenol of the Five Diphenyl primary-Alkyl Carbinols: Diphenyl Ethyl Carbinol, Diphenyl n-Propyl Carbinol, Diphenyl n-Butyl Carbinol, Diphenyl iso-Butyl Carbinol, and Diphenyl n-Amyl Carbinol.

From the fractional distillation of the non-phenolic fractions, two types of compounds were obtained,

diphenyl alkenes, resulting from the dehydration of the carbinols, and small amounts of high-boiling, viscous materials distilling over wide ranges (180-250°/ 3 mm.). These latter materials probably contained dimers of the diphenyl alkenes but were not investigated because they occurred in amounts too small to permit their purification.

The principal products isolated from the phenolic fractions were, besides unused phenol, the condensation products (p-hydroxy triphenyl primary-alkyl methanes). Small amounts of higher boiling materials (above 230° at 3 mm.) were obtained. Because they could not be crystallized, or distilled without decomposition, they were not investigated. They may consist of disubstituted phenols or products resulting from the condensation of the unsaturated dimers of the diphenyl alkenes with phenol. Their solubility in aqueous KOH indicates that they are not disubstituted phenols.

The diphenyl alkenes, 1,1 diphenyl 1-propene, 1,1 diphenyl 1-butene, 1,1 diphenyl 1-pentene, 1,1 diphenyl 2 methyl 1-butene, and 1,1 diphenyl 1-hexene resulting from the dehydrations of diphenyl ethyl carbinol, diphenyl n-propyl carbinol, diphenyl n-butyl carbinol, diphenyl iso-butyl carbinol, and diphenyl n-amyl carbinol respectively, were also condensed with phenol with the formation of the same products as from the condensations of the corresponding carbinols with phenol.

The p-hydroxy triphenyl primary-alkyl methanes were obtained, for the most part, in yields of 30% to 40%.

(2) Products from the Condensations with Phenol of the Two Diphenyl sec-Alkyl Carbinols: Diphenyl iso-Propyl Carbinol and Diphenyl sec-Butyl Carbinol.

From the fractional distillation of the non-phenolic fraction, obtained from the condensation of diphenyl iso-propyl carbinol with phenol, were isolated iso-propyl benzene, 1,1 diphenyl 2 methyl 1-propene (from the dehydration of the carbinol), and a small amount of a viscous liquid (B.P. 200-50°/ 3 mm.). This viscous material was not investigated.

From the phenolic fraction were isolated unused phenol, p-benzyl phenol, p-hydroxy triphenyl iso-propyl methane, and a small amount of higher boiling material (above 220°/ 3 mm.) which decomposed on distillation. The yields of p-hydroxy triphenyl iso-propyl methane varied greatly (from 9% to 73%).

Identical products were obtained from the condensation of 1,1 diphenyl 2 methyl 1-propene with phenol.

From the condensation of diphenyl sec-butyl carbinol with phenol were obtained, in the non-phenolic fraction, sec-butyl benzene, 1,1 diphenyl 2 methyl 1-butene, and a small amount of high boiling, viscous material, and, in the phenolic fraction, phenol, p-benzyl

phenol, p-hydroxy triphenyl sec-butyl methane, and a small amount of higher boiling material. The yields of p-hydroxy triphenyl sec-butyl methane were 12% and 13%.

Because it could not be obtained in sufficient amounts, 1,1 diphenyl 2 methyl 1-butene was not condensed with phenol.

In two condensations of diphenyl iso-propyl carbinol and diphenyl sec-butyl carbinol with phenol, where the condensation mixtures were decomposed with ice only and the phenolic and non-phenolic fractions immediately separated with the use of alcoholic KOH and petroleum ether, small amounts of the carbinol were recovered in the non-phenolic fractions. Apparently, in the presence of HCl, the temperature necessary to remove the diethyl ether is sufficiently high to cause dehydration of the carbinols.

(3) Products from the Condensation of Diphenyl tert-Butyl Carbinol with Phenol

The attempted condensation of diphenyl tert-butyl carbinol with phenol, by the procedure used for the other carbinols, gave only phenol, 2,2 diphenyl 3 methyl 3-butene, and 2,2 diphenyl 3 chloro 3 methyl butane. When a mixture of phenol and diphenyl tert-butyl carbinol, dissolved in petroleum ether, was added dropwise, with stirring, to anhydrous aluminum chloride suspended in petroleum ether, a 6% yield of 2,2 diphenyl 3 (p-hydroxy phenyl) 3 methyl butane was obtained. The conden-

sation of 2,2 diphenyl 3 methyl 3-butene , the dehydration product of diphenyl tert-butyl carbinol, with phenol gave a 15% yield of 2,2 diphenyl 3 (p-hydroxy phenyl) 3 methyl butane. In the condensations with diphenyl tert-butyl carbinol and 2,2 diphenyl 3 methyl 3-butene, only very small amounts of higher boiling materials were formed.

Products of the Condensation of the Diphenyl

Alkyl Carbinols with Phenol

Condensation Product	B.P.	B.P.
p-hydroxy triphenyl ethyl methane	198-199°/ 1 mm.	259-260°/ 15 mm.
p-hydroxy triphenyl n-propyl methane	196-197°/ 1 mm.	256-257°/ 15 mm.
p-hydroxy triphenyl iso-propyl methane	198-199°/ 1 mm.	*245-255°/ 16 mm.
p-hydroxy triphenyl n-butyl methane	182-183°/ 1 mm.	237-238°/ 13 mm.
p-hydroxy triphenyl iso-butyl methane	196-197°/ 1 mm.	261-262°/ 15 mm.
p-hydroxy triphenyl sec-butyl methane	195-196°/ 1 mm.	
#p-hydroxy triphenyl tert-butyl methane	205-206°/ 1 mm.	
2,2 diphenyl 3 methyl 3 (p-hydroxy phenyl) butane	195-200°/ 1 mm.	
p-hydroxy triphenyl n-amyl methane	183-184°/ 1 mm.	256-257°/ 15 mm.

* The distillation of p-hydroxy triphenyl iso-propyl methane at 16 mm. resulted in noticeable decomposition.

The p-hydroxy triphenyl tert-butyl methane was prepared from diphenyl tert-butyl chloro methane and p-anisyl magnesium bromide.

M.P.	Molecular Formula	Calculated		Determined	
		C	H	C	H
113-3.5°	C ₂₁ H ₂₂ O	87.46%	6.99%	87.21%	7.22%
<hr/>					
*	C ₂₂ H ₂₂ O	87.37%	7.33%	87.30%	7.40%
<hr/>					
	C ₂₂ H ₂₂ O	87.37%	7.33%	87.25%	7.32%
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*	C ₂₃ H ₂₄ O	87.30%	7.64%	87.30%	7.75%
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	C ₂₃ H ₂₄ O	87.30%	7.64%	87.15%	7.75%
<hr/>					
	C ₂₃ H ₂₄ O	87.30%	7.64%	87.18%	7.62%
<hr/>					
	C ₂₃ H ₂₄ O	87.30%	7.64%	87.38%	7.36%
<hr/>					
	C ₂₃ H ₂₄ O	87.30%	7.64%	87.55%	7.84%
<hr/>					
*	C ₂₄ H ₂₆ O	87.22%	7.90%	87.20%	7.98%

* These compounds were crystallized but, due to their great viscosities and low melting points, they failed to lose their crystalline form when heated above their melting points.

(3) preparation of Derivatives

The preparation of solid derivatives of the p-hydroxy triphenyl alkyl methanes and of 2,2 diphenyl 3 (p-hydroxy phenyl) 3 methyl butane was exceedingly difficult and not very successful. The derivatives attempted were: phenyl urethanes, alpha naphthyl urethanes, diphenyl urethanes, aryloxy acetic acids, p-nitro benzyl ethers, bromo derivatives, nitro derivatives, and the benzene sulfonyl, p-bromo benzene sulfonyl, benzoyl, p-anisoyl, 3,5 dinitro benzoyl, p-chloro benzoyl, and p-bromo benzoyl esters. The derivatives that were successfully prepared are described, in tabular form, on pages 18 and 19.

Derivatives of the p-Hydroxy Triphenyl Alkyl Meth-
Butane

Parent Compound	Derivative	M.P.
p-hydroxy triphenyl ethyl methane	benzoyl ester	106-6.5°
p-hydroxy triphenyl ethyl methane	p-bromo benzene sulfonyl ester	*121° (needles) *129° (cubes)
p-hydroxy triphenyl n-propyl methane	3,5 dinitro benzoyl ester	133-4°
p-hydroxy triphenyl n-butyl methane	p-chloro benzoyl ester	158-9°
2,2 diphenyl 3 (p-hydroxy phenyl) 3 methyl butane	p-chloro benzoyl ester	183-4°
p-hydroxy triphenyl tert-butyl methane	p-chloro benzoyl ester	169-70°

* The derivative crystallized in two crystalline forms.

The analyses of halogen were carried out by the Parr bomb method. The analysis of nitrogen was by the micro Dumas method.

anes and 2,2 Diphenyl 3 (p-Hydroxy Phenyl) 3 Methyl

Molecular Formula	Analyses	
	Calculated	Determined
$C_{28}H_{24}O_2$	C-85.67% H-6.16%	C-85.55% H-6.29%
$C_{27}H_{23}O_3SBr$	Br-15.75%	Br-15.61%
$C_{29}H_{24}O_6N_2$	N-5.64%	N-5.80%
$C_{30}H_{27}O_2Cl$	Cl-7.79%	Cl-7.75%
$C_{30}H_{27}O_2Cl$	Cl-7.79%	Cl-7.90%
$C_{30}H_{27}O_2Cl$	Cl-7.79%	Cl-7.62%

(4) Identification of Compounds and Proofs of Structure

The compounds, other than the condensation products, which were isolated from the condensations of the diphenyl alkyl carbinols with phenol, were identified as follows:

1,1 Diphenyl 1-propene was identified by its melting point.

1,1 Diphenyl 1-butene, 1,1 diphenyl 2 methyl 1-propene, 1,1 diphenyl 1-pentene, 1,1 diphenyl 3 methyl 1-butene, 1,1 diphenyl 2 methyl 1-butene, and 1,1 diphenyl 1-hexene were identified by their physical constants (boiling points, densities, and indices of refraction).

2,2 Diphenyl 3 methyl 3-butene was identified by converting it to 2,2 diphenyl 3 chloro 3 methyl butane by the method of Bateman and Marvel (36). 2,2 Diphenyl 3 chloro 3 methyl butane was identified by its melting point, 108-9°(34).

Diphenyl iso-propyl carbinol was identified by its melting point.

Diphenyl sec-butyl carbinol was identified by its physical constants.

p-Benzyl phenol was identified by its melting point and by its mixed melting point with a sample of p-benzyl phenol prepared from benzyl chloride, phenol, and aluminum chloride.

Iso-propyl benzene and sec-butyl benzene were iden-

tified by the melting points of their p-acetamino derivatives (106° and 126°), prepared by the method of Ipatieff and Schmerling (38).

The proof of structure of the condensation product of diphenyl methyl carbinol and phenol was accomplished by Welsh and Drake (6) by allowing the chloride of the carbinol to react with p-anisyl magnesium bromide and by subsequent conversion of the methoxyl group to a hydroxyl. The compound, p-hydroxy triphenyl methyl methane, was also prepared by Julian and Gist (39) from fuchsone (diphenyl methylene quinone) and methyl magnesium iodide and they prepared the corresponding methoxy compound from p-anisyl diphenyl chloro methane and methyl magnesium iodide.

The method of Welsh and Drake was not thought to be generally desirable, except for the synthesis of p-hydroxy triphenyl tert-butyl methane, for the following reasons: The chlorides of the diphenyl primary-alkyl and diphenyl secondary-alkyl carbinols are difficult to prepare. They eliminate HCl at room temperature to form the diphenyl alkenes. The point of attachment of the chlorine atom is not proved. Their use involves the assumption that the OH of the carbinol is replaced directly by Cl or, in case the reaction takes place by preliminary dehydration and addition of HCl to the resulting double bond, the assumption that the chlorine atom is

directed to the position previously held by the hydroxyl group. This latter assumption is supported by Markownikoff's rule for the chlorides of the diphenyl primary-alkyl carbinols but not for the chlorides of the diphenyl secondary-alkyl carbinols. The chloride of diphenyl tert-butyl carbinol is readily prepared, stable, and its structure has been established by Ramart-Lucas (34).

The synthesis of the p-hydroxy triphenyl alkyl methanes from p-anisyl diphenyl methyl halides and alkyl magnesium halides (one of the methods of Julian and Gist) was tried without success. The reactions of p-anisyl diphenyl chloro methane with ethyl magnesium bromide and of p-anisyl diphenyl bromo methane with sec-butyl magnesium bromide both gave p-anisyl diphenyl methane instead of the desired products, p-anisyl diphenyl ethyl methane and p-anisyl diphenyl sec-butyl methane. Apparently this method is successful only when the Grignard reagent used is incapable of exhibiting any reducing action. Two attempts to prepare fuchsone by the method of Bistrzycki and Herbst (41) were unsuccessful.

The structure of the condensation product of diphenyl n-butyl carbinol and phenol was proved by the following method:

p-Anisyl diphenyl carbinol was prepared from

p-anisyl magnesium bromide and benzophenone and from p-anisoyl chloride and phenyl magnesium bromide. It was condensed with malonic acid (and the product decarboxylated) by the method of Fosse (42) to give 3,3,3 p-anisyl diphenyl propanoic acid. The acid chloride was prepared with the use of thionyl chloride and allowed to react with ethyl magnesium bromide. The resulting ketone, 1,1,1 p-anisyl diphenyl 3-pentanone, was reduced by the Clemmensen method (40) and the methoxyl group changed to hydroxyl by the procedure of Welsh and Drake (6). The p-chloro benzoyl esters of the condensation product and the synthesized product melted at 158-9 , mixed melting point 158-9 .

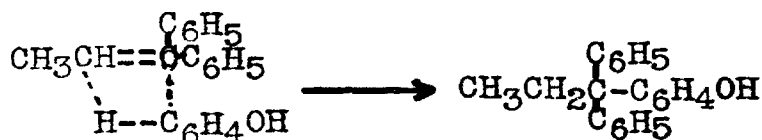
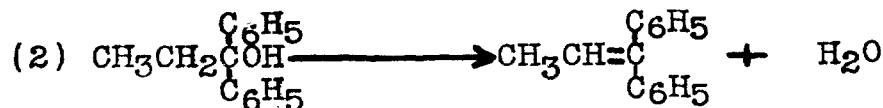
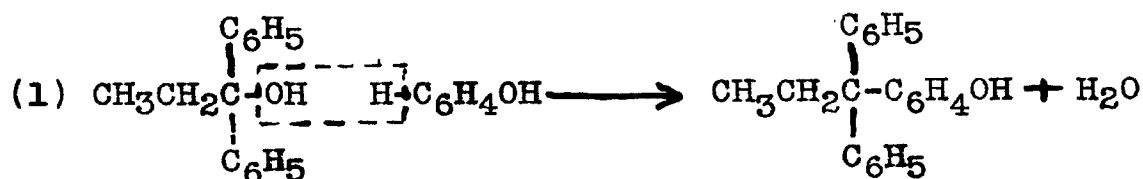
In an attempt to establish the structure of the condensation product of diphenyl iso-propyl carbinol and phenol, diphenyl iso-propyl chloro methane, prepared from the carbinol and dry HCl gas, was allowed to react with p-anisyl magnesium bromide. The product was converted to p-hydroxy triphenyl iso-propyl methane (or 1,1 diphenyl 2 (p-hydroxy phenyl) 2 methyl propane) by refluxing with conc. HBr and phenol. No solid derivatives of this product or of the condensation product could be prepared.

p-Hydroxy triphenyl tert-butyl methane, the expected condensation product of diphenyl tert-butyl carbinol and phenol, was synthesized from p-anisyl magnesium

bromide and diphenyl tert-butyl chloro methane (34), with subsequent demethylation by the usual procedure. The condensation product was compared with it and found to be different. The condensation product was found to be identical, by mixed melting points of the p-chloro benzoyl esters, with the product obtained from the condensation of 2,2 diphenyl 3 methyl 3-butene with phenol. It was therefore assumed to be 2,2 diphenyl 3 (p-hydroxy phenyl) 3 methyl butane. To establish its structure more definitely, attempts were made to condense 2,2 diphenyl 3 chloro 3 methyl butane (36) with phenol in the presence of aluminum chloride, with sodium phenolate in toluene solvent, and with p-anisyl magnesium bromide. All three attempts were unsuccessful.

(5) Interpretation of Results

In the condensation of tert-alcohols with phenol in the presence of aluminum chloride, two of the mechanisms advanced have been, (1) direct elimination of water from the OH of the carbinol and the para H of the phenol, and (2) dehydration of the carbinol followed by addition of phenol to the resulting ethylenic double bond.



The 'direct' condensations of the diphenyl primary-alkyl and diphenyl secondary-alkyl carbinols with phenol would be expected to give the same products as would the condensations of the carbinol's dehydration products. Thus, the fact, that the carbinols and the corresponding diphenyl alkenes both condense with phenol to give identical products, demonstrates only that the second mechanism is a definite possibility.

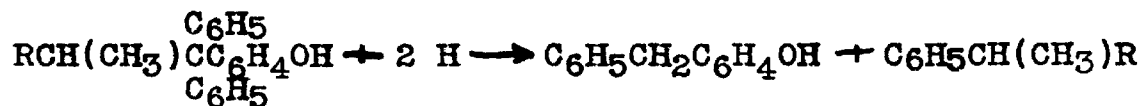
In one condensation of diphenyl ethyl carbinol with phenol, in which less than the theoretical amount of aluminum chloride (The theoretical amount is assum-

ed to be one mole of aluminum chloride to three moles of the carbinol.) was added to the solution of the carbinol and phenol in petroleum ether, a small yield (19%) of p-hydroxy triphenyl ethyl methane was obtained. If complete dehydration of the carbinol were necessary before any condensation could take place, no condensation product would have been formed. This evidence, though far from being conclusive, favors the first mechanism.

In the condensation of diphenyl tert-butyl carbinol with phenol, 'direct' condensation would be expected to give p-hydroxy triphenyl tert-butyl methane. Condensation by the second mechanism, as well as condensation of the dehydration product (2,2 diphenyl 3 methyl 3-butene) with phenol, would be expected to give 2,2 diphenyl 3 (p-hydroxy phenyl) 3 methyl butane. The products obtained from the condensation of the carbinol and of its dehydration product were proved to be identical. Therefore, at least in the case of diphenyl tert-butyl carbinol, the condensation takes place by the second mechanism. The failure of 2,2 diphenyl 3 chloro 3 methyl butane to condense with phenol eliminates the chloride as a possible intermediate.

The formation of p-benzyl phenol and iso-propyl benzene and p-benzyl phenol and sec-butyl benzene respectively from the condensations of diphenyl isopropyl carbinol and diphenyl sec-butyl carbinol with

phenol was first thought to result from the breakdown (with hydrogenation) of the condensation products under the influence of aluminum chloride.



The isolation of p-benzyl phenol from the products formed when p-hydroxy triphenyl iso-propyl methane is distilled, with decomposition, at 15 mm. pressure, supported this idea. However, when p-hydroxy triphenyl iso-propyl methane was dissolved in ligroin and treated with aluminum chloride, no p-benzyl phenol or iso-propyl benzene could be isolated. The products isolated, in addition to undecomposed p-hydroxy triphenyl iso-propyl methane and higher boiling materials, were phenol and 1,1 diphenyl 2 methyl 1-propene. Thus, it appears that p-benzyl phenol and the sec-alkyl benzene are formed during the process of condensation and not by decomposition of the condensation product. The hydrogen donor was not determined.

Condensations with Phenol

Carbinol	grams moles		Phenol	
	grams	moles	grams	moles
diphenyl ethyl carbinol	106	1/2	94	1
diphenyl ethyl carbinol	106	1/2	94	1
diphenyl ethyl carbinol	53	1/4	47	1/2
diphenyl ethyl carbinol	53	1/4	24	1/4
diphenyl n-propyl carbinol	45	1/5	40	
diphenyl iso-propyl carbinol	113	1/2	73	3/4
diphenyl iso-propyl carbinol	113	1/2	73	3/4
diphenyl n-butyl carbinol	120	1/2	73	3/4
diphenyl iso-butyl carbinol	120	1/2	73	3/4
diphenyl sec-butyl carbinol	120	1/2	73	3/4
diphenyl tert-butyl carbinol	120	1/2	73	3/4
diphenyl tert-butyl carbinol	60	1/4	37	3/8
diphenyl n-amyl carbinol	127	1/2	73	3/4

AlCl ₃		Condensation	Product	p-Benzyl	Alkyl
grams	moles	grams	% yield	Phenol	Benzene
35	1/4	57	40		
35	1/4	126	87		
10	1/14	14	19		
35	1/4	10	14		
15		26	46		
35	1/4	14	19	15 g.	10 g.
35	1/4	110	73	15 g.	10 g.
35	1/4	48	30		
35	1/4	63	40		
35	1/4	21	13	33 g.	10 g.
35	1/4	no condensation			
18	1/8	4	6		
35	1/4	46	30		

Condensations with Phenol				Phenol	
Compound		grams	moles	grams	moles
1,1 diphenyl 1-propene	64	1/3	40		
1,1 diphenyl 1-butene	90		47	1/2	
1,1 diphenyl 2 methyl 1-propene	105	1/2	47	1/2	
1,1 diphenyl 2 methyl 1-propene	85	2/5	55		
1,1 diphenyl 1-pentene	75	1/3	35	1/3	
1,1 diphenyl 3 methyl 1-butene	75	1/3	35	1/3	
1,1 diphenyl 3 methyl 1-butene	55	1/4	35	1/3	
2,2 diphenyl 3 methyl 3-butene	40	1/6	35	1/3	
1,1 diphenyl 1-hexene	80	1/3	35	1/3	
2,2 diphenyl 3 chloro 3 methyl butane	65	1/4	47	1/2	

AlCl ₃		Condensation	Product	p-Benzyl	Alkyl
grams	moles	grams	% yield	Phenol	Benzene
5		54	56		
20		50	42		
5		17	11	----	----
20		57	47	3 g.	5 g.
25	1/6	40	36		
5		15	14		
15		14	18		
25	1/6	8	15		
5		5	4		
25	1/6	no condensation			

IV Experimental

Preparation of the Diphenyl Alkyl Carbinols

In a dry 3 L. 3 neck round bottom flask, fitted with separatory funnel and CaCl_2 tube, reflux condenser and CaCl_2 tube, and mechanical stirrer with glycerol seal, place 60 g. magnesium, a few crystals of iodine, and 10 g. bromo benzene dissolved in 100 cc. anhydrous ether. Heat the mixture on the water bath until the reaction begins. Remove the water bath and then add, with stirring, a solution of 377 g. bromo benzene in 1 L. anhydrous ether at such a rate that the mixture refluxes gently. Continue stirring for one hour after addition is complete.

To the Grignard reagent, add dropwise, with cooling and stirring, one mole of acid chloride or ethyl ester (or two moles of phenyl alkyl ketone) dissolved in 500 cc. anhydrous ether.

Decompose the mixture with ice and add sufficient conc. HCl to barely dissolve the basic magnesium salts that are formed. Separate, and extract the aqueous layer twice with 300 cc. portions of ether. Dry the combined ether solutions with a mixture of anhydrous Na_2SO_4 and anhydrous Na_2CO_3 . After removal of the ether (steam bath), the remaining liquid is cooled and allowed to crystallize or is fractionally distilled at 2-3 mm. pressure. The yield is 65-90% of the theoretical, based

on the acid chloride, ester, or ketone.

Condensation of the Diphenyl Alkyl Carbinols (and
Diphenyl Alkenes) with Phenol

In a 1 L. 3 neck round bottom flask, fitted with mechanical stirrer and glycerol seal, and CaCl_2 tube, place 70 g. phenol, 1/2 moles diphenyl alkyl carbinol (or diphenyl alkene), and 100 cc. petroleum ether. To the mixture, with stirring, add 35 g. anhydrous aluminum chloride in small portions over a period of two hours. Continue stirring for 4-6 hours and allow the mixture to stand for 3-4 days.

Decompose the mixture with ice and HCl , separate the petroleum ether layer, and extract the aqueous layer twice with 50 cc. portions of diethyl ether. Combine the ether solutions and remove the ether (steam bath). To the residue add 500 cc. alcoholic KOH (1 g. KOH / 5 g. H_2O / 4 g. methyl alcohol) and extract the mixture twice with 100 cc. portions of petroleum ether. The petroleum ether extracts are combined, dried with anhydrous Na_2SO_4 , the ether removed (steam bath), and the residue subjected to fractional distillation. The alcoholic KOH layer is acidified with 1-1 HCl and twice extracted with 100 cc. portions of diethyl ether, the ether removed (steam bath), and the residue fractionally distilled. The condensation product, which occurs

in this fraction, boils in the neighborhood of 190 to 230°/ 3 mm. pressure.

Condensation of Diphenyl tert-Butyl Carbinol with Phenol

In a 500 cc. 3 neck round bottom flask, fitted with mechanical stirrer and glycerol seal, CaCl₂ tube, and separatory funnel, place 20 g. anhydrous aluminum chloride and 100 cc. petroleum ether. Add dropwise, with stirring, a solution of 60 g. diphenyl tert-butyl carbinol and 37 g. phenol in 100 cc. petroleum ether, over a period of one hour. Continue stirring for 4-6 hours and allow the mixture to stand 3-4 days. The remaining procedure is identical with the preceding one.

Synthesis of p-Hydroxy Triphenyl n-Butyl Methane

In a 1 L. 3 neck round bottom flask, fitted with mechanical stirrer and glycerol seal and condenser set for downward distillation, place 290 g. malonic acid and 115 g. p-anisyl diphenyl carbinol. Heat on an oil bath, with stirring, at 120-30° for six hours and then raise the oil bath temperature to 170-80° for an additional hour. Discard the distillate, which consists of water and acetic acid, cool the remaining liquid, and add 300 cc. 20% alcoholic KOH and reflux for two hours. Cool the mixture, dilute it with an equal volume of water, and extract it with 100 cc. ether. The ether

layer, which contains p-anisyl diphenyl carbinol, is discarded. To the alcoholic KOH layer, add sufficient conc. HCl to make the solution acid to Congo Red paper, cool, and extract the solution twice with 100 cc. portions of ether. Combine the extracts and dry with anhydrous Na_2SO_4 . Distill off the ether (steam bath) and remove the last traces of ether and malonic acid by heating on an oil bath at 180° under reduced pressure. The yield of crude 3,3,3 p-anisyl diphenyl propanoic acid is 85 g.

To the crude acid, add 50 g. thionyl chloride and reflux the mixture for three hours. Remove the excess thionyl chloride by distillation. The last traces of it are removed by heating on an oil bath at 180° under reduced pressure. Crude 3,3,3 p-anisyl diphenyl propanoyl chloride is a dark red, glassy, non-crystalline solid.

In a 250 cc. erlenmeyer flask fitted with reflux condenser and CaCl_2 tube, place 1.5 g. magnesium and a few small crystals of iodine. Add 50 cc. anhydrous ether and 1 cc. ethyl bromide and warm the flask (water bath) until the reaction begins. Add, in small portions, 6 g. ethyl bromide dissolved in 75 cc. anhydrous ether, allowing the reaction to subside after each addition.

In a 500 cc. erlenmeyer flask fitted with a reflux condenser, place 20 g. 3,3,3 p-anisyl diphenyl propanoyl chloride dissolved in 200 cc. anhydrous ether. In

the top of the condenser, place a 250 cc. separatory funnel held in place by a notched cork. Through the separatory funnel, add dropwise, with cooling and agitation, the solution of ethyl magnesium bromide. Decompose the mixture with ice and HCl and extract it with 400 cc. ether. Wash the ether layer with 10% Na₂CO₃ solution and remove the ether (steam bath). The residue is crude 1,1,1 p-anisyl diphenyl 3-pentanone, yield, 18 g.

The 1,1,1 p-anisyl diphenyl 3-pentanone is reduced to p-anisyl diphenyl n-butyl methane by the Clemmensen method (40) and the latter is converted to p-hydroxy triphenyl n-butyl methane by the method of Welsh and Drake (6).

Synthesis of p-Hydroxy Triphenyl iso-Propyl Methane and p-Hydroxy Triphenyl tert-Butyl Methane

In a dry 1 L. 3 neck round bottom flask fitted with reflux condenser and CaCl₂ tube, mechanical stirrer and glycerol seal, and separatory funnel, place 6 g. magnesium and a few crystals of iodine. Add a solution of 2 g. p-bromo anisole in 50 cc. anhydrous ether and warm (water bath), with stirring until the reaction begins. Add dropwise, with stirring, a solution of 48 g. p-bromo anisole in 100 cc. anhydrous ether at such a rate that the mixture refluxes gently. After addition is complete, continue stirring for 2-3 hours.

To the p-anisyl magnesium bromide thus prepared, add slowly 30.5 g. diphenyl iso-propyl chloro methane (or 32 g. diphenyl tert-butyl chloro methane) dissolved in 100 cc. anhydrous ether. The flask is then transferred to the steam bath, the ether removed, and the residue heated at 90-100° for 6-8 hours. The residue is decomposed with ice and HCl and extracted with ether. The ether is removed (steam bath) and the residue is distilled under reduced pressure. The fraction boiling at 180-220°/ 3 mm. is crude p-anisyl diphenyl iso-propyl methane (or p-anisyl diphenyl tert-butyl methane). The p-anisyl diphenyl iso-propyl methane and p- anisyl diphenyl tert-butyl methane are converted to p-hydroxy triphenyl iso-propyl methane and p-hydroxy triphenyl tert-butyl methane by the method of Welsh and Drake (6).

Diphenyl iso-propyl chloro methane was prepared from diphenyl iso-propyl carbinol and dry HCl:

In a 100 cc. separatory funnel, place 28 g. diphenyl iso-propyl carbinol dissolved in 25 cc. benzene, and 10 g. CaCl_2 . Surround the separatory funnel with ice-water and bubble dry HCl gas through the solution of the carbinol, at the rate of 4-5 bubbles a second, for one hour. Immediately transfer the separatory funnel to the flask containing the p-anisyl magnesium bromide and add the solution of diphenyl iso-propyl chloro methane to the Grignard reagent. (Diphenyl iso-propyl chloro meth-

ane is very difficult to prepare because it spontaneously gives off HCl, at room temperature, to form 1,1 diphenyl 2 methyl 1-propene. Its preparation was attempted unsuccessfully five times before it was finally obtained.

Diphenyl tert-butyl chloro methane was prepared from diphenyl tert-butyl carbinol and thionyl chloride. The excess of thionyl chloride was removed by heating at 60 under reduced pressure.

Preparation of the p-Chloro Benzoyl Esters

In a 6 in. pyrex test tube, place 1.5 g. of the phenol and 1 g. of p-chloro benzoyl chloride. Heat the mixture gently with a very small flame until HCl fumes cease to be evolved. Reflux the mixture very gently for an additional five minutes, cool, and add 5 g. solid Na_2CO_3 and 20 cc. water and heat the mixture (steam bath) for 4-5 hours to hydrolyse the excess acid chloride. Cool the tube, place its contents in a 250 cc. separatory funnel, and dissolve the ester with 100 cc. ether. Wash the ether solution with 10% Na_2CO_3 solution, dry with anhydrous Na_2SO_4 , and evaporate the ether solution to dryness. Recrystallize the ester from ligroin.

V Summary

(1) Five of the diphenyl primary-alkyl carbinols have been condensed with phenol to give the expected p-hydroxy triphenyl primary alkyl methanes.

(2) Two of the diphenyl secondary alkyl carbinols have been condensed with phenol to give the p-hydroxy triphenyl secondary-alkyl methanes, p-benzyl phenol, and secondary alkyl benzenes.

(3) Diphenyl tert-butyl carbinol has been condensed with phenol to give 2,2 diphenyl 3 (p-hydroxy phenyl) 3 methyl butane.

(4) p-Hydroxy triphenyl tert-butyl methane has been synthesized.

(5) The structure of one of the p-hydroxy triphenyl primary alkyl methanes has been established by synthesis.

(6) A new alcohol, diphenyl sec-butyl carbinol, has been prepared, its structure established, and some of its physical constants determined.

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