hydroxyls in retronecine or platynecine, structures have been deduced for retronecine, desoxyretronecine, platynecine and anhydroplatynecine, which agree with all the available experimental facts.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Condensation of Some of the Diphenyl Alkyl Carbinols with Phenol in the Presence of Aluminum Chloride

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Previous papers from this Laboratory[2] have described the condensation of benzyl alcohol and some of the phenylalkylcarbinols with phenol in the presence of aluminum chloride. Welsh and Drake[3] have reported the condensation of diphenylmethylcarbinol with phenol. To extend the scope of these investigations, the following diphenylalkylcarbinols, *viz.*: diphenylethylcarbinol,[4] diphenyl-*n*-propylcarbinol,[5] diphenyl-*iso*-butylcarbinol,[4] diphenyl-*s*-butylcarbinol, diphenyl-*t*-butylcarbinol,[6] and diphenyl-*n*-amylcarbinol[5] were prepared from phenylmagnesium bromide and the chlorides of *n*-butyric, isobutyric, *n*-valeric, isovaleric, methylethylacetic, trimethylacetic and caproic acids by the procedure of Gilman, Fothergill and Parker[7] and from the ethyl esters of propionic, *n*-butyric, isobutyric and caproic acids by the procedure of Sabatier and Murat.[4]

Diphenyl-*s*-butylcarbinol was prepared as follows: sixty grams of magnesium, a few crystals of iodine, and 10 g. of bromobenzene dissolved in 100 cc. of anhydrous ether, were placed in a three-liter three-necked round-bottom flask, fitted with separatory funnel with calcium chloride tube, reflux condenser with calcium chloride tube, and mechanical stirrer with glycerol seal. The mixture was heated on a water-bath until the reaction began. The water-bath was removed and a solution of 375 g. of bromobenzene in one liter of anhydrous ether was added, with stirring, at such a rate that the mixture refluxed gently. Stirring was continued for one hour after the addition was complete. One hundred twenty-one grams of methylethylacetyl chloride, dissolved in 500 cc. of anhydrous ether, was added dropwise, with cooling and stirring, to the Grignard reagent. The mixture was decomposed with ice and there was added a sufficient amount of concentrated hydrochloric acid to barely dissolve the basic magnesium salts that formed. After separation, the aqueous layer was extracted twice with 300-cc. portions of ether. The combined ether solutions were dried with anhydrous sodium sulfate and anhydrous sodium carbonate. After removal of the ether on the steam-bath, the remaining liquid was subjected to fractional distillation at 2–3 mm. pressure. The yield of diphenyl-*s*-butylcarbinol was 70% of the theoretical, based on the acid chloride. Its structure was established by dehydration and oxidation of the resulting unsaturated hydrocarbon with chromic acid. Benzophenone and methyl ethyl ketone were isolated, the latter being identified as its semicarbazone, m. p. 143°[8]; physical constants: b. p. 126–127° (1 mm.), 185–186° (15 mm.); sp. gr.$^{25}_{25}$ 1.0445, n^{25}D 1.5664.

Condensation of the alcohols with phenol was effected, using the following general procedure: seventy grams of phenol, one-half mole of diphenylalkylcarbinol and 100 cc. of petroleum ether were placed in a one-liter three-necked round-bottom flask fitted with mechanical stirrer, glycerol seal, and calcium chloride tube. To the mixture was added, with stirring, 35 grams of anhydrous aluminum chloride in small portions over a period of two hours. Stirring was continued for from four to six hours and the mixture was allowed to stand three to four days. After decomposing with ice and hydrochloric acid, the petroleum ether layer was separated and the aqueous layer was extracted twice with 500 cc. portions of diethyl ether. The ether solutions were combined and the ether removed on the steam-bath. The residue was treated with 500 cc. of alcoholic potassium hydroxide (100 g. potassium hydroxide, 500 g. water, 400 g. methyl alcohol) and extracted twice with 100-cc. portions of petroleum ether. The petroleum ether extracts were combined and dried with anhydrous sodium sulfate. The alcoholic potassium hydroxide layer was acidified with 1:1 hydrochloric acid, cooled, and twice extracted with 100-cc. portions of diethyl ether, the ether removed, and the residue fractionally distilled. The condensation product in this fraction boiled in the neighborhood of 190–230° (3 mm.).

In the condensation of diphenyl-*t*-butylcarbinol with the phenol, this procedure was modified by adding a solution of the carbinol and phenol in petroleum ether to the anhydrous aluminum chloride suspended in petroleum ether.

In addition to the expected *p*-hydroxyphenyl-*s*-alkylmethane, diphenyl-*s*-propylcarbinol and di-

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(1) Abstract from thesis presented in partial fulfillment of requirements for Ph.D. degree.

(2) (a) Huston, THIS JOURNAL, **46**, 2775 (1924); (b) Huston, Lewis and Grotemut, *ibid.*, **49**, 1365 (1927).

(3) Welsh and Drake, *ibid.*, **60**, 58 (1938).

(4) Sabatier and Murat, *Ann. chim. phys.*, [9] **4**, 296 (1915).

(5) Schlenk and Bergman, *Ann.*, **479**, 42 (1930).

(6) Ramart-Lucas, *Ann. chim. phys.*, [8] **30**, 349 (1913).

(7) Gilman, Fothergill and Parker, *Rec. trav. chim.*, **48**, 748 (1929).

(8) Veibel, *Bull. soc. chim.*, [4] **41**, 1410 (1927).

phenyl-*s*-butylcarbinol gave considerable amounts of *p*-benzylphenol.

The petroleum ether extracts of the alcoholic potassium hydroxide solutions were distilled. Those from the diphenyl-*n*-alkylcarbinols and diphenyl-*i*-butylcarbinols gave in each case the diphenylalkene; that from diphenyl-*s*-propylcarbinol gave 2-phenylpropane and 1,1-diphenyl-2-methyl-1-propene; that from diphenyl-*s*-butylcarbinol gave 2-phenylbutane and 1,1-diphenyl-2-methyl-1-butene and that from diphenyl-*t*-butylcarbinol gave mostly 2,2-diphenyl-3-methyl-3-butene with some 2,2-diphenyl-3-chloro-3-methylbutane. In all cases, a small amount of high boiling product was obtained. The identification of 2-phenylpropane and 2-phenylbutane was accomplished through the melting points of their *p*-acetamino derivatives.[9]

When 1-*p*-hydroxyphenyl-1,1-diphenyl-2-methylpropane was treated with aluminum chloride under the conditions of condensation it decomposed partially with the formation of 1,1-diphenyl-2-methyl-1-propene but neither 2-phenylpropane or *p*-benzylphenol was formed. It appears that these latter products were formed during the condensation rather than from the decomposition of 1-*p*-hydroxyphenyl-1,1 diphenylalkane under the influence of aluminum chloride.

The structure of 1-*p*-hydroxyphenyl-1,1-diphenylpentane was established by the following synthesis: *p*-anisyldiphenylcarbinol was prepared from *p*-anisoyl chloride and phenylmagnesium bromide and identified by converting it to the chloride, m. p. 122–123°.[10] A mixture of 100 g. of the carbinol and 290 g. of malonic acid was placed in a one-liter three-necked round-bottom flask, fitted with a mechanical stirrer with glycerol seal and condenser set for downward distillation. After heating on an oil-bath with stirring, for six hours at 120–130°, the temperature was raised to 170–180° for an additional hour. The distillate was discarded and the remaining liquid cooled. Three hundred cc. of 20% alcoholic potassium hydroxide was added and the mixture refluxed for two hours. After cooling, an equal volume of water was added before extraction with 100 cc. of ether. The ether layer, which contained *p*-anisyldiphenylcarbinol, was discarded. A sufficient amount of concd. hydrochloric acid was added to the alcoholic potassium hydroxide layer to make the solution acid to congo red paper. This was cooled and extracted twice with 100-cc. portions of ether. The extracts were combined and dried with anhydrous sodium sulfate. The ether and malonic acid were removed by heating on an oil-bath at 180° under reduced pressure. The yield of crude 3-*p*-anisyl-3,3-diphenylpropanoic acid was 85 g.[11] To the crude acid, 50 g. of thionyl chloride was added and the mixture refluxed for three hours. The excess thionyl chloride was removed by distillation under reduced pressure.

One and one-half grams of magnesium and a few crystals of iodine were placed in a 250 cc. Erlenmeyer flask fitted with reflux condenser and calcium chloride tube. Anhydrous ether and 1 cc. ethyl bromide were added and the flask warmed until the reaction began. Six grams of ethyl bromide dissolved in 75 cc. anhydrous ether was then added in small portions, allowing the reaction to subside after each addition. A solution of 20 g. of 3-*p*-anisyl-3,3-diphenylpropanoyl chloride in 200 cc. of anhydrous ether was placed in a 500-cc. Erlenmeyer flask fitted with a reflux condenser. By means of a separatory funnel, held in the top of the condenser by a notched cork, the solution of ethylmagnesium bromide was added dropwise with agitation and cooling. After decomposition with ice and hydrochloric acid, the mixture was extracted with 400 cc. of ether. The ether layer was washed with 10% sodium carbonate solution and the ether removed by distillation, leaving a residue of 1-*p*-anisyl-1,1-diphenyl-3-pentanone, yield 18 g. The ketone was reduced to 1-*p*-anisyl-1,1-diphenylpentane by the Clemmensen method[12] and this was demethylated by the method of Welsh and Drake.[3] The phenol was proved to be identical with 1-*p*-hydroxyphenyl-1,1-diphenylpentane obtained from the condensation of diphenyl-*n*-butylcarbinol with phenol by the mixed melting points of the *p*-chlorobenzoyl esters.

The Synthesis of 1-*p*-Hydroxyphenyl-1,1-diphenyl-2,2-dimethylpropane.—A solution of 2 g. of *p*-bromoanisole in 50 cc. of anhydrous ether was added to 6 g. of magnesium and a few crystals of iodine and the mixture warmed with stirring until the reaction began. A solution of 48 g. of *p*-bromoanisole in 100 cc. of anhydrous ether was added dropwise with stirring at such a rate that the mixture refluxed gently. After addition was complete, stirring was continued for two to three hours. To the *p*-anisylmagnesium bromide thus prepared was added slowly 32 g. 1,1-diphenyl-1-chloro-2,2-dimethylpropane[6] dissolved in 100 cc. of anhydrous ether. The flask was then transferred to the steam-bath, the ether removed and the residue heated at 90–100° for six to eight hours. The residue was decomposed with ice and hydrochloric acid and extracted with ether. The ether was removed and the residue distilled under reduced pressure. The fraction boiling at 180–210° (3 mm.) was crude 1-*p*-anisyl-1,1-diphenyl-2,2-dimethylpropane. It was converted into 1-*p*-hydroxyphenyl-1,1-diphenyl-2,2-dimethylpropane by the method of Welsh and Drake.[3]

The product from the condensation of diphenyl-*t*-butylcarbinol with phenol was compared with the above synthetic product and found to be different. The condensation product was found to be identical, by the mixed melting point of the *p*-chlorobenzoyl derivatives, with the product obtained from the condensation of the dehydration product of the alcohol[13] (2,2-diphenyl-3-methyl-3-butene) with phenol. This, according

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(9) Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

(10) Bent, Dorfmann and Bruce, *ibid.*, **54**, 3250 (1932).

(11) Fosse, *Bull. soc. chim.*, [4] **49**, 159 (1931).

(12) Clemmensen, *Ber.*, **47**, 51 (1914).

(13) Bateman and Marvel, THIS JOURNAL, **49**, 2914 (1927).

TABLE I

CONDENSATION OF DIPHENYL ALKYL CARBINOLS WITH PHENOL

Product	Yield, %	B. p., °C. 1 mm.	B. p., °C. 15 mm.	Mol. formula	Calcd. % C	Calcd. % H	Found % C	Found % H
1-p-Hydroxyphenyl-1,1-diphenylpropane	87[d]	198–199	259–260	$C_{21}H_{20}O$	87.46	6.99	87.21	7.22
1-p-Hydroxyphenyl-1,1-diphenylbutane	46[a]	196–197	256–257	$C_{22}H_{22}O$	87.37	7.33	87.30	7.40
1-p-Hydroxyphenyl-1,1-diphenyl-2-methylpropane	73	198–199	[b]245–255	$C_{22}H_{22}O$	87.37	7.33	87.25	7.32
1-p-Hydroxyphenyl-1,1-diphenylpentane	30[a]	182–183	237–238	$C_{23}H_{24}O$	87.30	7.64	87.30	7.75
1-p-Hydroxyphenyl-1,1-diphenyl-3-methylbutane	40	196–197	261–262	$C_{23}H_{24}O$	87.30	7.64	87.15	7.75
1-p-Hydroxyphenyl-1,1-diphenyl-2-methylbutane	13	195–196		$C_{23}H_{24}O$	87.30	7.64	87.18	7.62
1-p-Hydroxyphenyl-1,1-diphenyl-2,2-dimethylpropane	[c]	205–206		$C_{23}H_{24}O$	87.30	7.64	87.38	7.36
3-p-Hydroxyphenyl-2,2-diphenyl-3-methylbutane	6	195–200		$C_{23}H_{24}O$	87.30	7.64	87.55	7.84
1-p-Hydroxyphenyl-1,1-diphenylhexane	30[a]	183–184	256–257	$C_{24}H_{26}O$	87.22	7.90	87.20	7.98

[a] 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. [b] The distillation of 1-p-hydroxyphenyl-1,1-diphenyl-2-methylpropane at 15 mm. resulted in noticeable decomposition. [c] The 1-p-hydroxyphenyl-1,1-diphenyl-2,2-dimethylpropane was prepared from diphenyl t-butylchloromethane and p-anisylmagnesium bromide. [d] M. p. 113–113.5°.

TABLE II

ESTERS OF p-HYDROXY-TRI-PHENYL ALKYL METHANES

Parent compound	Ester	M. p., °C.	Formula	Analyses, %	Calcd.	Found
1-p-Hydroxyphenyl-1,1-diphenyl-	Benzoyl	106–106.5	$C_{28}H_{24}O$	C	85.67	85.55
-propane				H	6.16	6.29
-propane	p-Bromobenzenesulfonyl	121[a] 129[a]	$C_{27}H_{23}O_3SBr$	Br	15.75	15.61
-butane	3,5-Dinitro benzoyl	133–134	$C_{29}H_{24}O_6N_2$	N	5.64	5.80
-pentane	p-Chloro benzoyl	158–159	$C_{30}H_{27}O_2Cl$	Cl	7.79	7.75
-2,2-dimethylpropane	p-Chloro benzoyl	169–170	$C_{30}H_{27}O_2Cl$	Cl	7.79	7.62
3-p-Hydroxyphenyl-2,2-diphenyl-3-methylbutane	p-Chloro benzoyl	183–184	$C_{30}H_{27}O_2Cl$	Cl	7.79	7.90

[a] This derivative crystallized in two distinct forms.

to the Markownikoff rule, would be 3-p-hydroxyphenyl-2,2-diphenyl-3-methylbutane.

The unsaturated hydrocarbons (1,1-diphenyl-1-propene, 1,1-diphenyl-1-butene, 1,1-diphenyl-2-methyl-1-propene, 1,1-diphenyl-1-pentane, 1,1-diphenyl-3-methyl-1-butene, and 1,1-diphenyl-1-hexene) obtained by dehydration of the carbinols, were also condensed with phenol, using the same technique as in the condensation of the alcohols except that the half-mole of alcohol was replaced by a half-mole of the unsaturated hydrocarbon. Products identical to those from the corresponding carbinols were obtained.

The assignment of the para position to the substituted group of these phenols is based upon a study of the condensation of a large number of tertiary alcohols with phenol[14] and upon the synthesis of p-hydroxyphenyl-diphenyl-n-butylmethane.

Yields, properties and analyses of the phenols are summarized in Table I. Derivatives were prepared and analyzed (see Table II).

Summary

1. Five diphenyl-*primary*-alkyl carbinols have been condensed with phenol to give the expected 1-p-hydroxyphenyl-1,1-diphenyl alkanes.

2. Two diphenyl-s-alkyl carbinols have been condensed with phenol to give the 1-p-hydroxyphenyl-1,1-diphenyl-2-methyl alkanes, p-benzyl phenol, and s-alkyl benzenes.

3. Diphenyl-t-butyl carbinol has been condensed with phenol to give 3-p-hydroxyphenyl-2,2-diphenyl-3-methylbutane.

4. 1-p-Hydroxyphenyl-1,1-diphenyl pentane and 1-p-hydroxyphenyl-1,1-diphenyl-2,2-dimethylpropane have been synthesized.

5. A new alcohol, diphenyl-s-butyl carbinol, has been prepared, its structure established and some of its physical constants determined.

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[14] Huston and Hsieh, THIS JOURNAL, **58**, 439 (1936); Huston and Hedrick, *ibid.*, **59**, 2001 (1937); Huston and Guile, *ibid.*, **61**, 69 (1939); unpublished theses by L. Snyder and W. K. Langdon.