Anal. Calcd. for $C_{14}H_{14}O_4$: C, 69.42; H, 4.16. Found: C, 69.68; H, 4.18.

2,2′-Bi-(3-methyl-6,7-dimethoxy-1,4-naphthoquinone), (Desapogossypolone Tetramethyl Ether) (V).—A mixture of 27.5 g. of 2,3-dimethoxybutadiene and 2.75 g. of 6,6′-dimethyl-2,5,2′,5′-biphenyldiquinone was heated in a loosely stoppered flask on the steam-bath for twenty hours. The excess 2,3-dimethoxybutadiene was recovered by distillation at 30 mm. (bath temp. below 70°). The residue was a viscous gum from which no crystalline material could be obtained. It was dissolved in 40 cc. of xylene, 12 g. of chloranil added and the mixture refluxed for four hours. The black solution was diluted with 100 cc. of benzene and extracted with 100 cc. of 5% aqueous sodium hydroxide. The emulsion which formed was broken by filtration through an asbestos mat. The organic layer was extracted twice more with alkali and then washed with water. The solvent was evaporated from the orange solution and the last traces removed by a stream of air. The gummy residue thus obtained was digested with 30 cc. of warm methanol for fifteen minutes. The gum gradually changed to an orange powder. After cooling, it was filtered (3 g.). The product was purified by two crystallizations from methyl ethyl ketone followed by three from benzene–petroleum ether (b. p. 60–110°); orange prisms, m. p. 251–254° (cor.).

Desapogossypolone tetramethyl ether obtained by degradation of gossypol was reported as melting at 245–248° (uncor.); when corrected this is 251–254° (cor.). A mixture of synthetic and natural specimens gave no depression when melted.

Anal. Calcd. for $C_{26}H_{22}O_8$: C, 67.50; H, 4.76. Found: C, 67.79; H, 4.66.

2,2′-Bi-(1,4-diacetoxy-3-methyl-6,7-dimethoxynaphthyl) (IX).—A mixture of 0.095 g. of pure 2,2′-bi-(3-methyl-6,7-dimethoxy-1,4-naphthoquinone), 0.095 g. of freshly fused sodium acetate, a few tenths of a gram of zinc dust and 2 cc. of acetic anhydride was refluxed for fifteen minutes. The solution was filtered hot and the zinc washed with two 5-cc. portions of acetic acid. The filtrate and washings were poured into water. The product was purified by recrystallization from methanol; white crystals, m. p. 264–265° (uncor.) or 272–273° (cor.). This melting point is identical with that of the substance obtained by similar treatment of natural desapogossypolone tetramethyl ether and a mixed melting point showed no depression.

Anal. Calcd. for $C_{34}H_{34}O_{12}$: C, 64.35; H, 5.36. Found: C, 64.52; H, 5.56.

Summary

The compound 2,2′-bi-(3-methyl-6,7-dimethoxy-1,4-naphthoquinone) has been prepared by condensation of 2,3-dimethoxybutadiene with 6,6′-dimethyl-2,5,2′,5′-biphenyldiquinone and oxidation with chloranil of the intermediate adduct. It proved to be identical with desapogossypolone tetramethyl ether obtained from gossypol. The synthetic product on reductive acetylation gave a substance identical with that resulting from a similar treatment of desapogossypolone tetramethyl ether. This synthesis confirms the earlier postulation that gossypol is a binaphthyl derivative.

URBANA, ILLINOIS RECEIVED OCTOBER 14, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Structure of Monocrotaline. VI. The Structure of Retronecine, Platynecine and Retronecanol[1]

BY ROGER ADAMS AND E. F. ROGERS

It has been shown that the alkaloid monocrotaline, $C_{16}H_{23}O_6N$, on catalytic hydrogenation, gives retronecanol, $C_8H_{15}ON$, and monocrotalic acid, $C_8H_{12}O_5$. When saponified, the alkaloid, yields retronecine, $C_8H_{13}O_2N$, and the alkaline decomposition products of monocrotalic acid, carbon dioxide and α,β-dimethyllevulinic acid. The two reactions together indicate that monocrotaline is an ester of retronecine in which an hydroxyl group of the alkamine is covered by monocrotalic acid.

In the hydrogenation of monocrotaline, two moles of hydrogen are absorbed, hydrogenolysis occurs at the ester grouping and the double bond of retronecine is reduced with the formation of the saturated monohydroxy base, retronecanol. A hydrogenation of this type was first observed by Menshikov,[2] who found that the alkaloid heliotrine, $C_{16}H_{27}O_5N$, which could be saponified to heliotridine, $C_8H_{13}O_2N$ (probably a diastereoisomer of retronecine), and heliotrinic acid, $C_8H_{16}O_4$, gave as reduction products oxyheliotridane, $C_8H_{15}ON$, and heliotrinic acid. Barger[3] observed that retrorsine hydrogenates in a similar manner. He found, moreover, that diacetylretronecine reduces to acetylretronecanol and

(1) For previous papers see (a) Adams and Rogers, THIS JOURNAL, **61**, 2815 (1939); (b) Adams, Rogers and Sprules, *ibid.*, **61**, 2819 (1939); (c) Adams, Rogers and Long, *ibid.*, **61**, 2822 (1939); (d) Adams and Long, *ibid.*, **62**, 2289 (1940); (e) Adams and Rogers, *ibid.*, **63**, 228 (1941).

(2) Menshikov, *Ber.*, **68**, 1051 (1935).

(3) Barger, Seshadri, Watt and Yabata, *J. Chem. Soc.*, 11 (1935).

acetic acid and that retronecine can be reduced directly to retronecanol, if platinum oxide is used as a catalyst. It thus appears that retronecine and the isomeric base, heliotridine, contain a remarkably labile hydroxyl group since room temperature hydrogenolyses of carbon–oxygen linkages are not common.

For convenience, in this and succeeding papers from this Laboratory the hydroxyl groups of retronecine will be designated as α and β, the α to represent the stable hydroxyl present in retronecanol (or oxyheliotridane), the β to represent the labile hydroxyl which is lost by hydrogenation. In the alkaloid, monocrotaline, the β-hydroxyl is esterified, since monocrotalic acid is a hydrogenolysis cleavage product. In heliotrine, similarly, β-esterification exists. The alkaloid retrorsine is retronecine probably with the β-hydroxyl esterified with a dibasic acid. If the hydroxyl groups in retronecine or heliotridine are replaced by chlorine and the resulting dichlorides subjected to hydrogenation with the aid of platinum as a catalyst, a saturated monochloride results due to replacement of one chlorine by hydrogen and addition of two hydrogens to the double bond. Presumably the chlorine corresponding to the β-hydroxyl is more labile than the other. The ease of hydrogenolysis of β-substituents may be represented as OH < OCOR < Cl.

Both retronecine and heliotridine will yield upon esterification mono- and diesters.[4] In all cases, the β- or labile hydroxyl appears to be more readily esterified than the α- or stable hydroxyl.

The catalytic hydrogenation of monocrotaline and retronecine has now been studied under various conditions. From monocrotaline in the presence of either platinum oxide or Raney nickel if the reduction is stopped after one mole equivalent of hydrogen is absorbed, monocrotalic acid and a base, $C_8H_{13}ON$, are obtained. The name desoxyretronecine is suggested for the new base since, as the formula indicates, an hydroxyl group has been lost although the double bond is still present. The double bond in this case is readily reduced with formation of retronecanol.

If retronecine, instead of an ester of the base, is reduced under certain conditions using Raney nickel as catalyst, only one mole of hydrogen is absorbed with saturation of the double bond and formation of platynecine. The product agrees in all its properties with the base obtained by saponification of the alkaloid platyphylline. The identity in configuration of the hydroxyl groups in retronecine and platynecine, which has been suspected since Orekhov[5] found esters of both in *Senecio platyphyllus*, is thus confirmed. With the relationship of retronecine and platynecine proved, the observation is significant that the latter forms a mono- or dibenzoate depending on the conditions used in synthesis and that one hydroxyl esterifies much more readily than the other.[6] It is thus evident that the presence of the double bond in retronecine is not the primary cause for the difference of the reactivity of the two hydroxyls in that molecule; it must be due to some other factor which persists as well in the saturated molecule.

Platynecine is not reduced further by hydrogen and nickel or platinum even at 80°. Moreover, while monobenzoyl retronecine is hydrogenolyzed and reduced by nickel and hydrogen to give benzoic acid and retronecanol, neither in presence of nickel nor platinum is hydrogenolysis of monobenzoyl platynecine possible.

The reactions are summarized in Table I. They indicate that hydrogenation of the β-hydroxyl in retronecine is dependent, at least primarily, on the presence of the double bond.

TABLE I

REDUCTION OF VARIOUS BASES

Compound hydrogenated	Moles of hydrogen absorbed	Catalyst (room temp. unless otherwise specified)	Products
Monocrotaline	1	Pt	Desoxyretronecine and monocrotalic acid
Monocrotaline	2	Ni	Retronecanol and monocrotalic acid
Desoxyretronecine	1	Pt or Ni	Retronecanol
Retronecine	2	Pt	Retronecanol
Retronecine	1	Ni	Platynecine
Monobenzoyl retronecine	2	Pt	Retronecanol and benzoic acid
Platynecine	0	Ni Pt (25° and 80°)	
Monobenzoyl platynecine	0	Pt	

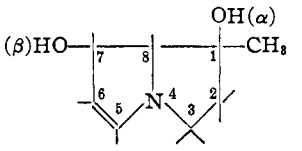
Accepting the basic nucleus of retronecine as 1-methyl pyrrolizidine,[1e,7] it is now possible to propose for retronecine structure I.

(4) Manske, *Can. J. Research*, **5**, 651 (1931); Menshikov, *Ber.*, **66**, 875 (1933).

(5) Orekhov and Tiedebel, *ibid.*, **68**, 650 (1935).

(6) Orekhov, Konovalova and Tiedebel, *ibid.*, **68**, 1886 (1935); Konovalova and Orekhov, *ibid.*, **69**, 1908 (1936).

(7) Menshikov, *Bull. Acad. Sci. (U. S. S. R.) Classe sci. math. Ser. chim.*, 1035 (1937).



I

The facts used in the deduction of this formula are summarized as follows:

(1) The hydrogenolysis of the β-hydroxyl in retronecine takes place with ease whereas under similar conditions the α-hydroxyl is stable. β,γ-Unsaturated alcohols and the α-hydroxyamines (or presumably vinylogous α-hydroxyamines) readily undergo hydrogenolysis under mild conditions.[8]

(2) The two hydroxyls in retronecine or in the corresponding saturated molecule, platynecine, esterify at different rates. One hydroxyl in each of these molecules is difficult to esterify.

(3) The β-hydroxyl in platynecine is stable under reducing conditions which cause hydrogenolysis of the β-hydroxyl in retronecine.

(4) Retronecine contains no readily enolized ketone as demonstrated by the inability to isolate a ketone derivative. This was attempted first by Barger[3] and confirmed by us. Retronecine gives no color with ferric chloride.

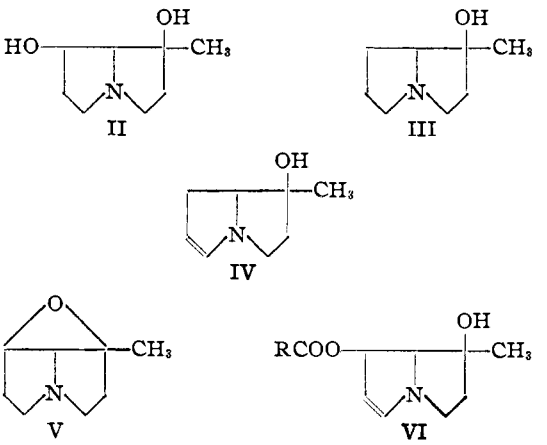
(5) Menshikov[9] subjected oxyheliotridane (stereoisomeric with retronecanol) to exhaustive methylation and reported the isolation of a tertiary alcohol.

(6) Orekhov[5,6] found that platynecine when treated with a variety of reagents undergoes loss of a molecule of water between the two hydroxyl groups to give anhydroplatynecine. In the pyrrolizidine nucleus, the 1,7 positions are more favorable stereochemically for formation of an oxygen bridge than any other two.

Each of these facts may be satisfactorily explained by structure I; what is more important is that any other orientation of the α- and β-hydroxyls and double bond fails to satisfy entirely one or more of them. Thus from a variety of structures which will clarify the ease of hydrogenolysis of the β-hydroxyl, it is found that (1) the α-hydroxyl must be represented as allylic and will therefore be unstable or that (2) the corresponding saturated compound, platynecine, will have one of its hydroxyls an α-hydroxyamine thus susceptible to reduction or the two hydroxyls secondary which will result in essentially identical esterification rates or that (3) the β-hydroxyl is tertiary which will not explain its ease of esterification.

Structure I explains also that in the dichloride obtained by replacement of the two hydroxyls in retronecine by chlorine, the β-chloride which is allylic is much less stable to reduction than the tertiary α-chloride. The relative difficulty of dehydration of retronecanol to heliotridene is surprising; it resembles that often found in the introduction of a double bond by dehydration into certain other fused ring systems. The resistance of the tertiary hydroxyl to dehydration also may serve to explain the somewhat greater ease of esterification of the α-hydroxyl than is usually found with aliphatic tertiary alcohols.

On the basis of the structure I for retronecine, platynecine would be represented by formula II, retronecanol by formula III, desoxyretronecine by formula IV and anhydroplatynecine by formula V. Finally the alkaloid monocrotaline would be represented by formula VI where RCOO- represents a monocrotalic acid residue.



Experimental

Hydrogenation of Monocrotaline with Raney Nickel as Catalyst.—A solution of 5.4 g. of monocrotaline in 100 cc. of ethanol, to which 3 g. of Raney nickel was added, was hydrogenated at 2–3 atmospheres pressure. Two mole equivalents of hydrogen were absorbed. After filtration, removal of ethanol *in vacuo* and solution of the residue in 17 cc. of *N* hydrochloric acid, the products were isolated as previously described[1a]; yield 2.38 g. of monocrotalic acid, m. p. 181–182° (cor.) and 2.22 g. of retronecanol, m. p. 95–96° (cor.).

Limited Hydrogenation of Monocrotaline with Platinum Oxide as Catalyst: Desoxyretronecine Hydrochloride.—A solution of 43.2 g. of monocrotaline in 136 cc. of *N* hydro-

(8) Skita and Keil, *Ber.*, **63**, 34 (1930); Wagner, THIS JOURNAL, **55**, 724 (1933); Forsee and Pollard, *ibid.*, **57**, 1788 (1935).

(9) Menshikov, *Bull. Acad. Sci. (U. S. S. R.) Classe sci. math. Ser. chim.*, 969 (1935).

chloric acid, was hydrogenated at approximately 2–3 atmospheres pressure until an amount of hydrogen corresponding to one mole equivalent was absorbed. Using 0.1 g. of platinum oxide catalyst, the time of reduction varies between five and twenty minutes. The solution was filtered and exhaustively extracted with ether. The ether extract yielded 15.5 g. of monocrotalic acid, m. p. 181–182° after one recrystallization from acetone–petroleum ether. The aqueous hydrochloric acid solution was clarified with Filter-cel and evaporated to dryness *in vacuo*. The sirupy residue was taken up in a small volume of boiling methanol and mixed with a tenfold volume of acetone. Crystallization was complete in two days at icebox temperature. The crude salt was recrystallized in the same manner. Seeds were first obtained from methanol–ether crystallization. Desoxyretronecine hydrochloride crystallizes in white plates, m. p. 182–183° (cor.).

Anal. Calcd. for $C_8H_{13}ON\cdot HCl$: C, 54.70; H, 7.97; N, 7.97; Cl, 20.20. Found: C, 54.92; H, 7.84; N, 8.09; Cl, 20.14.

Rotation. 0.5390 g. made up to 10 cc. with water at 24° gave α_D −1.72°; *l*, 2; $[\alpha]^{24}D$ −15.9°.

Desoxyretronecine.—The free base was obtained by decomposition of the hydrochloride with strong alkali and extraction with ether. After drying the ether extract and removing the solvent, the desoxyretronecine was distilled, b. p. 120° (20 mm.). The distillate crystallized; it was purified by crystallization from petroleum–ether (b. p. 30–60°) and formed white rods, m. p. 77–78° (cor.).

Anal. Calcd. for $C_8H_{13}ON$: C, 69.06; H, 9.35; N, 10.07. Found: C, 68.98; H, 9.33; N, 10.06.

Desoxyretronecine Picrate.—Prepared in and recrystallized from ethanol, the picrate formed yellow needles; m. p. 157–158° (cor.).

Anal. Calcd. for $C_8H_{13}ON\cdot C_6H_3O_7N_3$: N, 15.22. Found: N, 15.25.

Hydrogenation of Desoxyretronecine.—A solution of 1.4 g. of desoxyretronecine in 10 cc. of *N* hydrochloric acid was hydrogenated at slightly above atmospheric pressure in the presence of 0.05 g. of platinum oxide. One mole equivalent of hydrogen was absorbed. The solution was then filtered, made strongly alkaline and extracted with ether. There was obtained 1.35 g. of retronecanol which after distillation had a melting point of 95–96° (cor.).

Desoxyretronecine was also quantitatively reduced to retronecanol by Raney nickel in ethanol.

Hydrogenation of Retronecine to Platynecine.—A solution of 10.3 g. of retronecine in 50 cc. of ethanol, to which was added 3 g. of Raney nickel, was hydrogenated at 2–3 atmospheres pressure. Absorption of 1.1 moles of hydrogen occurred, after which the reduction was very slow and was stopped. After filtration, the ethanol was removed *in vacuo* and the sirupy product taken up in 100 cc. of boiling acetone. The platynecine crystallized readily from the cooling solution, although when first prepared, considerable scratching was necessary; yield 6.2 g., and a further 0.4 g. on concentrating the mother liquors. The remaining base presumably was an uncrystallizable mixture of retronecanol and platynecine.

Platynecine was purified by crystallization from acetone; long, rodlike prisms; m. p. 148–149° (cor.). Sometimes thin platelets were obtained.

Anal. Calcd. for $C_8H_{15}O_2N$: C, 61.14; H, 9.55; N, 8.91. Found: C, 61.26; H, 9.76; N, 8.71.

Rotation. 0.150 g. made up to 10 cc. with chloroform at 30° gave α_D −1.73°; *l*, 2; $[\alpha]^{30}D$ −57.7°.

The reported constants for platynecine[10] are: m. p. 148–148.5°; rotation, $[\alpha]D$ −56.8° in chloroform.

Platynecine Methiodide.—This was prepared as described by Orekhov and Konovalova[6]; long needles, m. p. 207–207.5° (cor.).

Anal. Calcd. for $C_8H_{15}O_2N\cdot CH_3I$: C, 36.14; H, 6.06. Found: C, 36.25, 36.13; H, 6.23, 5.94.

Platynecine was recovered unchanged after reductions with platinum oxide in ethanol solution at 25° and at 80° (150 atm. press.).

Monobenzoyl Platynecine.—This was prepared and described by Orekhov and Konovalova.[6] It crystallized from ether–petroleum ether (b. p. 30–60°) in prisms, m. p. 118–119° (cor.). The reported melting point is 119–120°.

Anal. Calcd. for $C_{15}H_{20}O_3N$: N, 5.34. Found: N, 5.33.

This base was not reduced by platinum oxide in ethanol solution at room temperature.

Hydrogenation of Monobenzoyl Retronecine Hydrochloride.—A solution of 3 g. of monobenzoyl retronecine hydrochloride[4] in 30 cc. of ethanol was reduced catalytically in the presence of 0.05 g. of platinum oxide. When hydrogen absorption was complete (2 mole equivalents), the solution was filtered, the ethanol was distilled *in vacuo* and the residue was taken up in 30 cc. of boiling water. On cooling, benzoic acid of m. p. 121–122° crystallized (weight 0.90 g.). From the filtrate retronecanol m. p. 95–96° was obtained as previously described (weight 1.20 g.).

Summary

1. By catalytic reduction under specified conditions, retronecine is converted into retronecanol or platynecine, and monocrotaline is converted to retronecanol or desoxyretronecine.

2. Desoxyretronecine was shown to be a molecule in which merely the easily removed (β) hydroxyl of retronecine was replaced by hydrogen.

3. Platynecine was formed by reduction of the double bond in retronecine without elimination of either hydroxyl. This establishes the relationship of platynecine and retronecine and indicates that the hydroxyls are in comparable positions.

4. On the basis (1) of the stability of the hydroxyls in platynecine to reduction and the failure of monobenzoyl platynecine to hydrogenolyze in contrast to the ease of reduction of one of the hydroxyls in retronecine and ease of hydrogenolysis of the monoesters of retronecine, and (2) of the difference in the ease of esterification of the two

(10) Drekhor, *Ber.*, **68**, 1886 (1935).

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

URBANA, ILLINOIS RECEIVED OCTOBER 21, 1940

[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

BY RALPH C. HUSTON AND RICHARD I. JACKSON[1]

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-

(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).