Reduction of Benzil with Aluminum Amalgam and Aqueous Ammonium Hydroxide.—The aluminum amalgam was prepared by adding small pieces of aluminum foil to a dilute solution of mercuric chloride. A vigorous reaction took place and after standing a few minutes, the amalgam was poured upon a Büchner funnel and well washed with water and then with alcohol. This amalgam must be used immediately because of its great reactivity.

Twenty grams of this aluminum amalgam was covered with 300 cc. of alcohol and then 25 g. of benzil in a mixture of 30 cc. of concentrated ammonium hydroxide and 50 cc. of water was added. Stirring caused the mixture to become warm. Stirring was continued for two hours and the mixture was allowed to stand till the next day. The yellow color of benzil disappeared, and a thick gray colored precipitate separated. The reaction mixture was poured into a large excess of dilute hydrochloric acid to dissolve the precipitated aluminum hydroxide. The precipitate was filtered and extracted with boiling alcohol. On cooling, 15 g. or 60% of crude hydrobenzoin melting at 128–130° was obtained. Recrystallization from alcohol gave iridescent plates melting at 135°. The mixed melting point with pure hydrobenzoin was 135°.

In an analogous manner benzil was subjected to the action of a number of reducing agents under various conditions. The conditions and data of these experiments are listed in Table I.

Whereas most of these reducing agents give high yields of benzoin, such reductions are only of theoretical interest because benzil itself is prepared from benzoin. However, the other reductions are valuable for the preparation of certain of the other reduction products of benzil.

Attempted Reductions of Benzil.—Whereas reaction of benzil with zinc and sodium hydroxide in water solution yielded didesyl, the reaction with zinc and sodium hydroxide in alcoholic solution gave a 90% yield of benzilic acid melting at 150°.

No reactions on benzil were obtained with aluminum and sodium hydroxide in alcoholic solution or with zinc amalgam and sodium hydroxide in water solution or with magnesium amalgam in water solution.

Summary

The effects of a number of various reducing agents and reducing conditions on benzil have been studied. Six new reduction products of benzil, namely, stilbene, phenylbenzylcarbinol, isostilbene, didesyl, isodidesyl, and β-desoxybenzoin pinacone have been obtained directly from benzil.

SEATTLE, WASHINGTON RECEIVED SEPTEMBER 21, 1937

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

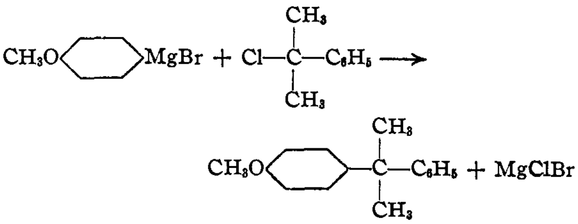
The Condensation of Some Tertiary Aryl Substituted Carbinols with Phenol in the Presence of Aluminum Chloride

BY LLEWELLYN H. WELSH WITH NATHAN L. DRAKE

Various types of carbinols have been condensed with aromatic compounds in the presence of aluminum chloride. Primary,[1] secondary[2] and tertiary[3,4] aliphatic alcohols, and primary and secondary aryl substituted carbinols[5] have been found to react with benzene under suitable conditions to yield alkyl- and arylalkyl-benzenes. These same types of alcohols[4,6,7,8], also have been condensed with phenol to form, usually, para-substituted phenols.

The purpose of the present work was to effect the condensation of some tertiary aryl substituted carbinols with phenol in the presence of aluminum chloride, and to obtain additional evidence concerning the mechanism of reactions between alcohols and aromatic compounds. Phenol rather than an aromatic hydrocarbon was selected as a reactant because greater ease of reaction and more efficient separation of products from reaction mixtures were anticipated.

Dimethylphenylcarbinol reacted with phenol to give 68–72% yields of *p*-(α,α-dimethylbenzyl)-phenol. That the dimethylbenzyl group entered para to the hydroxyl was proved by the following synthesis



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(1) Tzukervanik and Vikhrova, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 632 (1937); *C. A.*, **31**, 5779 (1937).

(2) Tzukervanik and Tokareva, *ibid.*. **5**, 764 (1935); *C. A.*, **30**, 442 (1936).

(3) Tzukervanik, *ibid.*, **5**, 117–120 (1935); *C. A.*, **29**, 4746 (1935).

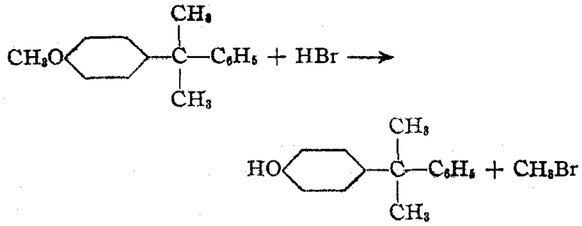
(4) Huston and Hsieh, THIS JOURNAL, **58**, 439 (1936).

(5) Huston and Friedemann, *ibid.*, **38**, 2527 (1916); *ibid.*, **40**, 785 (1918).

(6) Tzukervanik and Nazarova, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 623 (1937); *C. A.*, **31**, 5778 (1937).

(7) Huston, THIS JOURNAL, **46**, 2775 (1924).

(8) Huston, Lewis and Grotemut, *ibid.*, **49**, 1365 (1927).

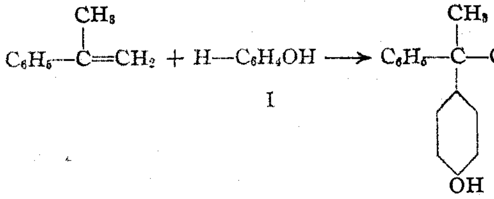


The principal by-product of the carbinol–phenol reaction was 1,1,3-trimethyl-3-phenylhydrindene, the saturated dimer of α-methylstyrene.[9]

Methyldiphenylcarbinol and phenol reacted to yield 80% of the theoretical quantity of *p*-(α,α-diphenylethyl)-phenol. There were also obtained 1,1-diphenylethylene and a resinous material which was probably a polymerization product of that olefin.

Triphenylcarbinol and phenol condensed more completely and readily than the other two less highly phenylated carbinols to give a 95% yield of *p*-triphenylmethylphenol.

The formation of olefins (or their polymerization products) in the dimethylphenylcarbinol and methyldiphenylcarbinol condensations would indicate that the probable reaction mechanism in these instances is that of addition of aromatic compounds to double bonds, according to the equations



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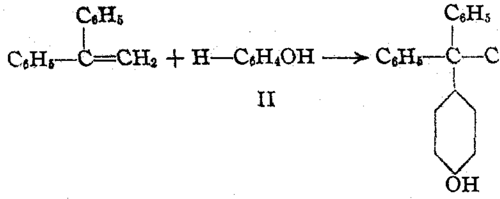

II

Tzukervanik[3] has considered this as a possible course of reaction for condensations of tertiary aliphatic alcohols with benzene and toluene in the presence of aluminum chloride. McKenna and Sowa,[10] employing boron fluoride as condensing agent, have proposed a like mechanism to account for side-chain rearrangements observed in their study of the alkylation of benzene with aliphatic alcohols. McGreal and Niederl[11] have explained the formation of *p*-(α-methylbenzyl)-phenol instead of the expected *p*-(β-phenylethyl)-phenol in the condensation of β-phenylethanol and phenol by means of zinc chloride to be the result of addition of phenol to the double bond of the olefin first formed. Further evidence that such condensations proceed according to this scheme whenever the nature of the carbinol and experimental conditions favor olefin formation has been obtained from the action of aluminum chloride on a benzene solution of benzyldiphenylcarbinol.[12] *sym*-Tetraphenylethane, rather than the unsymmetrical isomer, was the principal reaction product. This phenomenon seems best interpreted as the addition of benzene to triphenylethylene, and is under further investigation at the present time.

The same course of reaction obviously cannot be postulated for those cases in which the alcohol employed is incapable of dehydration to olefin, *e. g.*, benzyl alcohol,[7] benzohydrol[8] and triphenylcarbinol. In such cases the reaction may proceed, in effect, by elimination of water from the hydroxyl group and nuclear hydrogen. The fact that triphenylcarbinol and phenol will react at elevated temperatures without the presence of catalyst or condensing agent[13] would appear to admit of this possibility.

Experimental

The phenol used in these condensations was obtained by distillation of Eastman phenol of practical purity. Aluminum chloride was of Mallinckrodt C. P. reagent quality.

Condensation of Dimethylphenylcarbinol and Phenol.—This reaction was investigated more thoroughly than the condensations of the other two carbinols. A number of preliminary runs indicated that the yield of *p*-(α,α-dimethylbenzyl)-phenol was adversely affected by temperatures below 100° and aluminum chloride in excess of 0.50 mole per mole of carbinol because of increased formation of hydrindene derivative. When molar proportions of phenol and carbinol reacted in petroleum ether solution by addition of 0.50 mole of aluminum chloride at 20–30°, the yield of product was of the order of 30–40%. Reactions employing less than 0.50 mole of catalyst at temperatures above 100° were not carried out.

The best yields of condensation product were obtained by the following procedure: 11 g. (0.083 mole) of aluminum chloride was added rapidly, with stirring, to 50 g. (0.53 mole) of molten phenol contained in a 3-necked flask connected with a trap for hydrogen chloride absorption. The flask was then heated on the steam-bath while a mixture of 22.7 g. (0.167 mole) of carbinol and 16 g. of phenol was added dropwise, with efficient stirring. On completion of the addition, the heating and stirring were

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[9] Bergmann, Taubadel and Weiss, *Ber.*, **64**, 1493 (1931).

[10] McKenna and Sowa, THIS JOURNAL, **59**, 470 (1937).

[11] McGreal and Niederl, *ibid.*, **57**, 2625 (1935).

[12] L. H. Welsh, Master's thesis, University of Maryland, 1935

[13] Boyd and Hardy, *J. Chem. Soc.*, **133**, 630 (1928).

continued for one hour, at the end of which time the reaction mixture was decomposed with dilute hydrochloric acid and the aqueous layer extracted with ether. The solvent was removed from the combined non-aqueous layers by distillation, excess phenol distilled off at 25 mm. and the residue completely distilled at *ca.* 1 mm. The distillate (31 g.) was liquefied by warming, and 75 ml. of 30–60° petroleum ether added with vigorous stirring. The resulting sludge of crystals was then cooled to 0–5°, filtered with suction, and the crystals washed with two 50-ml. portions of cold petroleum ether. The yield of dry *p*-(α,α-dimethylbenzyl)-phenol[14] was 25.6 g. (72%); m. p. 72.5–73°.[15] The substance is best recrystallized from 30–60° petroleum ether from which it is deposited as prisms which, when pure, melt at 73°. It distills at 213–214° at 25 mm. (bath temperature 255°).

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.59. Found: C, 84.56; H, 7.65.

Evaporation of the petroleum ether leachings yielded an oil which was dissolved in 5 ml. of methanol and chilled: there resulted 1.5 g. of crude 1,1,3-trimethyl-3-phenylhydrindene which, after recrystallization from methanol, melted at 52°. A mixed melting point determination with an authentic specimen of the saturated dimer of α-methylstyrene gave no depression. The residue obtained by evaporation of the mother liquor of the crude hydrindene was distilled at *ca.* 1 mm. The following fractions were obtained: (a) up to 115°, 0.6 g.; (b) 115–122°, 1.2 g.; (c) 122–135°, 0.5 g.; (d) 135–150°, 0.5 g. Fraction (a) partly solidified, and decolorized bromine in carbon tetrachloride. It consisted principally of diphenyl which was present in small amount in the original carbinol which was prepared by the action of phenylmagnesium bromide on acetone. Fraction (b) almost completely solidified when seeded with the hydrindene derivative and also gave evidence of containing unsaturated compounds. The unsaturation of these two fractions was probably due to the presence of the unsaturated dimer of α-methylstyrene.[9] Fraction (c) had a refractive index of 1.582 and was not investigated further. The last fraction crystallized when seeded with the phenolic condensation product.

A duplicate condensation gave a 68% yield of *p*-(α,α-dimethylbenzyl)-phenol.

Coupling of *p*-Anisylmagnesium Bromide and Dimethylphenylchloromethane.—Forty-seven grams (0.25 mole) of *p*-bromoanisole was reacted with 6.5 g. of magnesium turnings in 200 ml. of dry ether. Forty grams of dimethylphenylchloromethane, prepared according to Klages' procedure,[16] was added dropwise, with stirring, while the mixture was allowed to reflux. The reaction mixture was then decomposed and worked up in the usual manner. The residue, after removal of ether, was distilled under diminished pressure. A large forerun, principally anisole, was obtained before collection of the fraction of *p*-(α,α-dimethylbenzyl)-anisole boiling at 140–141° at *ca.* 3 mm. This fraction weighed 15 g. (26%); n^{25}D 1.569.

Cleavage of *p*-(α,α-Dimethylbenzyl)-anisole with Hydrobromic Acid.—Five grams of the ether, 6 ml. of 48% hydrobromic acid and 50 g. of phenol were refluxed three hours and the phenol then removed by steam distillation. The residual oil was solidified by cooling and seeding. After three recrystallizations from 30–60° petroleum ether there was obtained 3.5 g. of pure white prisms which melted sharply at 73° and gave no depression of melting point when mixed with the primary product of the condensation of dimethylphenylcarbinol and phenol.

Methylation of *p*-(α,α-Dimethylbenzyl)-phenol.—This methylation was effected with dimethyl sulfate and aqueous-alcoholic alkali. The following physical constants of *p*-(α,α-dimethylbenzyl)-anisole were determined: n^{25}D 1.5685; d^{25} 1.0367; b. p. (25 mm.) 198–199°; *M*R, 71.50 (*M*R calcd., 70.86). The distillation temperature is influenced considerably by the bath temperature; the above distillation range was observed when the bath temperature was 240°.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.91; H, 7.93.

Diphenylurethan and Aryloxyacetic Acid of *p*-(α,α-Dimethylbenzyl)-phenol.—These derivatives were prepared according to the directions of Kamm.[17] The diphenylurethan crystallizes as leaflets from alcohol; m. p. 126°.

Anal. Calcd. for $C_{28}H_{25}NO_2$: N, 3.44. Found: N, 3.29.

The aryloxyacetic acid is deposited as shining leaflets from ethanol–water or petroleum ether–benzene; m. p. 117°.

Neutral equiv. Calcd. for $C_{15}H_{15}OCH_2COOH$: 270. Found: 272, 273.

Condensation of Methyldiphenylcarbinol and Phenol.—Thirty-three grams (0.167 mole) of the carbinol was reacted with phenol under the conditions of the previous condensation. After standing for two days, the reaction mixture was decomposed with dilute hydrochloric acid and the excess phenol distilled off under diminished pressure. The residue was removed to a beaker, dissolved in the minimum volume of benzene, 5 volumes of petroleum ether added and the mixture cooled. The resulting pinkish, crystalline material (38.5 g.) was dissolved in the minimum volume of petroleum ether–benzene, filtered to remove a small amount of insoluble red material, and the filtrate chilled: 33 g. of slightly yellow *p*-(α,α-diphenylethyl)-phenol[18] resulted: m. p. 121–121.5°. Combination of mother liquors, evaporation and recrystallization of the residue yielded an additional 2.5 g. of pure condensation product. The mother liquor was extracted with Claisen's alcoholic potash.[19] Dilution and acidification of the alkaline layer resulted in the precipitation of a thick oil which when dissolved in petroleum ether–benzene and cooled deposited an additional gram of condensation product: m. p. 119.5–121.5°. The total yield of this compound amounted to 36.5 g. (80%). On evaporation of the petroleum ether–benzene layer there resulted an oil which was separated into two fractions by distillation. The unsaturated, lower boiling material (1.5 g.) possessed the following physical constants: b. p. (25 mm.) 155°; n^{30}D 1.6035; f. p. 7–9°. These values are in excellent

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[14] Britton and Martin, U. S. Patent 2,028,043; *C. A.*, **30**, 1395 (1936).

[15] All melting points are corrected.

[16] Klages, *Ber.*, **35**, 2638 (1902).

[17] Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, 1932.

[18] Baeyer and Villiger, *Ber.*, **36**, 2794 (1903).

[19] Claisen, *Ann.*, **442**, 224 (1925).

agreement with those reported in the literature[20] for 1,1-diphenylethylene. The higher boiling fraction consisted of a resinous material which distilled at 250–260° at *ca.* 1 mm. From this resin, which probably consisted of a mixture of polymers of 1,1-diphenylethylene, no crystalline compounds could be isolated.

Condensation of Triphenylcarbinol and Phenol.—Five grams of aluminum chloride was added, with stirring, to a mixture of 20 g. of triphenylcarbinol and 20 g. of phenol. After heating for ten minutes on the steam-bath, 75 ml. of 50–70° petroleum ether was added, the reaction mixture refluxed an additional fifty minutes and then decomposed by heating with 200 ml. of 5% hydrochloric acid. This heating removed the volatile solvent. The solid matter was filtered off, the lumps crushed and washed first with hot water then with two 75-ml. portions of alcohol. After drying, the yield of *p*-triphenylmethylphenol was 24.5 g. (95%); m. p. 281–283.5°.

We wish to acknowledge our indebtedness to J. R. Adams and J. K. Wolfe for the carbon, hydrogen and nitrogen determinations.

Summary

1. Dimethylphenylcarbinol, methyldiphenylcarbinol and triphenylcarbinol have been condensed with phenol in the presence of aluminum chloride.

2. Mechanisms for these condensations have been postulated.

3. The methyl ether, diphenylurethan and aryloxyacetic acid of *p*-(α,α-dimethylbenzyl)-phenol have been prepared.

COLLEGE PARK, MD. RECEIVED NOVEMBER 1, 1937

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[20] Beilstein, "Handbuch der organischen Chemie," 4th ed., 1922, Vol. V, p. 639; Supplement, 1930, Vol. V, p. 308.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

I. The Atomic Weight of Lead from a Specimen of St. Joaquimsthal Pitchblende. II. The Lead–Uranium Ratio of this Pitchblende

BY GREGORY P. BAXTER AND WALLACE M. KELLEY

I. The Atomic Weight

Although it has been clear from earlier work[1] that St. Joaquimsthal (Bohemia) pitchblende is badly contaminated with common lead, since we had the opportunity of examining a fine specimen of pitchblende stated to be from this locality it seemed worth while to determine the atomic weight of the lead and the lead–uranium ratio on identical material. The results correspond to earlier evidence with pitchblende from the same source.[1]

The original specimen, which weighed over a kilogram, was streaked with veins of colored calcite. The search for galena in a polished section was negative.

About 450 g. of this mineral was crushed in a clean chipmunk crusher and then finely ground in a nutmeg mill. A sample of about 25 g. of the powder was set aside for analysis. Treatment with 1% hydrochloric acid removed most of the calcite. A small amount of lead sulfide (± 50 mg.) was obtained from the solution. Treatment of the pitchblende with hot nitric acid left a considerable residue, a large part of which dissolved in hot aqua regia. The material remaining insoluble was then evaporated with redistilled hydrofluoric acid in platinum, and then again with sulfuric acid. After removal of the excess sulfuric acid by fuming, the lead sulfate was extracted with ammonium acetate and precipitated as sulfide. Lead was recovered from the nitric acid and aqua regia solutions either by crystallization as chloride or by precipitation as sulfide. All the lead was at least once converted to sulfate by evaporation with excess sulfuric acid. This was washed with dilute sulfuric acid, and dissolved in ammonium acetate. After filtration lead sulfide was precipitated, converted to chloride and crystallized (13 g.). Conversion to nitrate by evaporation with nitric acid followed.

The nitrate was then recrystallized from nitric acid five times, twice in glass and three times in quartz. To convert the nitrate to chloride it was evaporated to dryness with 20% hydrochloric acid three times. Five crystallizations as chloride from 10% hydrochloric acid in quartz and two distillations in quartz in a current of dry hydrogen chloride completed the purification.

In the course of the purification it early became evident that the lead contained bismuth as chief impurity. The final product when examined with a quartz spectrograph on pure carbon electrodes seemed to be free from this element as well as copper and silver.

This material was used in Analyses 4, 5 and 6. For Analyses 7 and 8 the residues from the first purification were further purified as sulfide and sulfate and combined with material contained in the lead nitrate solutions resulting from Analyses 4–6. The combined material was crystallized as nitrate and chloride and distilled in hydrogen chloride as before.

To prepare the lead chloride for weighing it was fused in a current of nitrogen and hydrogen chloride in a small quartz boat contained in the quartz tube of a Richards bottling apparatus. After sweeping out the bottling apparatus with nitrogen followed by air, the weighing

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[1] Bull. Nat. Res. Council, The Age of the Earth, 305 (1931).