[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

THE EFFECT OF UNSATURATION ON THE ACTIVITY OF ALCOHOLIC HYDROXYL. I. ACTION OF ALLYL ALCOHOL ON BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

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Continuing our studies on the condensation of aromatic alcohols and aromatic hydrocarbons in the presence of aluminum chloride, an attempt was made to condense phenylethyl alcohol and benzene by means of aluminum chloride. The results were negative in so far as the production of diphenylethane was concerned. Attempts to prepare symmetrical diphenylpropane from phenylpropyl alcohol and benzene were also unsuccessful.

Our earlier work had shown that both methylphenylcarbinol and ethylphenylcarbinol readily condense with benzene, and the failure of their isomers to respond under similar treatment was regarded as significant. *Of the aromatic alcohols studied, only those in which the hydroxyl is on the carbon atom adjacent to the ring were found to react.*

The method was next applied to a number of aliphatic alcohols; methyl, ethyl, propyl, secondary propyl, *n*-butyl, *iso*butyl and *iso*-amyl alcohols were included. In no case was there evidence of the formation of the corresponding alkyl benzene.

This lack of reactivity of the simple aliphatic alcohols was expected. Goldschmidt[1] was able to effect condensation in the presence of zinc chloride only at relatively high temperatures, while Brochet and Borlinger[2] obtained a small yield of the alkyl benzene by heating the alcohol and benzene for several hours at 175–200° in the presence of an excess of sulfuric acid.

From the results it is apparent that the activity of the hydroxyl group is greatly enhanced when it is attached to a carbon atom which is in turn attached to a carbon of the benzene ring, and the question naturally arose as to what effect unsaturation, other than that of the benzene ring, would have upon the activity of the hydroxyl group.

This paper describes experiments in which a simple unsaturated aliphatic alcohol, allyl alcohol was mixed with an excess (5 molecular equivalent) of benzene and treated with aluminum chloride (0.5 equivalent) at room temperature. The principal product of the reaction was allyl benzene: $CH_2{=}CH{-}CH_2OH + C_6H_6 \longrightarrow CH_2{=}CHCH_2C_6H_5 + H_2O$. It was identified by conversion into propenylbenzene, by boiling with alcoholic

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[1] Goldschmidt, *Ber.*, **15**, 1066 (1882).

[2] Brochet and Borlinger, *Compt. rend.*, **117**, 235 (1893).

potassium hydroxide.[3] The yield was smaller than that obtained in those condensations where aromatic alcohols were used, 16% as compared with 67% for benzyl alcohol.

From the higher-boiling portion of the reaction product there was isolated by repeated fractionation under reduced pressure a considerable amount of chloropropylbenzene. This was probably the result of addition of hydrochloric acid to allylbenzene under the catalytic influence of aluminum chloride: $C_6H_5CH_2CH{=}CH_2 + HCl \longrightarrow C_6H_5CH_2CHClCH_3$. The formation of this compound is in part responsible for the low yield of allylbenzene.

The next higher fraction was freed from halogen by boiling in ether solution with sodium and was refractionated. After purification it came over at 277–280° (745 mm.). It has the properties of a saturated hydrocarbon and is probably 1,2-diphenylpropane. Silva[4] obtained this compound when he attempted to prepare allylbenzene from allylchloride and benzene by the Friedel and Crafts reaction. He attributed its formation to the intermediate formation of 1,2-dichloropropane from allyl chloride or of β-chloropropylbenzene from allylbenzene. The isolation of β-chloropropylbenzene from our reaction product would indicate the correctness of his second hypothesis. One experiment with a small amount of material indicated the formation of 1,2-diphenylpropane directly from allylbenzene, benzene and aluminum chloride.

The literature gives no definite data on the preparation and properties of β,γ-dibromopropylbenzene. This was prepared by treating pure allylbenzene in chloroform solution with the calculated amount of bromine.

Discussion

In the compounds studied, there appears to be a very definite relationship between reactivity of the hydroxyl group and the state of saturation of the alpha carbon atom. *Only those compounds in which the alpha carbon is a member of the benzene ring or is double bonded show appreciable reactivity.*

In the aromatic alcohols the difference in activity of the phenylalkylcarbinols and those isomers in which the hydroxyl is on the second or third carbon atom from the ring, is also apparent in their behavior toward heat. When heated under atmospheric pressure to their boiling points, phenylmethylcarbinol and phenylethylcarbinol lose water to form the corresponding unsaturated hydrocarbons, while phenylethyl alcohol and phenylpropyl alcohol may be distilled without decomposition at atmospheric pressure.

It is also well known that benzyl alcohol, benzohydrol, phenylmethylcarbinol and phenylethylcarbinol, react more readily with halogen acid to

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[3] Tiffeneau, *Compt. rend.*, **139**, 1482 (1904).

[4] Silva, *Compt. rend.*, **89**, 606 (1879).

form halogen derivatives, than do those compounds in which the hydroxyl is more distant from the phenyl group.

A certain parallelism is evident between the activity of the hydroxyl group and halogen. Claisen[4a] has explained the formation in benzene or toluene solution, of different amounts of *o*-allyl- or *o*-benzylphenol (and the lack of formation of *o*-alkyl phenol) from the corresponding halide, on the basis of a loosening effect of the double bond or benzene ring on the bond between carbon and halogen. Conant and Kirner[5] found a sharp decrease in reactivity of the halogen toward potassium iodide in passing from benzyl chloride to phenylethyl chloride and the higher homologs. An especially interesting comparison is found in the reactivity of propyl halide, allyl halide and benzyl halide toward potassium iodide,[6] sodium thiosulfate[7] and pyridine.[8] With all three reagents the allyl halide has a reactivity greater than the propyl halide, and less than the benzyl halide. Our work has shown the same relative order of reactivity in the alcohols when condensed with benzene in the presence of aluminum chloride.

Experimental Part

Allyl Alcohol, Benzene and Aluminum Chloride.—Eighty-seven g. of allyl alcohol, b. p. 95–97°, was dissolved in 585 g. of benzene and the solution stirred constantly during the addition of 99 g. of aluminum chloride. The addition of the chloride took, in general, from two to three hours, during which time the temperature was maintained at 20–25°. Hydrogen chloride was copiously evolved. The stirring was continued for about eight hours, while the mixture gradually became dark reddish-brown. The next morning it was decomposed with ice and dil. hydrochloric acid. The benzene layer was separated and the aqueous portion extracted thrice with ether. The ether was distilled and the residue added to the benzene portion. This was fractionated with a 20cm. column; 510 g. of benzene and 30 g. of allyl alcohol were recovered from those portions which came over below 105°. The residue weighed 28 g. This was combined with the products of two other runs, and fractionated eight times. The fractions obtained were as follows: 105–165° 45 g.; 85–105 (18 mm.) 10 g.; 105–135 (18 mm.) 1 g.; 135–170 (18 mm.) 14.5 g.; tarry residue 14 g. Practically all of the fraction boiling at 105–165° (746 mm.) proved to be allyl benzene (b. p., 157–159°).

In order to verify the identification, 4 g. of allyl benzene was heated on the water-bath with 8 g. of potassium hydroxide in 80 cc. of 95% alcohol for three hours. Most of the alcohol was then distilled and 250 cc. of water added. After the solution was neutralized with hydrochloric acid, it was extracted with ether. The ether was distilled and the propenylbenzene treated in chloroform solution with 2 cc. of bromine. After two crystallizations from alcohol the α,β-dibromopropylbenzene melted sharply at 66–66.5°.[9]

The 85–105 (18 mm.) fraction came over after repeated distillation at 90.5 to

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[4a] Claisen, *Ann.*, **442,** 216, 213 (1925).

[5] Conant and Kirner, THIS JOURNAL, **46,** 232 (1924).

[6] Conant, Kirner and Hussey, *ibid.*, **47,** 476 (1925).

[7] Slator, *J. Chem. Soc.*, **85,** 1286 (1904); **87,** 481 (1905); **95,** 93 (1909).

[8] Clarke, *ibid.*, **97,** 416 (1910); **99,** 1927 (1911); **101,** 1788 (1912); **103,** 1689 (1913).

[9] Hell and Bauer, *Ber.*, **36,** 206 (1903).

92.5° (18 mm.). When distilled under atmospheric pressure it had the correct boiling point for β-chloropropylbenzene,[10] 205–207°. A determination of chlorine (Carius) gave 21.75%. When boiled with dil. nitric acid (10%) it gave *p*-nitrobenzoic acid (m. p., 237–238°) the methyl ester of which melted at 96°. Oxidation with potassium permanganate gave benzoic acid.

The fraction boiling at 135–170° (18 mm.) did not give a sharp boiling point after ten distillations. A Carius determination for chlorine gave 5.53%. The entire fraction was dissolved in 50 cc. of ether, the solution treated with 1 g. of finely chipped sodium and refluxed on a water-bath for four hours. The mixture was filtered, the ether evaporated and the residue fractionated. After three distillations 6.5 g. came over at 277–280° (745 mm.). This fraction was entirely free from halogen. Its properties were those of a saturated hydrocarbon. It is probably 1,2-diphenylpropane,[3] $C_6H_5CHCH(C_6H_5)CH_3$.

Allylbenzene, Benzene and Aluminum Chloride.—Eleven g. of allylbenzene and 34.5 g. of benzene were treated with 6 g. of aluminum chloride under the usual conditions. The temperature was kept below 25°. The mixture turned dark brown and hydrogen chloride was evolved. Decomposition, extraction and distillation were effected as in the preceding experiment. The following fractions were obtained: 105–270°, 2 g.; 270–285° (mostly 276–280°), 4.5 g.; 285–320°, 1 g.; residue, 6 g.

β,γ-Dibromopropylbenzene.—Twenty g. of allylbenzene dissolved in 125 cc. of chloroform was treated with bromine in 0.25cc. portions until 8.75 cc. (28 g.) had been added, when the bromine color ceased to disappear (calculated amount, 27.12 g.). The chloroform was allowed to evaporate and the residue distilled under reduced pressure. After two fractionations, 39 g. of β,γ-dibromopropylbenzene distilled at 114–115° (5 mm.). It boils under atmospheric pressure at 242–244° with considerable decomposition; d_4^{20}, 1.62.[11]

Calcd. for $C_9H_{10}Br_2$: Br, 57.51. Found: 57.52, 57.70.

Effect of Aluminum Chloride on Mixtures of Benzene with Phenylethyl Alcohol, Phenylpropyl Alcohol and Saturated Aliphatic Alcohols

The conditions in each case were as nearly the same as those used with allyl alcohol and the aromatic alcohols as possible. Two molecular equivalents of the alcohol were dissolved in ten equivalents of benzene and treated with one equivalent of aluminum chloride. The temperature was kept at 20–25°. Hydrogen chloride was slowly evolved, but there was no evidence of vigorous reaction. After standing overnight the mixture was decomposed, extracted and distilled as usual.

In the following table there is recorded the amount of distillate which came over in the second distillation within a range of 10° on either side of the boiling point of the expected alkyl benzene.

Alcohol	methyl	ethyl	propyl	*iso*propyl	butyl	*iso*butyl	*iso*-amyl	phenyl-ethyl	phenyl-propyl
Temp., °C.	103–122	126–146	149–169	143–163	170–190	161–181	180–204	274–294	280–300
Distil-late, g.	0.30	0.10	0.15	0.10	0.00	0.00	0.00	0.15	0.20

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[10] Errera, *Gazz. chim. ital.*, **16**, 320 (1886); *J. Chem. Soc.*, **52**, 35 (1887).

[11] Luib, *Ann.*, **283**, 304 (1894).

Summary

1. Of the alcoholic derivatives of aromatic hydrocarbons, only those in which the hydroxyl is on the carbon atom adjacent to the ring condense with benzene in the presence of aluminum chloride.

2. The saturated aliphatic alcohols up to and including amyl alcohol do not react with benzene in the presence of aluminum chloride to form alkylbenzenes.

3. Allyl alcohol condenses with benzene to give a fair yield (16%) of allylbenzene: $CH_2{=}CHCH_2OH + C_6H_6 \longrightarrow CH_2{=}CHCH_2C_6H_5 + H_2O$.

4. Unsaturation on the carbon atom, adjacent to the alcoholic group, increases the reactivity of the hydroxyl toward the dehydrating effect of aluminum chloride.

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THE CONSTITUTION OF CATECHIN. IX. SOME NEW DISINTEGRATION PRODUCTS OF ACACATECHIN

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Various formulas have been suggested by Freudenberg and his collaborators for catechin including Formula I, which was considered untenable[1] in 1924, but is now regarded as the correct formula for epicatechin[2] and catechin[3] respectively, since cyanidin chloride (II) may be reduced to epicatechin. It is beyond the limits of the present communication to discuss the validity of this formula of cyanidin chloride and reference must be made to (1) Willstätter and Mallison,[4] from whom it will become evident that the formula of cyanidin chloride is based on very slender evidence and (2) to Willstätter, Zechmeister and Kindler[5] as well as to the work of Pratt and Robinson[6] from which it will also become evident that so far no convincing synthesis of cyanidin chloride has been accomplished by these workers since the synthetic products obtained by them have been shown only to be similar to but not convincingly identical with cyanidin chloride. As the matter stands at present there is as much evidence in favor of Formula IV for cyanidin chloride as for Formula II[7] and the production of catechin from cyanidin chloride may well be quoted in favor of the author's formula (V) for acacatechin.

[1] Freudenberg, Orthner and Fikentscher, *Ann.*, **436**, 290 (1924).

[2] Freudenberg, Fikentscher, Harder and Schmidt, *Ann.*, **444**, 135 (1925).

[3] Freudenberg, Carrara and Cohn, *Ann.*, **446**, 87 (1925).

[4] Willstätter and Mallison, *Ann.*, **408**, 24 (1915).

[5] Willstätter, Zechmeister and Kindler, *Ber.*, **57**, 1944 (1924).

[6] Pratt and Robinson, *J. Chem. Soc.*, **127**, 172 (1925).

[7] Compare Ref. 4, p. 23.