[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Condensation of Aliphatic Alcohols with Aromatic Compounds in the Presence of Aluminum Chloride. I[1]

BY R. C. HUSTON AND T. Y. HSIEH[2]

Papers from this Laboratory[3] have described the condensation of aromatic and unsaturated aliphatic alcohols with aromatic hydrocarbons and phenols by means of anhydrous aluminum chloride. These experiments indicated that unsaturation of the alpha-carbon atom, whether it be double bonded or a member of the benzene ring favors condensation. The following saturated aliphatic alcohols did not condense to an appreciable extent with benzene under the same conditions used in the condensation of aromatic or unsaturated alcohols, *viz.*, methyl, ethyl, propyl, isopropyl, isobutyl, isoamyl, phenylethyl and phenyl propyl alcohols.

By using a slightly modified technique fair yields of condensation products have now been obtained with benzene and the following secondary alcohols: isopropyl, *s*-butyl, methyl-*n*-propylcarbinol and methylisopropylcarbinol. Under the same conditions primary alcohols up to and including *n*-hexyl alcohol did not react.

In these condensations 0.5 equivalent of aluminum chloride was added to from 2 to 5 equivalents of benzene. The mixture was vigorously stirred while one equivalent of the carbinol was added drop by drop from a dropping funnel. The temperature was kept below 30°. The usual reaction phenomena were exhibited: hydrochloric acid was evolved and the reaction mixture turned a deep red. After standing overnight, the mixture was decomposed with ice and hydrochloric acid. The benzene layer was removed and the aqueous portion extracted with ether. The combined ether and benzene extract was finally fractionated through a 30-cm. column.

Dimethylphenylmethane[4] (cumene) (b. p. 152–154°), methylethylphenylmethane[5] (b. p. 172–174°), methyl-*n*-propylphenylmethane[6] (b. p. 191–193°), methylisopropylphenylmethane[7] (b. p. 189–191°) were prepared in this way by condensation of the corresponding secondary alcohols with benzene, with yields of 25–28%.

Application of a similar technique to the condensation of *t*-butyl alcohol and benzene gave a 67% yield of trimethylphenylmethane.

Of a number of alcohols studied, those containing the tertiary groups were found to be much more reactive than the secondary alcohols, indicating as a second factor a relationship between the number of alkyl groups on the carbinol carbon atom and the tendency of the hydroxyl group to combine with a hydrogen of the aromatic ring to form water.

Condensation with Phenol

Investigations of the condensation capabilities of primary aliphatic alcohols (ethyl, propyl and butyl) in which aluminum chloride was added to a solution of the alcohol and phenol in an inert solvent, gave negative results. Under similar conditions, *s*-propyl alcohol reacted to give a small amount of a compound still under investigation which does not correspond in properties to any of the known propyl phenols or phenyl propyl ethers. Secondary butyl alcohol did not react.

Tertiary aliphatic alcohols were found to condense readily with phenol to give the *para* alkyl phenol. In these condensations a technique similar to that employed in the condensation of aromatic alcohols and phenols was used.[8]

A mixture of the tertiary alcohol (0.25 mole) and phenol (0.25 mole) was suspended in a suitable inert solvent such as petroleum ether and stirred mechanically while anhydrous aluminum chloride (0.125 mole) was added at a rate which maintained the temperature between 25 and 30°. The mixture was allowed to stand for several hours and was then decomposed with ice and hydrochloric acid. The alkyl phenol was isolated either by fractionation of the ether extract or by crystallization. Yields varied between 45 and 60%.

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(1) The material in this paper, together with information on the condensation of *t*-butyl, *t*-amyl and *t*-hexyl alcohols with benzene was presented before the Organic Section of the American Chemical Society at its meeting Sept. 10–14, 1934, at Cleveland, Ohio. See Tzukervanik, *J. Gen. Chem. U. S. S. R.*, **5**, 117, 764, 767 (1935) (*C. A.* **29**, 4746 (1935); **30**, 443 (1936)).

(2) From a thesis submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) R. C. Huston and K. Goodemoot, THIS JOURNAL, **56**, 2432 (1934); R. C. Huston and A. L. Houk, *ibid.*, **54**, 1506 (1932).

(4) Jacobsen, *Ber.*, **8**, 1260 (1875); Gustavson, *ibid.*, **11**, 1251 (1878); Radziewanoski, *ibid.*, **28**, 1137 (1895).

(5) Klages, *ibid.*, **35**, 2642, 3509 (1902).

(6) Klages, *ibid.*, **35**, 3509 (1902).

(7) Klages, *ibid.*, **36**, 3691 (1903).

(8) R. C. Huston, THIS JOURNAL, **46**, 2775 (1924).

TABLE I

CONDENSATIONS OF TERTIARY ALCOHOLS WITH PHENOL

Product	B. p., °C. (740 mm.)	M. p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-*t*-Butylphenol[9]	236–238	99–100				
p-*t*-Amylphenol[10]	248–250	94–95				
Di-Me-*n*-Pr-*p*-OH-Ph-methane	259–261	37–38	80.89	80.74	10.11	10.06
Di-Me-*i*-Pr-*p*-OH-Ph-methane	266–268	105–106	80.89	80.80	10.11	10.00
Di-Et-Me-*p*-OH-Ph-methane	268–269	59–60	80.89	80.95	10.11	10.17

Proof of Structure of Tertiary Hexyl Phenols.—The *t*-hexyl alcohols were condensed with benzene and each tertiary alkyl benzene was then nitrated by treatment with an equal weight of fuming nitric acid (1.52) at room temperature for two hours.[11] After washing and drying, the products were distilled under reduced pressure.

TABLE II

p-NITRO-*t*-ALKYLBENZENES, $C_{12}H_{17}O_2N$

Compound, -methane	B. p., °C. (3 mm.)	Nitrogen, % Calcd.	Nitrogen, % Found
p-Nitrophenyl-dimethyl-*n*-propyl-	124–126	6.76	6.81
p-Nitrophenyl-dimethyl-*i*-propyl-	122–124	6.76	6.73
p-Nitrophenyl-diethyl-methyl-	123–125	6.76	6.70

TABLE III

p-AMINO-*t*-ALKYLBENZENES, $C_{12}H_{19}N$

Compound, -methane	B. p., °C. (3 mm.)	Nitrogen, % Calcd.	Nitrogen, % Found
p-Aminophenyldimethyl-*n*-propyl-	107–109	7.91	7.78
p-Aminophenyldimethyl-*i*-propyl-	109–111	7.91	7.95
p-Aminophenyldiethylmethyl-	108–110	7.91	7.85

A 2-g. portion of each of these nitro compounds was oxidized by heating with 25 cc. of dilute nitric acid (1.20) in a Carius tube at 130° for from ten to fifteen hours.[10] The mixture was poured into 400 cc. of water. The *p*-nitrobenzoic acid was suction filtered, washed with cooled ether and recrystallized to a melting point of 238–240°. A mixed melting point determination showed no depression.

Each of the above *p*-nitro-hexylbenzenes was reduced to the amino derivative by means of tin and hydrochloric acid under the following conditions.

Thirty grams of tin in a 500-cc. round-bottomed flask fitted with an air condenser was treated with 100 cc. of concentrated hydrochloric acid and then 20 g. of *p*-nitro-*t*-hexylbenzene. After eight hours the mixture was treated with water and made alkaline with sodium hydroxide. The amine was steam distilled, extracted with ether, dried over solid potassium hydroxide and distilled under reduced pressure.

Diazotization of the amines gave in each case the same phenol as was produced directly by condensation of the alcohol with phenol by means of aluminum chloride. The following technique was used.

Five grams of *p*-amino-*t*-hexylbenzene was treated with 2.5 cc. of concentrated sulfuric acid in 15 cc. of water. The solid salt was suspended in 300 cc. of water cooled to 5° and diazotized with 1.9 g. of sodium nitrite in 8 cc. of water. This was added slowly beneath the surface of the stirred

TABLE IV

BENZOYL ESTERS OF *p*-*t*-ALKYLPHENOLS

Compound	M. or b. p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-*t*-Butylphenol[12]	M 81–82					
p-*t*-Amylphenol[11]	M 60–61					
Di-Me-*n*-Pr-*p*-OH-Ph-methane	B 169–171(3 mm.)	$C_{19}H_{22}O$	80.80	80.66	7.86	7.65
Di-Me-*i*-Pr-*p*-OH-Ph-methane	M 54–55	$C_{19}H_{22}O$	80.80	80.71	7.86	7.81
Di-Et-Me-*p*-OH-Ph-methane	M 77–78	$C_{19}H_{22}O$	80.80	80.72	7.86	7.79

TABLE V

BENZENE SULFONYL ESTERS OF *p*-*t*-ALKYLPHENOLS

Compound	M. or b. p., °C. (3 mm.)	Formula	Sulfur, % Calcd.	Sulfur, % Found
p-*t*-Butylphenol	M 70–71	$C_{16}H_{18}O_3S$	11.03	10.97
p-*t*-Amylphenol	B 184–185	$C_{17}H_{20}O_3S$	10.52	10.26
Di-Me-*n*-Pr-*p*-OH-Ph-methane	B 174–175	$C_{18}H_{22}O_3S$	10.06	9.88
Di-Me-*i*-Pr-*p*-OH-Ph-methane	B 178–179	$C_{18}H_{22}O_3S$	10.06	9.91
Di-Et-Me-*p*-OH-Ph-methane	B 183–184	$C_{18}H_{22}O_3S$	10.06	9.98

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(9) Kreysler, *Ber.*, **18**, 1717 (1885); Studer, *Ann.*, **211**, 246 (1882).

(10) Anschütz and Beckerhoff, *ibid.*, **327**, 219 (1903).

(11) Malherbe, *Ber.*, **52**, 319 (1919).

(12) Kreysler, *ibid.*, **18**, 1717 (1885).

TABLE VI

p-TOLUENE SULFONYL ESTERS OF *p*-*t*-ALKYLPHENOLS

Compound	M. or b.p., °C. (3 mm.)	Formula	Sulfur, % Calcd.	Sulfur, % Found
p-*t*-Butylphenol	M 109–110	$C_{17}H_{20}O_3S$	10.52	10.44
p-*t*-Amylphenol	M 54–55	$C_{18}H_{22}O_3S$	10.06	9.93
Di-Me-*n*-Pr-*p*-OH-Ph-methane	B 194–195	$C_{19}H_{24}O_3S$	9.64	9.72
Di-Me-*i*-Pr-*p*-OH-Ph-methane	B 187–188	$C_{19}H_{24}O_3S$	9.64	9.57
Di-Et-Me-*p*-OH-Ph-methane	B 188–189	$C_{19}H_{24}O_3S$	9.64	9.60

suspension from a dropping funnel the delivery tube of which had been drawn to a capillary. The diazotized solution was then warmed on a water-bath and steam distilled. The tabulated esters were prepared by the pyridine method.[13]

Summary

1. Aliphatic tertiary alcohols condense with phenol in the presence of aluminum chloride to give good yields of *p*-tertiary-alkyl phenols.

2. The benzoyl, benzene sulfonyl and *p*-toluene sulfonyl esters of five phenols were prepared.

3. Aliphatic secondary and tertiary alcohols condense with benzene to give the corresponding alkylbenzenes. The tertiary alcohols react much more readily and give higher yields than the secondary alcohols.

4. Aliphatic primary alcohols do not condense with either phenol or benzene in the presence of aluminum chloride, under the given experimental conditions.

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[13] Einhorn and Holland, *Ann.*, **301**, 95 (1898).

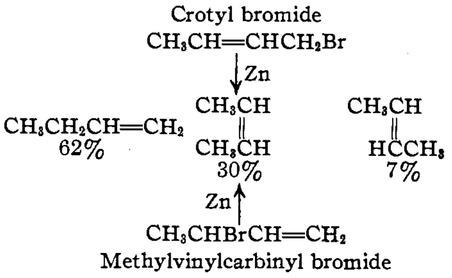
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. III. The Action of Zinc on Crotyl and Methylvinylcarbinyl Bromides[1]

BY WILLIAM G. YOUNG AND SAUL WINSTEIN

A previous communication from this Laboratory[2] mentioned the possibility of allylic rearrangement during the preparation of butenes from mixtures of crotyl and methylvinylcarbinyl bromides by the formation and hydrolysis of the Grignard reagents of these bromides or by treatment of the bromides with zinc in alcohol. Recently we were able to show that rearrangement to an equilibrium took place during the preparation and hydrolysis of the Grignard reagents of these bromides.[3] It is the purpose of this paper to present evidence that an allylic rearrangement to a different equilibrium takes place in the analogous process of reducing the bromides with zinc, as shown below.

We have treated various mixtures of crotyl and methylvinylcarbinyl bromides with zinc in alcohol and have analyzed the resulting butene mixtures by the dibromobutane reaction rate method.[4]



The same butene mixture was obtained from all of the bromide mixtures.

Experimental Part

The preparation of mixtures of crotyl and methylvinylcarbinyl bromides was carried out as previously described.[5] None of the products used in this work contained butyl bromide. Carius analyses gave values within 0.15 of the calculated value of 59.20% Br. The refractive indices of the bromide mixtures and the corresponding compositions are given in the Table of Results.

The conversion of the bromides to butenes was carried out in the same apparatus used for the preparation of the Grignard reagents.[6] The bromides were dropped into zinc dust in boiling aqueous alcohol, the evolved butene

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(1) This work was accomplished with the aid of a grant from the Board of Research of the University of California.

(2) Young and Prater, THIS JOURNAL, **54**, 404 (1932).

(3) Young, Winstein and Prater, *ibid.*, **58**, 289 (1936).

(4) (a) Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930); (b) Young and Winstein, *ibid.*, **58**, 102 (1936).

(5) Winstein and Young, *ibid.*, **58**, 104 (1936).

(6) Young, Prater and Winstein, *ibid.*, **55**, 4908 (1933).