ACTION OF THE TERTIARY ALIPHATIC CARBINOLS WITH AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE

THESIS FOR THE DEGREE OF M. S.

Wallace Burgess Fox

1934

R. C. Huston
5/24/34

ACTION OF THE TERTIARY ALIPHATIC CARBINOLS WITH AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE

ACTION OF THE TERTIARY ALIPHATIC CARBINOLS WITH AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE

by

WALLACE BURGESS FOX

THESIS

Submitted to the faculty of Michigan
State College of Agriculture and
Applied Science as partial fulfillment of the requirements for the
degree of Master of Science

JUNE, 1934

6-29-54
a
l

ACKNOWLEDGEMENT

This thesis signifies the completion of a task. It is with a feeling of deep appreciation that the author realizes that it was the helpful co-operation of Dr. R. C. Huston which made the consummation of this work possible.

CONTENTS

page

Historical

Experimental

Condensations

Theoretical

HISTORICAL

A. Condensations

The condensation of aromatic alcohols with aromatic compounds to form derivatives of di- or triphenylmethane is commonly brought about by the following dehydrating agents: sulfuric acid (Meyer and Wurster, *Ber.*, 6, 964, 1873; Becker, *Ibid.*, 15, 2091, 182; Noelting, *Ibid.*, 24, 3127, 3136, 1891; Gatterman and Koppert, *Ibid.*, 26, 2811, 1893; Bistrzycki and Flatau, *Ibid.*, 28, 989, 1895; Fritsch, *Ibid.*, 29, 2300, 1896; Bistrzycki and Simonis, *Ibid.*, 31, 2812, 1898; etc.), phosphorus pentoxide (Hemilian, *Ber.* 7, 1203, 1874; Michael and Jeanpretre, Ibid., 25, 1615, 1892; etc.), zinc chloride (Fischer and Roser, *Ber.*, 13, 674, 1879; *Ann.*, 206, 113, 155, 1880; Liebmann, *Ber.*, 15, 152, 1882; Kippenberg, *Ibid.*, 30, 1140, 1897; etc.), dilute or concentrated hydrochloric acid (Sunis, *Bull.*, 3, 17, 517, 1897; D.R.P. 27032; Noelting, *Ber.*, 24, 3127, 1891; Noelting, *Ibid.*, 24, 553, 1891; etc.), sulfuric and acetic acids (Paterno and Fileti, *Gazz.*, 5, 381, 1875; Mohlau and Klopfer, *Ber.*, 32, 2147, 2149, 1899), absolute alcohol (Mohlau and Klopfer, *Ber.*, 32, 2150, 2153, 1899), stannic chloride (Bistrzycki, *Ibid.*, 37, 659, 1904), and acetic acid (Khotinski and Patzewitch, *Ibid.*, 42, 3104, 1909).

Aluminum chloride has been used as a dehydrating agent in organic chemistry by Merz and Weith (*Ber.*, 14, 189, 1881), Shell and Seer (Ann., 394, 119, 1912), Wass (Ber., 15, 1128, 1882), Graebe (Chem. Ztg., 25, 268, 1901; Ber., 34, 1778, 1901), Jaubert (Compt. rend., 132, 841, 1901), Frankforter and Kritchevsky (J. Am. Chem. Soc., 36, 1511, 1914; 37, 385, 1915), Frankforter and Kokatnur, Ibid., 36, 1529, 1914, and others (Ber., 40, 1694, 1907; D.R.P. 136,015; etc.).

To include all condensations and reactions which have been carried out in the presence of aluminum chloride is somewhat beyond the scope of this paper. However, it was felt necessary to include a brief resumé of those experimentations which have dealt with the reactions of alcohols with aromatic compounds in the presence of aluminum chloride. These several alcohols include aromatics, aliphatics, and mixed aromatic aliphatics.

The first work reported in connection with the dehydrating action of aluminum chloride on aromatic alcohols and aromatic compounds was that of Huston and Friedemann (J. Am. Chem. Soc., 38, 2527, 1916). They found that the principal product of the reaction between benzyl alcohol and benzene in the presence of aluminum chloride was diphenylmethane:

$$C_6H_5CH_2OH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + H_2O$$

If equimolecular amounts of the reacting substances are used, the yield of diphenylmethane is not large (about 30%) and the yields of secondary products (p- and o-dibenzylbenzene, anthracene and tar) are quite large. If, however, an excess (5 mols) of benzene is used the yield of diphenylmethane is greatly increased, while the yields of secondary products are correspondingly decreased.

Later work done by Huston and Friedemann (*J. Am. Chem. Soc.*, 40, 785, 1918) showed definitely that secondary aromatic alcohols condense with benzene under the dehydrating influence of anhydrous aluminum chloride according to the following general equation:

$$C_6H_5\text{-}\underset{R}{CHOH} + C_6H_6 \xrightarrow{AlCl_3} C_6H_5\text{-}\underset{R}{CH}C_6H_5 + H_2O$$

When R is the phenyl group the reaction is smoother and a larger yield of the condensation product is obtained than when R is methyl or ethyl. The ethyl group has a greater retarding effect on the reaction than the methyl group. An excess of aluminum chloride tends to eliminate a phenyl or an alkyl radical from the product especially if the temperature is not kept low.

Huston (*J. Am. Chem. Soc.*, 46, 2775, 1924) reports that benzyl alcohol reacts with phenol at low temperatures in the presence of aluminum chloride to form p-benzyl phenol:

$$C_6H_5CH_2OH + C_6H_5OH \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4OH + H_2O$$

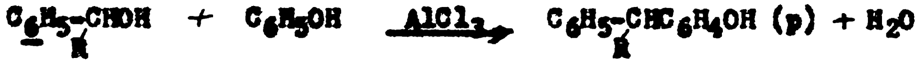
The methyl and ethyl esters of p-benzylphenol may be prepared in good yield by condensing benzyl alcohol with anisole or phenetole. The phenolic hydroxyl group does not interfere with the substitution of the benzyl group in the benzene ring by means of the aluminum chloride.

The action of aliphatic alcohols were next considered. Huston and Sager (*J. Am. Chem. Soc.*, 48, 1955, 1926) report that the saturated aliphatic alcohols do not condense with benzene. These alcohols included methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl and iso-amyl. Also, phenyl ethyl alcohol and phenyl propyl alcohol show no condensation with benzene. It is interesting to note that phenylmethyl carbinol and phenylethyl carbinol when heated under atmospheric pressure to their boiling points, lose water to form the corresponding unsaturated hydrocarbon, while phenylethyl alcohol and phenylpropyl alcohol may be distilled without decomposition at atmospheric pressure. This behavior was considered significant in that only those compounds in which the alpha carbon is a member of the benzene ring or is double bonded (as will be shown with allyl alcohol) show appreciable reactivity.

The unsaturated aliphatic alcohol, allyl alcohol was found to condense with benzene to give a fair yield (16%) of allyl benzene:

$$CH_2=CHCH_2CH + C_6H_6 \xrightarrow{AlCl_3} CH_2=CHCH_2C_6H_5 + H_2O$$

Similar to Huston and Friedemann's work on aromatic alcohols with benzene, Huston, Lewis and Grotemut (*J. Am. Chem. Soc.*, 49, 1365, 1927) found that methylphenyl carbinol, ethylphenyl carbinol and benzhydrol were condensed with phenol by means of anhydrous aluminum chloride according to the equation:



$$C_6H_5\text{-}\underset{R}{C}HOH + C_6H_5OH \xrightarrow{AlCl_3} C_6H_5\text{-}\underset{R}{C}HC_6H_4OH\ (p) + H_2O$$

Where R is methyl, ethyl or phenyl. A relatively large yield from benzhydrol further confirms the hypothesis that unsaturation of carbon atoms adjacent to the alcoholic groups increases the reactivity of the hydroxyl group.

Later work has shown that such compounds as diphenylethyl carbinol and diethylphenyl carbinol dehydrate when heated and do not themselves show any condensation with benzene. In the latter of these two cases, this inability to condense was explained by the fact that the phenyl and two alkyl groups seem to draw the OH group rather closely to its Carbon atom, thus inhibiting the action of the OH to split off a molecule of water with an H from the benzene ring.

Summarizing these several results, we can say:

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 (normal and iso- compounds, not tertiary aliphatics) up to and including amyl alcohol do not

react with benzene in the presence of aluminum chloride to form alkylbenzenes.

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

4. Of the mixed tertiary carbinols worked with, no condensation has been reported, but rather in its stead, dehydration of the carbinol to give the corresponding hydrocarbon.

B. Other Methods of Preparing the Tert-alkyl Benzenes

I. Tert-butyl benzene.

Shoesmith and Mackie (*J. Chem. Soc.*, 2334, 1928) tells that Schramm (*Monatsh.*, 9, 615, 1888) proved that *iso-* or *tert*-butyl chloride condensed with benzene in presence of aluminum chloride to give *tert*-and not *iso*-butyl benzene.

Shoesmith and Mackie (loc. cit.) go on to state that iso-butyl alcohol was converted to a mixture of iso- and tert-butyl chlorides by means of zinc chloride and phosphorous trichloride (Dehn and Davis, *J. Am. Chem. Soc.*, 29, 1322, 1907), but only a 32% yield could be obtained, the chief product being apparently a mixture of polymerised butylenes. The m ixed chlorides were condensed with benzene; continuous stirring and efficient apparatus improved the yield, and white aluminum chloride of very good quality was found to be advantageous. The tert-butyl benzene had b. p. 165-170° C.

Verley (*Bull.*, 3, 19, 72, 1898) prepared tert-butyl benzene from iso-butyl alcohol and benzene, using 30% fuming sulfuric acid as the dehydrating agent. His procedure:

"Mix 500 gm. of iso-butyl alcohol and 2 kilograms of benzene. Stir continually, cool, and add 2 kilograms of 30% fuming sulfuric acid. At the end of ¾ hour of stirring, wash the entire mass with water, and fractionate.

These quantities are obtained:

263 gm. at 75-78° (22 mm.)

150 " " 120-121° (22 mm.)

The first portion boils at 165-166° under ordinary pressure; it is pur tert-butyl benzene.

As for the portion at 120-121°, which crystallises, it corresponds to the formula of diiso-butyl benzene".

(It seems that Verley is referring here to p-di-tert-butyl benzene. The authors have prepared that compound (see page 14). It boils at 114-116° (18 mm.) and is crystalline in nature)

Boedtker (*Bull.*, 3, 31, 966, 1904) prepared tert-butyl benzene by treating tert-butyl alcohol with gaseous hydrochloric acid. The chloride formed is treated with benzene and aluminum chloride.

II. Tert-Amyl Benzene

Gleditsch (*Bull.*, 3, 35, 1094, 1906) prepared this hydrocarbon from iso-amyl chloride and benzene with aluminum chloride. Iso-amyl alcohol was treated with gaseous HCl and heated in a sealed tube. From 180 gm. of iso-amyl chloride and 30 gm. aluminum chloride, 80 gm. of tert-~~butyl~~ amyl benzene, $C_6H_5-C(CH_3)_2-C_2H_5$. B.P. 189-190°; density, $^{21.5°}_{4°}$ = .8657; $N_D^{23°}$ = 1.4915.

III. Dimethyl n-Propylphenyl Methane

Dimethyl n-propylphenyl methane is prepared (*J. fur* *praktische Chem.*, 2, 82, 293) by heating 2-chlor 2-methyl pentane with benzene and aluminum chloride; B. P. 205-206°.

EXPERIMENTAL

Materials.----Tert-butyl alcohol was obtained commercially. Tert-amyl alcohol was a laboratory classroom preparation by use of acetone and ethylmagnesium bromide. It was dried over anhydrous magnesium sulfate and purified by fractionation. It boils at 102° C. at atmospheric pressure.

Dimethyl n-propyl carbinol was prepared in a similar manner n-propyl bromide and acetone by Grignard reaction. It was first necessary to prepare the bromide from the corresponding alcohol and hydrobromic acid (sodium bromide and sulfuric acid). The carbinol boils at 122-124° C. at atmospheric pressure.

Dimethyl iso-propyl carbinol was prepared from iso-propyl bromide and acetone. Again it was first necessary to prepare the bromide from the alcohol. The carbinol boils at 119-120° C.

Chemically-pure thiophene-free benzene was used in all condensations. The anhydrous aluminum chloride was a good grade commercial product.

Condensations

A.

Tert-butyl Alcohol, Benzene and Aluminum Chloride, I.--

18½ gm.	-	¼	mole	-	1 eq.	alcohol
97½ "	-	5/4	"	-	5 "	benzene
17 "	-	1/8	"	-	½ "	$AlCl_3$

The alcohol, b.p. 83°, was dissolved in the benzene and the solution stirred constantly during the addition of the aluminum chloride. Two hours elapsed during this operation. Copious amounts of hydrogen chloride were evolved during the reaction. A temperature of not over 30° was maintained easilty; a water bath being necessary only occasionally. The entire mixture was stirred for an additional two hours. Solution turns a dark red-brown. Allowed to stand over night. It was then decomposed with ice and dilute hydrochloric acid. The benzene layer was separated and the aqueous portion extracted thrice with ether. In the ether extraction, it is necessary to add HCl to destroy the ether-water emulsion which results. Anhydrous calcium chloride was used to dry the solution. The ether was distilled and the residue added to the benzene portion. This was fractionated three times. These fractions were obtained:

110-165°	2.5 gm.
166-170°	8.0 "
above 170°	1.7 "

The fraction boiling at 166-170° is tert-butyl benzene.

Equation of the reaction:

$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH + C_6H_6 \xrightarrow{AlCl_3} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_5 + H_2O$$

Tert-butyl Alcohol, Benzene and Aluminum Chloride, II.-- Same amounts as I, above, were used. Instead of dissolving the alcohol in the benzene and then proceeding as usual, adding aluminum chloride from time to time, the aluminum chloride was added in its entirety to the benzene. The alcohol was allowed to drop slowly into the stirred solution. It was necessary to add a small amount of petroleum ether to the alcohol to prevent its precipitation (M.P. 25°). As the alcohol is added, the solution darkens rapidly; hydrogen chloride is given off freely. Temperature not over 30°. Allow to stand overnight. Decompose with ice and dilute HCl. Extract with ether. Distill and fractionate three times:

110-166°	4.4 gm.	
166-170°	17.2 "	tert-butyl benzene
above 170°	5.4 "	

Tert-butyl Alcohol, Benzene and Aluminum Chloride, III.-- Same amounts and procedure as II, above. However, the stem of the dropping funnel used was pulled out into a capillary, thus simplifying the dropping of the alcohol into the stirred solution. After about tw-thirds of the alcohol had been added, it seemed to adhere to the side of the jar. No more HCl gas is given off. Two hours elapsed during the addition. After refraction:

110-166°	3.4 gm.	
166-170°	14.7 "	tert-butyl benzene
above 170°	3.9 "	

Tert-butyl Alcohol, Benzene and Aluminum Chloride, IV.-- It was felt that perhaps, all of the alcohol was not used up in the previous condensation, so accordingly, 146 gm. benzene and 25½ gm. aluminum chloride (½ more equivalents of each) were used with the original amount of alcohol. Three hours elapsed in adding the alcohol. HCl was given off during the entire addition of the alcohol. After fractionating:

110-166°	2.4 gm.	
166-170°	12.6 "	tert-butyl benzene
above 170°	5.6 "	

The additional aluminum chloride seems to lower the yield of tert-butyl benzene and cause a subsequent increase in yield of the higher boiling fraction.

Tert-butyl Alcohol, Benzene and Aluminum Chloride, V.--- Same conditions and procedure as II and III, above. Double quantities of each compound were used. 48 gm. of tert-butyl benzene were obtained.

Tert-butyl Alcohol, Benzene and Aluminum Chloride, VI.-- Same as V, above. 37 gm. of tert-butyl benzene obtained.

The higher boiling fractions of these condensations were combined and re-fractionated. A fraction at 230-235°, atmospheric pressure, was separated. After standing for some time (several months), several crystals were noted on the neck of the flask. The liquid was seeded with one of these crystals and the whole placed in the refrigerator for several days. 1½ grams were obtained, which when crystallized from alcohol, melt at 77°. It is p-di tert-butyl benzene. The crystals have a quite definite shape, which is best described as being long rhombic.

Table of Results

	Benzene			t-butyl alcohol			aluminum chloride			t-butyl benzene	
No.	gm.	eq.	mol.	gm.	eq.	mol.	gm.	eq.	mol.	gm,	% yield
I	97½	5	5/4	18½	1	¼	17	½	1/8	8.0	24%
II	"	"	"	"	"	"	"	"	"	17.2	51%
III	"	"	"	"	"	"	"	"	"	14.2	44%
IV	146	7½	1 7/8	"	"	"	25½	¾	3/16	12.6	37%
V	195	5	2½	37	"	½	34	½	¼	48.0	67%
VI	"	"	"	"	"	"	"	"	"	37.0	55%

It will be noted that in V and VI when larger quantities are used, the yield is more than accordingly increased. With the exception of I, the aluminum chloride was added to the benzene and the alcohol dropped into the stirred solution. All these condensations were run at or below 30°.

B.

Tert-butyl Alcohol, tert-butyl Benzene, Aluminum Chloride, I-- Seven and one-half grams of aluminum chloride mixed with 45 gm. of tert-butyl benzene. Eight grams tert-butyl alcohol dropped into stirred solution. Temperature rose to 40°; cooled down to 30°. HCl given off. Solution darkens. Stand overnight. Decompose with ice and HCl. Upon fractionation:

28.1 gm. tert-butyl benzene recovered

3.5 " p-di-tert-butyl benzene, B.P. 235° (736 mm)
114-116°(18 mm)

The p-di-ert-butyl benzene solidifies. Crystallize from ethyl alcohol twice. White plates. M.P. 77-78°.

The reaction:

$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH + C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{AlCl_3} (CH_3)_3C-C_6H_4-C(CH_3)_3\ (p) + H_2O$$

Tert-butyl Alcohol, tert-butyl Benzene, Aluminum Chloride, II-- Identical to above. Upon fractionation:

27.5 gm. tert-butyl benzene recovered

4.5 " p-di-tert-butyl benzene

Table of Results

No.	t-butyl benzene gm.	eq.	mol.	t-butyl alcohol gm.	eq.	mol.	aluminum chloride gm.	eq.	mol.	p-di-t-butyl benzene gm.	% yield
I.	45	3	1/3	8	1	1/9	7½	½	1/18	3.5	17%
II.	"	"	"	"	"	"	"	"	"	4.5	22%

C.

Tert-amyl Alcohol, Benzene, and Aluminum Chloride, I.---22 grams alcohol; 97½ gm. benzene; 17 gm. aluminum chloride. $AlCl_3$ in benzene. Alcohol added through capillary. Stir. 1½ hours. HCl given off. Darkening of solution. After about 2/3 of alcohol had been added, coagulation on side of jar with little or no appreciable amount of gas given off. 50 cc. of benzene added. Stand overnight. Decomposed. Extracted. Distilled. After three fractionations:

180-189° 4.5 gm.
189-191° 13.5 " tert-amyl benzene
above 191° 10.0 "

The reaction:

$$H_3CH_2C-\underset{CH_3}{\overset{CH_3}{C}}-OH + C_6H_6 \xrightarrow{AlCl_3} H_3CH_2C-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5 + H_2O$$

Tert-amyl Alcohol, Benzene, and Aluminum Chloride, II.---Identical conditions and materials as above. Temp. 25-30°. No rising of temperature and No cooling with water necessary. These fractions:

85-189°	5.5 gm.	
189-191°	15.0 "	tert-amyl benzene
above 191	8.5 "	

Note that there is less amount of the higher fraction with a corresponding increased in yield of the alkyl benzene as compared with the first condensation.

Tert-amyl Alcohol, Benzene, and Aluminum Chloride, III.---Double the quantities of I above. Water bath used to cool condensing material. After ½ of alcohol had been added, $AlCl_3$ formed a dark mass making stirring difficult. Water bath removed allowing temp. to rise (32°); $AlCl_3$ mass broke up, stirring continued. HCl given off during rest of addition of alcohol. After fractionating:

85-189°	2.5 gm.	
189-191°	45.2 "	tert-amyl benzene
above 191°	9.0 "	

Table of Results

	Benzene			t-amyl alcohol			aluminum chloride			t-amyl benzene	
No.	gm.	eq.	mol.	gm.	eq.	mol.	gm.	eq.	mol.	gm.	% yield
I	97½	5	5/4	22	1	¼	17	½	1/8	13.5	36.5%
II	"	"	"	"	"	"	"	"	"	15.0	41%
III	195	"	2½	44	"	½	34	"	¼	45.2	61%

Note here, as with the tert-butyl compound, there is a considerable increase in the percentage of yield when a larger quantity is used in the starting materials.

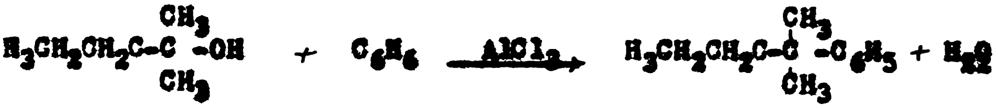
D.

Dimethyl n-propyl Carbinol, Benzene and Aluminum Chloride, I.-- $25\frac{1}{2}$ gm. carbinol; $97\frac{1}{2}$ gm. benzene; 17 gm. aluminum chloride. $AlCl_3$ added to benzene. Carbinol added drop by drop. HCl given off. The usual mechanism.

115-87°(15 mm.)	2.3 gm.	
87-87.5°(15 mm.)	23.5 "	dimethyl n-propyl phenyl methane
Above 87.5°(15 mm.)	4.5 "	

Under atmospheric pressure, the alkyl benzene boils at 205-6° (745 mm)

The reaction:



$$H_3CH_2CH_2C-\underset{CH_3}{\overset{CH_3}{C}}-OH + C_6H_6 \xrightarrow{AlCl_3} H_3CH_2CH_2C-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5 + H_2O$$

Dimethyl n-propyl Carbinol, Benzene and Aluminum Chloride, II.-- $38\frac{1}{2}$ gm. carbinol; 147 gm. benzene; 25 gm. aluminum chloride. After fractionating:

115-87°(15 mm.)	3.2 gm.	
87-87.5°(15 mm.)	~~23.0~~ 18.0 "	dimethyl n-propyl phenyl methane
above 87.5°(15 mm.)	5.2 "	

Table of Results

No.	Benzene gm.	Benzene eq.	Benzene mol.	dimethyl *n*-propyl carb. gm.	dimethyl *n*-propyl carb. eq.	dimethyl *n*-propyl carb. mol.	aluminum chloride gm.	aluminum chloride eq.	aluminum chloride mol.	dimethyl n-propyl phenyl methane gm.	dimethyl n-propyl phenyl methane % yield
I	97½	5	5/4	25½	1	¼	17	½	1/8	18.0	44%
II	147	"	1 7/8	38¼	"	3/8	25	"	3/16	23.0	38%

E.

Dimethyl iso-propyl Carbinol, Benzene and Aluminum Chloride, I and II.---Amounts and procedure as in II, immediately above. 21.5 gm. and 20 gm. of dimethyl iso-propylphenyl methane (B.P. 86-87° at 15 mm.; 209° at 745 mm.) were obtained in the two respective condensations.

The reaction:

$$C_6H_6 + HO-\underset{CH_3}{\overset{CH_3}{C}} - \underset{H}{\overset{CH_3}{C}}-CH_3 \xrightarrow{AlCl_3} C_6H_5-\underset{CH_3}{\overset{CH_3}{C}} - \underset{H}{\overset{CH_3}{C}}-CH_3 + H_2O$$

It had been thought that due to the close proximity of the methyl groups on the two adjacent C atoms of the carbinol, that the $AlCl_3$ would dehydrate the carbinol, producing tetramethyl ethylene, (B.P. 73°). This was not found to happen to any appreciable degree.

Table of Results

No.	Benzene gm.	Benzene eq.	Benzene mol.	dimeth iso prop. carb. gm.	dimeth iso prop. carb. eq.	dimeth iso prop. carb. mol.	aluminum chloride gm.	aluminum chloride eq.	aluminum chloride mol.	dimeth iso-propyl phenyl methane gm.	dimeth iso-propyl phenyl methane % yield
I	147	5	17/8	38¼	1	3/8	25	½	3/16	21.5	36%
II	"	"	"	"	"	"	"	"	"	20.0	34%

Nothing could be found in the literature on dimethyl isopropylphenyl methane. Combustion of it gave the following analysis for carbon and hydrogen:

Wt. sample	wt CO_2	% C	wt. H_2O	% H
0.2150	.6966	88.35	.2134	11.13
0.2019	.6566	88.69	.1986	11.01
Calculated for $C_{12}H_{18}$		88.81		11.19

Molecular weight determination for dimethyl iso-propyl phenyl methane gave the following result:

Wt. sample	Temp. diff.	Wt. Benzene	Mol. Wt.
0.5972	0.430	22.4098	165
Calculated for $C_{12}H_{18}$			162

The higher boiling fractions of each group of condensations have not, as yet, been separated. None of them give definitely boiling fractions.

Determination of Physical Constants

The density of each alkyl benzene was determined by means of a picnometer. Values given are for the compound at 20°, in relation to water at 4°.

The index of refraction was determined by use of the Abbé refractometer.

The Harkins (J. Am. Chem. Soc., 41, 499, 1919; 38, 228, 246, 1916) drop weight method was used to determine the surface tension of each compound. The radius of the dropping tip was .27122 cm. Temperature, 20°. The surface tension was calculated by this formula:

$$\gamma = \frac{m\,g}{2\pi r\ f(r/V^{1/3})}$$

where

γ = surface tension in dynes per centimeter

m = mass of drop in grams

g = pull of gravity (981 dynes)

r = radius of tip in cm.

V = volume of drop (is equal to m/density)

$f(r/V^{1/3})$ = fraction of ideal drop which falls

The molecular volume is calculated by dividing the molecular weight of the compound by its density. The molecular volume is the volume occupied by the molecular weight of the substa[illegible].

The observed parachor is equal to the molecular weight divided by the density times the ¼ power of the surface tension. Or more simply, the molecular volume times the ¼ power of the surface tension.

$$P = \frac{M}{D}\gamma^{1/4}$$

Table of Physical Constants

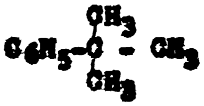
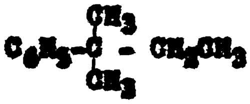
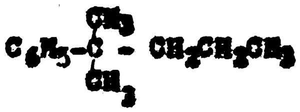
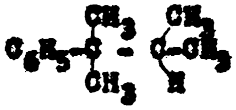
	mol. wt.	B.P.	Density $\frac{20^\circ}{4^\circ}$	$N_D^{20^\circ}$	wt. of drop	surface tension	V_m	Parachor (obs.)
t-butyl benzene	134.11	168-170° (740 mm)	.8659	1.4923	.02920	28.04 dynes	154.87	356.4
t-amyl benzene	148.13	189-191° (740 mm)	.8720	1.4924	.03011	28.91	169.88	393.9
dimethyl n-propyl phenyl methane	162.14	205-206° (745 mm) 87-87.5° (15 mm)	.8718	1.4934	.03015	28.95	185.97	431.4
dimethyl iso-propyl phenyl methane	162.14	209° (745 mm) 86-87° (15 mm)	.8814	1.4988	.03082	29.59	183.95	429.0

THEORETICAL

The condensation of the tertiary aliphatic carbinols with benzene is in itself significant. It definitely proves that of the simpler tertiary aliphatics, the OH is readily replaced by an aromatic group under the influence of anhydrous aluminum chloride. As with aromatic carbinols, one molecular equivalent of carbinol with five molecular equivalents of benzene in the presence of 0.5 molecular equivalent of aluminum chloride undoubtly gives the highest yield of the alkyl benzene. The higher boiling fractions which resulted from the condensations were not identified.

The reaction of tert-butyl benzene with tert-butyl alcohol to give in good yields (17 - 22%) p-di-tert-butyl benzene again substantiates the fact that when a substitient enters the nucleus of tert-butyl benzene it does so almost exclusively in the para-position, i.e., as far as possible from the tert-butyl group.

The Molecular Volume Problem

	$V_m\left(\frac{\text{Mol. wt.}}{\text{density}}\right)$	Difference
 $C_6H_5-C(CH_3)_2-CH_3$	154.87 cc.	
		15.01
 $C_6H_5-C(CH_3)_2-CH_2CH_3$	169.88 cc.	
		14.09
 $C_6H_5-C(CH_3)_2-CH_2CH_2CH_3$	185.97 cc.	
		14.07
 $C_6H_5-C(CH_3)_2-CH(CH_3)_2$	183.95 cc.	

The normal observed difference in V_m for each CH_2 is 16.27. However, we note here that the difference between tert-butyl benzene and tert-amyl benzene is 15.01. This is due to the fact that the third methyl group has a greater eurogenic effect than does the ethyl group in the tert-amyl benzene; thus, the density of tert-butyl benzene is decreased and the V_m is greater than it normally should be.

With tert-amyl benzene and dimethyl n-propylphenyl methane, the effectof the ethyl and n-propyl groups are about the same. The two methyl groups of each compound excert the same eurogenic effect and we find the difference in V_m of the two compounds is very near to that of the normally expected difference.

The most striking fact is the decrease of V_m of the dimethyl iso-propylphenyl methane in comparison to the V_m of dimethyl n-propylphenyl methane. This lowering is due to "heaping" of euregenic groups on adjacent carbon atoms. This seems paradoxical since euregens are these groups (CH_3, Cl, Br, $C=O$, OH, etc.) which increase V_m when "heaped". However, as has already been said, when this "heaping" is present on adjacent carbon atoms there is a lowering of molecular volume and, as will be seen later, a subsequent lowering of the parachor.

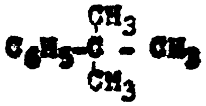
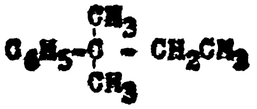
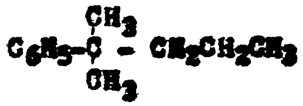
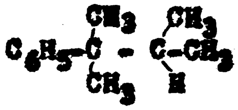
The lowering of the V_m in dimethyl iso-propylphenyl methane (the compound in which "heaping" is the greatest) is explained by the greater strain in the molecule. Molecular volume and parachor are directly related. And since the parachor is virtually a measure of molecular volume under comparable conditions as regards internal pressure, and is, therefore, more or less independent of the cohesion between molecules, the contraction referred to as strain constants would appear to connote a real diminution of molecular volume, brought about by the closer packing of atoms and groups within the molecule. This is found to be the case.

Note the boiling points of the last two compounds prepared:

Dimethyl n-propylphenyl methane,	205-206° (745 mm.)	Density,	.8718
Dimethyl iso-propylphenylmethane,	209° (745 mm.)	"	.8814

The more-branched chain would be expected to have the lower boiling point. The opposite of this which occurs in this instance is best explained by referring to the above explanation of the difference in V_m. By simple reasoning, since $V_m = \frac{\underline{\text{mol. wt.}}}{\text{density}}$, if V_m is less for the *iso* compound, then it follows that the density must be greater (which it is). Of the two isomeric compounds, the one with the greater density, will have the higher boiling point.

The Parachor Problem

	Observed	Calculated			
		Sugden	% Diff.	Mumford & Phillips	% Diff.
 $C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	356.4	363.1	+ 1.8	359.4	+ .8
 $C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CH_3$	393.9	402.1	+ 1.6	399.4	+ 1.4
 $C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CH_2CH_3$	431.4	441.1	+ 2.2	439.4	+ 1.8
 $C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_3$	429.0	441.1	+ 2.7	436.4	+ 1.7

Sugden's (*J. Chem. Soc.*, 125, 1177, 1924) constants for the calculation of the parachor were mainly evaluated from the earlier members of the various series of organic compounds irrespective of whether they had straight or branched chains. The atomic constants for carbon and hydrogen were deduced from molecular parachors in a rational manner. Says Sugden: "The values for a particular atom appear to be independent of the manner in which it is situated in the compound and with a few exceptions, position isomerism seems to cause no change in the parachor". However he did predict that this simple addition of atomic and constitutional factors will require some modifications when more precise values for the parachors are available.

Sugden's atomic and structural parachors:

$C = 4.8$ Double bond $= 23.2$

$H = 17.1$ 6-membered ring $= 6.1$

$CH_2 = 39.0$

Later work by Mumford and Phillips (*J. Chem. Soc.*, 33, 2112, 1929) considered the branched chain and its lessening effect on the parachor. Thier values:

$C = 9.2$ Double bond $= 19.0$

$H = 15.4$ 6-membered ring $= 0.8$

$CH_2 = 40.0$

The decrement due to chain branching in aliphatics has been fixed at -3.0 for all branched groups of the type CHR_2, and double this value for CR_3 radicals and doubly-branched compounds CHR_2——CHR_2.

With the tert-alkyl benzenes, the values of Mumford and Phillips give values for the parachor which check more closely with the observed than do these of Sugden.

If a -3.0 be added to each of these new values (as according to M & P) for the effect of the Ph group, a still closer check is obtained. The following values are obtained:

	Observed	Calculated	% Difference
tert-Butyl benzene	356.4	356.4	± 0.0
tert-Amyl benzene	393.4	396.4	+ 0.7
Di-methyl n-propyl phenyl methane	431.4	436.4	+ 1.1
Di-methyl iso-propyl phenyl methane	429.0	433.4	+ 1.0

SUMMARY

1. The tertiary aliphatic carbinols condense readily at or not over 30° with benzene in the presence of anhydrous aluminum chloride, according to the general equation

$$R'-\overset{R}{\underset{R}{C}}-OH + C_6H_6 \xrightarrow{AlCl_3} R'-\overset{R}{\underset{R}{C}}-C_6H_5 + H_2O$$

where R is a methyl group, and R' is a methyl, ethyl, n-propyl, or iso-propyl group. More specifically,

Tert-butyl alcohol, tert-amyl alcohol, dimethyl n-propyl carbinol, dimethyl iso-propyl carbinol condense with benzene in the presence of aluminum chloride to give the corresponding alkyl benzene according to the equation above.

2. There is a definite lessening of the parachor of hydrocarbons due to the effect of chain branching.

3. The "heaping" effect of euregens on adjacent carbon atoms with the subsequent increase in boiling point, density, and surface tension, and the decrease of molecular volume and parachor in relation to structural isomers, is definitely shown.

Pocket has: 1 Suppl.