[From the Kedzie Chemical Laboratory, Michigan State College]

FRAGMENTATION OF ALCOHOLS IN THE PRESENCE OF ALUMINUM CHLORIDE. II. 2,3,3-TRIMETHYL-2-BUTANOL

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The prediction of the course of aluminum chloride induced reactions is difficult because of the varied reactivity of this substance with most organic compounds. The first report of this series (1) has shown that the low yields of tertiary alkyl benzenes obtained from the condensation of highly branched aliphatic alcohols with benzene are due to fragmentation of the alcohol. The particular configuration of the alcohol determines the type of fragmentation, the fragments in some cases forming lower alkyl benzenes.

The carbinol, 2,3,3-trimethyl-2-butanol, is reported to give a seven per cent yield of the corresponding alkyl benzene (2), the lowest yield of any of the isomeric heptylbenzenes formed by the condensation of tertiary heptyl alcohols with benzene. A discussion of the results of the condensation of this alcohol, referred to as the carbinol, its chloride, 2,3,3-trimethyl-2-chlorobutane, referred to as the chloride, its unsaturated derivative, 2,3,3-trimethyl-1-butene, referred to as the alkene, follows.

Under the particular conditions of low temperature (10–15°), a 0.5/1.0 mole ratio of aluminum chloride to carbinol, and slow addition of the carbinol to a suspension of the aluminum chloride in benzene, there are two stages in the reaction. During the addition of the first half of the carbinol, hydrochloric acid is given off and the aluminum chloride in the flask is converted to a heavy red-orange complex. During the addition of the second half of the carbinol, no hydrochloric acid is given off and the red-orange complex is replaced by a dark red tarry complex. When either the chloride or the alkene of the carbinol is condensed with benzene, the dark red tarry complex is formed immediately. Hydrogen chloride is given off throughout the addition of the chloride; very little hydrochloric acid is given off during the addition of the alkene.

Analysis of the organic layer after hydrolysis shows that each condensation forms the same products, the expected *tert.*-heptylbenzene, lower *tert.*-alkylbenzenes, alkyl halides and the alkene. When the *tert.*-heptylbenzene produced by the above condensations is mixed with benzene and aluminum chloride at room temperature the same characteristic fragmentation products, *i.e.*, lower alkylbenzenes, are produced.

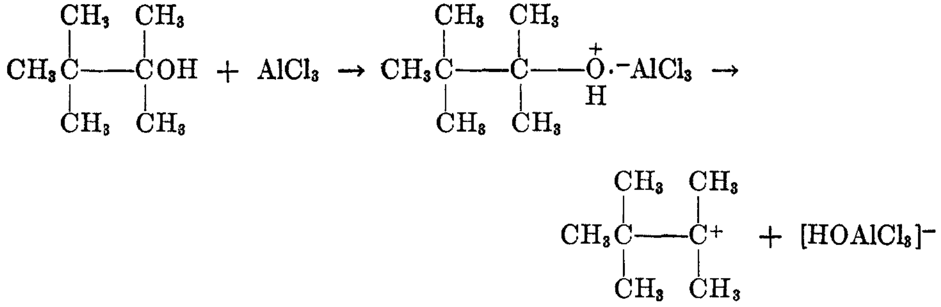
The presence, as reaction products, of chloromethane, 2-methylpropane, 2-chloropropane, 2,3,3-trimethyl-1-butene, 2,3,3-trimethyl-2-chlorobutane, 2-methyl-2-phenylpropane, 2-methyl-2-phenylbutane, 2,3-dimethyl-2-phenylbutane, and 2,3,3-trimethyl-2-phenylbutane is explained by the assumption that the initial step of the reaction is the combination of carbinol and aluminum

TABLE I

YIELDS OF PRODUCTS

CONDENSATION	1	2	3	4	5	6	7
Compound condensed (A)	Carbinol	Carbinol	Carbinol	Carbinol	Chloride	Alkene	*t*.-Heptylbenzene
Temperature, °C	10	10	10	40	10	10	20
Charged: Moles per mole of A							
A	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$AlCl_3$	0.43	0.50	0.66	0.65	0.50	0.50	0.50
Benzene	5.00	5.00	5.00	5.00	5.00	5.00	4.00
Recovered: Moles per mole of A							
HCl given off	0.35	0.42	0.62	0.46	—	—	—
Aqueous layer analysis							
Al	0.41	—	0.66	0.65	—	—	—
Cl	0.48	—	0.91	1.18	—	—	—
OH	0.81	—	1.07	0.78	—	—	—
Organic layer analysis							
Chloromethane	0.12	0.11	0.13	0.12	—	—	—
2-Methylpropane	0.02	0.03	0.04	0.05	—	—	—
2-Chloropropane	0.08	0.10	0.11	0.09	0.04	0.03	—
2,3,3-Trimethyl-1-butene	0.12	0.12	0.21	0.46	0.01	0.01	0.0
2,3,3-Trimethyl-2-chlorobutane	0.25	0.30	0.22	0.12	0.02	0.01	0.0
Benzene	4.60	4.50	4.49	4.60	4.0	4.0	3.8
2,3,3-Trimethyl-2-butanol	0.18	0.05	0.02	0.0	0.0	0.0	0.0
2-Methyl-2-phenylpropane	0.10	0.12	0.11	0.094	0.3	0.3	0.1
2-Methyl-2-phenylbutane	0.037	0.018	0.027	0.017	0.1	0.1	0.05
2,3-Dimethyl-2-phenylbutane	0.034	0.081	0.061	0.079	0.1	0.1	0.1
2,3,3-Trimethyl-2-phenylbutane	0.15	0.15	0.14	0.12	0.3	0.2	0.8
Higher boiling	0.06	0.10	0.17	0.07	0.2	0.3	0.1

chloride by means of a dative bond and the formation of an alkyl cation (3). 2,3,3-Trimethyl-2-chlorobutane may form the same cation through a dative bond while 2,3,3-trimethyl-1-butene may add a proton to give the cation or condense with benzene directly (4).



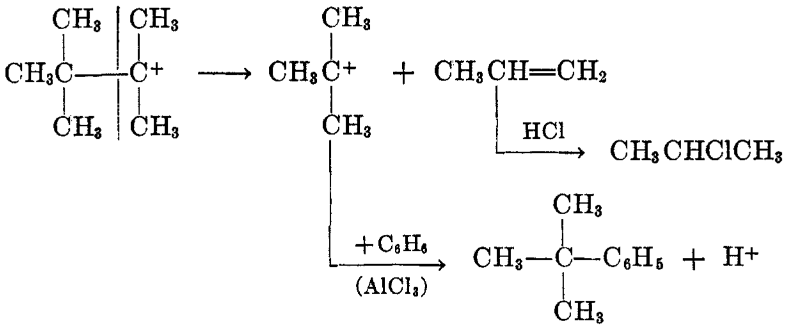
$$CH_3C(CH_3)_2-C(CH_3)_2OH + AlCl_3 \rightarrow CH_3C(CH_3)_2-C(CH_3)_2-\overset{+}{O}(H)\cdot{}^{-}AlCl_3 \rightarrow CH_3C(CH_3)_2-C^{+}(CH_3)_2 + [HOAlCl_3]^{-}$$

The alkyl cation may condense (1) with benzene to form 2,3,3-trimethyl-2-phenylbutane, lose a proton to form 2,3,3-trimethyl-1-butene or add a chlorine ion to form 2,3,3-trimethyl-2-chlorobutane.

When 2,3,3-trimethyl-2-phenylbutane is treated with aluminum chloride, the same cation is formed by reversal of the process of condensation (3).

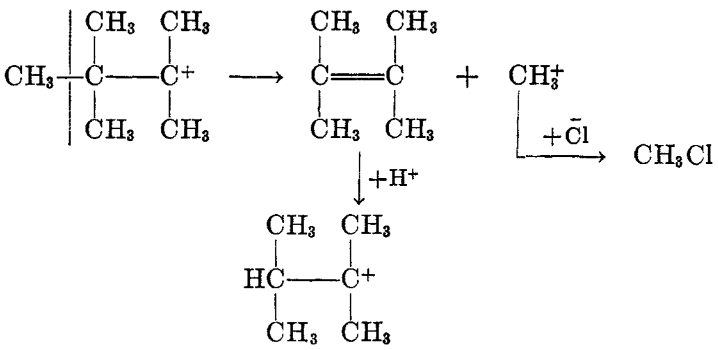
Since, with this particular carbinol, the total moles of alkyl benzenes are approximately equal to the moles of aluminum chloride charged, it would appear that aluminum chloride is necessary to carry the reaction to completion. [With lower tertiary alcohols and less branched tertiary heptyl alcohols, the moles of alkyl benzenes are higher than the moles of aluminum chloride charged (6).] After equal molar quantities of carbinol and aluminum chloride are present, the addition of more carbinol may form a dative bond with the $AlCl_2OH$ but the catalyst is not active enough to convert alkyl groups to alkyl benzenes. Upon hydrolysis at this stage the excess carbinol is recovered as its chloride. The addition of still more carbinol may or may not form a dative bond with $AlCl(OH)_2$ but in either case hydrolysis yields unchanged carbinol.

Fragmentation of the heptyl cation may yield *tert.*-butyl cation and isopropyl chloride.

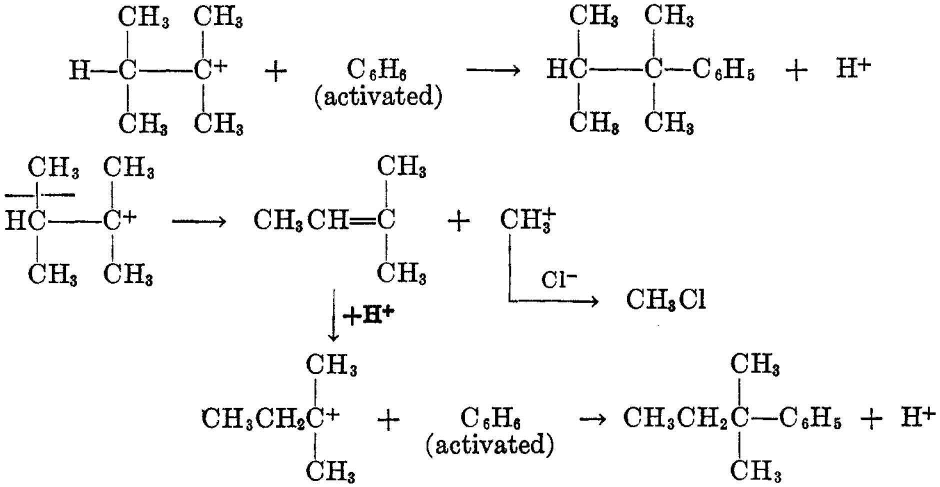


$$CH_3C(CH_3)_2-C^{+}(CH_3)_2 \longrightarrow CH_3C^{+}(CH_3)_2 + CH_3CH{=}CH_2$$
$$CH_3CH{=}CH_2 \xrightarrow{HCl} CH_3CHClCH_3$$
$$CH_3C^{+}(CH_3)_2 \xrightarrow[(AlCl_3)]{+C_6H_6} CH_3-C(CH_3)_2-C_6H_5 + H^{+}$$

Because of branching and proximity of the positive carbon, the wave functions are concentrated around the number two carbon and a positive methyl is eliminated (5).



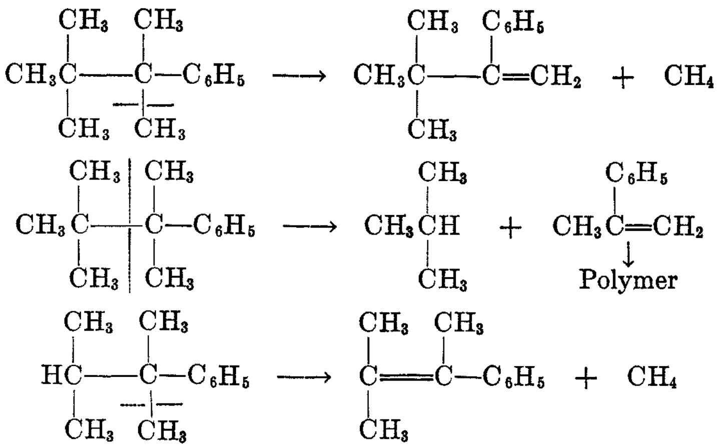
The hexyl cation again may either attack benzene or fragmentate again at the β-carbon.



It should be noted that all of the tertiary alkylbenzenes were found which are made possible by the fragmentation of the cation from 2,3,3-trimethyl-2-butanol. We could find no evidence of the formation of secondary alkylbenzene (2-phenylpropane).

The formation of the small amount of 2-methylpropane may be accounted for by the reduction of isobutene or/and by the direct cracking of 2,3,3-trimethyl-2-phenylbutane. 2-Methylpropane is a by-product in a large number of hydrocarbon-aluminum chloride reactions. In case of reduction, the unsaturated fragment of the hydrogen donor would tend to polymerize.

The distillates which came over between 185° and 215° contained, besides alkylbenzenes, some unsaturated compounds (see experimental part). It has been shown (7) that alkyl groups tend to split from the α-carbon of alkylbenzenes and and that this carbon has a tendency toward free radical formation (8). With this in mind, the following are proposed as possible fragmentations to form 2-methyl-3-phenyl-2-butene, 3,3-dimethyl-2-phenyl-1-butene, and 2-methylpropane.



Gaseous products which did not condense in the dry-ice trap burned with a faintly luminous flame.

EXPERIMENTAL

Synthesis of 2,3,3-trimethyl-2-butanol. The carbinol was prepared in 70–80% yield, by the reaction of pinacolone with methylmagnesium bromide (9). It was obtained as the crystalline hydrate (m.p. 80°), which was dried in ether solution by metallic sodium and then distilled from sodium (b.p. 128–130°). The hydrate is formed from the carbinol in moist air; it can be sublimed without decomposition. Pinacolone was prepared by the method given in Organic Syntheses (10).

2,3,3-Trimethyl-2-chlorobutane was prepared from the carbinol by use of thionyl chloride. It is a solid (m.p. 127°) which decomposes when distilled at atmospheric pressure to give HCl and the alkene (2,3,3-trimethyl-1-butene).

2,3,3-Trimethyl-1-butene was prepared from the carbinol by slow distillation from iodine at atmospheric pressure (11) (b.p. 78°).

Condensation of the carbinol and its derivates. The condensations were carried out in a three-necked flask fitted with a reflux condenser, mechanical stirrer, and dropping-funnel. A tube from the top of the condenser led to a dry-ice trap, then to a water scrubber (to absorb the HCl) and then to a liquid nitrogen trap which was connected to a manometer.

The carbinol (or the alkene) was added slowly to a suspension of aluminum chloride in benzene. The chloride was dissolved in half the benzene to facilitate addition. The reaction mixture was stirred for three hours and then hydrolyzed on ice. The organic layer was separated and washed with water until the washings were neutral. The combined aqueous layers were analyzed in the usual manner for aluminum and chloride.

The material in the dry ice and nitrogen traps was changed to a low-temperature Podbielniak column and fractionated. Orsat analysis was made on the individual fractions to establish their purity. No olefins were found to be present.

The organic layer was fractionated in a 25-plate column until all of the benzene had been taken off. The material in the kettle was then changed to a 100-plate column and fractionated at reduced pressure (20 mm.). The boiling temperatures reported in Table II were corrected to 760 mm. pressure.

Mixed melting points of the known and unknown derivatives in each case gave less than one degree melting point depression from that of the unknown.

Estimation of yields of 2,2,3-trimethyl-1-butene and 2,2,3-trimethyl-2-chlorobutane. The chloride was decomposed during fractionation at atmospheric pressure and came over as the alkene and hydrochloric acid along with benzene. The hydrochloric acid was taken up in standard sodium hydroxide. The benzene fractions were washed with water and the combined aqueous layers titrated. The per cent of alkene in the benzene fraction was approximated by density measurements. The moles of chloride present in the unfractionated mixture was assumed to be equal to the moles of hydrochloric acid given off during fractionation. The alkene was determined by subtracting the moles of chloride from the moles of alkene. Since the mixture contains small amounts of lower tertiary alkyl chlorides, formed as by-products of fragmentation, the calculated yields should be considered as good approximations.

Identification of unsaturated compounds in the 2,3-dimethyl-2-phenylbutane and 2,3,3-trimethyl-2-phenylbutane fractions. The boiling points of these fractions were less constant than the others. They gave positive tests for unsaturation.

TABLE II

FRACTIONATION PRODUCTS

COMPOUND IDENTIFIED	BOILING RANGE, °C	DENSITY 20/4		SOLID DERIVATIVE	MELTING POINT, °C	
		Known	Unknown		Known	Unknown
Chloromethane	−26 to −23	—	Inert to cold conc'd H_2SO_4			
2-Methylpropane	−13 to −11	—	Inert to cold conc'd H_2SO_4			
2-Chloropropane	24 to 30	0.8603	0.8587	Anilide	103	102
2,3,3-Trimethyl-1-butene	76 to 78	0.7050	—	None		
2,3,3-Trimetyl-2-chlorobutane	76 to 78	—	—	None		
2,3,3-Trimethyl-2-butanol	128 to 130	—	—	Hydrate	80	80
2-Methyl-2-phenylpropane	167 to 169	0.8623	0.8629	*p*-Acetamino derivative	169	169
2-Methyl-2-phenylbutane	187 to 191	0.8720	0.8743	*p*-Acetamino derivative	139	138
2,3-Dimethyl-2-phenylbutane	207 to 211	0.8819	0.8835	*p*-Acetamino derivative	119	117–118
2,3,3-Trimethyl-2-phenylbutane	224 to 227	0.8867	0.8873	*p*-Nitro derivative	108	108

The 189–191° cut was found to contain trimethyl styrene (2-methyl-3-phenyl-1-butene). Cuts from several condensations were combined, hydrogenated with sodium and ethyl alcohol, and the extracted hydrocarbons fractionated. The 186–188° cut from this fractionation was nitrated, reduced, and acetylated to give a *p*-acetamino derivative (m.p. 147°) which showed no melting point depression when mixed with the known derivative of 2-methyl-3-phenylbutane. The unknown derivative did show melting point depression when mixed with the corresponding derivative of 2-methyl-2-phenylbutane.

Oxidation of this 189–191° cut with CrO_3 in glacial acetic acid at room temperature for 24 hours, yielded some acetophenone, which was identified by its semicarbazone (m.p. 193°). Mixed melting point showed no depression. This indicates that the double bond is on the α-carbon.

Oxidation of the 207–211° cut with CrO_3 in glacial acetic acid at room temperature for 24 hours yielded some phenyl *tert.*-butyl ketone, b.p. 85–89° (10 mm.). This was identified by its semicarbazone, which melted at 168°. 3,3-Dimethyl-2-phenyl-1-butene was made from pinacolone and phenylmagnesium bromide. It was oxidized in the same manner, and the ketone converted to the semicarbazone. Mixed melting point showed no depression.

Preparation of solid derivatives. The anilide of isopropyl chloride was prepared by the method given in Shriner and Fuson, "Identification of Organic Compounds."

The hydrate of the carbinol, as noted above, forms in moist air.

The *p*-acetamino derivatives were prepared by the method given by Ipatieff and Schmerling (12).

The nitro derivative was prepared by nitration of the *tert.*-heptylbenzene. This is the only one of the *tert.*-heptylbenzenes which forms a solid mononitro derivative.

SUMMARY

The condensation of 2,3,3-trimethyl-2-butanol with benzene in the presence of aluminum chloride, has given, in addition to the expected *tert.*-heptylbenzene (2,3,3-trimethyl-2-phenylbutane), a number of fragmentation products. These products were identified as chloromethane, 2-methylpropane, 2-chloropropane, 2,3,3-trimethyl-1-butene, 2,3,3-trimethyl-2-chlorobutane, 2-methyl-2-phenylpropane, 2-methyl-2-phenylbutane, and 2,3-dimethyl-2-phenylbutane.

Small amounts of 2-methyl-3-phenyl-2-butene and 3,3-dimethyl-2-phenyl-1-butene were found in the 2,3-dimethyl-2-phenylbutane and the 2,3,3-trimethyl-2-phenylbutane fractions respectively.

The condensation of 2,3,3-trimethyl-2-chlorobutane and of 2,3,3-trimethyl-1-butene produced these same fragmentation products. The tertiary heptylbenzene, when mixed with benzene and aluminum chloride, has also produced some of the same products. The theory of the intermediate formation of an alkyl cation from the carbinol or its derivatives and its fragmentation gives a satisfactory explanation.

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