

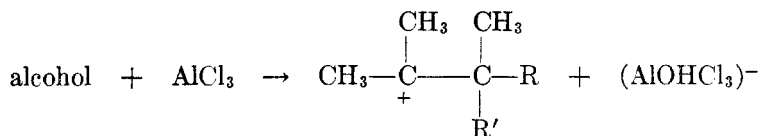
FRAGMENTATION OF 2,3,4-TRIMETHYL-2-PENTANOL WHEN
CONDENSED WITH BENZENE IN THE PRESENCE
OF ALUMINUM CHLORIDE

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In a previous paper (1) from this laboratory, it was observed that attempts to condense 2,3,4-trimethyl-2-pentanol with benzene in the presence of aluminum chloride at a temperature of -15° resulted in a mixture of hydrocarbons which distilled over a wide range below the boiling points of the octylbenzenes. There was no isolation of 2,3,4-trimethyl-2-phenylpentane.

In other fragmentation studies (2, 3, 4) of various tertiary alcohols, large yields of tertiary butylbenzene have been obtained. It is presumed that the fragmentation results from the carbonium ion, which was present in each of the above cases, either directly by the removal of the hydroxyl ion, or indirectly by rearrangement.



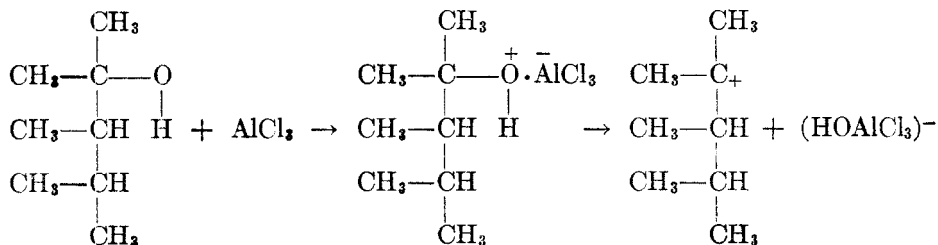
R' = methyl or H.

R = methyl, ethyl, or isopropyl.

Condensation of 2,3,4-trimethyl-2-pentanol with benzene, activated by aluminum chloride, gave the following products: 2-methylpropane (7%); 2,3,4-trimethyl-2-chloropentane (23%); 2-methyl-2-phenylpropane (28%); olefin, $\text{C}_{11}\text{H}_{22}$ (2%); 2-methyl-2-phenylbutane (3%); olefin, $\text{C}_{12}\text{H}_{24}$ (5.5%); 2,3,4-trimethyl-2-phenylpentane (6%); plus other alkyl chlorides.

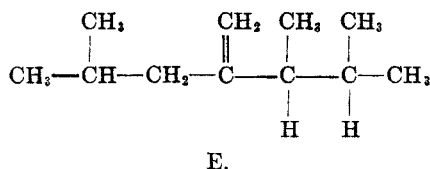
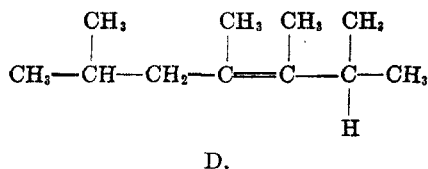
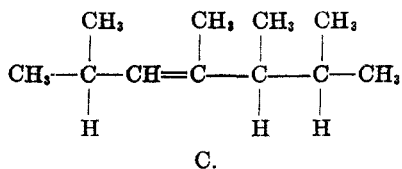
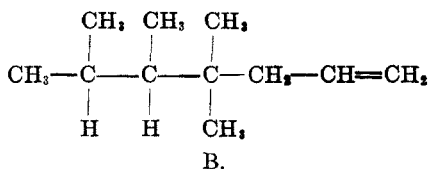
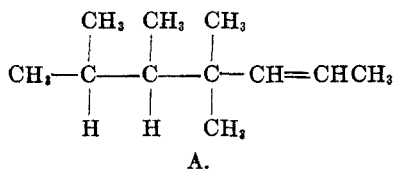
To facilitate separation of the fractions, the products were treated with 50% alcoholic potash to give olefins in place of the alkyl chlorides.

It is assumed, as in other reactions of alcohol and aluminum chloride (2, 3), that the initial step is the formation of the dative bond between the nucleophilic catalyst and the carbinol, followed by the formation of the octyl cation.



Normally one would expect the octyl carbonium ion to react with the activated benzene nucleus, but due to the instability of the cation only 6% of the octylbenzene is obtained.

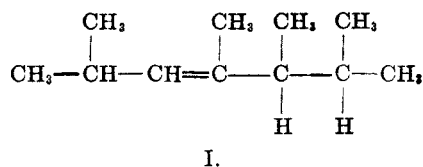
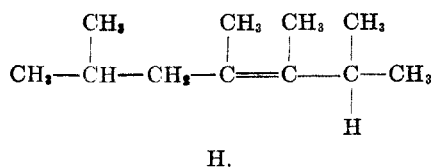
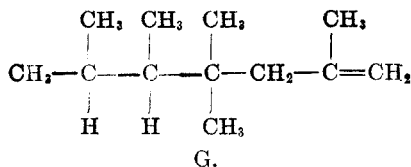
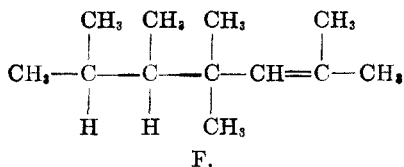
It is believed that the octyl cation adds to propene to give two isomeric eleven-carbon olefins (A and B) after loss of a proton. Although less likely according to polymerization studies, three other possible olefins (C, D, and E) could form by the addition of the isopropyl cation to 2,3,4-trimethyl-1-pentene.

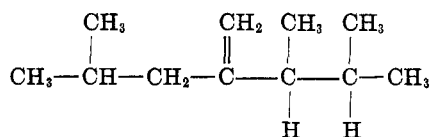


In the dehydration of an analogous alcohol, 4,4-dimethyl-2-pentanol, Whitmore (7) has shown that the ratio of 4,4-dimethyl-2-pentene to 4,4-dimethyl-1-pentene is 4.5 to 1. This would indicate a preponderance of A over B.

In a similar manner the octyl cation can add to isobutene to give two isomeric twelve-carbon olefins. Theoretically possible, also, are three other olefins (H, I, and J) formed by the addition of the tertiary butyl cation to 2,3,4-trimethyl-1-pentene. Although all five of the olefins may be present, the formation of F and G seems most plausible.

In the dehydration of 2,4,4-trimethyl-2-pentanol, Whitmore (8) has shown that the ratio of 2,4,4-trimethyl-1-pentene to 2,4,4-trimethyl-2-pentene is four-to-one. By analogy, one would expect a greater amount of G in this fraction.





J.

When the twelve-carbon olefins were hydroxylated and oxidized with perchloric acid, acetone was found present in small amounts. This should indicate the presence of F.

The proof of the structure of 2,3,4-trimethyl-2-phenylpentane was made by nitration, reduction of the amine, and diazotization to 2,3,4-trimethyl-2-*p*-hydroxyphenylpentane. The phenol thus obtained was identical with the product of the condensation of the carbinol with phenol. This was ascertained by the mixed melting points of their α -naphthylurethan derivatives.

In the condensation of 2,3,4-trimethyl-2-pentanol with phenol, less fragmentation took place and the chief product was the *p*-octylphenol with lesser amounts of *p*-*t*-butylphenol and a trace of 2-methylpropane. There was also evidence of the presence of some 2,4,4-trimethyl-2-*p*-hydroxyphenylpentane.

EXPERIMENTAL

Preparation of 2,3,4-trimethyl-2-pentanol. The alcohol was prepared by the reaction of methyl Grignard and ethyl 2,3-dimethylbutanoate. The ester was prepared by a series of reactions developed by Huston and Goerner (9). They include a Reformatsky reaction of acetone and ethyl 2-bromopropionate to give ethyl 3-hydroxy-2,3-dimethylbutanoate; this was followed by dehydration with phosphorus pentoxide to give two isomeric unsaturated esters, and subsequent hydrogenation of these unsaturated esters with platinum catalyst gave ethyl 2,3-dimethylbutanoate.

The total yield of carbinol based on the bromo ester was 35–40%; b.p. 49.5°/7 mm; n_D^{20} 1.4350; d_4^{20} 0.8432.

Condensation of 2,3,4-trimethyl-2-pentanol. A 1-liter 3-necked flask was equipped with dropping-funnel, stirrer, and condenser which contained a delivery tube through a Dry Ice-acetone trap. In a typical run, 130 g. (1 mole) of carbinol was added dropwise with vigorous stirring to a suspension of 44.5 g. ($\frac{1}{3}$ mole) of aluminum chloride in 450 ml. (5 moles) of anhydrous, thiophene-free benzene. The temperature was kept at $34 \pm 1^\circ$. After the addition of the carbinol (2.5 hours), the mixture was stirred for an additional hour, allowed to stand all night, and hydrolyzed with 125 ml. of ice-water.

The benzene layer was separated, washed with water and with sodium carbonate. After drying over sodium sulfate the benzene was removed at atmospheric pressure and the condensation products fractionated. The gas collected in the Dry Ice trap was combined with the gas given off when the benzene was removed.

Identification of 2-methylpropane. The gas collected in the Dry Ice-acetone trap was fractionally distilled until free from hydrogen chloride and benzene. An Anschütz thermometer then measured the boiling point at -11° to -10° . Since refractive index readings are often better indications of purity than boiling points, an adaptation of a method by Grosse (10) for determining refractive indices at low temperatures was used.

The two lenses of the refractometer were protected from frosting over with the moisture of the room by covering them with a glass plate sealed on the sides with vaseline. A thermometer was calibrated at -25° , and acetone with some solid carbon dioxide was passed back and forth through the system. After becoming familiar with the apparatus, a temper-

TABLE I
(3-MOLE BASIS)
FRACTIONATION OF PRODUCTS

FRACTION IDENTIFIED	B.P., °C. (738 MM.)	n_D^{20}		DERIVATIVE OR MEANS OF IDENTIFICATION	YIELD, GRAMS
		Obs.	Lit.		
2-Methylpropane	-11 to -10	1.3515 (-25°)	1.3514 (10)	Phys. Const.	25
2,4,4-Trimethyl-1-pentene	101-102	1.4099	1.4089 (11)	Phys. Const.	4
2,3,4-Trimethyl-1-pentene	107-108	1.4145	1.4146 (12)	Phys. Const.	45
2,3,4-Trimethyl-2-pentene	114-115	1.4230	1.423 (11)	Phys. Const.	55
2-Methyl-2-phenylpropane	168.5	1.4918	1.4918	<i>p</i> -acetamino deriv., m.p. 168°	115
C ₁₁ H ₂₂	177-180	1.4490		Calc'd: C, 85.71; H, 14.29; M.W., 154 Fd: C, 85.62; H, 14.13; M.W., 153.5	8
2-Methyl-2-phenylbutane	189	1.4928		<i>p</i> -acetamino deriv., m.p. 138-39°	13
C ₁₂ H ₂₄	189-197	1.4620		Calc'd: C, 85.71; H, 14.29; M.W., 168 Fd: C, 85.89; H, 14.05; M.W., 171	25
2,3,4-Trimethyl-2-phenylpentane*	235	1.4958		Calc'd: C, 88.33; H, 11.67; M.W., 190 Fd: C, 88.27; H, 11.50; M.W., 193 α -naphthylurethan of <i>p</i> -hydroxy deriv. m.p. 139°	35

*Four grams of distillate came over between 230° and 233°. This had an index of refraction of 1.4935 which is near that of 2,4,4-trimethyl-2-phenylpentane. It was not pure enough to give sharp melting derivatives.

ature of $-25 \pm 1^\circ$ could be maintained. Three possible gases possess the following physical properties:

Compound	B. P., °C.	n_D^{25}
<i>n</i> -butane.....	-0.5	1.3621
isobutane.....	-10.2	1.3514
isobutylene.....	-6.0	1.3814

The observed refractive indices varied from 1.3512 to 1.3518 in about ten readings, using different samples from different condensations.

Fractionation of the condensation product. This was accomplished at reduced pressure in a 24-inch Fenske type column, packed with $\frac{1}{8}$ inch glass helices. To facilitate separation, the condensate was refluxed three to four hours with an equal volume of 50% alcoholic potassium hydroxide. The resulting emulsion was washed with water, dried over sodium sulfate, and fractionated. The fractions are shown in table I.

Identification of 2,3,4-trimethyl-2-phenylpentane. One-half mole of aluminum chloride was mixed with 200 ml. of Skellysolve in the apparatus described under the condensation of the carbinol. The phenol (1.2 moles) was dissolved in 1 mole of carbinol and the solution added slowly through the dropping-funnel, with the temperature of the reaction flask maintained at 25–30°. After all of the solution had been added, the mixture was allowed to stand all night and hydrolyzed the next morning with ice-water. The organic layer was dried and the solvent removed at atmospheric pressure. At this time 1 g. of 2-methylpropane, which had been dissolved in the Skellysolve, was collected in a Dry Ice-acetone trap.

Careful fractionation gave the two olefins resulting from the dehydration of the carbinol, 2,3,4-trimethyl-2-chloropentane, and unreacted phenol.

The residual mass was transferred to a small flask and distilled through a 12-inch Vigreux column. Two main fractions were obtained.

I. 110–125°/5 mm.....	10 g.
II. 130–140°/5 mm.....	23 g.

Repeated crystallizations after redistillation of I yielded a solid phenol, m.p. 95–96°. The benzoyl ester of this phenol melted at 80–81°. Mixed melting point with the benzoate of *t*-butylphenol showed no depression.

Fraction II had the m.p. 80–83°. Fractional crystallization resulted in a phenol, melting at 88–89°. Its α -naphthylurethan melted at 138–139°, and its benzoate at 113–115°. The initial melting range of fraction II indicates the presence of some 2, 4, 4-trimethyl-2-hydroxyphenylpentane with 2, 3, 4-trimethyl-2-*p*-hydroxyphenylpentane (13).

Nitration, reduction, and diazotization of 2,3,4-trimethyl-2-phenylpentane gave a phenol whose α -naphthylurethan or benzoate showed no melting point depression when mixed with those obtained directly from condensation of the alcohol with phenol.

EAST LANSING, MICH.

SUMMARY

1. 2,3,4-Trimethyl-2-pentanol was condensed with benzene in the presence of aluminum chloride. Only 6% of the expected 2,3,4-trimethyl-2-phenylpentane was obtained.

2. Proof of the structure of 2,3,4-trimethyl-2-phenylpentane was obtained by nitration of the octylbenzene, reduction, and diazotization to give an octylphenol identical with one obtained by direct condensation of the carbinol with phenol.

3. The gas, 2-methylpropane, was identified by its b.p., and refractive index at –25°.

4. Chain rupture, both before and after rearrangement, gave a small amount of *t*-amylbenzene, and a 28% yield of *t*-butylbenzene. Possible mechanisms are suggested.

5. Mixed eleven- and twelve-carbon olefins were found.

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