

A STUDY OF THE REDUCTION AND FRAGMENTATION OF SOME
TERTIARY CARBINOLS WHEN CONDENSED WITH BENZENE
IN THE PRESENCE OF ALUMINUM CHLORIDE

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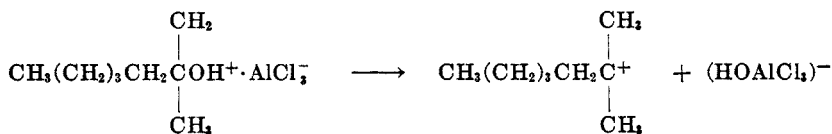
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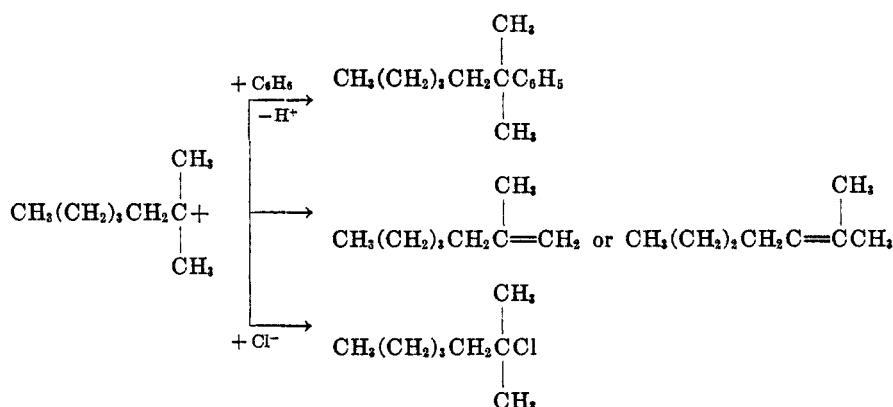
Previous papers (1, 2) from this laboratory showed that when tertiary alcohols having alkyl groups, particularly methyl, on the carbon atom adjacent to the carbinol carbon were condensed with benzene in the presence of aluminum chloride rearrangement followed by fragmentation or fragmentation without rearrangement took place. In any event, the relatively low energy-containing 2-methylpropane and 2-methyl-2-phenylpropane were isolated from the reaction products.

Other investigations (3, 4, 5) in which alkyl aryl carbinols were condensed with benzene and phenol in the presence of aluminum chloride showed that the alcohol was reduced to the corresponding hydrocarbon to an extent of approximately ten percent. In 1945 Dr. G. L. Goerner, of this laboratory, isolated from the condensation products of 3-ethyl-3-hexanol a saturated paraffin hydrocarbon fraction which was tentatively identified as 3-ethylhexane.

Sixteen tertiary alcohols (8 octanols, 4 heptanols, 2 hexanols, 1 pentanol, and 1 butanol) having only primary groups attached to the carbinol carbon have been condensed with benzene in the presence of anhydrous aluminum chloride. Separation of the reaction products showed that reduction of the alcohols to the corresponding hydrocarbons had taken place in varying amounts depending on their size and structure. Fragmentation of those alcohols having methyl groups attached to the second carbon from the carbinol carbon took place without preliminary rearrangement at such a point as to favor the formation of the *tert*-butyl carbonium ion which further reacted to form 2-methyl-2-phenylpropane and 2-methylpropane. Branching on the carbon atom third removed from the carbinol carbon is apparently too distant to bring about appreciable fragmentation.

Making the usual assumptions as to the formation of a dative bond and a carbonium ion, the reactions involved in the condensation of 2-methyl-2-heptanol may be outlined as follows:

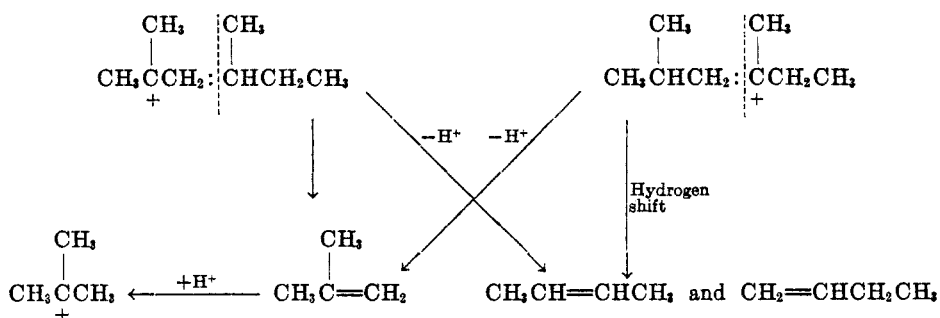




Both olefins and alkyl chlorides have been isolated and both are known alkylating agents. Furthermore either may act as a hydrogen acceptor and would yield, in the presence of a suitable donor, 2-methylheptane.

As examples of fissionable alcohols 2,4-dimethyl-2-hexanol and 2,4-dimethyl-4-hexanol will be used. In both cases the reactions would lead to the formation of an octylbenzene, a mixture of octenes and an octyl chloride.

The carbonium ion from 2,4-dimethyl-2-hexanol or 2,4-dimethyl-4-hexanol would undergo fragmentation as follows:



It should be noted that in one case fission takes place between the positive carbon and the adjacent carbon, while in the other case the fission is between the adjacent carbon and the next adjacent. No evidence has been found of the formation of secondary alkylbenzenes; however, secondary alkyl chlorides have been isolated. In either case the 2-methylpropene, the *tert*-butyl carbonium ion or the chloride would condense with benzene to give 2-methyl-2-phenylpropane, or in the presence of a suitable hydrogen donor they would be reduced to 2-methylpropane.

There are many examples of dehydrogenating and hydrogenation effects of aluminum chloride and similar catalysts (6-9). Many of these reactions are accompanied by the formation of biphenyl, anthracene, and indane derivatives, and more generally, by large amounts of resinous material. Each of these side reactions is a possible source of hydrogen.

One can only postulate as to what form the hydrogen acceptor is in during the reduction. If one assumes that the formation of olefin is necessary, some other hypothesis must be advanced to explain the formation of triphenylmethane, when triphenylcarbinol is condensed with benzene in the presence of aluminum

TABLE I
PREPARATION OF ALCOHOLS AND DERIVATIVES

METHOD OF PREPARATION	ALCOHOL	3,5-DINITROBENZOATES		
		M.P., °C.	N	
			Calc'd	Found
$\text{CH}_3(\text{CH}_2)_4\text{MgBr}$ and CH_3COCH_3	2-Methyl-2-heptanol (11)	43-44	8.63	8.40
$\text{CH}_3(\text{CH}_2)_3\text{MgBr}$ and $\text{CH}_3\text{COCH}_2\text{CH}_3$	3-Methyl-3-heptanol (12)	53-54	8.63	8.88
$\text{CH}_3(\text{CH}_2)_2\text{MgBr}$ and $\text{CH}_3\text{COOC}_2\text{H}_5$	4-Methyl-4-heptanol (13)	55-56	8.63	8.59
$\text{CH}_3\text{CH}_2\text{MgBr}$ and $\text{CH}_3(\text{CH}_2)_2\text{COOH}$	3-Ethyl-3-hexanol (12)	62-63	8.63	8.74
CH_3 $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{MgBr}$, CO_2 and CH_3MgBr	2,4-Dimethyl-2-hexanol (14)	48.5-49.5	8.63	8.69
$\text{CH}_3\text{CH}_2\text{MgBr}$ and O $\text{CH}_3\text{CCH}_2\text{CH}(\text{CH}_3)_2$	2,4-Dimethyl-4-hexanol (15, 16)	52-53	8.63	8.93
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{MgBr}$ and CH_3COCH_3	2,5-Dimethyl-2-hexanol (17)	61-62	8.63	8.95
$(\text{CH}_3)_3\text{COH}$, H_2SO_4 , HI , and Ag_2O	2,4,4-Trimethyl-2-pentanol (18)	89.5-90.5	8.63	8.81
$\text{CH}_3(\text{CH}_2)_3\text{MgBr}$ and CH_3COCH_3	2-Methyl-2-hexanol (12)	53-54	9.02	8.68
$\text{CH}_3(\text{CH}_2)_2\text{MgBr}$ and $\text{CH}_3\text{COC}_2\text{H}_5$	3-Methyl-3-hexanol (12)	43-44	9.02	9.54
$\text{CH}_3\text{CH}_2\text{MgBr}$ and $\text{C}_2\text{H}_5\text{OCOOC}_2\text{H}_5$	3-Ethyl-3-pentanol (19)	118-119	9.02	9.17
CH_3MgBr and $\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$	2,4-Dimethyl-2-pentanol (20)	69-70	9.02	9.07
$\text{CH}_3(\text{CH}_2)_2\text{MgBr}$ and CH_3COCH_3	2-Methyl-2-pentanol (12)	71-72		
$\text{CH}_3\text{CH}_2\text{MgBr}$ and $\text{CH}_3\text{COC}_2\text{H}_5$	3-Methyl-3-pentanol (21)	95.5-96.5		

chloride (10). If one assumed that the carbonium ion or complex is reduced, one must postulate the formation of hydride ions.

A free radical mechanism is not favored inasmuch as this would involve the formation of such fragments as $(\text{CH}_3)_3\text{C}\cdot$ which is not considered as an intermediate in the formation of 2-methyl-2-phenylpropane.

It is perhaps logical to assume that a necessary prerequisite for reduction is the formation of an alkyl chloride which may be reduced by atomic hydrogen

with the formation of a paraffin hydrocarbon and hydrogen chloride. Twelve grams of 2-methylpropane were isolated from a three-mole condensation (AlCl_3) of *tert*-butyl chloride with benzene, in contrast to only five grams from a similar run using *tert*-butyl alcohol.

TABLE II
HYDROCARBONS ISOLATED IN THE CONDENSATION OF ALCOHOLS WITH BENZENE

ALCOHOL	YIELD, %				ALKYL BENZENE, %
	2-Methyl- propane	Paraffin Hydrocarbon		2-Methyl- 2-phenyl- propane	
2-Methyl-2-heptanol	—	2-Methylheptane	8.8	—	2-Methyl-2-phenyl- heptane (23) 27.4
3-Methyl-3-heptanol	—	3-Methylheptane	9.5	—	3-Methyl-3-phenyl- heptane 24.2
4-Methyl-4-heptanol	—	4-Methylheptane	12.0	—	4-Methyl-4-phenyl- heptane (23) 33.1
3-Ethyl-3-hexanol	—	3-Ethylhexane	14.3	—	3-Ethyl-3-phenyl- hexane (23) 25.1
2,4-Dimethyl-2-hex- anol	3.1	2,4-Dimethylhex- ane	3.8	1.30	2,4-Dimethyl-2- phenylhexane (23) 19.6
2,4-Dimethyl-4-hex- anol	4.6	2,4-Dimethylhex- ane	3.9	2.20	2,4-Dimethyl-4- phenylhexane (23) 19.2
2,5-Dimethyl-2-hex- anol	—	2,5-Dimethylhex- ane	5.7	—	2,5-Dimethyl-2- phenylhexane (23) 21.5
2,4,4-Trimethyl-2- pentanol	4.6	2,4,4-Trimethyl- pentane	—	20.00	2,4,4-Trimethyl-2- phenylpentane (23) 14.0
2-Methyl-2-hexanol	—	2-Methylhexane	2.1	—	2-Methyl-2-phenyl- hexane (24) 31.3
3-Methyl-3-hexanol	—	3-Methylhexane	1.6	—	3-Methyl-3-phenyl- hexane (24) 30.0
3-Ethyl-3-pentanol	—	3-Ethylpentane	2.3	—	3-Ethyl-3-phenylpen- tane (24) 33.2
2,4-Dimethyl-2-pen- tanol	2.2	2,4-Dimethylpen- tane	—	2.80	2,4-Dimethyl-2- phenylpentane (24) 22.2
2-Methyl-2-pentanol	—	2-Methylpentane	7.0	—	2-Methyl-2-phenyl- pentane (24) 32.7
3-Methyl-3-pentanol	—	3-Methylpentane	10.2	—	3-Methyl-3-phenyl- pentane (24) 35.9
2-Methyl-2-butanol	—	3-Methylbutane	1.8	—	2-Methyl-2-phenyl- butane (24) 40.0
2-Methyl-2-propanol	2.2	—	—	55.0	(<i>p</i> -Di- <i>tert</i> -butylben- zene) (M.p. 76°) 1.2

EXPERIMENTAL

Preparation of alcohols: Table I gives the methods used in the preparation of all of the alcohols used with the exception of 2-methyl-2-butanol and 2-methyl-2-propanol. These were purified to a boiling-point range of two degrees and their refractive indices and densities were checked against those given in the references. They were further characterized by the preparation and analysis of the new 3,5-dinitrobenzoyl derivatives.

TABLE III
IDENTIFICATION OF PARAFFIN HYDROCARBON FRACTIONS

HYDROCARBON	B.P. °C.	MM.	n_D^{20}	d_4^{20}	MR Calc'd (Found)	INFRARED MAXIMA (in microns at 25°)				
						8.30	9.57	11.17	13.24	
2-Methylheptane (25)	115-116	743	1.3962 (1.3949)	0.7001 (0.6979)	39.16	8.30 8.55 8.75 9.25	9.57 10.41 10.66 10.86	11.17 11.88 12.26 12.99	13.24 13.79	
3-Methylheptane (25)	117.5	749.5	1.3980 (1.3985)	0.7055 (0.7058)	39.16	8.05 8.25 8.70 8.77	9.30 9.89 10.05 10.47	10.72 10.99 11.15 12.95	13.74	
4-Methylheptane (25)	116-117	749	1.3980 (1.3979)	0.7044 (0.7040)	39.16	8.22 8.69 8.76 9.35	9.55 9.70 9.90 10.10	10.48 11.03 11.17 11.44	11.94 12.12 13.06 13.49	
3-Ethylhexane (25)	115-116	746	1.3980 (1.4016)	0.7052 (0.7139)	39.16	7.90 8.03 8.18 8.70	8.90 9.35 9.62 9.75	9.88 9.76 10.95 11.24	12.14 12.88	
2,4-Dimethylhexane (25)	109-109.5	745	1.3970 (1.3953)	0.7012 (0.7004)	39.16	6.81 7.31 7.70 7.79	8.10 8.54 8.69 9.22	9.55 9.87 10.04 10.31	10.85 11.05 11.37 11.61	12.43 13.04
2,5-Dimethylhexane (25)	107-108	736	1.3930 (1.3925)	0.6952 (0.6936)	39.16	6.79 7.22 7.31 7.93	8.17 8.54 9.17 9.58	9.64 10.54 10.69 10.87	11.92 12.28 12.46 13.28	
2-Methylhexane (25)	89.5	750	1.3855 (1.3876)	0.6790 (0.6787)	34.53	6.80 7.23 7.30 7.47	7.72 7.97 8.18 8.53	8.73 9.30 9.53 9.71	9.85 10.88 11.04 11.17	12.16 12.81 13.74
3-Methylhexane (25)	89.5-91	733	1.3895 (1.3887)	0.6890 (0.6870)	34.53	7.24 8.11 8.65 8.72	9.29 9.88 10.16 10.38	10.77 11.36 12.96 13.55		

3-Ethylpentane (25)	92.5-93	741	1.3940 (1.3934)	0.6995 (0.6982)	34.53 (34.73)	6.84 7.25 7.50 7.59	7.66 7.85 8.03 8.57	8.68 8.87 9.59 9.96	11.13 11.83 12.03 12.68	13.05 13.69
2-Methylpentane (25)	60-60.5	742	1.3725 (1.3716)	0.6558 (0.6532)	29.91 (30.18)	7.22 7.29 7.84 8.05	8.52 8.70 9.35 9.62	9.90 10.45 10.65 10.87	11.20 11.59 12.18 13.50	
										6.85 7.25 7.69 7.99
3-Methylpentane (25)	61.5-62	741	1.3780 (1.3765)	0.6655 (0.6643)	29.91 (30.00)	6.85 7.25 7.69 7.99	8.66 8.88 9.58 9.86	10.15 10.50 11.39 12.85		
									1.3552 (1.3537)	0.6197 (0.6212)
2-Methylbutane (25)	26-28	742	1.3552 (1.3537)	0.6197 (0.6212)	25.29 (25.32)					
2-Methylpropane (25)	--10.4	750	1.3518 ⁻²⁵							

A preliminary study of the methods of preparation showed the importance of selecting simple Grignard reagents. Isoalkylmagnesium bromides gave relatively small yields of alcohols contaminated with products of side reactions, *i.e.*, reduction, condensation, pinacol formation, enolization coupling, etc.

Condensations: As all condensations were carried out by the same procedure only one will be described. A 3-liter, 3-necked flask equipped with stirrer, dropping-funnel, and condenser to which was attached a solid carbon-dioxide trap, was charged with 1053 grams (13.5 moles) of anhydrous thiophene-free benzene and 179.5 grams (1.35 moles) of anhydrous aluminum chloride. The suspension was heated to reflux, with stirring, cooled to room temperature and 314 grams (2.7 moles) of 2,4-dimethyl-2-hexanol added dropwise at such a rate as to keep the temperature at $35^{\circ} \pm 1^{\circ}$. When the addition of alcohol was complete the mixture was stirred for two hours and then allowed to stand overnight. Cracked ice was used in the hydrolysis.

After hydrolysis the organic layer was separated from the aqueous layer, the latter was extracted with benzene, the combined organic layers washed with dilute sodium carbonate and dried over sodium sulfate. Fractionation was accomplished at atmospheric pressure by means of Fenske-type columns. In the final fractionations of the paraffin hydrocarbons a 92×0.8 cm. column, packed with $1/32$ in. glass helices, was used.

The gas collected in the solid carbon dioxide-acetone trap was combined with the gas given off during hydrolysis and was identified by its boiling point and refractive index as 2-methylpropane. An adaptation of the method of Grosse (22) for determining refractive indices at low temperatures was used.

Those octyl alcohols in which there was fragmentation gave unsaturated fractions which came over at 190 – 200° . These indicated the formation of dodecenes (2).

Table II lists the alcohols condensed with benzene and the hydrocarbons isolated.

The identification of 2-methyl-2-phenylpropane was accomplished by its physical constants and the acetamino derivative. The other alkylbenzenes were identified by their physical constants which have been reported in earlier work (23, 24).

Table III lists the isolated paraffin hydrocarbons together with their determined boiling points, densities, and refractive indices. The figures in parentheses are the "preferred" densities and refractive indices as reported under the American Petroleum Institute Project 44 at the National Bureau of Standards (25).

The infrared absorption maxima were determined at 25° and checked against those of pure samples of the hydrocarbons furnished by the National Bureau of Standards. Those of the octanes and heptanes were also checked against the spectrograms published in mimeograph form by the National Bureau of Standards as a part of the reports of the American Petroleum Institute Research Project 44 (26).

The greatest deviation from the preferred refractive index and density was found in 3-ethylhexane. It is worthy of note in this connection that 3,3-dimethylhexane (25) which is a possible rearrangement product has a lower "preferred" refractive index (n_D^{20} 1.4001) and density (d_4^{20} 0.7100) than 3-ethylhexane (25). The two hydrocarbons have infrared absorption maxima in common at 7.90, 8.20, 8.65, 8.90, 9.85, and 10.92μ (26). The presence of 3,3-dimethylhexane as a contaminant is not excluded.

SUMMARY

1. Sixteen tertiary alcohols having only primary alkyl groups attached to the carbinol carbon were prepared and condensed with benzene in the presence of aluminum chloride.

2. Fragmentation was shown to take place with those alcohols having branching on the *beta*-carbon. Fission of the alkyl carbonium ion always took place at such a point as to favor the formation of 2-methylpropane and 2-methyl-2-phenylpropane.

3. Reduction was shown to take place as evidenced by the isolation of the paraffin hydrocarbon corresponding to the structure of the alcohol condensed. 2-Methylpropane was isolated in all cases where fragmentation occurred.

4. Possible mechanisms have been proposed to explain the fragmentation and reduction.

5. 3,5-Dinitrobenzoates of the alcohols were prepared.

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