

FRAGMENTATION OF TERTIARY ALIPHATIC ALCOHOLS WHEN CONDENSED WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE. III¹

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Received July 17, 1952

Information reported here together with that in earlier papers (1-3) shows that, in the presence of benzene and aluminum chloride, a tertiary aliphatic alcohol in which there is branching on the *alpha* carbon atom may undergo the following reactions:

1. The alcohol may condense with benzene to form a phenylalkane.
2. The alcohol may form an alkyl chloride.
3. The alcohol may decompose to form an alkene or a mixture of alkenes of the same carbon content.
4. The alcohol may fragmentate directly or after rearrangement to form a tertiary fragment of smaller carbon content and an alkene. The smaller tertiary fragment may condense with benzene or it may be reduced to the alkane (usually 2-methylpropane). The alkene fragment may add hydrogen chloride to form an alkyl chloride.
5. Incidental to the migration of a methyl group in rearrangement, a methyl group may split off and form, with negative chlorine, methyl chloride. The resulting fragment containing one less carbon than the original alcohol may condense with benzene, or it may rearrange and fragmentate into a tertiary butyl fragment and an alkene of smaller carbon content. This process of demethylation may continue as long as there is methyl branching on the *alpha* carbon (2).
6. Reduction may occur to give the alkane corresponding to the alcohol (4).
7. Alkene fragments may combine with the original carbonium complex, or with themselves to give alkenes of higher carbon content (3).

Formulations of these proposed reaction types are given in the earlier articles of this series. Some demethylation may occur after the combination of fragments followed by rearrangement and refragmentation (5).

In this communication are reported the results of condensation and fragmentation of five highly branched carbinols: 2,3-dimethyl-2-butanol; 2,3-dimethyl-2-pentanol; 2,3,3-trimethyl-2-butanol; 2,2,3-trimethyl-3-pentanol; and 2,3,3-trimethyl-2-pentanol.

The yields given in Tables I to IV are based on weight-% of the alcohol. The yields of methane reported (Tables III and IV) were the parts of the total gases formed which escaped solution in the reaction mixture and in the liquids which condensed in the cold traps, and were analyzed by gas analysis apparatus.

The yields of methyl chloride and 2-methylpropane consisted of condensates

¹ Part of this investigation was presented before the 114th meeting of the American Chemical Society at St. Louis, Missouri, September 1948.

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of gases which escaped solution in the reaction mixture. Repeated fractionation of these low-boiling compounds further reduced the apparent yields.

CONDENSATION AND FRAGMENTATION PRODUCTS OF 2,3-DIMETHYL-2-BUTANOL

The condensation of 2,3-dimethyl-2-butanol was characterized by a good yield of 2,3-dimethyl-2-phenylbutane and a small amount of fragmentation (See Table I).

The small yield of 2-methyl-2-phenylpropane and the failure to isolate 2-methylpropane indicated a limited amount of methyl migration.

TABLE I
CONDENSATION AND FRAGMENTATION PRODUCTS OF 2,3-DIMETHYL-2-BUTANOL

PRODUCT	B.P., °C./MM.	d_4^{20}	n_D^{20}	DERIVATIVE, M.P., °C.	YIELD, %
2,3-Dimethyl-1-butene	54-56/750 (55.6/760) (6)	0.6824 (0.6780) (6)	1.3915 (1.3904) (6)		15
2,3-Dimethyl-butane	58-60/750 (58/760) (7)	0.6619 (0.6616) (7)	1.3760 (1.3749) (7)		3
2,3-Dimethyl-2-butene	72-74/750 (73.2/760) (6)	0.7076 (0.7080) (6)			4
2-Chloro-2,3-dimethyl-butane	108-110/740 (112/750) (8)	0.8772 (0.8784) (8)	1.4298		18
2-Methyl-2-phenylpropane	166-169/750 (169.1/760) (9)	0.8632 (0.8665) (9)	1.4910 (1.4902) (9)	Acetamino 168-169 (2)	0.9
2,3-Dimethyl-2-phenylbutane	206-208/740 (208-210/745) (11)	0.8814 (0.8814) (11)	1.4980 (1.4988) (11)	Acetamino 118-119 (2)	40

The yield of 2,3-dimethylbutane was small. This type of reduction is in general more pronounced with alcohols in which there is no methyl branching on the carbon adjacent to the carbinol carbon (4).

A highly unsaturated fraction (3 g.) distilled at 100-105°. This range includes the boiling points of several octenes which might be formed by the combination of fragments (3). Another small alkene fraction came over at 150-160°.

An aromatic and unsaturated fraction (4 g.) distilled at 187-192°. Oxidation gave a small amount of acetophenone which was identified by the melting point of its semicarbazone (193°). This mixture would contain any 2-phenyl-3-methyl-2-butene (b.p. 189°) and 2-phenyl-3-methyl-1-butene (b.p. 191°) formed by the elimination of methane from 2,3-dimethyl-2-phenylbutane. This fraction would contain also any 2-methyl-2-phenylbutane (b.p. 190°) formed by the condensation of 2-methyl-2-butene with benzene. Since there was little fragmentation,

the lack of the formation of appreciable amounts of 2-methyl-2-butene was not surprising.

CONDENSATION AND FRAGMENTATION PRODUCTS OF 2,3-DIMETHYL-2-PENTANOL

In the condensation of 2,3-dimethyl-2-pentanol with benzene the yield of 2,3-dimethyl-2-phenylpentane was high while the amount of methyl migration as indicated by the yield of 2-methyl-2-phenylpropane was very small. No 2-methylpropane could be isolated (See Table II).

TABLE II
CONDENSATION AND FRAGMENTATION PRODUCTS OF 2,3-DIMETHYL-2-PENTANOL

PRODUCT	B.P., °C./MM.	d_4^{20}	n_D^{20}	DERIVATIVE, M.P., °C.	YIELD, %
2,3-Dimethyl-1-pentene	83-85/750 (85/760) (12)	0.7095 (0.7100) (12)	1.4025 (1.4030) (12)		10
2,3-Dimethyl-pentane	88-91/750 (89.79/760) (13)	0.6950 (0.6951) (13)	1.3912 (1.392) (13)		4
2,3-Dimethyl-2-pentene	95-98/750 (97/760) (12)	0.7304 (0.728) (12)	1.4205 (1.421) (12)		3
2-Chloro-2,3-dimethylpentane ^a	135-137/740 39-40/18 (38-39/20) (11)	0.8788	1.4278 ²⁵ (1.4264) (11)		14
2-Methyl-2-phenylpropane	165-168/740 (167/760) (9)	0.8631 (0.8665) (9)	1.4912 (1.4902) (9)	Acetamino 168-169 (10)	1
2,3-Dimethyl-2-phenylpentane	219-221/740 (222-223/745) (11)	0.8801 (0.8801) (11)	1.4958 (1.4966) (11)	Acetamino 85-86	42

^a Chlorine: Calc'd, 26.37; Found, 26.99.

There was sufficient reducing action to produce 2,3-dimethylpentane in about the same yield as that of 2,3-dimethylbutane from 2,3-dimethyl-2-butanol.

A mixture of alkenes (3 g.) came over at 150-160° (3) and another small fraction (2 g.) at 175-180°. Five grams of product distilled at 200-205°. Oxidation of this fraction gave a small amount of acetophenone, indicating the presence of 2-phenyl-3-methyl-2-pentene (b.p. 204°). We were unable to detect the presence of 2-phenyl-2-methylpentane (b.p. 205°), which would be formed by demethylation and condensation of the resulting fragment with benzene.

CONDENSATION AND FRAGMENTATION PRODUCTS OF 2,3,3-TRIMETHYL-2-BUTANOL

The products identified from the condensation of 2,3,3-trimethyl-2-butanol with benzene were the same as described in an earlier publication (2).

The compound, 2-chloro-2,3,3-trimethylbutane was further identified by its melting point 133–135° (14). It boiled at 129–131° (745 mm.).

A small amount (3 g.) of alkane (4) came over at 79–82°. There was evidence of the formation of small amounts of propene and ethene since 1,2-dibromopropane and 1,2-dibromoethane were recovered from the bromine trap. Separation was accomplished by fractional distillation of the combined products of several runs. The 1,2-dibromopropane was identified by its boiling point 138–140° (15) and by bromine analysis. The 1,2-dibromoethane was identified by its boiling point 130–132°, and its melting point 9.8–10.2° (16).

The formation of propene gave additional evidence of the type of fragmentation of 2,3,3-trimethyl-2-butanol. The formation of ethylene gave further evidence of the rearrangement and fragmentation of the demethylated fragment.

The distillation of the liquid products of the condensation gave evidence of the formation of small amounts of alkenes (3). One small fraction (2.5 g.) came over at 150–160° and another (3 g.) at 175–180°.

The method used in the identification of 3-methyl-2-phenyl-2-butene was by reduction with sodium and alcohol as described in the earlier publication (2). It should be pointed out that any 3-methyl-2-phenyl-1-butene present would be reduced also by sodium and alcohol to 3-methyl-2-phenylbutane.

CONDENSATION AND FRAGMENTATION PRODUCTS OF 2,2,3-TRIMETHYL-3-PENTANOL

The 2,2,3-trimethyl-3-phenylpentane fraction from the condensation of 2,3,3-trimethyl-3-pentanol with benzene appeared to be impure.

Fragmentation accounts for the recovery of 2-chlorobutane, 2-methylpropane, and 2-methyl-2-phenylpropane.

Loss of water from 2,2,3-trimethyl-3-pentanol would give a mixture of 3,4,4-trimethyl-2-pentene (b.p. 112°) and 3,3-dimethyl-2-ethyl-1-butene (b.p. 110.4°). These would be present in the C_8H_{16} fraction together with any small amount of 2,2,3-trimethylpentane, b.p. 109.8° (4). Reduction of the C_8H_{16} fraction with sodium and alcohol gave pure 2,2,3-trimethylpentane, b.p. 108–110°; d_4^{20} 0.7165; n_D^{20} 1.4031 (29).

Demethylation followed by condensation would give 2,3-dimethyl-3-phenylpentane. Repetition of this process would give 3-methyl-3-phenylpentane.

A portion of the fraction which came over at 200–206° was oxidized and gave some propiophenone. Reduction of the 200–206° fraction gave 2-methyl-3-phenylpentane which came over at 198–200° (26) and was separated, by repeated fractionation, from 3-methyl-3-phenylpentane which distilled at 204–206°.

It will be noted that the physical constants reported for 2,2,3-trimethyl-3-phenylpentane are practically identical with those of 2,3,3-trimethyl-2-phenylpentane. Nitration, reduction, and diazotization of either gave phenolic mixtures which did not give sharp-melting α -naphthylurethans. It has been shown in this laboratory (28) that 2,2,3-trimethyl-3-pentanol condenses with phenol to give octylphenols which are identical with the two octylphenols formed by the condensation of 2,3,3-trimethyl-2-pentanol with phenol.

TABLE III
CONDENSATION AND FRAGMENTATION PRODUCTS OF 2,2,3-TRIMETHYL-3-PENTANOL

PRODUCT	B.P., °C./MM.	d_4^{20}	n_D^{20}	DERIVATIVE, M.P., °C.	YIELD, %
Methane ^a					1
Methyl chloride ^b	-24 to -22/740 (24.2/760) (17)		1.3480-25 (1.3830-25) (18)		1.5
2-Chlorobutane ^c	68-70/760 (68/760) (19)	0.8712 (0.8788) ¹⁵ (20)	1.3969 (1.3994) ¹⁵ (20)		1
2-Methylpropane	-11 to -10/745 (-10.2/760) (21)		1.3516-25 (1.3514-25) (18)		1
C ₈ H ₁₆ ^d	108-112/750	0.7282 (22)	1.4232 (22)		10
3-Chloro-2,2,3-trimethylpentane ^e	158-160/745	0.8840	1.4609		20
2-Methyl-2-phenylpropane	168-170/755 (169.1/760) (23)	0.8686 (0.8665) (23)	1.4912 (1.4902) (9)	Acetamino 168-170 (10)	10
2,3-Dimethyl-3-phenylpentane	223-225/750 (226/760) (11)	0.8820 (0.8803) (11)	1.5012 (1.4974) (11)	α -Naphthylurethan of 2,3-dimethyl-3- <i>p</i> -hydroxyphenylpentane, 110-112 (24)	4
2-Methyl-3-phenylpentene and 3-methyl-3-phenylpentane	200-206/750			Dinitrophenylhydrazone of propiophenone, 196. ^f Benzoyl ester of 3- <i>p</i> -hydroxyphenyl-3-methylpentane, 77-78 (25)	13
2,2,3-Trimethyl-3-phenylpentane ^e	230-233/745 (27)	0.8901	1.5031	α -Naphthylurethan of <i>p</i> -hydroxyderiv. 110-114 ^g	10

^a Determined by combustion of gases which had passed through cold trap below -50° ^b Chlorine, Calc'd: 70.23; Found, 69.85. ^c Chlorine, Calc'd: 38.3; Found, 38.04. ^d Carbon, Calc'd: 85.61; Found, 85.55; Hydrogen, Calc'd: 14.38; Found, 13.91. ^e Chlorine, Calc'd: 23.86; Found, 23.63. ^f This was checked by mixed melting point with the dinitrophenylhydrazone of the known propiophenone. ^g Carbon, Calc'd: 88.38; Found, 88.29; Hydrogen, Calc'd: 11.66; Found, 11.73. ^h Melting point shows evidence of mixture (27).

PRODUCT	B.P., °C./MM.	d_4^{20}	n_D^{20}	DERIVATIVE, M.P., °C.	YIELD, %
Methane ^a					0.9
Methyl chloride	-24 to -22/745 (-24.2/760) (17)		1.3482 ²⁶ (1.3830 ⁻⁴³) (18)		1.5
2-Chloropropane	35-37/750 (29, 30)			2-Methylpropionanilide 105-107° (2)	1.0
2-Methylbutane	27-29/750 (30/747) (31)		1.3581 ²⁵ (1.3579 ¹⁶) (32)		10
2, 3, 3-Trimethyl-1-pentene	107-109/744 (108/760) (22)	0.7366 (0.737) (22)	1.4185 (1.4178) (22)		10
2, 3, 3-Trimethylpentane	113-115/750 (114.7/760) (29)	0.7265 (0.7262) (29)	1.4081 (1.4075) (29)		3
2-Methyl-2-phenylpropane	166-169/750 (169.1/760) (23)	0.8630 (0.8665) (23)	1.4912 (1.4902) (23)	Acetamino, 168-170 (10)	10
2-Chloro-2, 3, 3-trimethylpentane ^b	156-159/740	0.8645	1.4629		15
2-Methyl-2-phenylbutane	189-192/741 (189.6/760) (33)	0.8735 (0.8737) (33)	1.4931 (1.4934) (33)	Acetamino, 139-142 (33)	2
2, 3-Dimethyl-2-phenylpentane	219-221/740 (222-223/745) (11)	0.8801 (0.8801) (11)	1.4960 (1.4988) (11)	Acetamino, ^c 85-86°	5
3-Methyl-2-phenylpentene and 2-methyl-2-phenylpentane	200-206/750			α -Naphthylurethan of 3-methyl-2- <i>p</i> -hydroxyphenylpentane, 100-102° (34). α -Naphthylurethan of 2-methyl-2- <i>p</i> -hydroxyphenylpentane, 126-127 ^d	12
2, 3, 3-Trimethyl-2-phenylpentane	230-233/740	0.8868	1.5011	Acetamino, 90-93°	10

^a Determined by the combustion of gases which had passed through the cold trap below -50°. ^b Chlorine, Calc'd: 23.86; Found, 23.70. ^c Mixture melting point with the acetamino derivative of the hydrocarbon prepared from 2, 3-dimethyl-2-pentanol and benzene showed no depression. ^d Mixed melting point with the α -naphthylurethan of the phenol prepared from 2-methyl-2-pentanol and phenol (24) showed no depression. ^e The wide melting point indicates a mixture.

One small fraction of alkenes (not shown in the Table) came over at 190–196° (3).

CONDENSATION AND FRAGMENTATION PRODUCTS OF 2,3,3-TRIMETHYL-2-PENTANOL

The probability of contamination of 2,3,3-trimethyl-2-phenylpentane by methyl migration prior to condensation (see above), was evidenced by the formation of a considerable amount of 2-methyl-2-phenylpropane. The compound, 2-methylpropane, was not formed in sufficient quantity for isolation and purification (See Table IV).

The large yield of 2-methylbutane and the small yield of 2-methyl-2-phenylbutane indicates that the five carbon fragment from 2,3,3-trimethyl-2-pentanol undergoes reduction more readily than condensation.

The formation of a small amount of 2,3,3-trimethylpentane was probably the result of reduction of 2,3,3-trimethyl-1-pentene or 2-chloro-2,3,3-trimethylpentane.

Demethylation followed by condensation with benzene would give 2,3-dimethyl-2-phenylpentane. Repetition of this process starting with protonized 2,3-dimethyl-2-pentene would give as the final products, methyl chloride and 2-methyl-2-phenylpentane.

The presence of 3-methyl-2-phenyl-2-pentene in the fraction boiling at 200–206° was indicated by oxidation of a small portion of the fraction and the identification of acetophenone by the melting point of its semicarbazone (193°). The 200–206° fractions from several runs were combined and reduced. The reduced mixture contained 3-methyl-2-phenylpentane, which distilled at 198–202°, and 2-methyl-2-phenylpentane which came over at 204–206°.

EXPERIMENTAL

PREPARATION OF THE CARBINOLS

2,3-Dimethyl-2-butanol. Methyl isopropyl ketone was added to methylmagnesium bromide. After hydrolysis the product was purified to the boiling range 118–120° @ 740 mm.

2,3-Dimethyl-2-pentanol. Acetone was added to *sec*-butylmagnesium bromide. The purified alcohol boiled at 129–131° @ 750 mm.

2,3,3-Trimethyl-2-butanol. Pinacolone was added to methylmagnesium bromide. After hydrolysis the alcohol distilled at 129–130° @ 750 mm.

2,2,3-Trimethyl-3-pentanol. Pinacolone was added to ethylmagnesium bromide. After hydrolysis the alcohol distilled at 148–150° @ 750 mm.

2,3,3-Trimethyl-2-pentanol. This alcohol was prepared by two methods. (a) Methyl tert-amyl ketone (35) was added to methylmagnesium bromide.

(b) 2,2-Dimethylbutanoic acid was prepared by the carbonation of tert-amylmagnesium chloride and the acid was added to three moles of methylmagnesium bromide (28, 36). The purified alcohol distilled at 155–157° @ 750 mm.

CONDENSATIONS

The condensations were made in a three-necked flask equipped with a glycerine-sealed stirrer, a Freas dropping-funnel, and a water-cooled condenser. The condenser was attached to a trap cooled by a mixture of ice and salt followed by a second trap cooled by a mixture of Dry Ice and acetone. Dewar flasks were used for both types of mixtures. A mer-

cury trap and manometer were attached to the last trap cooled by Dry Ice and acetone to a temperature of -40 to -60° . A stop-cock system permitted the by-passing of the cooled traps when necessary. A trap containing bromine was attached to the mercury trap. A nitrometer containing 50% aqueous potassium hydroxide completed the condensation apparatus. The Freas dropping-funnel permitted the washing out of the entire system with carbon dioxide. The latter was dried by passage through concentrated sulfuric acid before entering the system. The first trap condensed small amounts of carbinol and benzene. The second trap condensed low-boiling substances, such as methyl chloride, while all gases not reacted or condensed were collected in the nitrometer for transfer and analysis.

The condensations were made in the ratio of one mole of carbinol, one-third mole of aluminum chloride, and five moles of benzene. The temperature was maintained at $40-45^{\circ}$ in order to obtain the maximum amount of fragmentation. The aluminum chloride was suspended in the benzene and heated to the reflux temperature for one hour. Carbon dioxide was passed through the system until the benzene and suspended aluminum chloride were cooled to room temperature. The evolution of gases began to decrease when one-third of the carbinol was added. When one-half of the carbinol was added, 200-300 mm. of back pressure was created in the system. After two-thirds of the carbinol was added, rapid addition of the remaining one-third did not increase the temperature, but the yields were decreased if this last one-third was not added. At this two-thirds point, both the temperature and the back pressure decreased. The system was washed out with carbon dioxide after all of the carbinol was added. The liquids which condensed in the traps were fractionated at low temperatures. The gases collected in the nitrometer were analyzed for hydrocarbons and oxygen with the Fisher Gas Analyzer. The products in the main reaction flask were stirred at least one hour after all of the carbinol was added, were hydrolyzed without additional acid, and the aqueous layer was extracted with benzene. The combined organic layers were washed with water and with sodium carbonate. After drying over sodium sulfate, the mixture was fractionated with a 30" Fenske type column equipped with a take-off head. For the redistillation of small portions shorter columns were used. The distillation flask was heated with a Glas-Col mantle. The heating of the flask and column was controlled electrically through a variable transformer.

The 200-206° fraction from 2,2,3-trimethyl-3-pentanol. A 10-ml. portion was oxidized with chromic acid in glacial acetic acid for 24 hours. Propiophenone was formed and identified as its dinitrophenylhydrazone, m.p. 196° . A mixture melting point with a sample of dinitrophenylhydrazone prepared from known propiophenone showed no depression. The 200-206° fractions from three condensations were combined and reduced with a platinum catalyst. Repeated fractionation gave 2-methyl-3-phenylpentane at $198-200^{\circ}$ (26) and 3-methyl-3-phenylpentane at $204-206^{\circ}$, d_4^{20} 0.8693, n_D^{20} 1.5005 (11). Nitration, reduction, and diazotization of the latter gave 3-*p*-hydroxyphenyl-3-methylpentane which was identified by the melting point, $77-78^{\circ}$, of its benzoyl ester (25).

The 200-206° fraction from 2,3,3-trimethyl-2-pentanol. A 10-ml. portion gave acetophenone when oxidized with chromic acid in glacial acetic acid. This was identified by the melting point of its semicarbazone, 193° (2). The 200-206° fractions from three condensations were combined and reduced catalytically.

The reduced mixture was fractionated repeatedly and two fractions were collected, one at $198-202^{\circ}$, and one at $202-206^{\circ}$. The $198-202^{\circ}$ fraction was nitrated, reduced, and diazotized to 3-methyl-2-*p*-hydroxyphenylpentane which gave an α -naphthylurethan melting at $101-102^{\circ}$ (34). Nitration, reduction, and diazotization of the $204-206^{\circ}$ fraction gave a phenol which came over at $258-261^{\circ}$ and gave an α -naphthylurethan which melted at $126-127^{\circ}$. Then, 2-methyl-2-*p*-hydroxyphenylpentane was prepared from 2-methyl-2-pentanol and phenol (25). A mixture melting point of the α -naphthylurethans showed no depression.

SUMMARY

1. Five highly branched alcohols, 2,3-dimethyl-2-butanol, 2,3-dimethyl-2-pentanol, 2,3,3-trimethyl-2-butanol, 2,2,3-trimethyl-3-pentanol, and 2,3,3-

trimethyl-2-pentanol, were reacted with benzene in the presence of aluminum chloride.

2. Condensation and fragmentation reactions are proposed to account for the products identified.

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