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The Dehydration of Tertiary Carbinols Containing the Neopentyl Group

BY FRANK C. WHITMORE AND EWALD ROHRMANN

While the dehydration products of a considerable number of tertiary carbinols have been studied, only a limited number of these carbinols have contained the neopentyl group, $(CH_3)_3CCH_2$–. Whitmore and Laughlin[1] studied the dehydration products of several tertiary carbinols having the hydroxyl group attached to a neopentyl group and found rearrangement to the extent of 6 to 25%. Similar tertiary carbinols with the hydroxyl group not attached to the neopentyl group gave no rearrangement.

The only tertiary carbinol containing the neopentyl group, $(CH_3)_3CCH_2$–, which Whitmore and Laughlin studied was methylethylneopentylcarbinol. This carbinol upon dehydration yielded largely 2,2,4-trimethyl-4-hexene (dehydration from the ethyl group), less than 5% of 2,2,4-trimethyl-3-hexene (dehydration from the neopentyl group) and only traces of 4,4-dimethyl-2-ethyl-1-pentene (dehydration from the methyl group).

Whitmore and Wrenn[2] dehydrated dimethylneopentylcarbinol by different procedures and observed in every case that the olefin mixture obtained was about 80% 2,4,4-trimethyl-1-pentene (dehydration from the methyl group) and 20% 2,4,4-trimethyl-2-pentene (dehydration from the neopentyl group).

In the present work the dehydration products of diethylneopentylcarbinol and of methyl-*n*-butylneopentylcarbinol have been studied. The olefins were determined by examination of their ozonolysis degradation products.[3] Diethylneopentylcarbinol gave about 90% of 2,2-dimethyl-4-ethyl-4-hexene (dehydration from the ethyl group) and less than 10% of 2,2-dimethyl-4-ethyl-3-hexene (dehydration from the neopentyl group). If all of the secondary hydrogen atoms adjacent to the carbinol carbon were of the same degree of reactivity the olefin yields would be in a ratio of 2:1 instead of about 9:1.

Methyl-*n*-butylneopentylcarbinol on dehydration yielded about 10% of 4,4-dimethyl-2-*n*-butyl-1-pentene (dehydration from the methyl group), a trace of 2,2,4-trimethyl-3-octene (dehydration from the neopentyl group) and over 80% of 2,2,4-trimethyl-4-octene (dehydration from the *n*-butyl group).

These results together with the previous observations show conclusively that the neopentyl group enters into such dehydrations only with difficulty. Its secondary hydrogen atoms are much less easily released as protons than are those of groups such as ethyl and *n*-butyl. The cause of the lack of reactivity is unknown but it may possibly be associated with the symmetrical electron arrangement typical of the neopentyl group.

The dehydrations herein reported were carried out using anhydrous copper sulfate in order to avoid any possible complications from the use of iodine or of strongly acidic agents. In no case was there any evidence of a rearrangement.

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[1] Whitmore and Laughlin, THIS JOURNAL, **55**, 3732 (1933).

[2] Whitmore and Wrenn, unpublished work, presented at the Pittsburgh meeting of the A. C. S., Sept., 1936.

[3] Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932); Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).

Experimental

Distillation Apparatus.—Two fractionating columns of the adiabatic, total reflux, variable take-off type packed with single turn glass helices were used. Column A, packed section 1.5 × 65 cm., 10 theoretical plates; column B, 0.9 × 45 cm., 10 theoretical plates.

Diethylneopentylcarbinol.—The carbinol was prepared by the addition of ethyl *t*-butylacetate to a large excess of ethylmagnesium bromide at room temperature: yield 78%, b. p. 32° at 3 mm., n^{20}D 1.4398–1.4408.

Dehydration of Diethylneopentylcarbinol.—The apparatus used consisted of a 200-ml. round-bottom two-necked flask equipped with a small Liebig condenser and a dropping funnel. A mixture of 30 g. of anhydrous copper sulfate and 8 g. of pulverized pumice was placed in the flask and the mixture heated to 180–190° in an oil-bath. Diethylneopentylcarbinol (473 g., 3 moles) was added dropwise to the catalyst over a period of nineteen hours while the olefins were distilled over as rapidly as formed. The distillate consisted of 53 ml. of water and 394 g. of crude olefins. The olefin layer was dried over sodium sulfate and fractionated through column A. The fractions obtained were combined in the following groups:

Group	B. p.	n^{20}D range	G.	Moles
A	147–148°	1.4278–1.4295	30.4	0.217
B	148.3–149.5	1.4298–1.4303	178	1.27
C	149.6–150	1.4307–1.4312	90.5	0.645
D	150–90.3 (110 mm.)	1.4317–1.4320	36.5	.260
E	90.4–91 (110 mm.)	1.4328–1.4365	39.4	.281

The yield of fractionated olefins was 375 g. (2.38 moles), 79.5%.

Ozonolysis of Decenes.—The olefins were ozonized and decomposed as already described.[3] A special low boiling (0–30°) olefin-free hydrocarbon solvent was used and the ozonides were decomposed with zinc dust and water in the presence of traces of hydroquinone and silver nitrate.

An aliquot part of the material from the salt–ice traps was used in the determination of acetaldehyde. This yielded a dimetol derivative, m. p. and mixed m. p. 138–139°. Trimethylacetaldehyde, diethyl ketone and ethyl neopentyl ketone were identified by formation of 2,4-dinitrophenylhydrazones which gave m. p. and mixed m. p. of 206–207.5°, 154–155.5° and 134–135.5°, respectively.

SUMMARY OF OZONOLYSIS DATA FOR DECENES FROM THE DEHYDRATION OF DIETHYLNEOPENTYLCARBINOL

Olefin group ozonized	A		B		C		D		E	
	Moles	%	Moles	%	Moles	%	Moles	%	Moles	%
Moles	0.207		0.40		0.40		0.26		0.28	
MeCHO	.11	53	.20	51	.21	52	.15	58	.15	53
Me_3C-CHO	.024	12	.013	3	.005	1	Trace	..	..	..
Et_2CO	.03	14	.027	7	.03	7	Trace	..	..	..
$EtCOCH_2CMe_3$	.15	70	.25	62	.3	75	0.18	72	0.2	70

Methyl-*n*-butylneopentylcarbinol.—The carbinol was prepared in 73% yield (based on the ketone used) by the addition of methyl neopentyl ketone to the theoretical amount of *n*-butylmagnesium bromide in ether solution at 0°, b. p. 55–56° at 5 mm., n^{20}D 1.4397–1.4404.

Dehydration of Methyl-*n*-butylneopentylcarbinol.—The apparatus and method described for the dehydration of diethylneopentylcarbinol was used. The catalyst consisting of 30 g. of anhydrous copper sulfate and 8 g. of pulverized pumice was heated to 193–198° and 498 g. (3.08 moles) of methyl-*n*-butylneopentylcarbinol was added dropwise over a period of twelve hours. The crude olefin layer weighing 445 g. was dried over sodium sulfate and fractionated through column A. The sixty-six fractions obtained were combined into the following groups:

Group	B. p., °C.	n^{20}D	G.	Moles
F	to 169.7	1.4311–1.4313	91.6	0.595
G	169.9	1.4316–1.4321	236	1.54
H	170	1.4321–1.4329	67	0.435

The total yield of fractionated olefins was 394.6 g. (0.256 mole) or 83.5% (based on the carbinol).

Portions of the materials from each of these olefin groups were ozonized in the same manner as the decenes. The water layer resulting from the decomposition of the ozonide gave a 2.6% yield of the dimetol derivative of formaldehyde, m. p. and mixed m. p. 188–189°. *n*-Butyraldehyde, trimethylacetaldehyde and methyl neopentyl ketone were identified as the 2,4-dinitrophenylhydrazones of m. p. and mixed m. p. 123–124°, 206° and 99–100°, respectively. There were also obtained the dimetol derivative of *n*-butyraldehyde, m. p. and mixed m. p. 134.5–135.5°, and the semicarbazone of methyl neopentyl ketone, m. p. and mixed m. p. 176.5–177.5°. *n*-Butyl neopentyl ketone gave a semicarbazone of m. p. and mixed m. p. 115–117°.

SUMMARY OF OZONOLYSIS DATA FOR THE UNDECENES FROM THE DEHYDRATION OF METHYL-*n*-BUTYLNEOPENTYLCARBINOL

Olefin Group ozonized	F		G		H	
	Moles	%	Moles	%	Moles	%
Moles	0.4		0.4		0.4	
CH_2O	.011	2.7	.01	2.6	.011	2.7
PrCHO	.06	14	.07	17	.09	18
Me_3C-CHO	Trace		Trace		Trace	
$MeCOCH_2CMe_3$	.16	40	.14	36	.19	47
$BuCOCH_2CMe_3$			.087	7.5		

Summary

1. Diethylneopentylcarbinol upon dehydration with anhydrous copper sulfate gave 90% of 2,2-dimethyl-4-ethyl-4-hexene (dehydration from the ethyl group) and less than 10% of 2,2-dimethyl-4-ethyl-3-hexene (dehydration from the neopentyl group).

2. Methyl-*n*-butylneopentylcarbinol upon dehydration in a similar manner gave over 80% of 2,2-dimethyl-4-methyl-4-octene (dehydration from the *n*-butyl group), about 10% of 4,4-di-

methyl-2-*n*-butyl-1-pentene (dehydration from the methyl group), and a trace of 2,2-dimethyl-4-methyl-3-octene (dehydration from the neopentyl group).

3. The sluggishness of the neopentyl group in giving hydrogen for a dehydration reaction is further confirmed and emphasized.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Polymerization of Olefins. V.[1] The Isomers in Triisobutylene

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The Isomers in Triisobutylene

The preparation of "triisobutylene" was first described in 1879 by Butlerow,[3] who obtained an oil boiling at 177.5–179° by dissolving isobutylene in a cold mixture of five parts of sulfuric acid and one of water. The structures of the compounds in this oil have since been investigated.[4,5,6] Work in this Laboratory on polymerization of olefins cast doubt on some of the earlier work and made necessary a complete study of the problem.

The fractionation of the triisobutylenes was undertaken in an attempt to separate the various isomers because the structure and the ratio of these olefins are important in the work on polymerization in progress in this Laboratory since 1932. We used the highly efficient large scale fractionating columns developed during the work on the fractionation and composition of gasoline in the Petroleum Refining Laboratory.[7]

After repeated fractionations of crude triisobutylene about 90% boiled 177–179° and about 10% 183–185°. Calculations[8] show that a column of perhaps five hundred theoretical plates would be needed to separate sharply the low boiling fractions. Actually a column of 75 plates was used first. This was followed by repeated refractionation through a smaller column having 90–100 plates. Cooling curves on the various fractions indicated no pure isomers.

The degree of separation was followed during the distillations by careful determination of the index of refraction, Cottrell boiling point, and density. The Kauri-butanol number[9] was also determined. Examination of these constants for the final fractions shows that the triisobutylene had been divided by distillation into three parts. A summary of the physical constants is given in Table I. These results summarize many distillations carried out from 1933 to date.

TABLE I

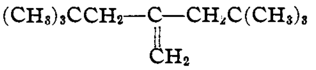
PHYSICAL CONSTANTS OF TRIISOBUTYLENE FRACTIONS

Group	A	B	C
% of total triisobutylene	75	15	10
Cottrell b. p. °C. at 760 mm.	177.7	179.0	183–185
$n^{20}D$	1.4300	1.4318	1.4415
d^{20}	0.7587	0.7597	0.7765
K. b. number	28.5	28.5	36.5

The hundreds of fractions making up Group A had a constant index of refraction. Repeated fractionation of this material through a 100-plate column gave no further separation. Extraction with methyl alcohol and with aniline also did not alter the composition. Likewise equilibrium melting gave no change.

Six possible triisobutylenes have been formulated.[10] Ozonolysis of the Group A material gave trimethylacetaldehyde, methyl neopentyl ketone, formaldehyde, dineopentyl ketone, and the related acids, thus proving the fractions to contain 2,2,4,6,6-pentamethyl-3-heptene (I) and 2-neopentyl-4,4-dimethyl-1-pentene, 1,1-dineopentylethylene (II).

$(CH_3)_3CCH{=}C(CH_3)CH_2C(CH_3)_3$ (I)



$(CH_3)_3CCH_2{-}\underset{\underset{\displaystyle CH_2}{\|}}{C}{-}CH_2C(CH_3)_3$ (II)[6]

The Group B material gave a larger yield of fragments from I than did the Group A fractions.

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(1) Whitmore and Mixon, THIS JOURNAL, **63**, 1460 (1941).

(2) Submitted in partial fulfillment for the Ph.D. degree.

(3) Butlerow, *Ber.*, **12**, 1482 (1879).

(4) Lebedev and Kobliansky, *ibid.*, **63B**, 103, 1432 (1930).

(5) McCubbin, THIS JOURNAL, **53**, 356 (1931).

(6) Bartlett, Fraser and Woodward, *ibid.*, **63**, 495 (1941).

(7) Fenske and co-workers, *Ind. Eng. Chem.*, **24**, 408 (1932); **26**, 1169 (1934); **29**, 70, 571 (1937).

(8) Rose, THIS JOURNAL, **62**, 793 (1940).

(9) Baldeschwieler, Troeller and Morgan, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 374 (1935); Beard, Ship and Spelhouse, *ibid.*, **5**, 307 (1933).

(10) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).