

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

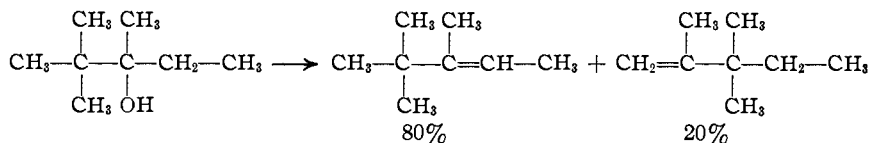
THE DEHYDRATION OF TERTIARY CARBINOLS CONTAINING A NEOPENTYL SYSTEM. I. METHYLETHYL-TERTIARY-BUTYLCARBINOL AND DIMETHYL-TERTIARY-AMYL CARBINOL¹

BY FRANK C. WHITMORE AND KENNETH C. LAUGHLIN

RECEIVED MAY 17, 1932

PUBLISHED OCTOBER 5, 1932

Methylethyl-*tert.*-butylcarbinol has been prepared previously by Clarke and Jones² and converted to an olefin by treating its iodide with alcoholic potassium hydroxide. This olefin was erroneously assumed to be *unsym.*-ethyl-*tert.*-butylethylene. The present study was undertaken to determine the nature of the olefinic products obtainable from this carbinol, especially in relation to the possible rearrangement of the neopentyl system. As will be recalled, primary and secondary alcohols having the hydroxyl attached to this system rearrange during dehydration or replacement of the hydroxyl by halogen.³ In view of the extraordinary ease with which tertiary alcohols are dehydrated by heating with a trace of iodine, it seemed possible that an alcohol in which the hydroxyl is both tertiary and part of a neopentyl system might be dehydrated without rearrangement. At first this seemed to be the case since the dehydration product obtained from methylethyl-*tert.*-butylcarbinol was 2,2,3-trimethylpentene-3, the "normal" dehydration product. When the process was studied more minutely, however, it was found that the dehydration product also contained 20% of the rearranged olefin, 2,3,3-trimethylpentene-1. None of the olefin assumed by Clarke and Jones was found. The structure of the olefins was determined by ozonolysis and the preparation of semicarbazones of the methyl-*tert.*-butyl ketone and the methyl-*tert.*-amyl ketone thus formed.



Dimethyl-*tert.*-amylcarbinol was prepared from methyl-*tert.*-amyl ketone and methylmagnesium chloride. Its dehydration with iodine gave mainly the "normal" dehydration product, 2,3,3-trimethylpentene-1, which was identified by ozonolysis. The small amount of by-product has not yet been identified.

¹ Presented by Kenneth C. Laughlin in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

² Clarke and Jones, *THIS JOURNAL*, 34, 170 (1912).

³ See *THIS JOURNAL*, 54, 3279 (1932).



Experimental

Methylethyl-*tert.*-butylcarbinol.—Methyl-*tert.*-butyl ketone, b. p. 103–106° (735 mm.), was prepared from acetone.⁴ Ethylmagnesium bromide was prepared from 327 g. (3 moles) of ethyl bromide in 750 cc. of dry ether and an aliquot part was titrated; yield, 80%.

To 1.9 moles of ethylmagnesium bromide solution in a 3-liter flask equipped with a stirrer, was added 190 g. (1.9 moles) of the ketone in 600 cc. of dry ether at about four drops per second. A small amount of unsaturated gas was evolved. The mixture was heated for one hour on the steam-bath and then stirred for three hours more. The mixture was poured on ice and 50 g. of ammonium chloride. The ether layer was decanted and the water layer was treated with dilute sulfuric acid until it just turned clear (still alkaline to litmus). It was then extracted twice with 250-cc. portions of ether. The ether solutions were dried overnight with 75 g. of freshly calcined potassium carbonate. After filtering and removing the ether on the steam-bath, the residue was distilled through an 85 × 2 cm. total condensation column.

Fraction	B. p., °C.	Pressure, mm.	Amt.	n_D^{20}
A 1	25–45	240	27 cc.	1.3738
2	45–90	240–100	76 cc.	1.4316
3	76.2–75.8	41–39	147 g.	1.4353
4	Residue		15 cc.	

The yield was 60%.

Dehydration of the Carbinol and Distillation of the Products.—The methylethyl-*tert.*-butylcarbinol (147 g.) was refluxed with a crystal of iodine under a column connected with a device for separating the water distilled out. When no more water was formed, the product was dried with 25 g. of potassium carbonate. The yield of crude olefin was 111 g. or 86%. The distillation of 86 g. of this material through the 85 × 2 cm. column gave the following at 740 mm.

Fraction	B. p., °C.	Wt., g.	n_D^{20}
B 1	104–107	6	1.4170
2	107–108	4	1.4199
3	108–108.8	15	1.4219
4	108.8–109.2	42	1.4230
5	Residue	16	1.4262

Identification of 2,2,3-Trimethylpentene-3.—Fraction B 4 (42 g.) was ozonized⁵ and the ozonide was decomposed with zinc dust and hot water. The oily layer of the distillate was combined with ether extracts of the water layer and dried, and distilled through a 40 × 0.8 cm. total condensation column at 741 mm.

Fraction	B. p., °C.	Amt., cc.	n_D^{20}
C 1	40–90	3	1.3831
2	90–98	6	1.3919
3	98–103	5	1.4945
4	103–106	7	1.3939
5	Residue		1.4120

⁴ "Organic Syntheses," 1925, Vol. V, p. 87.

⁵ See THIS JOURNAL, 54, 3710 (1932).

The semicarbazone was prepared from 0.5 cc. of Fraction C 4 by adding 0.5 g. of semicarbazide and 0.7 g. of sodium acetate in 5 cc. of water, adding alcohol to form a clear solution, and warming on the steam-bath until cooling to 0° produced crystals. The crude semicarbazone melted at 150°. Recrystallization from petroleum ether raised the m. p. to 153–154°. The melting point was not lowered by a known sample of the semicarbazone of methyl-*tert.*-butyl ketone. The water layer of the distillate from the ozonide decomposition had a strong aldehyde odor but gave no test for formaldehyde (ferric chloride and resorcinol tests), thus indicating acetaldehyde. These results demonstrated the formation of the normal dehydration product of the carbinol, 2,2,3-trimethylpentene-3. The presence of so much lower boiling olefin indicated the necessity for a more exhaustive study of the olefinic products.

Isolation and Identification of the Rearranged Dehydration Product, 2,3,3-Trimethylpentene-1.—The pinacolone for this run was prepared in 20–50% yields by adding *tert.*-butylmagnesium chloride to an excess of acetyl chloride.⁶ The other steps were the same, giving a 52% yield of methylethyl-*tert.*-butylcarbinol (163 g.). Dehydration of 122 g. of the carbinol with a trace of iodine was followed by refluxing with 1 g. of sodium for one hour. The yield of crude olefin with n_D^{20} 1.4222, was 95.5% (100 g.). This was carefully fractionated in a 90 × 1.2 cm. adiabatic, *partial condensation*, column packed with 5-mm. copper gauze cylinders.⁷ The temperature was not recorded because the amount of vapor passing the thermometer was insufficient to give significant readings.

Fraction	Amt.	Reflux ratio	n_D^{20}
D 1	3.5 cc.	100:1	1.4185
2	3.5 cc.	100:1	1.4191
3	3.5 cc.	100:1	1.4192
4	3.5 cc.	100:1	1.4191
5	3.5 cc.	75:1	1.4198
6	3.5 cc.	60:1	1.4200
7	3.5 cc.	100:1	1.4203
8	5.5 cc.	300:1	1.4203
9	3.5 cc.	200:1	1.4207
10	3.5 cc.	150:1	1.4212
11	62 g.	Residue	1.4230

The residue was fractionated through the same column to give final values of n_D^{20} 1.4232 and b. p. 109° (740 mm.).

The lower fractions were redistilled through the same column, giving 7 cc. of material of refractive index, 1.4180. This was ozonized as usual. The water layer of the distillate from the zinc dust decomposition gave a strong test for formaldehyde (resorcinol). The oil layer was dried, distilled and converted to a semicarbazone, m. p. 134–136°. The semicarbazone of pure methyl-*tert.*-amyl ketone melted at 138–139° and a mixture of the two melted at 135–136°. This demonstrated the formation of the rearranged dehydration product, 2,3,3-trimethylpentene-1. Calculations based on the distillation data and on the refractive indices of the pure substances and the crude olefin mixture indicated that the normal and rearranged dehydration products were formed in the ratio of 4:1.

Preparation and Dehydration of Dimethyl-*tert.*-amylcarbinol.—Methyl-*tert.*-amyl ketone (60 g., b. p. 129–131° (731 mm.), n_D^{20} 1.4097), prepared by D. E. Badertscher of this Laboratory from acetyl chloride and tertiary amyl magnesium chloride,⁸ was

⁶ Whitmore and Badertscher, *THIS JOURNAL*, **54**, 825 (1932).

⁷ See *THIS JOURNAL*, **54**, 3453 (1932).

⁸ The tertiary amyl alcohol was kindly supplied by the Sharples Solvents Corporation of Philadelphia.

diluted with an equal volume of dry ether and added to a slight excess of methylmagnesium chloride in the usual way. The product was decomposed with ammonium chloride and worked up as usual. The 125 cc. of crude carbinol was distilled through a 38 × 1.5 cm. total condensation column. The yield was 65%.

Fraction	B. p., °C.	Pressure, mm.	Amt.	n_D^{20}
F 1	80	84	10 cc.	1.4118
2	80-82	58	9 cc.	1.4280
3	82-85	58	45 g.	1.4280
4	Residue		5 cc.	

The carbinol, 35 g. of Fraction F 3, was dehydrated with iodine as usual, dried and fractionated through the 40 × 0.8 cm. column at 742 mm.

Fraction	B. p., °C.	Amt.	n_D^{20}
G 1	104-106	0.5 cc.	1.4172
2	106-106.7	22 g.	1.4179
3	Residue	5 cc.	1.4200

Fraction G 2 represented a yield of 65%. This was ozonized and decomposed in the usual way. The oily layer was dried and distilled at 737 mm.

Fraction	B. p., °C.	Amt., cc.	n_D^{20}
H 1	to 115	4	1.4056
2	115-128	4	1.4062
3	128-132	4	1.4090
4	Residue	3.5	1.4252

Fraction H 3 corresponded to methyl-*tert.*-amyl ketone, b. p. 129-131° (731 mm.) and n_D^{20} 1.4097. The semicarbazone from this fraction melted at 135-136°. Its melting point was not lowered by a known sample of the semicarbazone of methyl-*tert.*-amyl ketone. These data show that the chief product of the dehydration of dimethyl-*tert.*-amylcarbinol is the normal dehydration product, 2,3,3-trimethylpentene-1. The other products are being studied.

The properties of the substances prepared in this research are as follows

	B. p., °C.	n_D^{20}
Methylethyl- <i>tert.</i> -butylcarbinol	76 (40 mm.)	1.4353
2,2,3-Trimethylpentene-3	109 (740 mm.)	1.4232
2,3,3-Trimethylpentene-1	106-106.7 (742 mm.)	1.4179
Dimethyl- <i>tert.</i> -amylcarbinol	82-85 (58 mm.)	1.4410

Summary

1. Two carbinols in which the hydroxyl is both tertiary and a part of a neopentyl system have been prepared and dehydrated.
2. The main product is the result of dehydration without rearrangement. One of the carbinols also gave 20% of the rearranged olefin.
3. The study of the dehydration of this type of carbinol is being continued.