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

The Dehydration of Tertiary Alcohols Containing a Neopentyl System. II.[1] Methylisopropyl-*tert*-butylcarbinol, Methyldi-*tert*-butylcarbinol, and Methylethylneopentylcarbinol

BY FRANK C. WHITMORE AND KENNETH C. LAUGHLIN[2]

The three alcohols, methylisopropyl-*tert*-butylcarbinol, methyldi-*tert*-butylcarbinol, and methylethylneopentylcarbinol, were selected as representing various types of tertiary alcohols containing a neopentyl group. The study of the dehydration of methylethyl-*tert*-butylcarbinol and dimethyl-*tert*-amylcarbinol has been continued.[1]

Dehydration of methylethyl-*tert*-butylcarbinol with β-naphthalenesulfonic acid gave the same mixture of olefins as with iodine.[1] Ozonolysis of intermediate fractions failed to give positive evidence for any olefin formed by dehydration from the methyl group. Dehydration of dimethyl-*tert*-amylcarbinol gave less than 6% of 2,2,3-trimethylpentene-3 formed by rearrangement of a methyl group.[1] The rearrangement of the ethyl group would give the same olefin as would the normal dehydration.[1,3]

Methylisopropyl-*tert*-butylcarbinol gave 3,3-dimethyl-2-isopropylbutene-1 (by normal dehydration involving the methyl group) and the rearrangement product 2,3,3,4-tetramethylpentene-1 in the ratio 3 : 1, with only traces of 2,3,4,4-tetramethylpentene-2 (by normal dehydration involving the isopropyl group). The sluggishness of the isopropyl group in losing a proton is noteworthy and is being further studied.[4] Methyldi-*tert*-butylcarbinol gave over 90% of 2-*tert*-butyl-3,3-dimethylbutene-1 (by dehydration involving the methyl group), and some low-boiling material which has not been identified. Methylethylneopentylcarbinol was dehydrated without rearrangement, giving mainly 2,2,4-trimethylhexene-4 (from the ethyl group), with less than 5% of 2,2,4-trimethylhexene-3 (from the neopentyl group) and only traces of 4,4-dimethyl-2-ethylpentene-1 (from the methyl group).

These results show the tendency of tertiary alcohols to dehydrate without rearrangement, in contrast to related primary and secondary alcohols containing a neopentyl group, which dehydrate mainly with rearrangement.[5]

With the hydroxyl group directly attached to the neopentyl system, the amount of rearrangement varied from less than 6% in the case of dimethyl-*tert*-amylcarbinol and methyldi-*tert*-butylcarbinol to 25% in the

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(1) Whitmore and Laughlin, THIS JOURNAL, **54**, 4011 (1932).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Whitmore, THIS JOURNAL, **54**, 3276 (1932).

(4) Unpublished results, T. S. Oakwood of this Laboratory. *Cf.* Whitmore and Houk, *ibid.*, **54**, 3716 (1932); Whitmore and Evers, *ibid.*, **55**, 814 (1933).

(5) For references see Whitmore and Meunier, *ibid.*, **55**, 3721 (1933).

case of methylisopropyl-*tert*-butylcarbinol. No rearrangement was found when the hydroxyl group, as in methylethylneopentylcarbinol, was not attached to the neopentyl system.

Experimental Part

Distillation Equipment.—The Johnston column has been described.[6] Column N[7] was of the same partial condensation type, but with a thermometer at the top of the packing so as to obtain significant temperature readings. The packed section, 130 × 1.4 cm., filled with 4-mm. glass helixes,[8] was equivalent to 16.5 theoretical plates.

Columns K, 44 × 1.4 cm., 9.6 theoretical plates, and L, 40 × 0.8 cm., 7.7 theoretical plates, were also packed with glass helixes. They were of the total condensation, variable take-off type previously described.[6] The 65 × 2.3 cm. column, and column A, 38 × 1.5 cm., were of the same type, but were packed with glass tubes (5 × 5 mm.). Column B, 25 × 0.8 cm., of the partial condensation indented type with no packing, was fitted with a 50-cc. pear-shaped flask by a ground-glass joint.

Preparation and Dehydration of Methylethyl-*tert*-butylcarbinol.—Methyl *tert*-butyl ketone (2 moles)[9] with 2.5 moles of ethylmagnesium bromide gave a 64% yield of methylethyl-*tert*-butylcarbinol, b. p. 76.1–76.6° (50 mm.), n_D^{20} 1.4354, d_4^{20} 0.849. The alcohol was dehydrated by distilling from 0.1 g. of β-naphthalene sulfonic acid through column K. The yield of olefin after drying and redistilling was 138 g. (95%). This was distilled through column N, the resulting curve showing the presence of 2,2,3-trimethylpentene-3 and 2,3,3-trimethylpentene-1 in the ratio 4:1 the same as with iodine as the dehydrating agent.[1] The following physical properties were determined:

	Cottrell b. p. °C., 760 mm.	n_D^{20}	d_4^{20}
2,2,3-Trimethylpentene-3	111.9	1.4232	0.739
2,3,3-Trimethylpentene-1	108.2	1.4178	0.736

In the search for some dehydration involving the methyl group, the intermediate fractions from two distillations (88 g.) were redistilled through column N without any indication of material with either a constant b. p. or refractive index. Since no third olefin could be separated by distillation, the intermediate fractions were again combined (73 g.) and ozonized as usual.[10] Formaldehyde was formed. The oily products were fractionated through column L, and the material of b. p. 116–126° (740 mm.) was treated with 2,4-dinitrophenylhydrazine. The main product was the derivative of methyl *tert*-amyl ketone (m. p. 111–111.5°). Careful fractional crystallization yielded no higher melting derivative. Thus no ethyl *tert*-butyl ketone (2,4-dinitrophenylhydrazone m. p. 145°[11]) was present, and consequently there was no dehydration from the methyl group.

Preparation and Dehydration of Dimethyl-*tert*-amylcarbinol.—Ethyl dimethylethylacetate, b. p. 140–140.8° (730 mm.), n_D^{20} 1.4040, was prepared in 37% yield from *tert*-amylmagnesium chloride and ethyl chlorocarbonate.[12] The ester, 0.75 mole, was dissolved in an equal volume of dry ether and added to 2 moles of methylmagnesium chloride. The yield of dimethyl-*tert*-amylcarbinol was 78%. The material from two runs (145 g.) was distilled through column K under reduced pressure to give 135 g. of

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(6) Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

(7) Constructed by C. W. Nash of this Laboratory.

(8) Wilson, Parker and Laughlin, THIS JOURNAL, **55**, 2795 (1933).

(9) Adams, Adams, Hill and Flosdorf, "Organic Syntheses," Vol. V, 1925, pp. 87, 91.

(10) Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

(11) Prepared by E. E. Stahly of this Laboratory.

(12) Whitmore and Badertscher, THIS JOURNAL, **55**, 1563 (1933).

carbinol, b. p. 86.5° (60 mm.), n^{20}_{D} 1.4420, d^{20}_{4} 0.861. The carbinol was dehydrated by twice distilling from 0.1 g. of β-naphthalene sulfonic acid through a steam-jacketed condenser. After drying with 5 g. of potassium carbonate and 0.5 g. of sodium, the olefin was distilled rapidly through column K and again dried over 0.1 g. of sodium. The yield was 112 g. (96.5%).

Isolation and Identification of the Rearrangement Product.—The olefin mixture (112 g.) was distilled through column N with a reflux ratio of more than 50:1. Fourteen fractions (90 cc.) were collected, b. p. 106.0–107.4° (732 mm.), n^{20}_{D} 1.4178–1.4183. The middle fractions were used to determine the physical properties of 2,3,3-trimethylpentene-1. The residue, 27 cc., was distilled through column K to give six fractions b. p. 107.5–108.7° (743 mm.), n^{20}_{D} 1.4187–1.4198, and a residue of 4.5 cc. This was distilled from a small flask to give a liquid of n^{20}_{D} 1.4260. The six fractions and residue were combined (17 g.) and ozonized as usual,[10] using an ether wash bottle to collect the acetaldehyde. The acetaldehyde-ammonia formed, m. p. 90.5–91°, did not lower the m. p. of a known sample. The oily layer was distilled through column L and the fraction (1 cc.) b. p. 100–110° (732 mm.), n^{20}_{D} 1.3983, was identified as methyl *tert*-butyl ketone by conversion to the 2,4-dinitrophenylhydrazone, m. p. 123–124°, which did not lower the m. p. (125°) of a known sample. The formation of acetaldehyde and methyl *tert*-butyl ketone by ozonolysis proves the presence of 2,2,3-trimethylpentene-3. The refractive index of the original mixture of olefins (1.4182) shows that this olefin was less than 6% of the total.

Preparation of Pentamethylacetone.—(1) *Tert*-butylisopropylcarbinol was prepared in 35% yield from isobutyraldehyde, b. p. 62.3–62.9° (735 mm.), and *tert*-butylmagnesium chloride.[13] The crude carbinol of n^{20}_{D} 1.428 was oxidized with chromic acid at 40° giving a 67% yield of pentamethylacetone,[14] b. p. 133–135° (738 mm.), n^{20}_{D} 1.4057, oxime m. p. 139–140°.[15]

(2) Methyl *tert*-butyl ketone, dimethylated in one operation by the sodamide method,[16] gave a 33% yield of pentamethylacetone. One mole of methyl *tert*-butyl ketone, b. p. 104–106° (739 mm.),[9] was dissolved in 1 liter of dry ether and 200 cc. of dry benzene. One mole (50 g. of 80%) of finely ground sodamide was added and the mixture was refluxed vigorously with good stirring for two hours. The mixture was cooled and one mole of methyl iodide was added over a period of two hours. After refluxing for fifteen minutes, the mixture was cooled, 1.4 moles (70 g.) of sodamide was added and the refluxing was continued until no more ammonia was evolved. The mixture was cooled and 1.75 moles of methyl sulfate dissolved in an equal volume of dry ether was added slowly, then refluxed for half an hour. The excess methyl sulfate was decomposed by vigorously stirring overnight with 200 cc. of water and 100 cc. of ammonium hydroxide. The upper layer was washed with 100 cc. of 5% sulfuric acid, 100 cc. of 5% sodium carbonate, and dried over 25 g. of potassium carbonate. After removal of the ether and benzene the residue was treated with 50 cc. of phenylhydrazine to remove any ethyl *tert*-butyl ketone, and the mixture was distilled to a residue of 50 cc. The distillate was washed with four 100-cc. portions of dilute hydrochloric acid, 100 cc. of water, and dried over 10 g. of potassium carbonate, giving 76 g. of material which was distilled through the 65 × 2.3 cm. column, collecting 42 g. of pentamethylacetone, b. p. 132–134° (730 mm.), n^{20}_{D} 1.4082, yield 33%. On account of the toxicity of methyl sulfate and phenylhydrazine, all the above operations were carried out in a good hood.

(3) Pentamethylacetone was prepared in 54% yield by treating diisopropyl

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(13) Whitmore and Houk, THIS JOURNAL, **54**, 3714 (1932).

(14) Fawórsky, *J. prakt. Chem.*, [2] **88**, 651 (1913).

(15) Nef, *Ann.*, **310**, 329 (1900).

(16) Haller and Bauer, *Ann. chim. phys.*, [8] **29**, 318 (1913).

ketone[17] in toluene solution with sodamide and methyl sulfate as above. The combined product from three runs was 227 g., b. p. 133–134° (739 mm.), n^{20}_{D} 1.4071.

Preparation and Dehydration of Methylisopropyl-*tert*-butylcarbinol.—Pentamethylacetone, 2.1 moles, with 2.25 moles of methylmagnesium chloride gave a 67% yield of the carbinol, b. p. 62° (12 mm.), n^{20}_{D} 1.4440, d^{20}_{4} 0.856. A second run gave a 68% yield.

(A) The carbinol, 90 g., was dehydrated with a crystal of iodine under a 90 × 2 cm. column provided with a water separator at its top. The dried olefin mixture (82% yield) was distilled through the Johnston column to give fourteen fractions (total 49 g.) and a residue of 19 g., n^{20}_{D} 1.4302: fractions 1–2, 7 g., n^{20}_{D} 1.4149; fractions 3–14, 42 g., n^{20}_{D} 1.4159–1.4163, Cottrell b. p. 120.1° (734 mm.).

(B) The carbinol, 130 g., was dehydrated by distilling from 0.1 g. of β-naphthalene sulfonic acid through a steam-jacketed condenser, giving a 92.5% yield of dried olefin. This was distilled through the Johnston column to give 27 fractions (total 87 g.) and a residue of 11 g., n^{20}_{D} 1.4357, having a strong odor of the carbinol. Fraction 1, 1.8 g., n^{20}_{D} 1.4152, was not identified. Fractions 2–13, 62 g. 3,3-dimethyl-2-isopropylbutene-1, n^{20}_{D} 1.4174–1.4176, Cottrell b. p. 121.6° (760 mm.), d^{20}_{4} 0.737, and fractions 23–27, 8 g., 2,3,3,4-tetramethylpentene-1, n^{20}_{D} 1.4305, b. p. 132.6° (743 mm.), d^{20}_{4} 0.761, were identified by ozonolysis. The intermediate fractions 14–22, n^{20}_{D} 1.4184–1.4298, totaled 14 g. The olefins 3,3-dimethyl-2-isopropylbutene-1 and 2,3,3,4-tetramethylpentene-1 were present in the ratio 3:1 as calculated from the refractive indices.

Identification of 3,3-Dimethyl-2-isopropylbutene-1.—(1) Ozonolysis of fractions 1–14 from (A) 49 g. according to the technique of Church[10] yielded 18 g. of ozonide (33%) which on decomposition gave a strong test[18] for formaldehyde and an oil which was dried and distilled through column B at 739 mm.: fraction 1, 0.5 cc., b. p. 85–123°, n^{20}_{D} 1.3943, fractions 2–4, 7.5 cc., 123–131°, 1.3997, and a residue of 5 cc., 1.4123, were obtained. Fraction 4 was identified as pentamethylacetone by the oxime, m. p. and mixed m. p. 139–140°.

(2) Because of the low yield of ozonide, the process was repeated. The low-boiling olefin (44 g.) from (B) was ozonized and the ozonides were decomposed in the presence of the hydrocarbon solvent.[10] Careful fractionation through Column L showed that only about two-thirds of the olefin had reacted with ozone. The unchanged olefin was again ozonized and again only about two-thirds of it reacted. The ozonolysis products were the same in both cases. The possibility of an equilibrium in ozonization is being further investigated in this Laboratory.

Identification of 2,3,3,4-Tetramethylpentene-1.—Fractions 23–27 from (B) and similar fractions from another preparation (14 g.) were ozonized to give formaldehyde and an oil which was fractionated through Column L to give about 4 cc. of material of b. p. 135–150° (743 mm.), n^{20}_{D} 1.4300, which proved to contain 3,3,4-trimethylpentanone-2. The 2,4-dinitrophenylhydrazone, after five crystallizations from absolute alcohol, melted at 145.5–146.5°. The semicarbazone, crystallized twice from 50% ethanol and once from 50% methanol, melted at 146.5–148.5°. The known semicarbazone kindly supplied by Professor Locquin[19] melted at 147–150° and a mixture melted at 147–149.5°. The structure of the ketone was further proved by oxidation with sodium hypobromite according to the method of Sandborn and Bousquet[20] to give an acid, m. p. 45–47°, and an amide of m. p. 128° which did not lower the melting point of a known sample of dimethylisopropylacetamide prepared from the acid obtained by the action of carbon dioxide on dimethylisopropylcarbinylmagnesium chloride.

Identification of 2,3,4,4-Tetramethylpentene-2.—One fraction from the above

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(17) This Journal, **54**, 4392 (1932).

(18) Schryver, *J. Chem. Soc.*, Abs., **98**, II, 334 (1910).

(19) Locquin and Leers, *Compt. rend.*, **179**, 55 (1925); *Bull. soc. chim.*, [4] **39**, 436 (1926).

(20) "Organic Syntheses," Vol. VIII, 1928, p. 108.

ozonolysis, 0.5 g., b. p. 95–118° (742 mm.), n^{20}_{D} 1.4090, gave a 2,4-dinitrophenylhydrazone, m. p. 128–129°, which was shown by mixed melting point determinations to be identical with the crystalline modification, m. p. 131°, obtained by melting the known derivative (m. p. 125°) of methyl *tert*-butyl ketone. Thus a small amount of 2,3,4,4-tetramethylpentene-2 occurred in the higher boiling fractions.

Preparation and Dehydration of Methyldi-*tert*-butylcarbinol.—Hexamethylacetone was prepared from diisopropyl ketone by the sodamide synthesis.[16] Three moles, 342 g., of diisopropyl ketone[17] was dissolved in xylene and treated with sodamide and methyl iodide for the first step, sodamide and methyl sulfate for the second. The reaction was carried out without isolating the intermediate product. Because of the difficulty of separating hexamethylacetone from pentamethylacetone and xylene by distillation, the mixture of products was treated with methylmagnesium chloride until a positive test was obtained with Gilman's reagent.[21] The product was worked up as usual and distilled through column A under reduced pressure. The carbinol (135 g.), collected at 122.5–123° (100 mm.), m. p. 42°,[22] represented a yield of 29% from the diisopropyl ketone.

The carbinol, 112 g., was dehydrated by distilling from 0.1 g. of β-naphthalene sulfonic acid through a steam-jacketed reflux condenser. No gas was formed. After drying with 5 g. of potassium carbonate and 1 g. of sodium, the olefin (90 g., 90% yield) was distilled at 731 mm. through the Johnston column to give twenty-five fractions totaling 95.5 cc. and a residue of 11 cc.: fractions 1–2, 3 cc., b. p. 78°, n^{20}_{D} 1.4129–1.4130, rapidly decolorized a solution of bromine in carbon tetrachloride; fractions 3–8, 13.5 cc., n^{20}_{D} 1.4275–1.4362, could not be further separated by redistillation through column L; fractions 9–15, 45 cc., n^{20}_{D} 1.4364, d^{20}_{4} 0.770, Cottrell b. p. 149.5° (760 mm.), were identified as 2-*tert*-butyl-3,3-dimethylbutene-1; fractions 16–25, 34 cc., 1.4365–1.4388, yielded on redistillation through the same column 13 cc. with n^{20}_{D} 1.4364. The residue, 11 cc., n^{20}_{D} 1.4457, distilled from a small distillation flask at 156–185°. The last portion of the distillate solidified in the condenser and was proved by mixed melting point to be unchanged carbinol.

Identification of 2-*Tert*-butyl-3,3-dimethylbutene-1.—A 32-g. portion of fractions 9–15 was ozonized as usual. After fifteen hours the tube plugged due to formation of a solid ozonide. The solution was decanted to another tube and ozonization was completed in less than an hour. The hydrocarbon solution was decomposed as usual, and the solid ozonide was washed into the reaction flask with 300 cc. of acetic acid and likewise decomposed. A positive test for formaldehyde[18] was obtained. The oil layer was dried with 3 g. of potassium carbonate and distilled through column L at 737 mm. to give the principal fractions with b. p. and n^{20}_{D} as follows: 6 cc., 140–149°, 1.4164; 9 cc., 149.0–149.5°, 1.4198; residue, 7 cc., 1.4222. The middle fraction was identified as hexamethylacetone by reaction of 5 cc. with methylmagnesium iodide prepared from 2.4 g. of magnesium and 14 g. of methyl iodide. After decomposing and drying as usual the product distilled from a small distillation flask at 100–117° (100 mm.). The solid carbinol thus obtained, m. p. 41.5°, did not lower the melting point of pure methyldi-*tert*-butylcarbinol. From a consideration of the distillation and ozonolysis results it was concluded that 2-*tert*-butyl-3,3-dimethylbutene-1 constituted over 90% of the dehydration products.

Preparation and Dehydration of Methylethylneopentylcarbinol.—The carbinol was prepared in 67% yield from 2.3 moles of methyl neopentyl ketone, b. p. 123–123.2° (736 mm.), n^{20}_{D} 1.4027, and 2.5 moles ethylmagnesium bromide. The carbinol, 144 g. collected from 62–62.5° (14 mm.), n^{20}_{D} 1.4340, was dehydrated with 3 g. of β-naphthalene sulfonic acid by distilling through a steam-jacketed condenser. The olefin, obtained in 95% yield, was dried over 1 g. of sodium and distilled through the Johnston

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[21] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

[22] Conant and Blatt, *ibid.*, **51**, 1236 (1929).

column to give 18 fractions amounting to 120 cc. and a residue of 9 cc., n_D^{20} 1.4292. Cottrell boiling points at 734 mm., n_D^{20} and volumes of the constant refractive index materials were as follows: fractions 5–6, 128.0°, 1.4220, 8 cc.; fractions 12–13, 129.4°, 1.4230, 11 cc.; fractions 17–18, 130.2°, 1.4237, 14 cc.

Identification of the Dehydration Products.—Fractions 2-6, 18 g., gave 20 g. of ozonide which on decomposition gave formaldehyde[18] and 12 g. of an oil layer which was dried and distilled through column B at 725 mm. to give fractions of wts., boiling ranges, and n_D^{20} as follows: No. 1, 2 g., 75–100°, 1.3915; No. 2, 3 g., 100–121°, 1.4035; No. 3, 5 g., 121–126°, 1.4049; No. 4, 1 g., 126–131°, 1.4051; residue, 1 g., 1.4158. Fraction 3 gave a 2,4-dinitrophenylhydrazone m. p. 99° which did not lower the melting point of the derivative prepared from pure methyl neopentyl ketone. From fraction 1, two 2,4-dinitrophenylhydrazones were isolated: one of m. p. 207° which did not lower the melting point of the derivative prepared from known trimethylacetaldehyde, and one m. p. 109–110° which melted at 112° when mixed with the derivative (m. p. 115°) prepared from methyl ethyl ketone. These products proved the presence of 2,2,4-trimethylhexene-4 and 2,2,4-trimethylhexene-3. The presence of 4,4-dimethyl-2-ethylpentene-1 was indicated by the formation of formaldehyde and by the high refractive index of the residue, but attempts to isolate a derivative of ethyl neopentyl ketone were unsuccessful. Since no physical constants for this compound could be found in the literature, it was synthesized from *tert*-butylacetyl chloride and ethylzinc iodide. The following constants for ethyl neopentyl ketone were determined: b. p. 143° (736 mm.), n_D^{20} 1.4110, d_4^{20} 0.812, 2,4-dinitrophenylhydrazone m. p. 135.5°, semicarbazone m. p. 160–161°.

The original olefin fractions 10–14, 23 g., and 15–18, 23 g., gave practically identical results on ozonolysis. The water layers gave no test for formaldehyde,[18] and the oil layers, 15 g. each, gave very similar results when distilled through column B at 727 mm. One of these distillations gave fractions as follows: No. 1, 0.5 g., b. p. 74–100°, n_D^{20} 1.3920; No. 2, 1 g., 100–121°, 1.4014; No. 3, 4 g., 121–123°, 1.4029; No. 4, 3.5 g., 123–124°, 1.4029; No. 5, 1.5 g., 124–126°, 1.4031; No. 6, **1** g., 126–129°, 1.4037; res., 2.5 g., 1.4199. Fraction 3 was identified as methyl neopentyl ketone as before. The distillation and ozonolysis results show that methylethylneopentylcarbinol dehydrates mainly to the ethyl group, with less than 5% dehydrating from the neopentyl group, and only traces due to dehydration from the methyl group. No evidence of rearrangement during the dehydration of methylethylneopentylcarbinol was detected. The expected rearrangement products would yield, on ozonolysis, formaldehyde and 3,4-dimethylhexanone-2, and acetone and methyl *sec*-butyl ketone, respectively. These ketones were not formed. 3,4-Dimethylhexanone-2 has been variously reported with b. p. 152–154°, semicarbazone, m. p. 119°,[23] and b. p. 158°, semicarbazone m. p. 124–126°.[24] The semicarbazone prepared from the residue, n_D^{20} 1.4199, melted at 160–165°, and no material melting lower than 135° could be obtained from the mother liquor, hence no 3,4-dimethylhexanone-2 was present. The other residues proved equally barren of this material.

Methyl *sec*-butyl ketone[25] has b. p. 118°, n_D^{18} 1.4002, semicarbazone m. p. 95.6°. In the search for this material all ozonolysis products were combined and distilled through column L. The semicarbazone prepared from the fraction b. p. 110–120° (736 mm.), n_D^{20} 1.4039, melted at 175° after one crystallization from alcohol (methyl neopentyl ketone semicarbazone m. p. 176°). No material melting lower than 135° could be obtained by fractional crystallization of the mother liquor, so no methyl *sec*-butyl ketone was present. These results prove the absence of rearrangement in the dehydration of methylethylneopentylcarbinol.

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(23) Colonge, *Bull. soc. chim.*, [4] **49**, 444 (1931).

(24) Powell and Secoy, THIS JOURNAL, **53**, 768 (1931).

(25) Beilstein, 4th ed., I, 693 (1918).

Summary

1. The dehydration of tertiary alcohols containing a neopentyl system has been studied with relation to rearrangement.

2. In no case was the rearrangement greater than 25%.

3. No rearrangement took place during the dehydration of methylethylneopentylcarbinol.

4. In the case of methyldi-*tert*-butylcarbinol no rearrangement products were found. Over 90% of the normal dehydration product was isolated.

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The Isoelectric Point of Orange Seed Globulin

By D. C. Carpenter and F. E. Lovelace

A crystalline protein was first isolated from California orange seed in 1931 by Saunders.[1] He obtained the protein in a crystalline form by dialysis of ammonium sulfate solutions of the protein and named it pomelin. The writers have been unable to obtain a crystalline product from Florida or California orange seed by Saunders' method, the product being in all cases in our experience an amorphous mass instead of definite crystals. However, the writers have been successful in preparing a crystalline globulin from orange seed by an adaptation of the method used by Vickery, Wakeman, and Leavenworth[2] for the extraction of the globulin from tobacco seed and its preparation in crystalline form.

Csonka, Murphy and Jones[3] record the isoelectric point of a number of proteins as deduced from data on minimum solubility. A large amount of their data deals with various plant globulins for which the various individual isoelectric points range between *P*H's 5.0 and 5.5.

The point of electrical neutrality of a colloid may be determined in either of two ways, *i. e.*, by the moving boundary method described by Tiselius[4] in which the movement of a column of colloidal particles under a known potential is measured, or the somewhat different method[5] in which the rate of movement of the individual colloidal particle or an aggregate is observed under the microscope. In many cases a substance such as powdered quartz has been added to a sol on which the colloid was supposedly adsorbed and which powder then behaved as the colloid itself.[6]

From the Helmholtz–Lamb equation $V = \zeta HD/4\pi h$, where V is velocity

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(1) Saunders, This Journal, **53**, 696 (1931).

(2) Vickery, Wakeman and Leavenworth, *Conn. Agr. Expt. Sta. Bull.*, [II] **339**, 625 (1932).

(3) Csonka, Murphy and Jones, This Journal, **48**, 763 (1926).

(4) Tiselius, *Nova Acta Reg. Soc. Sci. Upsaliensis*, Series IV, **7**, No. 4 (1930).

(5) Northrup, *J. Gen. Physiol.*, **4**, 629 (1922).

(6) Freundlich and Abramson, *Z. physik. Chem.*, **133**, 51 (1928).