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Hydrogenolysis of 2,2,3-Trimethyl-1-butanol

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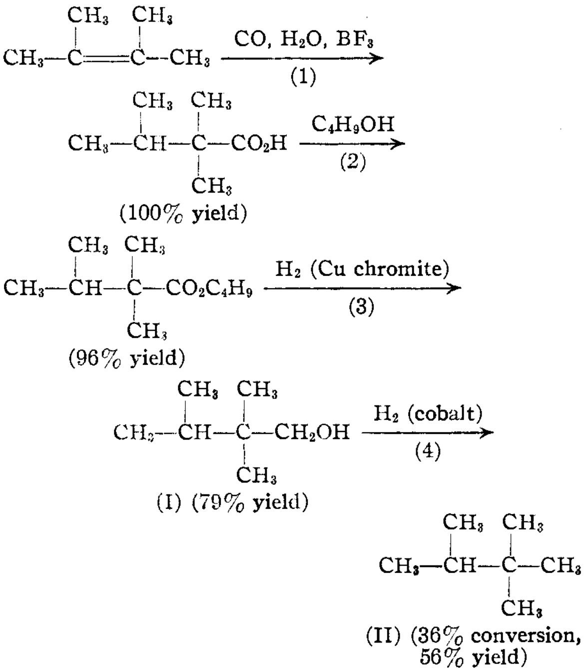
The neopentyl-type alcohol, 2,2,3-trimethyl-1-butanol (I), has been converted to the hydrocarbon trimethylbutane (triptane) (II) without rearrangement by hydrogenolysis over a cobalt catalyst at high temperature and pressure. The reactions involved, including the synthesis of the trimethylbutanol starting with tetramethylethylene, have been carried out on a laboratory scale as indicated in the scheme



$$CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3 \xrightarrow[(1)]{CO,\ H_2O,\ BF_3}$$

$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CO_2H \xrightarrow[(2)]{C_4H_9OH}$$

(100% yield)

$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CO_2C_4H_9 \xrightarrow[(3)]{H_2\ (Cu\ chromite)}$$

(96% yield)

$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2OH \xrightarrow[(4)]{H_2\ (cobalt)}$$

(I) (79% yield)

$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

(II) (36% conversion, 56% yield)

The carboxylation of tetramethylethylene (reaction 1) was carried out by injecting the olefin into boron fluoride trihydrate at a temperature of 75° under 600 atm. carbon monoxide pressure.[1] The acid obtained was converted to the *n*-butyl ester (reaction 2) for hydrogenolysis.[2] In the third step it was found desirable to operate at high temperatures and pressures (280°, 1000 atm.) in order to get a high conversion of this rather inert ester to the alcohol. No hydrocarbon was observed in the products of hydrogenolysis of the ester or alcohol over copper chromite catalyst. The hydrogenolysis of the alcohol to triptane (reaction 4) was carried out at 300° and 1000 atm. hydrogen pressure. Over a cobalt-on-alumina catalyst,[3] the conversion of the alcohol to triptane was approximately 36% and the yield, allowing for recovered alcohol, was 56%. The hydrocarbon was unequivocally identified as triptane by comparison of its infrared absorption spectrum (Fig. 1) with that of an authentic sample prepared by the Grignard synthesis as described by Brooks, Howard and Crafton.[4]

Alloy skeleton nickel also catalyzed this hydrogenolysis reaction, but the triptane was not so pure as when formed in the presence of cobalt catalyst. Neither catalyst was effective in bringing about hydrogenolysis of the ester directly to triptane.

Reaction (4) is novel in that it represents the first example of the hydrogenolysis of an aliphatic alcohol incapable of simple dehydration. The fact that this reaction proceeds to give the corresponding hydrocarbon without rearrangement gives rise to speculation as regards its mechanism. It is generally accepted that heterolytic fission[5] of the carbon–oxygen bond in neopentyl alcohols in homogeneous systems results in a rearrangement of the carbon skeleton.[6,7,8] Thus Whitmore and Rothrock[7] found that the reaction of neopentyl alcohol with hydrogen bromide gave 72% of *t*-amyl bromide, 8% of a secondary bromide, and 20% of one or more primary bromides. Therefore, the fission in our hydrogenolysis reaction cannot be heterolytic unless adsorption on the catalyst surface provides a stabilizing influence that hinders rearrangement. We consider it more likely that the fission is homolytic; this is consistent with the non-rearrangement of the neopentyl group in the chlorination of neopentane.[9] It is impossible to say at present whether stabilization by adsorption is involved where homolytic fission does not lead to rearrangement. However, this may be found to be the case in view of the known migration of phenyl and possible migration of methyl observed[10] with neophyl radicals in homogeneous solution.

Experimental

Synthesis of 2,2,3-Trimethylbutanoic Acid by Carboxylation of Tetramethylethylene.—A silver-lined high-pressure

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[1] (a) Larson, U. S. Patent 2,022,244 (Nov. 26, 1935); (b) Loder, U. S. Patent 2,135,459 (Nov. 1, 1938).

[2] German investigators (see "Library Bulletin of Abstracts," Universal Oil Products Company, Vol. 23, p. 39; T. O. M. Microfilm Reel No. 138) are reported to have studied the direct hydrogenation of 2,2,3-trimethylbutanoic acid to triptane while employing a nickel sulfide–tungsten sulfide catalyst.

[3] The cobalt-on-alumina catalyst was prepared essentially as described by Signaigo, Example IV, U. S. Patent 2,166,183 (July 18, 1939).

[4] Brooks, Howard and Crafton, *J. Research Nat. Bur. Standards*, **24**, 37 (1940).

[5] The term heterolytic fission is used to describe the fission of a covalent bond to yield an ion-pair as opposed to homolytic fission leading to two free radicals. See Hey, "Ann. Reports on Progress Chemistry" (Chem. Soc. London), **41**, 181 (1944).

[6] Whitmore, THIS JOURNAL, **54**, 3274 (1932).

[7] Whitmore and Rothrock, *ibid.*, **54**, 3431 (1932).

[8] Whitmore and Homeyer, *ibid.*, **54**, 3435 (1932).

[9] Whitmore and Fleming, *ibid.*, **55**, 4161 (1933).

[10] Urry and Kharasch, *ibid.*, **66**, 1438 (1944).

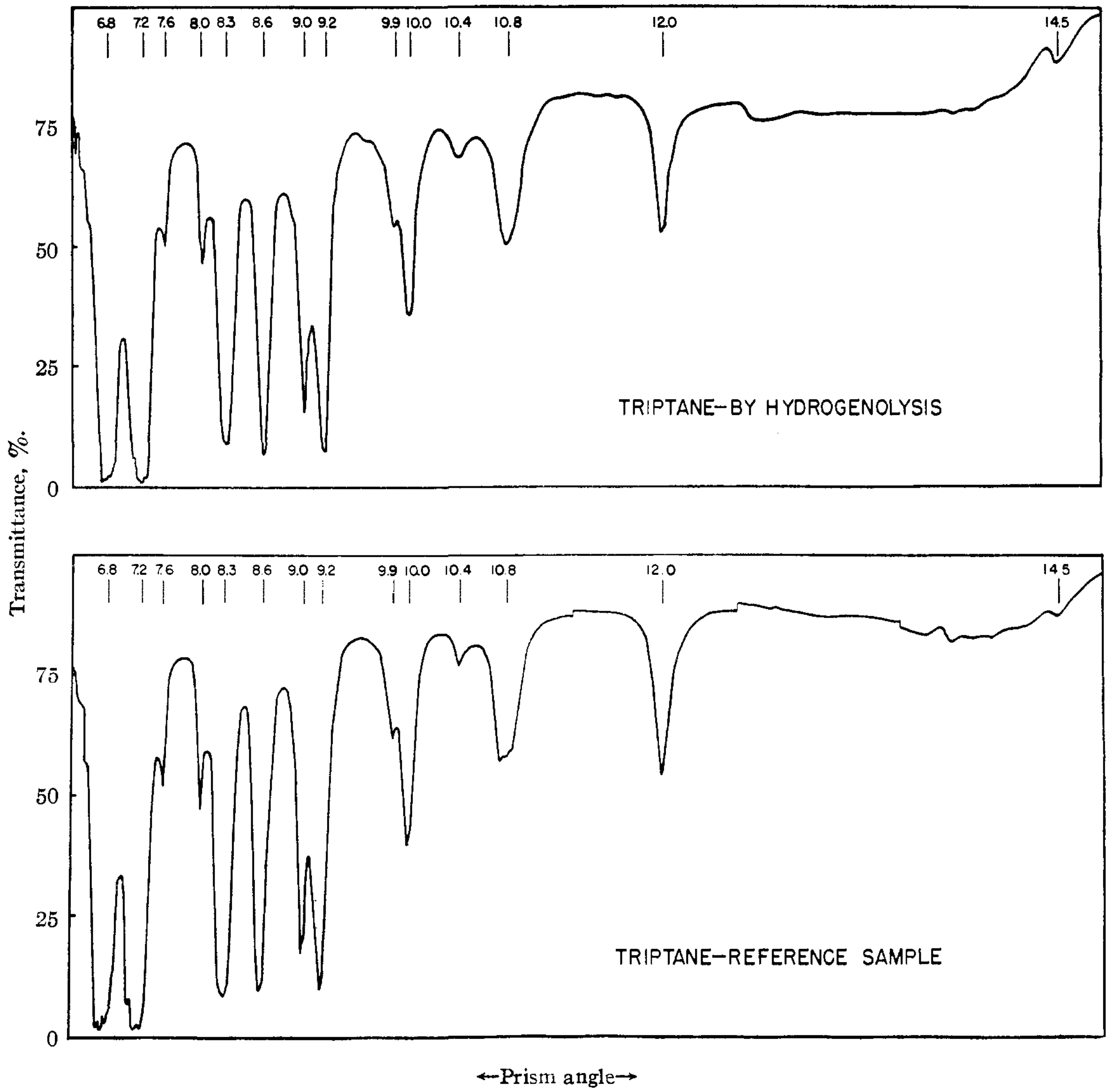

Fig. 1.—Direct tracings of infrared absorption spectra of triptane reference sample and triptane obtained by hydrogenolysis. Wave length in microns is marked on each absorption band.

shaker tube of 400 ml. capacity was charged with 121.8 g. of boron fluoride trihydrate (1 mole), and was cold-pressured to 400 atm. with carbon monoxide. The tube was then heated to 75°, at which temperature the pressure was about 600 atm. Seventy-three grams of tetramethylethylene[11] (0.87 mole) was injected into the tube over a period of two and one-half hours, and heating at 75–77° was continued for a total of nine and one-half hours. After cooling and opening, the tube was discharged and the product diluted with water and extracted with benzene. On distillation there was obtained 113 g. of 2,2,3-trimethylbutanoic acid boiling at 100–101° (11 mm.). The amide of this acid, prepared by the action of ammonia on the acid chloride, melted at 130–130.5°, as compared with 133–134° reported by Haller and Bauer.[12]

Grignard Synthesis of 2,2,3-Trimethylbutanoic Acid.—The acid was also prepared on a small scale by the Grignard synthesis starting with 2-chloro-2,3-dimethylbutane. Fifteen grams of 2-chloro-2,3-dimethylbutane, b. p. 111–112° (prepared by the action of hydrochloric acid on the corresponding alcohol), was dissolved in 50 ml. of dry ether and added to 4 g. of magnesium turnings in 50 ml. of dry ether. When the reaction was completed the product was saturated with carbon dioxide, and hydrolyzed by the addition of 10 ml. of concentrated hydrochloric acid in 50 ml. of water. The ether was separated and extracted with dilute sodium hydroxide. This alkaline solution was then acidified with dilute sulfuric acid and the free organic acid was extracted with ether. The acid was heated with thionyl chloride and after the excess thionyl chloride was distilled off, the acid chloride was added to concentrated ammonia. An amide was obtained which, after recrystallizing from water and from a mixture of petroleum ether and ethyl alcohol, melted at 129–130°. No depression in melting point resulted when this compound was mixed with the amide of the acid obtained by the carboxylation of tetramethylethylene.

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[11] Tetramethylethylene was prepared by the action of 2 moles of methylmagnesium chloride on 1 mole of methyl isobutyrate as described by Hodgson and Risher, American Petroleum Institute, Hydrocarbon Research, Fifth Annual Report, Sept. 1, 1942–August 31, 1943, p. 6.

[12] Haller and Bauer, *Compt. rend.*, **149**, 6 (1909).

Preparation of *n*-Butyl-2,2,3-trimethylbutanoate.—The *n*-butyl ester of 2,2,3-trimethylbutanoic acid was prepared by refluxing a solution of 229 g. of 2,2,3-trimethylbutanoic acid, 3 ml. of concentrated sulfuric acid and 400 g. of *n*-butyl alcohol for twenty-four hours with intermittent removal of the water of reaction. The product was washed successively with 10% sodium carbonate and water, and fractionated to obtain 316 g. of *n*-butyl ester, b. p. 90–91° (16 mm.), $n^{20}D$, 1.4220.

Hydrogenolysis of *n*-Butyl 2,2,3-Trimethylbutanoate to 2,2,3-Trimethyl-1-butanol.—A stainless-steel shaker tube was charged with 220 g. of *n*-butyl 2,2,3-trimethylbutanoate and 20 g. of copper chromite catalyst. After closing, the vessel was cold-pressured to 210 atm. with hydrogen and the temperature was raised and held at 269–281° over a period of six and one-half hours, during which time the pressure was maintained in the neighborhood of 1000 atm. by intermittent pressuring with hydrogen. There was a total pressure drop of 310 atm. The vessel was then cooled, bled of excess hydrogen, opened and discharged. After filtering off the catalyst, the product was distilled to give 108 g. of 2,2,3-trimethyl-1-butanol, b. p. 157–158°, $n^{20}D$ 1.4320.

Hydrogenolysis of 2,2,3-Trimethyl-1-butanol to Triptane.—A stainless-steel shaker tube was charged with 100 g. of 2,2,3-trimethyl-1-butanol and 20 g. of cobalt-on-alumina catalyst, closed, and pressured with hydrogen to 225 atm. The temperature was then raised to 300° and held in the range of 298–308° for eighteen hours, during which time the pressure dropped from a maximum of 965 atm. to 740 atm. The vessel was cooled, bled of hydrogen, discharged, and the product was filtered and dried. Distillation yielded the fractions

Fraction	Boiling point, °C.	Weight, g.	Composition
I	67–81	5.6	Foreshot
II	81–82	27.0	Triptane
III	82–157	8.0	Triptane and alcohol
IV	157–157.5	28.0	Recovered alcohol
Holdup	....	4.0	Recovered alcohol

Acknowledgments.—The Grignard synthesis of the triptane used as a reference compound in this work was carried out by Dr. J. C. Thomas, and the infrared characterization of triptane by Dr. J. R. Downing.

Summary

A method for the conversion of 2,2,3-trimethyl-1-butanol, a neopentyl-type alcohol, to the hydrocarbon trimethylbutane (triptane) has been worked out. This method involves hydrogenolysis over a cobalt catalyst at 1000 atmospheres pressure.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Urea–Formaldehyde Kinetic Studies

BY GEORGE A. CROWE, JR.,[1] AND CECIL C. LYNCH

During polarographic studies of the reaction of various substances with formaldehyde in dilute basic solutions, it was observed that the reaction of urea and formaldehyde to form monomethylolurea did not go to completion. Also, when alkali was added to a dilute solution of monomethylolurea, polarographic measurements indicated that free formaldehyde was liberated.

Smythe,[2] on the basis of kinetic studies, found that in neutral solutions the reaction of urea and formaldehyde to form monomethylolurea proceeded to more than 95% completion. The reaction was essentially bimolecular.

The kinetic study described in this paper has shown that the reaction is reversible

$$NH_2CONH_2 + HCHO \rightleftarrows NH_2CONHCH_2OH$$

In dilute basic solutions, the forward reaction was found to be bimolecular and the reverse reaction monomolecular.

Experimental

The polarographic measurements were made with an E. H. Sargent and Company Model XII Polarograph. The dropping mercury electrode was of the original Heyrovsky type.[3,4] The mercury mass, *m*, was 1.495 mg. sec.$^{-1}$, and the drop time, *t*, was 5.01 sec. in 0.05 *N* lithium hydroxide containing dissolved air, and with an open electrical circuit. The $m^{2/3}t^{1/6}$ value was 1.71.

The polarographic method for formaldehyde analysis was similar to that of Jahoda,[4,5] although 0.05 *N* lithium hydroxide was used as the supporting electrolyte instead of 0.03 *N* sodium hydroxide. The diffusion current, i_d, due to formaldehyde was proportional to the formaldehyde concentration over the range used. The half-wave potential of formaldehyde in 0.05 *N* lithium hydroxide was −1.56 volts *vs.* the mercury pool electrode, and −1.67 volts *vs.* the saturated calomel electrode.

The diffusion current constant,[6] *I*, for formaldehyde in 0.05 *N* lithium hydroxide containing dissolved air (oxygen not removed) at 25.0°, using maximum galvanometer swing values was

$$I = i_d/Cm^{2/3}t^{1/6} = 1.26$$

(where i_d is diffusion current in microamperes and *C* is concentration in millimolar solution.

The urea was J. T. Baker Analyzed, C.P. and was dried for two and one-half hours at 105°; combined moisture and volatile matter was 0.2%.

The formaldehyde was Merck and Co. neutral reagent grade. The formaldehyde content was 36.7% by the hydroxylamine hydrochloride method.[2] The solution was diluted to 0.00346 *M* for polarographic measurements.

Lithium hydroxide (Merck, lithium hydrate) was made up to 0.100 *N* by standardization against a primary sulfuric acid standard solution. Titration with the sulfuric acid solution was made to phenolphthalein and methyl orange end-points, to correct for a small amount of carbonate (less than 0.001 *M*).

Monomethylolurea was prepared by the method of Ein-

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[1] Present address, Hercules Powder Company, Experiment Station, Wilmington, Delaware

[2] Smythe, *J. Phys. Colloid Chem.*, **51**, 369 (1947).

[3] Polarographic kinetic studies for several other organic reactions are reviewed in Heyrovksy, "Polarographie," Springer Verlag, Vienna, 1941.

[4] Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

[5] Jahoda, *Coll. Czechoslov. Chem. Commun.*, **7**, 415 (1935).

[6] Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).