fied at room temperature; yield 5.5 g., 19.4%. The yields in 1.0 and 2.0 mole runs were 18 and 13%, respectively.

Summary

1. Practical methods have been developed for making hexamethylethane.

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

Some Aspects of the Tschugaeff Reaction for Dehydrating Alcohols[1]

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Tschugaeff was the first to suggest the dehydration of alcohols by decomposition of their xanthates.[3] His original paper dealt with the preparation of menthene from menthol, and gave two possible alternative reactions for the decomposition of the xanthate upon heating

$$C_nH_{2n-1}OCS_2R \xrightarrow{\text{Heat}} C_nH_{2n-2} + COS + RSH \quad (1)$$

$$C_nH_{2n-1}OCS_2R \xrightarrow{\text{Heat}} C_nH_{2n-2} + CS_2 + ROH \quad (2)$$

It has since been found that (1) is the reaction. The yield is best when R is methyl.

By the same method Tschugaeff[4] also prepared thujene from thujyl alcohol, limonene from carvone, cholesterylene from cholesterylin, and bornylene from borneol. Others have extended the application of the method. Gandurin[5] prepared guajene from guajol. Kurssanoff[6] dehydrated benzhydrol to give tetraphenylethylene and phenylcyclohexylcarbinol to give benzylidene cyclohexane.

In the aliphatic series Fomin and Sochanski[7] prepared tertiary-butylethylene from pinacolyl alcohol. More recently Stevens[8] dehydrated *dextro*-2-methyl-3-ethoxybutanol-2 to secure *dextro*-3-ethoxy-2-methylbutene-1.

In all these preparations the general method was the same. Sodium or potassium (preferably the latter) reacted with the alcohol in a solvent such as xylene. Carbon disulfide was added to form the xanthate of the metal,

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(2) Submitted in partial fulfilment of the requirements for the M.S. degree.

(3) Tschugaeff, *Ber.*, **32**, 3332 (1899).

(4) Tschugaeff, *ibid.*, **33**, 3118, 735 (1900); **34**, 2276 (1901); **37**, 1481 (1904); **42**, 4631 (1909); **45**, 1293 (1912); *Ann.*, **375**, 288 (1910); **388**, 280 (1912).

(5) Gandurin, *Ber.*, **41**, 4362 (1908).

(6) Kurssanoff, *Chem. Centr.*, I, 997 (1921); *Ber.*, **64**, 2297 (1931).

(7) Fomin and Sochanski, *ibid.*, **46**, 246 (1913).

(8) Stevens, THIS JOURNAL, **54**, 3736 (1932).

which was then converted to the methyl xanthate by refluxing with methyl iodide or sulfate. The methyl xanthate gave the olefin when strongly heated.

Apparently in all these instances only the normal dehydration product was formed, that is, no rearrangement took place. The method thus appeared satisfactory for certain secondary and tertiary alcohols, but it was untried for primary alcohols until the present research. It has now been found to give normal dehydration here also. It is suitable for the preparation of pure isopropylethylene from isoamyl alcohol and of pentene-1 from *n*-amyl alcohol. Capryl alcohol gives a mixture of almost equal parts of octene-1 and octene-2.

The particular advantage of the Tschugaeff method is that it avoids rearrangements. This has been confirmed in the present work by the conversion of isoamyl alcohol to pure isopropylethylene, whereas trimethylethylene is the chief product when isoamyl alcohol is subjected to other methods of dehydration. However, the Tschugaeff method is generally avoided since in the original form it was dangerous and inconvenient. This objection was overcome in the present work by modifying the preparation of the metallic xanthate. This consists in reaction of the alcohol with equimolecular quantities of sodium or potassium hydroxide and carbon disulfide, thus forming the xanthate in one step in a larger yield than is secured by the original method. The best results are obtained when an excess of the alcohol is used, with no other solvent, but by using only equimolecular quantities of the alcohol and a neutral solvent such as a mixture of diethyl ether and carbon tetrachloride the yields are lowered only slightly. This modification makes the Tschugaeff reaction much less hazardous and more practicable than the original method. The following reactions represent the modified reaction

$$\mathrm{ROH} + \mathrm{NaOH} + \mathrm{CS_2} \longrightarrow \mathrm{H_2O} + \mathrm{ROCS_2Na} \xrightarrow{\mathrm{MeI}} \mathrm{ROCS_2Me} \xrightarrow{\mathrm{Heat}} \mathrm{Olefin} + \mathrm{COS} + \mathrm{MeSH}$$

The chief obstacle in applying the method to primary alcohols was found to be the comparatively great stability of the primary xanthates toward heat. They can be distilled *in vacuo*, and even when boiled at atmospheric pressure their decomposition is slow and incomplete, so that only small yields of olefins can be secured. Apparently the secondary and tertiary xanthates are much less stable and, consequently, give better yields of olefins.

Experimental

The alcohols were carefully purified by distillation, and only the purest fractions were used in these experiments. The other liquid chemicals were purified by distillation after drying.

Each of the three alcohols was dehydrated by both the original and the modified

Tschugaeff method, and it was found that the latter gave slightly better yields, as may best be indicated by comparing the yields of xanthates.

The yields of about 15% listed for isopropylethylene and pentene-1 may be regarded as conservative and may be almost doubled by more care in purifying and distilling the products obtained from the decomposition of the xanthates.

Original Tschugaeff Method on Isoamyl Alcohol.—A 2-mole run will be taken as typical of the procedure of this method.

Clean potassium (84 g.) was placed in a 5-liter flask containing 1500 cc. of xylene. The flask was attached to a trident fitted with a mechanical stirrer, a Pyrex reflux condenser and a dropping funnel; then 180 g. of isoamyl alcohol was added dropwise with very vigorous stirring and the mixture was warmed to about 65° to melt the potassium and form tiny beads which reacted vigorously so that the reaction was practically all completed in three hours. Then the mixture was diluted with 1500 cc. of diethyl ether and 305 g. of carbon disulfide added with stirring. After standing overnight the mixture was warmed and stirred for three hours longer, and then 570 g. of methyl iodide was added dropwise and the mixture was stirred and refluxed for six hours. After filtering off the potassium iodide the lower-boiling constituents were removed by distillation and the residual xanthate was distilled at 10 mm. through a 68 × 1.1 cm., indented, total-condensation column.[9] The yellow distillate, b. p. 100–105°, weighed 230 g. Redistillation gave 216 g., b. p. 101–103°, while a third distillation gave 142 g., b. p. 102.5–103° (10 mm.), n^{20}_{D} 1.5230 and d^{20}_{4} 1.036.

The material of b. p. 101–103° (216 g.) was heated in a 1-liter flask under a partial-reflux column for seven and one-half hours by a free flame, the distillate being condensed by a copper coil packed in an ice–salt mixture. The undecomposed residue amounting to 43 and 45 g. of colorless distillate was collected. The distillate was purified by three extractions with 40% potassium hydroxide solution and one treatment with 20 cc. of saturated mercuric chloride solution to remove the mercaptan; then it was dried over anhydrous sodium sulfate and distilled through the 68 × 1.1 cm. column. It boiled at 19–20° (740 mm.). It was thus mainly isopropylethylene.

Original Method on *n*-Amyl Alcohol.—Practically the same procedure was followed here as in the case of isoamyl alcohol. For a 2-mole run, 180 g. of alcohol gave 207 g. of xanthate, b. p. 108–108.5° (10 mm.), n^{20}_{D} 1.5247, d^{20}_{4} 1.040. After heating for nine hours there remained 66 g. of residue, while the distillate amounted to 50 g. ,which after purification distilled at 28.5–29.0° (735 mm.). This boiling point checks that recently established for pentene-1 by Dykstra, Lewis and Boord.[10]

Original Method on Capryl Alcohol.—261 g. of alcohol gave 98 g. of olefin, distilling at 120.5–121.2° (725 mm.), n^{20}_{D} 1.4113, after purification by refluxing over sodium. In this case the xanthate could not be distilled because it was found to decompose upon boiling, even at 5 mm. At atmospheric pressure, heating in an oil-bath at 165° gave almost complete decomposition.

Modified Tschugaeff Method on Isoamyl Alcohol.—This was a 1-mole run. In a 2-liter flask were placed 40.5 g. of finely pulverized sodium hydroxide, 89 g. of isoamyl alcohol, 600 cc. of diethyl ether and 50 cc. of carbon tetrachloride. The flask was attached to the same apparatus as in the original method, and the mixture was stirred for half an hour to dissolve part of the base and form a finely divided suspension of the remainder. Then 76 g. of carbon disulfide was added during one hour, with the temperature below 30°. After three hours of stirring, 149 g. of methyl iodide was added dropwise and the mixture was stirred and refluxed for six hours longer. The remainder of the procedure was the same as for the original method described above. Distillation of the xanthate gave 126 g., b. p. 100–102° (10 mm.), n^{20}_{D} 1.5234.

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[9] Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

[10] Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930).

A run using potassium hydroxide gave the same yield. Still another run, using no other solvent than excess isoamyl alcohol, gave slightly higher yields than when ether and carbon tetrachloride were used as solvents.

Modified Method on *n*-Amyl Alcohol.—From 90 g. of alcohol was obtained 112 g. of xanthate, b. p. 105–107.5° (10 mm.), n^{20}_{D} 1.5253. The olefin boiled at 29° (740 mm.).

Modified Method on Capryl Alcohol.—This was a 2-mole run using 260 g. of capryl alcohol which had been distilled through the 16-meter column;[11] 134 g. of crude olefin was secured by decomposing the crude xanthate. The residue was practically all capryl alcohol. The olefin was purified as usual. The distillate boiled at 120–122° (738 mm.), n^{20}_{D} 1.4115, and weighed 108 g. This was allowed to stand over sodium for several days and was distilled through the 90 × 2.1 cm. partial condensation column built by Franklin Johnston and described in a paper by Whitmore and Lux.[12]

No definite cuts could be obtained, but 12 g. of n^{20}_{D} 1.4095 and 23 g. of n^{20}_{D} 1.4143 were obtained at the lower and upper extremes, respectively. These two fractions were identified by ozonolysis, etc.,[13] as containing octene-1 and octene-2, as follows. The aldehydes secured by decomposing the ozonides were identified by mixed melting points of their semicarbazones and 2,4-dinitrophenylhydrazones with known samples of these same derivatives made from pure heptaldehyde and pure hexaldehyde kindly supplied by John M. Herndon[13] of this Laboratory.

The Tschugaeff reaction applied to capryl alcohol thus gave a mixture of octene-1 and octene-2 of n^{20}_{D} 1.4115, which represents a mixture of about 47% octene-2 and 53% octene-1, according to data supplied by Mr. Herndon, who found octene-1 had n^{20}_{D} 1.4149 and octene-2 n^{20}_{D} 1.4085.

Summary

1. Isoamyl alcohol, *n*-amyl alcohol and capryl alcohol have been dehydrated by the Tschugaeff method.
2. Isoamyl alcohol gave isopropylethylene, *n*-amyl alcohol gave pentene-1 and capryl alcohol gave a mixture of equal parts of octene-2 and octene-1.
3. Primary xanthates are much more stable to heat than are secondary and tertiary xanthates.
4. An advantageous modification of the Tschugaeff technique has been developed.

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[11] Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

[12] Whitmore and Lux, THIS JOURNAL, **54**, 3453 (1932).

[13] *Cf.* Whitmore and Herndon, *ibid.*, **55**, 3428 (1933).