3. Not all enol ethers undergo these reactions.
4. A mechanism for the transformation is advanced. It involves complex formation between two ether molecules followed by rearrangement in either of the two parts of the complex body.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# Syntheses in the Olefin Series. V. Completing the Survey of the Hexenes and Including Certain Heptenes and Octenes[1]

BY IMAN SCHURMAN[2] AND CECIL E. BOORD

In the third paper of this series Schmitt[3] and one of us in a survey of the hexenes, described eleven of the thirteen isomers as prepared by the bromo ether method. This method is not applicable to the tetra-alkylethylenes, type V, or to the *tert*-alkylethylenes of type I. It has seemed desirable, therefore, to seek other methods for the preparation of tetramethylethylene, the highest boiling hexene, and *tert*-butylethylene, the lowest boiling member of this family, and to measure their physical constants under conditions wholly comparable with those used for the other isomers.

Tetramethylethylene has been described by numerous investigators, its physical constants having been measured under widely varying conditions. It is most conveniently prepared by the dehydration of isopropyldimethylcarbinol, this method yielding also *as*-isopropylmethylethylene in smaller amounts.[4]

$$(CH_3)_2COH—CH(CH_3)_2 \longrightarrow \left\{ \begin{array}{l} (CH_3)_2C{=}C(CH_3)_2 \\ (CH_3)_2CH—(CH_3)C{=}CH_2 \end{array} \right.$$

For the present purpose the above carbinol was dehydrated over anhydrous oxalic acid, the two heptenes being obtained in yields of 80 and 20%, respectively. Their physical constants were measured under the conditions previously used in this series.

It is well known that *tert*-butylmethylcarbinol (pinacolin alcohol) does not yield the normally expected *tert*-butylethylene as the principal dehydration product. Alcohols of this type upon dehydration undergo a skeletal rearrangement. Such rearrangements have been frequently studied, and most recently by Whitmore and his co-workers,[5] who found only 3% of

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[1] (a) For the earlier papers of this series see Soday and Boord, THIS JOURNAL, **55**, 3293 (1933). (b) Presented before the Organic Division of the American Chemical Society in Washington, March, 1933, and before the Chemical Section of the Ohio Academy of Science, May, 1933.

[2] Research Associate under a Grant-in-Aid from the National Research Council, to whom our best thanks are due for making this work possible.

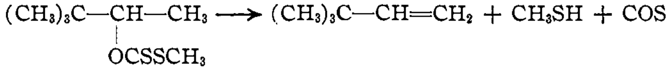
[3] Schmitt and Boord, THIS JOURNAL, **54**, 751 (1932).

[4] (a) Henry, *Bull. soc. chim. Belg.*, **22**, 140 (1907); (b) Couturier, *Bull. soc. chim.*, [4] **9**, 898 (1911).

[5] Whitmore, THIS JOURNAL, **54**, 3274 (1932); Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933); Whitmore and Meunier, *ibid.*, **55**, 3721 (1933).

*tert*-butylethylene among the dehydration products of the above carbinol.

The one method which above all others has proved most successful for the preparation of *tert*-butylethylene is the decomposition of the methyl xanthate of *tert*-butylmethylcarbinol.



$$(CH_3)_3C{-}\underset{\displaystyle OCSSCH_3}{\underset{|}{C}H}{-}CH_3 \longrightarrow (CH_3)_3C{-}CH{=}CH_2 + CH_3SH + COS$$

Fomin and Sochanski[6] adapted the method first used by Tschugaeff[7] in an extended study of the terpenes, to this one case among the simple olefins. The results of these authors have been confirmed in every detail.

In the earlier papers of this series it has been pointed out, from time to time, that the β-olefins of type II boil lower than the corresponding saturated hydrocarbons. And it will be further shown, in a general paper now in preparation concerning the relation of the physical constants of the simple olefins to their structure, that this rule is general for the olefins of type II.

Faworski and Alexejewa,[8] by the action of alcoholic potassium hydroxide upon 2,2-dimethyl-3-bromopentane, obtained a heptene boiling at 84–86° which they designated as *s*-*tert*-butylmethylethylene. If this olefin has the boiling point indicated it forms a marked exception to the above rule. The question is raised, therefore, does the heptene described have the structure assigned? Edgar, Calingaert and Marker[9] found this method as well as the dehydration of 2,2-dimethyl-3-pentanol to yield a mixture of heptenes having a wide boiling range. Furthermore, this mixture upon hydrogenation did not give an individual heptane. It seems obvious that a rearrangement takes place during the dehydration of the latter carbinol analogous to that found in the case of the simpler pinacolin alcohol.

The heptene obtained by the decomposition of the methyl xanthate of *tert*-butylethylcarbinol was found to boil at 76.9° (760 mm.). Upon hydrogenation it yielded 2,2-dimethylpentane identical with that prepared by Edgar and his co-workers by the condensation of *n*-propylmagnesium bromide with *tert*-butyl chloride. One must conclude, therefore, that Faworski and Alexejewa's hydrocarbon was probably a mixture and that pure 4,4-dimethyl-2-pentene boils at the lower temperature indicated above and thus conforms to the rule.

The present authors have found the xanthic ester synthesis to be a method which may be depended upon to yield the *tert*-alkyl derivatives of ethylene true to structure. Advantage has been taken of this peculiarity of the method to extend the surveys being made of the hexene, heptene and octene families. The present paper describes: 3,3-dimethyl-1-butene, 3,3-dimethyl-1-pentene, 4,4-dimethyl-2-pentene, 4,4-dimethyl-2-hexene

[6] Fomin and Sochanski, *Ber.*, **46**, 246 (1899).

[7] Tschugaeff, *ibid.*, **32**, 3332 (1899).

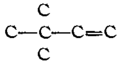
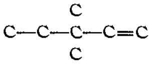
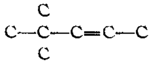
[8] Faworski and Alexejewa, *J. Russ. Phys.-Chem. Soc.*, **50**, 561 (1918).

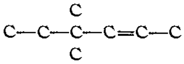
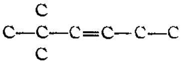
[9] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1485 (1929).

and 2,2-dimethyl-3-hexene. The physical constants of these olefins are recorded in Table I.

TABLE I

PHYSICAL CONSTANTS OF THE OLEFINS

| | | | |
|---|---|---|---|
| Structure |  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{=}C}$ |  $\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}C{=}C}$ |  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{=}C{-}C}$ |
| Type | I | I | II |
| B. p., °C. at (mm.) | 40.2–40.4(747)<br>41.0–41.2(760)<br>41.2[a](760) | 76.0(745)<br>76.9(760) | 75.0–75.1(739)<br>76.0–76.1(760)<br>84–86[b] |
| $d_4^{20}$ | 0.6510 0.6549$_4^{18}$[a] | 0.6961 | 0.6881 0.7220[b] |
| $n_D^{20}$ | 1.3759 1.37667[a] | 1.3991 | 1.3986 |
| MR, obs. | 29.76 29.53[a] | 34.06 | 34.44 |
| MR, calcd. | 29.44 | 34.06 | 34.06 |

| | | |
|---|---|---|
| Structure |  $\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}C{=}C{-}C}$ |  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{=}C{-}C{-}C}$ |
| Type | II | II |
| B. p., °C. at (mm.) | 103.5–104.1(739)<br>105.4–106.0(760) | 99.0(750.5)<br>100.1(760) |
| $d_4^{20}$ | 0.7202 | 0.7048 |
| $n_D^{20}$ | 1.4120 | 1.4068 |
| MR, obs. | 38.91 | 39.14 |
| MR, calcd. | 38.68 | 38.68 |

[a] Fomin and Sochanski, *Ber.*, **46**, 246 (1913).

[b] Faworski and Alexejewa, *J. Russ. Phys.-Chem. Soc.*, **50**, 561 (1920).

## Experimental Part

**Dehydration of Isopropyldimethylcarbinol.**—Four moles (408 g.) of isopropyldimethylcarbinol and 1200 g. of anhydrous oxalic acid were heated on an oil-bath under a reflux condenser, at 100°, for about eight hours. The condenser was then turned down and the mixture distilled. The distillate was washed six times with ice water, dried over calcium chloride and distilled repeatedly over sodium. After several fractionations through a 46 × 1.3 cm. column, closely packed with carborundum, and using a ratio of return to take off of 10 to 1, the mixture of heptenes was separated chiefly into two fractions boiling at 55.0–55.4° (748 mm.) and 72.3–72.6° (747 mm.), respectively.

The high boiling isomer, tetramethylethylene (2,3-dimethyl-2-butene), showed the following physical constants: b. p. 72.3–72.6° (747 mm.), 72.9–73.2° (760 mm.); $d_4^{20}$ 0.7081; $n_D^{20}$ 1.41153, $n_\alpha^{20}$ 1.40867, $n_\beta^{20}$ 1.41775; MR. obs. 29.49, calcd. 29.44; melting

TABLE II

METHYL XANTHATES OF SECONDARY CARBINOLS

| Carbinol | B. p. (uncorr.), °C. | Yield, % | Methyl xanthates[a] B. p. °C. | (mm.) | $d_4^{20}$ | $n_D^{20}$ | Yield, % | Olefin yield % on ester | % on carbinol |
|---|---|---|---|---|---|---|---|---|---|
| Methyl-*tert*-butyl | 116–119 | 60 | 85–87 | (6) | 1.0255 | 1.5242 | 73.5 | 58 | 41.6 |
| Methyl-*tert*-amyl | 142–145 | 50 | 110–112 | (8) | 1.0235 | 1.5250 | 75.0 | 67 | 51.0 |
| Ethyl-*tert*-butyl- | 132–135 | 58 | 92–92.5 | (5) | 1.0014 | 1.5206 | 60.0 | 73 | 44.0 |
| Ethyl-*tert*-amyl- | 156–160 | 25 | 118–120 | (8) | 1.0160 | 1.5210 | 41.0 | 55 | 22.5 |
| *n*-Propyl-*tert*-butyl- | 151–155 | 57 | 112–114 | (8) | 0.9950 | 1.5122 | 63.0 | 63 | 40.0 |

[a] The methyl xanthates are completely decomposed when distilled under atmospheric pressure. Apparently they are partially decomposed when distilled under the low pressures indicated. The methyl xanthate of ethyl-*tert*-butylcarbinol upon analysis for sulfur gave 31.69 and 31.92%. The theoretical value is 31.09%.

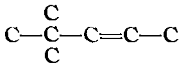
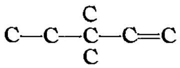
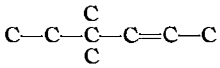
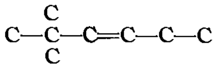
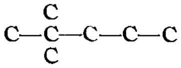
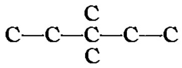
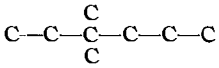
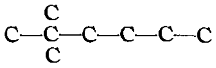
### TABLE III

### OLEFIN DIBROMIDES

| Name | B. p., °C. | (mm.) | $d_4^{20}$ | $n_D^{20}$ | MR, (obs.) | MR. (calcd.) | Bromine, % Found | Bromine, % Calcd. |
|---|---|---|---|---|---|---|---|---|
| 1,2-Dibromo-3,3-dimethylpentane | 95.3–95.6 | (10) | 1.5615 | 1.5109 | 49.77 | 50.05 | 61.82 | 61.92 |
| 2,3-Dibromo-4,4-dimethylpentane | 92.8–93.0 | (14) | 1.5538 | 1.5080 | 49.47 | 50.05 | 61.65 | 61.92 |
| 2,3-Dibromo-4,4-dimethylhexane | 92.0–93.0 | (4) | 1.5148 | 1.5113 | 54.21 | 54.67 | 58.70 | 58.82 |
| 3,4-Dibromo-2,2-dimethylhexane | 96.5–97.0 | (8) | 1.4856 | 1.5032 | 54.54 | 54.67 | 58.04 | 58.82 |

### TABLE IV

### HYDROGENATION OF OLEFINS

| | | | | | |
|---|---|---|---|---|---|
| Olefin | Structure |  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{=}C{-}C}$ |  $\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}C{=}C}$ |  $\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}C{=}C{-}C}$ |  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{=}C{-}C{-}C}$ |
| | G. | 12 | 10 | 8 | 12 |
| Saturated hydrocarbons | Structure |  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{-}C{-}C}$ |  $\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}C{-}C}$ |  $\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}C{-}C{-}C}$ |  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{-}C{-}C{-}C}$ |
| | Yield, g. | 10 | 7 | 6.5 | 9 |
| | B. p., °C. (760) | 78.8 78.9[a] | 85.9–86.0 86.0[a] | 110.7–111.2 111–112[b] | 106.8–107.1 106–107[b] |
| | $d_4^{20}$ | 0.6736 0.6737[a] | 0.6926 0.6934[a] | 0.7078 0.7116[b] | 0.6953 0.6967[b] |
| | $n_D^{20}$ | 1.3822 1.38233[a] | 1.3910 1.39114[a] | 1.3992 1.3998[b] | 1.3930 1.3931[b] |
| | Mol. ref. Obs. | 34.60 34.61[a] | 34.35 34.32[a] | 39.03 38.8[b] | 39.17 39.0[b] |
| | Mol. ref. Calcd. | 34.526 | 34.526 | 39.14 | 39.14 |

[a] Edgar and Calingaert, THIS JOURNAL, 51, 1540 (1929).

[b] Noller, *ibid.*, 51, 594–599 (1929).

point −76.4°.[10] The low boiling isomer, *as*-isopropylmethylethylene (2,3-dimethyl-1-butene), gave: b. p. 55.0–55.4° (748 mm.), 55.6–56.0° (760 mm.); $d_4^{20}$ 0.6810; $n_D^{20}$ 1.3899; MR (obs.) 29.27; calcd. 29.44; melting point −120 to −123°.

**Methyl Xanthates.**—One and one-tenth moles of metallic potassium was caused to react with an equivalent amount of *tert*-amyl alcohol dissolved in 1500 cc. of toluene, by boiling under a reflux condenser. One mole of the appropriate secondary carbinol was added to the hot solution, it being thus converted, according to Tschugaeff,[11] into the alcoholate. After cooling, 1.5 moles (115 g.) of carbon disulfide was slowly added causing the precipitation of the yellow potassium xanthate. Since much heat was evolved by this reaction the mixture was again cooled to room temperature and 1.1 moles (156 g.) of methyl iodide added and the mixture heated on the water-bath from four to five hours. After filtering, to remove the precipitated potassium iodide, the toluene and alcohol were distilled from the xanthic ester under a pressure of about 70 mm. The ester was then transferred to a modified Claisen flask and distilled under strongly diminished pressure. In later runs the methyl iodide was replaced by an equivalent amount of methyl sulfate with equally good results. The yields and physical constants of the methyl xanthates are recorded in Table II.

**Decomposition of the Methyl Xanthates.**—The purified ester was placed in a flask which was provided with a short upright condenser. The top of this condenser was in turn connected to the top of a coil condenser, set vertically, through which ice water was circulated. The receiver was immersed in a bath of ice and salt. By heating the flask gently the ester was slowly decomposed with a quiet ebullition.

The distillate was washed three times with strong potassium hydroxide solution, twice with ice water and then dried over calcium chloride. It was finally purified by distilling over a mixture of freshly cut sodium and potassium. The physical constants of the olefins prepared in this way are recorded in Table I.

**Dibromides.**—Ten or twelve grams of the olefin was dissolved in 50 cc. of chloroform and slowly treated with an equivalent amount of dry bromine dissolved in an equal volume of the same solvent. The bromination was carried out below 5° and in diffused light. The solvent was removed by distillation and the residual dibromides distilled under diminished pressure. The physical constants and analyses of the resulting dibromoparaffins are recorded in Table III.

**Hydrogenation of the Olefins.**—Ten or twelve grams of the olefin was dissolved in 75 cc. of ordinary alcohol and hydrogenated in a Burgess–Parr apparatus by the method of Voorhees and Adams.[12] The saturated hydrocarbon was precipitated by dilution with water, separated and washed with concentrated sulfuric acid to remove the last traces of water, alcohol and olefin. Final purification was effected by distillation from a modified Claisen flask having a 20.3 × 1.3 cm. Vigreux column "built in" to the side-arm. The physical constants of the saturated hydrocarbons are shown in Table IV in comparison with those previously recorded in the literature.

## Summary

The physical constants of tetramethylethylene (2,3-dimethyl-2-butene) have been remeasured, under the conditions used for the isomeric hexenes, and those of *tert*-butylethylene (2,2-dimethyl-1-butene) confirmed, thus completing the survey of the hexenes.

The methyl xanthate synthesis has been extended to the preparation of

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[10] The authors are greatly indebted to Mr. Earl O. Long for the determination of the melting points of this and the following heptene.

[11] Tschugaeff, *J. Russ. Phys.-Chem. Soc.*, **36**, 1253 (1904), through *J. Chem. Soc.*, **88**, 166 (1905).

[12] Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922).

3,3-dimethyl-1-pentene, 4,4-dimethyl-2-pentene, 4,4-dimethyl-2-hexene and 2,2-dimethyl-3-hexene and their physical constants are recorded. These olefins are new.

As evidence that a skeletal rearrangement did not take place in the formation of these olefins, 4,4-dimethyl-2-pentene was hydrogenated to 2,2-dimethylpentane, 3,3-dimethyl-1-pentene to 3,3-dimethylpentane, 4,4-dimethyl-2-hexene to 3,3-dimethylhexane and 2,2-dimethyl-3-hexene to 2,2-dimethylhexane.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF BROWN UNIVERSITY]

# Aliphatic Germanium Derivatives. III. Ethylgermanium Trihalides

BY E. A. FLOOD

Methods of preparation of ethylgermanium trihalides and some reactions of these compounds are described herein. In the preceding paper of this series it was pointed out that considerable difficulty is encountered in attempting to substitute a second bromine atom for an ethyl group in triethylgermanium bromide by the direct action of bromine.[1] It was therefore anticipated that the bromination of tetraethylgermane would not be a feasible method of obtaining monoethylgermanium derivatives. However, ethylgermanium triiodide can be obtained in almost quantitative yields from ethyl iodide and germanous iodide, which react according to the equation $C_2H_5I + GeI_2 = C_2H_5GeI_3$. Since germanium is readily extracted from its ore, germanite, as the volatile germanous sulfide which when treated with hydriodic acid yields $GeI_2$,[2] this method of preparing monoethylgermanium derivatives is simple and direct.

**Ethylgermanium Triiodide,** $C_2H_5GeI_3$.—When germanous iodide and an excess of ethyl iodide are heated together, in the absence of air, to a temperature of 110° reaction takes place over a period of several days with the formation of ethylgermanium triiodide, while if the reaction is carried out at a temperature of 140° a mixture of products is obtained, the chief constituents being germanium tetraiodide, unidentified gases and only very little ethylgermanium triiodide.

**Preparation.**—The following is a typical preparation of the triiodide from crude germanous iodide.

A mixture consisting of 18.5 g. of germanous iodide and 40 g. of ethyl iodide in an air-free sealed tube was heated to a temperature of 110° during three days. At the end of this period most of the solid had disappeared. The tube was opened and the liquid

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[1] E. A. Flood, THIS JOURNAL, **54**, 1663 (1932).

[2] Johnson, Morey and Kott, *ibid.*, **54**, 4278 (1932).