intermediate product, evidence is presented to show that these acyl exchanges are preceded by the formation of some sort of a triacyl complex as the result of an acetoacetic ester type of condensation. Through the decomposition of such a complex the various products obtained from the reaction are explained.

MADISON, WISCONSIN RECEIVED MAY 16, 1941

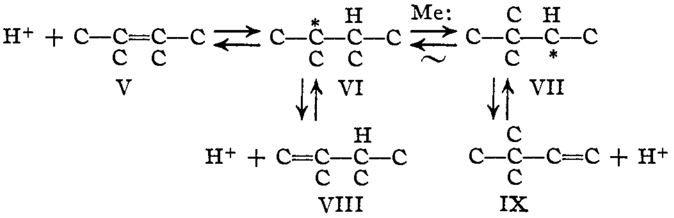
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Polymerization of Olefins. VI.[1] The Dimers Obtained from Tetramethylethylene. Preliminary Paper[2]

BY FRANK C. WHITMORE AND PAUL L. MEUNIER[3]

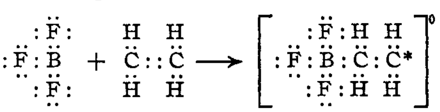
The present work was undertaken to throw further light on the mechanism of the polymerization of olefins by acid catalysts.[1,5]

Brunner and Farmer in 1937[4] published their results on the action of boron trifluoride on tetramethylethylene to form 2,2,3,5,6-pentamethyl-3-heptene and a trimethylheptylethylene. These authors[4] discussed various theories of polymerization and concluded that the products were best explained by the Whitmore mechanism.[5] Although the work on tetramethylethylene has been continued, little has been added to the problem as it stood in 1936. Consequently we are now reporting on it although it is still incomplete. Tetramethylethylene was polymerized with 80% sulfuric acid. The dimer mixture was distilled and ozonized. Identified were pinacolone, methylisopropylacetaldehyde, acetone, methyl neopentyl ketone, trimethylacetaldehyde, 3,5,5-trimethyl-2-hexanone, formaldehyde and dineopentyl ketone roughly in that order of decreasing abundance. Our work confirms the formation of 2,2,3,5,6-pentamethyl-3-heptene (I) as found by Brunner and Farmer.[4] We proved their other product to be 2,3,4,6,6-pentamethyl-2-heptene (II). We also found 2,2,4,6,6-pentamethyl-3-heptene (III) and the closely related isomer 1,1-dineopentylethylene (IV). Of these four products the percentages in the dimer were about 50, 10, 25 and 0.2, respectively. No product was found which was directly related to the starting material through the simple application of the Whitmore mechanism.[5] In each case rearrangement apparently took place both before and after the initial addition of a positive activated fragment to an olefin.[5] As was shown earlier[6] tetramethylethylene with an acid catalyst comes to equilibrium with its related isomers



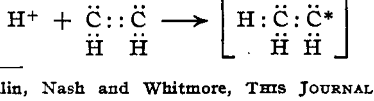
$$\begin{array}{ccccc}
H^+ + C{-}\underset{C}{C}{=}\underset{C}{C}{-}C & \rightleftarrows & C{-}\underset{C}{\overset{*}{C}}{-}\underset{C}{\overset{H}{C}}{-}C & \underset{\sim}{\overset{Me:}{\rightleftarrows}} & C{-}\underset{C}{\overset{C}{C}}{-}\underset{*}{\overset{H}{C}}{-}C \\
\text{V} & & \downarrow\uparrow\ \text{VI} & & \downarrow\uparrow\ \text{VII} \\
 & & H^+ + C{=}\underset{C}{C}{-}\underset{C}{\overset{H}{C}}{-}C & & C{-}\underset{C}{\overset{C}{C}}{-}C{=}C + H^+ \\
 & & \text{VIII} & & \text{IX}
\end{array}$$

Boron trifluoride[4] functions exactly like the proton from the acid catalyst by adding to one electron pair of the double bond and making the other carbon of the ethylene grouping electronically deficient as indicated by the asterisk. This deficiency can be overcome by the migration of an electron pair with the attached methyl group or proton (Me: ~ or H: ~) or by the migration of an electron pair to form a double bond with the liberation of a proton (loss H^+).[7] It should be



$$\begin{array}{c}:\ddot{F}:\\ :\ddot{F}:\ddot{B}\\ :\ddot{F}:\end{array} + \begin{array}{c}H\quad H\\ \ddot{C}::\ddot{C}\\ \ddot{H}\quad \ddot{H}\end{array} \longrightarrow \left[\begin{array}{c}:\ddot{F}:H\quad H\\ :\ddot{F}:\ddot{B}:\ddot{C}:\ddot{C}^*\\ :\ddot{F}:\ddot{H}\quad \ddot{H}\end{array}\right]^0$$

noted that this activated complex is electrically neutral in spite of its electronically deficient carbon, whereas the activated fragment formed from an olefin by the addition of a proton from the catalyst has an electronically deficient carbon and is electrically positive.



$$H^+ + \begin{array}{c}H\quad H\\ \ddot{C}::\ddot{C}\\ \ddot{H}\quad \ddot{H}\end{array} \longrightarrow \left[\begin{array}{c}H\quad H\\ H:\ddot{C}:\ddot{C}^*\\ \ddot{H}\quad \ddot{H}\end{array}\right]^+$$

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[1] V, THIS JOURNAL, **63**, 2035 (1941).

[2] Presented at the Pittsburgh meeting of the American Chemical Society, 1936.

[3] Full details are available in the Ph.D. Thesis, 1936, on file in the College Library, Willard P. Lewis, Librarian.

[4] Brunner and Farmer, *J. Chem. Soc.*, 1039 (1937).

[5] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

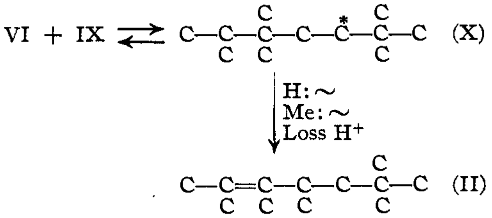
[6] Laughlin, Nash and Whitmore, THIS JOURNAL, **56**, 1395 (1934).

[7] *Cf.* ref. 4 and Whitmore, *ibid.*, **54**, 3274 (1932); *cf.* Hunter and Yohe, *ibid.*, **55**, 1248 (1933).

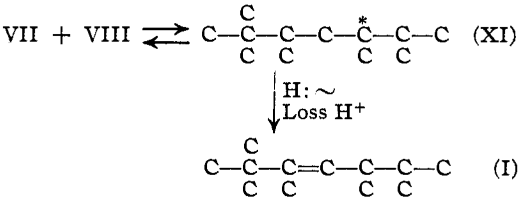
This important difference is undoubtedly related to the fact that boron trifluoride tends to give much higher polymers than do proton catalysts. The electrically neutral activated fragment should have less tendency to chain termination than the corresponding positively charged fragment.

The equilibrium mixture of V, VIII and IX contains about 60, 30 and 5%, respectively, of these substances. The indicated increasing rearrangement ability in presence of acid catalysts agrees with the dimerization results. The three olefins are, respectively, tetra-, di- and monosubstituted. Steric relations apparently increase their polymerization activity in that order. The activated complexes VI and VII are, respectively, tertiary and secondary. The ability of the first to add to an olefin should be less than that of the second. In the dimerization through the union of an electronically deficient complex with an olefin[5] the mathematically possible combinations are: (a) V + VI, (b) V + VII, (c) VI + VIII, (d) VI + IX, (e) VII + VIII, (f) VII + IX. Of these the first three are apparently inoperative.

No product corresponding to (a), (b) or (c) was found. This is not strange because they would involve, respectively, the union of the tetra substituted olefin and a tertiary fragment or a sterically hindered secondary fragment (pinacolyl) and the union of a tertiary fragment with the disubstituted olefin. This failure of a sterically hindered fragment to add to a sterically hindered double bond is like the failure of a *t*-butyl fragment to add to 2,4,4-trimethyl-2-pentene to give the long sought 1,1-di-*t*-butyl-2,2-dimethylethylene.[1,8] On the other hand, combination (d) involves a tertiary fragment and a monosubstituted olefin. It apparently takes place to a fair extent with the following rearrangements to give the observed product 2,3,4,6,6-pentamethyl-2-heptene (II).

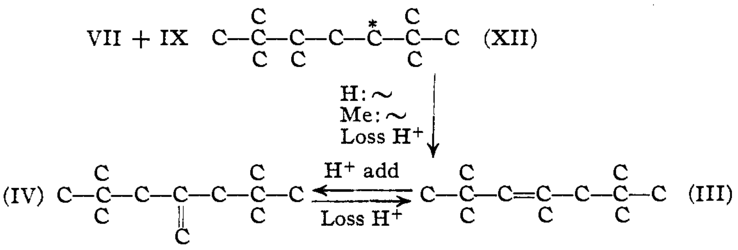


It is interesting to note that a 1,3-shift of methyl[9] in (X) would give the intermediate for the chief product (I) below. We have found no experimental way of choosing between these mechanisms. Combination (e) involves the secondary fragment and the disubstituted olefin.



This is the chief dimer.

Combination (f) involves the secondary fragment and the monosubstituted olefin. The combinations of rearrangements necessary to explain the observed products III and IV is again fantastic.



Olefins III and IV are the other products identified in the dimer mixture. A 1,3-shift of methyl[9] in XII would give no net change. It should be emphasized that *breaking a complex process like one of these polymerizations into steps is like analyzing an avalanche by slow motion photography and then assuming that there are fixed static points in the process.* Of course, both the slide and the chemical change keep moving to a stable end-point.

In spite of years of careful search no olefins corresponding to the non-rearranged primary addition complexes X, XI and XII have been found. It is hoped that it will be possible to continue the study of tetramethylethylene with larger amounts of material and the improved columns and techniques now available.

A polymerization of 1,1-methylisopropylethylene (VIII) gave a mixture of dimers indistinguishable from that obtained from tetramethylethylene (V).

We wish to thank N. C. Cook of this Laboratory for selecting and arranging material for publication from the large amount of data in the Thesis.[3]

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(8) Bartlett, This Journal, 63, 495 (1941).

(9) *Cf.* Whitmore and co-workers, *ibid.*, 63, 756, 1120 (1941).

Experimental

Preparation of Tetramethylethylene.—Tetramethylethylene, b. p. 72–72.4° at 740 mm., $n^{22}\text{D}$ 1.4120, and 1,1-methylisopropylethylene, b. p. 55–55.4°, $n^{20}\text{D}$ 1.3904, were prepared by the dehydration of pinacolyl alcohol and dimethylisopropylcarbinol. The olefins were prepared in two to five mole runs by means of anhydrous oxalic acid and β-naphthalene sulfonic acid. An average ratio of about 60% tetramethylethylene to 40% methylisopropylethylene was obtained.

Polymerization.—Two runs of 1.35 and 2 moles of the tetramethylethylene were polymerized to furnish the dimer. The olefin in each case was added slowly with stirring to 600 g. of 80% sulfuric acid at about 0°. The mixture was then allowed to warm up to room temperature overnight. The hydrocarbon layer was separated and washed with three 100-cc. portions of water, then with three 75-cc. portions of 10% sodium carbonate solution and dried over 25 g. of calcium chloride.

The polymerized material was distilled through an efficient column. An over-all yield of 62% dimer with a b. p. range of 70–110° at 100 mm. pressure and an $n^{20}\text{D}$ 1.4280–1.4351 was obtained from the distillation. The material was redistilled by parts and divided into four fractions of the following properties: 1, 9.1 g., b. p. 83–95° at 100 mm., $n^{20}\text{D}$ 1.4299–1.4328; 2, 13.5 g., b. p. 95–107° at 100 mm., $n^{20}\text{D}$ 1.4294–1.4313; 3, 21.6 g., b. p. 107–109° at 100 mm., $n^{20}\text{D}$ 1.4320–1.4333; 4, 33.7 g., b. p. 108–109.8° at 100 mm., $n^{20}\text{D}$ 1.4340–1.4377.

Identification.—Each of these cuts was ozonized separately in low boiling petroleum ether containing no unsaturated materials. They were then decomposed by dropping into boiling water containing zinc dust. The oil layer was steam distilled and collected. In each case traps were provided to catch any low boiling material.

In every case the identity of a listed product was confirmed by a mixed m. p. determination. Fraction 1 gave acetone, 2,4-dinitrophenylhydrazone m. p. 125–126°; 3,5,5-trimethyl-2-hexanone, 2,4-dinitrophenylhydrazone 63–64°, semicarbazone, 168–169°; trimethylacetaldehyde, 2,4-dinitrophenylhydrazone 204–206°; methyl neopentyl ketone 2,4-dinitrophenylhydrazone 98–99.5°; and formaldehyde dimetol 185–187°.

Fraction 2 gave trimethylacetaldehyde, methyl neopentyl ketone, semicarbazone m. p. 163–165°, formaldehyde and dineopentyl ketone, oxime m. p. 75–78°.

Fraction 3 gave pinacolone, 2,4-dinitrophenylhydrazone 125–126°, methylisopropylacetaldehyde, 2,4-dinitrophenylhydrazone 121.5–122.5°, dimetol 156.5–157.5°; trimethylacetaldehyde; methyl neopentyl ketone and formaldehyde. Fraction 4 gave mainly pinacolone and methyl isopropyl ketone, with some formaldehyde.

Polymerization of 1,1-Methylisopropylethylene.—The olefin, 173.5 g., was polymerized and distilled as near like the experiments with tetramethylethylene as possible. A yield of 43% dimer with a boiling range 70–111° and $n^{20}\text{D}$ 1.4257–1.4353 was obtained from the distillation. On ozonolysis there were identified trimethylacetaldehyde, methyl neopentyl ketone, pinacolone, methylisopropylacetaldehyde, and formaldehyde. These materials were present in approximately the same proportions as before.

Synthesis of Unknown Ozonolysis Products.—3,5,5-Trimethyl-2-hexanone was synthesized by the addition of methylmagnesium chloride to methylneopentylacetyl chloride.[10] The 2,4-dinitrophenylhydrazone and semicarbazone melted at 63–64° and 168–169°, respectively.

The methylisopropylacetaldehyde was obtained by the hydrolysis of the dibromide of 1,1-methylisopropylethylene. Although the methylisopropylacetaldehyde was contaminated with pinacolone its presence was confirmed by positive Schiff tests and the formation of a dimetol melting at 159–160°. A 2,4-dinitrophenylhydrazone, m. p. 123–124°, was obtained, which on mixing with the derivative of pinacolone, lowered the m. p. to 105–109°.

Summary

1. Tetramethylethylene has been polymerized at 0° with 80% sulfuric acid.

2. The results of Brunner and Farmer using boron trifluoride have been confirmed and extended.

3. The chief products in the dimer are: 2,2,3,5,6-Me_5-3-heptene (*ca.* 50%), 2,2,4,6,6-Me_5-3-heptene (*ca.* 25%), 2,3,4,6,6-Me_5-2-heptene (*ca.* 10%), 1,1-dineopentylethylene (2-neopentyl-4,4-Me_2-1-pentene, *ca.* 0.2%).

4. All the observed products correspond to rearrangements both before and after the union of the parts of the dimers.

5. Although the formation of the dimers cannot be explained by any existing theory of polymerization it fits a combination of the rearrangement and polymerization theories current in this Laboratory.

STATE COLLEGE, PENNSYLVANIA RECEIVED MAY 13, 1941

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[10] Whitmore and co-workers, THIS JOURNAL, **63**, 2028 (1941).