of aluminum chloride monomethanolate) was sealed into the autoclave and 100 cc. (56 g.) of isobutane and 5 g. of hydrogen chloride were pressed in. The stirrer was started and 800 cc. (456 g.) of a mixture of about four parts of isobutane to one of the olefin was added during two to three hours from a charger equipped with a calibrated Jerguson gage. Stirring was continued for an additional one-half hour, after which the autoclave was cooled to room temperature, if necessary, and the gaseous product was slowly led through a soda lime tower into a trap immersed in a Dry Ice–acetone-bath. The autoclave was then cooled to 0° and opened. The liquid product was separated from the catalyst, combined with product from two or three similar experiments, washed and dried. A portion of the washed material was analyzed for chlorine; the remainder was distilled through an 18-inch total reflux fractionation column (wire spiral).[12] The product boiling up to 125° was divided into two parts, one of which was carefully fractionated through a high-temperature Podbielniak column and the various fractions were analyzed[13] by means of their infrared spectra. The other part was used for the octane number determination.

The catalyst was recovered as a dark brown viscous liquid (15–20 g.) when aluminum chloride was used and as a dark brown mixture of crystals and very viscous liquid (15–19 g.) when aluminum chloride monomethanolate was used. The recovery was incomplete owing to difficulty in removing the viscous material from the autoclave; nevertheless, the indications were that more of the hydrocarbon charge was tied up with the catalyst when using the pure aluminum chloride than with the other catalyst.

The alkylates obtained with the aluminum chloride monomethanolate contained unusually large amounts of chlorine (1.0–1.6%) which was present chiefly in the form of *s*-butyl chloride. Its removal from the gasoline, had it been desired, could have been accomplished quite readily by any of several known methods.

No normally liquid product was obtained in an experiment in which a mixture of isobutane and 2-butene was added to a well-stirred mixture of isobutane, hydrogen chloride and **aluminum chloride dimethanolate** at 72° using the above-described procedure.

Acknowledgment.—The writer wishes to thank Dr. W. S. Gallaway for the analyses of the products by the infrared method and Mr. E. E. Meisinger for assistance in the experimental work.

Summary

1. The respective alkylates obtained by the reaction of isobutane with 1-butene and with 2-butene in the presence of aluminum chloride monomethanolate and hydrogen chloride differed markedly in that the former contained about 60% of dimethylhexanes and 10% of trimethylpentanes whereas the latter contained about 65% of trimethylpentanes and only 4% of dimethylhexanes. A similar difference in composition of the two products was observed when unmodified aluminum chloride was used as catalyst; the alkylation was, however, accompanied by more side reaction.

2. Alkylation of isobutane with propene using aluminum chloride monomethanolate as catalyst yielded a liquid product more than half of which was heptane and consisted of approximately equal amounts of 2,3- and 2,4-dimethylpentane.

3. The mechanism of the alkylation is discussed and the difference in composition of the butene products is explained.

RIVERSIDE, ILLINOIS RECEIVED SEPTEMBER 1, 1945

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[12] C. L. Thomas, H. S. Bloch and J. Hoekstra, *Ind. Eng. Chem., Anal. Ed.*, **10**, 153 (1938).

[13] Analyses by Dr. W. S. Gallaway, Physics Division, Universal Oil Products Company. A description of the analytical method as well as data obtained for the present samples will be given in a paper submitted to the *Analytical Edition of Industrial and Engineering Chemistry*.

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

The Depolymerization of 3,4,5,5-Tetramethyl-2-hexene and 3,5,5-Trimethyl-2-heptene in Relation to the Dimerization of Isoamylenes[1,2]

BY FRANK C. WHITMORE AND WILLIAM A. MOSHER[3]

The polymerization of the isoamylenes by the action of sulfuric acid gives chiefly the two decenes 3,4,5,5-tetramethyl-2-hexene (V), and 3,5,5-trimethyl-2-heptene (I).[4,5] In acid media both of these olefins may give rise to a carbonium ion[6] containing $R_3C—C—C+$ by the addition of a proton.[7] Such a carbonium ion has been shown by Whitmore and Stahly[1,8] to split readily giving two smaller olefins. The action of 1-chloro-4-naphthalenesulfonic acid upon the present decenes yielded significant information, especially regarding the formation of 3,4,5,5-tetramethyl-2-hexene which has been recognized as an abnormal polymerization product.[4,5]

Whitmore called attention to the fact that the

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[1] The Polymerization of Olefins. IX. Paper VIII of this series, THIS JOURNAL, **67**, 2168 (1945).

[2] From a part of the dissertation submitted by W. A. Mosher in partial fulfillment of the degree of Doctor of Philosophy, The Pennsylvania State College, 1940.

[3] The Eastman Kodak Co. Research Fellow in Chemistry, 1939–1940. Present address: University of Delaware, Newark, Delaware.

[4] Drake, Kline and Rose, THIS JOURNAL, **56**, 2076 (1934).

[5] Whitmore and Mosher, *ibid.*, **63**, 1120 (1941).

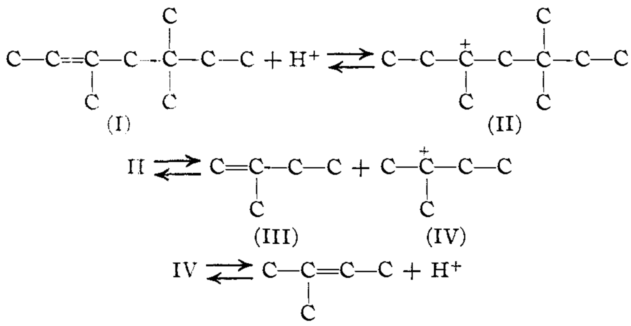
[6] The term "carbonium ion" is used in the sense employed by L. P. Hammett in "Physical Organic Chemistry," McGraw-Hill Company, 1940, but with the reservations stipulated by the present senior author in reference 7. The "+" sign is used in place of the "*" previously employed to indicate the carbon atom having only a sextet of electrons, this electronic deficiency being due usually to the decomposition of an oxonium compound or to the addition of a proton or other electrophyllic group or compound to a multiple linkage but rarely to a simple ionization such as that of the trityl halides in liquid sulfur dioxide.

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

[8] Whitmore and Stahly, *ibid.*, **55**, 4153 (1933).

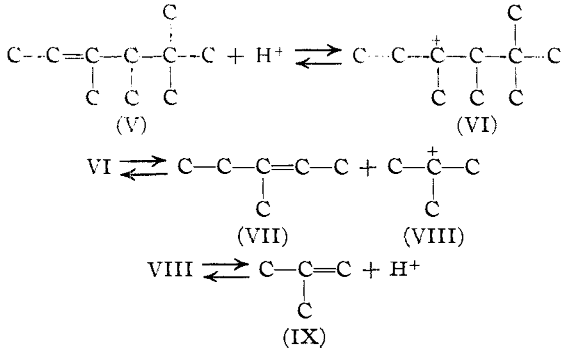
polymerization of the isoamylenes would probably be complicated by rearrangements.[9] The agents which catalyze polymerizations also are effective in bringing about rearrangements. Wachter[10] has also emphasized this possibility. Whitmore postulated 2,3,4,4-tetramethyl-2-hexene as one of the most probable of the diisoamylenes. This compound, however, has not been found. The possibility that the observed 3,4,5,5-tetramethyl-2-hexene could be formed from 2,3,4,4-tetramethyl-2-hexene was realized by Drake and his co-workers. However, they considered the rearrangement too complicated to be probable. It was hoped in the present work that the rearrangement, if it did occur, might be reversible under the influence of hydrogen ion and that fragments resulting from the depolymerization of the rearranged form might be obtained. Such proved to be the case.

According to the mechanism advanced by Whitmore[1,8,9] the depolymerization of decene I should take place as shown.



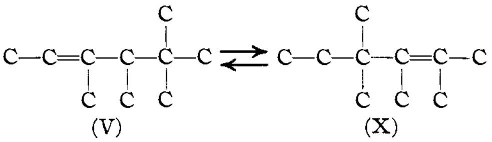
The depolymerization of I followed this prediction, yielding 83% isoamylenes, mostly trimethylethylene as would be expected from the above and the known ready formation of the latter from III.[11] The other product was unchanged decene I.

The depolymerization of decene V would be expected to be as follows



The depolymerization of V gave the products predicted but also gave C_5 and C_6 products in substantial amounts due to rearrangements as discussed below. The predicted products included 11.6% isobutylene (IX), 24.8% 3-methyl-2-pentene (VII) and 3.8% diisobutylene from the union of IX and VIII. The rearrangement products included 21.5% trimethylethylene, 3.6% 1,1-methylethylethylene, and 3.8% nonenes from the union of VIII the trimethylethylene. Unchanged decene V was obtained in 27.5% yield. The formation of trimethylethylene from V was confirmed by three separate experiments in one of which the percentage ran as high as 45.

V cannot split to give trimethylethylene. The following rearrangement taking place through the corresponding carbonium ions is the most probable one



X is the simplest rearranged product of V which would readily depolymerize to give only isoamylenes. This rearrangement involves a "1,3-shift" of a methyl group. It was considered improbable by Kline and Drake[12] but was considered the probable course by Wachter[10] who interpreted it as a "double pinacol rearrangement." Such a 1,3-rearrangement of methyl had been observed in this Laboratory by K. C. Laughlin in 1933 during the "copolymerization" of tertiary and secondary butyl alcohols to give 2,3,4-trimethyl-2-pentene in addition to the expected products. This was regarded as such an unusual rearrangement that it was not published until it had been observed repeatedly[13] and was supported by the similar findings of Drake, Kline and Rose[4] which were also confirmed in this Laboratory.[5]

The various postulated courses of the reaction are given in Chart I.

Careful searches have failed to detect XIV or any probable products from it or the related carbonium ion XIII either in the original polymerization[5] or in the present depolymerization studies. Thus, the successive 1,2-shifts of H and methyl are probably excluded. The successive 1,2-shifts of methyl at the right of Chart I correspond to the "double pinacol rearrangement" of Wachter.[10] This course cannot be excluded because it gives XV which corresponds to the fact of the formation of amylenes in addition to the finding of V and its expected splitting products. On the other hand, the formation of XVI with its two neo carbons seems less probable than the formation of XV by a direct 1,3-shift.

The importance of various industrial products apparently corresponding to a 1,3-shift of methyl

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

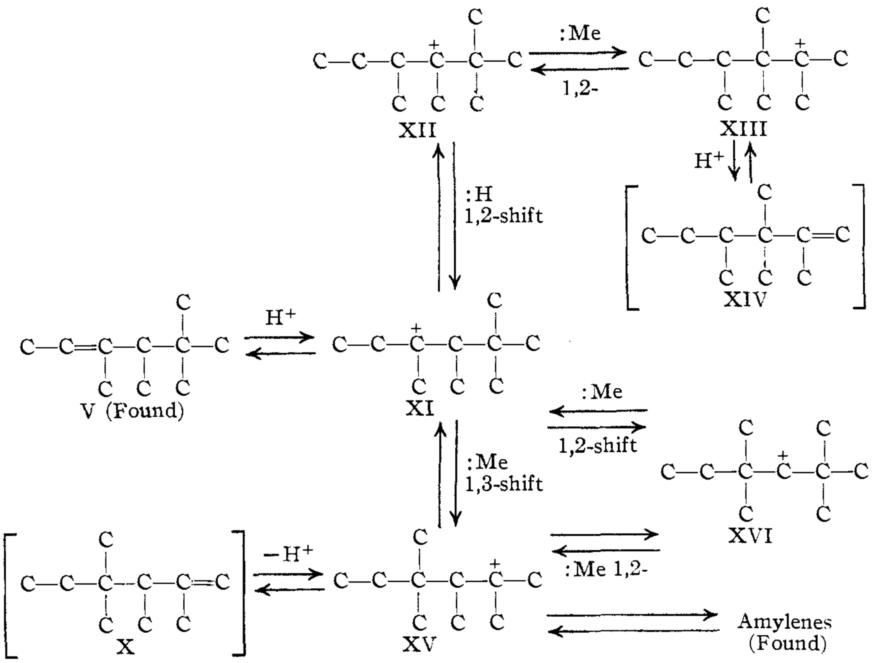
[10] Wachter, *ibid.*, **30**, 822 (1938).

[11] *Cf.* Whitmore, *et al.*, THIS JOURNAL, **64**, 2970 (1941).

[12] Kline and Drake, *J. Research Natl. Bur. Standards*, **13**, 705 (1934).

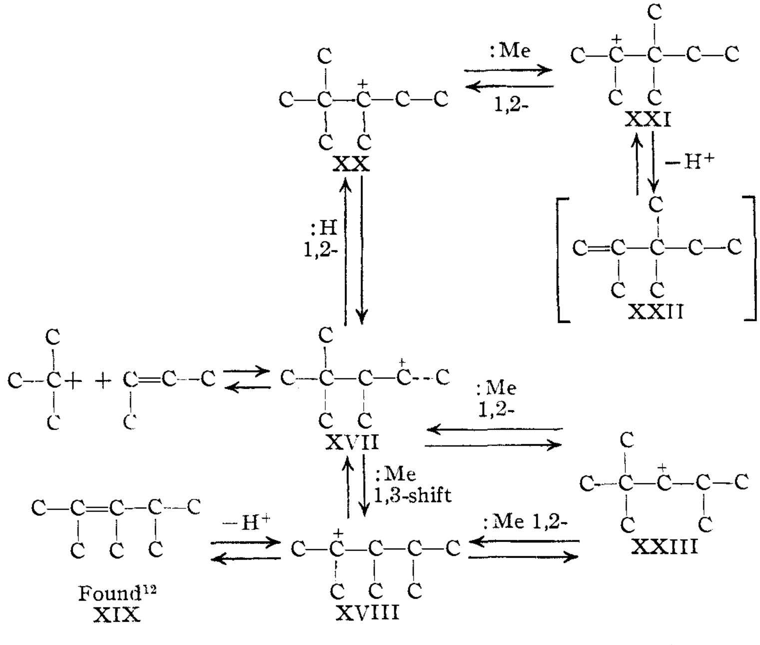
[13] Whitmore, Laughlin, Matuszeski and Surmatis, THIS JOURNAL, **63**, 746 (1941).

CHART I



warrants Chart II covering the possibilities in the earlier work.[13]

CHART II



Again the failure to find XXII or products related to it and XXI indicates that the successive 1,2-shifts of hydrogen and methyl cannot take place to any large extent under the conditions used.

The two successive 1,2-shifts of methyl to give XVIII by way of XXIII cannot be directly excluded since the latter is less sterically "crowded" than XVII and would also give rise to one of the observed products, namely, diisobutylene. It should be noted that both XVII and XX, by loss of a proton, give the principal product formed in this copolymerization, 3,4,4-trimethyl-2-pentene.

The probability of a 1,3-shift of methyl is seen to be greater on considering the steric relations of 3-carbon system having five and six alkyl groups attached to it as in XVII and XI. Such an accumulation of alkyl groups is known to favor the closing of a 3-membered ring and retard its opening. The effect of the alkyl groups is to decrease the effective valence angle and thus bring the 1- and 3-carbons closer in space.[14] It should also be noted that the same arguments hold for the effect of the alkyl groups on a 4-membered ring in case the 1,3-shift is regarded as involving a Walden inversion type of rearward attack on the shifting group.[15]

Conclusions

The dimerization of isoamylene consists in the addition of *t*-amyl carbonium ions tetramethylethylene and 1,1-methylethylethylene[16] according to Chart III.

The facts obtained in the dimerization of isoamylenes[5] and in the present depolymerization studies of olefins corresponding to II and XI correspond entirely with the compounds in Chart III except for the absence of the olefins corresponding to XV which were predicted by Whitmore[9] at a time when it was not recognized sufficiently that the polymerization of branched olefins may be greatly complicated by rearrangements and by depolymerizations. It would appear that of the two closely related carbonium ions XV and XI, the former will depolymerize much more readily because in it the electron pair taken by the electronically deficient carbon comes from a

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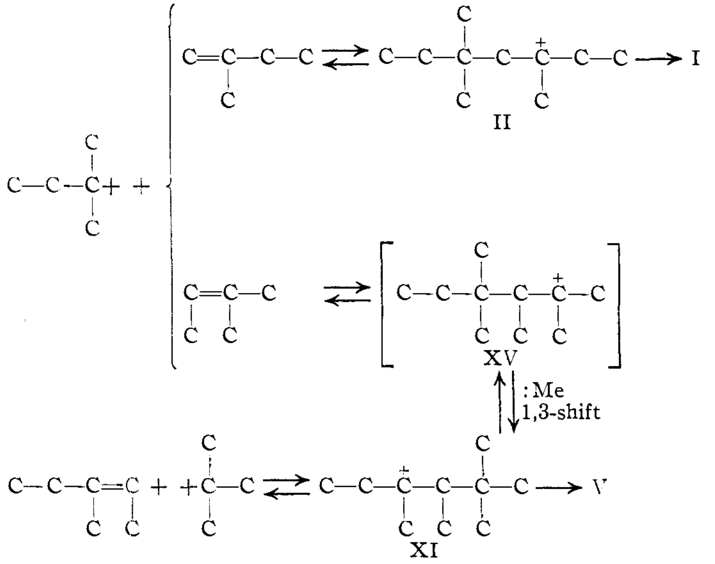
[14] Ingold and Thorpe, *J. Chem. Soc.*, **119**, 305 (1921); 1318 (1928).

[15] *Cf.* L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 157 *et seq.*

[16] Compare ref. 8.

CHART III



t-amyl group instead of a *t*-butyl group. The result is that as fast as XV is formed it shifts to the more stable XI which gives V. In other words, under comparable conditions a *t*-amyl group is lost by a carbonium ion much more readily than a *t*-butyl group. This recalls the results obtained in the "copolymerization" of *t*-butyl and *t*-amyl alcohols[17] in which only 10% of the stable final product (nonenes) contained the *t*-amyl group while the rest contained *t*-butyl.

Experimental

Depolymerization of 3,5,5-Trimethyl-2-heptene.—This olefin was obtained by the fractionation of the polymer from methylisopropylcarbinol through a column equivalent to 85 theoretical plates.[5] The purity of the olefin was confirmed by the fact that it yielded only acetaldehyde and 4,4-dimethyl-2-hexanone on ozonolysis. The depolymerization was performed using the method of Whitmore and Stahly.[8] The reactions were carried out under a column 1 × 50 cm. packed with single turn glass helices and equivalent to 15 theoretical plates.[18] The receiver was attached to two cold traps in series, one immersed in ice water to catch pentenes which might evaporate from the water cooled receiver and the other in Dry Ice–acetone to trap isobutylene and other low-boiling products. The olefin, 35 g. (0.25 mole) was heated with 1 g. of 1-chloro-4-naphthalenesulfonic acid; the temperature of the bath was 200–225°. Nothing was caught in the cold traps. The product consisted of 29 g. of isoamylenes, b. p. 30–38°, $n^{20}D$ 1.3788–1.3852, largely trimethylethylene. The trimethylethylene was identified by bromination and hydrolysis of the resulting dibromide to methyl isopropyl ketone.[8] The pot residue, 4.2 g., $n^{20}D$ 1.4409, was unchanged decene.

The Depolymerization of 3,4,5,5-Tetramethyl-2-hexene.—The olefin was obtained and depolymerized as above. The olefin yielded only acetaldehyde and 3,4,4-trimethyl-2-pentanone on ozonolysis. The olefin, 85 g. (0.6 mole), b. p. 152° (742 mm.), $n^{20}D$ 1.4358, was heated with 2 g. of the sulfonic acid. The Dry Ice trap caught 7.8 g. of liquid; no liquid was caught in the ice water trap. Refractionation of 60 g. of the product yielded the following fractions: (1) b. p. 26–28° (728 mm.), 2.2 g., $n^{20}D$ 1.3792, 1,1-methylethylethylene; (2) b. p. 38°, 13.8 g., $n^{20}D$ 1.3867–1.3889 trimethylethylene, identified as above; (3) b. p. 66–68°, 16.7 g., $n^{20}D$ 1.3995–1.4041, 3-methyl-2-pentene, identified by ozonolysis to give acetaldehyde and methyl ethyl ketone; (4) b. p. 90–115°, 2.8 g., $n^{20}D$ 1.4085–1.4135, largely diisobutylenes; (5) b. p. 115–140°, 4.3 g., $n^{20}D$ 1.4197–1.4300, nonenes; (6) b. p. 147–152°, 16.2 g., $n^{20}D$ 1.4320–1.4364, decenes. The ozonolysis of cut 6 showed the presence of the original decene. The distillation residue was 4 g., $n^{20}D$ 1.4385. There was no material refluxing between 68 and 90°. Fractions before and after this break were tested for the presence of tetramethylethylene by the use of nitrosyl chloride.[19] No indication of this olefin was found. The contents of the Dry Ice trap were vaporized and proved to be isobutylene by its complete absorption in 68% sulfuric acid.[20]

Summary

1. 3,5,5-Trimethyl-2-heptene has been depolymerized with 1-chloro-4-naphthalenesulfonic acid to yield trimethylethylene.

2. 3,4,5,5-Tetramethyl-2-hexene has been depolymerized with 1-chloro-4-naphthalenesulfonic acid to yield isobutylene, isoamylenes, 3-methyl-2-pentene, diisobutylenes and nonenes.

3. The dimerization of isoamylene is discussed in detail especially in relation to the absence of the predicted 2,3,4,4-tetramethylhexenes.[9]

4. Further evidence is presented and discussed for a 1,3-shift of methyl in certain carbonium ions.

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(17) Whitmore and Mixon, THIS JOURNAL, **63**, 1460 (1941).

(18) Whitmore and Lux, *ibid.*, **54**, 3451 (1932).

(19) *Cf.* Simonsen, "The Terpenes," Vol. 1, Cambridge, 1931, p. 141–142.

(20) Marcowitch and Moore, *Natl. Petroleum News*, Oct. 14, 15, 1931.