

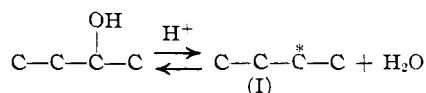
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Polymerization of Olefins. II.¹ The Copolymerization of *s*-Butyl and *t*-Butyl Alcohols by Sulfuric Acid

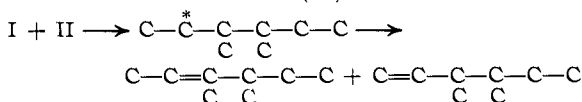
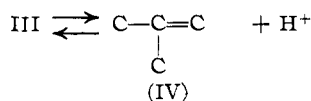
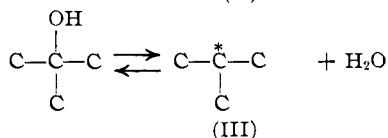
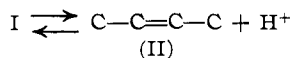
BY FRANK C. WHITMORE, KENNETH C. LAUGHLIN, JOHN F. MATUSZESKI AND J. D. SURMATIC

The copolymerization of *s*-butyl and *t*-butyl alcohols was studied in connection with the mechanism of the polymerization of olefins by acid catalysts as presented from this Laboratory.¹ The symmetrical nature of the chief olefin formed by the dehydration of *s*-butyl alcohol, 2-butene, should serve to limit the isomers in the polymer.

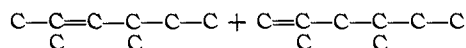
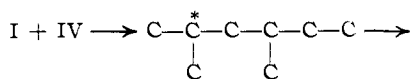
A study of the products of the reaction of equimolar amounts of *s*-butyl and *t*-butyl alcohols with an excess of sulfuric acid has been made by means of fractionation and ozonolysis. Possible reactions are formulated below¹ along with the actual results obtained in the study of the 78% yield of octylenes:



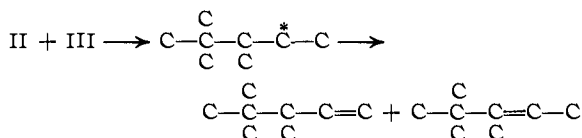
The asterisk indicates a deficiency of an electron pair. This is preferred to the use of a plus sign because it emphasizes the reactivity of the fragment as due to its electronic deficiency and avoids any confusion with the properties expected of an ordinary positive ion.²



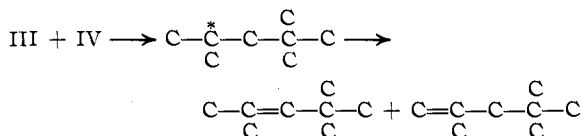
No trace of these products was indicated in the fractionation or ozonolysis studies. Thus the addition of the secondary butyl fragment to 2-butene does not take place appreciably in competition with the other possible reactions.



These products also failed to appear in appreciable amounts. Thus the secondary butyl fragment fails to add to isobutylene.

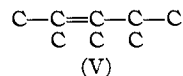


The first of these olefins was not found but the second, 3,4,4-trimethyl-2-pentene, constituted 40% of the octylene product from the alcohols. Since this was the chief product, there is evidently a strong tendency for the *t*-butyl fragment to add to 2-butene.



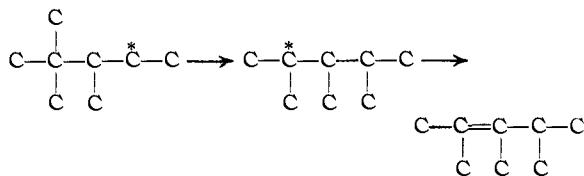
These are the diisobutylenes ordinarily formed from *t*-butyl alcohol and sulfuric acid.³ In the present work these diisobutylenes formed only 25% of the octylenes obtained.

In addition to the predictable diisobutylenes and the 3,4,4-trimethyl-2-pentene there was obtained an unexpected product, 2,3,4-trimethyl-2-pentene, V, to the extent of 35% of the octylenes.



This compound must be a product of an intramolecular rearrangement. When its formation was first observed in 1933 the rearrangement involved appeared unique, but almost immediately other workers observed a similar 1,3-shift of a methyl group during the polymerization of the olefins from methylisopropylcarbinol.⁴ Since that time the presence of the rearranged product 2,3,4-trimethyl-2-pentene (V) has been confirmed repeatedly in this Laboratory. It may be pictured merely as a 1,3-shift followed by the loss of a proton

(1) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).(2) Cf. Whitmore, *This Journal*, **54**, 3277, Note 12 (1932).(3) Cf. Whitmore and co-workers, *ibid.*, **53**, 3136 (1931); **54**, 3706, 3710 (1932).(4) Drake, Kline and Rose, *ibid.*, **56**, 2076 (1934).



The discussion of the similar rearrangement observed by Drake and his co-workers is presented in a paper to follow this one. A carefully drawn distillate *vs.* refractive index curve indicates the possible presence of a small amount of the 1-isomer of compound V but no ozonolysis products corresponding to it were obtained.

The octylenes from *t*-butyl alcohol and *s*-butyl alcohol thus appear to be formed by the addition of the *t*-butyl fragment to the isobutylene and the 2-butene to the extent of 25 and 75%, respectively. In the latter case about half of the product is formed by the peculiar 1,3-shift observed in this study.

Experimental

Materials.—Commercial *t*-butyl alcohol (4 l.) was refluxed for twelve hours with 40 g. of metallic sodium and then fractionated through a column equivalent to 16 theoretical plates. Alcohol melting at 25.0–25.5° was used in the polymerization studies. *s*-Butyl alcohol (Eastman Kodak Co.) was fractionated through the 16-plate column. Material of b. p. 98.5–99.0° (735 mm.), n_D^{20} 1.3972 was used.

Polymerization.—A typical run is given. Purified *s*-butyl alcohol (740 g., 10 moles) was dissolved in 2975 g. of a cooled solution of 75% (by wt.) sulfuric acid (about 21 moles). The solution of alcohol in acid was heated to 64° in a flask fitted with a sealed stirrer, separatory funnel, and reflux condenser. *t*-Butyl alcohol (740 g., 10 moles) was added slowly with stirring over a period of eleven hours. The mixture was allowed to cool, the oil layer siphoned off and then washed with water and 5% sodium carbonate solution. The yield of oil was 873 g., n_D^{20} 1.4230, 78% of the theoretical. The oil was dried over calcium chloride and fractionated repeatedly through the 16-plate column.

Identification of the Products.—The products of the polymerization were identified by ozonolysis using the methods of Whitmore and Church⁵ and of Church, Whitmore and McGrew⁶ with the exception that glacial acetic acid was used as the solvent during the preparation of the ozonides. The solution of the ozonide was added directly to the boiling mixture of water, zinc, and catalysts. The material ozonized is indicated by the Roman numerals on the unpublished curve.

Ozonolysis I.—Fractions 2–11, b. p. 100–104° (741 mm.), n_D^{20} 1.4082–1.4122, 65.5 g., were ozonized to yield 16 g. of oil on decomposition. The fractionation of this oil through a 20-plate column yielded 13 g. of oil which gave the 2,4-dinitrophenylhydrazone of methyl neopentyl ketone, m. p. and mixed m. p. 99–100°. Formaldehyde

was demonstrated in the water layer of the decomposition by the isolation of its "dimetol" derivative, m. p. and mixed m. p. 186–187°.

Ozonolysis II.—Fractions 12–22, b. p. 105.5–106.8° (740 mm.), 1.4132–1.4176, 88.6 g., were ozonized to yield 23.5 g. of oil on decomposition. Fractionation of the oil through the 20-plate column gave 2.5 g. of oil which yielded the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde, m. p. and mixed m. p. 208°; 2 g. of oil which gave the 2,4-dinitrophenylhydrazone of pinacolone, m. p. and mixed m. p. 125–126°; and 15 g. of oil which gave the 2,4-dinitrophenylhydrazone of methyl neopentyl ketone. The water layer contained formaldehyde identified by the preparation of its "dimetol" derivative. The dry-ice trap gave a derivative when treated with anhydrous ammonia which melted at 89–90°, thus showing the presence of acetaldehyde. The odor of acetaldehyde was plainly observed during the decomposition.

Ozonolysis III.—Fractions 23–33, b. p. 107.5–109.5° (726 mm.), 1.4184–1.4200, 100.5 g., were ozonized and the ozonide decomposed to yield 28 g. of oil. The fractionation of the oil gave 1.2 g. which yielded the 2,4-dinitrophenylhydrazone of 3,4-dimethyl-2-pentanone, m. p. and mixed m. p. 94°; 4.8 g. which gave the 2,4-dinitrophenylhydrazone of methyl neopentyl ketone; and 9 g. which gave the 2,4-dinitrophenylhydrazone of pinacolone. Formaldehyde was found in the water layer and acetaldehyde was demonstrated in the trap contents by the formation of acetaldehyde-ammonia, m. p. 88–90°.

Ozonolysis IV.—Fractions 34–41, b. p. 110–111° (728 mm.), 1.4220–1.4225, 83 g., were ozonized to yield 63.7 g. of oil on decomposition. On fractionation, the product gave only the 2,4-dinitrophenylhydrazone of pinacolone. Acetaldehyde was found in the contents of the dry-ice trap.

Ozonolysis V.—Fractions 42–45, b. p. 112–112.6° (743 mm.), 1.4232–1.4240, 84 g., were ozonized to yield 32.5 g. of oil on the decomposition of the ozonide. Fractionation of the oil gave 11.6 g. of oil which gave the 2,4-dinitrophenylhydrazone of methyl isopropyl ketone, m. p. and mixed m. p. 121–122°; 8.1 g. of the oil gave the 2,4-dinitrophenylhydrazone of pinacolone. Acetaldehyde was identified in the dry-ice trap. The 2,4-dinitrophenylhydrazone of acetone was obtained from the water layer.

Ozonolysis VI.—Fractions 58–60, b. p. 113.5–115° (745 mm.), 1.4252–1.4242, 84 g., were ozonized to give 22.2 g. of oil on decomposition. On fractionation this proved to be a mixture of methyl isopropyl ketone, 70%, and pinacolone, 30%. Acetaldehyde was found in the dry-ice trap, and the 2,4-dinitrophenylhydrazone of acetone, m. p. and mixed m. p. 123–124°, was prepared from the water layer from the decomposition of the ozonide.

Summary

The copolymerization of *s*-butyl and *t*-butyl alcohols with 75% sulfuric acid yields 25% diisobutylenes, 40% 3,4,4-trimethyl-2-pentene, and 35% 2,3,4-trimethyl-2-pentene. The last compound is formed by an unusual type of rearrangement, involving a 1,3-shift of a methyl group.

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(5) Whitmore and Church, *THIS JOURNAL*, **54**, 3710 (1932).

(6) Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).