Summary

Isoprene has been ethylated; 4-methyl-4-octene was formed exclusively. The structure of this nonene is in agreement with the usual behavior of a conjugated double bond system. This type of addition is further evidence in favor of the hypothesis which regards the polymerization of isoprene to synthetic rubber as the formation of long chains of isoprene units linked together by ordinary valences in the 1,4-position.

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NATURAL AND SYNTHETIC RUBBER. V. TETRAMETHYLOCTADIENE

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The third paper of this series[1] has shown how the polymerization of isoprene to synthetic rubber could be stopped at the dimeric stage by addition of an atom of hydrogen to each terminal carbon of the transitory dimer.

A similar experiment can be carried out with dimethylbutadiene substituted for isoprene. Although details differ, the general trend of the reaction remains the same, the reaction products are comparable and the conclusions are similar.

If the views presented before are correct, the linkage of two molecules of dimethylbutadiene, during polymerization to methyl-rubber, should form the transitory compound

$$\text{—}H_2CC(CH_3)=C(CH_3)CH_2CH_2C(CH_3)=C(CH_3)CH_2\text{—}$$

Should polymerization be allowed to proceed further, the unstable molecules would link together by their terminal free valences and form a long chain; methyl-rubber would be the final product. This agrees with Kondakow's ideas.[2] On the other hand, should polymerization be stopped by addition of an atom of hydrogen on each end of the unstable dimeric derivative, a duodecadienic hydrocarbon should result. This hydrocarbon has been isolated and analyzed. As expected, it was 2,3,6,7-tetramethyl-2,6-octadiene.

The polymerization of dimethylbutadiene can never be entirely stopped at the dimeric stage; an appreciable amount of a rubber-like material is always formed. The amount of this compound varies with the experimental conditions. This can be used as an evidence that the formation of tetramethyloctadiene and that of methyl-rubber are simultaneous and

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[1] Midgley and Henne, This Journal, 51, 1294 (1929).

[2] I. L. Kondakow, "Scientific Memoirs of the Imperial Yuriev University for the year 1901."

analogous processes. Consequently, the structure of the tetramethyloctadiene will have a very close relation to the structure of methyl-rubber. Moreover, since isoprene and dimethylbutadiene behave in a similar way, the structure of ordinary synthetic rubber may be postulated by analogy with that of methyl-rubber.

Experimental

The apparatus, procedure and proportions of reagents have been described previously. Runs were made at 0, 25 and 70°. In each case, 200 g. of dimethylbutadiene has been used. The best yield was obtained by running at 70°; 65 g. of $C_{12}H_{22}$ was collected and 45 g. of C_6H_{10} recovered, the balance being polymerized to methyl-rubber (15 g.) or carried out with the escaping hydrogen. The tetramethyloctadiene, purified by fractionation under reduced pressure, exhibited the following constants: b. p. (18 mm.) 87.5–88.5°, d_4^{25} 0.7971, n_D^{25} 1.45963. Molecular refraction found, 57.0; calcd., 56.7. The determination of the number of double bonds was made by bromination with a $KBr-KBrO_3$ mixture, and by hydrogenation in the presence of platinum oxide; in each case 4 atoms were accepted per molecule of hydrocarbon. To complete the analysis, a combustion, a molecular weight determination by freezing point lowering in benzene and an oxidation with ozone were performed. The ozonization was carried out in glacial acetic acid, as reported previously.[3] Two compounds were obtained and characterized: acetone and acetonylacetone. Not a trace of any other derivative could be detected. The result of the examination thus proves that the formula of the tetramethyloctadiene is $(CH_3)_2C{=}C(CH_3)CH_2CH_2(CH_3){=}C(CH_3)_2$.

The physical constants of the compound obtained by hydrogenation have been measured. They are: b. p. (20–22 mm.) 92°, d_4^{25} 0.7593, n_D^{25} 1.42527; mol. refr. found, 57.2; calcd., 57.6. A combustion and a molecular weight determination agree with the expected values. From its method of formation this compound should be 2,3,6,7-tetramethyloctane.

It is to be noted that when the polymerization is carried out at a low temperature the sample of tetramethyloctadiene obtained is considerably less pure; its boiling point is not constant, it can be fractioned into portions whose densities and refractive indexes vary between d_4^{25} 0.7980 and 0.8003 and n_D^{25} 1.45952 and 1.46111. The odor of the compound strongly resembles that of turpentine. Particularly, the addition of bromine or hydrogen to the double bonds is strongly hampered. This gave the impression that only one double bond was present and led to the erroneous belief that a ring compound had been formed. A better interpretation would be to consider that tetramethyloctadiene formed at low temperature is contaminated by a small quantity of cyclic or even dicyclic compound, which would account for the odor, the higher density and the high refractive index.

Summary

Dimethylbutadiene treated with potassium and alcohol gives 2,3,6,7-tetramethyl-2,6-octadiene and methyl-rubber. The structure of the first hydrocarbon has been established, and is used as an evidence that the methyl-rubber formula must be a long, open chain. This is also regarded as an evidence in favor of the chain formula of natural rubber.

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[3] Midgley and Henne, THIS JOURNAL, **51**, 2676 (1929).