7. The collective results lead to the conclusion that sucrose is β-glucosido-α-(γ)-fructose and that the *iso*-sucrose now described is β-glucosido-β-(γ)-fructose.

ST. ANDREWS, SCOTLAND

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. II. REDUCTION OF ISOPRENE BY Na–NH_3

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED DECEMBER 7, 1928 PUBLISHED APRIL 5, 1929

The reduction of isoprene by sodium in liquid ammonia was attempted to determine: (1) whether reduction would take place in preference to polymerization and (2) the location of the added hydrogen.

Isoprene was added to sodium dissolved in liquid ammonia and a 60% yield of 2-methyl-2-butene resulted. No other volatile hydrocarbon was found. High molecular weight hydrocarbons were formed but were not investigated. It is thus shown: (1) that the predominant reaction proceeds in accordance with the equation $C_5H_8 + 2Na + 2NH_3 = C_5H_{10} + 2NaNH_2$ and (2) that hydrogen adds to isoprene in the 1,4-position, in agreement with Thiele's theory.

The hydrogen addition is similar to the bromination of isoprene at low temperature.[1] If properly conducted the latter reaction stops after 2 atoms of bromine have been added to 1 molecule of isoprene; the resulting compound, 1,4-dibromo-2-methyl-2-butene, is characterized by the inactivity of its double bond toward bromine. Similarly, 2-methyl-2-butene obtained by reduction of isoprene is not reduced to *iso*pentane by an excess of Na–NH_3 reagent.

Procedure.—750 cc. of liquid ammonia are placed in a one-liter round-bottomed flask (Pyrex) and 46 g. of sodium is dissolved in it. The flask is equipped with a rubber stopper carrying a separatory funnel and an abduction tube. One mole of isoprene is slowly dripped into the liquid; the stem of the separatory funnel should nearly reach the surface of the ammonia in order to prevent abduction of isoprene by the escaping ammonia vapors. When the isoprene drops strike the ammonia, a clear sound is heard which can be used to regulate the delivery. The ammonia vapors carry the reduced hydrocarbon, together with a small quantity of unchanged isoprene, through an empty safety bottle to a cylinder filled with cracked ice. Ammonia dissolves immediately, the ice melts and the water flows into a large separatory funnel; the hydrocarbon, which condenses on the ice, is carried with the water and collects as an upper

[1] Staudinger, *Helv. Chim. Acta*, **5**, 756–767 (1922).

layer in the separatory funnel. By rerunning, the hydrocarbon can be completely freed of isoprene.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. III. DIMETHYLOCTADIENE

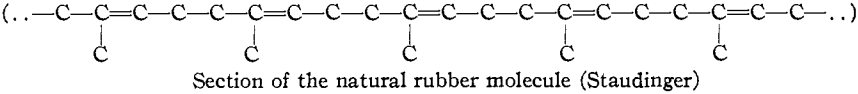
BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED DECEMBER 7, 1928 PUBLISHED APRIL 5, 1929

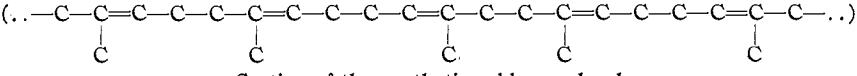
The polymerization of isoprene to synthetic rubber has long been known. The mechanism of this reaction has, however, so far escaped detection. To throw light upon this question, it was decided to polymerize isoprene in the presence of active hydrogen, with the hope that polymerization might be stopped at the dimer stage. This was accomplished in the following manner.

Well-purified isoprene, active toward polymerization, was placed in contact with metallic potassium chips and ethyl alcohol slowly added at a rate just sufficient to give a moderate evolution of hydrogen at the surface of the potassium. A good yield of a light yellow oil resulted, which upon analysis proved to be a mixture of 2,6-, 2,7- and 3,6-dimethyl-2,6-octadienes. These isomers are the dihydro dimers of isoprene resulting from a junction at the 1,4-, the 4,4- or the 1,1-carbon atoms, respectively, and the addition of hydrogen to the 1,8-positions of the dimer. No trace of a compound of cyclic nature could be detected.

These results suggest that the polymer of isoprene produced by contact with alkali metals and called "sodium rubber" (the commonest of the synthetic rubbers) is a long chain formed of isoprene units linked together by means of their 1 and 4 carbon atoms. This chain very closely resembles the long-chain structural formula of natural rubber proposed by Staudinger[1] and his associates, except that the recurring methyl groups may be placed at either side of the double bond, thus



Section of the natural rubber molecule (Staudinger)



Section of the synthetic rubber molecule

It should be noted that in the natural product the groups attached to each double bond may be expected to present always the same *cis*- or *trans*-configuration, whilst such uniformity can hardly be hoped for in the synthetic product.

[1] Staudinger, *Helv. Chim. Acta*, **5**, 785–805 (1922), and later papers.