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

ITHACA, NEW YORK

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

NATURAL AND SYNTHETIC RUBBER. III. DIMETHYLOCTADIENE

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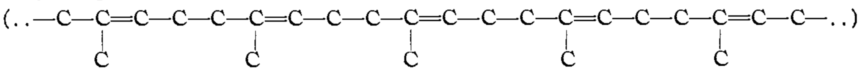
The polymerization of isoprene to synthetic rubber has long been known. The mechanism of this reaction has, however, so far escaped detection. To throw light upon this question, it was decided to polymerize isoprene in the presence of active hydrogen, with the hope that polymerization might be stopped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

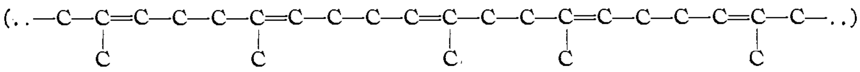
Well-purified isoprene, active toward polymerization, was placed in contact with metallic potassium chips and ethyl alcohol slowly added at a rate just sufficient to give a moderate evolution of hydrogen at the surface of the potassium. A good yield of a light yellow oil resulted, which upon analysis 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



$$(..\text{—C—}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{=C—C—C—}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{=C—C—C—}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{=C—C—C—}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{=C—C—C—}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{=C—C—}..)$$

Section of the natural rubber molecule (Staudinger)



$$(..\text{—C—}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{=C—C—C—}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{=C—C—C—C=}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{—C—C—}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{=C—C—C—C=}\underset{\substack{|\\ \text{C}}}{\text{C}}\text{—C—}..)$$

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.

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

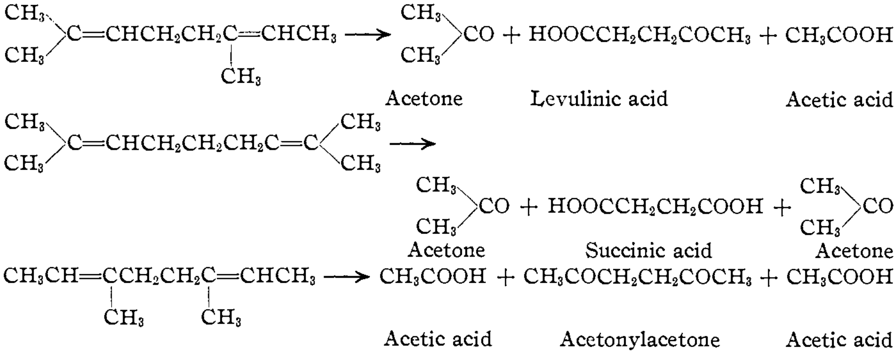
The products of the side reactions appear to be high polymers; their constitution is being studied at the present time. It is thought that a small amount of 2-methyl-2-butene was formed during the reaction but it was lost with the escaping hydrogen excess.

Procedure.—The apparatus comprises a 500-cc. round-bottomed flask equipped with a reflux condenser and a separatory funnel. The top of the condenser is connected to a glass tube whose end dips into a test-tube containing a little alcohol, thus making it possible to judge the rate at which hydrogen escapes.

Two-gram molecules of isoprene were placed in the flask, 4-g. atoms of potassium shavings quickly added and the flask connected to the condenser and separatory funnel; alcohol was dripped in at such a rate that a hydrogen excess escaped slowly from the apparatus. During the reaction the potassium remained shiny; when it was completely used, the potassium ethylate formed during the reaction was decomposed by adding water slowly through the separatory funnel. The reaction product was decanted, washed, dried and distilled. The mixture of dimethyloctadienes had the following constants: b. p., 163–167°; d_{20}^{20}, 0.769; n_{D}^{20}, 1.4457; mol. wt., 136.8 (138, theoretical). The bromination number determined with a $KBrO_3$–KBr mixture gives 2 double bonds per $C_{10}H_{18}$. Combustion checks the previous formula. Hydrogenation requires 2 moles of hydrogen and yields 2,6-, 2,7- and 3,6-dimethyloctanes.

Analysis of the Dimethyloctadienes.—The hydrocarbon was oxidized by means of a solution of CrO_3 in acetic acid. After removal of the bulk of Cr_2O_3 as $Cr_2(SO_4)_3$, insoluble in H_2SO_4, the following products were detected: acetone, 2,5-hexanedione, levulinic acid and succinic acid. These compounds are all very easily characterized: acetone by means of its mercury compounds, acetonylacetone by its dioxime and its unusually strong reaction with bromine, levulinic acid by its reaction with sodium nitroprusside and succinic acid by the pyrrole–pine shaving reaction.

The following diagram compares the oxidation products with the hydrocarbons from which they are formed.



$$(CH_3)_2C{=}CHCH_2CH_2\underset{\mathrm{CH_3}}{C}{=}CHCH_3 \longrightarrow \underset{\text{Acetone}}{(CH_3)_2CO} + \underset{\text{Levulinic acid}}{HOOCCH_2CH_2COCH_3} + \underset{\text{Acetic acid}}{CH_3COOH}$$

$$(CH_3)_2C{=}CHCH_2CH_2CH_2C{=}C(CH_3)_2 \longrightarrow \underset{\text{Acetone}}{(CH_3)_2CO} + \underset{\text{Succinic acid}}{HOOCCH_2CH_2COOH} + \underset{\text{Acetone}}{(CH_3)_2CO}$$

$$CH_3CH{=}\underset{\mathrm{CH_3}}{C}CH_2CH_2\underset{\mathrm{CH_3}}{C}{=}CHCH_3 \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Acetonylacetone}}{CH_3COCH_2CH_2COCH_3} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Although one of the oxidation products probably was acetic acid, it is obvious that it could not be detected, since the oxidation was carried out in an acetic acid solution. It is nevertheless evident that the hydrocarbon obtained by polymerization and simultaneous reduction of isoprene is a mixture of 2,6-, 2,7- and 3,6-dimethyl-2,6-octadienes.

Summary

The dimer of isoprene formed under conditions which normally produce "sodium rubber" has been stabilized by the addition of hydrogen. This partially hydrogenated dimer is a mixture of three isomeric dimethyloctadienes; its formation indicates that the mechanism of the polymerization of isoprene to synthetic rubber is the joining of many isoprene molecules by linkage of the 1,1-, the 1,4- or the 4,4-carbon atoms to produce a long-chain molecule.

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NEW BOOKS

Annual Survey of American Chemistry. Vol. III, July 1, 1927, to July 1, 1928. Edited by CLARENCE J. WEST. Prepared under the auspices of the Division of Chemistry and Chemical Technology, National Research Council. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1928. 395 pp. 13.5 × 21.5 cm. Price $3.00.

This volume of the Survey contains forty-six chapters which deal with the more actively studied fields in chemistry. A change in policy by the editorial board is announced in the foreword. This consists in "varying the subjects treated from year to year, which will mean that certain less active fields will be covered only every second or third year. Different authors also will be asked to write the reviews, thus distributing the effort of preparing the chapters among the authorities in the fields involved, and giving the readers more than one man's point of view on a particular subject."

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JAMES F. NORRIS

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition, completely rewritten. **Sodium.** System No. 21. Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin, W 10, Germany; 1928. 18 + 33 + 992 pp. 75 figs. 17 × 25 cm. Price, to subscribers, M. 118; singly, M. 150 (postage included).

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