period of eight hours. The solution was then cooled with an ice-bath and 30 cc. of concentrated hydrochloric acid added slowly and with stirring. The precipitated acid was filtered from this mixture, dried *in vacuo* at room temperature, and its rotation taken as follows: 0.1073 g. of acid made up to 15 cc. in acetone at 20° gave α_D $-0.76°$, $l = 1$, $[\alpha]^{20}_D$ $-105.8°$.

(c) A 0.1236-g. sample of the *l*-acid, $[\alpha]^{20}_D$ $-105.3°$ in acetone, was dissolved in 20 cc. of a solution that had been prepared by saturating an acetic acid solution, which contained 5% of water, with hydrogen chloride. The resulting solution was refluxed for eight hours, then cooled in an ice-bath and 50 cc. of concentrated hydrochloric acid added. After permitting the cooled mixture to stand for one-half hour, the precipitated acid was filtered from it, dried *in vacuo* at room temperature, and its rotation taken as follows: 0.0967 g. of acid made up to 15 cc. in acetone at 20° gave α_D $-0.54°$, $l = 1$, $[\alpha]^{20}_D$ $-83.4°$.

(d) A 0.1535-g. sample of the *l*-acid was made up to 15 cc. in a 5% sodium carbonate solution at 20° and its rotation taken: α_D $-2.13°$, $l = 1$, $[\alpha]^{20}_D$ $-208.0°$. This pale yellow solution was permitted to stand in a sealed tube at room temperature for seven days, during which period it developed an amber color. Its rotation was then taken and found to be: α_D $-2.11°$, $l = 1$, $[\alpha]^{20}_D$ $-206.3°$.

An attempt was made to heat the solution in a sealed tube to a temperature of 50–60°, but after eight hours of this treatment the solution had developed such a deep red color that its rotation could not be taken.

Summary

1. The compound 2,4,6,2′,4′-pentanitro-3-carboxydiphenyl has been prepared and resolved. This is the first diphenyl derivative with three of the same groups in the 2,2′,6-positions which has been resolved.

2. The active forms could not be racemized in acid, neutral or alkaline solution.

3. Discussion is given of what properties may be anticipated of various 2,2′,6-trisubstituted diphenyls.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. IV. 4-METHYL-4-OCTENE BY ISOPRENE ETHYLATION

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

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In preceding papers[1] it has been shown that when isoprene accepts hydrogen, or when two molecules of isoprene link together, the reaction affects only the 1- and 4-positions. This behavior has been regarded as a general property, and it has been used to explain the polymerization of isoprene to synthetic rubber.

The present paper offers one more evidence of the 1,4-addition. Two ethyl groups have been attached to an isoprene molecule

$$H_2C{=}C(CH_3)CH{=}CH_2 + 2C_2H_5Br \xrightarrow{Na} CH_3CH_2CH_2C(CH_3){=}CHCH_2CH_2CH_3$$

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[1] Midgley and Henne, THIS JOURNAL, **51**, 1215, 1293, 1294 (1929).

The experimental conditions were precisely those which are required for the formation of synthetic rubber: the reaction took place at room temperature in the presence of an alkaline metal and, in each case, a certain amount of synthetic rubber was formed. This favors the view that the ethylation of isoprene is a process very analogous to its polymerization.

As was expected, the ethyl groups linked exclusively to the first and the fourth carbon atoms; a hydrocarbon was thus obtained which on examination proved to be 4-methyl-4-octene. The criteria used for its identification were a combustion, a molecular weight determination by freezing point depression in benzene, a double bond determination by hydrogenation and by bromination, a computation of the molecular refraction and finally an oxidation with ozone.

Since the experimental results support the postulation that isoprene accepts radicals *exclusively* on its 1- and 4-carbon atoms (under the conditions required for synthetic rubber formation), they also fortify the hypothesis that the chain formula of natural rubber proposed by Staudinger[2] and his associates is much more acceptable than any formula involving the formation of a ring.

Experimental

Two-gram molecules of metallic potassium are covered with one gram molecule of isoprene, which has been sufficiently purified to be capable of rapid polymerization. Two-gram molecules of ethyl bromide (or one gram molecule of ethyl sulfate) is dissolved in a like volume of dry ether, and added gradually to the isoprene. A gentle shaking is maintained, and heat is applied sufficiently to maintain a moderate ebullition. Much gas is evolved; the decomposition of the ethylation agent is the predominant reaction. After twenty-four hours, the residual metal is eliminated by the cautious addition of alcohol, and the ethylate is then decomposed with water. The mixture is washed with dilute hydrochloric acid and water, decanted, dried and fractionated. About 4% of the theoretical amount of C_9H_{18} is obtained. This compound shows the following physical constants: b. p. 136–144° (chiefly 139°), d^{20}_{20} 0.7495, n^{20}_{D} 1.4228, $\Delta =$ 1.0 per C_9H_{18}. The molecular weight determined by freezing point depression in benzene was found to be 122: theory requires 126, but the discrepancy is within the permissible experimental error of 3%. A combustion checked the formula already evident. The molecular refraction computed from the density and the refractive index by means of the Lorentz–Lorenz formula was found to be 42.8. This value compares favorably with the theoretical value 43.3.

To prove that isoprene had accepted the ethyl groups exclusively on the 1- and 4-carbon atoms, it was necessary to locate the double bond in the resulting nonene, and this was done by ozone oxidation in a glacial acetic acid solution. The ozonization procedure has been previously recommended.[3] After decomposition of the ozonide with a dilute potassium dichromate solution, two compounds were isolated and characterized: methyl butyl ketone, and butyric acid. No trace of any other compound was detected. The results of the ozonization were in complete agreement with the formula postulated for the nonene.

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[2] Staudinger and co-workers, *Helv. Chim. Acta*, **5**, 785 (1922), and later papers.

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

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

$$—H_2CC(CH_3)=C(CH_3)CH_2CH_2C(CH_3)=C(CH_3)CH_2—$$

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."