The author wishes to express his appreciation to Professor Victor Lenher, at whose suggestion and under whose direction this work was carried out.

Summary

1. The reactions between selenium oxychloride and ethylene, propylene, butylene and amylene have been studied.

2. The mechanism of the reaction between selenium oxychloride and the olefins has been formulated and has been compared with that of selenium monochloride and the olefins.

3. It has been shown that with selenium oxychloride and the olefins, the dichlorides of the corresponding alkyl selenides are always formed regardless of whether the oxychloride or the olefin is in excess during the course of the reaction.

4. It has been shown that the final reaction products of selenium monochloride and the olefins are identical with those formed by the interaction of selenium oxychloride and the olefins.

5. The results obtained in these syntheses have been offered as further evidence in favor of the unsymmetrical structure for selenium monochloride.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE ACTION OF SELENIUM OXYCHLORIDE ON PURE RUBBER[1]

BY CARL E. FRICK

Received April 20, 1923

In the studies on the oxychloride of selenium which have been in progress in this Laboratory, Lenher[2] has shown that pure rubber, vulcanized rubber and vulcanite react chemically with selenium oxychloride. It seemed advisable to undertake a quantitative study of this reaction, if possible, as any information would be interesting in view of our incomplete knowledge of the nature of the rubber hydrocarbon. The products obtained by the action of selenium oxychloride on 2 wild, and 2 plantation rubbers, and a synthetic rubber prepared from isoprene, were investigated.

Preparation of Materials

Selenium Oxychloride.—The method of Lenher[3] was used.

Pure Rubber Hydrocarbon.—Samples[4] of crude, unworked rubber were washed

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[1] This paper is constructed from a part of a thesis submitted by the author to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, January, 1923.

[2] Lenher, THIS JOURNAL, **43,** 29 (1921).

[3] Lenher, *ibid.*, **42,** 2498 (1920).

[4] These samples were kindly furnished by Dr. W. C. Geer of the B. F. Goodrich Co. and Prof. H. E. Simmons of the University of Akron.

in frequent changes of water until dirt and soluble impurities were removed, dried, and freed from resins by extraction with boiling acetone for 24 hours. The residue was freed from acetone and the rubber hydrocarbon dissolved in pure carbon tetrachloride. The undissolved protein was filtered off and the rubber precipitated by absolute alcohol. The sample was freed from alcohol, redissolved in carbon tetrachloride, reprecipitated by alcohol 7 times, and finally redissolved and kept in pure carbon tetrachloride. The following natural rubbers were used in this study: Upriver, fine, hard Para; first latex Pale Crepe; Upper Caucho Ball; and ribbed Smoked Sheet.

Synthetic "Isoprene Rubber."—This was prepared from pure isoprene by the well-known method discovered practically simultaneously by Mathews[5] in England and Harries[6] in Germany, using metallic sodium to effect the polymerization. The rubbery mass was washed with acetone, dissolved in carbon tetrachloride, reprecipitated by alcohol, redissolved and reprecipitated several times, and thus purified in exactly the same manner as the natural rubbers. The sample was finally redissolved and kept in pure carbon tetrachloride.

Isoprene.—The isoprene was prepared from *dl*-limonene (dipentene) by passing the vapors over an electrically-heated platinum wire, using the principle of Harries' isoprene lamp.[7] The limonene was obtained from washed orange oil, which was over 96% pure limonene. The crude isoprene was freed from any contained amylene by allowing it to stand for several days in contact with barium dioxide, dried with fused calcium chloride and distilled, then dried with metallic sodium and redistilled, using a Vigreaux fractionation column. Ostromuislinskii's[8] method of purification by forming the tetrabromide and then removing the bromine by treatment with zinc dust at 0° in absolute alcohol solution was found to be impractical when it was desirable to prepare a liter or more of pure isoprene. The material was colorless; b. p., 33.2–33.8° (742 mm.).

Solvents.—Acetone was freshly distilled over anhydrous potassium carbonate, and the fraction boiling at 56–57° used. Carbon tetrachloride was purified by treatment with saturated chlorine water for several days in diffused sunlight. It was then washed thoroughly with distilled water, dried over fused calcium chloride and distilled.

Experimental Part

When crude rubber, vulcanized rubber or even vulcanite is placed in selenium oxychloride a vigorous reaction sets in and the rubber is dissolved with evolution of heat. The solution becomes reddish brown in color and contains selenium monochloride and selenium, in addition to the decomposition products of the rubber. In order to study this reaction, it became evident at once that the reaction would have to be more carefully controlled and further that the results would be the easier to interpret, the purer the samples of rubber used. The reactions of selenium oxychloride on the purified rubber hydrocarbon in solution in carbon tetrachloride, were carried out in all cases as follows.

To a known quantity of a 5% solution by weight of pure rubber in dry carbon tetrachloride, cooled to 0°, was added slowly, with vigorous stirring, an excess of a 5% solution of selenium oxychloride in dry carbon tetrachloride, also cooled to 0°. The selenium oxychloride was added in slight

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[5] Mathews and Strange, Brit. pat., 24,790, **1912.**

[6] Harries, *Ann.*, **383,** 157 (1911).

[7] Harries and Gottlob, *Ann.*, **383,** 228 (1911).

[8] Ostromuislinskii, *J. Russ. Phys. Chem. Soc.*, **47,** 1983 (1916).

excess as otherwise the solution could not be filtered because the excess of rubber clogs the filter. A yellowish-white, amorphous substance immediately settled. The solution was filtered quickly through a Büchner funnel, the precipitated material transferred to a beaker containing cold carbon tetrachloride and agitated in order to free the material from the slight excess of selenium oxychloride. This operation was repeated several times using fresh portions of cold, dry carbon tetrachloride. The precipitated material was finally brought onto the filter paper and the carbon tetrachloride replaced by ethyl ether. The ether was quickly evaporated, the dry, amorphous powder transferred to a glass-stoppered weighing bottle and this container kept at 0°. Due to its instability at ordinary room temperatures and the consequent evolution of hydrogen chloride, the material had to be handled in this way. This instability also prevented further purification of the material by any of the usual methods.

Table I shows the comparative results based on the averages of all of the complete analyses of the various reaction products of selenium oxychloride with the natural rubbers and the synthetic isoprene rubber

Table I

Average Analyses[9] of the Products of the Reaction between Rubber and Selenium Oxychloride

$SeOCl_2$ reaction products with	C %	H %	Se %	Cl %	(Diff.) %	Ratio C:H
"Isoprene Rubber"	23.72	4.67	22.57	23.79	25.25	10:23.3
Pale Crepe	23.75	4.37	22.81	24.23	24.84	10:22.3
Smoked Sheet	21.60	4.66	27.04	24.69	22.01	10:26.0
Para	23.85	4.42	26.74	26.03	18.96	10:22.1
Caucho Ball	24.49	4.37	26.09	25.35	19.70	10:21.1

Discussion

Attention is called to several points brought out in this table. (1) It will be noted that the average content of carbon in the various reaction products of either synthetic rubber from isoprene, or the natural rubbers, varies less than 1%, except in the case of the product from Smoked Sheet, which is about 2% lower. (2) The average contents of hydrogen in the various reaction products vary less than 0.4 of 1%. (3) The average content of selenium in the synthetic isoprene-rubber product is practically the same as in the plantation Pale Crepe product. The amount of selenium in reaction products of the other 3 natural rubbers, varies only within 1%, but all are 4 to 5% higher than in the case of the Pale Crepe or the synthetic isoprene rubber. It will be noted, however, that the products from all 3 of the natural rubbers in which the latex was coagulated by smoke have a selenium content of 26 to 27%. The Smoked Sheet comes from

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[9] The "average analyses" are the means of the results of 10 to 12 determinations on different samples of the same material handled under as nearly the same conditions as possible. The average analysis for each constituent is accurate to at least 1%.

exactly the same source as the Pale Crepe (cultivated *Hevea brasiliensis*), but the latex of Pale Crepe is coagulated by acetic acid, while the latex of Smoked Sheet is only partially coagulated by acetic acid and is then smoked to complete the process. Possibly this difference in the selenium content of the 2 reaction products can be attributed to the method of coagulation. (4) The average content of chlorine in the various reaction products from either the synthetic or the natural rubber varies about 2.2%. (5) The ratio of carbon to hydrogen has changed from $C_{10}H_{16}$ in the pure rubber, up to $C_{10}H_{26}$ in the reaction products. (6) Parallel with the chemical changes in the various kinds of rubber upon treatment with selenium oxychloride, there is a great change in their physical properties. The products are all amorphous powders, having lost their elasticity and swelling power, and are insoluble in the ordinary rubber solvents, such as benzene, carbon tetrachloride, chloroform and ether. (7) The two most important conclusions that can be drawn from the comparative data on these reaction products are: (a) the pure rubber hydrocarbon from natural, *Hevea* rubbers, shows a slightly different behavior in its reaction with selenium oxychloride, depending upon the source of the rubber and its method of coagulation; (b) judging by the behavior towards selenium oxychloride, there is no difference in empirical composition between the pure rubber from a typical natural rubber, such as Pale Crepe, and a synthetic rubber, made by the polymerization of isoprene by metallic sodium. This statement is in contradiction to the recent article of Kirchof.[10] Kirchof has compared the ultimate analyses that have been made on the rubber hydrocarbon from different sources and also the analyses of the various derivatives that have been reported. He concluded that synthetic rubber is a true polymer of the corresponding hydrocarbon, C_5H_8, but that the hydrocarbon of Para rubber has the empirical composition $C_{10}H_{17}$ and cannot be formed from the hydrocarbon C_5H_8 through polymerization, as Harries supposed. According to Kirchof, neither the empirical composition nor the structure of synthetic rubber is identical with that of Para rubber.

The present work tends to support the conclusion that Harries reached after a study of the hydrolysis products of the ozonides of various kinds of natural and synthetic rubbers, namely, that there is no essential difference in constitution between natural rubber and the polymerized isoprene.

The author wishes to express his appreciation to Professor Victor Lenher, at whose suggestion and under whose direction this work was carried out; also to Professor Homer Adkins for helpful suggestions.

Summary

1. The reactions between selenium oxychloride and the natural, *Hevea* rubbers, Pale Crepe, Smoked Sheet, Para and Caucho Ball, have been studied.

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[10] Kirchof, *Kolloidchem. Beihefte*, **16**, 47 (1922).

2. The reaction between selenium oxychloride and a synthetic rubber made by polymerizing isoprene has been studied.

3. It has been found that when the various rubbers are treated with selenium oxychloride their physical properties are changed. The products are all amorphous powders, having lost their elasticity and swelling power, and are insoluble in the ordinary solvents for rubber.

4. It has been shown that the pure rubber hydrocarbon from natural, *Hevea* rubbers, shows a slightly different behavior in its reaction with selenium oxychloride, depending upon the source of the rubber and its method of coagulation.

5. It has been shown definitely that, judging by their respective behaviors towards selenium oxychloride, there is no difference in empirical composition between the pure rubber hydrocarbon from the *Hevea* tree and the synthetic rubber made by polymerizing isoprene with metallic sodium.

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[CONTRIBUTION FROM THE LABORATORY OF THE J. B. WILLIAMS COMPANY]

DIPROPARGYL METHYLENE ETHER

BY HERBERT H. GUEST

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The statement has been made by Delange[1] that "as a rule, acetylenic linkages produce unpleasant odors.* * * *An exception is methylheptine carboxylate."[2] Apparently, the acetylenic linkage adjacent to an alcoholic group forms another exception of Delange's generalization. For example,[3] octin-2-ol-1 has a much pleasanter and more intense odor than octanol. Also,[4] 2-methylhexin-3-ol-2 has a very pleasant, flower-like odor. Finally, it is well known that propargyl alcohol itself possesses a pleasant odor.

It seemed of interest, therefore, to prepare a number of alcohols having the triple bond in the α position to the hydroxyl group and compare their odors with those of the corresponding saturated alcohols.

The only method so far available for the preparation of these alcohols is that of Moureu and Desmots[3] which depends upon the action of trioxymethylene on the sodium derivative of acetylene hydrocarbons. Unfortunately, the latter are not easily obtainable and, moreover, the yield of alcohol is very poor.

This paper describes the attempt to prepare these alcohols by the alkylation of the metallic derivatives of the methylal of propargyl alcohol.

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[1] Delange, *Perfumery Essent. Oil Record,* **13,** 352 (1922).

[2] Moureu and Delange, *Bull. soc. chim.,* [3] **29,** 648 (1903).

[3] Moureu and Desmots, *ibid.,* [3] **27,** 361 (1901).

[4] Dupont, *Compt. rend.,* **148,** 1524 (1909).