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

Received April 21, 1923

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).

This acetal was readily obtained by a method that parallels that of Claisen[5] for the preparation of propargyl-aldehyde acetals, such as $CH\colon C.CH(OCH_3)_2$. The starting point is β-dibromohydrin[6] which was readily converted into the corresponding acetal. The latter loses 2 moleculcs of hydrobromic acid on treatment with alcoholic potash to form the acetal of propargyl alcohol: $CH_2Br.CHBr.CH_2OH \longrightarrow (CH_2Br.CHBr.CH_2O)_2CH_2 \longrightarrow (CH\colon C.CH_2O)_2CH_2$.

It was hoped that the magnesium-bromide compound, $(MgBrC\colon C CH_2O)_2CH_2$, would react with alkyl bromides in a manner analogous to that observed by Grignard[7] in the preparation of phenylethyl alcohol from phenylmagnesium bromide and glycol chlorohydrin. The action of ethylmagnesium bromide on the acetylenic acetal proceeded normally with a steady evolution of ethane. After some hours or when the ethereal solution was warmed to complete the reaction, a product was formed which was insoluble in ether or benzene. This resinous material has not been identified and is probably the inter-reaction product of 2 or more molecules, in the manner observed by Tschitschibabin and Jelgasin[8] who found that acetals are acted upon by Grignard reagents to form ethers. When the reaction was stopped before this insoluble substance was produced and alkyl bromide added to the cold mixture, alkylation did not take place.

The silver compound $(AgC\colon C.CH_2O)_2CH_2$ was readily obtained but proved to be exceedingly inert. For example, prolonged boiling with excess of butyl bromide failed to give the desired butyl acetal. This result is in harmony with the observation of Reitzenstein[9] as to the inertness of the silver derivative of the acetal of propargyl aldehyde, $AgC\colon C.CH(OCH_3)_2$.

Metallic sodium did not react readily with the acetal of propargyl alcohol and when it was heated for a long time with sodium in toluene suspension a yellow solid was obtained which was not the normal reaction product of acetylenes and sodium.

Experimental Part

Bis(2,3-dibromopropyl)methylene Ether, $(CH_2Br.CHBr.CH_2O)_2.CH_2$.—Into 342 g. of dibromohydrin dry hydrogen chloride[10] was led until the weight of the mixture had increased 3.5 g.; 135 g. of paraformaldehyde was added and the mixture was allowed to stand at room temperature for 6 days. Ether was added and the excess of paraformaldehyde removed by filtration. The ethereal solution was dried over sodium carbonate. On distillation at 10 mm. pressure, a fraction boiling at 118° to 170° was collected, weighing 76 g., which consisted mostly of unaltered dibromohydrin, and a second fraction boiling at 170–235° which on redistillation gave 195 g. boiling at 220° under 7 mm. pressure. This yield of acetal corresponds to 55%.

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[5] Claisen, *Ber.*, **31**, 1022 (1896).

[6] Kohler, *Am. Chem. J.*, **42**, 381 (1909).

[7] Grignard, *Compt. rend.*, 141, 44 (1905).

[8] Tschitschibabin and Jelgasin, *Ber.*, **47**, 48 (1914).

[9] Reitzenstein, *J. prakt. Chem.*, [2] **86**, 73 (1912).

[10] Fischer and Giebe, *Ber.*, **30**, 3053 (1897).

Analysis. Subs., 0.3715: AgBr, 0.6218. Calc. for $C_7H_{12}O_2Br_4$: Br, 71.43. Found: 71.23.

This acetal was also prepared by the catalytic action of ferric chloride,[11] as follows: 75 g. of dibromohydrin, 25 g. of trioxymethylene and 3.5 g. of sublimed ferric chloride were mixed and heated at 125–150° for 2 hours. When the product was treated as in the previous case, 18 g. of unaltered dibromohydrin and 42 g. of acetal were obtained, duplicating the percentage yield. Finally, the same results were obtained by the use of dry calcium chloride[12] as catalyst to the extent of 20% of the weight of dibromohydrin taken.

This acetal is a viscous oil, insoluble in alcohol but soluble in ether or benzene.

Bis(α-bromo-allyl)methylene Ether, $(CH_2:CBrCH_2O)_2CH_2$.—This compound was obtained from the dibrompropyl acetal by the action of a slight excess of finely powdered potassium hydroxide in ether suspension, at a temperature below 25°. The reaction product was treated with water, the oil in ethereal solution dried over calcium chloride and distilled at 10 mm. pressure. On repeated redistillation an oil was obtained, b. p., 135–140° at 10 mm. pressure, which was soluble in organic solvents.

Analysis. Subs., 0.2773: AgBr, 0.3680. Calc. for $C_7H_{10}O_2Br_2$: Br, 55.9. Found: 56.48.

Dipropargyl Methylene Ether, $(CH \vdots C.CH_2O)_2CH_2$.—To 4 molecular proportions of potassium hydroxide dissolved in 4 times the weight of 95% alcohol and cooled to 25–30°, one molecular equivalent of the dibromopropyl acetal was gradually added and the mixture kept cold. After 1/2 hour at room temperature, this was heated under a reflux condenser on the steam-bath for 2 to 3 hours. The salt was separated on a filter by suction, the alcoholic filtrate made neutral with acetic acid and then the alcohol removed by distillation under diminished pressure at a low temperature. The residue was poured into water and the oil (400 g.) dissolved in ether, dried over sodium carbonate and distilled at 10 mm. pressure. Fraction 1, b. p. 70–100°, amounted to 98 g.; Fraction 2, b. p. 100–140°, weighed 57 g. and the residue weighed 5 g.

Fraction 1 was redistilled at 10 mm. pressure and the high-boiling portion added to Fraction 2. The united high-boiling fractions were then treated with alcoholic potassium hydroxide as before. On final distillation 56 g. of an oil was obtained which boiled at 75–80° under 10 mm. pressure and at 162° under 760 mm. pressure; yield, 50%. This oil was free from halogen.

Analyses. Subs., 0.2325: H_2O, 0.1340; CO_2, 0.5730. Calc. for $C_7H_8O_2$: C, 67.74; H, 6.45. Found: C, 67.22; H, 6.45.

SILVER SALT $(AgC \vdots C.CH_2O)_2CH_2$.—To a solution of 2 molecular proportions of silver nitrate in a small amount of water and much alcohol, ammonium hydroxide was added by drops until the precipitate that first formed redissolved. One molecular equivalent of acetal dissolved in alcohol was then added, and a white granular precipitate formed at once. This was separated by filtration with suction and washed with alcohol and ether. When dried at 60°, it turned brown; it exploded at 110°. It is insoluble in ammonium hydroxide, alcohol, ether or water.

Analysis. Subs., 0.1825: AgCl, 0.1545. Calc. for $C_7H_6O_2Ag_2$: Ag, 63.9. Found: 63.71.

This silver salt, while still moist, was added to an ethereal solution of a large excess of butyl bromide. The mixture was heated for 5 to 6 hours under a reflux condenser. As the appearance of the insoluble material did not change, the ether was removed, more butyl bromide added and the whole heated for 5 hours longer. The insoluble material

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[11] Trillat and Cambier, *Bull. soc. chim.*, [3] 11, 757 (1894).

[12] Compare Adkins and Nissen, THIS JOURNAL, **44**, 2749 (1922).

was removed by filtration and the filtrate distilled. The latter proved to be unaltered butyl bromide.

Action of Grignard Reagent on Acetal.—To a Grignard solution made from 50 g. of ethyl bromide was added gradually at 5–10° an ethereal solution of dipropargyl methylene ether. Ethane was evolved steadily and was collected and tested. After 24 hours outdoors, two layers formed in the liquid. To this mixture was then added 50 g. of butyl bromide, and the whole heated for 3 hours under a reflux condenser; dry toluene was then added and the ether removed. The heating was continued for 1 hour longer. No magnesium bromide separated. The reaction mixture was then treated with dil. sulfuric acid, and the upper layer dried and distilled. After removal of the solvent, no oil was obtained. The residue, which was insoluble in solvents, could not be resolved into any individual product.

This experiment was repeated several times under various conditions, but so far unsuccessfully.

Summary

1. Dipropargyl methylene ether was prepared from the acetal of β-dibromohydrin.
2. It was found that the silver derivative of dipropargyl methylene ether did not react with alkyl halides under the conditions indicated.
3. Dipropargyl methylene ether reacts with ethylmagnesium bromide but the resulting reaction product did not aid in the synthesis of the higher homologs of propargyl alcohol.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, HARVARD MEDICAL SCHOOL]

OBSERVATIONS ON THE PROPERTIES OF ARSPHENAMINE[1]

BY WALTER G. CHRISTIANSEN

Received April 26, 1923

The Relation of Arsphenamine to Some Methyl Ketones

In connection with an investigation of the ease of solution of arsphenamine in water, samples were precipitated from methyl alcohol solution by acetone instead of ether. Analytical data on material precipitated in this way confirm the conclusion of Fargher and Pyman[2] that the product contains 1 molecule of acetone in addition to the usual 2 molecules of water.

Calc. for $C_{12}H_{14}O_2N_2Cl_2As_2.2H_2O.(CH_3)_2CO$: As, 28.2; Cl, 13.3. Found: As, 28.1; Cl, 13.1.

Prolonged drying in a vacuum removes the 2 molecules of water but the acetone remains unchanged;[2] when the material is dried to constant

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[1] This is the twelfth of a series of studies on the properties contributing to the toxicity of arsphenamine being made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School; the work is under the general direction of Dr. Reid Hunt.

[2] Fargher and Pyman, *J. Chem. Soc.*, 117, 372 (1920).