Anal. Calcd. for $C_{10}H_9O_2Br_3$: Br, 59.81. Found: Br, 59.75.

The melting point of the propionate is 70.5°.

Anal. Calcd. for $C_{11}H_{11}O_2Br_3$: Br, 57.79. Found: Br, 57.85.

In the case of the butyrate the use of the anhydride did not give as satisfactory results as butyryl chloride, with which the carbinol was heated at 60–90° for three hours. Even after careful purification and distillation this ester does not solidify on standing for several weeks at room temperature. It is a thick viscous liquid of b. p. 205–207° at 220 mm., d_{20}^{20} 1.779.

Anal. Calcd. for $C_{12}H_{13}O_2Br_3$: Br, 55.90. Found: Br, 55.85.

The benzoate was prepared by treatment with benzoyl chloride according to the usual procedure of the Schotten–Baumann reaction. On recrystallization from 95% alcohol clusters of needles are obtained. It melts at 146°.

Anal. Calcd. for $C_{15}H_{11}O_2Br_3$: Br, 51.81. Found: Br, 51.76.

The average yield of all of these esters was 85%.

All of the esters are insoluble in water and with the exception of the benzoate readily soluble in carbon disulfide, ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform and carbon tetrachloride, the benzoate being much less readily soluble in ethyl and methyl alcohols than the others.

Summary

Tribromomethylphenylcarbinol and its acetic, propionic, butyric and benzoic esters have been prepared and studied.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND THE UNIVERSITY OF TARTU (DORPAT), ESTONIA]

SYNTHESIS OF 1,4-PENTADIENE

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Among various series of unsaturated hydrocarbons the least explored field is that of the 1,4-dienes. According to Beilstein's "Handbook" only a few open-chain 1,4-dienes are known, *i. e.*, hexadiene-1,4, and 4-propylheptadiene-1,4. The first member of the series of diolefins with isolated double bonds has attracted the attention of many chemists. Several investigators have tried to prepare 1,4-pentadiene. Demjanov[2] and Demjanov and Dojarenko[3] on heating pentamethylenediamine nitrate or treating 1,5-di-iodopentane with alcoholic potash obtained among other products a small amount of a substance which on bromination yielded the tetrabromide of 1,4-pentadiene. Thiele[4] and others tried to prepare the hydrocarbon by exhaustive methylation of piperidine but

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[1] Beilstein, "Handbuch org. Chem.," **1918**, Bd. I, p. 253.

[2] Demjanov, *J. Russ. Phys.-Chem. Soc.*, **26**, 665 (1894).

[3] Demjanov and Dojarenko, *Ber.*, **40**, 2589 1908).

[4] Thiele, *Ann.*, **319**, 228 (1901).

obtained its isomer, 1,3-pentadiene. Recently Dojarenko[5] found that on catalytic dehydration of cyclopentanol a small amount of 1,4-pentadiene is formed. All these investigators failed to obtain the pure hydrocarbon. The final stage of the above-mentioned reactions favors molecular rearrangements. It seemed to the author most natural to avoid high temperatures and strong reagents, and in a manner analogous to the preparation of diallyl from allyl bromide[6] to bind vinyl and allyl radicals, using their bromides and magnesium

$$CH_2{=}CHCH_2Br + CH_2{=}CHBr \xrightarrow{Mg} CH_2{=}CHCH_2CH{=}CH_2 + MgBr_2$$

Starting from this point of view the author treated a mixture of vinyl bromide and allyl bromide with magnesium in anhydrous ether; the experiment was successful but the yield of the hydrocarbon was rather low. To increase the yield various modifications of the method were studied. First of all it was attempted to prepare vinylmagnesium bromide, and treat this Grignard compound with allyl bromide. Contrary to expectation, which was based on the researches of Austerweil[7] and Krestinsky,[8] vinyl bromide did not react with magnesium in dry ether under ordinary conditions. Then it was tried *vice versa* to treat ally magnesium bromide with vinyl bromide, using an excess of the latter. The method of Gilman and McGlumphy[9] was used for preparation of allylmagnesium bromide. The Grignard compound was heated in a pressure bottle with three times the theoretical amount of vinyl bromide: the result was negative. One is inclined to assume that allylmagnesium bromide *in statu nascendi* is more active or "activates" vinyl bromide, thus favoring the formation of vinylmagnesium bromide.

Further it was found that the size of the magnesium turnings or particles has some effect on the yield of the hydrocarbon. The best results were obtained with magnesium-copper-alloy,[10] finely ground. Increase in the rate of the reaction also increases the yield of the diolefin. The 1,4-pentadiene obtained by this anomalous Grignard reaction is not pure; after removal of ether with strong hydrochloric acid,[11] the liquid contains a fair amount of vinyl bromide, 1,4-pentadiene and 1,5-hexadiene.

The only way to recover the pure 1,4-pentadiene is via its tetrabromide. The researches of Tissier and Grignard,[12] v. Braun and Sobecki,[13] and

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[5] Dojarenko, *J. Russ. Phys.-Chem. Soc.*, **58**, 29 (1926).

[6] Meisenheimer and Casper, *Ber.*, **54**, 1655 (1921).

[7] Austerweil, German Patent 245,180; *Chem. Centr.*, I, 1267 (1912).

[8] Krestinsky, *Ber.*, **55**, 2770 (1922).

[9] Gilman and McGlumphy, *Bull. soc. chim.*, [4] **43**, 1322 (1928).

[10] Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1928).

[11] Compare Cortese, THIS JOURNAL, 51, 2267 (1929).

[12] Tissier and Grignard, *Compt. rend.*, **132**, 835 (1901).

[13] V. Braun and Sobecki, *Ber.*, **44**, 1918 (1914).

others show that 1,2-dibromides react with magnesium, forming unsaturated hydrocarbons, *i. e.*, regenerating the double bond. The same method was used for regenerating 1,4-pentadiene from its tetrabromide, about 85% of the original hydrocarbon being recovered. The pure 1,4-pentadiene boils at 25.8–26.2°. The yield of the hydrocarbon is about 15% of the theoretical, based on vinyl bromide.

Experimental

Preparation of Vinyl Bromide.—The Swarts[14] method for preparation of vinyl bromide from ethylene bromide and alcoholic potash is not quite satisfactory for preparing larger quantities of vinyl bromide. Therefore the method was improved by introducing the following modifications.

A 1.5-l. flask with three necks is provided with a stirrer (through central neck), with a dropping funnel, and a dephlegmator or Vigreux column, surrounded by a jacket through which water at 17° is circulated (see Fig. 1). The column is connected (in succession) with a wash-bottle, calcium chloride tube and a Staedeler condenser (cooled by means of a freezing mixture). The receiver is also surrounded with freezing mixture. Into the flask is put an alcoholic solution of potassium hydroxide, made from 175 g. of potassium hydroxide, 350 cc. of water and 650 cc. of 96% ethyl alcohol. The solution is stirred and heated on a water-bath up to about 60°. Then 195 g. of ethylene bromide is dropped slowly into the flask. In a few minutes evolution of vinyl bromide begins. By circulating water in the jacket the speed of distillation is regulated so that the temperature of the vapor leaving the column is about 18°. The operation takes about an hour and a half. Then the solution of potassium hydroxide can be removed from the flask by a siphon, the dropping funnel charged with a fresh portion of ethylene bromide and the operation started again. The yield of vinyl bromide from 195 g. of ethylene bromide is 90–100 g. or about 85%. Vinyl bromide obtained by this method is dry and pure; b. p. 16–17°.

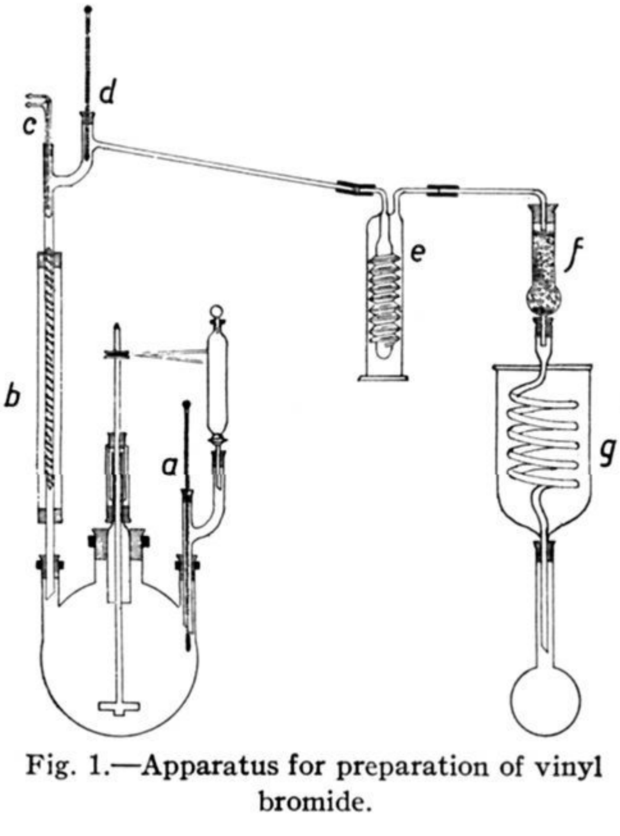

Fig. 1.—Apparatus for preparation of vinyl bromide.

Allyl bromide was prepared by the method of Adams;[15] the fraction of b. p. 70–71° was used.

Preparation of 1,4-Pentadiene. (1) Under Atmospheric Pressure.—A 100-cc. round-bottomed pyrex flask is provided with a mercury-sealed stirrer, dropping funnel and Staedeler condenser, surrounded with freezing mixture; 2.65 g. of magnesium, 0.5 g. of iodine and 0.1 mole of ethylene bromide dissolved in about 40 cc. of dry ether is intro-

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[14] Swarts, *Chem. Centr.*, II, 804 (1901); *Bull. acad. Roy. Belgique*, 383 (1901).

[15] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1921,** Vol. **I,** p. 3.

duced into the flask; 16–17 g. of allyl bromide in about 15 cc. of ether is then slowly dropped into the flask, with stirring of the mixture. In a few minutes the reaction starts. After the reaction ceases the flask is heated for about one hour and cooled. The reaction products are then distilled, using a Widmer column, and two fractions collected: one (i) taken up to the initial decomposition point of the etherates, and (ii) up to 36°. Both fractions are cooled in a freezing mixture, then bromine is slowly added (shaking the flasks) until the color of bromine remains. After bromination the flasks are allowed to stand in a freezing mixture for about two hours. Then the ether is evaporated under reduced pressure, and the contents of the flasks dissolved in hot alcohol. On cooling, crystals (colorless leaflets) of 1,4-pentadiene tetrabromide appear. The ii fraction always contains a certain amount of the tetrabromide of 1,5-hexadiene. The crystals are filtered, dried and weighed. After recrystallization from hot ethyl alcohol, the crystals of 1,4-pentadiene tetrabromide melt at 85.8–86°.

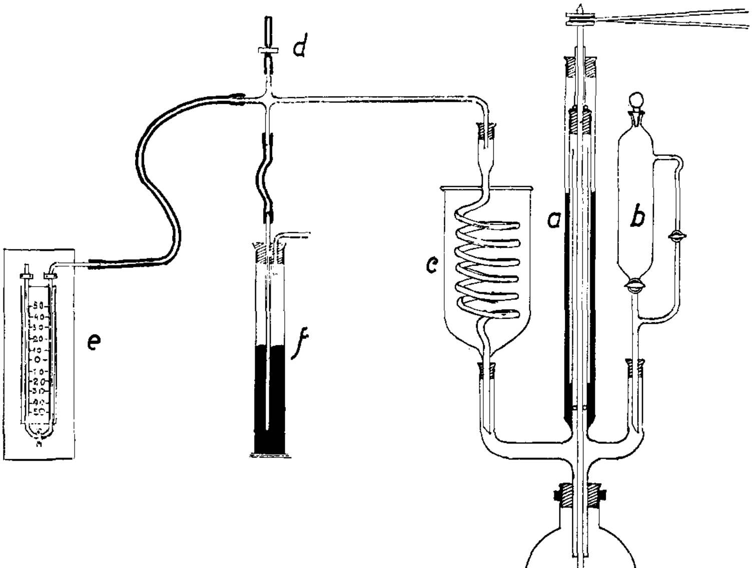

Fig. 2.—Apparatus for preparation of 1,4-pentadiene under pressure.

(2) **Under Pressure.**—When the reaction proceeds violently some vinyl bromide is carried through the condenser uncondensed. To avoid losses the reaction can be carried out in a closed system, under a pressure of 260–270 mm. For this purpose a 100-cc. round-bottomed flask is provided with a rubber stopper through which passes a tube with two side tubes; through the central tube is a mercury-sealed stirrer; the height of the mercury column is about 320 mm. (see Fig. 2a), one side tube is fitted with a dropping funnel, b, the other with Staedeler condenser, c. The body of the funnel is connected with its outlet tube below the stopcock by means of a narrow glass tube. The spiral condenser is connected with a manometer, e, and a mercury seal, f. The height of the mercury column in f is regulated so that the pressure in the apparatus does not exceed 280–290 mm.

For the production of larger quantities of the compound, a 750-cc. round-bottomed flask was used. and the dimensions of other parts of the apparatus were correspondingly larger.

Thirteen and two-tenth grams of magnesium and 0.5 g. of iodine were placed in the flask; from the dropping funnel about 100 cc. of anhydrous ether containing 1 g. of allyl bromide was added. In few minutes the reaction begins. The pinchcock clamp, d, is opened, and air is driven out by the ether vapor. Next 56 g. of vinyl bromide in 100 cc. of anhydrous ether is introduced into the flask, and then 75 g. of allyl bromide in 70 cc. of ether is slowly added in the course of about eighty to ninety minutes. During the reaction the manometer shows about 240–260 mm. pressure; when the pressure rises above that indicated, the flask must be cooled. After the whole portion of allyl bromide has been added the reaction mixture is heated on a water-bath until the pressure begins to fall. The reaction products are distilled, and the distillate is brominated. The yield of crude tetrabromide is about 45 g. or 22% of the theoretical from the vinyl bromide. After recrystallization from hot alcohol, about 25–28 g. of tetrabromide, m. p. 85–86°, is obtained.

Anal. Calcd. for $C_5H_8Br_4$: C, 15.47; H, 2.08; Br, 82.47; mol. wt., 387. Found: C, 15.53; H, 1.99; Br, 82.52; mol. wt., 376.

The yield of crystals under various conditions of the experiment is given in Table I.

TABLE I

Expt.	Mg, g.	CH_2=CHBr, g.	CH_2=CH—CH_2Br, g.	CH_2=CHCH_2Br, time of addition, min.	Bromine, cc.	Tetrabromide (crude), g.	Crystals, m. p. 85–86° g.	Remarks
1	2.65	10.8	16.2	18	0.8	1.9	1.2	Mg Schering Kahlbaum
2	2.65	12.7	18.3	110	.9	..	1.75	Mg Schering Kahlbaum
3	2.65	10.8	16.0	16	1.7	..	3.8	Ground Mg
4	2.65	12.7	17.4	120	2.2	6.7	4.0	Ground Mg
5	2.65	10.6	15.3	30	3.3	10.2	6.6	Finely ground Mg under pressure
6	2.65	10.8	15.9	75	2.4	7.1	4.5	Finely ground Mg under pressure
7	2.65	10.55	12.3	30	21	5.9	3.8	Finely ground Mg under pressure

Tetrabromides of 1,4-Pentadiene.—When the mother liquor from recrystallization of the solid tetrabromide is diluted with water, an oily liquid is precipitated. As theoretically two isomeric tetrabromides are possible, an attempt was made to isolate the other isomer. About 160 g. of washed and dried heavy liquid was distilled under reduced pressure using a Widmer column as still-head. From the distillate, on cooling, about 60 g. of crystalline pentadiene tetrabromide (m. p. 85–86°) and about 55 g. of diallyl tetrabromide were obtained; about 45 g. of the distillate remained liquid. After repeated fractionation crystals again separated from the distillates. Finally, about 10 g. of oily bromide, boiling from 115–123° (1–2 mm.) remained. The figures obtained on the analysis of the liquid did not closely correspond to the composition of pentadiene tetrabromide but were close to the diallyl tetrabromide. Anyhow, the supposed liquid tetrabromide is formed in comparatively small quantities or it might isomerize on distillation.

Regeneration of 1,4-Pentadiene from its Tetrabromide.—Regeneration of the diene was carried out in a flask provided with a stirrer, a dropping funnel and a Staedeler condenser. The condenser jacket was filled with freezing mixture. Between the flask and condenser is placed a T-piece for pushing in the dry tetrabromide (see Fig. 3).

The tetrabromide is put into the side tube, provided with a glass rod. By pushing forward the glass rod the solid tetrabromide is introduced into the condenser tube, wherefrom the ether vapor sweeps it down. This device allows the use of smaller quantities of ether because the solubility of the tetrabromide in ether is rather low, *i. e.*, about 13 g. in 100 cc. In the flask are placed 12.5 g. of magnesium, 0.5 g. of iodine and 3 g. of tetrabromide; then 35 cc. of dry ether is added. The reaction begins immediately and 33 g. of tetrabromide in 250 cc. of dry ether is then slowly added. After the dissolved tetrabromide has been added, 31 g. of tetrabromide is gradually pushed in through the T-piece. The reaction takes about two hours, after which the flask is warmed on a water-bath for about thirty minutes. From the reaction mixture the pentadiene and ether are distilled off. The distillate is placed in a separatory funnel, an equal amount of cooled concd. hydrochloric acid is added, and the contents of the funnel are shaken while cooling under the tap. The mixture is allowed to settle, the acid layer is drawn off and the operation is repeated. The ether-free pentadiene is successively washed with water, sodium bicarbonate solution, and again with water, then the liquid diene is dried over calcium chloride. The yield of the products from 145 g. of tetrabromide is 18.5 g. of 1,4-pentadiene, or about 73% of the theoretical.

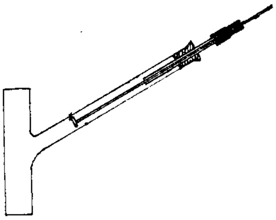
Fig. 3.—T-piece for pushing in solid pentadienetetrabromide.

The total amount of 1,4-pentadiene recovered, as determined by bromination of the distillate is about 85%.

The hydrocarbon was fractionated using a Widmer column as stillhead. A few drops of liquid passed over below 25° and about 70% of the liquid at 25.8–26.2°. The whole boiled below 26.6°. The liquid has a weak characteristic odor.

Properties of 1,4-Pentadiene.—B. p. 25.8–26.2° at 756 mm.; d_4^{20} 0.6594; n_D^{20} 1.3883; mol. refraction: calcd., 24.26; found, 24.26; mol. wt. (Victor Meyer method): calcd. 68.08· found, 68.66.

In conclusion, the author desires to record his thanks to Professor E. P. Kohler for his interest in the work, and to Mr. H. Raudsepp for checking the experiments.

Summary

1. An improved method for preparation of vinyl bromide has been worked out.

2. Two modifications of a new method for the synthesis of 1,4-pentadiene are described.

3. For the first time 1,4-pentadiene has been prepared in pure condition and its properties determined.

4. The bromination products of 1,4-pentadiene were investigated

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