dried as above; 95% yields were obtained in the regenerations.

The dibromobutane samples were then distilled at 50 mm. pressure through the column described by Lucas, Dillon and Young.[16] The first part of the distillation was conducted slowly to strip out the last possible residual traces of low-boiling impurities, the first distillate being collected in several small fractions, of which the first one or two were discarded. Refractive indices of the fractions indicated that the impurities when present were removed in the first part of the distillate. That no change in composition is wrought by the purification procedure used already has been definitely shown.[17]

The boiling ranges of the dibromobutane mixtures through the apparatus used were all approximately 76.2–79.4°. Carius analyses were in the range 73.80–74.18% Br, theoretical 74.03.

Analysis of the Dibromobutane Mixtures.—The reaction rate determinations necessary for the analysis of the dibromobutanes were carried out exactly as described by Dillon, Young and Lucas.[4] The methyl alcohol preparations in this work were those used by Young and Winstein.[17] Duplicate rate runs were always made. Eight tubes, titrated successively at two to two and one-half hour intervals after a lapse of sixteen to twenty hours, constituted a run. The results of duplicate runs never differed by more than 0.0003.

The average corrected pseudo-specific reaction rate constants, the densities corrected to vacuum and the compositions of the mixtures appear in the table of results. As a further check on the analyses a comparison of the calculated and observed refractive indices is also included.

The authors are indebted to Dr. G. Ross Robertson for his helpful suggestions.

Summary

An allylic rearrangement to an equilibrium has been shown to occur when different mixtures of crotyl and methylvinylcarbinyl bromides are converted into Grignard reagents and then decomposed to form butenes. The rearrangement apparently occurs only during the formation of the Grignard reagent.

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[16] Lucas, Dillon and Young, THIS JOURNAL, **52**, 1949 (1930).

[17] Young and Winstein, *ibid.*, **58**, 102 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

The Grignard Reaction on Alpha-Pinene Oxide

BY JOHN J. RITTER AND KENNETH L. RUSSELL[1]

The action of Grignard reagents upon alpha-pinene oxide (I) has been investigated recently by Prileshaev and Vershuk.[2] These authors stated that the reaction proceeds in a complicated manner with methyl, ethyl and isopropylmagnesium halides with the formation in each case of gaseous products and an alcohol (IV). Isobutyl and phenylmagnesium halides, however, appeared to act normally to form saturated alcohols (V).

We have repeated and extended this work, and have now secured evidence which indicates that the alcohol formed from alpha-pinene oxide and methylmagnesium iodide is methylcampholenol (III). The newly assigned structure is based upon the fact that campholenic aldehyde (II), prepared by isomerization of alpha-pinene oxide with anhydrous zinc bromide according to the method of A. Arbuzov[3] reacts with methylmagnesium iodide to yield methylcampholenol (III) identical with that obtainable directly from alpha-pinene oxide by the action of the same reagent. The products of the action of a series of Grignard reagents upon alpha-pinene oxide seem to be analogous to methylcampholenol, and probably possess the same type of structure.

It has been found recently by Arbuzov[3] that the Reformatzky reaction upon alpha-pinene oxide likewise involves a simultaneous isomerization to campholenic aldehyde (II). It may be noted also that products of ring isomerization in Grignard reactions with other cyclic olefin oxides have been observed occasionally.[4]

The volumes of gases evolved in these reactions were found to diminish greatly, and the yield of alcohol to increase correspondingly, when the reaction is allowed to take place for a longer period and at an elevated temperature. Even so, not inconsiderable amounts of gas are obtained, although the quantity is small in comparison with the yield of alcohol. The gases apparently arise

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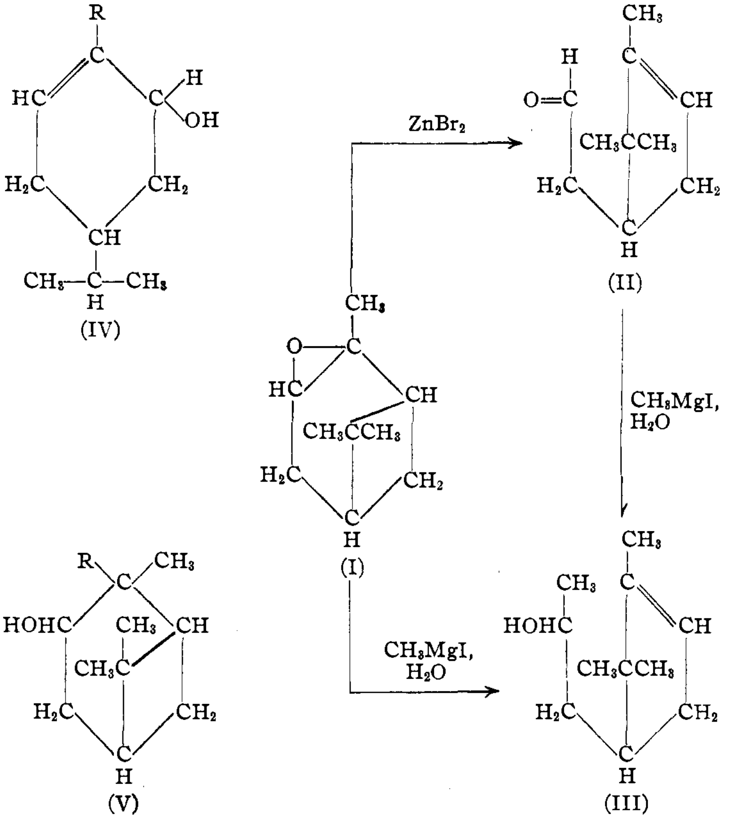
[1] This paper is based upon a portion of the Dissertation submitted by Mr. Russell to the Graduate School of New York University in December, 1935, in partial fulfilment of the requirements for the Ph.D. degree.

[2] Prileshaev and Vershuk, *J. Russ. Phys.-Chem. Soc.*, **61**, 473 (1929).

[3] A. Arbuzov, *Ber.*, **68**, 1430–1435 (1935).

[4] Bedos, *Compt. rend.*, **189**, 255 (1929); Godchot and Conquil, *ibid.*, **186**, 375, 954 (1928); Godchot, Conquil and Bedos, *Bull. soc. chim.*, **43**, 521 (1928); Vavon and Metchavetch, *Compt. rend.*, **186**, 702 (1928).

partly from the decomposition of unreacted alkylmagnesium halide and partly from side reactions which have been commonly observed hitherto in Grignard reactions.



Experimental

Perbenzoic Acid.—This was prepared by the method of B. T. Brooks.[5] The yield obtained (91%) equaled that reported by Brooks when the alternative procedure described in that publication was followed.

Pinene.—α-Pinene (Hercules Powder Company) was refluxed over sodium for one hour and then distilled, the fraction boiling at 155–156° (corr.) being collected separately and used for the following experiments. $[\alpha]^{22}_D$ varied between +24 and +26° for a number of preparations.

Alpha-Pinene Oxide.—α-Pinene ($[\alpha]^{22}_D$ 25.2°) is added to a 10% excess over one mole of perbenzoic acid dissolved in chloroform (15 g., 100 cc.). The addition is carried out very slowly (one hour) at 0° with constant mechanical stirring, care being taken to avoid a rise in temperature of more than five degrees. The reaction mixture is kept at 0–5° for three days, when the amount of unreacted perbenzoic acid (determined iodimetrically) corresponds closely to the 10% excess added initially.

The reaction mixture is then extracted with 10% sodium hydroxide solution to free it of benzoic acid, washed, dried over anhydrous sodium sulfate, and distilled under reduced pressure after removal of the chloroform on the water-bath: yield 70–75%; b. p. (12 mm.) 70–71°; d^{20}_4 0.9627; n^{16}_D 1.4709; $[\alpha]^{25}_D$ +65.3. This procedure is substantially the same as that of Prilezhaev.[6]

Methylcampholenol.—To magnesium (6.5 g., 0.27 mole) and ether (30 cc.), a solution of 38 g. (0.27 mole) of methyl iodide in 30 cc. of ether is added, following the usual technique of Grignard reagent preparations. An additional 60 cc. of ether is added shortly after the reaction has started. α-Pinene oxide (35 g., 0.23 mole) dissolved in 35 cc. of ether is then added during one and one-half hours. About 1200 cc. of methane is evolved during this operation. The reaction mixture is then refluxed for one hour, after which 125 cc. of benzene is added, and the ether distilled off (until the vapor temperature reaches 70°). The reaction is completed by an additional six hours' refluxing of the benzene solution. Hydrolysis of the addition product by dropwise addition of about 20 cc. of water releases an additional 150 cc. of methane. The precipitated magnesium hydroxide is dissolved by addition of 500 cc. of saturated ammonium chloride solution, the benzene layer separated, washed, dried over anhydrous sodium sulfate, and freed of benzene by distillation from the steam-bath. Distillation of the remaining material at 4 mm. yields 29 g. of the alcohol; b. p. 84–86°. Redistillation at 4 mm. yields 27 g. with the following constants: b. p. (4 mm.) 82–83°; (12 mm.) 107–108°; d^{20}_4 0.9162; n^{20}_D 1.4755; n^{16}_D 1.4770; $[\alpha]^{22}_D$ −4.0°; MR (calcd.) 51.75; found, 51.73.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.49; H, 11.98. Found: C, 78.36, 78.01; H, 12.25, 11.91.

Prilezhaev reported: b. p. (13 mm.) 109–110°; d^{15}_{15} 0.9275; n^{15}_D 1.4769; $[\alpha]^{22}_D$ +7.90° (from a *l*-rotatory α-pinene oxide). The use of benzene as solvent in the foregoing procedure was suggested by the method of E. E. Dreger.[7]

Determination of the Double Bond in Methylcampholenol.—(a) 4.990 g. of alcohol reacted with 3.67 g. of perbenzoic acid, indicating 0.92 double bond per molecule. (b) 0.2000 g. of the alcohol reacted with 0.2900 g. of iodine, or the equivalent of 0.966 double bond per molecule.

Analysis of the Gaseous Reaction Products.—These were analyzed by the ordinary procedure in each case, for which the details are omitted.

Methylcampholenone (α-Campholenic acid methyl ketone).—To a solution of sodium dichromate hydrate (10 g.), concentrated sulfuric acid (11 g.) and water (80 cc.) contained in a glass-stoppered bottle is added 10 g. of methylcampholenol. The mixture is shaken for one-half hour, and then allowed to stand overnight. It is

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[5] B. T. Brooks and W. B. Brooks, THIS JOURNAL, **55**, 4309 (1933).

[6] Prilezhaev, *Ber.*, **42**, 4814 (1909).

[7] E. E. Dreger, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York City, 1932, p. 299.

TABLE I

	I C_2H_5	II n-C_3H_7	III n-C_4H_9	IV iso-C_4H_9	V C_6H_5
Approx. vol. gas, cc.	1200	1300	1000	1500	None
Anal. gas (approx.) %	90 C_2H_6 10 C_2H_4	75 C_3H_8 25 C_3H_6	80 C_4H_{10} 20 C_4H_8	60 C_4H_{10} 40 C_4H_8	... ...
B. p., 4 mm.	88–89	100–101	110–112	106–107	140–142 (1.3 mm.)
d^{20}_4	0.9125	0.9024	0.8987	0.8939	1.0003
n^{20}_D	1.4740	1.4720	1.4721	1.4715	1.5308
$[\alpha]^{22}_D$	−2.9	−4.5	.....	.....	−5.7
MR found	56.11	60.96	65.52	65.58	78.17
MR calcd.	56.37	60.54	65.57	65.57	78.48
% C calcd.	79.04	79.69	79.92	....	83.43
% H calcd.	12.19	12.24	12.38	....	9.63
% C found	78.65	79.00	79.89	.....	83.01
% H found	12.28	12.36	12.11	.....	9.59
Double bond per mol.	0.94	.....	.....	0.94	0.96

then extracted with ether in two portions of 40 cc. each, the ether solution washed with water, 5% sodium carbonate solution, water again, and dried over anhydrous sodium sulfate. After removal of the ether the ketone (6 g.) is distilled at 4 mm.: b. p. 73–74° (4 mm.); d^{22}_4 0.9214; n^{22}_D 1.4690; semicarbazone, m. p. 175–176° (corr.).

Campholenic Aldehyde.—α-Pinene oxide was isomerized according to the method of Arbuzov:[3] 40 g. of the oxide is dissolved in 100 cc. of dry benzene and 0.5 g. of anhydrous zinc bromide added. The mixture is heated on the steam-bath for one and one-half hours. The violent reaction described by Arbuzov was not noted in this preparation. The benzene is distilled off from the steam-bath and the aldehyde distilled from the residue at 12.5 mm. Twenty-five grams of product (62.5%) is obtained; b. p. (12.5 mm.) 83–84°; n^{17}_D 1.4676; semicarbazone, m. p. 138–139° (corr.). Arbuzov[3] reported: b. p. (12.5 mm.) 83°; n^{17}_D 1.4668; semicarbazone, m. p. 138–139° (corr.).

Grignard Reaction on Campholenic Aldehyde.—Methyl magnesium iodide in ether, prepared in the usual manner is treated with 18 g. (one equivalent) of campholenic aldehyde, added during one half hour. About 200 cc. of a gas (probably methane) is evolved during the addition of the aldehyde. The mixture is refluxed for an additional two hours, then hydrolyzed by pouring into an ice and water mixture containing dilute sulfuric acid. The ether layer is separated, neutralized with 5% sodium carbonate solution, dried over anhydrous sodium sulfate, the ether removed, and the product distilled at 4 mm.: b. p. (4 mm.) 82–83°; d^{22}_4 0.9070; n^{20}_D 1.4750. The product is shown by oxidation to methylcampholenone to be identical with methylcampholenol obtained directly from α-pinene oxide: 8 g. of the product yields 5 g. of the ketone, b. p. (4 mm.) 73–74°; d^{22}_4 0.9224; n^{22}_D 1.4684; semicarbazone, m. p. 175–176°; mixed melting point with the semicarbazone of methyl campholenone described above showed no depression.

Additional Campholenols.—A few further alcohols in this series were also prepared by the action of Grignard reagents upon α-pinene oxide ($[\alpha]^{22}_D$ 65.2) by the procedure already described, using equimolar amounts of reagents in each case. The yields were close to 70% throughout. Significant data and the physical properties of the preparations are given in Table I.

Remarks.—Preparations I, IV and V were also described by Prilezhaev. Preparation I was oxidized to the ketone, ethyl campholenone: b. p. (2 mm.) 80–81°; d^{22}_4 0.9246; n^{22}_D 1.4720; semicarbazone, m. p. 148–149° (corr.).

Summary

A series of alcohols obtained by the action of Grignard reagents upon α-pinene oxide has been prepared and characterized. The structures of the alcohols have been shown to be different from those previously assigned.

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