that a study of the effect of various cations would lead to synthetic improvements in this typical S_N2 reaction.

When 2-ethylhexyl bromide was treated for two hours with absolute alcoholic solutions of metal alkoxides at reflux 2-ethyl-1-hexene and ethyl 2-ethylhexyl ether were formed in a ratio of about 2/1. The results recorded in Table I indicated that under these conditions the nature of the cation had no appreciable effect on the product composition. We were able to account for about 75–80% of the starting bromide with reasonably good duplication of results. Our conclusion is that the slight trend noted is not significant. Possibly more accurate work would reveal a significant trend but we decided to drop this study as it did not seem profitable to pursue it further.

TABLE I

PRODUCTS OF REACTION OF 1.5 N C_2H_5OM WITH 2-ETHYLHEXYL BROMIDE

Expt.	Olefin, %	Ether, %	Unreacted bromide, %	Ratio[a] olefin/ether
Li-1	42.0	18.8	15.3	
Li-2	46.0	19.6	16.2	2.29
Na-1	51.3	24.5	5.4	
Na-2	51.7	24.5	5.7	2.10
K-1	50.4	24.8	6.0	
K-2	50.2	25.1	5.1	2.02

[a] Average of two experiments. In all experiments 350 ml. of 1.5 N ethoxide in ethanol and 0.249 mole of 2-ethylhexyl bromide were used. A non-volatile residue of 9% by weight was obtained in each experiment.

Experimental

Absolute ethanol[3] was used in all experiments. 2-Ethylhexyl bromide, b.p. 65–67° at 5 mm., n^{25}_{D} 1.4520–1.4532, was used; the same batch in all experiments.

Ethyl 2-Ethylhexyl Ether.—Several hours was needed for 12.5 g. of sodium to dissolve in a solution of 70 g. of 2-ethyl-1-hexanol in 100 cc. of benzene. To this solution was added 77 g. of diethyl sulfate in 50 cc. of benzene. The reaction mixture became quite viscous and an additional 150 cc. of benzene was added. After one hour the reaction mixture was treated with ethanol and water. The crude product, b.p. 70–80° at 25–30 mm., had a disagreeable odor which was only removed from the desired narrower boiling range material, b.p. 55–56° at 6 mm., by heating with sodium for several hours. Redistillation afforded a material, b.p. 53–54° at 5 mm., which had the same index of refraction, 1.4099 at 28°, for four 5-g. cuts. The yield is not significant as attention was paid to securing very pure material.

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.9; H, 14.0. Found: C, 76.0; H, 13.8.

Analytical Methods.—In order to estimate the composition of mixtures of 2-ethylhexyl bromide and ethyl 2-ethylhexyl ether obtained from reaction mixtures, a composition–index of refraction curve was constructed by mixing weighed amounts of the components and determining the index.

2-Ethyl-1-hexene was determined by titration with bromine in acetic acid.[4] Values for the bromine number of about 108 were obtained in acetic acid and chloroform. The correct value of 143 was obtained only when 5 ml. or more of ethyl alcohol was added. The percentage of olefin found in various fractions of the reaction mixture was calculated by dividing the bromine number found by 143. Tests on all of the suspected impurities showed that they did not interfere or give blanks.

Bromine analyses of certain non-volatile residues were made by the Umhoefer method.[5] 2-Ethylhexyl bromide gave the theoretical value.

TABLE II

COMPOSITION–INDEX OF REFRACTION AT 28° OF MIXTURES OF 2-ETHYLHEXYL BROMIDE AND ETHYL 2-ETHYLHEXYL ETHER

Wt. % of bromide	n^{28}_{D}	Wt. % of bromide	n^{28}_{D}
0.00	1.4099	15.48	1.4148
3.48	1.4112	25.25	1.4177
4.94	1.4116	40.35	1.4230
8.53	1.4128	46.50	1.4248
13.37	1.4140		

General Procedure.—After several preliminary experiments to determine appropriate concentration, reaction time and method of working up the products, the following procedure was adopted: In a 1-liter, 3-necked flask equipped with stirrer, reflux condenser with calcium chloride drying tube, and dropping funnel was placed 350 ml. of a 1.5 N solution of the appropriate metallic ethoxide. This solution was brought to reflux temperature and 48.0 g. (0.25 mole) of 2-ethylhexyl bromide added in five minutes. Stirring at reflux temperature was continued for two hours. The reaction mixture was then cooled and treated with dilute sulfuric acid. The layers were separated and the aqueous layer salted out with sodium bromide and extracted with ether. No attempt was made to dry the combined organic layers at this point because of the large amount of ethanol present. The organic solution was fractionated and ether collected to a temperature of 35°. An intermediate cut and some of the ethanol was then collected from 35 to 78°. This intermediate cut contained an azeotrope of ethanol and 2-ethyl-1-hexene boiling at 74°. The olefin in this cut was titrated with a solution of bromine in acetic acid and the percentage of olefin present thus determined. Most of the ethanol was then fractionated from the remaining material. The residue, which now contained only a small amount of alcohol, consisted of two layers which were separated and the aqueous layer salted out with sodium bromide and extracted with ether. The combined organic layers were then dried over sodium sulfate. After fractionation of the ether, the residual material was dried at 5 mm. at room temperature and weighed. This residual material was then analyzed for bromine and the amount of non-volatile material present determined by distillation at 5 mm. The amount of ethyl 2-ethylhexyl ether present was determined by subtracting the amount of 2-ethylhexyl bromide and non-volatile material from the weight of the original residue and also by using the index of refraction–composition diagram (Table II). The values obtained by the two methods checked within 2 to 5%.

In each of the six experiments reported in Table I there remained about 9% (by weight) of non-volatile residue containing less than 1% of bromine.

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Isolation of a New Fraction from Wool Wax Acids

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RECEIVED APRIL 1, 1954

By the saponification of wool wax and the isolation of the acid fraction free of all alkali-insoluble material, it has been possible to separate chromatographically from the "acid" fraction a non-acidic material which apears to be a lactone of molecular formula $C_{20}H_{33}O_2$ representing 12% of the acid fraction. This material gave negative tests for nitrogen by the soda lime test, for unsaturation using bromine in carbon tetrachloride and for aldehyde or ketone using 2,4-dinitrophenylhydrazine reagent. Additional efforts to saponify this material and obtain an unsaponifiable fraction were unsuccessful. Infrared examination of the lactone fraction dis-

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[3] R. H. Manske, THIS JOURNAL, **53**, 1104 (1931).

[4] K. Uhrig and H. Levin, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 90 (1941).

[5] R. R. Umhoefer, *ibid.*, **15**, 383 (1943).

solved in carbon disulfide showed a carbonyl absorption band at 1738 kaysers[1] which agrees closely with a literature value[2] of 1740 kaysers for a δ-lactone carbonyl. The spectrum of the lactone fraction showed no absorption band near the higher frequency (1770 kaysers) given in the literature[2] for γ-lactones. On the other hand, authentic samples of γ-stearolactone, γ-valerolactone and γ-butyrolactone showed carbonyl bands at 1784, 1788 and 1786 kaysers, respectively.

Refluxing the lactone with methanol and sulfuric acid as catalyst yielded a derivative, presumably a methyl ester, whose infrared spectrum in carbon disulfide (7.6 g./l.) showed an ester carbonyl absorption band at 1744 kaysers and broad alcoholic hydroxyl absorption bands at 3370 and 3470 kaysers. The total area of these hydroxyl absorptions was appreciably less than that of methyl 12-hydroxystearate, whose major hydroxyl band occurred at 3630 kaysers with minor broad bands at 3370 and 3470 kaysers (8.7 g./l. in CS_2). The original lactone showed no hydroxyl bands.

The ease of δ-lactone formation is well established. From the data obtained it may be inferred that the lactone fraction is a δ-lactone. Such a compound would explain the difficulty encountered in obtaining wool wax acids free of an appreciable saponification number. Furthermore, the above data would indicate the presence of a δ-hydroxy acid in wool wax acids. Thus far the only hydroxy acids isolated from wool wax were α-hydroxy acids.[3-6]

Although the information available indicates the probability that the lactone is a $C_{20}H_{38}O_2$ compound, the data do not eliminate the possibility that we have a difficultly separable mixture of δ-lactones.

Experimental

A 500-g. sample of U.S.P. lanolin was saponified[7] and the resulting mixture was exhaustively extracted with petroleum naphtha (88–98°). From the extract there was isolated 243 g. of material having an acid number of 2.66 and a saponification number of 11.97. The soaps remaining in the lower layer in the continuous extractor were acidified with a 100% excess of concentrated hydrochloric acid and the acid mixture heated for four hours at 68°. The mixture was allowed to cool to room temperature and then continuously extracted with ether for 24 hours. The ether extract was evaporated leaving 261 g. of material having an acid number of 103.5 and a saponification number of 167.5. A 15-g. sample of this material in 30 ml. of reagent grade chloroform was chromatographed on a 4.5 cm. × 39 Florisil column.

The column was developed with petroleum ether (35–60°) (8 liters eluted 10% and an additional 12 liters eluted 2% more by wt.). The residue obtained by evaporating 20 liters of petroleum ether weighed 1.8 g. and contained no free acid.

Anal. Calcd. for $C_{20}H_{38}O_2$: sapn. equiv., 310.5; C, 77.36; H, 12.33. Found: sapn. equiv., 311.1; C, 77.7; H, 12.8; $[\alpha]^{26}D$ +13° (chloroform, c = 4); mol. wt. (cryoscopically in benzene), 316.

Methanolysis.—A 0.68-g. sample of lactone was refluxed for 6 hours with 250 ml. of methanol and 2 drops of concentrated sulfuric acid. The reaction mixture was diluted with 200 ml. of water, concentrated to approximately 200 ml. and ether-extracted. The organic layer was washed free of acid with water and then dried over anhydrous granular sodium sulfate. The dry extract was evaporated leaving a residue of 0.78 g., $[\alpha]^{26}D$ +5.0° (chloroform, c = 1.8).

Acknowledgment.—The authors wish to thank C. Roland Eddy for the infrared data and Virginia A. Schubert for the carbon and hydrogen analysis.

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[1] The term "kayser" is used in this paper as a unit of wave number (formerly cm.$^{-1}$) as recommended by the Joint Commission for Spectroscopy, *J. Optical Soc. Am.*, **43**, 410 (1953).

[2] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 881 (1951).

[3] A. W. Weitkamp, THIS JOURNAL, **67**, 447 (1945).

[4] D. H. S. Horn, F. W. Hougen and E. von Rudloff, *Chemistry and Industry*, 106 (1953).

[5] J. Tiedt and E. V. Truter, *ibid.*, 403 (1952).

[6] D. H. S. Horn, F. W. Hougen, E. von Rudloff and D. A. Sutton, *J. Chem. Soc.*, 177 (1954).

[7] C. S. Barnes, R. G. Curtis and H. H. Hatt, *Australian J. Appl. Sci.*, **3**, 88 (1952).

The Disproportionation of Allylic Chlorofluoro Compounds[1]

BY MAURICE PROBER

RECEIVED FEBRUARY 25, 1954

The utility of metal halides for the disproportionation of chlorofluoro compounds became of interest when an appreciable yield of a trichlorotrifluoropropene was isolated from a sample of tetrachloro-3,3-difluoropropene which had been contaminated with metal halides. Previously, aluminum halides have been used as disproportionation catalysts—aluminum chloride and bromide at moderate temperatures,[2] and aluminum fluoride at elevated temperatures.[3]

A series of metal halides was tested for catalytic activity by refluxing tetrachloro-3,3-difluoropropene with one mole per cent. of catalyst and noting qualitatively how fast the lower boiling trichlorotrifluoropropene was formed. The catalysts, arranged in order of decreasing activity, are antimony pentachloride > titanium tetrachloride > aluminum bromide, aluminum chloride > ferric chloride. Tin tetrachloride, zinc chloride, boron trifluoride etherate and aluminum fluoride did not effect disproportionation under these conditions.

The disproportionation of tetrachloro-3,3-difluoropropene by antimony pentachloride was repeated on a larger scale and the following reactions occurred

$$2CF_2ClCCl{=}CCl_2 \longrightarrow CF_3CCl{=}CCl_2 + CFCl_2CCl{=}CCl_2$$
$$2CFCl_2CCl{=}CCl_2 \longrightarrow CF_2ClCCl{=}CCl_2 + CCl_3CCl{=}CCl_2$$

Only the allylic chlorofluoro group was involved in the disproportionation. The identity of the products was proved by comparison of the physical constants with the literature values. In addition, the refractive indices of the isomeric chlorofluoro compounds which have been reported are different from those observed.

The yield data are summarized in Table I.

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[1] Presented at the 124th Meeting of the American Chemical Society, September, 1953.

[2] (a) U. S. Patent 1,994,035 (March 12, 1953); (b) U. S. Patent 2,426,637 (September 2, 1947); (c) U. S. Patent 2,426,638 (September 2, 1947); (d) W. T. Miller, E. W. Fager and P. Griswold, THIS JOURNAL, **72**, 705 (1950); (e) U. S. Patent 2,598,411 (May 27, 1952).

[3] U. S. Patent 2,478,201 (August 9, 1949); U. S. Patent 2,478,932 (August 16, 1949).