Racemization during Chromatography of Some Optically Active Halides[1]

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The action of the usual chromatographic adsorbents as catalysts for various organic reactions has been noted before.[2] It has now been found that silica gel and acid alumina are particularly potent catalysts for the racemization of tetrahydrolinalyl chloride and α-phenylethyl chloride. Optically active, α_{D}^{23} $-0.63°$ (obs.), methylethylisohexylcarbinyl chloride[3] (tetrahydrolinalyl chloride) was chromatographed on silica gel with pentane as eluent. The product isolated was a mixture containing about 60% tetrahydrolinalyl chloride and olefins derived from it. This mixture was optically inactive. Similarly, α-phenylethyl chloride, α_{D}^{22} $-62.98°$ (obs.), when chromatographed on silica gel with pentane as the eluent gave racemic chloride and a small amount of styrene. Chromatography of optically active tetrahydrolinalyl chloride on an ice jacketed silica gel column gave racemic chloride and a smaller amount of olefin than was found at room temperature. The same chloride chromatographed on activated acid alumina gave complete elimination. Chromatography of either halide on basic alumina caused little or no racemization. Optically active tetrahydrolinalyl methyl ether can be chromatographed on acid alumina without racemization.

These results show that acidic adsorbents are potent catalysts for the racemization of halides which can form relatively stable carbonium ions. A related reaction has been observed by Uskokvic, Dorfman, and Gut[4] who found that 20-chlorobisnorcholane-3β-ol acetate rearranges with loss of hydrogen chloride on acidic silica gel to give 17,-17a-dimethyl-D-homoandrost-17(17a)-en-3β-ol acetate. The action of the catalyst is undoubtedly due to its acidity and the polarity of the surface.[5] Certainly these results are most consistent with a carbonium ion or modified carbonium ion mechanism for the racemization.

Clearly the data serve as a warning to workers who may wish to purify halides chromatographically which form carbonium ions easily.

EXPERIMENTAL

Adsorbents. The silica gel (28–200 mesh) was obtained from Fisher Scientific Co., New York 14, N. Y. The activated acidic alumina, Aluminum Oxide Woelm, acid, activity grade 1, was obtained from Alupharm Chemicals, New Orleans, La. The basic alumina (80–200 mesh) was obtained from Aluminum Corporation of America, Pittsburgh, Pa.

Silica gel chromatography. (A) Optically active tetrahydrolinalyl chloride,[6] 1.0 g., α_{D}^{23} $-0.63 \pm 0.01°$ (obs.), was chromatographed on 19.0 g. of silica gel with pentane as the eluent. Approximately 200 ml. of pentane were collected from which 1.0 g. of a clear liquid residue was isolated by evaporation. Gas phase chromatography[7] of the residue indicated that about 60% was tetrahydrolinalyl chloride. The rest was a mixture of olefins. The total mixture was optically inactive, α_{D}^{23} $0.00 \pm 0.01°$ (obs.).

The same experiment was repeated using an ice-jacketed column with the same results.

(B) Optically active α-phenylethyl chloride, 2.0 g., α_{D}^{22} $-62.98 \pm 0.01°$ (obs.), was chromatographed on silica gel with pentane as eluent. Approximately 500 ml. of pentane were collected. Evaporation of the pentane afforded 1.5 g. of liquid residue. Gas phase chromatography showed this to be α-phenylethyl chloride plus a trace of styrene. The rotation of this fraction was α_{D}^{22} $0.00 \pm 0.01°$ (obs.).

Chromatography on acid alumina. (A) Optically active tetrahydrolinalyl chloride, 1.53 g., α_{D}^{23} $-0.63 \pm 0.01°$ (obs.), was chromatographed on 26.0 g. of Woelm alumina with hexane as the eluent. Approximately 200 ml. of hexane were collected from which 0.94 g. of liquid residue was isolated by evaporation of the solvent. Gas phase chromatography showed this material did not contain tetrahydrolinalyl chloride and that it was a mixture of olefins derived from the halide.

(B) Optically active tetrahydrolinalyl methyl ether, 2.41 g., α_{D}^{22} $-0.37 \pm 0.01°$ (obs.), was chromatographed on 26.0 g. of Woelm alumina with hexane as the eluent. Approximately 150 ml. of hexane were collected. Evaporation afforded 2.3 g. of liquid, α_{D}^{21} -0.31 ± 0.01 (obs.). Gas phase chromatography showed this to be essentially pure tetrahydrolinalyl methyl ether.

Chromatography on basic alumina. (A) Optically active tetrahydrolinalyl chloride, 1.0 g., α_{D}^{23} $-0.63 \pm 0.01°$ (obs.), was chromatographed on 26.0 g. of basic alumina with pentane as the eluent. Approximately 150 ml. of pentane were collected. Evaporation afforded 1.0 g. of a liquid, α_{D}^{23} $-0.58 \pm 0.01°$ (obs.). Gas phase chromatography showed this to be essentially pure tetrahydrolinalyl chloride.

(B) Optically active α-phenylethyl chloride, 2.0 g., α_{D}^{22} $-62.98 \pm 0.01°$ (obs.), was chromatographed on 60.0 g. of basic alumina with pentane as the eluent. Approximately 150 ml. of pentane were collected from which 1.7 g. of liquid was obtained by evaporation. The rotation of this material was α_{D}^{22} $-58.23 \pm 0.01°$ (obs.). Gas phase chromatography showed it to be essentially pure α-phenylethyl chloride.

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(2) (a) K. B. Wiberg, *Laboratory Technique in Organic Chemistry*, McGraw-Hill, New York, N. Y., 1960, Chap. 4. (b) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960) discuss the catalytic activity and intrinsic acidity of alumina.

(3) Prepared by the reaction of triphenyl phosphite with tetrahydrolinalyl hypochlorite at −78°. Details of this preparation will be published later.

(4) M. Uskokvic, R. Dorfman, and M. Gut, Abstracts of Papers, American Chemical Society Meeting, Atlantic City, N. J., 1959, p. 82P.

(5) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 621 (1956) has reviewed the evidence concerning the catalytic activity of acids in promoting carbonium ion reactions from alkyl halides in nonaqueous systems.

(6) The tetrahydrolinalyl chloride used in these experiments was contaminated to some extent with a mixture of olefins derived from it.

(7) All gas phase chromatography was carried out on a K and M Gas Chromatograph, model 17A. A two-foot glass column packed with 40% by weight polyethylene glycol 300 on 30–80 mesh Celite was used. Helium was used as the carrier gas at a flow rate of 60 ml./min. The temperature was 140°.