Stereochemistry of Vapor Phase Dehalogenation of *meso*- and DL-2,3-Dibromobutane with Zinc[1]

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We have observed that the elimination of bromine atoms from the isomeric 2,3-dibromobutanes occurs in a stereospecific manner, giving products expected for a "*trans*" debromination when the bromobutanes in vapor form are passed through a heated column of granular zinc.

Stereospecific elimination of halogens from vicinal dihalides has been reported using iodide ion[3] and metals.[4] An excellent summary of metal-promoted eliminations is given by Banthorpe.[5] Schubert and co-workers[4] obtained principally *trans* debromination products from *meso*- and *dl*-2,3-dibromobutane and *meso*- and *dl*-1,2-dibromo-1,2-dideuterioethane using either magnesium in tetrahydrofuran or zinc in water. Recently, Prince and Bremer have reported *trans* elimination of bromine atoms from the dibromobutanes using sodium selenide in both dimethylformamide and dimethyl sulfoxide.[6]

Using our system for elimination of vicinal halogens, the yield of alkenes increases with increasing temperature, decreasing flow rate, and increasing column length. Quantitative yields of ethylene were obtained from ethylene bromide using a column temperature of 100° and a helium flow rate of 8 ml/min. The dibromobutanes were debrominated at a considerably lower column temperature of 50°. Attempts are being made to ascertain the optimum conditions of flow rate, column temperature, and length for complete stereospecific debromination. *meso*-2,3-Dibromobutane gave *trans*-2-butene (92%) and *cis*-2-butene (8%); *dl*-2,3-dibromobutane gave *cis*-2-butene (89%) and *trans*-2-butene (11%).[7]

We are presently engaged in determining the stereospecificity of elimination of halogens from other vicinal dihalides and to what extent the stereochemistry of these reactions is affected by use of different metals in the dehalogenation column. A kinetic investigation of the reaction and evaluation of Arrhenius parameters should provide insight as to the nature of the metal-catalyzed reaction.

Experimental Section

Preparation of the Dibromobutanes.—Pure *dl*-2,3-dibromobutane was prepared by addition of bromine to *cis*-2-butene (Matheson Co., 99.82% pure) using the method of Young, Dillon, and Lucas.[8] The product was purified by two distillations through a 24-in. stainless steel spinning band column: bp 76–77° (50 mm), n^{25}_{D} 1.5120 (lit.[8] bp 75.6–75.8° (50 mm), n^{25}_{D} 1.5125). *meso*-2,3-Dibromobutane prepared from *trans*-2-butene (Matheson Co., 99.26% pure) was a colorless liquid: bp 73–74° (50 mm), n^{25}_{D} 1.5089 (lit.[8] bp 72.7–72.9° (50 mm), n^{25}_{D} 1.5092).

Debromination of Dibromobutanes.—The apparatus used in this study consisted of the following items in sequence: carrier gas supply and control, "vaporizer" with sampler, oven containing column packed with metal, exit sampler, and flowmeter. Pure helium was used to carry vaporized bromobutanes onto the column and to remove butenes formed by dehalogenation. The vaporizer was constructed of Pyrex glass in such a manner as to permit sampling of the vaporized dibromobutanes prior to their contact with the column. A 10 ft × 0.25 in. column packed with zinc (40 mesh, 99+% pure) was placed in a high mass oven capable of temperature stability to ±0.05°. Samples of the effluent gas from the column were analyzed by glpc. To demonstrate that isomerization of the dibromobutanes did not occur during vaporization, samples of the dibromobutanes were taken from the vaporizer at the beginning and the end of each run and the refractive indices were noted before and after heating; they were identical. Also, authentic samples of *cis*- and *trans*-butenes were passed through the column to determine if the heated column used for debromination could bring about isomerization of the butenes; it did not.

Analysis of Butenes.—Samples of the effluent gas from the column were taken using a syringe and injected into an Aerograph HY-Fi Model 600-D hydrogen flame gas chromatograph equipped with a 20-ft $\frac{1}{8}$-in. column packed with silver nitrate in benzyl cyanide (30%) on Chromsorb W connected to a 6-ft $\frac{1}{8}$-in. column packed with dimethylsulfolane (30%) on Chromsorb W. Retention times were 7.80 min for *cis* and 4.12 min for *trans* at a temperature of 35° and flow rate 30 ml/min.

Registry No.—*meso*-2,3-Dibromobutane, 5780-13-2; *dl*-2,3-dibromobutane, 14897-69-9; zinc, 7440-66-6.

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[2] This paper was taken in part from the thesis presented by James V. Hay to the Graduate School of Murray State University in partial fulfillment of the requirements for the degree Master of Science.

[3] S. Winstein, D. Pressman, and W. G. Young, *J. Am. Chem. Soc.*, **61**, 1645 (1939).

[4] W. M. Schubert, B. S. Rabinovitch, N. R. Larson, and V. A. Sims, *J. Am. Chem. Soc.*, **74**, 4590 (1952).

[5] D. V. Banthorpe in "Reaction Mechanisms in Organic Chemistry," Vol. 2, E. D. Hughes, Ed., Elsevier Publishing Co., The Netherlands, 1963, p 136.

[6] M. Prince and B. W. Bremer, *J. Org. Chem.*, **32**, 1655 (1967).

[7] These values represent the averages for ten consecutive runs. After each run the column was repacked with fresh zinc. The compositions of the mixtures of butenes are expected to change as the zinc:zinc bromide ratio changes, *i.e.*, as a given packing is continuously used.

[8] W. G. Young, R. T. Dillon, and H. J. Lucas, *J. Am. Chem. Soc.*, **51**, 2528 (1929).

The Reactions of Acidic Reagents with Diene–Quinone Adduct Epoxides. II

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In a previous communication,[1] the reactions of several diene–quinone epoxides with boron trifluoride etherate to afford ring-contracted indanedione derivatives were described. We now report the anomalous reactions of two such epoxides **1** and **2** upon treatment with mineral acid.

Treatment of **1** or **2** with 50% sulfuric acid in dioxane at 80° yielded two products in each case. Quinone **6** was identified by comparison with an authentic sample[2] and a sample of quinone **4** was independently synthesized by oxidation of the product

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[1] H. S. Wilgus, III, E. N. Oftedahl, W. J. Musliner, and J. W. Gates, Jr., *J. Org. Chem.*, **32**, 3208 (1967).

[2] R. F. Porter, W. W. Rees, E. Frauenglass, H. S. Wilgus, III, G. H. Nawn, P. P. Chiesa, and J. W. Gates, Jr., *J. Org. Chem.*, **29**, 588 (1964).