Stereospecific Dehydrobromination of *dl*- and *meso*-2,3-Dibromobutanes over Solid Catalysts

Makoto Misono and Yukio Yoneda

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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We have observed that the elimination of hydrogen bromide from the isomeric 2,3-dibromobutanes occurs in a stereospecific manner over some basic solid catalysts, giving products expected to be obtained by *anti*-elimination.

Elimination reactions in homogeneous liquid phase in the presence of basic catalyst usually proceeds stereospecifically by *anti*-elimination in *E*2 mechanism.[1] However, very few such stereospecific eliminations have been observed in the case of vapor phase elimination over solid catalyst. Non-catalytic debromination of 2,3-dibromobutanes with zinc was reported to give products expected by *anti*-elimination.[2] Pines and Manassen[3] postulated *anti*-elimination on the basis of the distribution of products obtained from the dehydration of cyclic alcohols such as menthol and neomenthol over alumina. Andreu *et al.*[4] reported that the dehydrobromination of 2,3-dibromobutanes over calcium chloride, sulfate and phosphate proceeded in a completely non-stereospecific way, leading them to propose an *E*1-like mechanism. If the elimination takes place by an *E*2-like mechanism as suggested by Pines and Manassen,[3] two sites on the surface of catalyst should simultaneously attack a reactant molecule, one from one side of the molecular plane and the other from the opposite side. It is of interest, also in this sense, to determine the steric course of reaction over solid catalyst.

We studied the products from the reaction of *meso*- and *dl*-2,3-dibromobutanes over sodium hydroxide and carbonate supported on silica gel (*ca.* 5 wt%) by a pulse technique at 120—200°C using hydrogen as a carrier gas. *dl*-2,3-Dibromobutane was prepared from *cis*-2-butene and bromine in methylene chloride. *meso*-2,3-Dibromobutane was prepared from *trans*-2-butene under the same conditions. Catalysts were prepared by impregnation on silica gel (Wako Chemicals, Q-12) from aqueous solution of each salt. Hydrogen was deoxygenated by a "Deoxo" purifier and dried by a dry ice trap. Products were analyzed by a glpc which was directly connected to a reactor and equipped with double columns, a dimethylsulfolane column for butene analysis and an Apiezon-grease column for the analysis of the rest. When necessary, products were analyzed after being collected with a trap inserted between the reactor and the glpc.

Table 1 Products from the elimination reaction of *dl*- and *meso*-2,3-dibromobutanes at 170°C

Catalyst	Reactant 2,3-Dibromobutane	% Conversion to 2-bromo-2-butene (-HBr)		2-butene ($-Br_2$)	
		trans	*cis*	*trans*	*cis*
$NaOH-SiO_2$	*dl*-	6.3	<0.3	<0.1	0.6
	meso-	<0.3	5.3	0.8	<0.1
$Na_2CO_3-SiO_2$	*dl*-	8.0	<0.3	<0.1	0.8
	meso-	<0.5	6.5	1.1	<0.1

Typical results are given in Table 1. No reaction of 2-bromo-2-butenes or butenes was detected under these conditions. Stereospecific *anti*-elimination is clearly seen in this table; *dl*-2,3-dibromobutane gave *trans*-2-bromo-2-butene and *meso*-2,3-dibromobutane gave *cis*-2-bromo-2-butene. The stereoselectivity was higher than 90% for both cases in the temperature range investigated. Butene, coming from minor reaction of debromination, also showed a stereospecific *anti*-elimination. In addition, it was noted that *dl*-2,3-dibromobutane reacted faster than *meso*-2,3-dibromobutane in dehydrobromination, while the latter reacted faster in debromination, indicating favorable formation of *trans*-olefins in both reactions. This is likely due to an eclipsing effect between two methyl groups at the transition state.

Over silica gel, which was slightly acidic, no bromobutenes were formed, but formation of butenes expected by *anti*-debromination was observed together with a small amount of butadiene.

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