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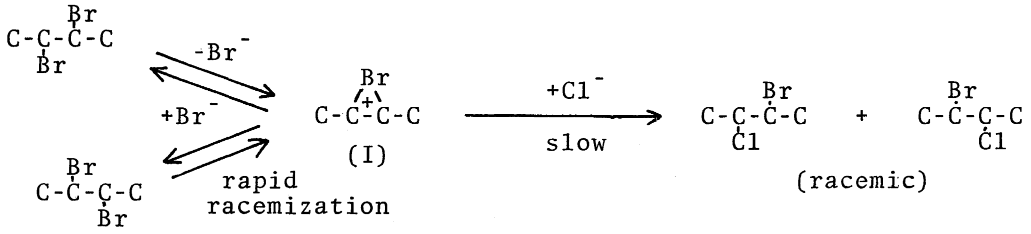
STEREOCHEMISTRY OF HALOGEN EXCHANGE AND DEHYDROBROMINATION REACTIONS OF 2-BROMOBUTANE OVER COPPER(II) CHLORIDE

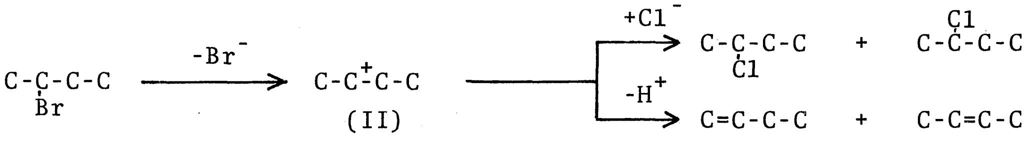
Makoto ISHIKAWA, Makoto MISONO*, and Yukio YONEDA
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Inversion of configuration and syn elimination were the favored steric paths, respectively for halogen exchange and for dehydrobromination of 2-bromobutane over $CuCl_2$ at about 100°C. This stereochemistry and slow racemization of 2-bromobutane are in contrast to those observed for 2,3-dibromobutane, and support the idea that the reaction intermediates are sec-butyl cation for 2-bromobutane and a cyclic bromonium ion for 2,3-dibromobutane.

We previously reported that 2,3-dibromobutane (C_4Br_2) exchanges halogen atoms with bivalent metal halides (substitution at a carbon atom) in a stereospecific way, i.e., retention of configuration, while the racemization of optically active C_4Br_2 took place very rapidly.[1] This stereochemical observation was reasonably explained by a cyclic bromonium-ion intermediate ((I) in Eq.1 and Fig.2 in Ref.1). Although a cyclic halonium ion is known as an intermediate of halogenation in liquid phase, its role has not been demonstrated on the solid surface.[2,3]



(1)



(2)

In this communication, we wish to report the results of 2-bromobutane (C_4Br). C_4Br forms sec-butyl cation (II) after heterolytic C-Br bond breaking. This ion has a non-cyclic structure, a cyclic hydrogen-bridged structure being less stable. In this case, the rotation about C^+-C bond is probably less restricted and the hydrogen shift between carbon 2 and 3 should be more difficult than those in the case of a bromine-bridged intermediate (I) from C_4Br_2. Therefore, it is expected that the stereochemistry of reactions and the rate of racemization are quite different between C_4Br and C_4Br_2.

Experimental procedure was essentially the same as before.[1] Optically active C_4Br was prepared from the reaction of optically active 2-butanol (Fluka) and PBr_3, and used after distillation and dilution with optically inactive C_4Br. erythro-C_4Br-3-d_1 was prepared and the isomeric composition was determined by the method similar to the previous one.[4]

Results with optically active C_4Br are compared with those of C_4Br_2 in Table 1. As expected, C_4Br was racemized much more slowly than C_4Br_2, while substitution to form 2-chlorobutane (C_4Cl) (S) and elimination to form butenes (E) took place more easily. It may be stated, therefore, that the rapid racemization of C_4Br_2 in the previous work is actually due to the effect of the bromine atom adjacent to the leaving bromine atom, i.e., the formation of a cyclic bromonium-ion intermediate. In Fig. 1, the optical activities of C_4Br unchanged and of C_4Cl formed are plotted against the conversion of C_4Br (S + E). The initial optical rotation of C_4Br, $[\alpha]_D^{20}$, was +6.8° or -8.2°. General trend in this figure seems to be unaffected by the variation of reaction temperature between 50° and 120°C. It is noted in this figure that (i) the extent of racemization increases as the conversion (S + E) increases, (ii) the optical rotation of C_4Cl is opposite to that of the starting C_4Br, i.e., inversion of configuration, and (iii) the racemization takes place considerably during the substitution reaction (compare the optical activities of C_4Br and C_4Cl at conversions less than 40%).[5]

In view of the relative reactivity of alkyl halides (sec-butyl > isopropyl > ethyl) and the relative activity of several metal chlorides (Cu, Ni > Ca, Ba > Li, Na), it seems reasonable to assume that sec-butyl cation (or ion pair) is the intermediate of the reactions of C_4Br. Therefore, the racemization which was observed during the substitution and elimination reactions should be due to (1) hydrogen shift between carbon 2 and 3 of the cation and/or (2) "roll over" of the cation on the surface which makes the two sides of the C^+-C plane indistinguishable.[8]

Table 1. Comparison of Reactions of Optically Active 2-Bromobutane (C_4Br) and 2,3-Dibromobutane (C_4Br_2) over Metal Chlorides at 80°C

Catalyst	Surface area (m^2/g)	Weight (mg)	Reactant	Substitution (%)	Elimination (%)	Racemization (%)
$CaCl_2$-SiO_2	430	58	C_4Br	0.3	0.5	9
		18	C_4Br_2	0	0	55
		41	C_4Br_2	0	0	83
$CaCl_2$	2.1	250	C_4Br_2	0	0	39
$CuCl_2$	4.8	34	C_4Br	1.3	0.3	4
		1000	C_4Br	7.6	1.7	43
		2021	C_4Br	25.4	2.4	80
		27	C_4Br_2	0	0	90
none	-	-	C_4Br, C_4Br_2	0	0	0

The stereochemistry of dehydrobromination of C_4Br over $CuCl_2$ was determined by use of C_4Br-3-d_1 as was done for silica gels.[4] The apparent %syn (the fraction of reaction which proceeded by syn elimination as determined by the previous method[4]) was about 80% when extrapolated to zero conversion and it decreased to about 60% at a 21% conversion. This decrease in %syn at higher conversions is obviously due to the racemization (or epimerization) described above. The actual %syn, if corrected for the racemization, must be as high as 80% or even higher.[11] Similarly, the degree of inversion of configuration in the substitution reaction can be higher than that seen from Fig. 1.

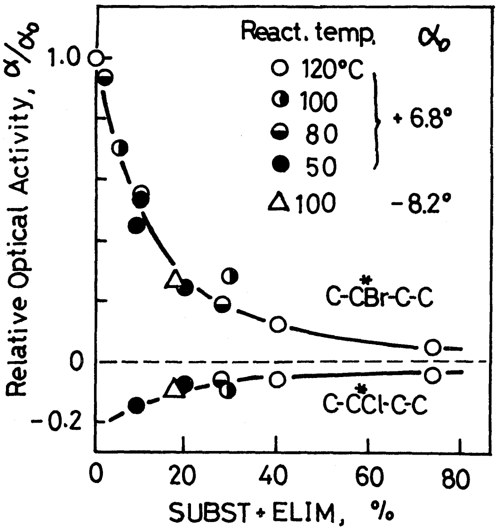


Fig. 1. Change in optical rotations of 2-bromo- and 2-chlorobutane during the reactions of optically active 2-bromobutane over $CuCl_2$

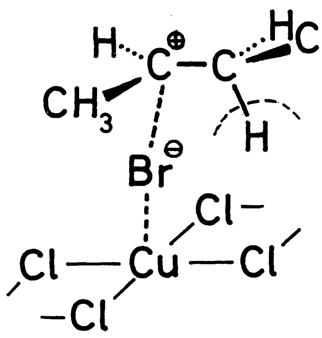
α_0 : initial optical rotation

Thus, the stereochemistry of the reactions of C_4Br was found to be in marked contrast to that of C_4Br_2, as summarized in Table 2. The fact that inversion of configuration is the favored mode of reaction on the solid surface is a little surprising and may be compared with S_N1 reactions in the liquid phase, which proceed sometimes with partial inversion.[13] Inversion of configuration in substitution and syn mode for dehydrobromination may tentatively be explained by the models given on the next page.

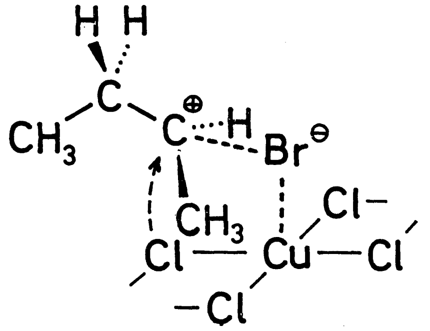
Results in the present communication were presented at the 34th National Meeting of the Chemical Society of Japan, Hiratsuka, April, 1976, and at the Symposium on "Molecular Catalysis," the Catalysis Society of Japan, Tokyo, May, 1976.

Table 2. Comparison of Stereochemistry of Reactions of 2-Bromobutane and 2,3-Dibromobutane

	$C-\underset{Br}{C}-C-C$	$C-\underset{Br}{C}-\underset{Br}{C}-C$[1]
Stereochemistry		
Substitution (Halogen exchange)	Inversion	Retention
Elimination		
-HBr	Syn	Non-specific
$-Br_2$	-	Anti
Racemization	Slow	Rapid
Intermediate	$C-C^{+}-C-C$	$C-\overset{\overset{Br}{/+\backslash}}{C-C}-C$



MODEL OF SYN ELIMINATION



MODEL OF SUBSTITUTION WITH INVERSION OF CONFIGURATION

References and notes

* To whom correspondence should be made.

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3) W.J.Hehre and P.C.Hiberty, J. Amer. Chem. Soc., 96, 2665 (1974); G.A.Olah, Angew. Chem. Intern. Ed., 12, 173 (1973).

4) M.Misono, Y.Aoki, and Y.Yoneda, Bull. Chem. Soc. Japan, 49, 627 (1976).

5) Specific rotatory power of C_4Cl (ca. 31°) is about 75% of C_4Br (ca. 42°).[6]

6) D.G.Goodwin and H.R.Hudson, J. Chem. Soc., B, 1968, 1333.

7) M.Misono and Y.Yoneda, presented at the Symposium on Catalysis, 3T09, Sendai, 1974.

8) Significant hydrogen shift actually took place, besides "roll over" of the cationic intermediate, in the reactions of C_4Br-3-d_1 and 2- or 3-bromopentane, as revealed by nmr and mass spectrometric analyses of products,[9] although the hydrogen shift was reported to be very slow on solid surface such as p-toluenesulfonic acid on silica gel.[10]

9) M.Misono, presented at the Symposium on "Molecular Catalysis," Tokyo, May, 1976.

10) Y.Sakurai, Y.Kaneda, S.Kondo, E.Hirota, T.Onishi, and K.Tamaru, Trans. Faraday Soc., 67, 3275 (1971).

11) Racemization was also observed with 2-butanol over metal phosphates.[12] It may be necessary in some cases to re-examine the stereochemistry of dehydration reported soforth.

12) M.Misono, H.Watanabe, and Y.Yoneda, unpublished results.

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