CHEMISTRY LETTERS, pp. 1089-1092, 1975. Published by the Chemical Society of Japan

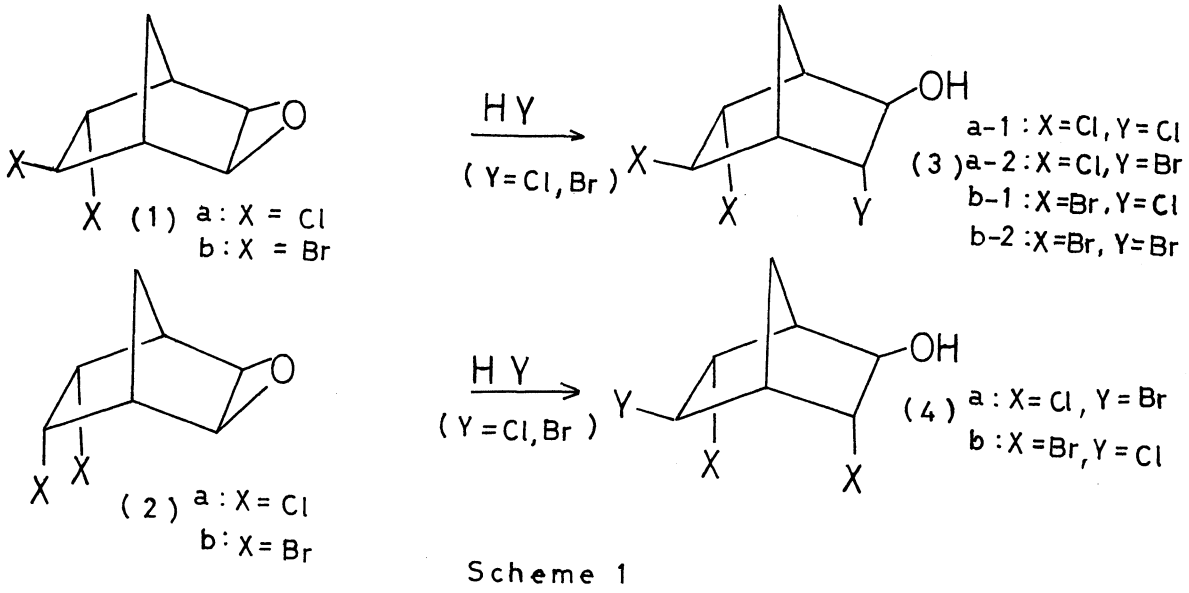
RING CLEAVAGE REACTION OF CERTAIN 5,6-DIHALO-SUBSTITUTED-2-NORBORNENE OXIDES

Yūji YANAGIDA, Yutaka SAKON, Masakatsu NOMURA, and Shōichi KIKKAWA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadakami, Suita, Osaka 565

Ring cleavage reactions of trans- and endo-cis-5,6-dichloro-(or dibromo-) 2-norbornene oxides by hydrogen halides have been investigated. Normal trans ring cleaved products were obtained in the case of trans-5,6-dihalonorbornene oxides, while the cleavage reaction of endo-cis-5,6-dihalonorbornene oxides gave the abnormal cleaved products via transannuler rearrangement of endo halogen substituent toward the resulting carbonium ion.

We have been interested in the substituent effect on the steric course of addition reaction to the double bond of 5,6-disubstituted-2-norbornenes,[1] and this time we have intended to investigate the acid-catalyzed ring cleavage reaction of two isomeric (trans- and endo-cis-) 5,6-dihalo-substituted-2-norbornene oxides as one of our extended interests of the remote substituent effect on the reaction center.

A typical experiment is as follows; 1 g of trans-5,6-dichloro-2-norbornene oxide (1a) was added to the solution of 25 ml of ether, 3.3 ml of water and 3.0 ml of conc. hydrochloric acid. Dry hydrogen chloride was bubbled into the solution during 14 hours at room temperature. After usual work up, the purification of the reaction mixture by silicagel column chromatography gave 864 mg of white solid (3a-1) as the cleaved product, mp 66-68°C. Additional cleavage reaction, using hydrogen bromide instead of hydrogen chloride as acid catalyst, was also carried out. These results are summarized in Scheme 1. The cleavage reaction of (1a) and endo-cis-5,6-dichloro-2-norbornene oxide (2a) gave the same product (3a-1), when they were treated with hydrogen chloride and this findings was true with the reaction of trans dibromide (1b) and endo-cis dibromide (2b) with hydrogen bromide, judging from their mp's and spectral analysis. Ir spectral data of all the products showed their ν_{C-O} absorption at near 1040 cm^{-1} and their elemental analysis and nmr spectral data supported that these products were the corresponding halohydrins. The properties of these halohydrins are shown in Table 1.



Scheme 1

Table 1. Properties of halohydrins

Reactant	Cleav. reagent	Product	Mp (°C)	Yield (%)	IR (KBr, ν_{C-O}, cm^{-1})
(1a)	HCl	(3a-1)	66-68	72	1040
(1a)	HBr	(3a-2)	76-77	64	1038
(2a)	HBr	(4a)	62-63	65	1042
(1b)	HCl	(3b-1)	59-61	74	1039
(1b)	HBr	(3b-2)	86-88	78	1038
(2b)	HCl	(4b)	65-66	72	1043

The nmr spectra of these products revealed the patterns similar to each other and consisted of eight characteristic groups of lines. The highest field peak except OH proton peak was assigned to bridge protons (H_7) and other two peaks over the range of τ=7.36-8.60 were also assigned to bridgehead protons (H_1 and H_4) consulting from our previous assignments of 2,3,5,6-tetrahalo-substituted norbornanes.[1] A peak at τ=8.80 was assigned to OH proton from its disappearance after the treatment with D_2O. The assignments of another signals in the lower field were undertaken by the combination use of their chemical shifts and spin decoupling techniques.

As a typical example, nmr spectrum of (3a-1) is shown in Fig. 1. τ; 8.80 (OH, doublet), 8.60 (H_7, doublet), 8.20 (H_4, doublet), 7.90 (H_1, doublet), 6.48 (H_2, septet),

6.12 (H_5, triplet), 6.00 (H_3, multiplet), 5.57 (H_6, double doublet) J_{1-2} = 4.0 Hz, J_{2-3} = 2.5 Hz, J_{4-5} = 3.0 Hz, J_{5-6} = 3.0 Hz, J_{6-7} = 1.0 Hz (solvent; C_6D_6).

Accordingly, the structure of (3a-1) has been decided to be trans, trans-3-hydroxy-2,5,6-trichloronorbornane from the values of J_{2-3} and J_{5-6} which are reasonable as trans vicinal coupling constants.

When 1.0 g of (3a-2) was treated with sodium pentoxide at 100°C for 4.5 hours, 127 mg (20 % yield) of (1a) was obtained. This result also suggests that (3a-2) possesses trans bromohydrin structure.[2)]

The most probable reaction mechanism is proposed in Scheme 2. In the case of trans isomer (1), the cleavage reaction would proceed by analogy with the previously reported bromine addition reaction[1)], in which initial addition of bromine to trans-5,6-dichloro-2-norbornene afforded bridged bromonium ion intermediate and required subsequent preferential endo attack of bromide and away from the endo halogen substituent. Thus the stereospecific trans cleavage reaction is realized.

However, in the cleavage reaction of endo-cis-5,6-dihalonorbornenes, the endo halogen substituents provide substantial interference for the attack of nucleophile (Y^-)

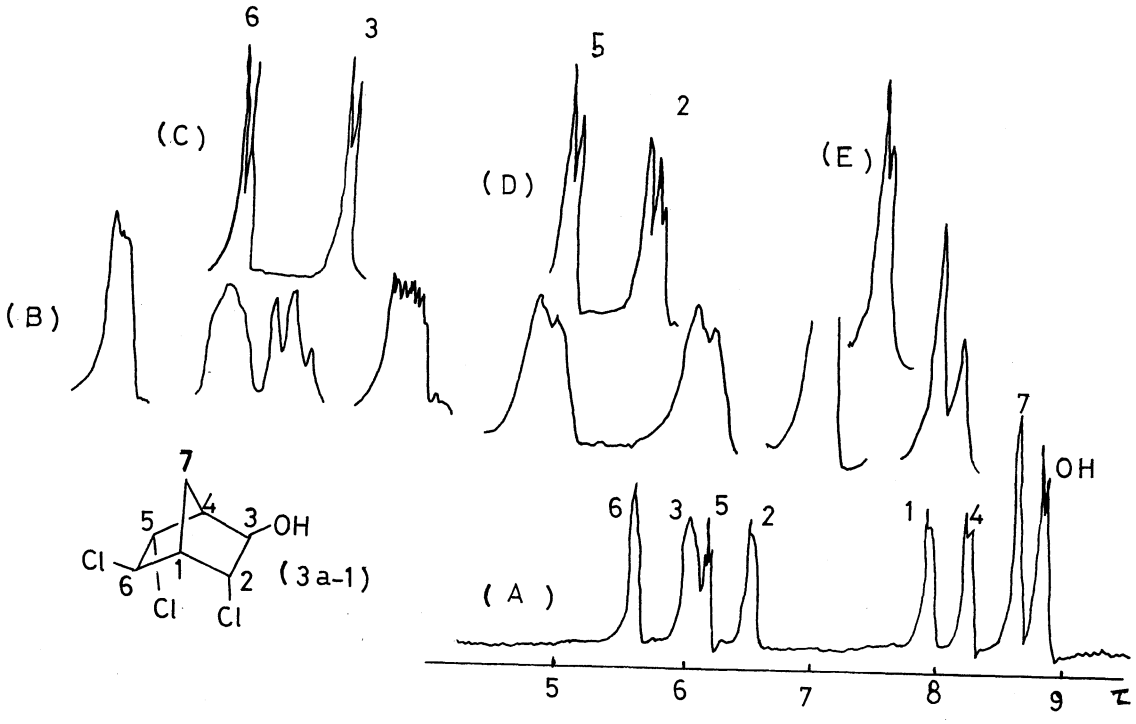
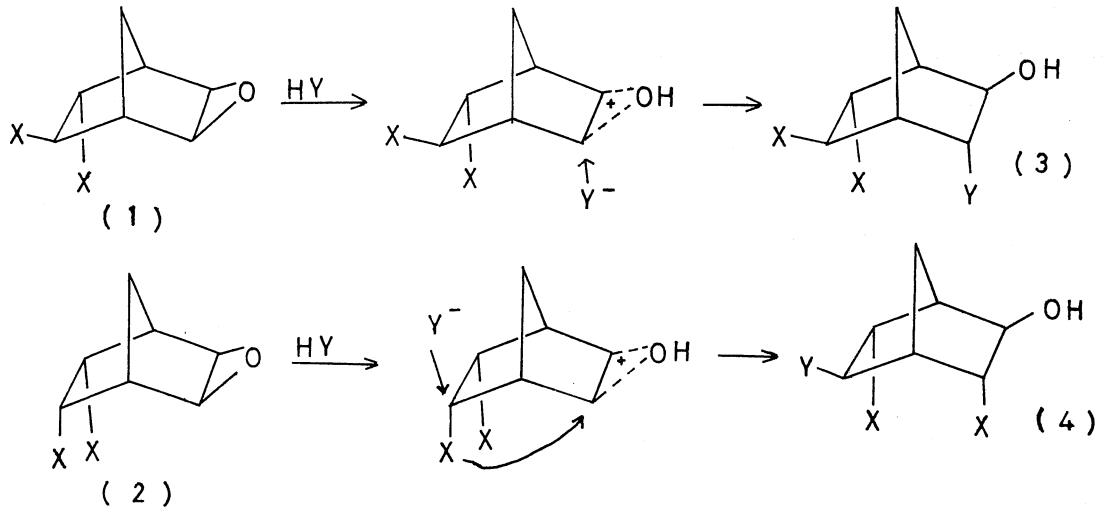


Fig. 1. NMR spectrum of (3a-1)

(A) Normal (B) Enlarged peaks (C) Decoupled from proton H_7

(D) Decoupled from proton H_4 (E) Decoupled from proton H_1

from the endo direction to the expected oxonium intermediate, and the electron-withdrawing halogen substituents appreciably deactivate the C_1–C_6 bond toward σ participation (Wagner-Meerwein rearrangement), and also eliminate hydride shifts where positive charge is developed adjacent to the halogen substituent. So the migration of either of endo halogen substituents to C_2 or C_3 where positive charge developed and from exo direction, Y^- attacks simultaneously to the carbon atom (C_5 or C_6) to which migrating group bonded before. Accordingly, the cleaved product is exo-3-hydroxy-, endo-2-, endo-5-, exo-6-trihalonorbornane. This results may be also explained in part by the steric repulsion among endo substituents.



Scheme 2

References

1) Y. Yanagida, H. Shigesato, M. Nomura and S. Kikkawa, Bull. Chem. Soc. Jap., 47, 677 (1974).
Y. Yanagida, H. Shigesato, M. Nomura and S. Kikkawa, Nippon Kagaku Kaishi, 652 (1975).
Y. Yanagida, T.Yokota, M. Nomura and S. Kikkawa, ibid., 657 (1975).
2) E. Tobler, D.E. Battin and D. J. Foster, J. Org. Chem., 29, 2834 (1964).

(Received July 17, 1975)