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Cis- and *Trans*-Chlorination of Cyclohexene by Antimony Pentachloride and Triethyloxonium Hexachloroantimonate

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Various methods for the preparation of *trans*-1,2-dichlorocyclohexane from cyclohexene have been reported by many investigators.[1–6] On the other hand, the formation of *cis*-1,2-dichlorocyclohexane was reported by Kawamoto and Komatsu[7] only in the case of the chlorination of cyclohexene by chlorine gas in the presence of cuprous chloride. However, the physical properties of the *cis*-1,2-dichloride reported by them are different from those reported by other investigators.[8,12] The chlorinations of cyclohexene by cupric chloride have been reported to yield *trans*-1,2-dichlorocyclohexane.[6,9] Therefore, we may suppose that the chlorination by chlorine in the presence of cuprous chloride does not give *cis*-1,2-dichloride. When we chlorinated cyclohexene by many metal halides without chlorine gas, we obtained *cis*-1,2-dichlorocyclohexane only in the case of chlorination by antimony pentachloride. While we were studying the chlorination of cyclohexene by antimony pentachloride, Uemura *et al.* reported the selective *cis*-chlorination of olefins by antimony pentachloride in carbon tetrachloride.[10] In this paper we wish to report some results on the chlorination of cyclohexene in liquid sulfur dioxide by antimony pentachloride and triethyloxonium hexachloroantimonate.

Experimental

General Procedure. The cyclohexene and antimony pentachloride were distilled into glass phials under a vacuum. The liquid sulfur dioxide was distilled into a reaction vessel in which the phials of the reactants have previously been placed. Breaking the phials, the chlorination reaction was started. After an appropriate time, an aliquot of the reaction solution was poured into a dilute alkaline aqueous solution. The products of the chlorination were analyzed by gas chromatography.

Materials. The triethyloxonium hexachloroantimonate was prepared according to the method of Meerwein *et al.*[11] Found: C, 16.26; H, 3.25%. Calcd for Et_3OSbCl_6: C, 16.46; H, 3.40%. Commercially-available metal halides and cyclohexene were purified by the usual methods. The liquid sulfur dioxide was distilled over phosphorous pentoxide.

Identification of the Chlorides. The products of the chlorination of cyclohexene were separated using 2.0 m silicone gum SE 30, 15% on a chromosorb w, column. The NMR or IR spectrum of each separated chloride coincided well with that of the respective authentic sample or that recorded in the literature.[12–14)]

A. Monochlorocyclohexane

Found: C, 60.68; H, 9.25%. Calcd for $C_6H_{11}Cl$: C, 60.75; H, 9.35%.

B. *trans*-1,2-Dichlorocyclohexane——NMR: δ 3.9—4.20 (2H), 2.60—1.2 (8H); IR: 692, 738, 745 cm^{-1}.

Found: C, 47.39; H, 6.66%. Calcd for $C_6H_{10}Cl_2$: C, 47.08; H, 6.58%.

C. *cis*-1,2-Dichlorocyclohexane——NMR: δ 4.10—4.35 (2H), 1.20—2.40 (8H); IR: 696, 744 cm^{-1}.

Found: C, 47.28; H, 6.39%. Calcd for $C_6H_{10}Cl_2$: C, 47.08; H, 6.58%.

D. *trans*-1,3-Dichlorocyclohexane——NMR: δ 4.0—4.5 (2H), 1.0—2.5 (8H).

Found: C, 47.61; H, 6.60%. Calcd for $C_6H_{10}Cl_2$: C, 47.08; H, 6.58%.

Results and Discussion

We obtained only monochlorocyclohexane in the chlorination of cyclohexene by aluminum trichloride, stannic chloride, molybdenum pentachloride, and phos-

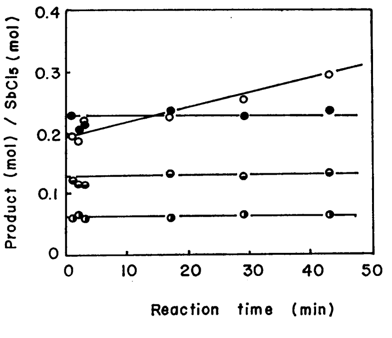

Fig. 1. The chlorination of cyclohexene by antimony pentachloride in liquid sulfur dioxide at 25°C.
$SbCl_5$ 0.14 mol/l, Cyclohexene 0.87 mol/l.
○: monochloro-, ●: *cis*-1,2-dichloro-, ◒: *trans*-1,2-dichloro-, ◑: *trans*-1,3-dichlorocyclohexane.

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Table 1. Distribution of chlorination products of cyclohexene by antimony pentachloride and triethyloxonium hexachloroantimonate

Chlorinating reagent	(mol/l)	Condition			Products mol %			
		Solvent	Temp (°C)	Cyclohexene (mol/l)	Mono-chloro-	*trans*-1,2-Dichloro-	*trans*-1,3-Dichloro-	*cis*-1,2-Dichloro-
$SbCl_5$[a)]	0.14	SO_2	25	0.87	31.7	21.1	10.7	36.5
$SbCl_5$[a)]	0.14	SO_2	25	2.49	29.1	20.2	14.2	36.5
$SbCl_5$[a)]	0.10	SO_2	−6	0.46	26.6	22.6	12.5	38.3
$SbCl_5$[a)]	0.30	*n*-hexane	25	1.86	20.8	30.7	4.0	44.5
Et_3OSbCl_6[b)]	0.15	SO_2	25	0.25	82.6	5.8	2.3	9.3

a) Initial reaction products. b) Reaction products at 2040 min.

phorous pentachloride. However, in the chlorination by antimony pentachloride, we obtained four chlorination products—monochlorocyclohexane, *trans*-1,2-dichlorocyclohexane, *trans*-1,3-dichlorocyclohexane, and *cis*-1,2-dichlorocyclohexane. As the reaction of monochlorocyclohexane with antimony pentachloride did not give the dichloride under our experimental conditions, the dichlorides were considered to result from the reaction of cyclohexene with antimony pentachloride. The yields of these products in liquid sulfur dioxide at 25 °C are plotted against the reaction time in Fig. 1. The yield of monochlorocyclohexane increased with the reaction time, but the yields of the dichlorides did not change with the reaction time. In the chlorination in *n*-hexane, we observed similar time-conversion curves. The distribution of the initial reaction products is listed in Table 1. At −70 °C in liquid sulfur dioxide, the chlorination reaction was very slow. As the reaction mixture prepared and kept for several hours at −70 °C was warmed up to 25 °C, however, the yield of the chlorination increased. In this case, however, only the chlorination product was monochlorocyclohexane, as is shown in Fig. 2. These results may be tentatively represented by the sequence of the reactions in Scheme 1. Path (c) may resemble the Diels-Alder reaction. As Path (c) does not occur at −70 °C, all of the antimony pentachloride may be converted to an intermediate, II. The hydrochlorination of cyclohexene may be a slow reaction at −70 °C. Scarecely no change of II to I may occur with an increase in the reaction temperature from −70 to 25 °C. The II intermediate is supposed not to be able to give dichlorides. Therefore, only monochlorocyclohexane was obtained upon increasing the reaction temperature from −70 to 25 °C. Upon the mixing of the reagents at 25 °C, two path, (b) and (c), may occur, thus giving both mono- and dichlorides. We obtained dichlorides in the chlorination by triethyloxonium hexachloroantimonate, as is shown in Fig. 3. The product distribution at 2040 min is shown in Table 1. Since the triethyloxonium cation is more stable than the cyclohexenyl cation, a little of the free hexachloroantimonate anion can exist in the case of triethyloxonium hexachloroantimonate, but in the case of the II intermediate none can exist. The free hexachloroantimonate anion may react with cyclohexene to give

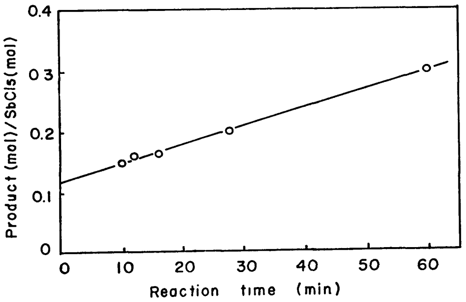
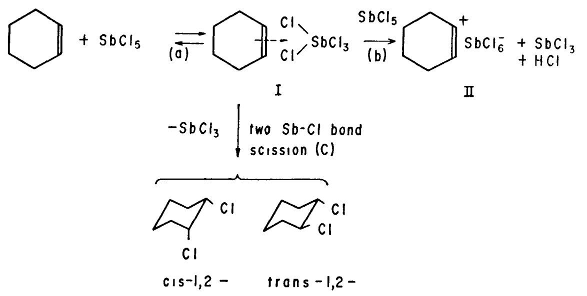


Fig. 2. The chlorination in the case that the reaction mixture was prepared at −70°C and then was warmed up to 25°C in liquid sulfur dioxide.
$SbCl_5$: 0.11 mol/l, Cyclohexene: 0.44 mol/l.
○: monochlorocyclohexane.



Scheme 1.

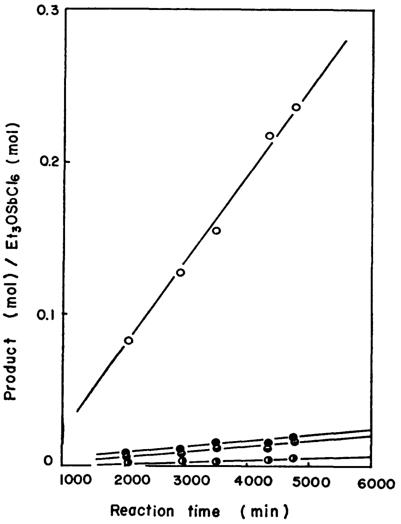


Fig. 3. The chlorination of cyclohexene by triethyloxoinum hexachloroantimonate in liquid sulfur dioxide at 25°C.
Et_3OSbCl_6 0.16 mol/l, Cyclohexene 0.25 mol/l.
○: monochloro-, ●: *cis*-1,2-dichloro-, ◒: *trans*-1,2-dichloro-, ◑: *trans*-1,3-dichlorocyclohexane.

dichlorides. However, contact-ion pairs of triethyloxonium salt or the II intermediate are considered not to give dichlorides.

The solvent effect of dichlorination is shown in Table 1. The predominance of the *cis*-chlorination is somewhat clearer in the less polar solvent, *n*-hexane, than in the more polar solvent, liquid sulfur dioxide.

At present, the mechanism of the formation of *trans*-1,3-dichlorocyclohexane is not yet clear.