BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (3), 692—697 (1974) [Vol. 47, No. 3

The Chlorination of Olefins with Antimony(V) Chloride[1)]

Sakae Uemura,* Akira Onoe, and Masaya Okano
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

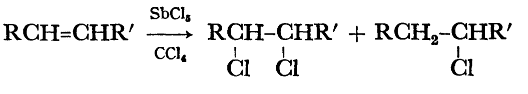
(Received August 8, 1973)

Antimony(V) chloride was revealed to be a good reagent for the *cis*-chlorination of simple olefins in chlorinated hydrocarbon solvents, such as 1,2-dichloroethane, dichloromethane, chloroform, and carbon tetrachloride. The higher the reaction temperature or the solvent polarity was, the higher the selectivity for *cis*-chlorination became. From 1,3-butadiene, *cis*-1,4-dichloro-2-butene was formed together with the *trans*-1,4- and 1,2-dichloro isomers. In the cases of cyclopentene and norbornene, the *trans*-1,2-dichloride and other various dichlorides were obtained without any formation of the *cis*-1,2-isomer. Probable mechanisms for this chlorination are briefly discussed.

Although antimony(V) chloride has been used as a reagent for the chlorination of aromatic hydrocarbons[2)] and alkanes[3)] and as an active catalyst for chlorine molecule addition to olefins,[4–6)] the direct chlorination of olefins with this reagent has not yet been studied except for only one case with α,β-dibromoethylene.[7)] After we published our preliminary data[1)] concerning a predominant *cis*-chlorination of certain olefins with antimony(V) chloride in carbon tetrachloride, an additional study of the same reaction in a more polar solvent, liquid SO_2, was described by Akiyama *et al.*[8)] In this report, all the results of the chlorination of several kinds of mono-olefins and 1,3-butadiene in less polar solvents, mainly chlorinated hydrocarbons, will be described in detail. In contrast to other metal or metalloidal chlorides,[9)] this chloride showed a striking product selectivity.

Results and Discussion

Reaction with Simple Olefins. When an olefinic hydrocarbon was added to a light-yellow homogeneous solution of antimony(V) chloride in carbon tetrachloride at room temperature, the reaction occurred exothermally to give the corresponding *vic*-dichloroalkane (**1**) in a good yield, occasionally together with small amounts of monochloride (**2**).



$$\mathrm{RCH{=}CHR'} \xrightarrow[\mathrm{CCl_4}]{\mathrm{SbCl_5}} \underset{\mathrm{Cl}\quad\mathrm{Cl}}{\mathrm{RCH{-}CHR'}} + \underset{\mathrm{Cl}}{\mathrm{RCH_2{-}CHR'}} \qquad (1)$$

1 **2**

Some typical data for several olefins are shown in Table 1. In contrast to the usual complete or predominant *trans*-addition in the chlorination using chlorine gas or other metal and metalloidal chlorides[9)] (*e.g.*, PCl_5, $CuCl_2$, $AuCl_3$, and $TlCl_3$), a favorable *cis*-addition is the most remarkable feature of this chlorination.[10)] Separate experiments revealed that no interconversion of *cis*- and *trans*-1,2-dichlorocyclohexanes occurred under the present reaction conditions. Moreover, as can be seen in Table 1, an elongation of the reaction time does not affect the ratio of *cis*- to *trans*-addition in the chlorination of *trans*-2-butene. Therefore, the observed ratio of *cis*- and *trans*-addition appears to be kinetically controlled. It should be noted that a rise in the reaction temperature resulted in a considerable increase in the *cis*-selectivity of this chlorination. The temperature dependence on the isomer ratio would indicate that both isomers may not arise from a common intermediate, as will be discussed later.

The reaction is clearly of an electrophilic nature,

Table 1. Chlorination of simple olefins by antimony(V) chloride in carbon tetrachloride [$SbCl_5$ 25 mmol, CCl_4 100 ml]

Run	Olefin	mmol	Temp. °C	Time min	Products, mmol 1 *cis*-add.	1 *trans*-add.	1 total yield, %[a)]	2	Ratio of *cis*- to *trans*-add.
1	*trans*-2-Buetne[b)]	71	73	10	19.7[f)]	4.3[g)]	96	0	4.6[l)]
2	*trans*-2-Butene[b)]	54	73	60	19.5[f)]	4.2[g)]	94	0	4.7[l)]
3	*trans*-2-Butene[b)]	30	2—6	10	17.5[f)]	7.5[g)]	100	0	2.3[l)]
4	*cis*-2-Butene[c)]	45	76	10	20.6[g)]	3.8[f)]	98	0	5.4[l)]
5	*cis*-2-Butene[c)]	61	0	10	18.0[g)]	5.9[f)]	96	0	3.1[l)]
6	*cis*-2-Octene[d)]	50	76	10	13.4[h)]	2.1[i)]	62	4.5	6.4[l)]
7	2-Octene[e)]	50	30—35	10	12.4[h)]	7.5[i)]	80	5.3	1.7
8	Cyclohexene	20	76	10	15.0[j)]	3.0[k)]	90	1.7	5.0
9[m)]	Cyclohexene	100	0—10	10	11.9[j)]	13.0[k)]	92	4.0	0.9
10	1-Octene	50	30—35	10	25.0		100	0	—
11	Allyl chloride	50	30	30	23.1		92	0	—

a) Based on $SbCl_5$. b) Contains 1% of *cis*-isomer. c) Contains 2.4% of *trans*-isomer. d) Contains 0.2% of *trans*-isomer. e) A mixture of *cis*- and *trans*-isomer (1: 1). f) *dl*-Isomer. g) *meso*-Isomer. h) *erythro*-Isomer. i) *threo*-Isomer. j) *cis*-Isomer. k) *trans*-Isomer. l) Correction based on contamination is not made. m) $SbCl_5$, 27 mmol.

because no reaction occurred with olefins having strong electron-withdrawing groups, such as acrylonitrile, ethyl maleate, ethyl fumarate, and tetrachloroethylene, even at the refluxing temperature in carbon tetrachloride, and all the olefins were recovered qualitatively. In a reaction with styrene or ethyl vinyl ether, a vigorous reduction of antimony(V) to antimony(III) occurred even at 0 °C, but only a resinous product was obtained; all attempts to isolate the dichlorinated compound were unsuccessful.

A radical pathway for the formation of **1** can be excluded by considering the following facts. First, no trace of 4-chloro-1-cyclohexene was found in the chlorination products from cyclohexene. Second, when the reaction was carried out in the presence of *m*-dinitrobenzene or oxygen, no change in the yield or in the *cis*/*trans* ratio of **1** was observed.

In order to ascertain the effect of solvents upon the stereoselectivity of the reaction, the chlorination of cyclohexene was carried out in several solvents. Some results are given in Table 2a. All the reaction mixtures were homogeneous. In chlorinated hydrocarbon solvents, the *cis*-dichloride generally predominated, and an increase in the ratio of *cis*- to *trans*-addition was observed when the dielectric constant of the solvent was increased. On the contrary, in a donor solvent such as carbon disulfide, a favorable *trans*-addition was observed. Certain polar solvents were not adequate for this chlorination; *i.e.*, when nitromethane was used as a solvent, only a slight amount of dichloride was formed from cyclohexene, and the reaction in acetonitrile afforded a tarry product. Alcohols, ethers (diethyl ether, 1,4-dioxane and tetrahydrofuran), dimethylformamide, and dimethyl sulfoxide could not be used as solvents because of a vigorous reaction or adduct formation between the solvent and antimony(V) chloride itself.

Table 2. Chlorination of cyclohexene by antimony(V) chloride

(a) Effect of solvents on the isomer ratio [$SbCl_5$ 25 mmol, solvent 100 ml]

Cyclohexene mmol	Solvent (ε)	Temp. °C	Time min	1,2-Dichlorides Yield,[a] %	*cis*/*trans* Ratio
20	$ClCH_2CH_2Cl$ (10.37)	83	10	88	8.3
20	$ClCH_2CH_2Cl$ (10.37)	20—30	10	89	4.6
100	CH_2Cl_2 (8.9)	40	10	89	4.0
100	$CHCl_3$ (4.70)	30—40	10	67	3.2
20	CCl_4 (2.23)	76	10	90	5.0
20	CCl_4 (2.23)	20—30	10	94	1.5
100	CCl_4 (2.23)	20—40	10	98	1.5
100	CS_2 (2.64)	30	10	77	0.81

(b) Effect of additives on the isomer ratio [Cyclohexene 100 mmol, $SbCl_5$ 25 mmol, CCl_4 100 ml, 76 °C, 10 min]

Additive mmol	1,2-Dichlorides Yield,[a] %	*cis*/*trans* Ratio
None	67	5.0
$SbCl_3$, 25	67	4.3
$TiCl_4$, 25	85	3.7
SbF_3, 25	52	1.2
$AlCl_3$, 25	25	0.8

a) Based on $SbCl_5$.

We should also consider briefly the source of hydrogen chloride, which gives **2** by addition to olefins. As the hydride-ion abstraction from triphenylmethane, 9,10-dihydroanthracene and cycloheptatriene with antimony(V) chloride has been established[11] to give hexachloroantimonate salts of stable carbonium ions, $SbCl_3$, and hydrogen chloride, it might be possible to assume that a similar abstraction may occur with olefins to produce hydrogen chloride. In fact, though we failed to isolate the corresponding antimonate salts or the hydrogen chloride addition product, α-chloroethylbenzene (**2**), because of the polymerization of styrene, the evolution of much hydrogen chloride was observed during the reaction of styrene. As the addition of hydrogen chloride is much easier to internal olefins than to terminal ones, **2** was not obtained from 1-octene and allyl chloride. Furthermore, the rate of the formation of **2** seems much slower than that of **1**; when the reaction was carried out using a smaller amount of cyclohexene than of antimony(V) chloride, the yield of chlorocyclohexane (**2**) became very low without affecting that of **1**. This may be a reason why **2** was not obtained from either *trans*- or *cis*-2-butenes, where the contact time of olefin and antimony(V) chloride is considered not to be very long. Another possible source of hydrogen chloride is the decomposition of antimony(III) chloride (formed through a reaction) or antimony(V) chloride by moisture.[12] However, even in the careful reaction under N_2 in a dried condition, the formation of **2** was observed, and so this possibility may be excluded.

Table 3. Chlorination of 1,3-butadiene by antimony(V) chloride in carbon tetrachloride [$SbCl_5$ 25 mmol, CCl_4 100 ml]

Diene mmol	Temp. °C	Time min	Products (mmol) and yield[a] (%)						
			Dichlorides				Tetrachlorides		
			3[b]	4[c]	5[d]	Total yield	6[e]	7[f]	Total yield
78	0	10	3.7	2.5	5.6	47	0.3	0.3	5
86	30	10	4.5	2.5	4.6	46	0.9	1.2	17
62	76	10	6.9	3.6	6.1	66	1.4	2.7	33

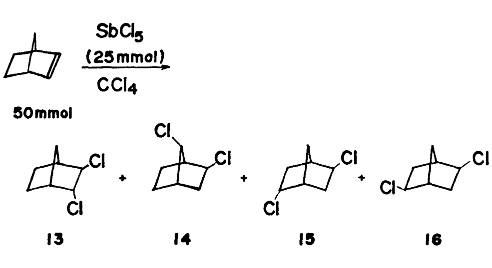
a) Based on $SbCl_5$. b) 3,4-Dichloro-1-butene. c) *cis*-1,4-Dichloro-2-butene. d) *trans*-1,4-Dichloro-2-butene. e) *dl*-1,2,3,4-Tetrachlorobutane. f) *meso*-1,2,3,4-Tetrachlorobutane.

Reaction with 1,3-Butadiene. By passing 1,3-butadiene through a CCl_4 solution of antimony(V) chloride, the following compounds were obtained as products: 3,4-dichloro-1-butene (**3**), *cis*- and *trans*-1,4-dichloro-2-butenes (**4** and **5** respectively), and two stereoisomers of tetrachlorobutanes [**6** (*dl*) and **7** (*meso*)]. Some typical data are shown in Table 3. Separate experiments eliminated the possibility of the interconversion of **3**, **4**, and **5** under the present reaction conditions. At higher temperatures the formation of **6** and **7** became prominent; they were apparently formed by a further reaction of **3**, **4**, and **5** with antimony(V) chloride. A rather high proportion of **4** (21—22%) to all the products should be noted here, together with the results of chlorination using $TlCl_3 \cdot 4H_2O$[13] (11%) and $CuCl_2$[14] (5%), because **4** has never[15] or only slightly (1%)[16] been formed in chlorination with a chlorine molecule. This fact suggests the existence of a certain interaction between metal chloride and both terminal carbons of 1,3-butadiene.

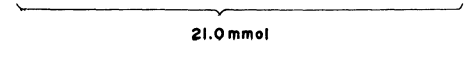
$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[CCl_4]{SbCl_5} \underset{\mathbf{3}}{CH_2{=}CHCHClCH_2Cl}$$

$$+ \underset{\mathbf{4}\ (cis)\ \&\ \mathbf{5}\ (trans)}{ClCH_2CH{=}CHCH_2Cl} + \underset{\mathbf{6}\ (dl)\ \&\ \mathbf{7}\ (meso)}{ClCH_2CHClCHClCH_2Cl} \quad (2)$$

Reaction with Cyclopentene and Norbornene. For cases of cyclopentene and norbornene, which might resist the *cis*-addition or *cis*-attack of the bulky species, the *trans*-1,2-dichloride and various unexpected dichlorides were obtained without the formation of the *cis*-1,2-isomer (Eqs. (3) and (4), where the figures in parentheses indicate a product distribution). All the dichlorides for each reaction seem to be formed by way of the corresponding carbonium ions, *i.e.*, the classical chlorocyclopentyl cation and the nonclassical chloronorbornyl cation, as will be discussed later. The reaction of cyclopentene with chlorine gas (neat or in CCl_4) has been reported[17] to yield only **10**; we found such a case also with copper(II) chloride (in acetonitrile). As to the chlorination of norbornene, the diversity of reaction products has previously been established. Thus, the chlorination with chlorine gas (in CCl_4) affords nortricyclyl chloride and *exo*-2-*syn*-7-dichloronorbornane, together with smaller amounts of *trans*-2,3- (**13**) and *exo*-*cis*-2,3-dichloronorbornane, by the ionic pathway,[18] and the reaction with gold(III) chloride (in cyclohexane) gives a mixture of *exo*-*cis*-2,5-dichloronorbornane (**16**), *exo*-2-*syn*-7-dichloronorbornane, and two unidentified isomeric dichlorides.[19] We have also confirmed that the chlorination with copper(II) chloride (in acetonitrile) yields mainly the *trans*-2,3- (**13**) and *exo*-*cis*-2,3-dichlorides, just as does the reaction with iodobenzene dichloride.[20]



(3)



(4)

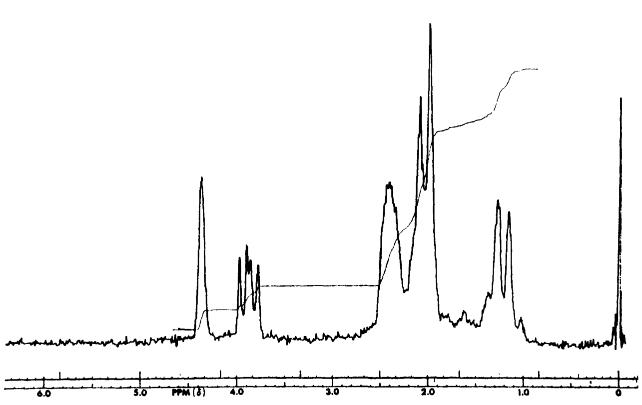


Fig. 1. NMR spectrum of **14** in CCl_4.

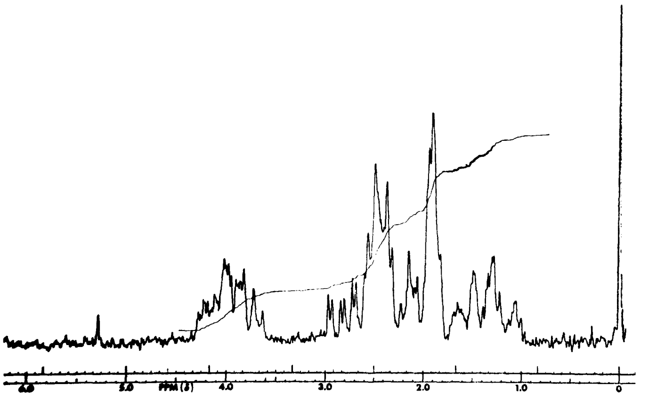
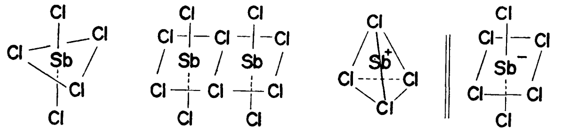


Fig. 2. NMR spectrum of **15** in CCl_4.

Probable Reaction Mechanisms. The nature of antimony(V) chloride in solutions appears to depend on the polarity of the solvents. Thus, in acetonitrile (ε 37.5) the conductivity data have shown that $SbCl_5$ is in equilibrium with $SbCl_4^+$ and $SbCl_6^-$,[21] while in carbon tetrachloride (ε 2.23) it has been established that the vibrational spectra are consistent with the D_{3h} symmetry expected for covalent antimony(V) chloride; *i.e.*, the predominant species is the monomeric molecules.[22] In contrast to such thermodynamic data, Kovacic and Sparka have assumed the attack of the $SbCl_4^+$ moiety formed from two molecules of antimony(V) chloride (see Eq. (5)) in the reaction of benzene, toluene, and chlorobenzene with antimony(V) chloride (below 40 °C), where an excess aromatic component (ε 2.27—5.61) is used as the solvent.[2] Since the reaction conditions of our chlorination and the electrophilic nature of the reaction are apparently similar to those of this aromatic chlorination, a similar participation of the ionic species—an initial attack of $SbCl_4^+$ on olefins, followed by a Cl^- transfer from $SbCl_6^-$ to give *trans*-dichlorides—might be expected, though the concentration of these species is believed to be very low. In this connection, a considerable decrease in the ratio of *cis*- to *trans*-addition was observed upon the addition of a strong Lewis acid (*e.g.*, $AlCl_3$ and SbF_3) to our chlorinating system (see Table 2b), where a complex formation of antimony(V) chloride with Lewis acid is to be expected (Eq. (6)).

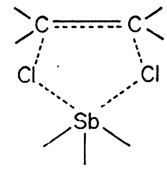
$$\underset{\mathbf{17}}{2SbCl_5} \rightleftarrows \underset{\mathbf{18}}{(SbCl_5)_2} \rightleftarrows \underset{\mathbf{19}}{SbCl_4^+\|SbCl_6^-} \qquad (5)$$



17 **18** **19**

$$SbCl_5 + MXn \rightleftarrows \underset{\mathbf{20}}{SbCl_4^+\|MXnCl^-} \qquad (6)$$

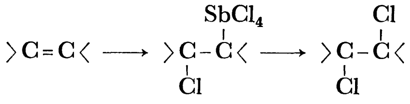
On the other hand, the formation of *cis*-dichlorides can presumably be explained by a concerted or near-concerted molecular addition of **17** or **18** to olefins, as has been proposed in connection with the chlorination of olefins by iodobenzene dichloride.[23] The distance



of any two chlorines is about 3.2—4.0 Å, assuming that the antimony-chlorine bond length of antimony(V) chloride is 2.29—2.34 Å[24] even in the liquid state; this is large enough for the interaction of two chlorines with two p-orbitals of simple olefins and even of 1,3-butadiene at the 1,4-position. The rather high proportion of *cis*-1,4-dichloro-2-butene (**4**) in the reaction products of 1,3-butadiene may be explained by assuming this interaction at the *s-cis*-conformation of 1,3-butadiene.

Since the ionization step in Eq. (5) is considered to be exothermic, like that of PCl_5,[25] the amount of **19** can be expected to increase when the temperature is lowered. The observed temperature effect on the isomer ratio in each solvent agreed with this expectation (see Table 2a). It is also anticipated that an increase in the solvent polarity would increase the proportion of ionized species. However, apparently a different trend was observed within a range of selected chlorinated hydrocarbon solvents (ε 2.23—10.37): namely, the higher the solvent polarity was, the higher the *cis*-selectivity became (see Table 2a). This may be explained by considering the large difference in the solvent effect on the rate between two chlorination reaction; *i.e.*, a change to a more polar solvent will increase the rate of the *cis*-addition (the reaction between two uncharged species) and will decrease that of the *trans*-addition (the reaction between uncharged and charged species).[26] The low *cis*-selectivity in carbon disulfide (ε 2.64) compared with that in carbon tetrachloride (ε 2.23) might be ascribed to the stabilization of **19** by solvation.

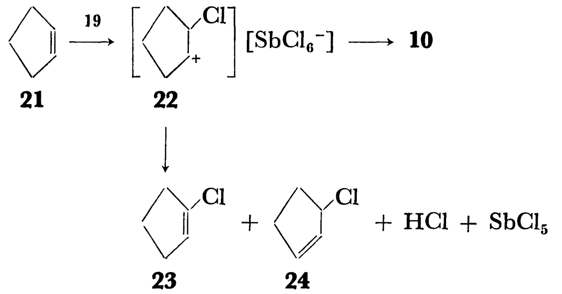
Another possible scheme for the chlorination is the addition of both chlorine and tetrachloroantimony species to olefin, followed by the displacement of antimony with chlorine (Eq. (7)), as has been estab-



$$>C=C< \longrightarrow >\underset{Cl}{C}-\overset{SbCl_4}{C}< \longrightarrow >\underset{Cl}{C}-\overset{Cl}{C}< \qquad (7)$$

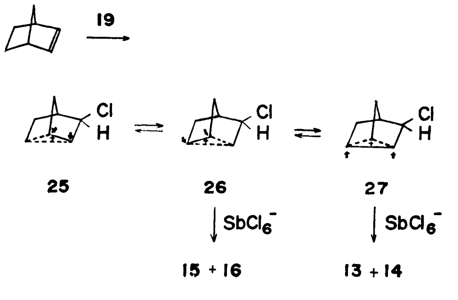
lished in the case of PCl_5.[27] However, the *trans* compound should be obtained preferably or exclusively by this scheme, as in the case of a reaction using PCl_5;[27] also, even careful experiments have failed to isolate the intermediate antimony compound. From these facts, this scheme can be excluded from consideration.

Finally, reasonable pathways to various unexpected chlorides derived from cyclopentene and norbornene were considered. If the *cis*-addition proceeds through a concerted or near-concerted transfer of chlorine between **17** or **18** and olefin, as has been described previously, quite a large steric hindrance would be unavoidable for both olefins and the attack of the $SbCl_4^+$ moiety of **19** may become important. In addition, an eclipsing effect at the Cl^--transfer step may affect the reaction products. In fact, the obtained 1,2-dichlorides consisted entirely of the *trans*-isomer. Further, the formation of 1,1- and 1,3-dichlorocyclopentanes from cyclopentene can be explained by assuming the deprotonation of the cation, **22** (Eqs. (8) and (9)). In the case of norbornene, the attack of $SbCl_6^-$ from a less crowding site upon each of the nonclassical



(8)

$$\left.\begin{array}{l} \mathbf{21} \xrightarrow{HCl} \mathbf{8} \\ \mathbf{23} \xrightarrow{HCl} \mathbf{9} + \mathbf{10} \\ \mathbf{24} \xrightarrow{HCl} \mathbf{10} + \mathbf{11} + \mathbf{12} \end{array}\right\} \qquad (9)$$



(10)

ions in equilibrium[28] may be expected, and all expected dichlorides were obtained except for those from **25** (Eq. (10)). The results seem to provide chemical evidence for the existence of such an equilibrium.

Experimental

Materials. Commercially-available *trans*-2-butene (contains 1% of the *cis*-isomer), *cis*-2-butene (contains 2.4% of the *trans*-isomer), and 1,3-butadiene were used without further purification, while $SbCl_5$ and all the other organic substrates and solvents were purified by distillation before use.

General Procedure. An appropriate amount of an olefinic hydrocarbon was added or bubbled into a homogeneous yellow solution of $SbCl_5$ (sometimes containing another Lewis acid salt as an additive) in a suitable solvent under stirring. The resulting black–red reaction mixture was cooled, aqueous NaOH was added, and the antimony(III) oxychloride or pentoxydichloride formed was filtered out.* The products in the filtrate sepatated from water were analyzed by glc with an appropriate internal standard material. The product composition was almost unchanged in the reverse reaction, *i.e.*, the drop-by-drop addition of $SbCl_5$ to a solution containing olefin.

a) 1,3-Butadiene: 1,3-Butadiene gas (4.6 g, 86 mmol) was bubbled into a CCl_4 (100 ml) solution of $SbCl_5$ (7.5 g, 25 mmol) at 30 °C for 10 min. The mixture was then treated as described above; the subsequent glc analysis of the CCl_4 layer showed the presence of these five components as products; 3,4-dichloro-1-butene (**3**; 0.56 g, 4.5 mmol), *cis*-1,4-(**4**; 0.31 g, 2.5 mmol) and *trans*-1,4-dichloro-2-butene (**5**; 0.58 g, 4.6 mmol), and *dl*-1,2,3,4- (**6**; 0.22 g, 1.2 mmol) and *meso*-1,2,3,4-tetrachlorobutane (**7**; 0.17 g, 0.9 mmol). A mixture of **4** and **5** (**4**: **5**=*ca.* 1: 2) was isolated by distillation (bp 51—53 °C/22 mmHg) from the reaction products of several runs. NMR (in $CDCl_3$) of the mixture; δ 6.05—5.7 (m, 2H), 4.2—4.0 (m, 4H). Found: C, 37.64; H, 4.72; Cl, 56.38%. Calcd. for $C_4H_6Cl_2$: C, 38.43; H, 4.84; Cl, 56.73%.

When 1,3-butadiene (3.5 g, 65 mmol) was passed into a CCl_4 (25 ml) solution of $SbCl_5$ (15 g, 50 mmol) at 76 °C for 10 min, a mixture of isomeric tetrachlorobutanes (**6** and **7**) was obtained as the main product (12.7 mmol, **6**: **7**=1: 2.7). Found: C, 24.53; H, 3.14; Cl, 72.33%. Calcd. for $C_4H_6Cl_4$: C, 24.52; H, 3.08; Cl, 72.39%. **7** was isolated as a solid and was revealed to be a *meso*-isomer; mp 72 °C from ethanol (lit.,[15] 72 °C).

b) Cyclopentene: The reaction of cyclopentane (3.4 g, 50 mmol) with $SbCl_5$ (7.5 g, 25 mmol) in CCl_4 (100 ml) at 25 °C for 5 min afforded a mixture of five products: **8** (7.4 mmol) and **9**—**12** (22.3 mmol, **9**: **10**: **11**: **12**=30: 31: 26: 13 by g.l.c.). A simple distillation gave 2.6 g, (18.7 mmol) of a mixture of **9**—**12**, which was revealed by analysis to be composed of isomeric dichlorocyclopentanes; bp 61—64 °C/42 mmHg. Found: C, 43.19; H, 5.97%. Calcd for $C_5H_8Cl_2$: C, 43.19; H, 5.80%. Further products, **9**, **10**, **11**, and **12**, were purely isolated by preparative glc, and comparisons of the NMR spectra and retention time on glc with those of the reported ones[29] revealed the compounds to be 1,1-, *trans*-1,2-, *trans*-1,3-, and *cis*-1,3-dichlorocyclopentane respectively. The chlorination of cyclopentene with a chlorine molecule in CCl_4[17] at room temperature afforded only **10** (by glc). **10** (1.2 g) could also be prepared by the reaction of cyclopentene (3.4 g) with $CuCl_2$ (3.4 g) in acetonitrile (25 ml) containing LiCl (1.1 g) at 80 °C for 3 hr; bp 50—51 °C/22 mmHg (lit.,[17] 53—53.5 °C/25 mmHg).

The reaction using 1,2-dichloroethane as a solvent at 84 °C for 10 min gave **9**, **10**, **11**, and **12** in the ratio of 18: 32: 30:: 20 (19 mmol).

c) Norbornene: The reaction of norbornene (4.7 g, 50 mmol) with $SbCl_5$ (7.5 g, 25 mmol) in CCl_4 (100 ml) at 26 °C for 10 min gave a mixture of four products (21 mmol, **13** : **14** : **15** : **16**=4 : 51 : 23: 22 by glc), all of which were revealed to be isomeric dichloronorbornanes by analysis; bp 92—98 °C/18 mmHg. Found: C, 50.72; H, 6.16%. Calcd for $C_7H_{10}Cl_2$: C, 50.93; H, 6.11%. After the fractional distillation of the mixture (a, bp 83—86 °C/13 mmHg; b, 86—87 °C/13 mmHg; c, 54—55 °C/2 mmHg), three products, **14**, **15**, and **16**, were purely isolated from Fraction a, b, and c respectively, by preparative glc. The NMR spectrum (in CCl_4) and the retention time on glc of **13** were identical with those of *trans*-2,3-dichloronorbornane, which was obtained from the reaction of norbornene (4.7 g) and $CuCl_2$ (13.4 g) in acetonitrile (200 ml) containing LiCl (4.2 g) at 84 °C for 3 hr; δ 4.3—4.1 (m, 1H), 3.7—3.6 (t, J=2 Hz, 1H) 2.6—2.3 (m, 2H), 2.1—1.1 (m, 6H). In the chlorination with $CuCl_2$, a slight formation of the *cis*-*exo*-2,3-dichloroisomer was also detected, together with **13** (yield, 6.7 g; *cis*: *trans*=*ca.* 1: 8). The NMR spectrum (in CCl_4) of **16** was identical with that of *exo*-*cis*-2,5-dichloronorbornane reported by Hüttel *et al.*;[19] δ 3.8—3.6 (t, J=5.5 Hz, 2H), 2.6—2.4 (m, 2H), 2.0—1.8 (m, 6H). The NMR spectra (in CCl_4) of **14** and **15** are shown in Figs. 1 and 2; **14**, δ 4.35 (s, 1H), 4.0—3.75 (m, 1H), 2.5—2.25 (m, 2H), 2.2—1.9 (m, 4H), 1.4—1.1 (m, 2H); **15**, δ 4.3—3.6 (m, 2H), 3.0—2.0 (m, 4H), 2.0—1.8 (m, 2H), 1.8—1.0 (m, 2H). The possibility of **14** and **15** being *cis*-*exo*-2,3- and *exo*-2-*syn*-7-dichloronorbornanes was eliminated, as well as the possibility of their being *cis*-*endo*-2,3-dichloroisomer (lit.,[18b] mp 70—72 °C), by a comparison of the retention time on glc and of the boiling point with the samples prepared by the reported method.[18a] Thus, **14** and **15** should be either *exo*-2-*anti*-7-, *trans*-2,5-, or *cis*- or *trans*-2,6-dichloronorbornane. In deuterated pyridine, a broad resonance near δ 2.4 of **14** in CCl_4 was split into two kinds of peaks, δ 2.15 (m) and 2.35 (m). Further, the sharp singlet peak at δ 4.35 of **14** can most reasonably be explained by identifying it as the *syn*-proton on C_7 bearing Cl. Thus, **14** is assigned to *exo*-2-*anti*-7-dichloronorbornane (lit.,[30] bp 77—81 °C/10 mmHg). A multiplet absorption at δ 4.3—3.6 in **15** shows the presence of both *exo*- (δ 4.3—4.0) and *endo*-(δ 4.0—3.6) protons; this appears to favor a *trans*-dichloride structure. If **15** is the *trans*-2,6-isomer, the peak of 2-*endo*-H can be expected to appear at a much lower field than usual because of the anisotropy of 6-*endo*-Cl. Thus, **15** can be assigned to *trans*-2,5-dichloronorbornane.

The reaction using 1,2-dichloroethane as a solvent at 84 °C for 10 min gave **13**, **14**, **15**, and **16** in the ratio of 5: 22: 40: 33 (20 mmol).

Attempted Isomerization of cis- *and* trans-*1,2-Dichlorocyclohexanes.* A mixture of the *cis*- and *trans*-dichlorides (2 g, *cis*/*trans*=1.6) was heated in 40 ml of CCl_4 containing 0.2 g of $SbCl_3$ and 0.3 g of $SbCl_5$ at a refluxing temperature (76 °C). Glc analysis after 2 hr gave an almost unchanged isomer ratio, *i.e.*, *cis*/*trans*=1.68.

Authentic Samples for glc. Both *meso*-2,3- (containing

---

* In separate experiments we have confirmed that the decomposition of $SbCl_3$ with water gave hydrogen chloride, which reacted easily with cyclohexene and 2-octene to afford monochloroalkanes (**2**) at room temperature. In order to avoid the formation of **2** by this route, the reaction mixture was treated with aqueous NaOH instead of water.

9.5% *dl*-isomer) and *dl*-2,3-dichlorobutane (containing 9.4% *meso*-isomer) were prepared by the reported method[31] by the reaction of *trans*- and *cis*-2-butenes with chlorine respectively at −40 °C. The *cis*-1,2-dichlorocyclohexane was obtained from the reaction of *trans*-2-chlorocyclohexanol with thionyl chloride in pyridine.[32] *trans*-1,2-Dichlorocyclohexane, 1,2-dichlooctane, and *threo*-2,3-dichlorooctane were prepared by the reaction of the corresponding olefins with Cl_2 or $CuCl_2$.[33] The *erythro*-2,3-dichlorooctane was isolated by the reaction of *cis*-2-octene with $SbCl_5$; bp 77—79 °C/10 mm, Found: C, 52.33; H. 8.91; Cl 38.24%. Calcd. for $C_8H_{16}Cl_2$: C, 52.47; H, 8.81; Cl, 38.73%. The monochloroparaffins, 1,2,3-trichloropropane, 3,4-dichloro-1-butene, and *trans*-1,4-dichloro-2-butene were commercially available.

Analytical Instruments. The IR and NMR spectra were determined by the use of a Hitachi EPT-S2 apparatus and a Varian A-60 (CCl_4 or $CDCl_3$ solvent, with TMS as the internal standard) apparatus respectively. Gas chromatographies were carried out by the use of two Shimadzu apparatuses 5APTF and 4BMPF [PEG 20M (25%)-Shimalite (3 m), PEG 6000 (25%)-Chromosorb-W (3 m), Apiezon L (30%)-Celite (1 m) and DEGS (25%)-Shimalite (3 m) columns; carrier gas, He].

References

1) Preliminary communication, S. Uemura, O. Sasaki, and M. Okano *Chem. Commun.*, **1971**, 1064.

2) P. Kovacic and A. K. Sparka, *J. Amer. Chem. Soc.*, **82**, 5740 (1960).

3) P. Kovacic and J-H. C. Chang, *J. Org. Chem.*, **36**, 3138 (1971) and references therein.

4) M. R. Radcliffe and C. E. Best, U. S. 2445729; *Chem. Abstr.*, **42**, 8207 (1948).

5) M. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Amer. Chem. Soc.*, **73**, 3329 (1951).

6) R. E. Buckles and D. F. Knaack, *J. Org. Chem.*, **25**, 20 (1960).

7) H. van de Walle, *Bull. Soc. Chim. Belg.*, **28**, 304 (1919).

8) F. Akiyama, T. Horie, and M. Matsuda, This Bulletin, **46**, 1888 (1973).

9) For a recent review, see S. Uemura and M. Okano, *Bull. Inst. Chem. Res. Kyoto Univ.*, **50**, 423 (1972).

10) A favorable *cis*-chlorination has been known for some olefins such as stilbene and acenaphtylene.[10a] Recent report of *cis*-chlorination of olefins by iodobenzene dichloride is also worth to be referred.[10b]

a) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, Amsterdam 1966, p. 92. b) M. Devillier and H. Bodot, *Bull. Soc. Chim. France*, **1972**, 227.

11) J. Holmes and R. Pettit, *J. Org. Chem.*, **28**, 1695 (1963).

12) In connection to this, see a footnote of experimental section.

13) S. Uemura, O. Sasaki, and M. Okano, This Bulletin, **45**, 1482 (1972).

14) W. C. Baird, Jr., J. H. Surridge, and M. Buza, *J. Org. Chem.*, **36**, 2088, 3324 (1971).

15) a) I. E. Muskat and H. E. Northrup, *J. Amer. Chem. Soc.*, **52**, 4043 (1930). b) K. Mislow and H. M. Hellman, *ibid.*, **73**, 244 (1951).

16) M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966).

17) H. L. Goering and F. H. McCarron, *J. Amer. Chem. Soc.*, **78**, 2270 (1956). We have confirmed the stereospecificity of the reaction by glc.

18) a) M. L. Poutsma, *ibid.*, **87**, 4293 (1965). b) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

19) R. Hüttel, H. Reinheimer, and K. Nowak, *Chem. Ber.*, **101**, 3761 (1968).

20) D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33**, 38 (1968).

21) L. Kolditz and H. Preiss, *Z. Anorg. Allg. Chem.*, **310**, 242 (1961).

22) a) G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963). b) I. R. Beattie, T. Gilson, K. Livingston, V. Fawcett, and G. A. Ozin, *J. Chem. Soc., A*, **1967**, 712. Further, we have confirmed that no appreciable absorption assigned to $SbCl_6^-$ is found in the Laser Raman spectrum (excited by Ar^+ 4880 Å) of $SbCl_5$ (in CCl_4). Measurement was kindly furnished by Professor T. Takenaka of our Institute.

23) D. H. R. Barton and E. Miller *J. Amer. Chem. Soc.*, **72**, 370 (1950).

24) S. M. Ohlberg, *ibid.*, **81**, 811 (1959).

25) R. W. Suter, H. C. Knachel, V. P. Petro, J. H. Howatson, and S. G. Shore, *ibid.*, **95**, 1474 (1973).

26) For leading references, *e.g.*, a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd Ed. Cornell University Press, Ithaca (1969), p. 457. b) K. B. Wiberg, "Physical Organic Chemistry", John Wiley, New York (1964), p. 374.

27) D. P. Wyman, J. Y. C. Wang and W. R. Freeman, *J. Org. Chem.*, **28**, 3173 (1963).

28) A spectral evidence for equilibrium of non-classical norbornyl (unsubstituted) cations was given by G. A. Olah *et al.* [*J. Amer. Chem. Soc.*, **92**, 4627 (1970)].

29) G. A. Russel and A. Ito, *ibid.*, **85**, 2983 (1963).

30) H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956).

31) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

32) B. Carroll, D. G. Kubler, H. W. Davis, and A. M. Whaley, *ibid.*, **73**, 5382 (1951).

33) K. Ichikawa, S. Uemura, T. Hiramoto, and Y. Takagaki, *Kogyo Kagaku Zasshi.*, **71**, 1657 (1968).