

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.

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 established¹¹ to give hexachloroantimonate salts of stable carbonium ions, SbCl₃, 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 N₂ in a dried condition, the formation of **2** was observed, and so this possibility may be excluded.

TABLE 2. CHLORINATION OF CYCLOHEXENE BY ANTIMONY(V) CHLORIDE
(a) Effect of solvents on the isomer ratio [SbCl₅, 25 mmol, solvent 100 ml]

Cyclohexene mmol	Solvent (ϵ)	Temp. °C	Time min	1,2-Dichlorides	
				Yield, ^{a)} %	<i>cis/trans</i> Ratio
20	ClCH ₂ CH ₂ Cl (10.37)	83	10	88	8.3
20	ClCH ₂ CH ₂ Cl (10.37)	20—30	10	89	4.6
100	CH ₂ Cl 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, SbCl₅, 25 mmol, CCl₄, 100 ml, 76 °C, 10 min]

Additive mmol	1,2-Dichlorides	
	Yield, ^{a)} %	<i>cis/trans</i> 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

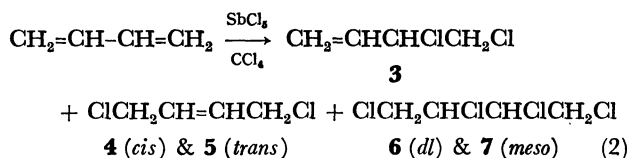
a) Based on SbCl₅.

TABLE 3. CHLORINATION OF 1,3-BUTADIENE BY ANTIMONY(V) CHLORIDE IN CARBON TETRACHLORIDE [SbCl₅, 25 mmol, CCl₄, 100 ml]

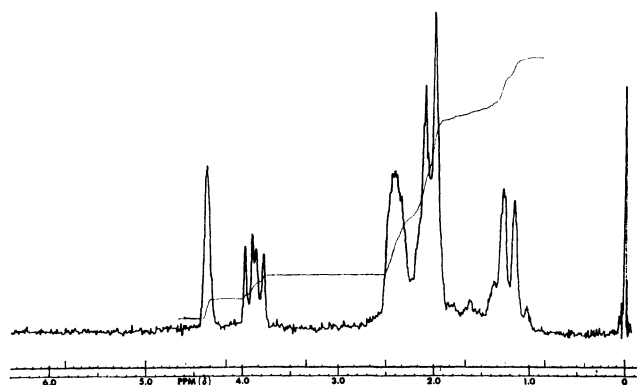
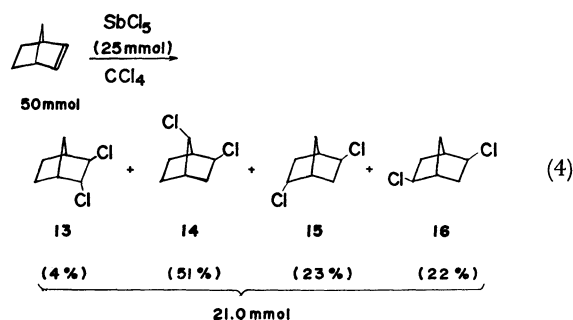
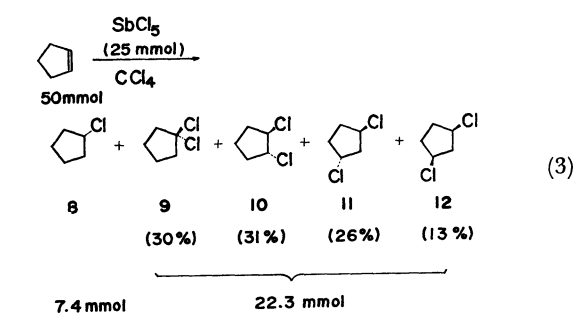
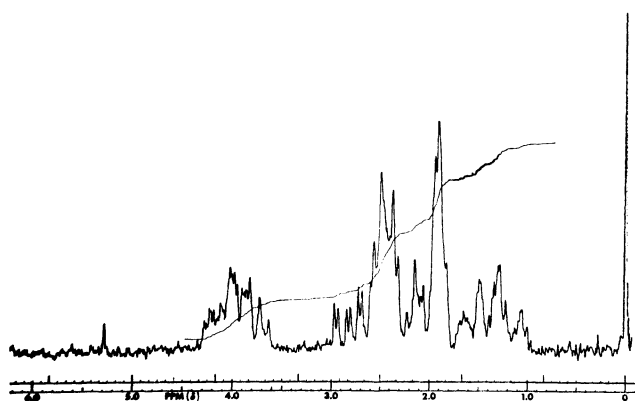
Diene mmol	Temp. °C	Time min	Products (mmol) and yield ^{a)} (%)						
			Dichlorides				Tetrachlorides		
			3 ^{b)}	4 ^{c)}	5 ^{d)}	Total yield	6 ^{e)}	7 ^{f)}	Total yield
78	0	10	3.7	2.5	5.6	47	0.3	0.3	5
86	30	10	4.5	2.5	4.6	46	0.9	1.2	17
62	76	10	6.9	3.6	6.1	66	1.4	2.7	33

a) Based on SbCl₅. 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 inter-conversion 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 $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ ¹³ (11%) and CuCl_2 ¹⁴ (5%), because **4** has never¹⁵ 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.



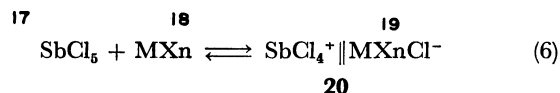
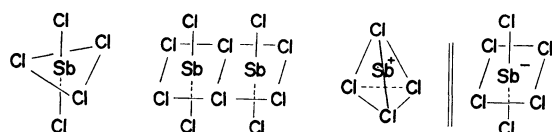
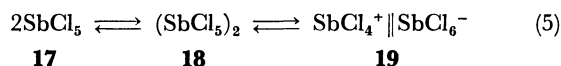
Reaction with Cyclopentene and Norbornene. For cases of cyclopentene and norbornene, which might resist the *cis*-addition or *cis*-attack of the bulky species, the *trans*-1,2-dichloride and various unexpected dichlorides were obtained without the formation of the *cis*-1,2-isomer (Eqs. (3) and (4), 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 reported¹⁷ to yield only **10**; we found

Fig. 1. NMR spectrum of **14** in CCl_4 .Fig. 2. NMR spectrum of **15** in CCl_4 .

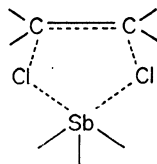
such a case also with copper(II) chloride (in acetonitrile). As to the chlorination of norbornene, the diversity of reaction products has previously been established. Thus, the chlorination with chlorine gas (in CCl_4) affords nortricyclyl chloride and *exo*-2-*syn*-7-dichloronorbornane, together with 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

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 2.27–5.51) is used as the solvent.² Since the re-

action 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)).



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

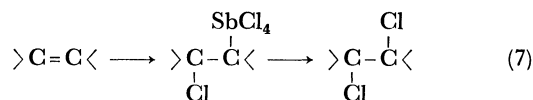


of any two chlorines is about 3.2–4.0 Å, assuming that the antimony-chlorine bond length of antimony(V) chloride is 2.29–2.34 Å²⁴⁾ even in the liquid state; this is large enough for the interaction of two chlorines with two p-orbitals of simple olefins and even of 1,3-butadiene at the 1,4-position. The 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 be-

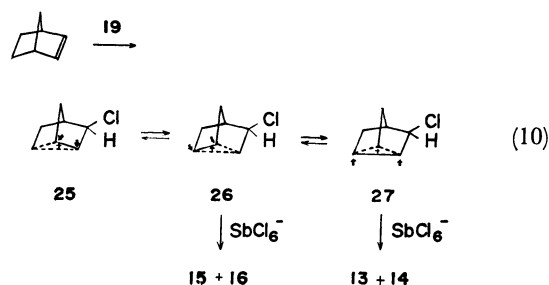
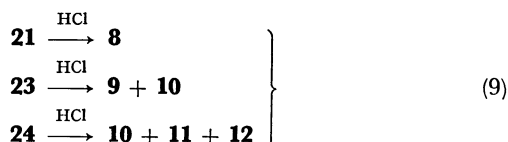
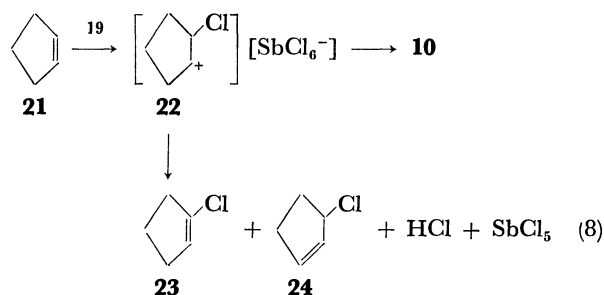
tween two uncharged species) and will decrease that of the *trans*-addition (the reaction between uncharged and charged species).²⁶⁾ The low *cis*-selectivity in carbon disulfide (ϵ 2.64) compared with that in carbon tetrachloride (ϵ 2.23) might be ascribed to the stabilization of **19** by solvation.

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-



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



ions in equilibrium²⁸⁾ 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 SbCl₅ 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 SbCl₅ (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 separated 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 SbCl₅ to a solution containing olefin.

a) 1,3-Butadiene: 1,3-Butadiene gas (4.6 g, 86 mmol) was bubbled into a CCl₄ (100 ml) solution of SbCl₅ (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 CCl₄ 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 CDCl₃) 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 C₄H₆Cl₂: C, 38.43; H, 4.84; Cl, 56.73%.

When 1,3-butadiene (3.5 g, 65 mmol) was passed into a CCl₄ (25 ml) solution of SbCl₅ (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 C₄H₆Cl₄: 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 cyclopentene (3.4 g, 50 mmol) with SbCl₅ (7.5 g, 25 mmol) in CCl₄ (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 C₅H₈Cl₂: 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 ones²⁹⁾ 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 CCl₄¹⁷⁾ 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 CuCl₂ (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 SbCl₅ (7.5 g, 25 mmol) in CCl₄ (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 C₇H₁₀Cl₂: 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 CCl₄) 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 CuCl₂ (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 CuCl₂, 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 CCl₄) 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 CCl₄) 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 CCl₄ 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 C₇ 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 CCl₄ containing 0.2 g of SbCl₃ and 0.3 g of SbCl₅ 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 SbCl₅ 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 method³¹⁾ 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-dichlorooctane, 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 $77-79^{\circ}\text{C}/10\text{ mm}$, Found: C, 52.33; H, 8.91; Cl 38.24%. Calcd. for $\text{C}_8\text{H}_{16}\text{Cl}_2$: 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

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