Chlorinations of Olefins and Dienes with Antimony Pentachloride

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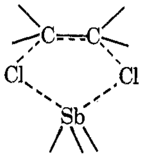
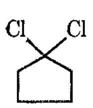
Received December 29, 1975

The addition of antimony pentachloride to several olefins and dienes is reported. In some cases, the reactions of the olefins and dienes and $SbCl_5$ have been examined in previous studies; we report on them here either because our data are in disagreement, or because we interpret these data differently. For example, it was reported previously that cyclopentene and $SbCl_5$ reacted to give 1,1-dichlorocyclopentane, *trans*-1,2-dichlorocyclopentane, *cis*-1,3-dichlorocyclopentane, and *trans*-1,3-dichlorocyclopentane by addition of HCl to intermediates 1-chlorocyclopentene and 3-chlorocyclopentene. Our data suggests that this cannot be the case since 1-chlorocyclopentene and 3-chlorocyclopentene do not react with HCl under the reaction conditions. We propose instead that all of the dichlorides result from addition of chloride ion to intermediate chlorocyclopentyl carbonium ions; the 1,1-dichloride and 1,3-dichlorides result from carbonium ions which are formed by hydride shifts. Two previous studies propose that $SbCl_5$ reacts with butadiene to give 3,4-dichloro-1-butene and *trans*-1,4-dichloro-2-butene by concerted additions. On the basis of our study on the reaction of cyclopentadiene and $SbCl_5$, we suggest that both butadiene and cyclopentadiene react with $SbCl_5$ by a carbonium ion mechanism. In spite of a report that *trans,trans*-2,4-hexadiene and $SbCl_5$ react to give only polymeric material, we found that 1,2- and 1,4-dichlorides are obtained under appropriate conditions. The 1,4 addition cannot be concerted since symmetry considerations indicate that a concerted addition should give only anti 1,4 addition; nearly equal amounts of syn and anti 1,4 additions were obtained experimentally. Evidence from previous studies on the reactions of $SbCl_5$ with olefins and dienes, and from our studies on cyclopentadiene, the isomeric 2,4-hexadiene, *cis*- and *trans*-piperylene, isoprene, and *cis*- and *trans*-β-methylstyrene, leads us to the conclusion that $SbCl_5$ can add to olefins and dienes either by a carbonium ion mechanism or a concerted mechanism, depending on the stability of the intermediate carbonium ion. As has been reported previously with butadiene, isoprene, *cis*- and *trans*-piperylene, *trans,trans*- and *cis,trans*-2,4-hexadiene, but not *cis,cis*-2,4-hexadiene, give *cis*-1,4-dichloride. Mechanisms for the reaction of $SbCl_5$ with these dienes to give the thermodynamically less stable *cis*-1,4-dichloride are discussed.

Recently Uemura and co-workers reported on the chlorination of several olefins, butadiene, and 1,5-octadiene with antimony pentachloride ($SbCl_5$).[1-3] With the simple olefins a preponderance of syn 1,2 addition was observed, with the exception of cyclopentene. They explained the syn 1,2 addition on the basis of a concerted molecular addition of $SbCl_5$ to the olefins as shown below.



In the case of cyclopentene they observed no syn 1,2 addition but reported the formation of the following products (some 1-chlorocyclopentane was also detected).



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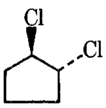

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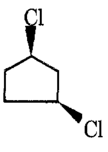

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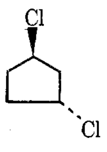

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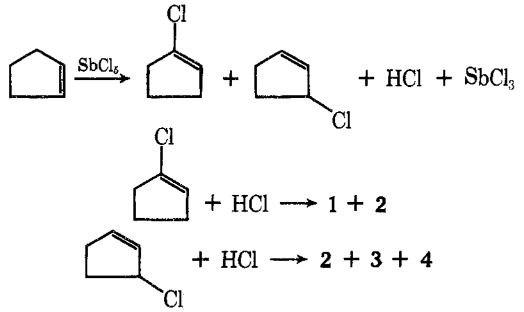
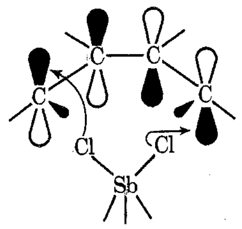
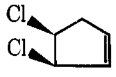
To account for these products they suggested that cyclopentene reacted with $SbCl_5$ to give initially 1-chlorocyclopentene and 3-chlorocyclopentene, and that these intermediates reacted further with HCl to give **1**, **2**, **3**, and **4**. However, they did not establish this experimentally.



Uemura and co-workers also observed that 1,3-butadiene reacts with $SbCl_5$ to give an unexpectedly large amount of *cis*-1,4-dichloro-2-butene, in addition to the expected 3,4-dichloro-1-butene and *trans*-1,4-dichloro-2-butene. They proposed that the cis 1,4 addition resulted from a concerted 1,4 addition of $SbCl_5$ to the s-cis conformer of butadiene. At this same time, Vignes and Hamer[4] also reported on the reaction of 1,3-butadiene and $SbCl_5$. Their experimental observations were essentially identical with those of Uemura and co-workers. Vignes and Hamer also accounted for the large amount of cis 1,4 addition on the basis of a concerted 1,4 addition to the s-cis conformer, but they correctly suggested that because of orbital symmetry control the addition must occur in an antarafacial direction, as shown below.



It seemed to us that an antarafacial addition of $SbCl_5$ to the s-cis conformer of butadiene was unlikely because of steric hindrance between the large antimony system and the cis 1,4-vinyl hydrogens. We felt that this proposed mechanism could be probed by studying the reaction of cyclopentadiene and $SbCl_5$. In the case of cyclopentadiene an antarafacial, concerted 1,4 addition is impossible because of interference between the antimony system and the methylene group in cyclopentadiene. Therefore if anti 1,4 addition does occur (to give *trans*-3,5-dichlorocyclopentene) it would mean either (or both) that cyclopentadiene and butadiene react with $SbCl_5$ by different mechanisms, or that another interpretation is required to explain the data from the reaction of butadiene and $SbCl_5$. It should also be pointed out that syn 1,4 addition of $SbCl_5$ to cyclopentadiene by a concerted mechanism is symmetry forbidden. We recently reported an investigation[5] of the chlorination of cyclopentadiene with molecular chlorine, and, therefore, the dichloride products (shown below) were already known.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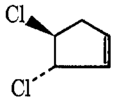
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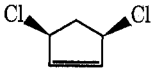
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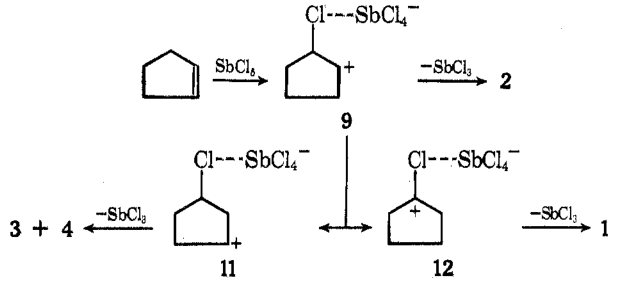
Results and Discussion

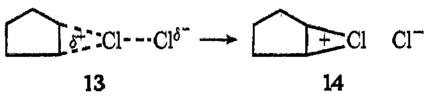
The results from the reaction of cyclopentadiene and $SbCl_5$ in different solvents are summarized in Table I, along with results from our previous study[5] with molecular chlorine, for comparative purposes. The data in Table I show that much larger amounts of *trans*-3,5-dichloropentene (**8**) were formed with $SbCl_5$ than were formed with chlorine. Therefore, at least in the case of cyclopentadiene, another mechanism other than a concerted 1,4 addition is required to account for the formation of **8**, and indeed of *cis*-3,5-dichlorocyclopentene (**7**).

At this point we carefully reexamined the reactions of $SbCl_5$ with cyclopentene, cyclohexene, and butadiene, and obtained essentially the same results as were reported previously. However, when we tested Uemura and co-workers' explanation for the formation of the dichlorides from cyclopentene, we found that it is incorrect since 1-chlorocyclopentene and 3-chlorocyclopentene *do not* react with HCl to give **1**, **2**, **3**, and **4**.

Scheme I



Scheme I outlines a series of reactions which we feel can be used to account for the dichloride products in the reaction of cyclopentene and antimony pentachloride.[6,7] According to Scheme I the ion-pair precursors (**11** and **12**) of dichlorides **3**, **4**, and **1**, respectively, result from appropriate hydride shifts[8,9] in intermediate **9**. We have established that molecular chlorine does not produce detectable amounts of a dichlorides **1**, **3**, or **4**, presumably because this reaction proceeds through a chloronium ion-type transition state (**13**) to give ion pair **14**, with little carbonium ion development in the transition state and no opportunity for hydride shift. Apparently intermediate **9** forms from transition state **15** and does not collapse to chloronium ion **14** because of stabilizing bonding between chlorine and the $SbCl_4^-$ ion.



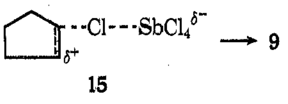
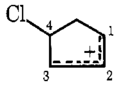


Table I. Reactions of Cyclopentadiene and $SbCl_5$

		Product distribution				
Chlorinating agent	Solvent[a]	5	6	7	8	Yield, %
$SbCl_5$	CCl_4	6	22	38	34	96
$SbCl_5$	CH_2Cl_2	7	12	52	29	27
$SbCl_5$	C_5H_{12}	19	21	27	33	71
Cl_2[b]	CCl_4	27	23	39	11	60
Cl_2[b]	CH_2Cl_2	38	35	18	9	52
Cl_2[b]	C_5H_{12}	13	29	29	29	68

[a] The mole fraction of diene was 0.02 in all cases. [b] See ref 5 for a description of this study.

We are now in a position to discuss the mechanism for the reaction of cyclopentadiene with $SbCl_5$. We have already shown that the products in this reaction cannot be accounted for on the basis of a concerted 1,4 addition. Therefore, since cyclopentene reacts with $SbCl_5$ by a carbonium ion mechanism, it would seem reasonable that cyclopentadiene would also react by this mechanism, particularly since the carbonium ion from the diene is both secondary and allylic, and, hence, more stable. Dichlorides **5**, **6**, **7**, and **8** would then result from an appropriate attack on cation **16**. The increase in anti 1,4 addition (**8**) with $SbCl_5$ compared to chlorine probably results from the fact that the large anion ($SbCl_4^-$) experiences little steric hindrance during anti attack at C_1. Conversely the small amount of syn 1,2 addition with $SbCl_5$ can be explained on the basis of increased steric interaction as the anion ($SbCl_4^-$) approaches C_3 from a syn direction.[10]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Vignes and Hamer[4] correctly suggested that the reaction of $SbCl_5$ with *trans,trans*-2,4-hexadiene (**16**) would be an excellent method for determining whether the 1,2 and 1,4 additions were symmetry controlled. However, when they attempted this reaction they obtained only polymeric material. We repeated this reaction under our conditions and obtained the products reported in Table II. Reactions between antimony pentachloride and the following dienes and olefins were also studied: *cis,cis*-2,4-hexadiene (**17**), *cis,trans*-2,4-hexadiene (**18**), *trans*- and *cis*-piperylene (**19** and **20**), and *trans*- and *cis*-β-methylstyrene (**21** and **22**). These results are reported in Table II.

The results which would be predicted if the reaction of *trans,trans*-2,4-hexadiene and $SbCl_5$ is symmetry controlled are outlined in Scheme II. As shown, a symmetry controlled 1,2 addition to **16** (concerted molecular addition) should occur in the syn direction to give the threo dichloride, and the 1,4 addition should occur from opposite sides (anti) of the diene (as illustrated earlier with butadiene and cyclopentadiene) to give the meso 1,4 dichloride. Anti 1,4 and syn 1,4 addition to **18** will give *dl*-1,4- and meso 1,4-dichlorides, respectively. Syn 1,2 additions to **17** will give the erythro 1,2-dichloride; the interpretation of syn 1,2 addition to **18** is more complex (see footnote *b*, Table II).[11]

The data in Table II indicate that 1,4 additions of $SbCl_5$ to **16** (and dienes **17** and **18**) is not under orbital control since the ratio of meso to *dl* attack is approximately equal. Perhaps one can imagine that some orbital control is involved since syn 1,4 addition should be favored inasmuch as the anion is generated on the same side of the diene as the attacking electrophile, and is situated correctly for syn 1,4 attack.[12]

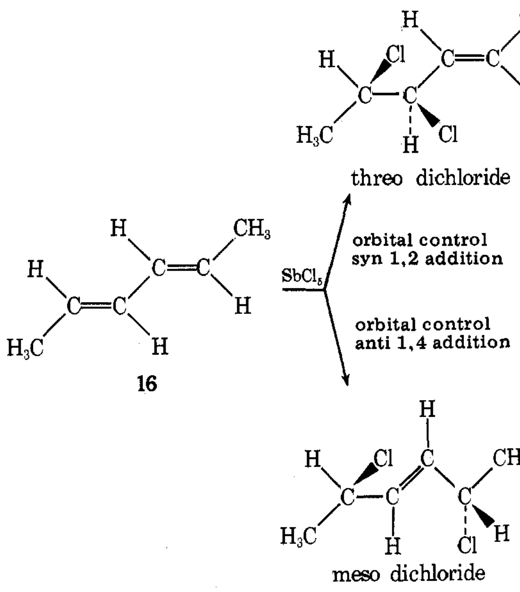
1,2 addition, in contrast to 1,4 addition, is highly stereospecific (syn) for the cis 2,4-hexadienes (**17**, **20**) but not for the

Table II. Chlorination of Dienes and Olefins with $SbCl_5$

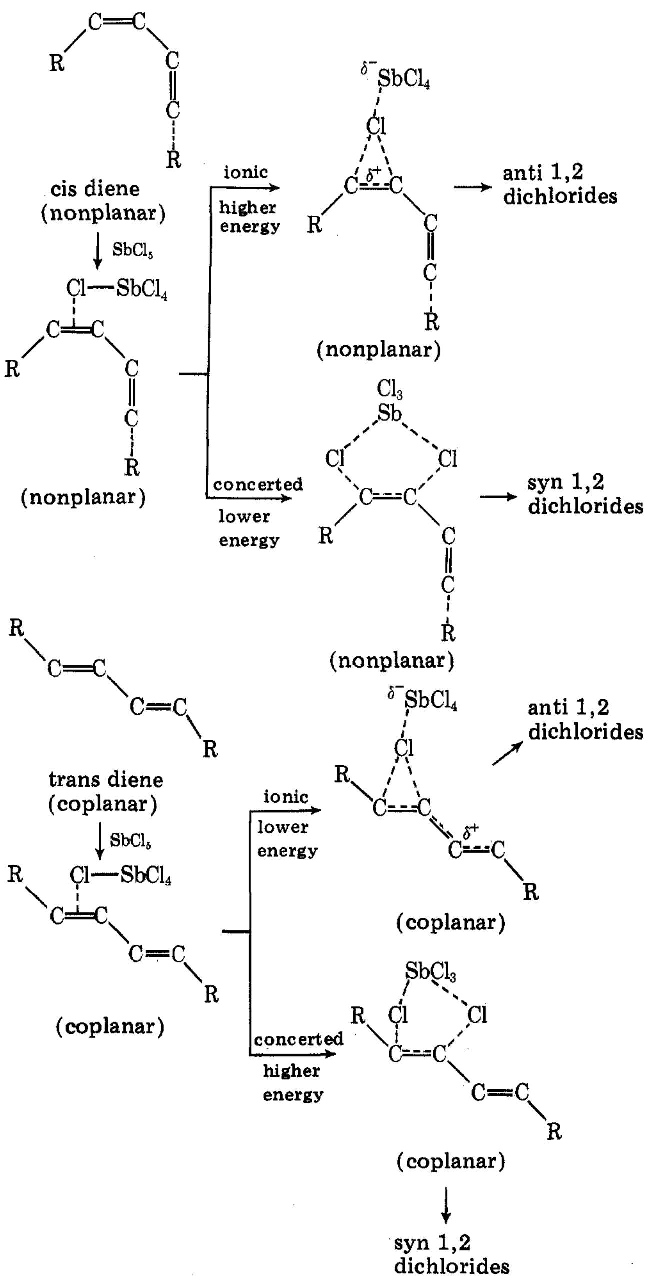
Diene or olefin	Threo/erythro	Syn 1,2 addition, %	*meso*-1,4-*dl*-1,4	Syn 1,4 addition, %	1,2/1,4	Yield, %
16	0.75	43	1.11	47	0.52	49[c]
17	0[a]	100	1.12	47	1.54	28
18	*b*	*b*	1.15	54	0.78	27
19[e]	0.11	10			0.77	94[d]
20[e]	0.41	71			1.05	34[d]
21	3.04	75				63
22	0	100				67

[a] Analysis procedures did not eliminate the possibility of a trace (2%) of threo product. [b] Since diene **18** has both a cis and trans bond, the stereochemistry of 1,2 addition must be stated for each bond: syn 1,2 addition (%) to the cis bond, 47; syn 1,2 addition (%) to the trans bond, 69. [c] Includes a 14% yield of a compound expected of being the cis 1,4-dichloride. [d] These percentages include the following yields (%) of the cis 1,4-dichlorides, respectively: 28 and 10. [e] Only 3,4-dichloro-1-pentene is formed.

Scheme II



Scheme III

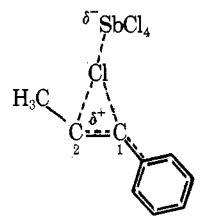


trans dienes (**16**, **19**). At least one explanation for these data is that $SbCl_5$ adds to the cis bonds by a concerted molecular mechanism, and to the trans bonds by an ionic mechanism. (In the ionic addition, the anion would undergo some reorientation leading to anti 1,2 product). Why should concerted addition be preferred for the cis dienes?

Conceivably, slight differences in the stabilities of the intermediate carbonium ions can determine whether $SbCl_5$ adds by a concerted or an ionic mechanism. For example, syn (concerted) addition is lowest[1-3] for those olefins and dienes involving the most stable carbonium intermediates (cyclopentene, *cis*-cyclooctene, *cis,cis*-1,5-cyclooctadiene, and norbornene), and highest for those olefins which would involve the least stable carbonium ion intermediates (2-butene, 2-octene, and cyclohexene). The lower stability of the latter intermediates may tip the scales in favor of a nonionic, concerted addition.[13]

The differences in intermediate carbonium ion stabilities may explain why addition of $SbCl_5$ is more stereospecific (concerted, syn) for cis dienes than for trans dienes. With cis dienes the two double bonds are probably nonplanar in the ground state because of 1,3 interactions between a methyl group and a hydrogen. This same type of interference also would be expected to exist in the transition state, hindering formation of the more stable, allylic carbonium ion, whose formation would require coplanarity of the double bonds. Thus the lower energy, concerted route becomes significant. With trans dienes this type of 1,3 interaction does not exist, an allylic carbonium ion is possible, and the ionic route is followed. These concepts are illustrated in Scheme III.[14]

The data in Table II show that chlorination of *cis*-β-methylstyrene (**22**) is completely stereospecific but that chlorination of *trans*-β-methylstyrene (**21**) is far less stereospecific. The line of reasoning which was used to explain the differences in stereospecificity of the cis and trans dienes also can be applied to these olefins. Attack of $SbCl_5$ on the trans olefin (**21**) could lead to a benzylic carbonium ion-type transition state (**23**), whereas formation of a benzylic ion with the cis olefin (**22**) would be hindered because of steric interaction between the methyl hydrogen and the ortho hydrogens of the phenyl ring, forcing the ring out of the plane of the C_1–C_2 bond, decreasing resonance stabilization (**24**). Concerted addition is of lower energy in the latter case.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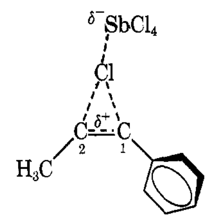
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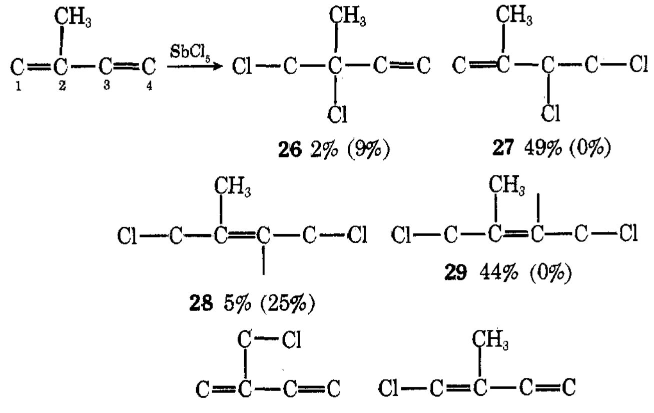
With the preceding discussion of ionic vs. concerted pathways as a background, we can now consider in some detail the chlorination of isoprene (**25**) with $SbCl_5$. The results of this study are summarized in the following reaction, along with the results from the chlorination[15] with molecular chlorine (in parentheses).



$$C{=}C(CH_3){-}C{=}C \xrightarrow{SbCl_5} Cl{-}C{-}C(CH_3)(Cl){-}C{=}C \quad C{=}C(CH_3){-}C(Cl){-}C{-}Cl$$

26 2% (9%) **27** 49% (0%)

$$Cl{-}C{-}C(CH_3){=}C{-}C{-}Cl \quad Cl{-}C{-}C(CH_3){=}C{-}C{-}Cl$$

28 5% (25%) **29** 44% (0%)

$$C{=}C(C{-}Cl){-}C{=}C \quad Cl{-}C{=}C(CH_3){-}C{=}C$$

30 0% (36%) **31** 0% (25%)

There are two principal differences in the chlorinations of isoprene with $SbCl_5$ and Cl_2: (a) Cl_2 attacks primarily (ionic) the 1,2 bond (**26** + **30** + **31** = 70%) and little at the 3,4 bond,[16] whereas $SbCl_5$ attacks significantly (nonionic) the 3,4 bond (**27**, 49%) and a trace at the 1,2 bond (**26**, 2%); and (b) $SbCl_5$ gives much cis 1,4 addition (**29**, 44%) and Cl_2 gives none.

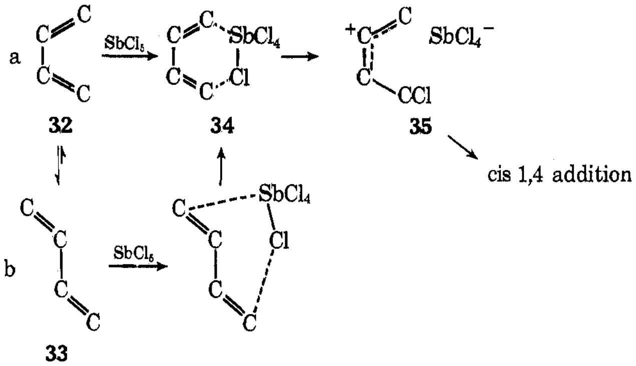
Chlorine attacks the 1,2 bond because it is most basic and because the most stable carbonium ion intermediate is formed (tertiary, allylic vs. secondary, allylic at the 3,4 bond). Perhaps $SbCl_5$ prefers to attack the 3,4 bond because of steric hindrance from the methyl group at the 1,2 bond. Reaction at the 3,4 bond appears to occur by a concerted mechanism since ionic products, $C{=}C(CH_3)C{=}CCl$ and **28**, are absent or formed in small amounts. Absence of an ionic reaction between $SbCl_5$ and **25** may result from the fact that formation of a stable, allylic cation in the transition state is hindered by nonplanarity of the double bonds (caused by 1,3 methyl, vinyl hydrogen interaction).

Certainly the most unexpected product in the reaction of butadiene and $SbCl_5$ is *cis*-1,4-dichloro-2-butene. Also a large amount of cis 1,4 addition (**29**) occurs with isoprene. Significant amounts of cis 1,4 addition products form with $SbCl_5$ and dienes **16** and **19**. *cis*-Piperylene (**20**) gives approximately one-third as much cis 1,4-dichloride as the trans isomer (**19**), and no cis 1,4-dichloride is formed from *cis,cis*-2,4-hexadiene (**17**).

The simplest explanation for the formation of cis 1,4-dichlorides is that $SbCl_5$ reacts with the s-cis (**32**) form of butadiene (used as an example) by the carbonium ion mechanism to give cis 1,4-dichloride (Vignes and Hamer[4] and Uemura and co-workers[2] suggested a concerted addition of antimony pentachloride to the s-cis form of butadiene). However, this explanation faces some real difficulties. For one thing, it was recently shown that butadiene exists in the s-trans conformation.[17] Another point is that all of the other chlorinating agents (Cl_2,[18] NCl_3,[19] and $C_6H_5ICl_2$[10]) give no more than a trace of cis 1,4 addition with butadiene.

Therefore, we conclude that the initial reaction is one in which $SbCl_5$ in some way is involved in enriching the concentration of the s-cis conformer (**32**). Two mechanisms for accomplishing this are suggested in Scheme IV. In one case (a) $SbCl_5$ complexes (**34**) extremely rapidly with the small amount of s-cis conformer (**32**), thus shifting the equilibrium in favor of **34**. In b, $SbCl_5$ reacts with the s-trans conformer (**33**) forming a complex which rearranges to the s-cis complex (**34**). Decomposition of **34** gives the cis allylic ion pair (**35**) which adds chloride ion giving cis 1,4 addition.

Scheme IV



Less cis 1,4 addition for **20** than **19** and none for **17** can apparently be explained on the basis of difficulty of formation of the s-cis conformer for these dienes because of steric hindrance between the vinyl hydrogen and methyl groups in **19** and the two methyl groups in **17**.

Experimental Section

Materials. All solvents were obtained commercially in high purity and were used without further purification. Cyclopentadiene was prepared from its dimer; all other olefins and dienes were obtained commercially in high purity. Antimony pentachloride was obtained from Ventron Corp.

Reaction Conditions. Antimony pentachloride, dissolved in solvent to give a 0.3 M solution, was added dropwise to a solution of the dienes and olefins in the corresponding solvent (mole fractions of dienes and olefins, 0.02) at 0 to −10 °C in such amount to react with ca. 25% of the dienes and olefins. Antimony pentachloride was also added neat to a solution of the hydrocarbons, but without effect on the ratio of products; the yield was somewhat reduced. As indicated in Table I, cyclopentadiene was studied in a variety of solvents; however, the other dienes and olefins were chlorinated with antimony pentachloride only in carbon tetrachloride since the yields were higher in this solvent. All yields were based on the amount of $SbCl_5$ added.

Identification of the Products and Analyses Procedures. Establishment of the structures of many of the dichloride products and the conditions for VPC analysis of them have been described previously: cyclopentadiene,[5,10] the 2,4-hexadienes and piperylenes,[12] and the β-methylstyrenes.[20] A modified procedure was used for the VPC analyses of the β-methylstyrenes: column (6 ft × 0.25 in., ss) at 65 °C, packed with SE-30 (2.5%) on 80–100 mesh Chromosorb W (AW DMCS) at a flow rate of 90 ml/min (He), and with retention times (min) of 28.3 and 33.1, respectively, for the erythro and threo isomers.

We suspect that *cis*-2,5-dichloro-3-hexene is formed in the reaction of *trans,trans*-2,4-hexadiene (**16**) with $SbCl_5$ since VPC analysis of the reaction product shows a substantial peak after the trans 1,4-

dichlorides. However, whenever this reaction solution was concentrated so that the suspected peak could be isolated by preparative VPC, the compound decomposed. Decomposition even occurred when the reaction solution was flash distilled and then concentrated. Conceivably, a trace amount of an unknown antimony compound catalyzes decomposition when the cis 1,4-dichloride is in a concentrated solution; perhaps the cis 1,4-dichloride is simply unstable, except when very dilute.

Information concerning the chlorination products from isoprene follows. **26**, **28**, **30**, and **31** have been described previously.[15] *cis*-1,4-Dichloro-2-methyl-2-butene (**29**) was obtained by preparative VPC. It was identified by its NMR spectrum, and by the similarity of its NMR spectrum to the spectrum of **28**: δ 1.92 (s, 3, CH_3), 4.03 (d, z, CH_2CH), 4.10 (s, z, CH_2CCH_3), 5.63 (t, 1, CH). 3,4-Dichloro-2-methyl-1-butene (**27**) was identified in three ways. (a) It was obtained by preparative VPC and confirmed by its NMR: δ 1.88 (s, 3, CH_3), 3.68 [d, 1, C(**H**)H, J = 5.0 Hz], 3.73 [d, 1, C(H)**H**, J_2 = 3.5 Hz], 4.50 (dd, 1, CH, J_1 = 5.0, J_2 = 3.5 Hz), 5.08 (m, 1, cis $CHCCH_3$), 5.17 (s, 1, trans $CHCCH_3$). (b) The NMR and ir spectra of VPC collected **27** were identical with those of **27** synthesized unambiguously by dehydration (P_2O_5) of 3,4-dichloro-2-methylbutan-2-ol. (c) Rearrangement of **27** by heating with zinc chloride gave small amounts of dichlorides **26**, **28**, and **29**, although extensive decomposition occurred.

Studies on the Addition of Hydrogen Chloride to 1-Chlorocyclopentene and 3-Chlorocyclopentene. Three experiments were conducted to establish that hydrogen chloride (HCl) does not add to 1-chlorocyclopentene[21] or 3-chlorocyclopentene.[22] (a) Gaseous HCl was added to a mixture of 1-chlorocyclopentene and 3-chlorocyclopentene in the appropriate solvent. No addition occurred to give **1**, **2**, **3**, and **4**. (b) Conceivably $SbCl_3$ or another antimony intermediate could catalyze the addition of HCl to the chlorocyclopentenes. To equimolar amounts of *trans*-1-phenylpropene and the chlorocyclopentenes under appropriate reaction conditions was added $SbCl_5$. **1**, **2**, **3**, or **4** were not formed during addition, or subsequently when gaseous HCl was added. *trans*-1-Phenylpropene should react more rapidly with $SbCl_5$, prehaps generating antimony intermediates and HCl which could then catalyze addition of the HCl (from the reaction or from that added) to the chlorocyclopentenes. This did not occur. (c) $SbCl_5$ was added to cyclopentene under appropriate reaction conditions (30% completion). The amounts of **1**, **2**, **3**, and **4** were determined. 1-Chlorocyclopentene and 3-chlorocyclopropene were added and HCl was bubbled into the solution. Analysis showed no increase in the amounts of **1**, **2**, **3**, and **4**.

Stability of the Dichlorides to the Reaction Conditions. A detailed study was made of the stability of the cyclopentadiene dichlorides to the reaction conditions. Since these dichlorides are probably the least stable of any of the dichlorides, they can serve as a model for stability. All of the cyclopentadiene dichlorides were found to be unaffected by antimony trichloride ($SbCl_3$). We determined that antimony pentachloride ($SbCl_5$) did not react with the dichlorides during the course of the reaction in the following manner. To an initial reaction mixture of diene and solvent was added a mixture of dichlorides. The appropriate amount of antimony pentachloride was now added to react with the diene. Analysis of this reaction product and subsequent calculations showed that the dichlorides that had been added originally were present at the end of the reaction.

Acknowledgment. Support for this work was provided by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Atlantic Richfield Foundation.

Registry No.—**16**, 5194-51-4; **17**, 6108-61-8; **18**, 5194-50-3; **19**, 2004-70-8; **20**, 1574-41-0; **21**, 873-66-5; **22**, 766-90-5; **27**, 53920-89-1; **28**, 51892-55-8; **29**, 51620-16-7; $SbCl_5$, 7647-18-9; HCl, 7647-01-0; cyclopentadiene, 542-92-7; isoprene, 78-79-5; 1-chlorocyclopentene, 930-29-0; 3-chlorocyclopentene, 96-40-2.

References and Notes

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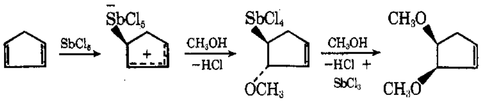
(6) The structure of the actual chlorinating agent is uncertain. Vignes and Hamer,[4] on the basis of conductivity studies, conclude that $SbCl_5$ is not ionized in carbon tetrachloride; Uemura et al.[2] are uncertain as to the structure of the chlorinating agent, but suggest that $SbCl_4^+$ may be the active chlorinating species. We show monomeric $SbCl_5$ as being the source of the chlorine atoms, but we have no evidence that $SbCl_4^+$ is not involved.

(7) Since antimony pentachloride is known to be a strong Lewis acid, we considered that the initial attack on the olefin might involve the antimony atom directly. However, when $SbCl_5$ was added to cyclopentadiene in carbon tetrachloride containing varying amounts of methanol, no dimethoxycyclopentene was detected. Dimethoxycyclopentene would be expected if the attack was made by antimony, as shown in the following equations.



(8) 1,2-Hydride shifts have been previously reported in cyclopentyl systems: J. L. Fry and G. J. Karabatos, "Carbonium Ions", Vol. II, Wiley-Interscience, New York, N.Y., 1970, p 522.

(9) Uemura et al.[3] accounted for the formation of 1,4-dichlorocyclooctane (mixture of cis and trans) from *cis*-cyclooctene and $SbCl_5$ on the basis of a 1,5-hydride shift.

(10) We have recently compared and discussed the stereochemistry of the dichlorides that result from chlorinating cyclopentadiene with Cl_2, $C_6H_5ICl_2$, NCl_3, and $SbCl_5$: V. L. Heasley, K. D. Rold, D. B. McKee, and G. E. Heasley, *J. Org. Chem.*, **41**, 1287 (1976).

(11) Orbital controlled addition to *cis,cis*-2,4-hexadiene (**17**) should give syn 1,2 addition (the erythro dichloride) and anti 1,4 addition (the meso dichloride). For a complete discussion of the stereochemical results of the additions to the 2,4-hexadienes see G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *J. Org. Chem.*, **38**, 4109 (1973).

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