dried over MgSO₄ and analyzed by glc. Quantitative data were obtained by adding a known amount of internal standard. Products were also identified by ir and nmr spectroscopy.

Attempted experiments to brominate unbranched alkanes, such as methane, ethane, propane, and *n*-butane, were carried out in Monel pressure bombs at elevated temperatures (50–100°).

Glc analyses were carried out on a Perkin-Elmer Model 226 chromatograph, equipped with an electronic Infrotronics Model CRS-1 integrator and an automatic readout system. Coated stainless steel open tubular (Golay) columns were used, with helium as the carrier gas. Nmr spectra were obtained on a Varian A60A and ir spectra on a Beckmann IR1o spectrometer.

Bromination of Adamantane. To 13.6 g (0.1 mol) of adamantane and 17.2 g (0.05 mol) of AgSbF₆ in 300 ml of CH_2Cl_2, immersed in a constant-temperature bath (−45°), a cold (−45°) solution of 8 g (0.05 mol) of bromine and 50 ml of CH_2Cl_2 was added and the reaction mixture thoroughly stirred. From time to time, samples were taken and quenched with ice-cold NaHSO₃ solution or with a solution of KOH in methanol at −60°. After dilution with water the reaction products were extracted with CH_2Cl_2 and the organic layer was dried over MgSO₄, and analyzed by glc (stainless steel open tubular column, 100 ft × 0.02 in.): stationary phases, butanediol 1,4-succinate; column temperature, 130°; 30 psi He; retention times (sec) adamantane (89), 1-fluoroadamantane (155), 1-bromoadamantane (170), 2-bromoadamantane (190), 1-hydroxyadamantane (280).

Glc Analytical Parameters. Isobutane: column A stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase, squalane; column temperature, 40°; 8 psi He; retention times (rt) (sec); *tert*-butyl bromide (787), isobutyl bromide (1597), *n*-butyl bromide (2377, standard); column B stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase, *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L; column temperature, 80°; 30 psi He; rt (sec) *tert*-butyl bromide (145), isobutyl bromide (167), *n*-butyl bromide (183, standard), isobutylene dibromide (420).

Isopentane: column B (80°/30 psi); rt (sec) *tert*-pentyl bromide (213), trimethylethylene dibromide (637), *n*-butyl bromide (183, standard).

Cyclopropane: column B (40°/30 psi or 80°/30 psi); rt (sec) and column temperature, isopropyl bromide (155, 40°), *n*-propyl bromide (182, 40°), 1,3-dibromopropane (683, 80°), *n*-butyl bromide (290, 40°; 183, 80°).

Cyclopentane: column B (80°/30 psi); rt (sec) cyclopentyl bromide (299), cyclohexyl bromide (692, standard).

Cyclohexane: column B (80°/30 psi); rt (sec) cyclohexyl bromide (692), cyclopentyl bromide (299, standard).

Norbornane: column C stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase, Carbowax 1540; column temperature, 60°; 30 psi He; rt (sec) norbornane (167), 7-bromonorbornane (993), *exo*-2-bromonorbornane (1045), *endo*-2-bromonorbornane (1067), *exo*-2-chloronorbornane (571, standard).

Electrophilic Reactions at Single Bonds. XVII.[1] SbF₅, AlCl₃, and AgSbF₆ Catalyzed Chlorination and Chlorolysis of Alkanes and Cycloalkanes

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Abstract: The electrophilic SbF₅ catalyzed chlorination of alkanes with chlorine in SO_2ClF solution at −78° resulted both in chlorination (substitution) and chlorolysis (chlorolytic cleavage). Under prevailing stable ion conditions dialkylchloronium ions are observed as the major reaction products in chlorination of methane, ethane, and propane. Higher alkanes give increasingly alkylcarbenium ions as stable ionization products. The AlCl₃ and AgSbF₆ catalyzed chlorination of alkanes and cycloalkanes gives besides direct electrophilic chlorination products also those of rearrangements and arising from electrophilic elimination–addition reactions.

The chlorination of saturated aliphatic hydrocarbons is usually achieved by free radical processes.[4] Since this reaction has great practical significance as well as being important in our understanding of radical chain processes, extensive investigations of both the photochemical and thermally induced chlorination of alkanes have been carried out. Except in the patent literature[5] where the use of certain Friedel–Crafts type of catalysts such as PCl₅, ZnCl₂, SbCl₅, and the chlorides of the rare earths were mentioned for the chlorination of tertiary isoalkanes with chlorine, no report of investigation of ionic chlorination of alkanes can be found in the literature. Generally it is considered that the presence of Lewis acids causes formation of polychlorinated compounds *via* dehydrochlorination-chlorine addition processes.[6] Obvious difficulties in controlling the Lewis acid catalyzed chlorinations arise from the fact that the reaction products formed are reactive toward the halide catalysts and thus subsequent rearrangement, elimination, and polymerization can occur *via* intermediate formation of carbenium ions.

In continuation of our studies into the electrophilic reactions of C–H and C–C single bonds,[7–10] we were

(1) Part XVI: G. A. Olah and P. Schilling, *J. Amer. Chem. Soc.*, **95**, 7680 (1973); for a preliminary communication, see G. A. Olah and Y. K. Mo, *ibid.*, **94**, 6864 (1972).

(2) Postdoctoral Research Investigator, 1969–1970.

(3) Postdoctoral Research Investigator, 1970–1972.

(4) For summaries, see (a) F. Asinger, "Paraffins, Chemistry and Technology," Pergamon Press, New York, N. Y., 1968; (b) M. L. Poutsma, "Methods in Free-Radical Chemistry," Vol. II, E. S. Huyser Ed., Marcel Dekker, New York, N. Y., 1969.

(5) G. W. Ayersant and E. E. Harton, U. S. Patent 2,542,107 (1951); *Chem. Abstr.*, **45**, 7135 (1951).

(6) H. P. Braendlin and E. T. McBee, "Friedel-Crafts and Related Reactions," Vol. III, Part 2, G. A. Olah, Ed., Wiley-Interscience, New York, N. Y., 1964, p 1578.

(7) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 1251 (1971).

(8) G. A. Olah and J. A. Olah, *ibid.*, **93**, 1256 (1971).

(9) G. A. Olah and H. C. Lin, *ibid.*, **93**, 1259 (1971).

(10) (a) G. A. Olah and P. Schilling *ibid.*, submitted for publication; (b) G. A. Olah, J. R. DeMember, and J. Shen, *ibid.*, submitted for publication.

interested to extend them to the investigation of the electrophilic chlorination of alkanes. We now report the results of the chlorination of alkanes in the presence of Friedel–Crafts catalysts of different strength, such as SbF_5, $AlCl_3$, and $AgSbF_6$.

Results and Discussion

SbF_5 Catalyzed Chlorination of Alkanes under Stable Ion Conditions. SbF_5–Cl_2 in SO_2ClF solution is a powerful electrophilic chlorinating agent. We studied previously its chlorinating ability on aromatic systems[11] and undertook now a study of its ability to chlorinate alkanes. It must be emphasized that chlorinations with this system were, in the present study, carried out at low temperature under conditions where the alkyl chlorides formed form stable complexes with SbF_5 or can undergo further ionization to the corresponding carbenium or dialkylhalonium ions, respectively. Thus, similarly to the case of Friedel–Crafts type acylations an equimolar amount of catalyst is used up in complex formation with the product (*i.e.*, alkyl chlorides) or the subsequent formation of carbenium or dialkylchloronium salts. These studies were obviously not intended for preparative purposes, but they prove the feasibility of electrophilic chlorination of alkanes under extremely limiting ionic conditions.

Methane reacts with SbF_5–Cl_2 in SO_2ClF solution at $-78°$ to give the dimethylchloronium ion. As in the SbF_5–SO_2ClF solution always a small amount of HF is present; a protolytic process of methane leading to the formation of CH_3^+ would also seem possible, with the methyl cation then reacting with chlorine to form methyl chloride. However, methane (as well as ethane, to be discussed subsequently) does not react with SbF_5 in SO_2ClF solution at $-78°$. In fact, protolytic condensation of methane can be achieved only at or above room temperature, in SbF_5 or SbF_5–FSO_3H solution, to give the trimethylcarbenium ion as the main reaction product. Furthermore, both methane and ethane do not react with Cl_2 in SO_2ClF in the absence of SbF_5 under the same reaction conditions. Consequently, the formation of dimethylchloronium ion from methane and chlorine in the presence of SbF_5 can be rationalized only as a chlorination process. The
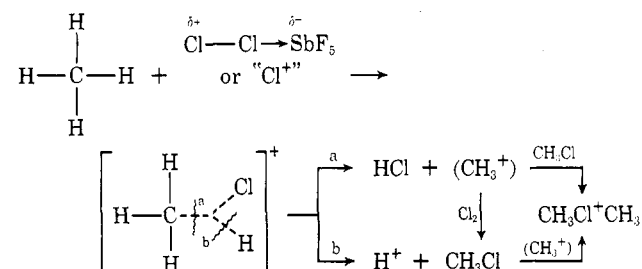
electrophile ("Cl^+")[12] attacks the C–H bond through a two-electron, three-center bonded carbonium ion type transition state to give either (CH_3^+) and HCl (a route) or H^+ and CH_3Cl (b route). Under the stable ion conditions dimethylchloronium ion is then formed.

Alternatively the $Cl\cdot^+$ (or $Cl_2\cdot^+$) radical cation (*i.e.*, the triplet state) could also be involved in the reaction.

(11) G. A. Olah, H. C. Lin, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3667 (1972).

(12) For simplicity, we are depicting the electrophile as "Cl^+" although there is presently no evidence for the existence of the chlorinium ion or any well defined cationic species in the system.

If this is the case hydrogen atom abstraction from methane would give HCl and $CH_3\cdot$ and the latter could initiate radical chain chlorination of methane. Methyl chloride subsequently could give dimethylchloronium ion in the presence of SbF_5. That the probability of radical chain chlorination in this system is very low could be demonstrated when toluene was allowed to react under identical conditions, and only electrophilic ring-chlorinated (with ortho and para substitution predominant) products were obtained. When excess methane was reacted with SbF_5–Cl_2 in SO_2ClF solution in a bomb at room temperature for 24 hr, besides the dimethylchloronium ion (in solution), methyl chloride (in the gas phase) was obtained. No methylene chloride is formed, indicating again the absence of less selective radical chlorination.

Ethane, under the same conditions (SbF_5–Cl_2 in SO_2ClF at $-78°$), gave dimethyl- and diethylchloronium ion (as well as some methylethylchloronium ion) in a ratio of 7:3. The identification of the dialkylchloronium ions (by nmr) is based on the increase of the pmr absorption intensities by adding authentic solutions of the corresponding dialkylchloronium ions. Methyl and ethyl chloride were also obtained as gaseous products in a ratio of 7:3 when the reaction was carried out in a bomb at room temperature for 24 hr. Chlorination and chlorolysis of ethane under these conditions represent competing electrophilic ("Cl^+") attack at C–H and C–C bonds as shown in Scheme I. It should be noted that the chlorolytic C–C bond reactivity is higher than that of the C–H bonds (similarly as found in protolytic[7] and nitrolytic[9] cleavage processes of ethane).

Propane, with SbF_5–Cl_2 in SO_2ClF solution at $-78°$, gave the diisopropylchloronium ion as the major product. Tertiary alkylcarbenium ions such as t-$C_4H_9^+$, t-$C_5H_{11}^+$, and t-$C_6H_{11}^+$ were also observed as minor products (10%).

Butanes, pentanes, hexanes, heptanes, and **octanes** also were studied under the same electrophilic chlorination conditions. In these cases stable tertiary alkylcarbenium ions were formed as the major products, depending on the reaction conditions and the nature of the alkane. Smaller amounts of dialkylchloronium ions were also observed. The results show that the initially formed alkyl chlorides are unstable under the reaction conditions and react further to give dialkylchloronium ions or the most stable tertiary alkylcarbenium ions, respectively.

In chlorination of the C–H bonds, besides the corresponding alkyl chlorides an equimolar amount of acid is generated, which could react with the alkanes and form alkylcarbenium ions by protolytic cleavage. However, the acid formed under the reaction conditions ($-78°$) is not used up to any significant degree and is observed by nmr (at δ 14.0 to 15.0). Since Cl_2 is

$$R\text{-}H + (Cl^+)SbF_5Cl^- \xrightarrow{-78°} R\text{-}Cl + H^+SbF_5Cl^-$$
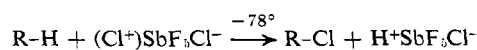
always present in large excess, chlorolysis and chlorination compete effectively with protolytic processes, even more so as the acid formed ($HSbF_6$) could protonate molecular chlorine (an n donor base) in preference to alkanes (σ donor). Cl_2H^+ itself could then be an effective chlorinating agent.

Neopentane with Cl_2–SbF_5 in SO_2ClF at $-78°$ gives

Scheme I

$$
CH_3-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H + (Cl^+) \longrightarrow
\begin{cases}
\left[\underset{CH_3\quad CH_3}{\overset{Cl}{|}}{C} \right]^+ & \longrightarrow CH_3\overset{+}{C}lCH_3 \uparrow \\
& \longrightarrow (CH_3^+) + CH_3Cl \\
\left[CH_3-CH_2\cdots\overset{Cl}{\underset{H}{}} \right]^+ & \longrightarrow (CH_3CH_2^+) + HCl \\
& \longrightarrow H^+ + CH_3CH_2Cl
\end{cases}
\longrightarrow (CH_3CH_2)_2Cl^+
$$
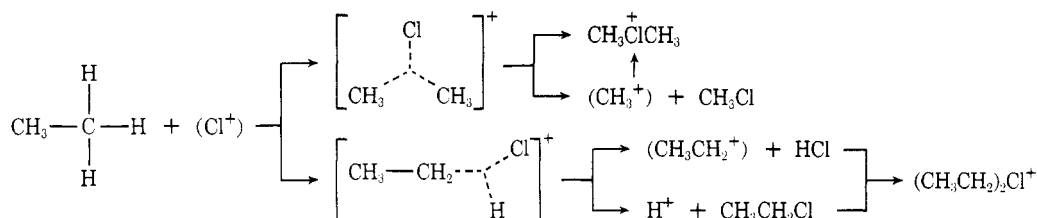
the dimethylethylcarbenium ion as the major product. **2,2,3,3-Tetramethylbutane** under the chlorinating conditions at $-78°$ gives dimethyl-*tert*-butylcarbenium ion and trimethylcarbenium ion in a ratio of $1:2.7$ (besides some dimethylchloronium ion). These results show that the electrophilic chlorinating agent, in contrast to protolylic reactions with superacids showing preference for C–C bond cleavage,[7] being larger and sterically more unfavorable for such attack, will preferentially interact with the more accessible terminal C–H bonds.

Having established the feasibility of electrophilic chlorination (and chlorolysis) of alkanes under stable ion conditions, we extended our studies to the more conventional $AlCl_3$ catalyzed chlorination.

$AlCl_3$ Catalyzed Chlorinations of Alkanes. It is known from the chlorination of benzene and toluene that $AlCl_3$ is a strong catalyst for aromatic chlorination,[13] although less reactive than SbF_5. In the $AlCl_3$ catalyzed chlorination of alkanes no stable ion conditions prevail. Consequently, most of the primary chlorination products obtained by reacting alkanes with chlorine in the presence of $AlCl_3$ in the dark at room temperature (for reaction conditions and reactant ratios see the Experimental Section) are unstable. In the presence of $AlCl_3$, rearranged end products or products formed by elimination–addition, polymerization, or condensation processes are obtained, due to ionization and subsequent reactivity of the initially formed alkyl chlorides.

Still it seems to be of interest to report the results found in our studies. Data obtained are summarized in Table I. Chlorine in the presence of $AlCl_3$ is obviously a weaker chlorinating agent than the SbF_5 catalyzed chlorinating system. The most striking difference between these two types of chlorinating systems is their differing ability to react with C–H and C–C bonds. As discussed previously, Cl_2 in the presence of SbF_5 generates electrophilic chlorine ("Cl^+") which shows high reactivity and only low selectivity. It was shown that in the case of ethane both chlorination (C–H bond substitution) as well as chlorolysis (C–C bond cleavage) occurred with the latter predominating. Cl_2 in the presence of $AlCl_3$, however, reacts with ethane to give exclusively C–H substitution, *i.e.*, ethyl chloride and polychlorinated products (formed by elimination–addition reactions) such as 1,2-dichloroethane. Based on this high selectivity (only C–H bonds are attacked), we can assume that in the presence of $AlCl_3$ the chlorinating agent is only a highly polarized complex of molecular chlorine which is to a higher degree space demanding when attacking a σ single bond than "positive chlorine" involved in the Cl_2–SbF_5–SO_2ClF system. Thus, steric hindrance can play a significant role in the chlorination reaction. The Cl_2–$AlCl_3$ system seems to react preferentially with
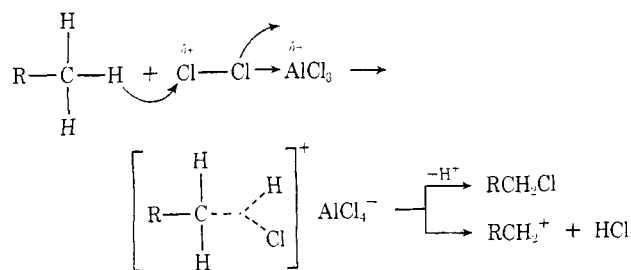
(13) G. A. Olah, S. J. Kuhn, and B. A. Hardie, *J. Amer. Chem. Soc.*, 86, 1055 (1964).

Table I. $AlCl_3$ Catalyzed Chlorination of Alkanes with Chlorine in the Dark at $25°$ [a]

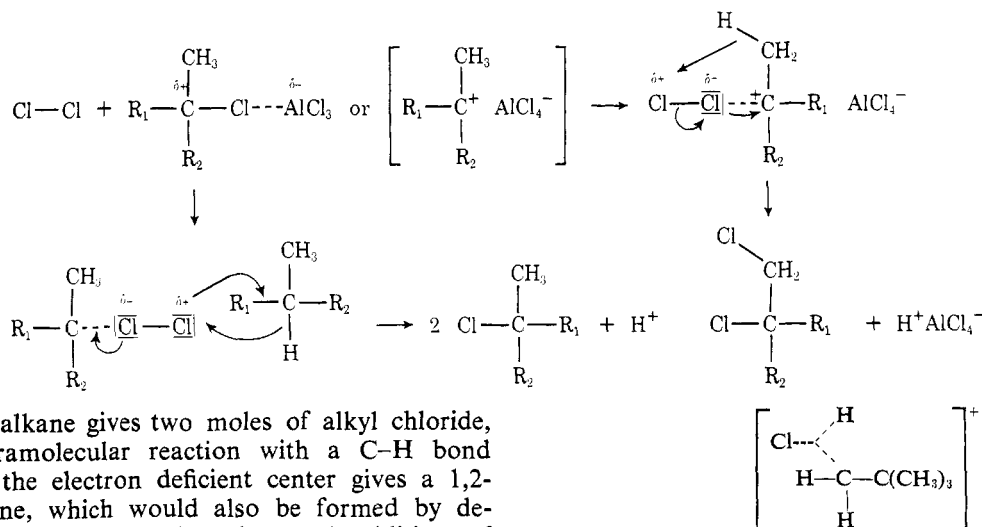| Alkane	Molar ratio $Cl_2:AlCl_3:$ alkane	Reaction time, hr	Reaction products[b] (%)
Methane	1:0.1:2	17	Methyl chloride[c] (1.0)
Ethane	1:0.1:1	23	Ethyl chloride (2.5) 1,1-Dichloroethane (1.5) 1,2-Dichloroethane (0.25) 1,1,1-Trichloroethane (0.75) Hexachloroethane (0.1)
Propane	1:0.1:1	17	1-Chloropropane (12.0) 2-Chloropropane (8.0)
n-Butane	1:0.1:1	18	More than 20 products 1-Chlorobutane (1.2) 2-Chlorobutane (1.6)
Isobutane	1:0.1:1	16	More than 20 products, no *tert*- or isobutyl chloride
Neopentane	1:0.1:1	17	1-Chloro-2,2-dimethylpropane (25.6) 1,1-Dichloro-2,2-dimethylpropane (16.8)
Norbornane[d]	1:0.1:1	15	2-*exo*-Chloronorbornane (16.6) 2-*endo*-Chloronorbornane (7.8) 7-Chloronorbornane (3.7)
Adamantane[d]	1:0.1:1	21	1-Chloroadamantane (63.2) 2-Chloroadamantane (2.9)

[a] Analysis by glc (see Experimental Section). [b] Yield based on the amount of chlorine. [c] Mass spectroscopic determination. [d] In CH_2Cl_2, all other chlorinations were carried out without solvent.

C–H bonds (chlorination) but not with the sterically more shielded C–C bonds (chlorolysis). As the mechanism for this chlorination we can again assume the formation of the two-electron, three-center bonded carbonium ion between a C–H bond and the chlorinating agent. Besides this reaction path which would explain the initial formation of alkyl chlorides by the interaction of alkanes with "positive" chlorine, we have to keep another possible mechanism in mind, a type of cationic chain propagation mechanism. As the initially generated alkyl chlorides react faster with the Lewis acid (due to the polarization of the C–Cl bond) than molecular chlorine, we can assume the alkyl chloride–$AlCl_3$ complexes, or in the limiting case the
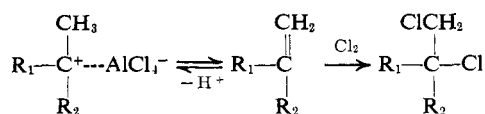
$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \ + \ \overset{\delta+}{Cl}-\overset{\delta-}{Cl}\rightarrow AlCl_3 \longrightarrow$$

$$\left[R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\cdots\overset{H}{\underset{Cl}{\triangle}} \right]^{+} AlCl_4^{-} \xrightarrow{-H^+} \begin{array}{l} RCH_2Cl \\ RCH_2^+ + HCl \end{array}$$

corresponding carbenium ions, will react with molecular chlorine to give a highly polarized carbenium ion-chlorine complex, or in the limiting case monoalkyl-chloronium ion. Intermolecular reaction with another

$$Cl-Cl \ + \ R_1-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle R_2}{|}}{\overset{\delta+}{C}}}-\overset{\delta-}{Cl}\text{---}AlCl_3 \ \text{ or } \ \left[R_1-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle R_2}{|}}{C^+}} \ AlCl_4^- \right] \longrightarrow \ \overset{\delta+}{Cl}-\overset{\delta-}{Cl}\cdots\overset{\ddagger}{\underset{\underset{\underset{\displaystyle R_2}{|}}{\overset{|}{}}}{\overset{\overset{\displaystyle H}{\diagup}\ \ \overset{\displaystyle CH_2}{}}{C}}}-R_1 \ AlCl_4^-$$

molecule of alkane gives two moles of alkyl chloride, whereas intramolecular reaction with a C–H bond adjacent to the electron deficient center gives a 1,2-dichloroalkane, which would also be formed by deprotonation of the carbenium ion and addition of chlorine to the corresponding olefin.

$$R_1-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle R_2}{|}}{C^+}}\text{---}AlCl_4^- \underset{-H^+}{\rightleftharpoons} R_1-\overset{\overset{\displaystyle CH_2}{||}}{\underset{\underset{\displaystyle R_2}{|}}{C}} \xrightarrow{Cl_2} R_1-\overset{\overset{\displaystyle ClCH_2}{|}}{\underset{\underset{\displaystyle R_2}{|}}{C}}-Cl$$

A similar pathway can also be visualized by protic acid catalysis. Molecular chlorine, as shown in our recent studies, is readily protonated with superacids to give the chloronium ion Cl_2H^+.[14] $HCl-AlCl_3$ is, therefore, considered to be capable of protonating chlorine and the chloronium ion Cl_2H^+ similarly to the discussed alkylchloronium ion; RCl_2^+ can then act as an electrophilic chlorinating agent. Despite the protic

$$RH + Cl_2^+HAlCl_4^- \longrightarrow RCl + 2HCl + AlCl_3$$

acid (HCl) generated in the progress of the chlorination, the formation of carbenium ions via direct alkane protolysis can be ruled out. By mass spectroscopic analysis no H_2 (the neutral reaction product of protolysis) could be detected, nor were typical protolytic cleavage products observed. σ basicity of alkanes is clearly lower than the n basicity of alkyl chlorides or molecular chlorine.

Methane and **neopentane**, having only primary C–H bonds, should react, if at all, very slowly with Cl_2–$AlCl_3$. As is observed in the case of methane, only about 1% of the methyl chloride was formed at 25° (under pressure). The very slow reaction of methane and chlorine probably takes place on the surface of $AlCl_3$. This seems to indicate that chlorination in the presence of

(14) G. A. Olah and J. Shen, *J. Amer. Chem. Soc.*, **95**, 3582 (1973).

$AlCl_3$ is, indeed, of ionic nature, since we would expect a much higher yield for a radical chlorination due to the chain propagation nature of the reaction, with kinetic chain lengths of the order of 10^6–10^7. Neopentane gives a much higher yield of chlorination (neopentyl chloride is formed in 25% yield, as compared with 1% methyl chloride from methane). This difference can be explained by assuming a significant C–C hyperconjugation effect by three methyl groups enhancing the C–H bond reactivity toward the electrophile. Alternatively, the inductive effect of the *tert*-butyl group and the threefold statistical abundance of the methyl hydrogens in neopentane, compared to methane, can also contribute to the enhanced reactivity. From the

$$Cl-\overset{\cdots}{\underset{}{Cl}}\cdots\overset{\overset{\displaystyle H}{\diagup}\ \ \overset{\displaystyle CH_2}{}}{C}-R_1 \ AlCl_4^-$$

$$\downarrow$$

$$2 \ Cl-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle R_2}{|}}{C}}-R_1 \ + \ H^+$$

$$Cl-\overset{\overset{\displaystyle CH_2}{|}}{\underset{\underset{\displaystyle R_2}{|}}{C}}-R_1 \ + \ H^+AlCl_4^-$$

$$\left[\begin{array}{c} Cl\text{---}\overset{\overset{\displaystyle H}{\diagup}}{\underset{\diagdown}{}} \\ H-\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}-C(CH_3)_3 \end{array} \right]^+$$

absence of any rearranged chlorides among the reaction products, which would certainly be found if a carbenium ion were first generated and then quenched by molecular chlorine or chloride ion, further evidence is obtained confirming the asssumption that the primary alkyl chlorides are formed exclusively via direct electrophilic attack of polarized chlorine on the C–H single bond. **Ethane, propane,** and *n*-**butane,** which have secondary C–H in addition to primary C–H bonds, react with Cl_2–$AlCl_3$ and give mixtures of chlorides which are formed from the initially obtained alkyl chlorides by subsequent rearrangements, dehydrochlorination–chlorination and polymerization processes. Due to the complexity of these reactions, no estimate of the selectivity of the initial electrophilic chlorination, for example, of the two different C–H bonds of isobutane, can be made. $AlCl_3$ is too active a catalyst since it enhances side reactions more than chlorination, with the result that no monochlorinated butanes could be detected anymore in the reaction mixture.

Norbornane with Cl_2–$AlCl_3$ gives a relative ratio of 2-*exo*-chloro-2-*endo*-chloro-7-chloronorbornane of 4:2:1. This isomer distribution differs considerably from that obtained by radical photochlorination of norbornane reported by Kooyman[15] (35:12.5:1) or by the Ag^+ catalyzed chlorination (8.7–11.5:2–3:1). Due to the strongly ionizing reaction conditions, we have to assume that in this case two rearrangements occurred (data of the $AlCl_3$ catalyzed isomerization of chloronorbornanes are reported separately)[16] and, therefore, the

(15) E, C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).
(16) G. A. Olah and T. Hockswender, unpublished results.

observed isomer distribution does not reflect the relative positional selectivity for the initial chlorination. This particularly relates to the relatively low exo:endo ratio.

Adamantane, which as a consequence of its rigid cage structure cannot form olefinic elimination products, simplifies the AlCl₃ catalyzed chlorination. The only ionic rearrangements possible in adamantane while maintaining its cage skeleton are intermolecular in nature. The isomer ratio of 1-chloro-:2-chloroadamantane = 32:1, obtained in the AlCl₃ catalyzed chlorination, indicates an ionic mechanism with little (or no) rearrangement. In contrast to this result the photochlorination of adamantane gives an isomer ratio of 1-:2-chloroadamantane of 0.6–2.1.[17] For the formation of 1-chloroadamantane we can again assume a direct electrophilic attack *via* a two-electron, three-center bonded carbonium ion type transition state leading to the chlorinated product. 2-Chloroadamantane, however, can be obtained either by direct chlorination of the secondary C–H bonds or by isomerization of 1-chloroadamantane by AlCl₃. Based on the recent findings of Geluk,[18] who reported the formation of 1.9% 2-hydroxyadamantane when 1-hydroxyadamantane is dissolved in 96% H₂SO₄ and then quenched, as well as Kovacic,[19] who reported that 2-chloroadamantane was found as a by-product when 1-chloroadamantane is prepared from adamantane and *tert*-butyl chloride in the presence of AlCl₃, the formation of 2-chloroadamantane in the reaction can be best attributed to intermolecular hydrogen transfer to the intermediately formed 1-adamantyl cation from a secondary C–H bond and then quenching of the 2-adamantyl cation by chloride (from AlCl₄⁻). In acetolysis 1- and 2-adamantyl tosylates show a relative rate of 10⁵:1, reported by Schleyer,[20] indicating the high reactivity of the tertiary bridgehead substituted adamantane.

Since there should be some similarity between the reactivity of 1- and 2-chloroadamantane toward solvolysis and the electrophilic substitution of adamantane in the 1 and 2 positions going through an ionic three-center bonded transition state, the direct chlorination in the 2 position should be very slow.

AgSbF₆ Catalyzed Chlorination of Alkanes. In electrophilic aromatic substitution silver ion catalyzed chlorination proved itself highly efficient. Thus, it was interesting to study this system in the chlorination of alkanes.

The AgSbF₆ catalyzed chlorination of alkanes was carried out in methylene chloride solution in the dark at temperatures between −15 and 25°. Addition of chlorine to a solution of AgSbF₆ did not cause any precipitation of AgCl₂ within 2 hr. However, subsequent addition of a reactive alkane such as adamantane or isobutane to the Cl₂–AgSbF₆ solution results in precipitation of AgCl and formation of the corresponding alkyl chlorides. That AgSbF₅–Cl₂ is only a relatively weakly polarized complex, and not an ionic

chlorine complex, is also shown by the competitive chlorination of benzene and toluene in methylene chloride soution at 0°. A substrate selectivity of $k_T/k_B = 110$ was obtained showing that AgSbF₆ is, indeed, a weak catalyst for electrophilic chlorination.

Table II. AgSbF₆ Catalyzed Chlorination of Alkanes with Chlorine in the Dark[a,b]

Alkane	Molar ratio Cl₂: AgSbF₆: alkane	Reaction temperature (°C) and time (min)	Reaction products[c] (%)
Isobutane	5:1:10	−15, 10	*tert*-Butyl chloride (7.1)
		0, 10	*tert*-Butyl chloride (5.3)
Isopentane	5:1:10	−15, 10	*tert*-Pentyl chloride (0.7)
		0, 10	*tert*-Pentyl chloride (1.4)
		10, 10	*tert*-Pentyl chloride (5.0)
Cyclopropane	5:1:10	−15, 10	n-Propyl chloride (40.0)
			Isopropyl chloride (31.5)
			1,3-Dichloropropane (1.2)
		−10, 10	n-Propyl chloride (39.2)
			Isopropyl chloride (36.0)
			1,3-Dichloropropane (1.4)
Cyclopentane	5:1:10	−15, 10	Cyclopentyl chloride (0.5)
			1,2-Dichlorocyclopentane (1.8)
		−15, 20	Cyclopentyl chloride (0.3)
			1,2-Dichlorocyclopentane (1.9)
		−15, 60	Cyclopentyl chloride (0.5)
			1,2-Dichlorocyclopentane (7.1)
		25, 180	Cyclopentyl chloride (0.3)
			1,2-Dichlorocyclopentane (3.0)
Cyclohexane	5:1:10	−15, 10	Cyclohexyl chloride (5.1)
		−15, 60	Cyclohexyl chloride (3.3)
Norbornane	5:1:10	25, 15	exo-2-Chloronorbornane (66.6)
			endo-2-Chloronorbornane (15.8)
			7-Chloronorbornane (7.6)
		25, 30	2-exo-Chloronorbornane (69.5)
			2-endo-Chloronorbornane (18.3)
			7-Chloronorbornane (6.0)
Adamantane	5:1:10	−15, 5	1-Chloroadamantane (62.4)
			2-Chloroadamantane (1.2)
			1-Hydroxyadamantane (36.3)

[a] In CH₂Cl₂. [b] Analysis by glc. [c] Yields of the reaction products based on the amount of AgSbF₆.

(17) (a) E. Muller and U. Trense, *Tetrahedron Lett.*, 2045 (1967); (b) G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961); (c) I. Tabushi, J. Hamuro, and R. Oda, *J. Amer. Chem. Soc.*, **89**, 7127 (1967); I. Tabushi, J. Hamuro, and R. Oda, *Nippon Kagaku Zasshi*, **89**, 789 (1968).

(18) H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, **24**, 5361 (1968).

(19) P. Kovacic and J. C. Chan, *J. Org. Chem.*, **36**, 3138 (1971).

(20) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 2700 (1961).

Results of the Cl_2-$AgSbF_6$ chlorination of alkanes are summarized in Table II, showing that the chlorinations are of high selectivity. Unbranched alkanes could not be chlorinated (even at elevated temperatures) whereas alkanes with tertiary C-H groups react readily. Cycloalkanes give increasing yields with rigidity of the systems (up to 80-100% in the case of norbornane and adamantane, based on the amount of $AgSbF_6$ in the chlorinating mixture). In control experiments, adamantane and isobutane did not react with $AgSbF_6$ or chlorine alone. Therefore, at least for the initial chlorination of the alkanes we have to assume that the polarized molecular chlorine complex acts as an electrophile. As in the reactions where HCl is eliminated, its reaction with $AgSbF_6$ gives fluoroantimonic acid ($HSbF_6$) which can initiate protolytic carbenium ion formations and subsequent quenching with chlorine to give some chlorination products.
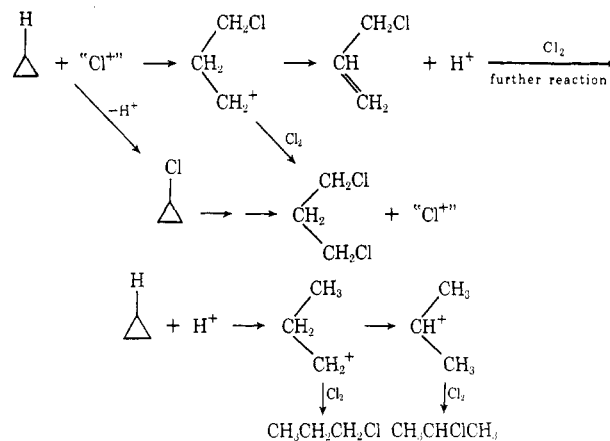
In the case of chlorination of **isobutane** and **isopentane**, the only products detected were the corresponding tertiary chlorides, showing the high selectivity of the chlorinating system. Since in the case of alkanes containing only primary and secondary C-H bonds no chlorination occurred under the reaction conditions, we have to assume that the tertiary chlorides are formed by direct attack of chlorine at the tertiary C-H bonds and that they are not the result of rearrangements. Compared with free radical photochlorination which gives in the case of isobutane a ratio of 1-chloro-:2-chloro-2-methylpropane of 2:1, the ionic chlorination is more selective. An explanation could be the effect of C-C and C-H hyperconjugation to stabilize the two-electron, three-center bonded carbonium ion type transition states in electrophilic chlorinations.

Chlorination of **cyclopropane**, besides of a smaller amount of 1,3-dichloropropane, gave 1- and 2-chloropropane as the major reaction products. The ratio of 1-:2-chloropropane is in the range of 1:0.77-0.92. Cyclopropyl chloride, the typical reaction product of the free radical photochlorination of cyclopropane, could not be detected. To explain the reaction products we have to assume initial electrophilic attack of chlorine on the C-C bond giving 2-chloroethylcarbenium ion, which either could lose a proton to form allyl chloride or react with chlorine to give 1,3-dichloropropane. However, to account for the high yield of propyl chlorides we have to assume protolytic cleavage of the C-C bond giving ethylcarbenium ion and, by rearrangement, dimethylcarbenium ion. The reaction of these ions with chlorine leads to the corresponding chlorides. The proton source either could come from the deprotonation of the 2-chloroethylcarbenium ion or from chlorine substitution of cyclopropane giving cyclopropyl chloride, which is unstable under the reaction conditions.

Cyclopentane and cyclohexane react at $-15°$ with Cl_2-$AgSbF_6$ to give low yields of monochlorinated products (up to 5%). Even at room temperature and with longer reaction times the yields could not be improved.

Norbornane, under similar conditions, gives a high yield of chloronorbornanes. The isomer ratio of chloronorbornanes formed is 2-*exo*-chloro-/2-*endo*-chloro-/7-chloronorbornane 8.7-11.5:2-3:1.

Adamantane reacts very fast at $-15°$, with 1-chloro-

adamantane as the main reaction product. The isomer distribution of 1-:2-chloroadamantane is 50:1, showing the ionic character of the chlorination. 1-Hydroxyadamantane which is also found among the reaction products is due to the quenching of the reaction mixture by water (*i.e.*, the 1-adamantyl cation formed by reaction of 1-chloroadamantane and $AgSbF_6$ is quenched by water).

Conclusions

The results obtained in our investigation of the Friedel-Crafts catalyzed chlorination of alkanes show that, similarly to electrophilic aromatic chlorination, the selectivity of the chlorinating agent can be changed by variation of the catalyst. SbF_5, the strongest catalyst used, promotes electrophilic chlorination (substitution) and chlorolysis (chlorolytic cleavage) of both C-H and C-C σ bonds of alkanes. $AlCl_3$ coordinates with chlorine but produces only a weaker electrophile, which gives only substitution reactions with alkanes. Chlorine in the presence of $AgSbF_6$ is the weakest and, therefore, the most selective chlorinating reagent studied and reacts only with tertiary isoalkanes (cycloalkanes) or strained, and therefore more reactive, systems.

Experimental Section

The alkanes used were of highest commercially available purity and used without further purification. $AgSbF_6$ (Cationics, Inc.) and $AlCl_3$ (MCB) were used without purification; SbF_5 (Allied Chemical) was purified by distillation. Chlorine was dried over concentrated H_2SO_4, and spectrograde CH_2Cl_2 was stored over Linde molecular sieves. All operations were carried out with usual care to avoid moisture (drybox handling).

SbF_5 Catalyzed Chlorination. About 100 mg of the individual alkane, which was cooled to $-78°$, was added to a solution of excess chlorine and 500 mg of SbF_5 in SO_2ClF (2 ml) and stirred for 5 min at $-78°$. Then the solution was transferred to an nmr tube and analyzed. Product identification was achieved by adding known amounts of a solution of the corresponding carbenium or halonium ions prepared, as described previously, by ionizing the corresponding halides. Methane and ethane were introduced as gases into the Cl_2-SbF_5-SO_2ClF solution.

$AlCl_3$ Catalyzed Chlorination. $AlCl_3$ (0.015 mol) was placed into a 50-ml Monel reaction bomb which was immersed in an acetone-Dry Ice bath and then 0.15 mol of the individual alkane was condensed into it (liquid alkanes were added undiluted; norbornane and adamantane were dissolved in a tenfold molar amount of CH_2Cl_2). Subsequently 0.15 mol of liquified chlorine was added. After closing the bomb the reaction mixture was allowed to warm up to room temperature and placed on a shaker and allowed to react for times specified in Table II.

Upon work-up of the reaction mixtures gaseous reaction products (*i.e.*, unreacted alkanes and chlorine) were trapped, washed (water), and extracted with ether. The ether solutions were

washed with aqueous NaHSO₃ solution and analyzed by glc. Liquid and solid reaction products were also dissolved in ether and analyzed, after washing with NaHSO₃, by ir, nmr, and glc (after adding an internal standard to the solutions for quantitative analysis). The volatile products, such as methyl chloride, were also analyzed by mass spectroscopy.

AgSbF₆ Catalyzed Chlorination. A sample (0.03 mol) of the individual alkane was dissolved in 10 ml of CH_2Cl_2 and added to a solution of 0.015 mol of chlorine in 10 ml of CH_2Cl_2 in the dark at −78°. This mixture was then added at once into a well stirred solution of 0.003 mol of AgSbF₅ in 10 ml of CH_2Cl_2, which was kept at −15 or 25°, respectively. After the reaction was completed (for reaction conditions and times, see Table II), the reaction mixture was poured into an ice-cold aqueous solution of NaHSO₃ (to remove unreacted chlorine). After separation and drying the organic layer, a known amount of an internal standard was added and the products analyzed by ir, nmr, and glc. Attempts to chlorinate unbranched alkanes were carried out at 25 or 70° in a Monel reaction bomb.

Analysis of Reaction Mixtures. Product analyses were carried out using the following. Nmr analyses were carried out using a Varian Associates Model A56/60A spectrometer, with gas chromatographic analysis performed on a Perkin-Elmer Model 226 chromatograph, equipped with an electronic integrator and automatic readout system. Ir spectra were obtained on a Beckmann Model IR 10 spectrometer.

Gas chromatographic conditions and retention time (rt) were as follows.

Ethane: column A stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase, squalane; column temperature, 60°; 12 psi He, pressure; retention times (sec) ethyl chloride (309), 1,1-dichloroethane (369), 1,2-dichloroethane (442), 1,1,1-trichloroethane (461), n-propyl chloride (506, standard).

Propane: column A (60°/12 psi); rt (sec), isopropyl chloride (464), n-propyl chloride (506), n-butyl chloride (610, standard).

n-Butane: column A (80°/12 psi); rt (sec) 2-chlorobutane (365), 1-chlorobutane (395), tert-butyl chloride (331, standard).

Isobutane: column B stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase; m-bis(m-phenoxyphenoxy)benzene + Apiezon L; column temperature, 40°; 20 psi He; rt (sec) tert-butyl chloride (220), n-butyl bromide (380, standard).

Isopentane: column B (40°/10 psi); rt (sec) 2-chloro-2-methylbutane (522), n-butyl bromide (780, standard).

Neopentane: column A (80°/20 psi); rt (sec) neopentyl chloride (265), 1,1-dichloro-2,2-dimethylpropane (650), norbornane (380, standard).

Cyclopropane: column B (40°/10 psi); rt (sec) isopropyl chloride (398), n-propyl chloride (429), n-butyl bromide (780, standard), 1,3-dichloropropane (339, 80°/30 psi).

Cyclopentane: column B (80°/30 psi); rt (sec) cyclopentyl chloride (324), 1,2-dichlorocyclopentane (490), cyclohexyl bromide (610, standard).

Cyclohexane: column B (80°/30 psi); rt (sec) cyclohexyl chloride (357), cyclohexyl bromide (610, standard).

Norbornane: column C stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase; Carbowax 1540; column temperature, 60°; 30 psi He; rt (sec) norbornane (167), 7-chloronorbornane (552), 2-exo-chloronorbornane (571), 2-endo-chloronorbornane (593).

Adamantane: column D stainless steel open tubular column, 100 ft × 0.02 in.; stationary phase, butanediole succinate; column temperature, 80°; 20 psi He; rt (sec) 1-chloroadamantane (175), 2-chloroadamantane (190), 1-hydroxyadamantane (503), adamantane (30).

Nucleophilic Alkylidene Transfer Reagents. Ethylides, Isopropylides, and Cyclopropylides Derived from Salts of Sulfoximines[1]

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Abstract: S-Ethyl-S-(p-tolyl)sulfoximine was converted to (dimethylamino)ethyl-p-tolyloxosulfonium fluoroborate (4), which provided ethylide 5 upon treatment with base. Ethylide 5 reacted to insert an ethylidene group across the double bond of the carbonyl of aldehydes and ketones, an imine, and electrophilic olefins to yield oxiranes, aziridine, and cyclopropanes (Table I). S-Isopropyl-S-(p-tolyl)sulfoximine was converted to (dimethylamino)isopropyl-p-tolyloxosulfonium fluoroborate, which was the precursor to ylide 9. Ylide 9 was also generated by reaction of ylide 5 with methyl iodide followed by treatment with 1 equiv of base. Isopropylide 9 was shown to react with benzalacetophenone to yield trans-1-benzoyl-2-phenyl-3,3-dimethylcyclopropane and with trans-dibenzoylethylene to give trans-1,2-dibenzoyl-3,3-dimethylcyclopropane. S-Phenyl-S-cyclopropylsulfoximine was prepared and converted to (dimethylamino)cyclopropylphenyloxosulfonium fluoroborate which upon treatment with sodium hydride provided the cyclopropylide 13. Ylide 13 reacted with benzalacetophenone to give trans-1-benzoyl-2-phenylspiropentane, with β-dimethylaminopropiophenone to give benzoylspiropentane, with α-methyl-β-dimethylaminopropiophenone to give 1-benzoyl-1-methylspiropentane, with mesityl oxide to give 1-acetyl-2,2-dimethylspiropentane, and with cyclohexanone to give 10-oxadispiro[2.0.5.1]decane which rearranged to spiro[3.5]nonan-1-one. (+)-(R)-(Dimethylamino)cyclopropyl-p-tolyloxosulfonium fluoroborate was prepared and used to generate a chiral cyclopropylide, from which several optically active spiropentanes were prepared. S-3-Chloropropyl-S-(p-tolyl)sulfoximine spontaneously cyclized to S-(p-tolyl)-N,S-trimethylenesulfoximine which was reacted with trimethyloxonium fluoroborate to yield 2-methyl-1-oxo-1-p-tolyl-2,1-azathiolanium fluoroborate.

S ulfonium ylides are extensively used in organic chemistry to achieve the stepwise insertion of a methylene or substituted methylene across the double

bond of a carbonyl, an imine, or an electrophilic olefin to yield an oxirane, an aziridine, or a cyclopropane,

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