addition of hydrogen fluoride or pyridine–poly(hydrogen fluoride)[18] to methyl isocyanate and isocyanic acid, respectively.[19] Other reagents were all commercially available.

Nmr and Ir Spectra. Varian Associates Model A-56/60 A spectrometer, equipped with a variable-temperature probe, was used. Chemical shifts are reported in ppm (δ) from external (capillary) tetramethylsilane or ppm (ϕ) from capillary fluorotrichloromethane. A Perkin-Elmer Model 421 grating spectrophotometer was used for ir spectroscopy.

Preparation of Solutions of Complexes and Ions. The procedure used in the preparation of solutions of protonated or metal halide complexes studied in this paper was identical with those described previously.[20]

Quenching of Ion Complexes. The fluorosulfuric acid–sulfur dioxide solution of the corresponding ion (or complex) at −78° was gradually poured into methanol (or wet SO_2), which was also cooled to −78°. The methanol (or SO_2) solution then was poured into ice–water to give a clear homogeneous solution, which was extracted by ether. The ether extract was dried over magnesium sulfate and evaporated. Finally the residue was distilled under reduced pressure. Products were identified by glc, nmr, and ir and compared with authentic samples. For example, methyl α,γ-dimethylallophanate was obtained by distillation at 104–107° (15 mm) (lit.[21] 104–105° (14 mm)). The nmr spectrum shows a doublet at δ 3.32 (J = 5.0 Hz) for γ-methyl, a singlet at 3.66 for α-methyl, a singlet at 4.24 for methoxyl group, and a broad peak at 8.92 for the imino group.

The procedure of quenching allophanyl cation by ethanol was almost the same as above, but ethyl allophanate was isolated as a crystalline material (mp 191° (lit.[22] 191–192°)).

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

(19) M. Linhard and K. Betz, *Ber.*, **73**, 177 (1940).
(20) G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, **89**, 5694 (1967).
(21) K. H. Slotta and R. Tschesche, *Ber.*, **60**, 295 (1927).
(22) R. Kreher and G. H. Berger, *Tetrahedron Lett.*, 369 (1965).

Electrophilic Reactions at Single Bonds. XVI.[1] $AgSbF_6$ Catalyzed Bromination of Alkanes and Cycloalkanes with Bromine in Methylene Chloride Solution

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Abstract: Anhydrous $AgSbF_6$ in methylene chloride solution catalyzes the electrophilic bromination of isoalkanes and cycloalkanes. Products of bromination are generally affected by silver catalyzed isomerization, as well as elimination and addition reactions.

In contrast to the extensive investigation on vapor phase photobrominations[3] or thermal gas phase brominations[4] of alkanes, only scattered results are available on brominations of saturated hydrocarbons in solution, which could have electrophilic nature. Stetter[5] reported the bromination of adamantane in neat bromine giving 1-bromoadamantane as the major reaction product and the preparation of di-, tri-, and tetrabromoadamantanes by $AlCl_3$–BBr_3 catalyzed bromination.[6] More recently Stetter also reported the reaction of several alkanes, having two adjacent tertiary hydrogens, with neat bromine at elevated temperatures.[7] In this case $\alpha,\alpha',\alpha'',\alpha'''$-tetrabromoalkanes were obtained as stable end products as the result of a sequence of bromination–dehydrobromination reactions. Straight chain unbranched alkanes failed to react even under forced conditions. Using different catalysts (mainly Lewis acids) only tarry reaction products were obtained.

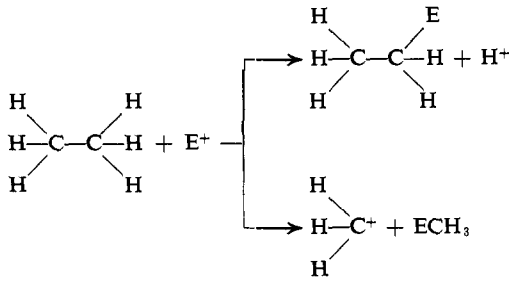
Deno[8] investigated the $FeBr_3$ and $AlCl_3$ catalyzed bromination of cyclopropane, a "bent" σ bonded more reactive cycloalkane.

One of the major difficulties in electrophilic bromination of alkanes arises due to the fact that alkyl bromides formed in the reactions themselves react further in the presence of acid catalyst (which are necessary for the generation of the electrophilic brominating agent) to give a variety of alkylation, condensation, and polymerization products characteristic of the behavior of alkyl halides with Friedel–Crafts catalysts. It seems that only cycloalkanes, such as adamantane, which cannot be readily deprotonated to an olefin, avoid this difficulty.

Recently we reported the reaction of typical electrophiles such as H^+, R^+, NO_2^+, and "Cl^+" with alkanes (σ donors). In these reactions electrophilic substitutions at C–H bonds, as well as electrophilic cleavage of the C–H and C–C bonds, took place. Both reaction types are assumed to proceed *via* a two-electron, three-center bonded carbonium ion type transition state, as shown

(1) Part XV: G. A. Olah and J. J. Svoboda, *J. Amer. Chem. Soc.*, **95**, 3794 (1973).
(2) Postdoctoral Research Investigator, 1970–1972.
(3) (a) P. C. Anson, P. S. Fredericks, and J. M. Tedder, *J. Chem. Soc.*, 918 (1959); (b) B. M. Eckstein, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **22** (1), 28 (1954); (c) M. S. Kharasch, Y. C. Liu, and W. Nudenberg, *J. Org. Chem.*, 20, 680 (1955); (d) J. D. Backhurst, *J. Chem. Soc.*, 3497 (1959); (e) U. Kh. Agaev, S. D. Mekhtiev, Zh. M. Mekhtieva, and N. F. Aliev, *Dokl. Akad. Nauk Azerb. SSR*, **23** (11), 18 (1967); (f) I. Tabuski, J. Hamuro, and R. Oda, *J. Amer. Chem. Soc.*, **89**, 7127 (1967).
(4) B. H. Eckstein, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **22** (1), 28 (1954).
(5) H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, **92**, 1629 (1959).
(6) (a) H. Stetter and C. Wulff, *Ber.*, **93**, 1366 (1960); (b) G. L. Baughman, *J. Org. Chem.*, **29**, 238 (1964).
(7) H. Stetter and E. Tresper, *Ber.*, **104**, 71 (1971).
(8) N. C. Deno and D. N. Lincoln, *J. Amer. Chem. Soc.*, **88**, 5357 (1966).

in the case of ethane.[1,9-11] To extend our studies of

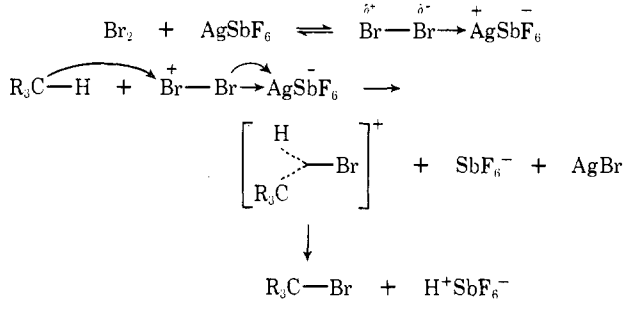


electrophilic substitution of alkanes, we now studied their bromination with a variety of Lewis acid catalysts and catalytic (metathetic) silver salts.

The system which gave the best results in our studies with a wide range of alkanes was the $AgSbF_6$ catalyzed bromination with bromine in methylene chloride solution. In contrast to Lewis acid catalysts the metathetic agent is removed from the reaction mixture as the reaction proceeds, since it is precipitated as AgBr. Thus only excess $AgSbF_6$ present during the course of the reaction can cause secondary reactions, by competing for the alkyl bromides produced.

Results and Discussion

As criteria that in homogeneous solutions ($AgSbF_6$ is soluble in CH_2Cl_2 without forming AgCl for at least 5 hr) the studied brominations are, indeed, of electrophilic nature, the following observations are indicative: (1) rapid reaction in the dark, (2) toluene under identical reaction conditions gives exclusively ring-brominated products (mostly *o*- and *p*-bromotoluenes), (3) no reaction occurred with bromine alone, (4) no reaction was observed between the alkanes and $AgSbF_6$ itself (for example adamantane did not react with $AgSbF_6$ within 24 hr at room temperature). That the electrophile involved is not a "free" form of positive bromine but only a polarized complex of molecular bromine with the silver salt is indicated, since there is no AgBr precipitation when the methylene chloride solutions of bromine and $AgSbF_6$ are combined. However, as soon as the substrate alkane is added, an immediate precipitation of AgBr can be observed. Therefore, at least for the initial stage of the bromination reaction the following mechanism can be assumed: (a) an equilibrium forming the polarized Br_2–$AgSbF_6$ complex



and (b) subsequent bromination of C–H bonds proceeding through a two-electron, three-center bonded carbonium ion type transition state. The σ base (*i.e.*, C–H bond) displaces the bromide ion, which is removed as the silver salt. Concerning the selectivity of the brominations only substitution of tertiary or reactive secondary bonds is taking place, but no apparent reaction with C–C bonds (bromolysis) is observed. This indicates a relatively bulky electrophile which cannot readily interact with less available (more crowded) bonds. The substrate selectivity observed in C–H bond substitution of alkanes and in ring substitution of aromatic systems also shows that the electrophile involved is relatively weak. Unbranched alkanes (methane, ethane, propane, *n*-butane) do not react at temperatures up to 70°. The scope of the bromination reaction is, therefore, somewhat limited. Branched alkanes with tertiary C–H bonds react fast, even at low temperature, but give mainly rearranged bromides or bromine addition products, derived from intermediate alkenes, as reaction products (see Table I). Generally the yields of alkyl bromides increase in more rigid cycloalkanes, where there is less possibility for elimination reactions.

From the competitive bromination of benzene and toluene under similar reaction conditions in methylene chloride at 0°, the relative reactivity value of k_T/k_B = 50.6 is obtained, with the isomer distribution o:m:p = 41.4:0.5:57.6%. The relatively high substrate selectivity and the high ratio of *p*-bromotoluene formed indicates that the bromine–$AgSbF_6$ system used is, indeed, a relatively weak electrophile.

Even if the bromination reactions are metathetic in nature, the Ag^+ ion being removed as AgBr during the reaction, there are obvious side reactions leading to rearranged and secondary products. (1) During the initial formation of the alkyl bromides there is an excess of Ag^+ ion present, which upon reaction with the alkyl bromide already formed can ionize it to the corresponding carbenium ion. The carbenium ion then can undergo rearrangement *via* proton elimination on the olefin which then can add bromine or collapse with the gegenion to give the corresponding alkyl fluoride, as observed in the case of adamantane. (2) In the bromination reactions $HSbF_6$ is formed as the by-product which is in equilibrium with SbF_5.

$$2HF + 2SbF_5 \rightleftharpoons H_2F^+Sb_2F_{11}^-$$

The strong protic acid generated can cause isomerization or the Lewis acid (SbF_5) can affect similar processes. (3) An excess of bromine during any stage of the reaction can react with alkyl bromides *via* dehydrobromination–bromine addition to give 1,2-dibromoalkanes. This reaction, which takes place in the dark, was extensively studied by Russel and Brown.[12]

The influence of these factors on the product distribution will be considered in connection with the discussion of the reaction of individual alkanes.

In the bromination of *fat*, the major product obtained is isobutyl bromide, the amount of which increases with increasing bromine concentration, which finally reaches a value which is eight times that of the amount of formed *tert*-butyl bromide (84.0 to 10.8%). Besides these monobromides, isobutylene dibromide is formed up to an amount of 7%. In spite of the fact that the primary isobutyl bromide is obtained as the

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

(10) (a) G. A. Olah and J. A. Olah, *J. Amer. Chem. Soc.*, **93**, 1256 (1971); (b) G. A. Olah, Y. K. Mo, and J. A. Olah, submitted for publication.

(11) G. A. Olah and H. C. Lin, *J. Amer. Chem. Soc.*, **93**, 1259 (1971).

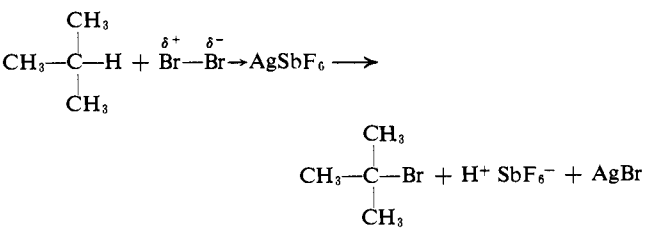
(12) G. A. Russel and H. C. Brown, *J. Amer. Chem. Soc.*, 77, 4025 (1955).

Table I. $AgSbF_6$ Catalyzed Bromination of Alkanes and Cycloalkanes in Methylene Chloride Solution

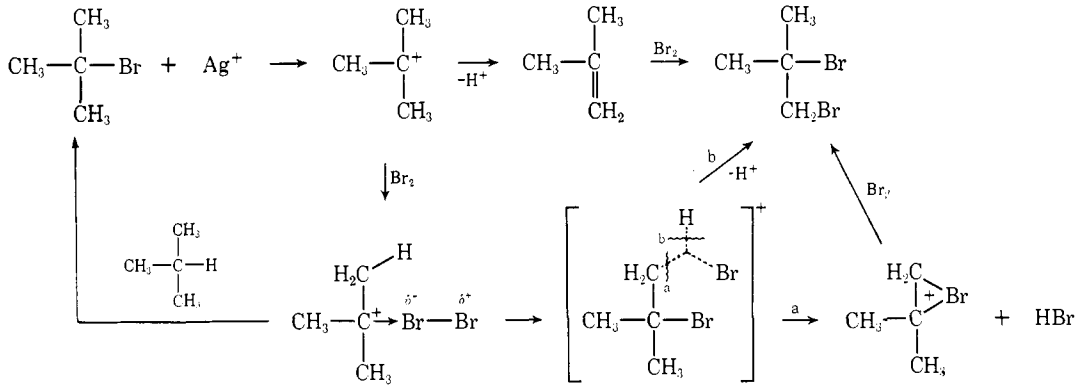
Alkane	Relative ratio Br_2: $AgSbF_6$: alkane	Reaction temp (°C) and time (min)	Reaction products[a] (%)
Isobutane	1:1:10	−15, 5	Isobutyl bromide (40.3) *tert*-Butyl bromide (6.0)
	2:1:10	−15, 5	Isobutyl bromide (77.5) *tert*-Butyl bromide (12.8) Isobutylene dibromide (4.3)
	5:1:10	−15, 5	Isobutyl bromide (75.0) *tert*-Butyl bromide (8.7) Isobutylene dibromide (7.1)
	5:1:10	−15, 10	Isobutyl bromide (84.0) *tert*-Butyl bromide (10.8) Isobutylene dibromide (6.2)
tert-Butyl bromide	1:1:10	−15, 10	Isobutyl bromide (3.0) Isobutylene dibromide (38.5)
	5:1:10	−15, 5	Isobutyl bromide (9.5) Isobutylene dibromide (49.1)
	5:1:10	0, 5	Isobutyl bromide (7.9) *n*-Butyl bromide (0.5) Isobutylene dibromide (188.5)
	5:−:10	−15, 10	Isobutylene dibromide (2.0)
	5:−:10	25, 10	Isobutylene dibromide (50.0)
Isobutylene dibromide (A) + isobutane (B)	A:−:B 2:1:10	−15, 10	Isobutyl bromide (38.2) Isobutylene dibromide recovered (20.0)
Isopentane	5:1:10	−15, 5	*tert*-Pentyl bromide (22.5) Trimethylethylene dibromide (66.0)
	5:1:10	−15, 10	*tert*-Pentyl bromide (10.2) Trimethylethylene dibromide (210.0)
Cyclopropane	5:1:10	−15, 5	*n*-Propyl bromide (52.2) Isopropyl bromide (20.4) 1,3-Dibromopropane (4.5)
	5:1:10	−15, 10	*n*-Propyl bromide (55.0) Isopropyl bromide (2.4) 1,3-Dibromopropane (5.1)
	5:−:10	−15, 10	No reaction
Cyclopentane	5:1:10	25, 10	Cyclopentyl bromide (0.2)
	5:1:10	25, 20	Cyclopentyl bromide (3.8)
	5:1:10	25, 30	Cyclopentyl bromide (4.5)
	5:1:10	25, 60	Cyclopentyl bromide (4.3)
Cyclohexane	5:1:10	−15, 15	Cyclohexyl bromide (1.5)
	5:1:10	25, 15	Cyclohexyl bromide (27.3)
	5:1:10	25, 60	Cyclohexyl bromide (26.6)
Norbornane	5:1:10	25, 15	*exo*-2-Bromonorbornane (71.4) *endo*-2-Bromonorbornane (12.3) 7-Bromonorbornane (16.3)
	5:1:10	25, 20	*exo*-2-Bromonorbornane (73.2) *endo*-2-Bromonorbornane (12.3) 7-Bromonorbornane (14.3)
Adamantane	10:1:2	−45, 5	1-Bromoadamantane (54.1) 2-Bromoadamantane (3.8) 1-Fluoroadamantane (3.0) 1-Hydroxyadamantane (4.1)
	10:1:2	−15, 5	1-Bromoadamantane (24.5) 2-Bromoadamantane (0.5) 1-Hydroxyadamantane (68.2) 2-Hydroxyadamantane (1.6)

[a] Reaction products determined by glc analysis; yields based on the amount of $AgSbF_6$.

major reaction product, it is considered improbable that it formed as a reaction product of the direct bromination. In the case of *n*-butane which has six primary and four secondary (thus more reactive) C–H bonds, no bromination takes place under identical conditions. The same consideration, therefore, can hold for the primary C–H bonds of isobutane. The initial reaction product in the case of isobutane is certainly *tert*-butyl bromide, which is formed in the early stages of the reaction by Ag^+ ion catalyzed bromination. During the progress of the reaction the

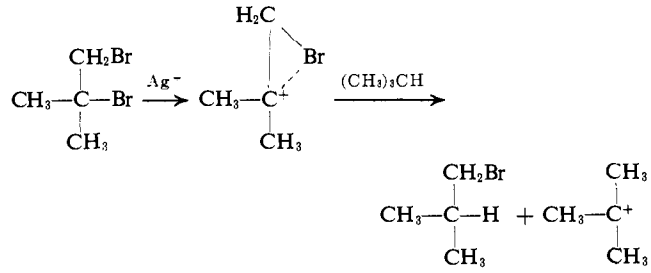


formation of *tert*-butyl cation as an intermediate must be taken into consideration, which then either can be deprotonated to form isobutylene or could be quenched

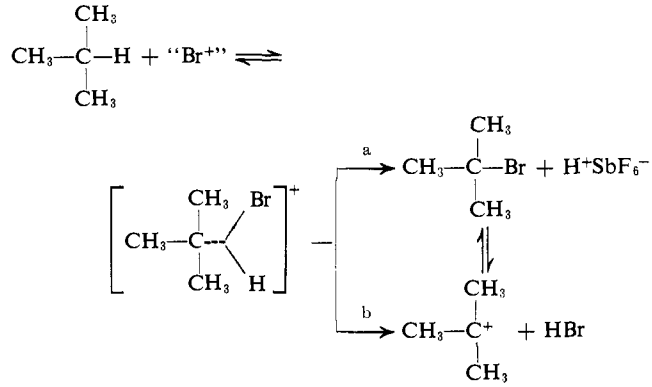


by bromine to re-form *tert*-butyl bromide and positive bromine "Br^+" which in turn then reacts with excess isobutane. This reaction thus could be the main pathway for the formation of the tertiary bromide in the later stages of the bromination. The initial quenching product can be considered as a polarized complex of molecular bromine with the *tert*-butyl cation interacting as a strong Lewis acid, which then can undergo further reaction. With excess isobutane it can form a second molecule of *tert*-butyl bromide or in an intramolecular electrophilic reaction a primary hydrogen can be abstracted to give 1,1-dimethylethylenebromonium ion as an intermediate for the consequent formation of isobutylene dibromide (route a). On the other hand, the dibromide could be formed directly through intramolecular bromination *via* a three-center bonded transition state without going through the cyclic bromonium ion as the intermediate (route b). The formation of isobutylene dibromide from *tert*-butyl bromide is obviously promoted by $AgSbF_6$, causing ionization to the *tert*-butyl cation, which *via* deprotonation and bromine addition gives the dibromide. Under the present reaction conditions ($-15°$) the catalytic effect of bromine itself plays only a minor role as the yields of isobutylene bromide (50% with Ag^+ and 2% without Ag^+) show.

Isobutyl bromide, the major observed reaction product, can be formed *via* two pathways. As it is seen from Table I, up to 9% isobutyl bromide is formed, besides the major reaction product isobutylene dibromide, when *tert*-butyl bromide is reacted with bromine in the presence of $AgSbF_6$. This could be understood if we assume the *tert*-butyl cation to be a partially H-bridged species (as a result of the hyperconjugative interaction of the empty p orbital of the carbenium enter with the C–H bonds of the methyl groups). Nucleophilic attack on the primary carbon gives isobutyl bromide; nucleophilic attack on the tertiary carbon regenerates the starting material or gives isobutylene dibromide as described earlier. However, as the reaction of isobutylene dibromide with $AgSbF_6$ in the presence of excess isobutane shows that the yield of isobutyl bromide *via* this pathway is much higher, this leads to the assumption that the former reaction sequence starting with the *tert*-butyl cation probably plays only a minor role. The major reaction path, therefore, can be assumed to be the abstraction of bromine from the tertiary carbon of isobutylene dibromide to give the corresponding bromonium ion (with the positive charge mainly concentrated at the tertiary carbon, as it was shown by cmr spectroscopy[13]), which by hydrogen transfer from isobutane gives isobutyl bromide and *tert*-butyl cation.



In contrast to other electrophilic reactions investigated previously, no C–C bond cleavage resulting in the formation of methyl bromide and isopropyl bromide could be observed. This is in accordance with the rather low electrophilicity of the used bromination agent, which is also showing a very high selectivity upon reaction with different C–H bonds. The Br^+ ion was never observed under long-lived conditions, in contrast to Br_2^+ and Br_3^+.[14] The high reactivity of the tertiary C–H bond can be explained by the fact that in the three-center bonded carbonium ion transition state the positive charge is more delocalized from the central carbon atom due to hyperconjugation by the three methyl groups, which may be responsible for a considerable decrease in energy of activation for reaction at the tertiary C–H bond.

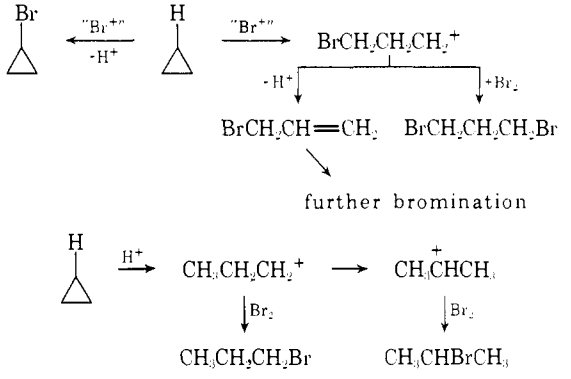


Isopentane, in reacting with $Br_2 + AgSbF_6$, gives with somewhat higher selectivity the tertiary bromide than does isobutane, but the major product is again trimethylethylene dibromide, the amount of which rapidly increases with prolonged reaction time. As the yield of the dibromide exceeds the stoichiometric amount

(13) G. A. Olah, Y. K. Mo, P. Westerman, and E. Melby, *J. Amer. Chem. Soc.*, submitted for publication.
(14) R. J. Gillespie and M. J. Morton, *Chem. Commun.*, 1565 (1968).

based on $AgSbF_6$ used, considerable contribution by reaction with excess bromine acting as a catalyst for the dehydrobromination–bromine addition reaction can be assumed.

Of the monocyclic hydrocarbons investigated the strained *fat* reacts much faster and gives higher yields of bromination products than five- and six-membered ring compounds. Recently Deno[8] investigated the bromination of cyclopropane under electrophilic conditions ($FeBr_3$, $AlCl_3$, and $AlBr_3$ as catalysts) over a wide temperature and time range. Besides the three isomeric dibromopropanes, the yields of which varied to a great extent with the reaction conditions, 1,1,2-tribromopropane was formed. In our studies, however, only a small amount of 1,3-dibromopropane was formed. The major products are *n*- and isopropyl bromide, respectively, in a relative ratio of about 2.5:1. Although there was no cyclopropyl bromide detected among the reaction products, it could play a major role in the bromination reaction. The formation of the propyl bromides can be best understood if we assume the formation of corresponding propyl cations as intermediates, which then are quenched by bromine to give the bromides. For this reaction sequence it is necessary to have a proton source in the reaction medium, which upon reaction with cyclopropane causes protolysis of the C–C bond, giving the 1-propyl cation (and by subsequent rearrangement the 2-propyl cation). To provide the proton source two reactions can be taken into consideration: (1) the bromination reaction of the C–H bond giving cyclopropyl bromide, which is unstable under the reaction conditions, or (2) the bromination of the bent C–C bonds forming the 2-bromoethylcarbenium ion, which is then deprotonated to allyl bromide and reacts by addition of bromine. That the formation of propyl bromides does not occur *via* hydrogen transfer from cyclopropane to the intermediate 2-bromoethylcarbenium ion is indicated from experiments in which 1,3-dibromopropane was reacted with $AgSbF_6$ in the presence of a large excess of cyclopropane. Also in



control experiments cyclopropane neither reacted with bromine or $AgSbF_6$ alone under the present experimental conditions.

Cyclopentane and cyclohexane under the same reaction conditions reacted much slower than cyclopropane with $Br_2 + AgSbF_6$, giving 5 and 27% cyclopentyl and cyclohexyl bromides, respectively. Although *norbornane* (bicyclo[2.2.1]heptane) consists of two fused cyclopentane rings, it gives much better yields of bromination than does cyclopentane (or cyclohexane). The bromination of norbornane shows high positional

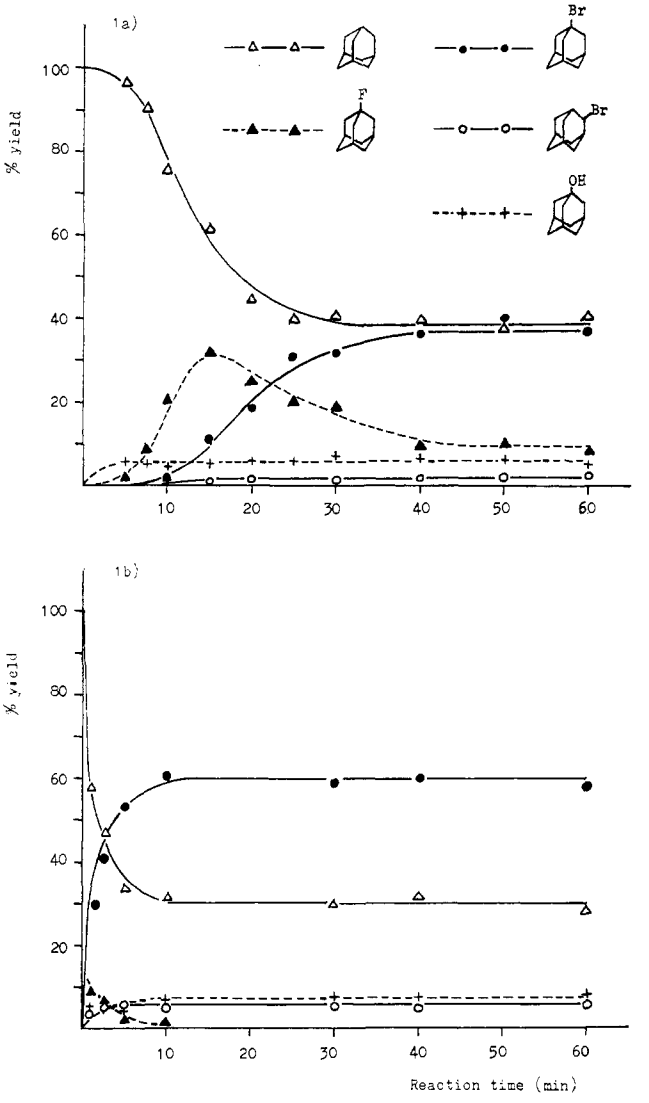
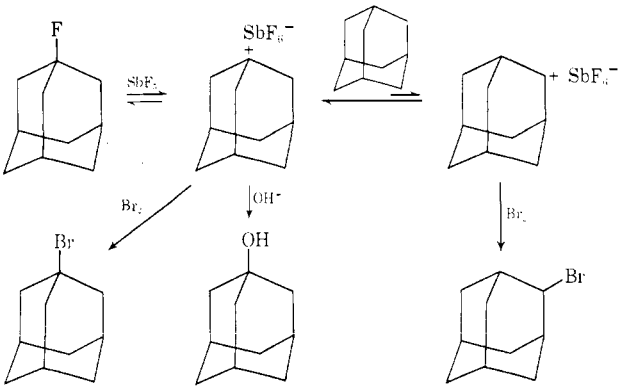


Figure 1. $AgSbF_6$ catalyzed bromination of adamantane in the dark at −45°: (a) molar ratio Br_2:$AgSbF_6$:adamatane = 1:1:2; (b) molar ratio Br_2:$AgSbF_6$:adamantane = 20:1:2.

selectivity with 2-*exo*-bromonorbornane as the dominant isomer. The ratio of 2-*exo*-bromo-2-*endo*-bromo-7-bromonorbornane is 6:1:2.5. 1-Bromonorbornane was not found in the reaction products. Due to the strongly ionizing reaction conditions it must be assumed that rearrangements occurred and the observed isomer distribution therefore does not necessarily reflect the relative positional selectivity for the initial bromination reaction (note the low exo:endo ratio and the 7-bromo compound, which could be formed by secondary rearrangement from the 2-bromo derivative).

Adamantane, a rigid and highly symmetrical hydrocarbon, was known to give good yields of 1-bromoadmantane with excess bromine at 60°.[5] Generally an ionic mechanism is proposed for this reaction. Since according to Bredts rule 1-bromoadamantane cannot readily undergo elimination, the reaction products are much simplified. The Ag^+ ion assisted bromination proceeds readily even at −45° to give 1-bromoadamantane (see Figure 1) as the major reaction product (with about 5% of the overall bromination product being the 2 isomer). At lower bromine concentration 1-fluoroadamantane is formed in a yield of

about 30% in the early stages of the reaction. Since 1-bromoadamantane is formed in increasing amounts during the later stages of the bromination, after the amount of 1-fluoroadamantane reached is highest value, it is obvious that the 1-bromoadamantane isolated does not originate entirely from the direct bromination of adamantane. As it is known that 1-haloadamantanes, especially the bromide, form with ease the stable 1-adamantyl cation,[15] we have to take into account that at the start of the reaction, when only a relatively small amount of 1-bromoadamantane is present, excess Ag^+ ion in the reaction mixture will ionize the bromide. In methylene chloride, an aprotic solvent with low dielectric constant, the ion pair will collapse with the SbF_6^- counterion forming 1-fluoroadamantane. As the reaction of 1-bromoadamantane and $AgSbF_6$ in CH_2Cl_2 at $-78°$ shows, a nearly quantitative amount of 1-fluoroadamantane is formed by the metathetic reaction. Although 1-fluoroadamantane is known to



react with bromine[16] at room or elevated temperatures, it is unlikely that this reaction takes place under the present extremely mild reaction conditions. We have, therefore, to assume that the 1-adamantyl cation which is in equilibrium with the ion pair, and thus with 1-fluoroadamantane, is quenched by bromine to give 1-bromoadamantane (or on work-up can be quenched with water, *i.e.*, OH^-, to give 1-hydroxyadamantane). As seen in Figure 1b, the rate of formation of bromoadamantane increases sharply when an excess of bromine is used. Only at the initial stages of the reaction is about 10% of 1-fluoroadamantane formed, which is then entirely converted into 1-bromoadamantane as the reaction progresses. For the formation of 2-bromoadamantane we have to consider two possibilities: (1) direct bromination of the secondary C–H bond, or (2) bromine quenching of the 2-adamantyl cation formed from the 1-adamantyl cation *via* intermolecular hydrogen transfer. Since for the direct bromination of a C–H bond a two-electron, three-center bonded carbonium ion type transition state is best proposed, we can compare the relative probability of the formation of such a transition state in the 1 and 2 positions with the relative rates of the SN1 type solvolysis of 1- and 2-adamantyl derivatives. The acetolysis of the tosylates at 25° shows, for example, a considerable difference in rates.[17] 1-Adamantyl tosylate reacts 10^5 times faster than 2-adamantyl tosylate. If we also take into account that norbornane, which has only secondary C–H bonds besides those of the bridgehead C–H bonds, does not react at this low temperature at all, it is reasonable to attribute the formation of 2-bromoadamantane not to direct bromination but to the quenching of the 2-adamantyl cation (formed *via* hydrogen transfer from 1-adamantyl cation and adamantane) by bromine. Although from pmr spectroscopic studies under stable ion conditions it is known that the 1-adamantyl cation is a stable species and 2-adamantyl precursors are readily rearranged into the tertiary ion by intermolecular hydrogen transfer,[15] Geluk,[18] as well as Kovacic,[19] found evidence also for the reverse reaction. As Geluk reported, 2-hydroxyadamantane is formed when 1-hydroxyadamantane is dissolved in 96% sulfuric acid at 28° (1.2% 2-hydroxyadamantane could be detected in the reaction mixture by glc analysis after 10 min). Recently Kovacic found the isomerization of 1-chloroadamantane to take place to 2-chloroadamantane in the presence of Lewis acid catalysts. To explain the 5% 2-bromoadamantane formed in the Ag^+ ion catalyzed bromination by this pathway thus seems to be reasonable.

The difference of the reactivity of the bridgehead C–H bonds of adamantane and norbornane toward electrophilic bromination also shows similarity to the behavior of the corresponding 1-bromoadamantane and 1-bromonorbornane under SN1 solvolytic conditions. Schleyer[17] reported the relative rates of solvolysis $k_{1\text{-Br-Ad}}$: $k_{1\text{-Br-Nor}} = 10^{-11}$. This result and the failure of norbornane to give 1-bromonorbornane in the bromination reaction seem to indicate that the partial positive charge at the bridgehead carbon in the three-center bonded carbonium ion type transition state of the electrophilic bromination is much more stabilized in the case of adamantane than at the more highly strained bridgehead center of norbornane.

Conclusions

The aim of the present study was to establish under mild (−45 to 25°) and typically electrophilic reaction conditions the scope of the Ag^+ catalyzed bromination of alkanes and cycloalkanes and to study the mechanism of the reaction. It seems to be well established that electrophilic bromination of alkanes (cycloalkanes) indeed takes place with ease, similarly to previously reported chlorination, as well as alkylation and nitration.

Experimental Section

Methylene chloride was twice distilled and kept over Linde 4A molecular sieves. The alkanes used were of highest commercially available purity and used without further purification. $AgSbF_6$ (Cationics, Inc.) was used freshly dissolved in CH_2Cl_2 (there is no precipitation of AgCl within 10 hr at 25°).

General Procedure of the Bromination. In a typical experiment 0.1 mol of the individual alkane (cycloalkane) was added to 8 g (0.05 mol) of bromine in 35 ml of CH_2Cl_2 in the dark (for lower and higher bromine concentration see Table I) and immersed into a constant-temperature bath (−15, 0, 25°). To this mixture a solution of 3.5 g (0.01 mol) of $AgSbF_6$ in 35 ml of CH_2Cl_2 at the same temperature was added. After a time interval (see Table I) the well-stirred mixture was quenched with ice–water saturated with $NaHSO_3$ to remove unreacted bromine. The organic layer was

(15) P. v. R. Schleyer, R. C. Fort, W. E. Watts, M. B. Commisarow, and G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 5679 (1964).
(16) M. P. Peterson, Jr., and G. H. Wahl, Jr., *Chem. Commun.*, 1552 (1968).
(17) P. v. R. Schleyer and R. D. Nicolas, *J. Amer. Chem. Soc.*, **83**, 2700 (1961).
(18) H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, **24**, 5361 (1968).
(19) P. Kovacic and J. C. Chang, *J. Org. Chem.*, **36**, 3136 (1971).

dried over $MgSO_4$ 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 IRlo spectrometer.

Bromination of Adamantane. To 13.6 g (0.1 mol) of adamantane and 17.2 g (0.05 mol) of $AgSbF_6$ 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 $NaHSO_3$ 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 $MgSO_4$, 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).

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Electrophilic Reactions at Single Bonds. XVII.[1] SbF_5, $AlCl_3$, and $AgSbF_6$ Catalyzed Chlorination and Chlorolysis of Alkanes and Cycloalkanes

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Abstract: The electrophilic SbF_5 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 $AlCl_3$ and $AgSbF_6$ 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 PCl_5, $ZnCl_2$, $SbCl_5$, 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.