oven was connected to a Mecaplex glovebox, to which the dried equipment can be transferred directly, without exposure to air. The nitrogen atmosphere in the glovebox was recirculated through molecular sieves (5 Å).

Preparations of solutions and transfers to reaction flasks were carried out in the glovebox, which also was used for storage of air- and moisture-sensitive compounds. Boiling and melting points are uncorrected.

Materials. **2,10-Diazabicyclo[4.4.0]dec-1-ene (1)** was synthesized according to our recently published method[2] and was sublimed directly before use in the kinetic experiments. On standing in dry air, some autoxidation of **1** occurs, probably forming the α-hydroperoxide of **1**.[36] Moreover, since **1** is sensitive to moisture, it was stored and handled in the glovebox.

2,10-Diazabicyclo[4.4.0]dec-1-ene hydrobromide (HBr-**1**) was obtained by shaking a solution of 0.7 mmol of **1** in 15 mL of CH_2Cl_2 with 1 mL of 3 M hydrobromic acid. The organic phase was dried with molecular sieves (4 Å), and the solvent was evaporated. The residue was dissolved in CH_2Cl_2, and Et_2O was added dropwise until the solution became opalescent. Crystals were formed when the solution was kept in the freezer. Filtration and drying afforded HBr-**1** (20%): mp 148–149 °C; ^{1}H NMR (CD_2Cl_2) δ 1.7 (m, 8 H), 2.4 (m, 1 H), 3.4 (m, 4 H), 9.6 (br s, 2 H). A 0.3 M solution of HBr-**1** in CH_2Cl_2 was prepared and used in the kinetic experiments.

Benzene (Merck, spectroscopic grade) was predried over molecular sieves (4 Å) and refluxed over and distilled from CaH_2 in a nitrogen atmosphere. The benzene was stored in the glovebox. Bromotrichloromethane (Fluka, purum) was shaken with 5 M NaOH solution and four portions of distilled water and dried with molecular sieves (4 Å). It was distilled in the dark in a nitrogen atmosphere, bp 104.9–105.0 °C (>99% purity from GLC, the content of CCl_4 was 0.7%). The distilled $CBrCl_3$ was stored in N_2 in the freezer in a flask which was placed in a larger jar filled with dry N_2 and silica gel. 9,10-Dihydroanthracene (EGA-Chemie, purum) was recrystallized from EtOH, mp 112–113 °C. Di-*tert*-butyl nitroxide (Polyscience) was used without further purification. 1,1-Dichloroethylene (Fluka, puriss.) was distilled directly before use, bp 32 °C. $CHCl_3$ (Fluka, p.a.) and $CDCl_3$ (Ciba-Geigy, > 99.5% D, from a newly opened ampule) were used directly or purified by distillation from anhydrous K_2CO_3. The distilled chloroform gave rates identical with those given by the chloroform used directly in the kinetic experiments.

Kinetics. General Procedure. A 30 mM solution of **1** in benzene was deoxygenated by bubbling N_2 or Ar through the solution for ca. 7 min. A 2.5-mL portion of the solution was transferred in the glovebox by means of a syringe to the reaction flask. The flask was wrapped in Al foil and thermostated at 25.0 °C. The reaction was initiated by adding $CBrCl_3$ with a syringe. The added amount of $CBrCl_3$ was determined by weighing the syringe before and after the addition. The syringe was filled in the glovebox and wrapped in Al foil. Six to nine aliquots (100 μL each) of the reaction mixture were withdrawn at different times with a 100-μL syringe under a flow of Ar. The kinetic runs were usually followed to 75% reaction of **1** and in the reactions with autocatalytic behavior up to 95% reaction of **1**.

Each aliquot was added to 600 μL of a mixture of EtOH containing 0.8 vol % DBN plus DBU (3.8 mM), which was used as an internal standard. The solution was immediately analyzed by HPLC. This method gave an accuracy of ±2.0 absolute % in the concentration determinations of **1**.

The rate constants were calculated by a linear least-squares analysis of the ln [**1**] vs. time plots using a programable Texas 59. Correlation coefficients typically better than 0.998 were obtained for the acid-catalyzed reactions.

Kinetic measurements in the presence of inhibitors and catalysts were performed by using the general procedure presented above except that the inhibitor or catalyst was added to the solution of **1**, which was then thermostated. 9,10-Dihydroanthracene was weighed and transferred to the reaction flask as a solid. Appropriate amounts of $(t\text{-Bu})_2NO$, $CH_2{=}CCl_2$, and 0.3 M HBr-**1** in CH_2Cl_2 were added by using a syringe.

Kinetics in Oxygen Atmosphere. In these experiments, the reaction flask was filled with oxygen before thermostating.

Hydrogen Isotope Exchange Measured by ^{2}H NMR. A solution of **1**(HH) (57 μmol) and HBr-**1** (0.8 μmol) in C_6H_6 (2.5 mL) in a 10-mm NMR tube equipped with septum and screw cap was thermostated at 25.0 °C in the NMR probe. $CDCl_3$ (102 μL, 1.3 mmol) was added with a syringe, and the α-D incorporation in **1** was measured at intervals by integration of the α-D signal by using the N–D signal as reference. The ^{2}H NMR experiments were performed with a spectral width of 250 or 500 Hz. The α-D/H-exchange rate for the reaction of **1**(DD) with $CHCl_3$ to **1**(HH) was measured as follows. C_6H_6 and chloroform in the above-mentioned solution of **1**(DD) was evaporated, and 2.5 mL of C_6H_6 was added to the solid residue. $CHCl_3$ (100 μL) was added to the solution, and the exchange rate was determined as above. The decrease of the α-D signal was measured relative to the growing signal from $CDCl_3$.

Kinetic Competition Experiments. To a thermostated solution of **1**-(HH) (100 μmol) and HBr-**1** (1.5 μmol) in C_6H_6 (2.5 mL) in an NMR tube equipped with septum and screw cap were simultaneously added 100 μL (1.2 mmol) of $CDCl_3$ and 150 μL (1.5 mmol) of $CBrCl_3$. ^{2}H NMR spectra were recorded as described above, and aliquots were withdrawn with a 100-μL syringe and analyzed by HPLC following the general procedure above.

These competition experiments were also performed in reaction flasks in the thermostat at 25.0 °C in order to obtain a more accurate determination of the dependence of the bromination rate on addition of $CHCl_3$ and $CDCl_3$. The experiments were carried out as in the general procedure except that $CHCl_3$ ($CDCl_3$) and $CBrCl_3$ were added simultaneously.

Acknowledgment. We thank the Swedish Natural Science Research Council for support.

Registry No. 1, 60832-40-8; **9**, 98821-50-2; deuterium, 7782-39-0.

(36) Investigations of the autoxidations of structurally related imines have been performed: Schumann, D.; Naumann, A.; Wirtz, K.-P. *Chem. Ber.* **1979**, *112*, 734–742.

Superacid-Catalyzed Alkylation of Adamantane with Olefins[1a]

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Abstract: The superacid catalyzed alkylation of adamantane with lower olefins (ethene, propene, and butenes) was investigated. Alkyladamantanes obtained show that the reaction occurs by two pathways: (a) adamantylation of olefins by adamantyl cation formed through hydride abstraction from adamantane by alkyl cations (generated by the protonation of the olefins) and (b) direct σ-alkylation of adamantane by the alkyl cations via insertion into the bridgehead C–H bond of adamantane through a pentacoordinate carbonium ion.

Studies of protonation and acid-catalyzed alkylation (by olefins) of saturated hydrocarbons are of importance both in terms of their usefulness in hydrocarbon conversion processes as well as mechanistic aspects involving carbocationic intermediates. The first

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Table I. Results of Acid Catalyzed Alkylation of Adamantane (AdH) in CCl_4 by Ethene and Propene at 0 °C

olefin	acid	acid:AdH ratio	flow rate, mL/min	reaction time, h	% yield[a] of 1-alkyladamantane	% yield[a] of polyalkyl-adamantanes
C_2H_4	CF_3SO_3H	1:1	3	0.5	5.8	7.7
C_2H_4	CF_3SO_3H	1:1	10	0.5	1.3	trace
C_2H_4	$CF_3SO_3H:B(OSO_2CF_3)_3$	1:10	3	0.16	31	6.7
C_2H_4	$CF_3SO_3H:B(OSO_2CF_3)_3$	1:10	3	1.0	trace	99.9
C_3H_6	CF_3SO_3H	1:1	3	0.5	2.6 (*n*-propyl), trace (2′-propyl)	2.4
C_3H_6	CF_3SO_3H	1:1	3	0.5	5.6 (*n*-propyl), 0.6 (2′-propyl)	7.6
C_3H_6	$CF_3SO_3H:B(OSO_2CF_3)_3$	1:10	3	0.5	32.0 (*n*-propyl), trace (2′-propyl)	39
C_3H_6	$CF_3SO_3H:B(OSO_2CF_3)_3$	1:10	10	0.5	1.1 (*n*-propyl), trace (2′-propyl)	complex mixture

[a] Yields are based on the amount of adamantane used and not based on the amount consumed. Trace amounts (≤0.1%) of 1-adamantanol were also obtained in all these reactions.

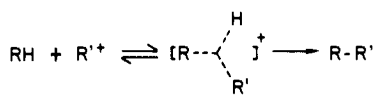
evidence for the protonation of alkanes under superacidic conditions has been reported independently by Olah and Lukas[2] as well as Hogeveen and co-workers.[3,4a] On the basis of Schmeerling's as well as Bartlett and Nentizescu's pioneering work,[4b] the conventional acid-catalyzed alkylation of isoalkanes by alkenes, from a mechanistic point of view, must be considered as the alkylation of alkenes by a trivalent alkyl cation produced via hydride abstraction from the isoalkane by the initial carbocation formed by the protonation of the alkene.

$$RCH{=}CH_2 + H^+ \rightleftharpoons R\overset{+}{C}HCH_3$$

$$R_3CH + R\overset{+}{C}HCH_3 \rightleftharpoons R_3C^+ + RCH_2CH_3$$

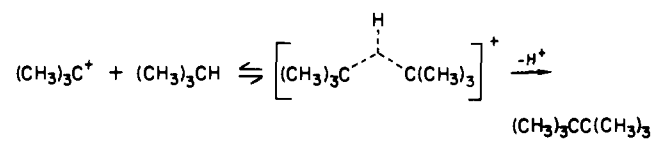
$$RCH{=}CH_2 + R_3C^+ \rightleftharpoons R\overset{+}{C}HCH_2CR_3 \xrightarrow{+H^-} RCH_2CH_2CR_3$$

This alkylation path is fundamentally different from that wherein an alkyl cation reacts directly with the alkane via three-center two-electron-bonded five-coordinate carbocation[4c] (σ-alkylation).



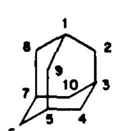
To understand the direct alkane–alkylation reactions, Olah et al. carried out experiments involving the alkylation of lower alkanes by stable alkyl cations under controlled superacidic stable-ion conditions.[5,6] Typical alkylation reactions are those of propane, isobutane, and *n*-butane by *tert*-butyl or *sec*-butyl cations. As intermolecular hydride transfer between tertiary and secondary alkyl cations and alkanes is generally much faster than the alkylation reactions, products obtained also included those derived from alkanes and alkyl cations formed in the hydride transfer reactions.

An interesting example of σ-alkylation is the reaction of *tert*-butyl cation with isobutane.[4d] Despite the highly unfavorable sterically crowded interaction, formation of small amounts of 2,2,3,3-tetramethylbutane has been demonstrated. The fast intermolecular Bartlett–Nentizescu–Schmerling type hydrogen-transfer reaction predominates but about 2% of 2,2,3,3-tetramethylbutane was also obtained, indicative of the common five-coordinate carbocation intermediate.



Results of protolytic reactions of hydrocarbons in superacidic media and alkylation reactions of alkanes by alkyl cations (both under stable-ion condition and under in situ formation from olefins) are indicative of the general electrophilic reactivity of covalent C–H and C–C single bonds of alkanes and cycloalkanes. The σ-donor ability of the C–C and C–H bonds in alkanes was demonstrated from a variety of examples. The order of reactivity of single bonds was found to be the following: tertiary C–H > C–C > secondary C–H ≫ primary C–H, although various specific factors such as steric hindrance can influence the relative reactivities. The reactivity is due to the σ-donor ability of a shared electron pair (of σ-bond) via two-electron, three-center-bond formation. The transition states of these reactions consequently are of three-center-bound pentacoordinate carbonium ion nature.

In continuation of our interest[7-11] in the chemistry of adamantane and its derivatives we undertook a study of the superacid-catalyzed alkylation of adamantane with olefins. Adamantane (**1**) has a unique geometry with tight interlocking of cyclohexane rings into rigid, relatively strain free chair confor-



1

mation. This rigid cage framework allows no formation of stable olefin and no back side (nucleophilic or electrophilic) attack. In adamantane there are four relatively crowded tertiary C–H bonds. Moreover, the 1-adamantyl cation that can be formed by hydride abstraction is highly stable.[10]

The basic mechanistic problem in acid-catalyzed alkylation of adamantane by olefins is to differentiate direct σ-alkylation of adamantane by alkyl cations (generated by the protonation of olefins) from the conventional π-adamantylation of olefins by 1-adamantyl cation (formed via hydride abstraction from adamantane by the initially generated alkyl cation). Our present study represents the triflic acid and triflic acid/boron tristriflate[12]

(1) (a) Considered as Electrophilic Reaction at Single Bonds. 21. For part 20, see: Olah, G. A.; Gupta, B.; Felberg, J. D.; Ip, W. M.; Husain, A.; Karpeles, R.; Lammertsma, K.; Melhotra, A. K.; Trivedi, N. *J. Am. Chem. Soc.*, in press. (b) Present address: Department of Chemistry, Kent State University, Kent, Ohio 44242.

(2) Olah, G. A.; Lukas, J. *J. Am. Chem. Soc.* **1967**, *89*, 2227, 4739.

(3) (a) Bickel, A. F.; Gaasbeek, G. J.; Hogeveen, H.; Oelderick, J. M.; Plattew, J. C. *Chem. Commun.* **1967**, 634. (b) Hogeveen, H.; Bickel, A. F. *Chem. Commun.* **1967**, 635.

(4) (a) Brouwer, D. M.; Hogeveen, H. *Prog. Phys. Org. Chem.* **1972**, *9*, 179. (b) Olah, G. A.; Prakash, G. K. S.; Sommer, J. "Superacids", Wiley-Interscience: New York, 1985. (c) For related σ insertions see: Olah, G. A.; Gupta, B. G. B.; Felberg, J. D.; Ip, W. M.; Husain, A.; Karpeles, R.; Lammertsma, K.; Mehrotra, A. K.; Trivedi, N. J. *J. Am. Chem. Soc.*, in press. Also see: Gal, C.; Rozen, S. *Tetrahedron Lett.* **1984**, 449. (d) For a review, see: Olah, G. A. "Carbocations and Electrophilic Reactions"; Verlag Chemie, John Wiley and Sons: New York, 1974.

(5) Olah, G. A.; Mo, Y. K.; Olah, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4939.

(6) Olah, G. A.; De Member, J. R.; Shen, J. *J. Am. Chem. Soc.* **1973**, *95*, 4952.

(7) Krishnamurthy, V. V.; Iyer, P. S.; Olah, G. A. *J. Org. Chem.* **1983**, *488*, 3373.

(8) Olah, G. A.; Shih, J. G.; Krishnamurthy, V. V.; Singh, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4492.

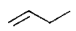
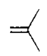
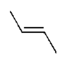
(9) Krishnamurthy, V. V.; Shih, J. G.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 1161.

(10) Olah, G. A.; Prakash, G. K. S.; Shih, J. G.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2764.

(11) Prakash, G. K. S.; Krishnamurthy, V. V.; Arvanaghi, M.; Olah, G. A. *J. Org. Chem.*, in press.

(12) Olah, G. A.; Laali, K.; Farooq, O. *J. Org. Chem.* **1984**, *49*, 4591.

Table II. Results of CF_3SO_3H Catalyzed Alkylation of Adamantane (**1**) in CCl_4 by Butenes at 0 °C

olefin	acid:AdH	flow rate, mL/min	reaction time, h	isomer distribution[a] 7	8	9	10	yield[b] of monobutyl-adamantane	yield[b] of polyalkyl-adamantane
	1:10	3	0.5	4.5	0.3	2.0	tr	6.8	trace
		10	0.5	0.5	2.0	3.8		6.3	trace
	1:10	3	0.5	3.0	0.12	2.5	4.5	10.12	1.2
		10	0.5	0.6	tr	2.9	1.1	4.6	0.5
	1:10	3	0.5	0.5	2.0	3.6	tr	6.1	1.6
		10	0.5	1.0	1.7	4.0		6.7	0.6
	1:10	3	0.5	1.4	1.1	4.2	tr	6.7	2.4
		10	0.5	1.3	0.7	3.3		5.3	1.1

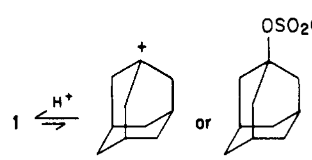
[a]The ratios are normalized to 100. [b]Yields are based on the amount of adamantane used and not based on the amount consumed. Trace (≤0.1%) amounts of 1-adamantanol were obtained in all these reactions.

catalyzed alkylation of adamantanes by lower olefins (ethene, propene, and butenes). Product alkyl adamantanes obtained indicate both direct σ-alkylation of adamantane by alkyl cations and conventional π-adamantylation of olefins by the 1-adamantyl cation.

Results and Discussion

The CF_3SO_3H or $CF_3SO_3HB(OSO_2CF_3)_3$[12] catalyzed alkylation of adamantane (**1**) with lower olefins (ethene, propene, 1-butene, *trasn*-2-butene, *cis*-2-butene, and 2-methylpropene) was carried out in dry CCl_4 at 0 °C. The olefins were passed into the solution of adamantane in CCl_4 (at different flow rates) containing 1 molar equiv or less of the acid. After the indicated reaction times, the solution was quenched with sodium bicarbonate–water and the products were analyzed by GC/MS. Authentic samples of alkyladamantanes were prepared independently by various routes[13,14] for GC/MS comparison. The results of the alkylation of adamantane by ethene and propene are given in Table I and those of isomeric butenes in Table II. In all reactions a significant amount of adamantane was recovered. The reported yields are based on the amount of adamantane used to set up the reaction (not the amount consumed in the reaction).

When adamantane was treated with 1 equiv or less of CF_3SO_3H in the absence of olefin, quenched, and analyzed, only trace amounts of 1-adamantanol (≤0.1%) were observed. However, the formation of 1-adamantanol increased up to 2% with higher (10:1) acid to adamantane molar ratio. This indicates the existence of a limited equilibrium between adamantane and 1-adamantyl cation (**2**) (and possibly 1-adamantyl triflate, (**3**) in the acid medium. In order to suppress the formation of 1-adamantyl cation



2 **3**

by protolysis in these acid systems during the alkylation reactions (and the subsequent adamantylation of olefins), all reactions reported in the present study were carried out with 1 equiv or less of superacid.

Reaction of adamantane with ethene in CF_3SO_3H gave 1.3 to 5.8% of 1-ethyladamantane (**4**), depending on the flow rate of ethene. In all reactions polyethylated adamantanes were also oberved along with ethene oligomers. Similar reaction of propene

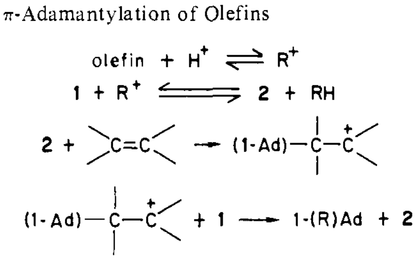
$$1 + CH_2{=}CH_2 \xrightarrow[CCl_4]{CF_3SO_3H} \underset{\mathbf{4}}{1(C_2H_5)Ad} + \text{polyethyladamantanes}$$

with CF_3SO_3H as the acid catalyst also gave monopropyl-

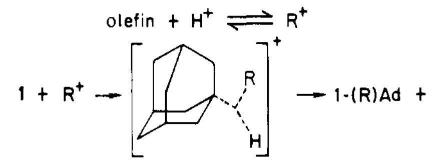
(13) Woodworth, C. W.; Bass, V.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1968**, 569.

(14) Osawa, E.; Majerski, Z.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 205.

Scheme I. π-Adamantylation of Olefins



Scheme II. σ-Alkylation of Adamantane



adamantane [both 1-*n*-propyl and 1-(2′-propyl)], along with polypropylated adamantanes.

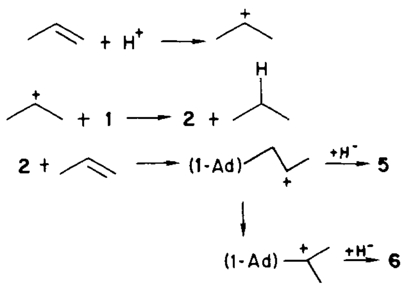
$$1 + CH_3CH{=}CH_2 \xrightarrow[CCl_4]{CF_3SO_3H} \underset{\mathbf{5}}{1\text{-}(n\text{-}C_3H_7)Ad} + \underset{\mathbf{6}}{1\text{-}(i\text{-}C_3H_7)Ad} + \text{polypropyladamantanes}$$

When a stronger acid system (1:1 triflic acid/boron tristriflate) was used the oligomerization of olefin became more predominant, but the yields of alkyl- and polyalkyladamantanes were also significantly higher. However, on prolonged reaction time only polyalkyladamantanes were obtained. The results summarized in Table I show that direct alkylation of adamantane by olefins with the lower acidity triflic acid system gave only low yields of alkyladamantanes. With a higher acidity system the yields of alkyladamantanes improved dramatically, but the extent of oligomerization of olefins also increased. Establishing the mechanism of the mode of formation of monoalkyadamantanes and not improving their yield was, however, our major goal in the present study.

The formation of alkyladamantanes can be visualized to take place either by π-adamantylation of olefins (Scheme I) or by σ-alkylation of adamantanes (Scheme II).

In situ formed alkyl cations (by protonation of olefins) can σ-alkylate adamantane by insertion into the tertiary (bridgehead) C–H bond through five-coordinated carbonium ion intermediate (Scheme II). Alternatively, the alkyl cation can hydride abstract from adamantane to generate the more stable 1-adamantyl cation which in turn adamantylates the olefin (Scheme I). The 1-adamantylalkyl cation formed in the adamantylation of olefin can then abstract hydrogen from another molecule of adamantane to give the alkyladamantane product (alternatively, the 1-adamantylalkyl cation can add to another molecule of olefin and form higher alkylated products). The intermolecular hydride transfer of adamantane is well-recognized. For example, it is

Scheme III



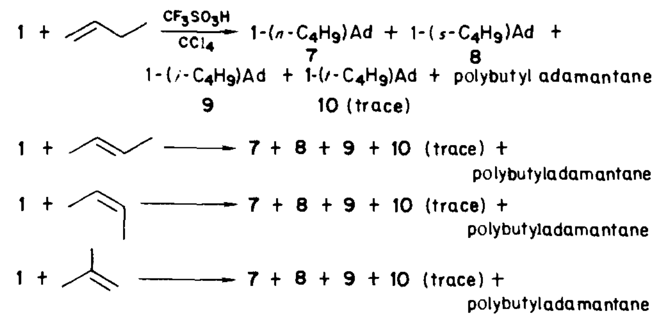
involved in the oxidation of adamantane to adamantanone in sulfuric acid medium.[15] 1-Adamantyl cation **2** readily generated from adamantane is a very stable carbocation since it cannot proton eliminate to adamantene, a highly strained anti-Bredt's olefin. Kramer has consequently recently utilized[16] adamantane as an excellent co-catalyst for the acid-catalyzed isomerization of hydrocarbons.

The formation of 1-ethyladamantane in the reaction with ethene can be explained by either route, and no differentiation between the two pathways is possible. However, more insight into the mechanism can be obtained considering the results of reactions with higher olefins such as propene and butenes (vide infra). The adamantylation of these olefins (Scheme I) should proceed by Markovnikov addition and thus give the more substituted 1-adamantylalkyl cations. Hydride transfer then leads to the corresponding alkylated products, i.e., 1-(*n*-propyl)adamantane (**5**) in the case of propene. However, direct σ-alkylation of adamantane with alkyl cations will give the anti-Markovnikov product, i.e., in case of propylation with propene 1-(2′-propyl)adamantane (**6**). Indeed, we observed both 1-(*n*-propyl)- and 1-(2′-propyl)adamantane in our study indicative of σ-alkylation competing with π-adamantylation of propene. To further study the σ-alkylation of adamantane we also carried out the reaction of adamantane with 2-propanol in CCl_4/CF_3SO_3H as well as with isopropyl cation, prepared from isopropyl chloride in $SbF_5–SO_2ClF$ in CH_2Cl_2 at −78 °C. In both reactions 1-(*n*-propyl)- and 1-(2′-propyl)adamantane were formed in 5:1 and 7:1 ratio, respectively. The formation of 1-*n*-propyladamantane in the reactions is due to the formation of propene by deprotonation of the isopropyl cation under the reaction conditions and its subsequent 1-adamantylation. These results are in accord with our previous results of the propylation of propane by isopropyl cation.[17]

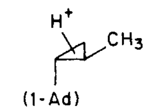
1-(2′-Propyl)adamantane is considered to be formed, both in the "control" reactions and in the reaction with propene by C–H insertion of the isopropyl cation into the tertiary C–H bond of adamantane, through the corresponding pentacoordinate carbonium ion (according to Scheme II). Alternatively, one could argue, however, that the 1-(2′-propyl)adamantane can also be formed by the rearrangement of the initially formed secondary cation formed by Markovnikov adamantylation of propene, as shown in Scheme III. Thus, both 1-(*n*-propyl)- and 1-(2′-propyl)adamantane could be products of adamantylation of propene. On the basis of the propylation data obtained no clear differentiation is possible.

Consequently, in order to gain further understanding of the mechanism of the formation of alkyladamantanes we subsequently studied the reaction of adamantane with butenes. The results are summarized in Table II.

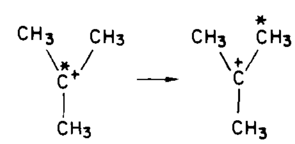
Butenes (*n*-butene, *trans*-2-butene, *cis*-2-butene, and 2-methylpropene) were reacted with adamantane in CCl_4/CF_3SO_3H with 10:1 adamantane to acid ratio with two flow rates of butenes (3 and 10 mL/min). Reactions with 2-butenes gave mostly 1-*n*-butyladamantane (**7**), 1-*sec*-butyladamantane (**8**), and 1-isobutyladamantane (**9**). Occasionally, trace amounts of 1-*tert*-butyladamantane (**10**) were also formed. Isobutylene (2-methylpropane), however, consistently gave relatively good yield of **10** along with other isomeric 1-butyladamantanes. 1-Butene gave only the isomeric butyladamantane **7**, **8**, and **9** with only trace amounts of **10**.



The formation of **7**, **8**, and **9** in these reactions can be explained through adamantylation of olefins (Scheme IV). In a control reaction when 1-butene was passed through CCl_4/CF_3SO_3H (under the usual reaction conditions) in the absence of adamantane, apart from large amounts of oligomeric products, both 2-butenes and 2-methylpropene were formed. Similarly 2-butenes were found to isomerize to 2-methylpropene in a control experiment. Even, 2-methylpropene was isomerized to 2-butenes under the reaction conditions. However, we were unable to quantify the isomerization results due to the formation of a large amount of oligomeric products in the absence of adamantane. Thus, the formation of **8** and **9** in the reaction with 1-butene and **9** in the reaction with 2-butene is readily explained. The formation of small amounts of **8** in the reaction with 2-methylpropene can be explained by an intramolecular rearrangement of the intermediate 1-(1-adamantyl)-2-methyl-2-propyl cation (formed by adamantylation of 2-methylpropene) to 2-(1-adamantyl)-2-butyl cation. Such a rearrangement in all probability involves a "protonated cyclopropane"-type intermediate (or a transition state) similar

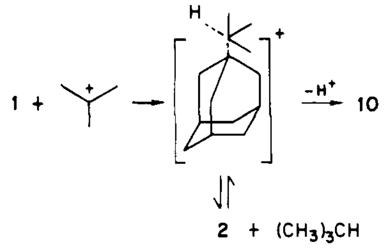


to that suggested in earlier studies.[18,19] ^{13}C scrambling has been observed in ^{13}C labeled *tert*-butyl cation[20] under stable ion conditions involving a protonated cyclopropane intermediate, although the process has a substantially high activation energy barrier.

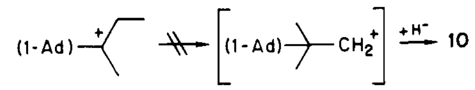


The formation of *tert*-butyladamantane, **10**, in the studied butylation reactions is significant. Since in control experiments attempted acid-catalyzed isomerization of isomeric 1-butyladamantanes did not give even trace amounts of 1-*tert*-butyladamantane the tertiary isomer must be formed in the direct σ-*tert*-butylation of adamantane by *tert*-butyl cation through a pentacoordinate carbonium ion. The same intermediate is involved in the concomitant formation of 1-adamantyl cation **2** via intermolecular hydrogen transfer (the indicated major reaction). The formation of even low yields of **10** in the reaction is a clear indication that the pentacoordinate carbocation does not attain a linear geometry ⩾C- - -H- - -⩽ (which could result only in hydrogen transfer), despite unfavorable steric interactions. This reaction is similar to the earlier discussed reaction between *tert*-butyl cation and isobutane to form 2,2,3,3-tetramethylbutane.

(15) Geluk, H. W.; Schlatmann, J. L. M. A. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 13 and references cited therein.
(16) Kramer, G. M., presented at the 1983 National Meeting of the American Chemical Society, Seattle, Petroleum Chemistry Division.
(17) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5801.
(18) (a) Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *5*, 53. (b) Saunders, M.; Budiansky, S. P. *Tetrahedron* **1979**, *35*, 929.
(19) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026.
(20) Prakash, G. K. S.; Husain, A.; Olah, G. A. *Angew. Chem.* **1983**, *95*, 51.



The alternate pathway for the formation of *tert*-butyladamantane through hydride abstraction of an intermediate 1-adamantylalkyl cation would necessitate involvement of an energetic "primary" cation or highly distorted "protonated cyclopropane" which is not likely under the reaction conditions.



We also carried out the reaction of adamantane with *tert*-butyl alcohol in CCl_4/CF_3SO_3H as well as with *tert*-butyl cation under stable-ion conditions. In both cases **8**, **9**, and **10** were observed in the ratios 1:7:2 and 1:4:1, respectively. In the latter reaction under stable-ion conditions 1-adamantanol was the major product formed by quenching of the initially formed 1-adamantyl cation.

This is again in accord with earlier studies on the alkylation of alkanes with *tert*-butyl cation under stable-ion conditions, although it is difficult to rationalize the formation of **8** and **9** (which should involve energetic primary and secondary butyl ions). Formation of trace amounts of **10** in the reactions of 1-butene and 2-butenes again probably occurs by the *tert*-butylation of adamantane by *tert*-butyl cation formed by the rearrangement of the secondary cations formed by the protonation of olefins.

The observation of 1-*tert*-butyladamantane **10** in the superacid-catalyzed reactions of adamantane with butenes provides unequivocal evidence for the σ-alkylation of adamantane by *tert*-butyl cation. As this involves an unfavorable sterically crowded tertiary–tertiary interaction, it is reasonable to suggest that similar σ-alkylation can also be involved in less strained interactions with secondary and primary alkyl systems. Although superacid-catalyzed alkylation of adamantane with olefins predominantly occurs via adamantylation of olefins, competing direct σ-alkylation of adamantane was also observed. As the adamantane cage allows attack of the alkyl group only from the front side, the reported studies provide significant new insight into the mechanism of electrophilic reactions at saturated hydrocarbons and the nature of their carbocationic intermediates.

Conclusions

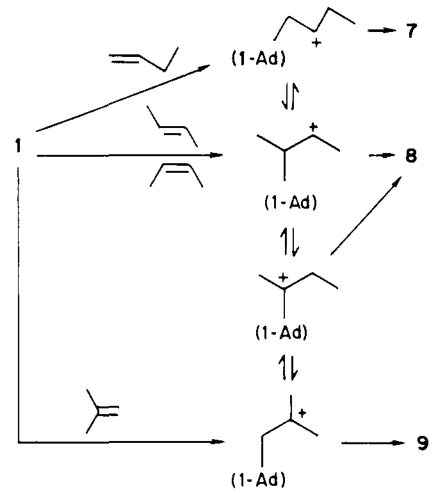
The superacid-catalyzed alkylation of adamantane with olefins gives alkyladamantanes which were found to be formed by two pathways: (a) adamantylation of olefins by adamantyl cation generated from adamantane via hydride abstraction by alkyl cations formed from the protonation of olefins and (b) σ-alkylation of adamantane by formed alkyl cations via insertion into the bridgehead C–H bond involving a pentacoordinate carbonium ion. Both these processes can occur simultaneously with path b generally being the minor competing with path a. Although the intermediate pentacoordinate carbocations of the alkylations are substantially crowded, alkylation of adamantane by alkyl cations via insertion into the C–H σ-bond (σ-alkylation) is still possible.

Experimental Section

Adamantane and all the olefins used in this study are commercially available (>99% purity) and were used as such (after analyzing with GC for their purity). Alkyladamantanes used in our study to identify products and for isomerization experiments are known compounds and were prepared following literature procedures.[13,14] Triflic acid was doubly distilled in an all-glass distillation unit. CCl_4 was dried by distillation over P_2O_5.

GC analyses were performed on a Varian Model 3700 gas chromatograph equipped with an on-line automatic integrator with a 50-m capillary and a 2-m packed column (OV 101). Olefins were analyzed on a Hewlett Packard GC Model 5730A with a porapak-Q column and in case of butenes with a BEEA column. GC–MS analyses were carried out on a Hewlett Packard or Finnigan Mass spectrometer interfaced with gas chromatographs.

Scheme IV



General Procedure of the Reaction of Adamantane with Olefins. A solution of adamantane (usually 2 g, 14.7 mmol) in 25 mL of CCl_4 was cooled in a Teflon reaction vessel to 0 °C. After adding the stated amounts of CF_3SO_3H or $CF_3SO_3H\text{–}B(OSO_2CF_3)_3$ superacid under dry nitrogen atmosphere, olefin was passed through the solution at the given flow rate and reaction times. The reaction mixture was quenched with ice–sodium bicarbonate solution, extracted with methylene chloride, separated, dried over $MgSO_4$, and analyzed (GC–MS).

Reaction of Isopropyl Alcohol with Adamantane. To a solution of adamantane (2.0 g, 14.7 mmol) and isopropyl alcohol (0.5 g, 0.83 mmol) in dry CCl_4 (25 mL) cooled to 0 °C was added triflic acid (2.7 g, 18 mmol) dropwise under dry nitrogen. The reaction was allowed to continue for 0.5 h at the same temperature. It was then quenched in ice–bicarbonate, extracted with *n*-pentane or petroleum ether, separated, dried over $MgSO_4$, and analyzed.

Reaction of Isopropyl Cation with Adamantane. To a solution of SbF_5 (5.0 g, 23 mmol) in SO_2ClF at −78 °C was added slowly isopropyl chloride (0.7 g, 0.89 mmol) with efficient vortex mixing. Isopropyl cation thus prepared at −78 °C was added in one portion to a stirred solution of adamantane (3.1 g, 22.8 mmol) in CH_2Cl_2 (5 mL) at −78 °C under dry nitrogen. The reaction was continued for 1 h, worked up, and analyzed.

Reaction of *tert*-Butyl Alcohol with Adamantane. To a solution of adamantane (3.0 g, 22.05 mmol) and *tert*-butyl alcohol (0.8 g, 10.6 mmol) in dry CCl_4 (25 mL) cooled to 0 °C was added triflic acid (3.3 g, 22 mmol) dropwise under dry nitrogen. After 1 h, the reaction was worked up in the usual way. The *n*-pentane extraction was dried over $MgSO_4$ and analyzed.

Reaction of *tert*-Butyl Cation with Adamantane. To 4.0 g (18.5 mmol) of SbF_5 in SO_2 in an NMR tube was added 0.8 g (0.86 mmol) of *tert*-butyl chloride with efficient vortex mixing. *tert*-Butyl cation, thus formed, was added to a vigorously stirred solution of adamantane (2.5 g, 18.4 mmol) in dry CH_2Cl_2 (15 mL) under dry nitrogen conditions at −78 °C. The reaction was continued for 1 h at this temperature. The mixture was subsequently quenched in ice–bicarbonate, extracted in petroleum ether, and dried over $MgSO_4$. The solution was passed through an alumina column to remove impurities imparting color to the solution. Part of the solvent was removed, and the concentrated solution was analyzed by GC.

Attempted Isomerization of Isomeric 1-Butyladamantane 7, 8, and 9. Isomeric 1-butyladamantane, 50 mg (0.26 mmol) dissolved in 5 mL of dry CCl_4, was treated with triflic acid (0.40 g, 0.26 mmol) at 0 °C for 0.5 h. Then the reaction mixture was subsequently quenched in ice–bicarbonate solution, extracted in petroleum ether, and dried over $MgSO_4$. Part of the solvent was removed, and the concentrated solution was analyzed by GC. In none of the experiments was isomerization observed, and the isomeric 1-butyladamantane was recovered intact.

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