

Electrophilic Reactions at Multiple Bonds. II.¹ Observation and Differentiation of Intermediate σ and π Complexes in Electrophilic Additions to Ethene, 2,3-Dimethyl-2-butene, and Adamantylideneadamantane

George A. Olah,* Peter Schilling,² Philip W. Westerman,³ and Henry C. Lin

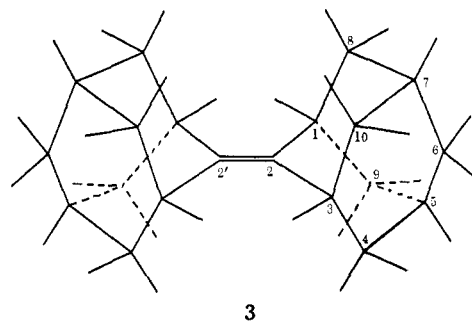
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received September 12, 1973

Abstract: The interaction of ethene, 2,3-dimethyl-2-butene, and adamantylideneadamantane with a series of electrophilic reagents has been studied under stable ion conditions in low-nucleophilicity media by nmr (¹³C and ¹H) spectroscopy. Chemical and spectral data indicate that in the case of adamantylideneadamantane alkonium type π complexes are formed preferentially as stable species which can be differentiated from open chain β -substituted alkenium ions or three-membered ring onium ions (σ complexes) formed with less hindered alkenes.

In the study of electrophilic reactions of alkenes the nature of the intermediate complexes is of substantial interest.^{4,5} In discussing the general concept of carbocations and their role in electrophilic reactions, it was suggested⁵ that the electron donor π bond first interacts with electrophiles, forming a two-electron three-center bonded alkonium ion (π complex) which subsequently opens up to the corresponding σ complex (alkenium ion). In the case of electrophilic halogenation, such as bromination, the nonbonded electron pairs on the halogen atom participate in forming a three-membered ring, σ -bonded halonium ion.^{1,6} Experimental differentiation of σ and π complexes in electrophilic reactions of alkenes has, however, so far not been achieved. Neither were any of the intermediate ionic complexes of electrophilic reactions, other than protonation of alkenes, directly observed. Alkylenehalonium ions, the suggested σ complex intermediates of electrophilic halogenations, were so far only obtained *via* neighboring group participation, *i.e.*, ionization of 1,2-dihaloalkanes under stable ion conditions.⁶

We have now undertaken a detailed study of the interaction of ethene (1), 2,3-dimethyl-2-butene (2), and adamantylideneadamantane (3) (olefins with increasing crowding of the π bond) with electrophiles in low-nucleophilicity media under stable ion conditions. Studied systems (using ¹H and ¹³C nmr) included protonation (with superacids), alkylation (with alkylcarbenium ions), halogenation, nitration (with nitronium ion), nitrosation (with nitrosonium ion), and complex formation with silver ion and antimony pentafluoride, an extremely powerful Lewis acid halide.

Ethene, the parent alkene, gives regular addition products with electrophiles, whereas 2,3-dimethyl-2-



butene, a slightly hindered alkene, fails to undergo a number of addition reactions. Adamantylideneadamantane (3), a sterically hindered alkene, shows exceptional behavior in its addition reactions to the double bond as Strating, Wieringa, and Wynberg⁷⁻⁹ recently found. It reacts with chlorine and bromine to form the stable 3-Br and 3-Cl adducts, respectively. Because of their insolubility in nonpolar solvents the halogen complexes of adamantylideneadamantane were assumed to be ionic bromonium and chloronium ions. No physical (spectroscopic) data were, however, available concerning their structure.

Results and Discussion

To study the interactions between alkenes and electrophiles in low-nucleophilicity solvent systems by nmr spectroscopy, it was necessary to first obtain the pmr and cmr spectral parameters for the parent alkenes 1, 2, and 3, in the same solvent. The pmr and cmr spectra of ethene^{10,11a} and 2,3-dimethyl-2-butene^{11b,c} have been reported, and our cmr results in SO₂ClF at -60° (Table I) are in good agreement. Solvent effects therefore are small compared with the shift changes which occur on addition of electrophiles. The pmr spectrum of adamantylideneadamantane 3 in CCl₄ (in-

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(3) Postdoctoral Research Investigator, 1971-1973.

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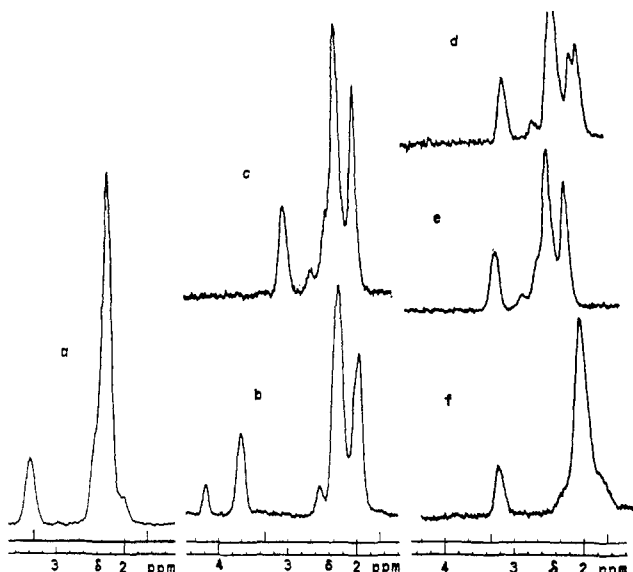


Figure 1. Pmr spectra (60 MHz) of (a) adamantylideneadamantane in CCl_4 at 25° , (b) adamantylideneadamantane in $\text{HSO}_3\text{F-SO}_2\text{ClF}$ at -30° , (c) adamantylideneadamantane in $\text{HF-SO}_2\text{ClF}$ at -30° , (d) 3-Br complex in HF-SO_2 at -30° , (e) 3- SbF_5 complex in SO_2ClF at -70° , (f) 3-Ag complex in SO_2 at -30° .

Table I. Olefinic Carbon-13 Chemical Shifts of σ and π Complexes of Adamantylideneadamantane, 2,3-Dimethyl-2-butene, and Ethene^a

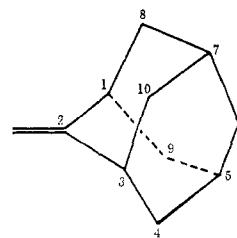
Complex	Ad=Ad (3)	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ (2)	$\text{CH}_2=\text{CH}_2$ (1)
Olefin	131.6 ^b	126.0 ^c 123.2 ^d	124.5 ^d (122.8) ^e
Epoxide	73.7 ^e	60.3 ^e	39.1 ^e
H	208.5 ^h	197.1 ^f	
HF^m	155.0		
Ag	143.6 ^e 141.0 ⁱ	131.0 ^f	118.2 ^e
Cl	157.7	151.6 ^f	74.0 ⁿ
Br	158.6 ^g	138.5 ^f	72.9 ^f
I	153.6	125 ⁱ	67.8
SbF_5	157.2 ^o		

^a δ in parts per million from TMS. ^b In benzene at 35° . ^c In SO_2ClF at -60° . ^d In SO_2ClF at -120° . ^e In CH_2Cl_2 at 20° . ^f In SO_2 at -60° . ^g In Br_2 at $30-35^\circ$. ^h In $\text{HSO}_3\text{F-SbF}_5$ (1:1)- SO_2 at -60° . ⁱ Reference 19. ^j In SO_2 at -30° . ^k Reference 11a. ^l Reference 11b. ^m In SO_2ClF at -70° . ⁿ G. A. Olah, D. A. Beal, and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3387 (1973). ^o In SO_2ClF at -80° .

soluble in SO_2 or SO_2ClF) consisted of broad singlets at δ 3.37 (4 H) and 2.2 (24 H) (Figure 1a and Table II). The proton-decoupled cmr spectrum of a solution of 3 in benzene was recorded at 35° , and the results are shown in Tables I and III. Assignments were made from a consideration of the relative peak intensities and from "off-resonance" decoupling experiments. The two signals at $\delta_{13\text{C}}$ 28.9 and 32.2, which both became doublets on "off-resonance" decoupling, were assigned to $\text{C}_{5,7}$ and $\text{C}_{1,3}$, respectively, by assuming a minimal substituent effect (compared with the corresponding shifts in adamantane) of the vinyl group (double bond) on $\text{C}_{5,7}$ (γ carbons).

Protonation. (a) In Superacid Systems. Ethene in fluoroantimonic acid (HF-SbF_5 ; 1:1)- SO_2 or SO_2ClF is protonated to the ethyl cation, which due to its great electron deficiency, even in this low-nucleophilicity medium, extracts fluoride ion to give the rapidly equi-

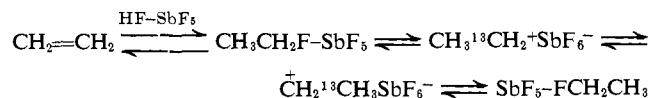
Table II. Proton Chemical Shifts of Adamantylideneadamantane Complexes^a



Compd	Solvent ^b	$\text{H}_{2,2'}$	$\text{H}_{1,1',3,3'}$	Others
3	CCl_4		3.37	2.2
3	$\text{HF-SO}_2\text{ClF}$ (-30°)		3.0	2.0-2.7
3-H	$\text{HSO}_3\text{F-SO}_2$ (-30°)	4.1-4.3	3.65	1.9-2.5
3-Br	$\text{Br}_2\text{-HF-SO}_2$ (-30°)		3.1	2.0-2.7
3-Br	Br_2		4.5	3.5-4.2
3-Cl	$\text{Cl}_2\text{-SO}_2\text{-HSO}_3\text{F}$ (-30°)		3.0	1.9-2.7
3-I	$\text{SO}_2\text{-HSO}_3\text{F-ICN}$ (-20°)		3.3	2.2-3.0
3- SbF_5	SO_2ClF (-80°)		3.55	2.35-2.6
3-Ag	CH_2Cl_2		3.35	1.8-2.2

^a Parts per million from TMS. ^b Probe temperature 37° unless otherwise indicated.

brating ethyl fluoride-antimony pentafluoride complex.¹² As shown by isotopic ^2H and ^{13}C scrambling experiments, the equilibration proceeds through the ion pair, *i.e.*



Protonation of 2,3-dimethyl-2-butene with HF-SbF_5 (5:1)- SO_2ClF at -120° results in the formation of the dimethylisopropylcarbenium ion,¹³ which is also a reasonable tertiary-tertiary model system for ion 3-H (*vide infra*) having the character of a rapidly equilibrating ion (δ_{H} 4.4; δ_{CH_3} 3.32; $\delta_{13\text{C}}$ (tertiary) 197.1).¹⁴

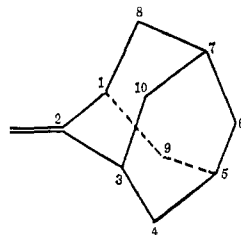
Although adamantylideneadamantane (3) is insoluble in SO_2 and SO_2ClF , addition of HSO_3F or 1:1 $\text{HSO}_3\text{F-SbF}_5$ at -70° gave a solution of the 2-(2'-adamantyl)-adamantyl cation whose nmr spectrum showed no temperature dependence between -70 and 25° . At room temperature in HSO_3F the ion was stable for several hours.

The methine proton chemical shift of δ 4.1-4.3 (Figure 1b) and the ^{13}C chemical shift of C_2 and C_2' ($\delta_{13\text{C}}$ 208.5) are indicative of a rapidly equilibrating carbenium ion. This is confirmed by comparison with data for dimethylisopropylcarbenium ion,¹⁴ which has been shown to be a rapidly equilibrating ion. In agreement with the proposed structure for 3-H, the signal at $\delta_{13\text{C}}$ 208.5 became a doublet on proton "off-resonance" decoupling. Unfortunately, the carbon-hydrogen coupling constant could not be measured from the proton-coupled cmr spectrum, because of line broadening arising from long-range carbon-proton coupling ($J_{\text{HC}_{1,3}\text{C}}$). The ^{13}C shifts for the remaining

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Table III. Carbon-13 Chemical Shifts of Adamantylideneadamantane Complexes^a

Compd	Solvent ^b	C _{2,2'}	C _{1,1',3,3'}	C _{4,4',9,9'} (C _{8,8',10,10'})	C _{8,8',10,10'} (C _{4,4',9,9'})	C _{5,5',7,7'}	C _{6,6'}
3	C ₆ H ₆	131.6	32.2	39.6	39.6	28.9	37.5
3-H	SO ₂ (-80°)	208.5	50.2	46.6	46.6	31.4	37.7
3-Br	Br ₂	158.6	39.8	45.0	42.9	29.3	38.8
	SO ₂ ClF (-40°)	157.6	39.7	44.8	42.3	29.0	39.1
3-Cl	SO ₂ (-70°)	157.7	37.6	43.3	39.6	27.3	36.6
3-I	SO ₂ (-70°)	153.6	38.4	43.9	43.3	27.9	37.7
3-SbF ₅	SO ₂ (-82°)	156.6	36.7	42.3	38.7	26.5	35.7
	SO ₂ ClF (-80°)	157.2	39.5	43.5	37.5	27.3	36.5
3-Ag	CH ₂ Cl ₂	143.6	36.7	44.0	44.0	30.2	38.7
	SO ₂ (-30°)	141.0	34.5	42.5	41.2	27.8 and 28.1	37.0
3-O	CH ₂ Cl ₂	73.7	33.6	39.3	37.0	29.2	38.9
3-HF	SO ₂ ClF (-80°)	155.0	35.9	41.5	38.0	25.9	35.1

^a Parts per million from TMS. ^b Probe temperature 30–35° unless otherwise indicated.

carbons occur at δ_{13C} 50.2, 46.6, 37.7, and 31.4 (HSO₃F–SbF₅, 1:1, SO₂). Assignments were made from a consideration of the relative peak intensities and from “off-resonance” decoupling experiments. The substituent effect of the protonated double bond in 3-H on the shifts of C_{8,10} and C_{4,9} apparently is the same, since there are only four carbon signals (excluding the C₂ signal), unlike the case of the bromo, chloro, iodo, and silver adducts where five or six carbon resonances in this region are observed. The C_{1,3} resonance is deshielded 18 ppm from the corresponding resonance in the parent alkene 3, indicating substantial positive charge at C₂. A comparison of the methyl carbon shifts in 2,3-dimethyl-2-butene^{11c} and in the dimethylisopropylcarbenium ion¹⁴ shows a similar α -substituent effect (22.1 ppm). This is additional evidence for the equilibrating carbenium ion structure of 3-H, since the α -substituent effect in olefin π complexes (alkonium ions) is much smaller (see Table III).

In addition to the methine proton signal (see above) the pmr spectrum of 3-H showed a broad singlet at δ 3.65, which was assigned to the tertiary bridgehead protons at C₁, C₃, C_{1'}, and C_{3'}. The resonances from the remaining 24 protons in the molecule have a completely different appearance from those in the parent olefin and occur as a multiplet between δ 1.9 and 2.5 in HSO₃F (Figure 1b) or between δ 2.3 and 2.9 in 1:1 HSO₃F–SbF₅.

On quenching ion 3-H with water or alkali at 0°, the parent alkene was recovered almost quantitatively. The failure to form the corresponding alcohol is in all probability due to the increased steric hindrance caused by the axial protons at C₄, C₉, C_{4'}, and C_{9'}, which prevent the nucleophile attacking the electron deficient C₂ and C_{2'} positions.

(b) **In Hydrogen Fluoride.** At higher temperature and generally under pressure, ethene reacts with hydrogen fluoride to form ethyl fluoride.¹⁵ When a stream of ethene is passed through liquid hydrogen

fluoride at –80°, a solution is obtained whose pmr and cmr spectra showed weak signals at δ 5.13 and δ_{13C} 120.4, respectively. The small changes in these shifts from those of ethene indicate that only weak solvent-solute interactions occur (outer π complex formation), and it is unlikely that an alkonium ion is formed.

2,3-Dimethyl-2-butene, in contrast, reacts almost quantitatively with hydrogen fluoride at –80° to give 2-fluoro-2,3-dimethylbutane: δ_{13C} 16.0 (CH₃), 21.8 (CH₃, $J_{C,F}$ = 147.9 Hz), 37.0 (CH, $J_{C,F}$ = 17.6 Hz), 112.0 (CF, J_{CF} = 20.5 Hz).

Adamantylideneadamantane (3), however, does not react with liquid hydrogen fluoride at –80°. In HF–SO₂ClF at the same temperature only a π complex type of interaction between the acid and the olefin is observed. Evidence for this interaction is provided in the pmr spectrum from the chemical shift of the bridgehead protons at δ 3.0 and the absence of any signal arising from a proton bonded to C₂ and C_{2'}, due to its rapid exchange with the acid. The remaining protons are found as three signals at δ 2.7 (2 H), 2.4 (14 H), and 2.0 (8 H) (Figure 1c). Also the cmr spectral data (Table III; in particular the C_{2,2'}, chemical shift) are indicative of a π type complex. On the addition of antimony pentafluoride to the solution at –60°, the (HF)_n aggregates are cleaved, forming the strong acid H₂F⁺SbF₆[–]. The π complex now reacts further to give the equilibrating ion 3-H, as shown by its pmr and cmr spectra.

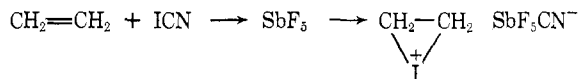
The spectral data indicate that in the more polar SO₂ solvent, protonation of adamantylideneadamantane to give 3-H occurs upon addition of hydrogen fluoride. In the addition reactions of hydrogen halides to olefins this is the first direct observation of the intermediate carbenium ion (not to be confused with protonation of olefins in the presence of strong Lewis acids,¹³ i.e., in superacids containing complex fluoride counterions).

Halogenation. Electrophilic additions of halogens to olefins show high stereoselectivity and consequently are assumed to take place *via* halonium ion inter-

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mediates. Alkylenehalonium ion complexes, which were observed and characterized in our preceding work,^{6,16} were prepared from 1,2-dihaloalkanes under stable ion conditions *via* neighboring halogen participation. They have not been, however, so far observed in direct electrophilic halogen additions to olefins.

The use of "positive halogen" complexes prepared from cyanogen iodide or bromide in the presence of a slight excess of SbF₅ in SO₂ or SO₂ClF solution at low temperature enabled us now to directly prepare alkylenehalonium ion complexes *via* electrophilic halogenation of alkenes. For example, ethene gave with ICN^{δ+}-SbF₅^{δ-} at -60° the etheniodonium ion 1-I, with



pmr spectral characteristics identical with those reported previously.^{16b} The reaction of ethene with cyanogen bromide-antimony pentafluoride resulted only in the formation of polymeric material. Cyanogen chloride-SbF₅ did not react with ethene (or with 2,3-dimethyl-2-butene and adamantylideneadamantane) to give the corresponding chloronium ion, perhaps indicating the reversed polarity of cyanogen chloride compared with the other halides. 2,3-Dimethyl-2-butenebromonium and -iodonium ions, prepared by direct halogenation with the appropriate cyanogen halide-antimony pentafluoride complexes, showed identical pmr spectra with the same ions prepared by ionization of 1,2-dihalo precursors.⁶

Using the highly polarized complexes, BrCN-SbF₅ and ICN-SbF₅ (in which SbF₅ is coordinated to the nitrogen), as electrophilic halogenating agents, the possibility of an addition-elimination reaction forming the halonium ion *via* neighboring group participation is excluded. Addition of cyanide cannot take place under the reaction conditions; furthermore, if such an addition would take place the resulting α-haloalkylnitrile would be unable to form an alkylenehalonium ion. These results directly show the formation of alkylenehalonium ions in the course of electrophilic addition of halogen to olefins.

The adamantylideneadamantane-bromine complex, 3-Br, is formed directly by the addition of bromine to a solution of parent alkene 3 in carbon tetrachloride.⁷ The complex is insoluble in nonpolar solvents and decomposes to the parent olefin when treated at room temperature with polar solvents such as acetone and pyridine. Similar decomposition occurs when irradiated or under high vacuum (10⁻⁷ Torr). Using neat bromine, bromine in methylene bromide, or bromine in SO₂ containing HF, HSO₃F, or AgSbF₆ as solvent, we were also successful in obtaining stable solutions of similar adducts. In neat bromine at 25° the complex 3-Br was stable for at least 60 hr. Dissolving the complex in acidic SO₂ gave bromine, indicating that the group bonded directly to the olefin-attached bromine atom had changed from Br₃ to Br, F, SO₃F, or SbF₅. In the case of AgSbF₆ being present in solution, silver bromide precipitated. Bromine complex 3-Br could be obtained by adding bromine, *N*-bromosuccinimide,

or cyanogen bromide to adamantylideneadamantane (3) in SO₂-HSO₃F. At -30°, ion 3-H also reacted slowly with bromine to form 3-Br. In 3-Br, the chemical shift of the bridgehead protons (H₁, H₃, H_{1'}, and H_{3'}) is found at δ 4.5 in neat bromine and δ 3.1 in HF-SO₂. The remaining 24 protons show three signals at δ 3.5-4.2 (neat bromine) and four signals at δ 2.0-2.7 (HF-SO₂; Figure 1d). The deshielding of the protons by approximately 1.5 ppm in neat bromine is most likely a solvent effect, since we found for adamantane, as model compound in CCl₄, a singlet at δ 2.2, while in neat bromine the singlet was found at δ 3.55.

The proton-decoupled carbon-13 nmr spectrum of 3-Br dissolved in excess bromine consisted of resonances at δ_{13C} 45.6, 42.9, 39.8, 38.8, and 29.3 (excluding the C-2 resonance). The shifts are only slightly affected by recording the spectrum in SO₂ClF-FSO₃H-Br₂ at -40°. On "off-resonance" decoupling the two peaks at δ_{13C} 29.3 and 39.8 became doublets, while the other three became triplets, indicating that the plane of symmetry in the parent olefin through carbons 1, 2, 3, and 6 as well as 1', 2', 3', and 6' no longer exists in 3-Br, otherwise there would be two and not three triplets in this region of the spectrum. The signal at δ_{13C} 38.8 is the least intense of the aliphatic carbon resonances and was assigned to C₆. For a 2-substituted adamantane, substituent effects at the 6 position should be minimal, and hence the C-6 chemical shift should be almost the same as the corresponding resonance in adamantane (δ_{13C} 38.2).¹⁷

There are only two doublets (of equal intensity) instead of the three we would expect on the disappearance of the above discussed plane of symmetry, which indicates that C-5 and C-7 must be equivalent. This suggests that the substituent effect at C-7 of the brominated double bond is negligible, since its effect at C-5 is almost certainly very small. The more shielded doublet at δ_{13C} 29.3, which is closer than the signal at δ_{13C} 39.8 to the shift of the corresponding carbons in adamantane (δ_{13C} 28.7)¹⁷ and the parent olefin 3, leads us to assign it to C-5 and C-7. The C_{1,3} shift, which is deshielded from that in the parent olefin, is compatible with the existence of positive charge at C-2 in ion 3-Br. Comparison of ¹³C chemical shift data for olefins and their corresponding bromonium complexes indicates that the substituent effect of an α carbon, caused by the introduction of the bromine atom, is deshielding.¹⁸

The chemical shifts of C-2 and C-2' should be important in determining if the bromine complex 3-Br is indeed a three-membered ring σ complex, a three-center bond π complex, or a rapidly equilibrating 2-bromocarbenium ion. The ¹³C chemical shifts of the corresponding carbons in the related ethylenebromonium and 2,3-dimethyl-2-butylenebromonium ions have been used to determine the structure of these ions.^{14,19} There is good evidence from chemical shifts as well as coupling constants for the three-membered ring nature of the ethylenebromonium ion.

The cmr data for the 2,3-dimethyl-2-butylenebromonium ion, however, need further consideration. The

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chemical shift of the tertiary carbons is δ_{13C} 138.5, or deshielded 65.6 ppm from that of the ethylenebromonium ion. The observed methyl substituent effect in the model system, ethylene oxide–tetramethylethylene oxide, is only 21.2 ppm. On the basis of this, and several other model systems, the observed shift in 2-Br was, in the first study of the ion considered, incompatible with either a bridged or equilibrating system, and consequently it was proposed that the ion existed as either a mixture of approximately 50% each of bridged and equilibration forms or a rapidly equilibrating pair of partially bridged ions. The data have been subsequently reinterpreted,¹⁸ in favor of the bridged ion species, on the basis of an equally large methyl substituent effect (74 ppm) observed in the ethylenebenzenium and 2,3-dimethyl-2-butylenebenzenium ions. It was argued that introduction of four methyl groups in cyclic ions produced a more profound effect on charge density, and hence on cmr shifts, than might be anticipated in a three-membered ring system in the absence of positive charge. More recent studies,¹⁹ however, of the temperature-dependent cmr spectra of alkylene halonium ions, have proved the existence of an equilibrium between bridged halonium ions and β -halocarbenium ions, particularly in systems involving tertiary carbenium ions.

A comparably large alkyl-substituent effect is observed in the carbon shifts of the ethylenebromonium ion and complex 3-Br (158.6 – 72.9 = 85.7 ppm). The corresponding chemical shift difference between the two related epoxides is only 34.6 ppm. An attempt to protonate 3-O with superacid at -70° in order to estimate the effect of charge on the C_2 and C_2' shifts did not give the protonated epoxide but rearrangement to the protonated spiro(adamantane-2,4'-homoadamantan-5'-one).²⁰

It is possible from a consideration of the geometry of complex 3-Br to exclude several structural possibilities (Figure 2). The restriction placed on the lateral movement of the bromine atom by the $C_{8,10}$ and $C_{8',10'}$ protons prevents the ion from being a rapidly equilibrating ion pair, a mixture of bridged and equilibrating forms, or a rapidly equilibrating pair of partially bridged ions. The chemical shift of the olefinic carbons C_2 and C_2' at δ_{13C} 158.6 also excludes the possibility of a rapidly equilibrating 2-bromocarbenium ion, as this would have an average shift of approximately δ_{13C} 200 (calculated from the average values of the tertiary carbon shifts in the trimethylcarbenium ion and *tert*-butyl bromide). Complex 3-Br is therefore most likely a bridged species but there are several data which suggest that it is a bridged species of a different type from the ethylenebromonium ion (*i.e.*, σ type complex). 3-Br obtained from bromine and 3 in CCl_4 transfers bromine irreversibly to cyclohexene or 2,3-dimethyl-2-butene forming the corresponding dibromides and adamantylideneadamantane. Also, all halogen adducts of 3, on quenching with nucleophiles, yield the precursor olefin, rather than the 1,2-addition product. Unlike ethene, adamantylideneadamantane (3) forms complexes with HF in SO_2ClF , or SbF_5 in SO_2ClF , which can readily be converted, by the addition of nucleophiles, to the starting material. The cmr shifts in these complexes

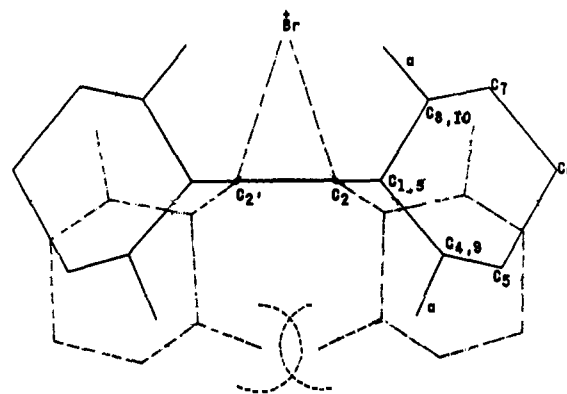


Figure 2. Steric repulsion between $H_{4,9}$ and $H_{4',9'}$ on formation of the three-membered ring bromonium ion from adamantylideneadamantane. Approximate geometry of olefin 3 (—), and bromonium ion (---).

are very similar to those observed for 3-Br. It is difficult to describe the HF and SbF_5 complexes in any other terms apart from a π type complex. A weak Mulliken outer complex type interaction alone cannot explain the total number of signals in the cmr spectrum of these complexes. These results indicate that the electrophile is bound to one side of the adamantylideneadamantane molecule and that consequently one element of symmetry, which is present in the parent compound, no longer exists.

Furthermore, we have found, in an attempt to obtain the X-ray photoelectron (ESCA) spectrum of 3-Br, that in the extremely high vacuum (10^{-8} Torr) bromine was pumped off, with the parent olefin remaining on the probe. This is a good indication that bromine is relatively loosely bound to the olefin. Similarly we observed that irradiation of crystals of 3-Br at room temperature with strong light tended to decompose 3 to bromine and the parent alkene, while in the dark the complex is stable at this temperature.

Consideration of molecular models also shows why the formation of a σ -bonded three-membered ring bromonium ion does not seem to be possible for the sterically hindered adamantylideneadamantane. As can be seen in Figure 2, the four axial hydrogens bound to $C_{4,9,4',9'}$ would strongly interact in case the molecule started bending toward its center as a result of a change in hybridization at $C_{2,2'}$ from sp^2 to sp^3 to form the σ bonded bromonium ion.

The above considerations therefore lead us to suggest that 3-Br has more the character of a two-electron, three-centered bonded π complex and not a three-membered ring σ complex (alkylenebromonium ion). Were the latter involved, it should contain considerably lengthened C-Br bonds allowing nucleophilic replacement from the side of the bromine atom. (To determine the distance of the bromine atom from the C_2 - C_2' bond in complex 3-Br, a single crystal X-ray diffraction study is presently attempted by Professor M. Simonetta.)

The bonding between alkene and bromine can be envisaged as arising from the initial interaction of the π system of the alkene with the electrophilic bromine, *i.e.*, the two p orbitals of the π bond interact with the back lobe of the antibonding orbital of bromine while the bromine-bromine covalent bond remains intact al-

(20) For a study of the acid-catalyzed rearrangement, see G. B. Gill and D. Hands, *Tetrahedron Lett.*, 181 (1971).

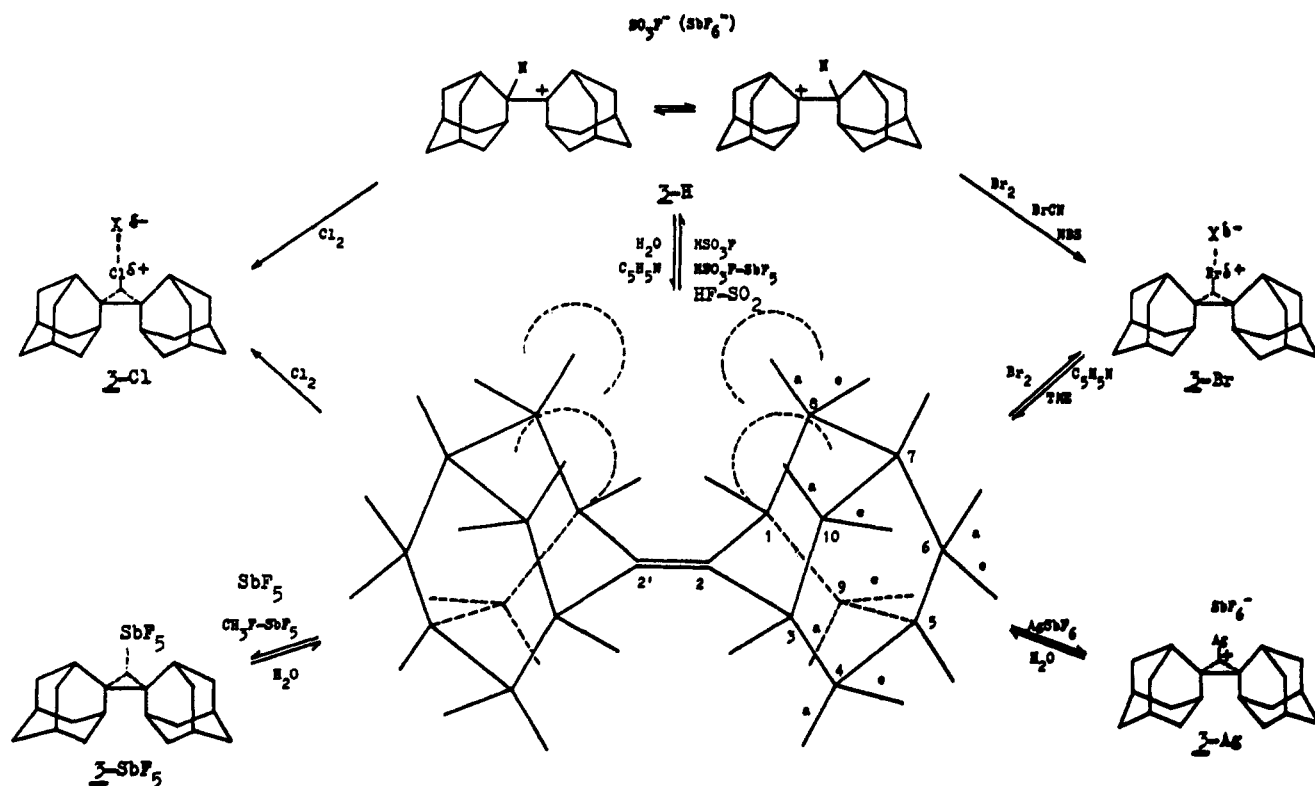


Figure 3. Outline of reactions for adamantylideneadamantane.

though polarized by another bromine molecule (a similar situation is found with BrCN-SbF_5 complexes with **3** (see ref 1, Figure 1). This interaction would then lead to a three-center bound π complex (alkonium complex) such as proposed in general for the reaction of electrophiles with alkenes^{1,5} and postulated for the reaction of the isoelectronic borane with alkenes.^{5,21} There may also be involved back-donation of electrons from the d_{xy} (or other $d\pi$ - p hybrid) orbitals of the bromine atom into the antibonding orbitals on the carbon atoms. Such a bonding situation has been postulated for many metal-olefin complexes.²² However, only in the process of cleavage of the bromine-bromine bond (or bromine-carbon bond in cyanogen bromide), involving rehybridization of the increasingly positive bromine atom, will opening of the three-center bond with more or less concerted participation of the non-bonded electron pairs on bromine with the developing carbenium center lead to formation of the three-membered ring alkylenebromonium ion.

The chlorine adduct **3-Cl** was obtained when molecular chlorine was introduced into a SO_2 solution of the protonated alkene **3-H** (HSO_3F) at -30° . The formation of the chlorine complex **3-Cl** from the equilibrating ion **3-H** is a relatively slow process at this temperature and can be observed by means of pmr spectroscopy. As the reaction proceeds, the disappearance of the methine proton and the shifting of the proton signals of the bridgehead protons from δ 3.68 to 3.00 can be followed. The remaining 24 protons of the chlorine adduct show a pattern of signals very similar to the bromine adduct **3-Br**, suggesting that **3-Cl** also may have π complex character.

(21) P. R. Jones, *J. Org. Chem.*, **37**, 1886 (1972).

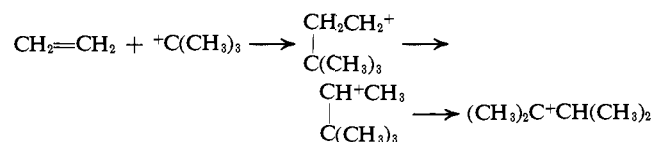
(22) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Interscience, New York, N. Y., 1973.

This is also indicated by the C_2 chemical shift (Table I) which is similar to the corresponding shift in **3-Br**. The other carbon chemical shifts for **3-Cl** are shown in Table III. Assignments were made in the same manner as for the bromine adduct, and much of the discussion for the cmr spectrum of this compound is also relevant for **3-Cl**.

The iodine adduct **3-I** was obtained by adding adamantylideneadamantane (**3**) to a solution of cyanogen iodide in $\text{SO}_2\text{-HSO}_3\text{F}$ at -20° . The pmr spectrum of **3-I** shows the signal for the bridgehead protons at δ 3.30 and the remaining 24 protons give five signals at δ 2.98, 2.80, 2.72, 2.40, and 2.20. The carbon chemical shifts for **3-I** are shown in Tables I and III.

The reactions by which the above adducts of adamantylideneadamantane are formed are summarized in Figure 3. The results of quenching experiments are also shown.

Alkylation. When ethene is introduced into a solution of excess *tert*-butyl cation (prepared with a minimum of free acid present) in SO_2 solution at -78° , the dimethylisopropylcarbenium ion is formed, indicating rearrangement of the initially formed neopentylcarbenium ion *via* 1,2-hydrogen and subsequent 1,2-alkyl shifts to the most stable tertiary cation.



Addition of a cold solution of 2,3-dimethyl-2-butene in SO_2ClF to a suspension of *tert*-butyl hexafluoroantimonate in SO_2ClF at -78° results in the formation of polymeric material, as indicated by the pmr spectrum. Adamantylideneadamantane does not react with the

above salt in SO_2ClF at -78° but on warming to -60° gives a complex mixture of as yet unidentified products. If the *tert*-butyl salt is prepared *in situ* by the reaction of 1-chloro-2-methylpropane with an excess of antimony pentafluoride, the alkene forms the SbF_5 complex (*vide infra*) and leaves the salt unreacted. Similarly, adamantylideneadamantane reacts with $\text{CH}_3\text{F-SbF}_5$ complex¹² in SO_2ClF at -78° to give the same SbF_5 complex. Additional peaks in the cmr and pmr spectrum were assigned (by comparison with authentic sample) to the $\text{CH}_3\text{OSO-F-SbF}_5$ complex¹² ($\delta_{13\text{C}}$ 69.7) and excess $\text{CH}_3\text{F-SbF}_5$.

When a cold stream of ethene is passed through a solution of $\text{CH}_3\text{F-SbF}_5$ in SO_2 at -78° , predominantly polymeric material is formed. From 2,3-dimethyl-2-butene, under similar conditions, formation of the expected tertiary carbenium ion (dimethyl-*tert*-butyl-carbenium ion) is predominant.¹²

There is, therefore, no evidence from the above results for the existence of a long-lived alkyl-bridged intermediate between any of the three olefins studied and the *tert*-butyl cation or methyl fluoroantimonate (*i.e.*, the $\text{CH}_3\text{F-SbF}_5$ complex).

Antimony Pentafluoride-Alkene Complexes. When ethene is introduced into a solution of SbF_5 in SO_2 or SO_2ClF at -78° , polymeric material is formed. 2,3-Dimethyl-2-butene reacts with SbF_5 in SO_2ClF at -70° to give a mixture of the trimethylcarbenium, dimethyl-*tert*-butylcarbenium, and dimethylisopropylcarbenium ions. As previously reported,²³ it was found that the latter ion decomposed on warming the solution to -20° , to give a mixture of the diethylmethylcarbenium and dimethylpropylcarbenium ions. In SO_2 , the pmr spectrum for the same reaction showed that small amounts of the trimethylcarbenium and dimethylisopropylcarbenium ions were present. In addition, unassigned signals were observed at δ 1.54, 6.1, 9.17, and 9.24.

When **3** is treated with SbF_5 in SO_2 or SO_2ClF at -70° , the complex **3-SbF₅** is formed. In the pmr spectrum of this adduct the signal for the bridgehead protons is found at δ 3.55 (SO_2ClF) and the remaining 24 protons show two signals at δ 2.6 (16 H) and 2.35 (8 H) (Figure 1e). Quenching of **3-SbF₅** with ice-water gives the parent olefin in quantitative yield. If a solution of **3-SbF₅** in SO_2 is allowed to warm up to -30° , the complex begins to decompose.

The cmr spectrum of **3-SbF₅** resembles that of the bromine complex **3-Br** and assignments were made on the basis of similar considerations used for the spectrum of that complex. The results are shown in Table II. The existence of five carbon signals between $\delta_{13\text{C}}$ 26 and 42 clearly indicates, as in the case of **3-Br**, that the plane of symmetry which exists in the parent olefin is no longer present in the complex.

The bonding for **3-SbF₅** mostly likely involves coordination of the antimony atom with the carbon-carbon double bond in a two-electron three-center bond.

Silver-Alkene Complexes. When ethene is introduced into a solution of silver hexafluoroantimonate in methylene chloride, the silver complex is formed whose proton decoupled cmr spectrum (Table I) shows a singlet absorption at $\delta_{13\text{C}}$ 118.2. This resonance is

shielded approximately 5 ppm relative to that of the free alkene, although part of this difference may arise from solvent effects. Similar shieldings have been observed for the silver(I) complexes of cyclopentene and cyclohexene, and it was proposed²⁴ that either there was an increase in the σ character of the bonds at the olefinic carbons, or that the π -orbital energy of the alkene is reduced by coordination with silver ion, so as to produce small changes in the excitation energy.

The silver(I)-alkene complex **3-Ag** was prepared by adding adamantylideneadamantane to a solution of excess silver hexafluoroantimonate in CH_2Cl_2 at room temperature, or SO_2 at -30° . The pmr spectrum in SO_2 (Figure 1f) shows peaks at δ 3.35 (H_1 and H_3) and 1.8-2.2. Carbon chemical shift data are shown in Table III and assignments were made in the same way as for the other complexes. There are only four signals in the spectrum of **3-Ag** in methylene chloride which may imply that the complex is in equilibrium with free silver ion and olefin. However, in SO_2 there are six carbon resonances, so that the silver ion must be tightly bound to one side of the carbon-carbon double bond. The C_2 resonance has shifted little in methylene chloride from that in SO_2 , so that if an equilibrium does exist in the former solvent there is an insignificant amount of free olefin present. It is of interest that this is the only complex (in SO_2) where C_5 and C_7 are nonequivalent.

The opposite situation is observed for adamantylideneadamantane and also for 2,3-dimethyl-2-butene (Table I) from that of ethene, since formation of a silver complex results in deshielding of their olefinic carbons by approximately 10 ppm (5 ppm for 2,3-dimethyl-2-butene). In terms of Dewar's concept²⁵ of the bonding in these complexes, we propose that the above downfield shifts result from a decrease in the π -electron density at the olefinic carbons (resulting from σ -overlap between the bonding alkene π orbital with a vacant s or sp hybrid orbital on the silver(I) ion being more than compensated for by back-donation from the metal d orbitals, thus making σ bonding less important than π bonding). It is also possible that the π orbital energy of the alkene is increased by coordination with silver ion, so as to produce small changes in the excitation energy.

The above results for the silver(I) complexes parallel those of the halonium ions in Table I. Shielding of the carbon shift of ethene occurs on formation of the halonium complex, whereas a deshielding of the corresponding carbon shifts occurs for adamantylideneadamantane and 2,3-dimethyl-2-butene.

Reaction with Nitrosonium Salts. Ethene does not react with a solution of nitrosonium tetrafluoroborate in SO_2 at -70° . The pmr spectrum shows a singlet at δ 5.13, coincident with that of the precursor under identical conditions. At the same temperature, 2,3-dimethyl-2-butene reacts with the nitrosonium salt to give polymeric products. When adamantylideneadamantane (**3**) is added to a suspension of NO^+PF_6^- in SO_2 at -70° a clear solution is obtained whose pmr spectrum showed singlets at δ 3.9 (4 H) and 1.8-2.2 (24 H) indicating the probable formation of a rapidly equilibrating nitrosocarbenium ion **3-NO** or a bridged

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(25) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

(23) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 4739 (1967).

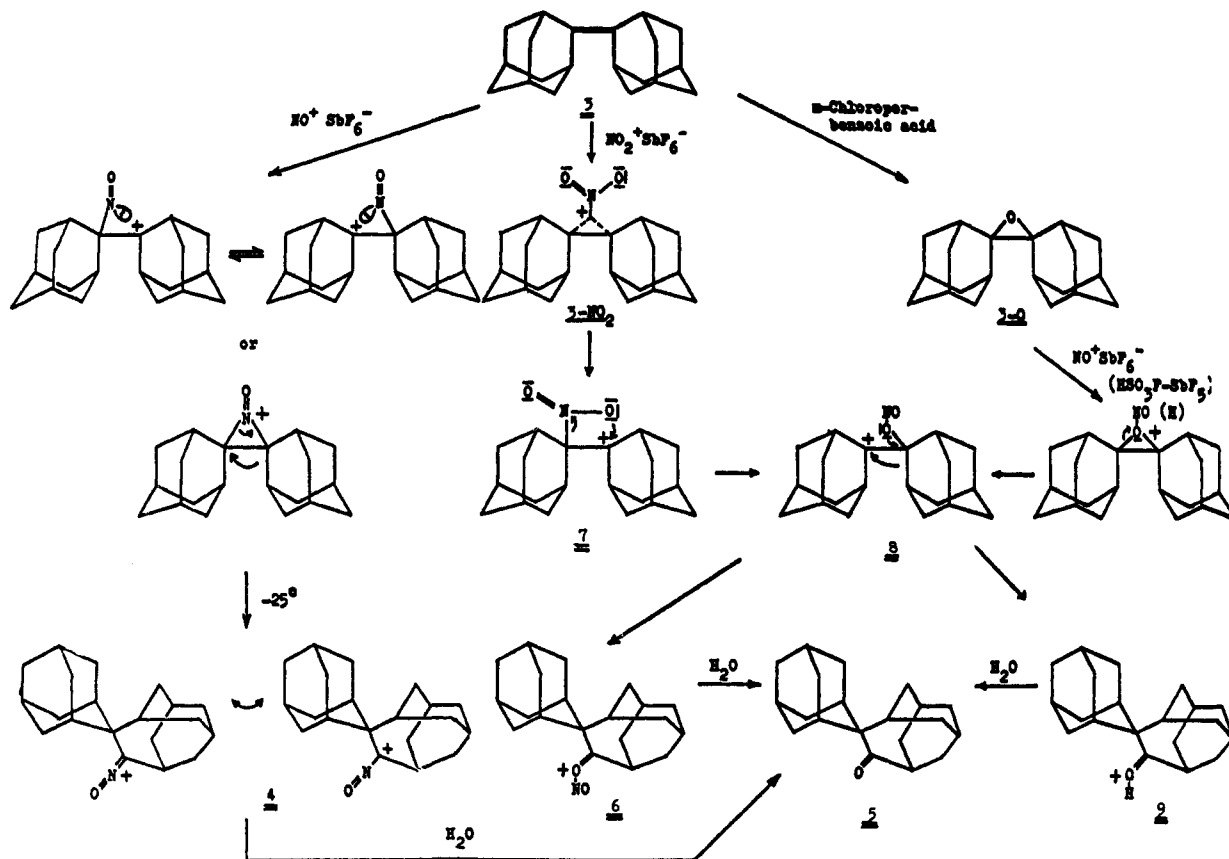


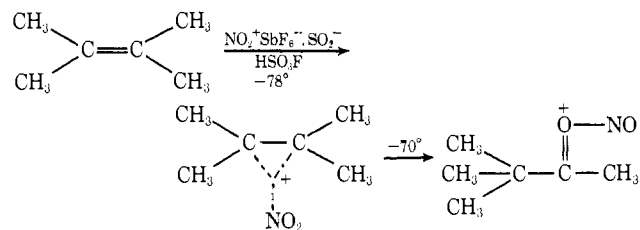
Figure 4. Proposed mechanisms of the reactions of adamantylideneadamantane with nitroso- and nitronium hexafluoroantimonate.

nitrosonium ion. We were unable to obtain a satisfactory cmr spectrum of this ion. Allowing the solution to stand at -20° for 2 hr gave spiro(adamantane-5'-nitroso-2,4'-homoadamantyl) cation 4 according to the mechanism in Figure 4. Quenching of ion 4 with water yielded spiro(adamantane-2,4'-homoadamantane-5'-one) (5), a compound which is also obtained by protonation of adamantylideneadamantane oxide.²⁰ In the pmr spectrum of ion 4 signals are at δ 4.2 (1 H), 3.0 (2 H), 2.5 (2 H), 2.2 (4 H), and 1.6–2.0 (17 H). The most deshielded signal was assigned to the proton on the tertiary carbon adjacent to the electron-deficient carbon center.

Reaction with Nitronium Salts. Ethene reacted with $\text{NO}_2^+\text{SbF}_6^-$ in SO_2 at -70° to give a solution whose pmr spectrum consisted of a singlet at δ 62.0. The observed deshielding of 1.1 ppm from the singlet of ethene indicates formation of a π complex. On warming the sample at -10° , it gave polymeric nitro group containing materials.

A π complex of 2,3-dimethyl-2-butene with nitronium salts could also be prepared by the addition of an SO_2 solution of the olefin to an $\text{SO}_2\text{-HSO}_3\text{F}$ solution of $\text{NO}_2^+\text{SbF}_6^-$ at -78° . (It was necessary to have acid present in order to obtain a homogeneous solution and thus a well resolved pmr spectrum). The nitronium π complex shows a single proton resonance at δ 2.42 for the 12 protons of the methyl groups (integrated against a known amount of internal reference), which is deshielded by 1.1 ppm from the parent alkene (δ 1.33, SO_2 at -70°). Since the alkene reacts with HSO_3F in the absence of the nitronium salt to give the corresponding fluorosulfate as does ethene (δ 1.65 t, 4.80 q

under the same conditions, the formation of fluorosulfate as well as the rapidly equilibrating protonated alkene (δ 4.4 m, 3.32 d)²³ can be ruled out. The π complex is very unstable and even at -70° upon standing undergoes rearrangement. The rearranged product (*O*-nitroso



ketone) shows a pmr spectrum with singlets at δ 2.45 (9 H) and 3.18 (3 H). On quenching with aqueous sodium bicarbonate solution at 0° , pinacolone is formed.

Upon addition of adamantylideneadamantane to a suspension of $\text{NO}_2^+\text{SbF}_6^-$ in SO_2 at -70° , a clear solution of the *O*-nitrosated spirocyclic ketone 6 is obtained. Due to the high reactivity of the nitronium ion and the subsequent fast rearrangement of the initially formed tertiary ion 7, neither the π complex 3- NO_2 nor the ions 7 and 8 can be observed by pmr spectroscopy. For the mechanism of the reaction we assume the initial formation of the π complex and its subsequent transformation through the incipient nitrocarbenium ion 7 to the nitrocarbenium ion 8 (a reaction somewhat similar to the hydroboration of alkenes). The reaction of adamantylideneadamantane oxide 3-O with NO^+PF_6^- also gives the same stable end product as the above reaction, thus confirming the intermediacy of ion 8. The structure for compound 6 was determined on the

basis of the close similarity of its pmr spectrum to that of the protonated spirocyclic ketone **9** (only the HO-proton signal at δ 14.25 is absent.) Quenching of ion **6** with ice-water gave the spirocyclic ketone **5** which is identical with the quench product from ion **9**.

Conclusion

The reported chemical and nmr spectral results allow differentiation of complexes formed between alkenes such as ethene, 2,3-dimethyl-2-butene, and adamantylideneadamantane with several electrophiles in solvents of low nucleophilicity into two differing classes: σ -bonded alkenium or halonium complexes, and π -bonded alkonium type complexes, containing an oriented two-electron, three-center bond between the carbon-carbon double bond and the electrophile (molecularly bound π complexes). These observations have substantial bearing on our understanding of electrophilic additions to multiple bonds where the transition state can lie either "early" on the reaction coordinate, thus being of alkonium type π complex nature, or "late," *i.e.*, resembling alkenium ions or σ complexes.

Experimental Section

Materials. Adamantylideneadamantane was prepared from adamantanone according to the method of Geluk.²⁶ Ethene and 2,3-dimethyl-2-butene were commercial materials of the highest purity. Silver hexafluoroantimonate, nitrosonium hexafluorophosphate, and nitronium hexafluoroantimonate were commercially available materials (Cationics, Inc.). Methyl fluoroantimonate was prepared as described by Olah, *et al.*¹²

Preparation of Ions and Complexes. Protonation. Adamantylideneadamantane when added directly to a mixture of FSO₃H-SbF₅ (1 ml) or FSO₃H (1 ml) in SO₂ or SO₂ClF (1 ml) at -70° gave a clear homogeneous solution of ion **3-H**. The same species was also prepared from the alkene and HF-SO₂ or HF-SbF₅ at -78°.

Bromine-Adamantylideneadamantane. A solution of bromine in carbon tetrachloride was added dropwise to adamantylideneadamantane dissolved in a minimum amount of carbon tetrachloride.⁷ The complex which precipitated from solution was filtered and washed with CCl₄. A sample was recrystallized from Br₂-CH₂Br₂. The bromo adduct could be dissolved in SO₂-HF, SO₂-

HSO₃F, or SO₂-AgSbF₆ at -70° or neat bromine at 25°. The alternate procedure for preparing this complex is to add adamantylideneadamantane to a mixture of SO₂-HSO₃F (1:1) and add bromine, *N*-bromosuccinimide, or cyanogen bromide at -30°.

Chlorine-Adamantylideneadamantane. A solution of adamantylideneadamantane in HSO₃F-SO₂ was saturated with excess chlorine at -70°, and allowed to stand at -30° for 15 min.

Iodine-Adamantylideneadamantane. A solution of this complex was prepared by adding adamantylideneadamantane to a solution of cyanogen iodide-SbF₅ (1:1) in SO₂ at -78°.

Silver(I)-Adamantylideneadamantane. Adamantylideneadamantane was added to a solution of silver hexafluoroantimonate (five-fold molar excess) in CH₂Cl₂ at 25° or SO₂ at -70° to yield a clear solution of the silver-olefin complex.

Silver(I)-2,3-Dimethyl-2-butene and Silver-Ethene. These complexes were prepared by adding an excess of the alkene to a solution of silver hexafluoroantimonate in methylene chloride at 25°. The solutions were evaporated *in vacuo* and the resulting material was dissolved in SO₂ (-70°) or CH₂Cl₂ in order to obtain the nmr spectrum.

Reaction of Adamantylideneadamantane with Nitrosonium and Nitronium Salts. Adamantylideneadamantane was added with vigorous stirring to a suspension of NO⁺PF₆⁻ or NO₂⁺SbF₆⁻. The clear upper layer was separated, for nmr spectral study, from the solid unreacted salts.

Quenching of the Ions and Complexes. Excess methanol or aqueous methanol was cooled to -78° and the SO₂ or SO₂ClF solutions of the ions or complexes were added with vigorous stirring. The methanolic solutions were subsequently added to cold saturated aqueous sodium bicarbonate solutions and the products isolated and purified in the usual way.

Nuclear Magnetic Resonance Spectra. Pmr spectra were obtained by using a Varian Associates Model A56/60A nmr spectrometer equipped with a variable temperature probe. External TMS (capillary tube) was used as reference. The cmr spectra were obtained by the rapid pulse Fourier transform method, using a Varian HA-100 nmr spectrometer, equipped with a variable temperature probe. External methyl iodide (capillary tube) was used both as reference and lock signal. Additional details of the instrument as well as the method used to determine chemical shifts have been described elsewhere.²⁷ Some of the cmr spectra were obtained by the FT method, using a Varian XL-100 nmr spectrometer and an external capillary of TMS as the reference.

Acknowledgment. Partial support of our work by the National Science Foundation is gratefully acknowledged.

(27) G. A. Olah, G. Liang, and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3698 (1973).

(26) H. W. Geluk, *Synthesis*, **2**, 652 (1970).