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Electrophilic Intermediates and Their Reactions in Superacids

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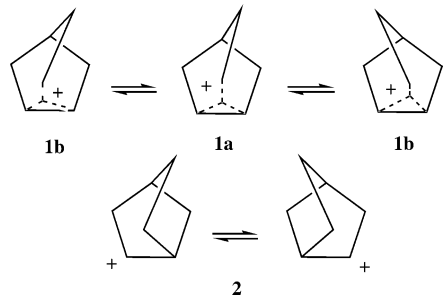
Acid-catalyzed reactions have played a major role in hydrocarbon chemistry involving electron-deficient intermediates such as carbocations, carbodications, onium ions, etc. The pioneering discovery of the use of superacids by George A. Olah, in the early 1960s, to characterize such intermediates under so-called long-lived stable ion conditions led to the understanding of their structures and reactivity patterns much more clearly. Continuing studies in this area in the past 30 years have resulted in a paradigm shift in comprehending the stability and reactivity of electrophilic intermediates in superacid media.

The significance of the carbocations and onium ions as true reaction intermediates has been highlighted by the award of the Nobel Prize to Professor George A. Olah in 1994. I had the distinct privilege of working with him, initially as a graduate student (1974−1978) and, subsequently, over the past 28 years, as a colleague and collaborator. The primary focus of the current perspective is to elaborate on certain new aspects of electrophilic hydrocarbon chemistry that was developed in collaboration with Professor Olah and other investigators. The discussion includes not only studies of some seminal carbocations, such as 2-norbornyl, cyclopropylcarbinyl, and related systems, but also carbodications such as pagodane dications. Studies on intriguing onium ions such as halonium, oxonium, and diazonium ions and their activation in superacids are also discussed. Some examples of new electrophilc reactions such as hydroxylations, aminations, alkylations, acylations, formylations, sulfurations, nitrations, etc., using superacid media are also included.

1. Studies on 2-Norbornyl and Related Cations. By the mid-1970s, the structure of the 2-norbornyl cation, **1**, had been investigated in exquisite detail under both solvolytic and stable ion conditions. It was at the epicenter of the well-publicized classical and nonclassical ion controversy.[1,2]

Based on the rate difference in the acetolysis of *exo*- and *endo*-2-norbornyl brosylates of 350, Winstein and Trifan had postulated[3] in 1949 the intermediacy of a σ-bridged (nonclassical) symmetrical norbornyl cation intermediate **1a** in the case of *exo*-derivative. On the other hand, Brown attributed these differences to steric effects.[2] He proposed that both *exo*- and *endo*-derivatives undergo unassisted ionzation involving trivalent (classical) 2-norbornyl cation **2**, which is capable of undergoing rapid Wagner−Meerwein shift. Saunders, Schleyer, and Olah,[4] by the methods discovered by Olah to generate long-lived carbocations in superacids,[5] were able to generate the 2-norbornyl cation and characterize the fluxional cation by ^{1}H NMR at 60 MHz. In subsequent ^{1}H NMR studies at 60 and 100 MHz at various temperatures (room temperature to −154 °C), Olah and co-workers determined[6−8] the barriers for 2,3 hydrogen shift as well as 6,1,2 hydrogen shift (in the nonclassical formulism; see Scheme 1) by line shape analysis and found them to be around 10.8 and 5.9 kcal/mol, respectively. However, the proton spectrum at −154 °C (at 100 MHz) in $SbF_5/SO_2ClF/SO_2F_2$ solvent system indicated unresolved peaks in the upfield methylene region. The ^{13}C NMR spectrum under similar conditions (at 25 MHz) had more problems because of viscosity-induced line broadening and lack of resolution.[8]



In the late 1970s, Frank Anet at UCLA had built a superconducting NMR spectrometer operating at 395 MHz field strength. We availed his facility to obtain a highly resolved ^{1}H NMR spectrum of the 2-norbornyl cation at −158 °C.[9] The ^{1}H NMR spectrum of the 2-norbornyl cation at room temperature

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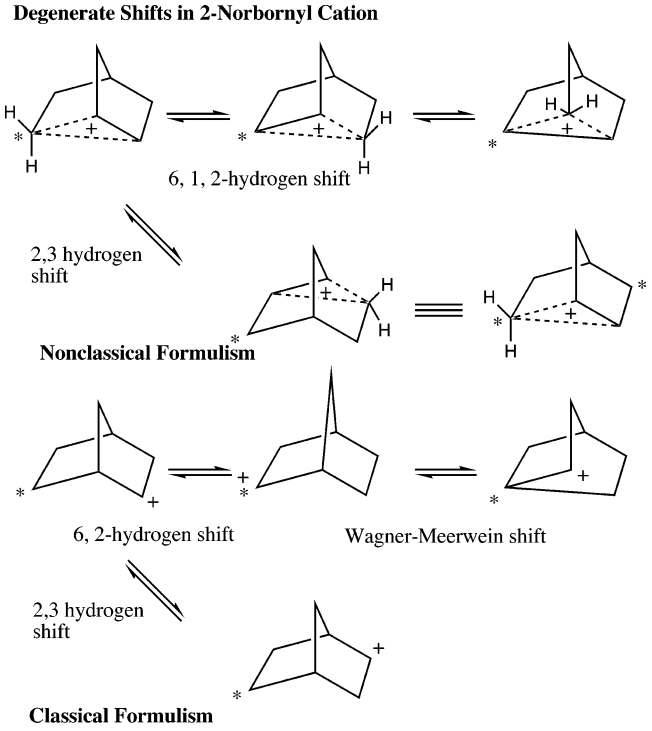
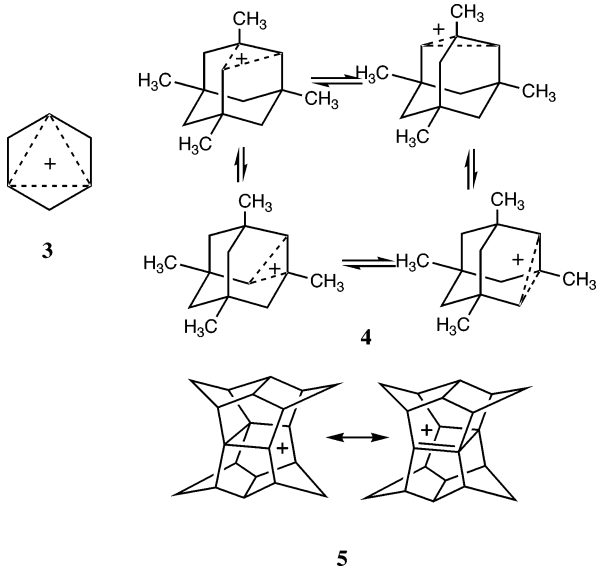
SCHEME 1



shows a single peak at δ ^{1}H 3.10 for all the protons indicating fast 2,3 hydrogen, 6,1,2 hydrogen shifts. Cooling the solution down to −100 °C at 395 MHz shows three peaks at δ ^{1}H 4.92 (4 protons), 2.82 (1 proton), and 1.93 (6 protons), indicating that the 2,3 hydrogen shift is fully frozen, whereas 6,1,2 hydrogen or 6,2 hydrogen and Wagner−Meerwin shifts are still fast on the NMR time scale. Cooling the solution further down to −158 °C resulted in significant changes in the spectrum. The peak at δ ^{1}H 4.92 decoalesced into two peaks at δ ^{1}H 6.75 and 3.17 in a ratio of 2:2. The high-field peak at δ ^{1}H 1.93 broadens and splits into two peaks at δ ^{1}H 2.13 and 1.37 in a ratio of 4:2. The peak at δ ^{1}H 2.83 remained unchanged. The line width (∼60 Hz) observed at 395 MHz at −158 °C compared to the previously observed line width of 30 Hz at 100 MHz at −154 °C has important implications. If there were any slow exchange processes occurring at these low temperatures, some of the resonances should have broadened 15.6 times at 395 MHz compared to the one observed at 100 MHz. The observation of comparably narrow line widths at 395 MHz demonstrated that either the 6,1,2 hydrogen shifts are completely frozen and the 2-norbornyl cation has a symmetrically bridged structure **1a** or the 6,2 hydrogen shift is frozen and so-called Wagner−Meerwein shift (in the classical formulism) is still fast on the NMR time scale with a barrier less than 3 kcal/mol. Moreover, if the Wagner−Meerwein shift is still possible with very low energy barrier, it can involve only unsymmetrically bridged cations **1b** and not classical trivalent ion **2**.

In the same study,[9] to obtain a well-resolved ^{13}C NMR spectrum at 50 MHz field strength, we synthesized 95% ^{13}C-enriched *exo*-2-chloronorbornane (the label present corresponded to one ^{13}C per molecule randomly distributed over C_1, C_2, and C_6 centers). The ionization of such a precursor led to 2-norbornyl cation, wherein the ^{13}C label distributed evenly on all seven carbon atoms due to fast 2,3 hydrogen and 6,1,2 hydrogen shifts. The ^{13}C NMR spectra were obtained at −80 and −159 °C in a relatively short period of time (within a few minutes because of the ^{13}C enrichment) at 50 MHz field strength. The supercooled $SbF_5/SO_2ClF/SO_2F_2$ ionic solution took some time to freeze at −159 °C. At −80 °C, three resonances were observed at δ ^{13}C 91.7, 37.7, and 30.8 indicating that the 2,3 hydrogen shift is frozen. Cooling the solution down to −159 °C showed a highly resolved ^{13}C NMR spectrum with the following five resonances at δ ^{13}C 124.5 (C_2 and C_6, d, 187.7 Hz), 36.3 (C_3 and C_7, t, 131.2 Hz), 37.7 (C_4, d, 150.9 Hz), 20.4 (C_5, t, 153.2 Hz), and 21.2 (C_7, t, 147.1 Hz), clearly demonstrating the σ-bridged nature of the species. The question of any possible fast Wagner−Meerwin shift was resolved by the solid-state cross-polarization magic angle spinning ^{13}C NMR spectrum at 5 K by Yannoni and Myhre, which fully endorsed the symmetrical structure **1a**.[10] If a hypothetical Wagner−Meerwein shift took place in the 2-norbornyl cation, 1 at 5 K, then such a barrier is less than 0.2 kcal/mol.[10] Many theoretical methods at increasingly higher levels also supported the symmetrical structure **1a**.[11] Interest in the structure of the 2-norbornyl cation led to development of many intriguing new methods for structural characterization of carbocations that include ESCA,[8] isotopic perturbation of resonance/equilibrium (notably by deuterium substitution) of Saunders,[12,13] IR and Raman spectroscopy,[7] microcalorimetry[14] (by comparing heats of ionizations), and X-ray.[15] All of these techniques were also applied to the 2-norbornyl cation problem with great success. The field has been extensively reviewed.[16−19]

Many other σ-bridged systems were also studied. These include trishomocyclopropenium cation **3**,[20] 1,3,5,7-tetramethyl-2-adamantyl cation **4**,[21] and the *seco*-pagodyl cation **5**.[22] The latter two systems show partial σ-bridging. In fact, the σ-bridging in carbocations can be partial to fully developed symmetrical bridging. Based on this realization, with Schleyer, Olah, and others, we developed the additivity of ^{13}C NMR chemical shift criteria relating to classical vs nonclassical carbocations in 1980.[21] The total ^{13}C NMR chemical shift difference between a carbocation and the corresponding neutral hydrocarbon provides a rough and useful index. Classical trivalent carbocations show a large chemical shift difference, typically 350 ppm or more, whereas related nonclassical carbocations display differences often 100 ppm or less depending on the extent of bridging.[21]



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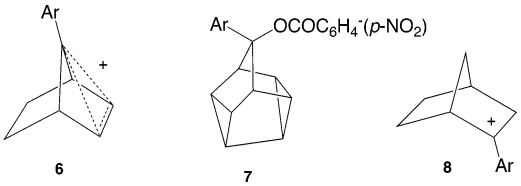
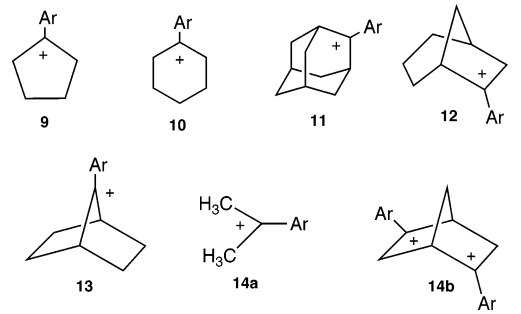
2. Application of ^{13}C NMR Spectroscopy to the Gassman−Fentiman Tool of Increasing Electron Demand to Carbocations. The Gassman−Fentiman "tool of increasing electron demand", originally applied to the solvolysis of 7-aryl-7-norbornen-2-yl systems,[23] was used by Richie et al.[24] in 1970 to measure the electron demand of the electron-deficient carbocationic center of long-lived 7-aryl-7-norbornen-2-yl cations **6** using NMR spectroscopy. Applying a similar technique, in 1977 Brown accepted[25] the existence of a nonclassical ion by comparing rate of solvolysis of 9-aryl-9-pentacyclo[4.3.0.^{2,4}0.^{3,8}0^{3,7}]nonyl *p*-nitrobenzoates **7**. The very low methyl/hydrogen and phenyl/methyl rate ratios observed were taken as criteria for a transition state stabilized by σ-bridging involving trishomocyclopropenium character. The system was originally studied by Coates and co-workers.[26] However, in the same study[25] Brown also stated that "*it should be pointed out that the application of same criteria to the 2-norbornyl cation fails to reveal such a participation under solvolytic conditions*".[27]



Farnum and Wolf using ^1H NMR spectroscopy were able to show[28] in a series of stable 2-aryl-2-norbornyl cations **8** the onset of nonclasical σ-delocalization by varying the substituents on the phenyl ring from electron-donating to electron-withdrawing ones. Since the ^1H NMR chemical shift scale is small and lacks range, we applied the method using ^{13}C NMR spectroscopy.[29] The method was extended to detect the onset of π-, $\pi\sigma$-, and σ-delocalization in a variety of cationic systems.[30] The ^{13}C NMR chemical shifts of the cationic carbons of a series of regular trivalent arylcyclopentyl (**9**), arylcyclohexyl, (**10**), 2-aryladamantyl (**11**), 6-arylbicyclo[3.2.1]octyl (**12**), 7-aryl-7-norbornyl (**13**) cations (so-called classical cations) correlate linearly with those of substituted cumyl cations (**14a**) over the entire range of substituents (generally from electron-releasing *p*-OCH_3 to the most electron-withdrawing 3,5-$(CF_3)_2$ groups).[31−34]

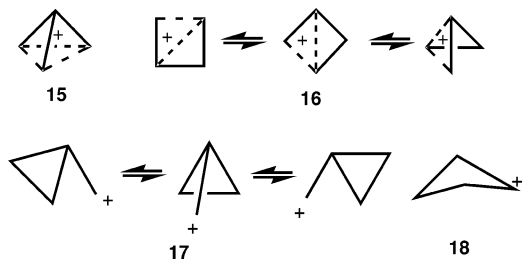


However, systems such as 2-norbornyl, **8**, show deviation from linearity in such chemical shift plots with electron-withdrawing substituents clearly indicating the onset of σ-delocalization.[29,34] This fully supports the nonclassical nature of the secondary 2-norbornyl cation. A similar investigation of 2,5-diarylnobornane-2,5-diyl dications (**14b**) reveals no onset of such σ-delocalization due to the presence of two positive charges in the bicyclic ring.[35] These conclusions were criticized by Brown.[36] In a comprehensive paper with Farnum and Olah, we showed major flaws in Brown's analysis.[34] Furthermore, in some cases, which contained phenyl and cyclopropyl, allyl, or propargyl groups, similar deviations were observed.[30,37] The origin of such effects may be entirely different. Brown attempted to explain all of the observed deviations by an inductive π-polarization phenomenon.[36] This suggestion was, however, shown to be incompatible with many experimental findings including the 2-norbornyl framework in question, which lacks π-electrons to be polarized.[30,34] We argued that judicious application of the tool of increasing electron demand coupled with ^{13}C NMR spectroscopy as the structural probe is useful to determine the onset of π-, $\pi\sigma$-, or σ-delocalization provided alternative explanations for the data are ruled out.[34] At times it was amusing to read Brown's concluding statement in one of his many papers published in 1982:[36] "*We have now shown that such deviations are not diagnostic of nonclassical σ-bridging. Thus this criteria must join the huge graveyard of disproved criteria for nonclassical structures*". In 1983, our reply was the following: "*It seems to us that this criterion, along with many others, "laid to rest" by Brown will, like Lazarus, refuse to accept this premature assignment to the tomb*".[34]

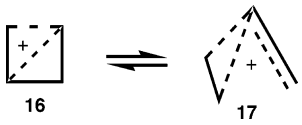
3. Cyclopropylcarbinyl Cations.

3.1. Cyclopropylcarbinyl, 1-Methylcyclopropylcarbinyl, and Related Systems. The nature of the cyclopropylcarbinyl cation, $C_4H_7^+$, has been under intense scrutiny by many groups of researchers using various techniques, ever since J. D. Roberts first carried out his pioneering solvolytic studies on the cyclobutyl and cyclopropylcarbinyl derivatives. Roberts initially proposed a pentacoordinated tricyclobutonium structure (**15**) to the cationic intermediate and named it as a "nonclassical" carbocation for the first time.[38,39] Bartlett's view that "*among the nonclassical ions, the ratio of conceptual difficulty to the molecular weight reaches a maximum with the cyclopropylcarbinyl-cyclobutyl system*" explains the enigma behind the structure of the $C_4H_7^+$ cation.[40] The structure of almost every carbocationic intermediate has first been proposed on the basis of solvolytic evidence, and the $C_4H_7^+$ ion is no exception. Roberts observed that the solvolysis of cyclopropylcarbinyl or cyclobutyl substrates and the diazotative deamination reactions of cyclopropylcarbinylamine or cyclobutylamine gave product mixtures consisting of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives in essentially the same ratio.[39] A common cationic intermediate of C_{3v} structure, tricyclobutonium ion **15**, was invoked to explain the above solvolytic behavior.[38] The tricyclobutonium ion structure was soon replaced by the equilibrating bridged bicyclobutonium ions **16** as further experimental results were not consistent with the proposed structure.[41] Brown, on the other hand, based on solvolysis of cyclopropylcarbinyl and cyclobutyl 2-naphthalene sulfonates, proposed equilibrating cyclopropylcarbinyl cations **17** involving the intermediacy of relatively unpopulated puckered cyclobutyl cation, **18**.[16]

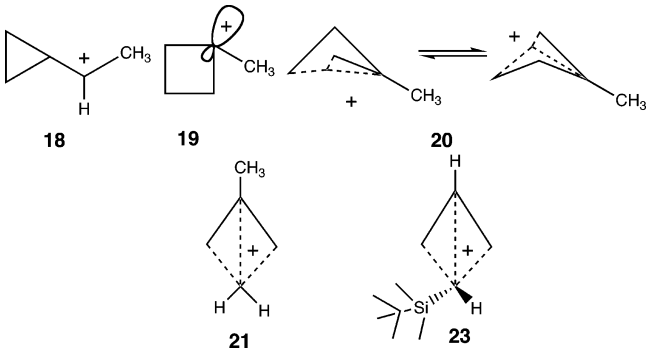
Olah et al. characterized the $C_4H_7^+$ cation by ^{13}C NMR spectroscopy under stable ion conditions.[42] Cyclopropylcarbinol or cyclobutanol upon ionization in superacids gave identical species. The ^1H NMR spectrum of the cation is interesting. It shows two overlapping quartets (J = 8 and 6.5 Hz) for the methyne protons and two sets of doublets for the methylene protons, δ ^1H 4.64 and 4.21. Thus, the methylene hydrogens are stereochemically nonequivalent, which is unexpected for the classical cyclopropylcarbinyl or cyclobutyl cations. The ^{13}C



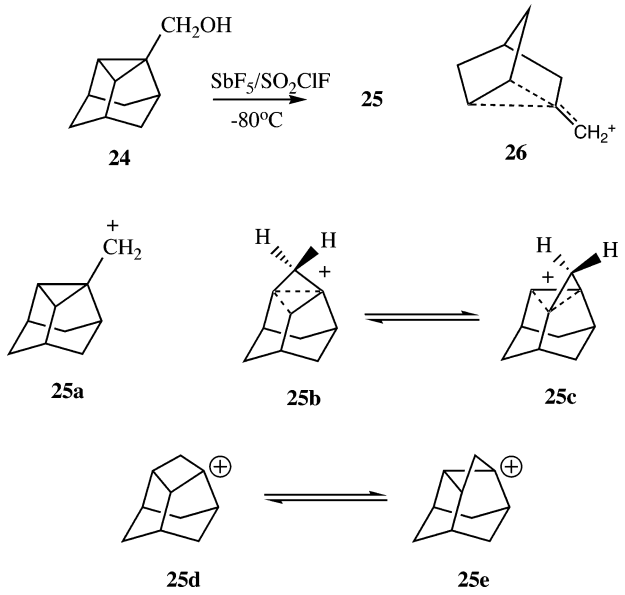
NMR spectrum shows only two resonances: δ ^{13}C 108.4 (CH) and 55.2 (CH_2, J_{CH} = 180 Hz). Thus, all three methylene carbons are identical, and the protons attached to each of them are nonequivalent. Equilibrating classical cyclopropylcarbinyl cations can be ruled out not only from the much-shielded averaged methylene carbons in the ^{13}C NMR spectrum but also from the dissimilar geminal protons on each of the methylene carbons. Only the pentacoordinated nonclassical bicyclobutonium ion could account for the observed results.[42] With Olah, Roberts, and co-workers, we have observed temperature-dependent chemical shifts for the $C_4H_7^+$ ion, prepared from cyclopropylcarbinol-1-^{13}C, between −61 and −132 °C.[43] The ion shows two signals at δ ^{13}C 107.56 and 57.41 for methine and methylene carbons, respectively, at −70 °C. The ^{13}C label was randomly distributed indicating facile hydride shifts. At −132 °C, the methine and methylene carbons moved to δ ^{13}C 111.32 and 50.89, respectively. This indicates that more than one species is involved in the rapid equilibration process. Based on these observations, we suggested an equilibration involving nonclassical bicyclobutonium ion, **16**, and the $\pi\sigma$-delocalized bisected cyclopropylcarbinyl cation, **17**, with the latter as minor equilibrating species.[42] Such a proposal has been affirmed by deuterium isotope studies,[12,13] solid-state NMR,[10] and high level of theory.[11]



Ionization of either 1-methylcyclopropylcarbinyl chloride or 1-methyl-1-cyclobutyl chloride with SbF_5-SO_2ClF at −80 °C gave the same ^{1}H NMR spectrum.[43] The ion showed two singlet resonances at δ ^{1}H 3.87 (CH_2) and 2.87 (CH_3) in a ratio of 2:1. This indicates that ring protons are rapidly equilibrated. At −25 °C, the ion rearranges to the static secondary (cyclopropyl methyl)carbinyl cation, **18**. The ^{13}C NMR spectrum at −80 °C shows three signals at δ ^{13}C 163.1 (singlet), 48.7 (triplet), and 25.4 (quartet). Later, Sorensen and Kirchen found that at −156 °C, the signal at δ ^{13}C 48.7 splits into two peaks at δ ^{13}C 72.72 and −2.83, respectively, whereas other absorptions remain unchanged. This indicates that only one species is involved in the 1-methylcyclobutyl cation case as opposed the cyclopropylcarbinyl/cyclobutyl cation system. This led Sorensen to suggest an sp^3-hybridized classical 1-methyl-1-cyclobutyl cation structure **19**. We reinvestigated the system and suggested a degenerate set of rapidly equilibrating bicylobutonium ions **20** rapidly interconverting through a symmetrical σ-delocalized species, **21**, or the static ion, **21** itself. Further studies of deuterium substitution[12,13,20b] as well as theoretical work[11] seem to support such a hypothesis. Siehl and co-workers have established that whereas 1-(trimethylsilyl)bicyclobutonium ion, **22**, undergoes 3-fold degenerate methylene rearrangement[44] as the parent system, the corresponding 3-*endo*-(*tert*-butyldimethylsilyl)bicyclobutonium ion is a static bicyclobutonium ion, **23**, providing a direct evidence for such nonclassical structures.[45] The system **23** is also stabilized by γ-silyl hyperconjugative effects.[45]



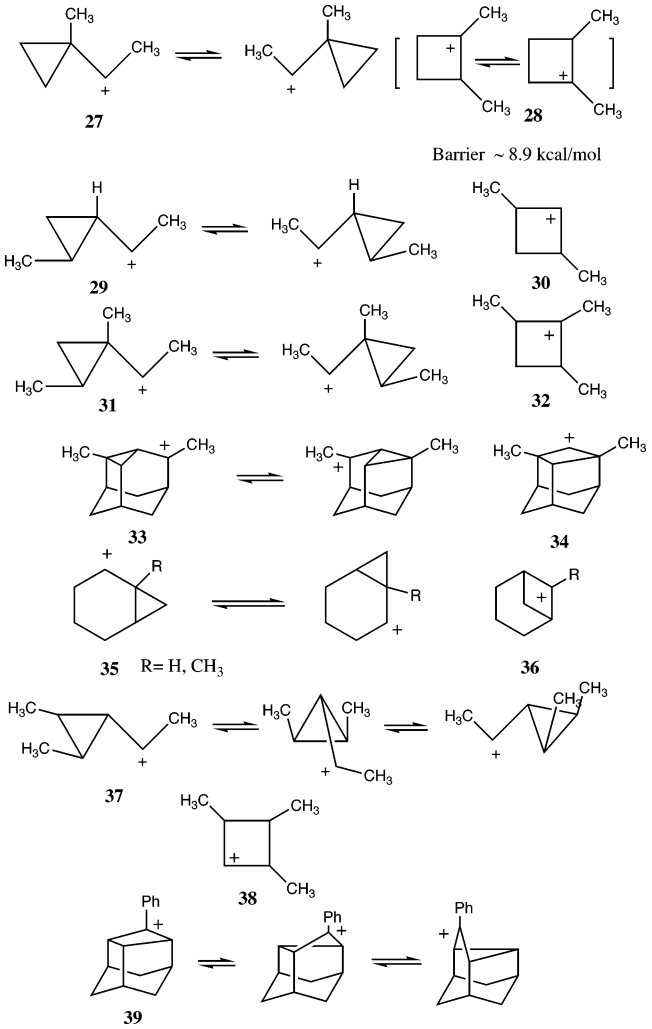
A highly stabilized cyclopropylcarbinyl cation, the noradamantylmethyl cation, **25**, derived by the ionization of noradamantanemethanol, **24**, was structurally characterized.[46] The cation seems to have a different structure than the norticyclylmethyl cation, **26**, studied previously by Sorensen.[47] The 75 MHz proton-decoupled ^{13}C NMR spectrum of the cation, 36 at −80 °C, shows only seven resonances (assigned on the basis of multiplicities and coupling constants): δ ^{13}C 147.9 (s), 97.6 (d, J_{CH} = 187.1 Hz), 52.7 (t, J_{CH} = 134.7 Hz), 47.3 (t, J_{CH} = 168.3 Hz), 43.4 (d, J_{CH} = 151.4 Hz), 38.7 (t, J_{CH} = 136.5 Hz), and 36.6 (d, J_{CH} = 149.9 Hz) in a ratio of 1:2:1:1:1:2:2, respectively. The chemical shifts remain constant over the temperature range of −100 to −40 °C. This is in accordance with either a single ground-state structure for the ion or a set of rapidly equilibrating unsymmetrical bicyclobutonium ion structures. Since the ion has apparent C_s symmetry, possible structures for **25** include the static bisected cyclopropylmethyl cation **25a**, a fast equilibrium between the nonclassical unsymmetrically bridged bicyclobutonium ions **25b** and **25c**, or a fast equilibrium of the classical 2,5-dehydro-3-protoadamantyl cations, **25d** and **25e**.



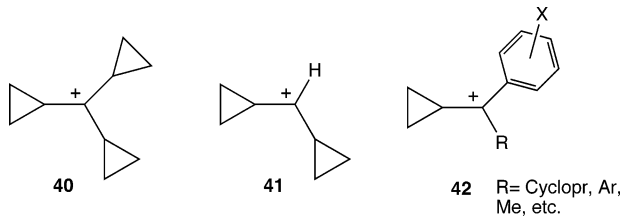
Based on theory and additivity of chemical shifts criteria,[21] the most likely structure for **25** is probably a set of rapidly

equilibrating bicyclobutonium ions (**25b/c**) with apparent C_s symmetry. The protoadamantyl cations (**25d/e**), on the other hand, should show much more classical character. Bisected structure similar to **42** is clearly ruled out based on IGLO calculations at the DZ//B3LYP/6-31G* level.[46]

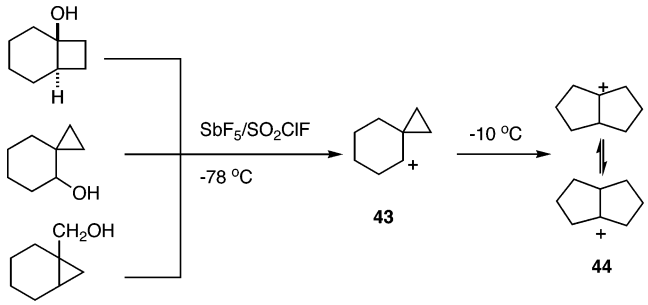
3.2. Other Fluxional Cyclopropylcarbinyl Cations. We have also studied a number of secondary cyclopropylcarbinyl cations, **27**, **29**, **31**, **33**, and **35**, which undergo rapid 2-fold degenerate rearrangements involving the respective cyclobutyl cations **28**, **30**, **32**, **34**, and **36** as high-lying intermediates. In all these cases, the secondary cyclopropylcarbinyl cations[48−51] were found as the global minima structures. In many cases, activation barriers for the degenerate rearrangements were determined. In one case, the interemediacy of degenerate 1,2-dimethylcyclobutyl cation **28** led to the determination of activation energy barrier for the 1,2-hydride shift in a cyclobutane skeleton.[48] A very low energy barrier 3-fold degenerate rearrangement was observed in the case of 1-(*cis*-2,3-dimethylcyclopropyl)ethyl cation **37**, proceeding through unpopulated cyclobutyl analogue, **38**.[49] Even 1,4-phenyl-2,5-dehydroprotoadamantyl cation, **39**, shows fluxionality, which can be frozen at low temperatures.[51]



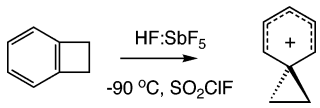
3.3. Static Cyclopropylcarbinyl Cations. Both tricyclopropyl and dicylopropylcarbenium ions, **40** and **41**, respectively, were found to be static in nature with substantial positive charge delocalization into the cyclopropyl skeleton.[52] The tricyclopropyl cation is even stable in sulfuric acid medium.[52] We have extensively investigated the relative charge-delocalizing ability of phenyl vs cyclopropyl in a series of benzylic cations **42** and found that a cyclopropyl group is superior to phenyl in stabilizing an adjacent positive charge.[53] A phenyl group is much more prone to steric effects since π-conjugation requires some coplanarity with the empty p-orbital of the cationic center.



The stabilization of an adjacent bisected spirocyclopropyl group was employed in the successful preparation of a secondary cyclohexyl cation. The spirocation, **43**, was prepared by three routes,[54,55] starting from 2-spirocyclopropylcyclohexanol, *trans*-bicyclo[4.2.0]octan-1-ol, or bicyclo[4.1.0]hept-1-yl methanol and SbF_5/SO_2ClF at −78 °C. The bisected nature of the cyclopropyl group is indicated by a single ^{13}C signal for the cyclopropyl methylene groups. The ion is stable up to −10 °C, where it rearranges to the equilibrating bicyclo[3.3.0]oct-1-yl cation, **44**. Attempted preparation of similar secondary spirocyclopropylcarbinyl cation bicyclo[2.2.2]octyl and bicyclo[2.2.1]heptyl skeletons were unsuccessful. The systems rearrange to allylic cations.[55−57]

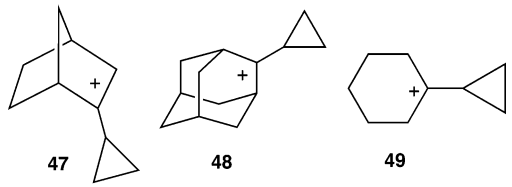


Over the years, we have also studied cyclopropyl-substituted allylic, dienylic, and propargylic systems.[37,50,58a,59,60] Crams's phenonium ion (spiro[2.5]octa-5,7-dien-4-yl cation), **43**, can be considered as a spirocyclopropylarenium ions (similar to a Wheland intermediate),[61,62] with substantial positive charge delocalization into the dienylic framework as well as the spirocyclopropyl group. Because of additional delocalization into the cyclopropyl skeleton, the C−C bond lengths in the six-membered ring are almost similar (∼1.401 Å) as demonstrated with theoretical calculations of Sieber, Schleyer, and Gauss.[63] The spiro carbon and methylene bond length, on the other hand, was computed to be longer (1.625 Å). This led Schleyer et al. to suggest[63] that the parent phenonium ion was nonclassical with the aromatic ring retaining substantial aromatic character. However, subsequently, we have shown that the structure of the phenonium ion, **45** is classical with substantial delocalization of the positive charge into the spirocyclopropane ring.[63] The ion **45** was also generated by the protonation of benzocyclobutene, **46**.[64]

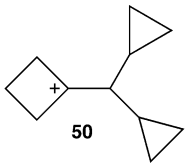


46 45

Some of the tertiary cyclopropylcarbinyl cations studied include **47**−**50**. In all these systems, the cationic center adopts a bisected conformation to facilitate positive charge delocalization into the cyclopropane ring.[29,48,50,65,66]

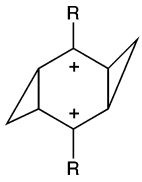


47 48 49

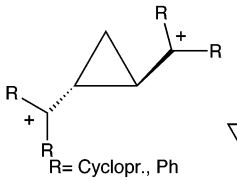


50

3.4. Cyclopropyl Group Stabilized Carbodications. A variety of cyclopropyl group stabilized dications, **51**−**53**, have also been observed. These include acyclic, cyclic, and polycyclic systems.[50,65,67,68]



51



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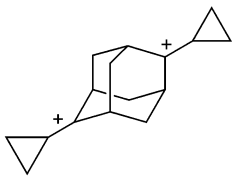
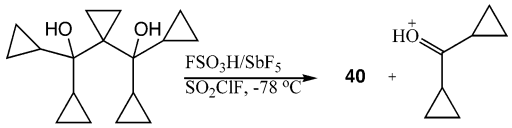


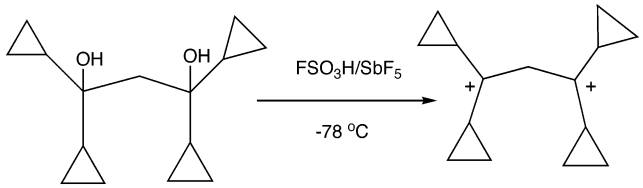
53

Ionization of the spirocyclopropyl-derived 1,1,3,3-tetracyclopropyl-1,3-propanediol, **54**, in FSO_3H/SbF_5-SO_2ClF at −78 °C also resulted in the formation of the disproportionated cationic products, the tricyclopropylcarbinyl cation (**40**), and the O-protonated dicyclopropyl ketone (**55**). No evidence for the formation of 1,3-carbodication was obtained. The spirocyclopropyl group, in fact, acts as a powerful neighboring group $\pi\sigma$-donor and usually gives the ring-opened rearranged carbocations.[69]

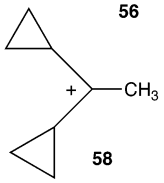


54 55

The ionization of the nonspirocyclopropyl analogue, the 1,1,3,3-propane-1,3-diol, **56**, in FSO_3H/SbF_5-SO_2ClF at −78 °C, on the other hand, gave the expected 1,3-carbodication, the 1,1,3,3-tetracyclopropyl-1,3-propanediyl dication, **57**[69] (δ^{13}C 262.8 (s, C^+), 47.1 (t, J = 134 Hz, C_2), 39.6 (d, J = 181 Hz) and 48.7 (d, J = 179 Hz, cyclopropyl CH), 38.2 (t, J = 182 Hz) and 46.6 (t, J = 171 Hz, cyclopropyl CH_2). The structure of the carbodication was further confirmed by matching the experimentally observed ^{13}C NMR chemical shifts with those obtained from theoretically calculated values (IGLO method using B3LYP/6-31G* optimized geometries).[69]



56 57

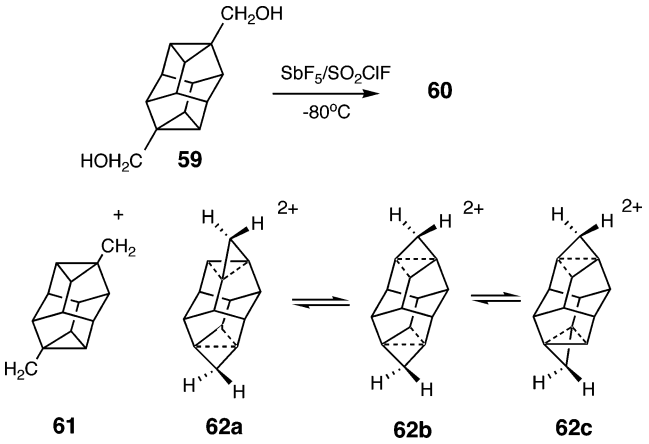


58

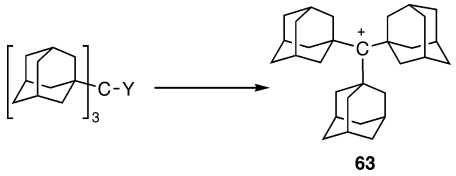
The cationic center of the carbodication **57** (δ^{13}C 262.8) is shielded by 12 ppm as compared to that of the 1,1-dicyclopropylethyl cation, **58**. The enhanced shielding of the cationic centers in the carbodication,. **57**, signifies the increased delocalization of the charge from the cationic centers into the neighboring cyclopropyl groups. The enhanced charge delocalization into the cyclopropyl groups, as compared to that of the monocation **58**, is also reflected in the relatively deshielded absorptions for the cyclopropyl methine ($\Delta\delta_{average}$ = 13.8) and methylene carbons ($\Delta\delta_{average}$ = 15.1). Despite the significant charge delocalization into the neighboring cyclopropyl groups, the carbodication **56** is a classical species as shown by the chemical shift additivity criterion.[21]

Ionization of the intriguing ditriaxane-2,10-dimethyl diol, **59**, with antimony pentafluoride (SbF_5) in SO_2ClF at −78 °C resulted in a dark yellow solution. The 75 MHz proton-decoupled ^{13}C NMR spectrum of the ion at −80 °C shows only five resonances, indicating the formation of a highly symmetric dication or a mixture of rapidly equilibrating dications with an apparent high symmetry: δ ^{13}C 135.7 (s, quaternary carbon), 118.9 (t, J_{CH} = 174 Hz, methylene), 105.0 (d, J_{CH} = 193.2, four beta CHs), 66.4 (d, J_{CH} = 148.8, two belt CHs), and 53.3 (d, J_{CH} = 156.1, four belt CHs) in a ratio of 1:1:2:1:2, respectively.[46] Considering the similar geometry and a correlation between charge density and ^{13}C chemical shifts, the downfield shift of the methylenes by 71 ppm compared to that of **25b/c** clearly indicates higher positive charge density on the methylene moieties in **60** and a lower degree of charge delocalization into the cyclopropylmethyl/cyclobutyl framework. On the other hand, this value is still relatively shielded when compared to Sorenson's nortricyclylmethyl cation **26**[47] by 72.5 ppm, indicating still substantial positive charge delocalization into the cyclopropane moiety, clearly ruling out the static bisected structure **61** for the ionization product of **59**.[46] Application of additivity criterion[21] indicates a overall deshielding of 250 ppm per unit positive charge. In addition, lack of line broadening between −30 and −100 °C clearly supports equilibrating degenerate biclobutonium structures **62a/b/c** for the dication **60** with rather low barriers.[46]

4. Sterically Crowded Carbocations. Highly hindered tris(*tert*-alkyl)methyl systems (R_3CX) are well suited for the study of steric crowding/strain energy relationships as well as the variation of the C−X bond length as a function of the steric bulk and strain energy of the R groups. Lomas[70a,b] has synthesized and examined by molecular mechanics (MM2)



calculations a series of tertiary alcohols containing combinations of *tert*-butyl, 1-adamantyl, 1-bicyclo[2.2.2]octyl, and 1-norbornyl ligands. However, MM2 theory is unable to predict the kinetic stability of tris(*tert*-alkyl)methyl cations. Previous work by Dubois et al.[70c,d] has indicated that highly hindered trialkylmethyl cations are formed more slowly than less crowded systems. Two effects working against each other are to be considered: the relief of steric strain associated with a change in hybridization from sp^3 to sp^2 is opposed by an increase of strain resulting from shortening of the C^+-C bond in the carbocation. We have achieved the preparation and NMR characterization of tris(1-adamantyl)methyl cation, **63**, possibly the most hindered trialkyl(or cycloalkyl)methyl cation that has yet been observed as a persistent (long-lived) ion.[71] Earlier, we have reported the generation of highly hindered trivalent carbocations, such as the bis(1-adamantyl)methyl cation under stable ion conditions.[72]

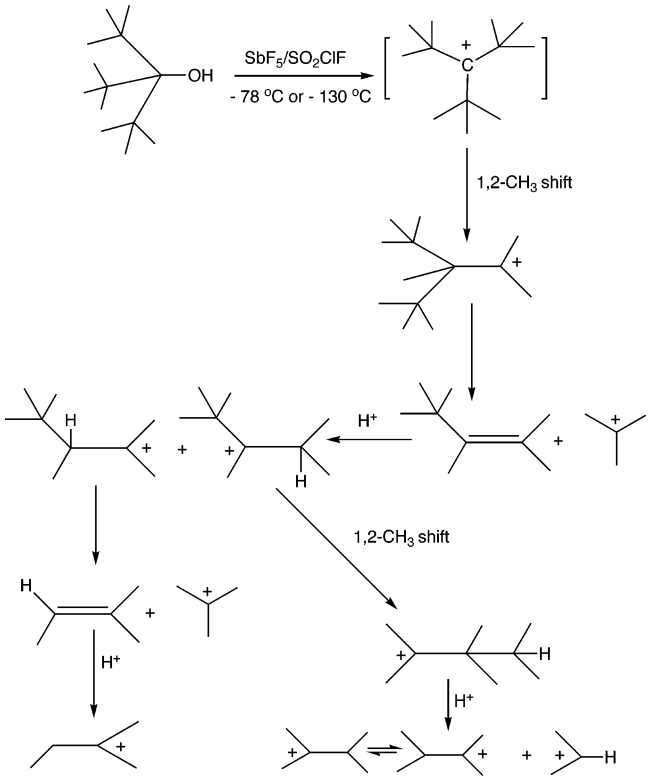


In the solvolysis of tris-*tert*-butylmethyl *p*-nitrobenzoate in a hydroxylic solvent under neutral conditions, Bartlett and Stiles observed[73] the formation of 3,3,4,4-tetramethyl-2-*tert*-butyl-1-pentene (a C_{13} olefin) via successive migration of methyl and *tert*-butyl group in the incipient tris(*tert*-butyl)methyl cation. No evidence was obtained for the capture of highly crowded tris(*tert*-butyl)methyl cation. Our attempts[74] at ionizing tris(*tert*-butyl)methanol in SbF_5/SO_2ClF at −78 or −130 °C led to a mixture of equilibrating *tert*-hexyl, *tert*-amyl, *tert*-butyl, and isopropyl cations by a cleavage mechanism as shown in Scheme 2.

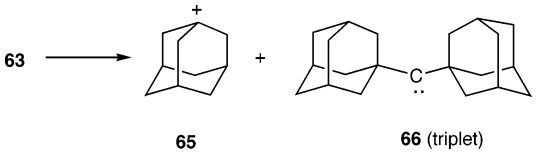
On the other hand, in tris(1-adamantyl)methyl cation, **63**, elimination to olefinic products is not favored, as this would entail the formation of a bridgehead olefin. Thus, **63** not unexpectedly has sufficient kinetic stability to allow its observation at low temperatures under stable ion conditions. In the highly hindered ion **63**, the cationic carbon displays a chemical shift of δ ^{13}C 335.2 and identical with that observed for α,α-bis(1-adamantyl)ethyl cation, **64a**.[72] The other shifts were δ ^{13}C 68.4 (C_2), 39.2(C_3), 34.0(C_5), and 27.9(C_4).

The crowded carbocation **63** is stable at −70 °C for about 30 min, after which it starts to decompose with the formation

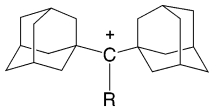
SCHEME 2



of 1-adamantyl cation, **65**, as the only identifiable species in the ^{13}C NMR spectrum of the solution. It is suggested that due to steric strain **63** loses 1-adamantyl cation, **65**, with formation of diadamantyl carbene, **66**[75] (in the triplet state).



We were also unsuccessful[72] in preparing the *tert*-butylbis-(1-adamantyl)methyl cation (**64c**) from the corresponding alcohol even at −130 °C. Probably this is due to its low kinetic stability and its possible fast cleavage−rearrangement. On the other hand, the tertiary ions **64a** and **64b** were found to be stable up to 0 °C.

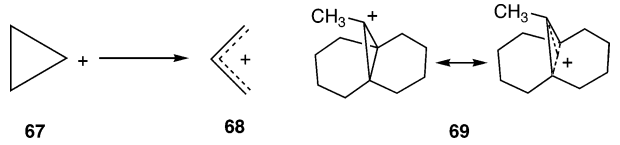


64a, R = CH_3
64b, R = CH_2CH_3
64c, R = $C(CH_3)_3$
64d, R = H

In the case of the less crowded secondary carbocation **64d**, ring expansion occurs rapidly to give a set of equilibrating 4-(1-adamantyl)-3-homoadamantyl cations.[72] No such C−C bond migration is possible in the case of ion **63** due to steric hindrance.

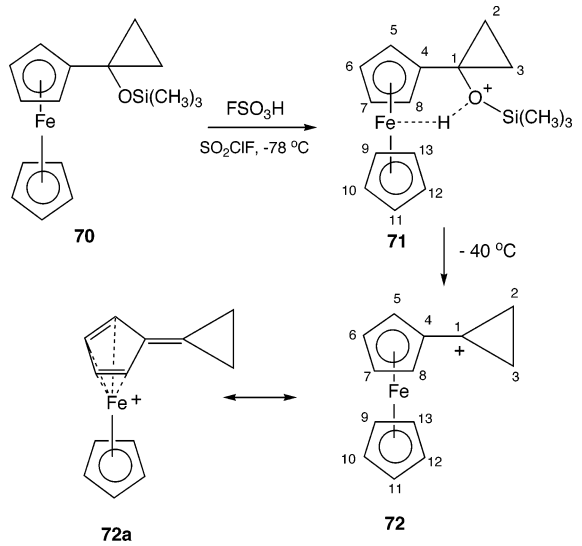
5. 1-Ferrocenyl-1-cyclopropyl Cation. The First Long-Lived Cyclopropyl Cation. Observation of a stable unencumbered cyclopropyl cation, **67**, was a challenge due to its facile

ring opening to the energetically more stable allyl cation **68**. Such a rearrangement is a low barrier Woodward−Hoffmann-allowed process.[76] A cyclopropyl-type cation built into a rigid framework under long-lived stable-ion conditions was studied by Olah and co-workers[77] relating to the geometrically constrained 11-methyl-11-tricyclo[4.4.1.0^{1,6}]undecyl cation, **69**, which shows significant β C−C bond interaction reflecting a half-opened cyclopropyl cation. Support for such a "half-opening" comes also from ab initio calculations.[78a] There were also some reports of NMR spectroscopic detection of 1-(methylthio)-2,2,3,3-tetramethylcyclopropyl cation from the corresponding chloride.[78b] However, the results were not clear. The constrained propellane systems in which the cyclopropyl group is "locked in" and related cyclopropyl derivatives have also been investigated under solvolytic conditions.[79,80] In the solvolytic reactions, unrearranged cyclopropyl products were obtained with retention of configuration.[79,80]



67 **68** **69**

Since a ferrocenyl group is a super-stabilizing group for adjacent carbocationic centers,[81] we envisioned preparation of 1-ferrocenyl-1-cyclopropyl cation.[82]



70 **71** **72a** **72**

Dissolution of 1-ferrocenyl-1-cyclopropyl trimethylsilyl ether, **70**,[82,83] in FSO_3H/SO_2ClF at −78 °C resulted in the formation of protonated ether **71**. Support for the formation of structure **71** comes from the observation of the highly shielded acidic proton on the ether oxygen at δ ^{1}H −3.21, which has strong agostic[84] interaction with the iron atom. Warming the ionic solution to −40 °C for 8 min followed by recooling to −60 °C showed irreversible changes, indicating the formation of 1-ferrocenyl-1-cyclopropyl cation **72**. The ^{13}C NMR spectrum consists of the following resonances: δ ^{13}C 117.1 (s, C_1) 94.8 (d, J_{CH} = 184.6, C_6, C_7), 94.3 (s, C_4), 84.3 (d, J_{CH} = 183.6 Hz, C_9, C_{10}, C_{11}, C_{12}, C_{13}), 83.5 (d, J_{CH} = 190.4 Hz, C_5, C_8), 7.6 (t, J_{CH} = 166.0 Hz, C_2, C_3). The observation of the cyclopropyl group methylene carbon signals at δ ^{13}C 7.6 supports the formation of a free cyclopropyl cation **72** with extensive charge delocalization into the ferrocenyl moiety as expressed in the resonance structure **72a**. Such delocalization is also supported by the observation of a signal for the carbocationic center at δ ^{13}C 117.1. The C_6 and C_7 cyclopentadienyl carbons are extensively deshielded (δ ^{13}C 94.8) compared to the C_5 and C_8 carbons. The assignments are also in accord with previously studied ferrocenyl substituted carbocations.[85] The ^{1}H NMR data [δ^1H 5.76 (s, H_6, H_7), 4.3 (s, H_9, H_{10}, H_{11}, H_{12}, H_{13}), 4.3 (s, H_5, H_8), 1.59 and 1.25 (s, H_2, H_3)] are also in accord with structure **72**. Support for **72** comes from the nonequivalence of H_2 and H_3 cyclopropyl protons as well.

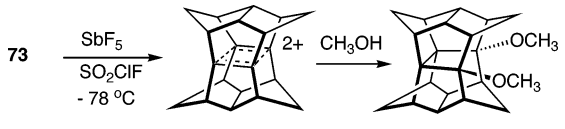
The large shielding of the cyclopropyl methylene carbons in **72** compared to **70** (by ca. 9.5 ppm) can be rationalized in terms of significant double bond character of the C_1-C_4 bond in the former. In fact, in going from methylcyclopropane to methylenecyclopropane, a shielding (3.2 ppm) of the ^{13}C NMR chemical shifts of the cyclopropyl methylene carbons is observed.[86]

6. Pagodane and Related Dications, Frozen Woodward−Hoffmann Transition-State Analogues. Prinzbach and co-workers at Frieburg have developed a synthetic route for the preparation of [1.1.1.1]pagodane **73**[87] as a promising precursor for the isomeric pentagonal dodecehedrane **74**. The total synthesis of **74** was achieved for the first time by Paquette et al.[88] in an endeavor termed "Mount Everest of Alicyclic Chemistry". Subsequently, the Frieburg group indeed developed many interesting routes to substituted dodecahedranes from related pagodanes.[89]

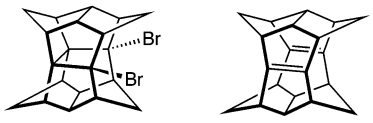
73 **74**

During the course of our collaborative investigations with the Frieburg group on superacid-catalyzed isomerization of **73** to **74**, we serendipitously discovered the formation of remarkably stable pagodane dication, **75**. The dication, **75** could be classified as a frozen Woodward−Hoffmann transition-state analogue.[90]

When **73** was reacted in 5-fold excess of freshly distilled SbF_5 in SO_2ClF −78 °C, the solution became instantaneously yellow. The proton spectrum recorded immediately comprised of complex broad signals in the aliphatic region, indicating the presence of paramagnetic radical cations.[91]



75 **76**

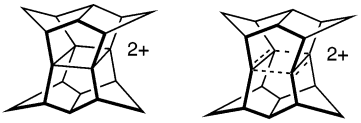


77 **78**

After ca. 3 h of standing at the same temperature, the proton and carbon spectra had simplified to the 4-line pattern represented. The solution showed a very clean ^{1}H NMR spectrum: δ ^{1}H 3.37 (br, 8 H), 3.68 and 2.72 (AX doublets, J_{H-H} = 13.2 Hz, 8 H), and 2.39 (br, 4 H). The 50-MHz ^{13}C NMR spectrum of the same solution at −80 °C showed only four signals at δ

^{13}C: 251.0 (singlet), 65.3 (triplet, J_{C-H} = 141.9 Hz). The observed symmetry and the extent of deshielding in both ^{1}H and ^{13}C NMR spectra of the species in SbF_5/SO_2ClF solution when compared to the progenitor pagodane **73** (δ^{1}H, 2.60 (4H, bridge-head), 2.24 (8H, bridgehead), 1.56 and 1.60 (8H, methylene, J_{AB} = 10 Hz); δ^{13}C, 62.9 (singlet), 59.6 (doublet), 42.7 (doublet) and 41.9 (triplet)) seem to imply that the species is ionic in nature and has the D_{2h} symmetry of the parent pagodane itself. The ion solution was found to be surprisingly stable. Quenching the ion solution with excess of cold methanol (at −78 °C) and usual aqueous $NaHCO_3$ workup provided a white crystalline product. The ^{13}C NMR spectroscopic analysis of the product in $CDCl_3$ solution indicated the main product to be **76**.

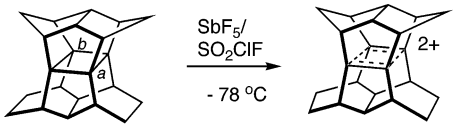
Under simialr ionizing conditions employed for pagodane **73**, ionization of dibromide **77** and oxidation of diene **78** gave the same dication, **75**.



75a **75b**

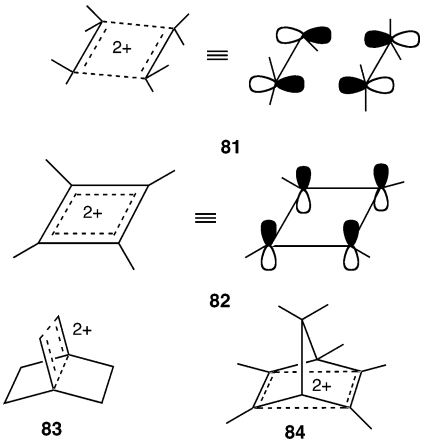
The "closed" dication **75a** (the "real tight pagodane dication") or the "open" dication **75b** (scission of bonds *b* in **73**) can safely be excluded as possible structures on the basis of the following facts: (i) the high tendency of cyclobutane radical cations toward "symmetry-allowed" ring opening,[92] (ii) the identity of dications obtained from structurally differing precursors **73**, **77**, and **78**, and (iii) ^{13}C NMR chemical shift analysis.[21,90] As the NMR spectra shown in were found to be temperature independent down to −130 °C, it must be presumed that the D_{2h} symmetry of the ionic species is not the result of a rapid equilibration processes (E_a < 3 kcal/mol) between other types of degenerate dications**.** In fact, there is ample experimental and computational evidence for such a preference: (i) the relative lengths of the cyclobutane bonds in **73** as calculated by different methods[93] and measured by X-ray analysis[90] indicate a weakening of bonds *a*; (ii) additions to pagodane, e.g., bromination to **77**, occur exclusively under opening of bonds *a*;[94,95] (iii) indications of hyperstability for diene **78** and derivatives[95] demonstrate the favorable geometrical situation; and (iv) the homoconjugation of β 2 eV for the bissecododecahedradiene, as determined by PE spectroscopy, which is basis for a ready and efficient [$\pi_2 + \pi_2$]-photocycloaddition,[96] provides proof of the optimal conditions for interactions between the perfectly collinear oriented π-orbitals, a situation that exactly is postulated in dication **75**.

Oxidative ionization of [2.2.1.1] pagodane, **79**, also gave a similar cyclobutane dication, **80**.[90]



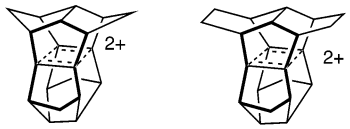
79 **80**

The dications **75** and **80** are considered as the first representatives of a novel class of 2π-"aromatic" pericyclic systems, topologically equivalent to the transition state **81** for the Woodward−Hoffmann "allowed" cycloaddition of ethylene to ethylene dication or dimerization of two ethylene radical cations.[97] In contrast to the well-studied cyclobutadiene dication **81** with conventional p-type delocalization,[98,99] in **81(75/80)** delocalization occurs among the orbitals in the plane of the (bishomo)-conjugated system. A precedent case of this type,



the assumed 1,4-bicyclo[2.2.2]octanediyl dication for which one canonical structure **83** is shown,[100a] was found in a reinvestigation to be the monocation−monodonor acceptor complex.[100b] Nevertheless, the theoretical arguments[100a] put forward in the context with **83** are still valid for **75** and **80**. Hogeveen et al. have also prepared and characterized octamethylnorbornadiene-diyl dication **84** wherein rapid skeletal scrambling results in only two ^{13}C NMR signals at δ^{13}C 151.7 and 16.9.[101]

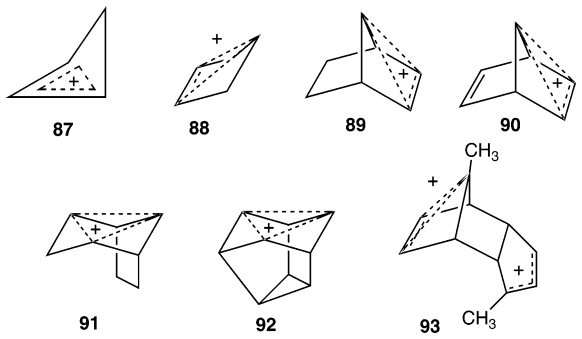
Similar cyclobutane dications, **85** and **86**, have been obtained by the oxidative ionization of [1.1.1.1] and [2.2.1.1]isopagodanes, respectively.[102,] Although the dications **85** and **86** are of σ-bishomoaromatic nature (4C/2e) and of similar geometry as **75** and **80**, they are chemically different in their properties.[102]



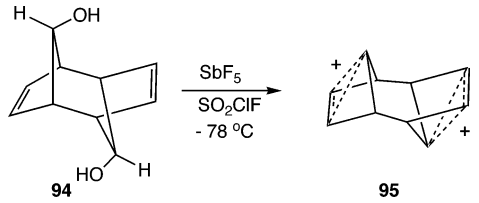
85 **86**

The cyclobutane dication structures in pagodane and isopagodane skeletons are fully supported by theory and are considered 4C/2e σ-bishomoaromatic dications.[103,] Attempted generation of dications in secododecahedradiene skeletons were unsuccessful demonstrating the limitations of the σ-bishomoaromaticity in strained systems.[104]

7. A Sandwiched Bis(bishomoaromatic) Dicationic System. The homoaromaticity concept was first advanced by Winstein more than 40 years ago.[105] Since then, it has been of great interest to experimental and theoretical chemists alike.[106,107] The question of homoaromatic overlap has been studied in six-π-electron as well as two-π-electron Huckeloid systems. The simplest two-π-electron monohomoaromatic cation is homocyclopropenium ion **87**.[108] The parent bishomoaromatic 4-cyclopentenyl cation, **88**, is still elusive, although the bishomoaromaticity in ethano- and etheno-bridged analogues (i.e., 7-norbornenyl and 7-norbornadienyl cations **89** and **90**) is well established.[109,110] Even several trishomoaromatic systems such as **3**, **91,** and **92** have been prepared and characterized.[20,111]



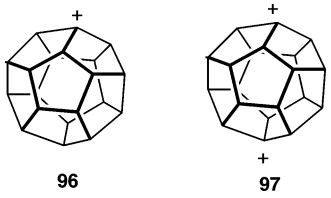
We have reported the generation and observation of *endo*-3,10-dimethyltricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-diyl dication, **93**, which encompassed an allylic cation as well as a bishomoaromatic cation framework.[112] In our search for new aromatic dications, we came across an interesting tricyclic diol, **94**, which would render itself for the generation of an interesting carbodication.[113]



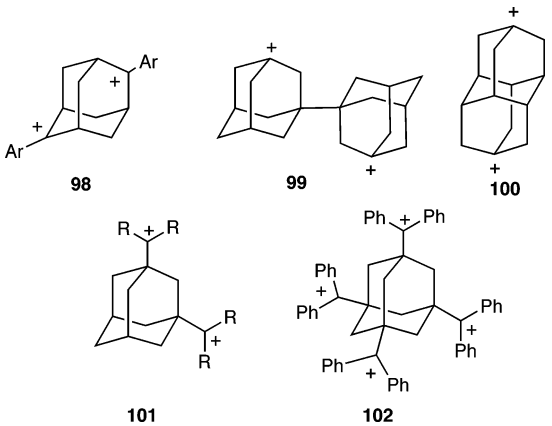
Ionization of *anti*-tricyclo[4.2.1.1^{2,5}]deca-3,7-diene-9-*endo*-10-*endo*-diol, **94**,[114] in freshly distilled protic acid free SbF_5 in 6-fold excess of SO_2ClF at −78 °C provided an ion whose 200 MHz ^{1}H NMR spectrum at −80 °C showed only three resonances at δ ^{1}H 6.31 (4 H), 3.52 (2 H), and 2.94 (4 H), indicating that the species in the superacid medium has the same symmetry as the progenitor, **94**. The ^{1}H NMR shifts of some of the protons are in fact more shielded than those of progenitor diol (δ^1H 6.73 (br, 4H; H_3, H_4, H_7, H_8), 4.24 (d, 2H, J_{H-H} = 12.5 Hz, OH), 3.95 (d, 2H, J_{H-H} = 12.5 Hz, H_9, H_{10}), and 2.64 (br, 4H, H_1, H_2, H_5, H_6)). The 50 MHz ^{13}C NMR spectra of the solution at −80 °C again showed three resonances at δ ^{13}C 131.7 (doublet, J_{C-H} = 219.2 Hz), 52.9 (doublet, J_{CH} = 219.2 Hz), and 38.1 (doublet, J_{C-H} = 169.6 Hz). These shifts, which are again shielded from those of progenitor diol (δ ^{13}C 141.2 (d, J_{C-H} = 171.1 Hz), C_3, C_4, C_7, C_8,), 83.6 (d, J_{C-H} = 159.4 Hz, C_9, C_{10}), 44.7 (d, J_{C-H} = 143.2 Hz, C_1, C_2, C_5, C_6), clearly indicate the formation of a highly symmetrical system which can be assigned the dicationic structure **95**, in which two bishomoaromatic cation frameworks are sandwiched together. Further proof for structure **95** is based on the comparison of the observed highly shielded ^{13}C NMR shifts with those of related bishomoaromatic 7-norbornenyl cation, **89**[109] [δ C_7 = 34.0 (J_{C-H} = 218.9 Hz), δ C_2C_3 = 125.9 (J_{C-H} = 192.8 Hz), and δ C_1C_4 = 58.0 (J_{C-H} = 173.0 Hz)]. However, the chemical shifts of **95** are much more deshielded than those in **89**. This can be rationalized by the presence of two positive charges in close proximity in **95**, which probably attenuates the degree of bishomoaromatic character in the individual frameworks. Furthermore, the observation of large C−H coupling constants in **95** is also diagnostic for the formation of sandwiched bishomoaromatic cationic frameworks which compare rather well with those in **89**.

Dication **95** can be considered as a four-π-electron bicyclo(polycyclo)aromatic system.[112] Goldstein and Hoffmann in their paper on "Symmetry, Topology, and Aromaticity"[97] discussed longicyclic ribbon aromatic systems. The dication **95** is the first example that can be considered as a longicyclic four-ribbon-four-π-electron [0,2,0,2] aromatic system. It appears that in four ribbon longicyclics [0,2,0,2] the four-π-electron interaction is the most stable one.[97] However, the extent of any such stabilization in dication **95** on the basis of the spectroscopic data, cannot be estimated. In a related study, Schleyer et al. could not find any evidence for longicyclic three-ribbon interaction in a number of benzobarrelene dications.[115a] More recently, Herges and co-workers have investigated the synthesis of a Mobius aromatic hydrocarbon.[115b]

8. Miscellaneous Systems. In collaboration with Leo Paquette, we were also able to generate dodecahedryl cation, **96**, and 1,-16-dodecahedryl dication, **97**.[116] Ionization of dodecahedrane and its chloro and hydroxy derivatives gave the bridgehead monocation, **95**. The ion **95** was static and showed no propensity for degenerate 1,2 hydrogen shifts, which could render all carbons and protons equivalent on the NMR time scale. The carbocationic center was highly deshielded at 363.9 ppm. Upon standing for 6−7 h, **96** protolytically ionizes further to the dication **97**. The dication **97** has the most deshielded carbocation center at 379.2 ppm. The formation of **97** from **96** can be rationalized by protolytic ionization.[116] According to semiempirical SCF-MO calculations, the dodecahdrane skeleton is not capable of accommodating a planar cation geometry. The situation appears to be more acute in the case the dication **97**, which can be characterized as a true sp^3 hybridized carbodication. The static nature of both **96** and **97** indicate unfavorable bending in the transition state for intramolecular 1,2-hydrogen shifts.[116]

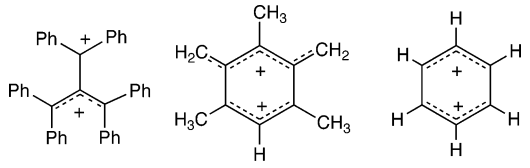


Several dications and polycations, **98**−**102**, have been prepared and characterized employing the adamantane and diamantane skeletons.[65,117−119]



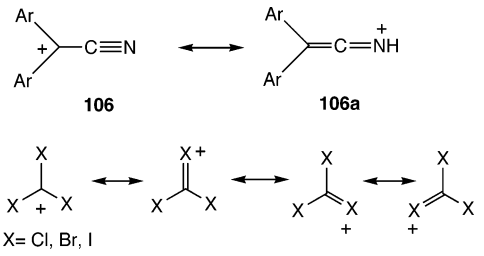
The novel tetrahedrally arrayed tetracation, **102**, may have applications in cationically induced dendridic polymerizations.[119] (Hexaphenyltrimethylene)methane dication, **103**, was found to

lack any "Y-aromatic" stabilzation.[120] The 2,6-dimethylmesitylene-2,6-diyl dication is a unique dienyl-allyl cation **104** and not so dissimilar to the elusive benzene dication, **105**.[121,122]



103 **104** **105**

Many carbocations containing electron-withdrawing substituents have been studied. These include halogen, nitro, trifluormethyl, and cyano groups.[123−126] Most notable ones are the α-cyanodiarylmethyl cations, **106**, which shows mesomeric nitrenium ion character (**106a**).[126] Of the trihalomethyl cations, **107**,[124] the trichloromethyl cation **107** (X = Cl) has been widely employed as a hydride abstracting agent.[127] More recent theoretical studies have indicated that the purported carbocationic carbon in **107** may even carry slight negative charge.[128]



106 **106a**

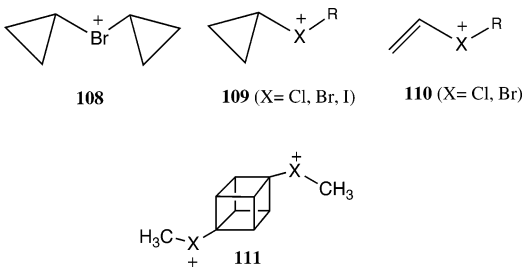
107

We have also investigated α- and *β*-trimethylsilyl-substituted carbocations.[58,129] *β*-Silyl stabilization in an allyl carbocation was also established.[129] Siehl et al. have pursued *β*-silyl effects in stabilizing long-lived vinyl cations.[130,131]

9. Onium Ions and Their Protolytic Activation. Onium ions are considered to be the positively charged higher coordinate compounds of nometallic elements. They are generally formed by protonation or alkylation of the related Lewis bases generally containing nonbonded pair of electrons. Onium ions play a major role in acid-catalyzed processes.[132]

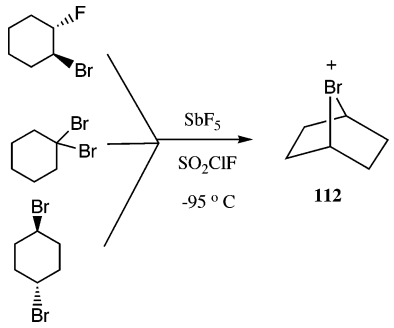
Remarkably, ionization of cyclopropyl bromide in SbF_5/SO_2ClF at low temperature resulted in dicyclopropyl bromonium ion, **108**, which could be formed only by an S_N2 substitution on an activated cyclopropyl bromide−SbF_5 complex by the nonbonded electron pair of the free cyclopropyl bromide.[133a] The ion, **108**, was characterized by ^1H and ^{13}C NMR spectroscopy. On the other hand, cyclopropyl chloride and cyclopropyl iodide under similar conditions gave ring-opened products. With alkylating agents, however, cyclopropyl halides could be efficiently alkylated to their respective halonium ions, **109**.[133a] Similarly, even vinyl chloride and bromide undergoes alkylation at the halogen to provide the vinyl alkyl halonium ions, **110**.[133b] The double bond appears to be less reactive than nonbonded electron pair of the halogens at low temperatures. We have also prepared cubyl-1,4-dimethyl dihalonium ions, **111**.[134]

A stable 1,4-bridged bicyclic bromonium ion, **112** (7-bromoniabicyclo[2.2.1]heptane), was prepared serendipitously by the ionization of a variety of cyclohexane precursors.[135] The formation of the bicyclic bromonium ion, **112**, should take place by an unprecedented transannular participation in a six-membered ring involving 1-bromo-4-cyclohexyl cation or its equivalents.[135]



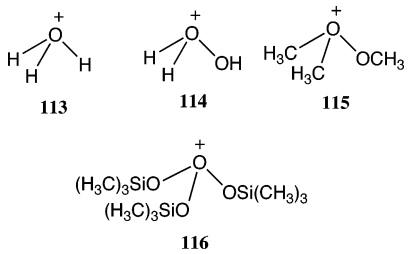
108 **109** (X= Cl, Br, I) **110** (X= Cl, Br)

111



112

We were also successful in studying a series of ^{17}O-enriched oxonium, carboxonium and acylium ions using ^{17}O NMR spectroscopy in superacids.[136] The parent hydronium ion, **113**, based on the magnitude of the $^{17}O-H$ coupling constant is clearly a pyramidal species.[136a] Protonated hydrogen peroxide, **114**, was also characterized.[136a] With Christe, we were also able to characterize trimethylperoxonium ion, **115**.[137] Even tris-(trimethylsilyl)oxonium ion, **116**, was prepared and characterized.[138] The ion **116** is an efficient source of trimethylsilyl cation for ring opening polymerization of cyclosiloxanes under almost living conditions.[139]



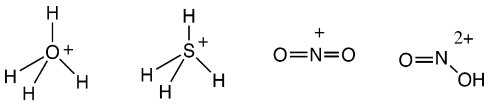
113 **114** **115**

116

Using ^{15}N-labeled ntrosonium tetrafluoroborate, we were able to diazotize ammonia, bis(trimethylsilyl)amine, and isocyanic acid, respectively. In all cases, $^{14}N^{15}N$ dinitrogen was produced involving the intermediacy of hitherto elusive parent diazonium ion (HN_2^+), **117**.[140]

We have also found that the parent hydronium ion, **113**, undergoes an unexpected hydrogen−deuterium exchange at extremely high acidities (HF−SbF_5 system), with an increase in exchange rate with increase in acid strength. This demonstrates that the nonbonded electron pair of oxygen in **113** is capable of interacting with the highly acidic proton through the involvement of protonated hydronium dication, **118**. The ab initio theoretical calculations performed at the HF-6.31G* level showed that although the dication H_4O^{2+}, **118**, is thermodynamically unstable (dissociation is exothermic by 59.2 kcal/mol), it is a minimum having substantial kinetic stability (deprotonation barrier, 39.4 kcal/mol).[141] The involvement of

H_4O^{2+}, **118**, moves the "leveling effect" many notches higher! Using isolobal analogy, analogues of **118** with $Au(PPh_3)$ ligands have been obtained by Schmidbauer.[142,143] At high acidities, evidence for the intermediacy of H_4S^{2+}, **119**, has also been obtained.[144]



118 **119** **120** **121**

The linear nitronium ion, **120**,[145] the de facto electrophilc nitrating agent in mixed nitric acid−sulfuric acid mixtures, can also be further protolytically activated to protontronium dication, **121**. Using MP2/6-31G* level optimization the protonitronium dication was found to be a minimum with substantial kinetic barrier of 17 kcal/mol for deprotonation.[146] Furthermore, ^{17}O NMR spectroscopic studies of nitronium ion by line broadening studies support the intermediacy of **121**.[147] The protonitronium dication, **121**, has also been observed in the gas phase by mass spectrometric techniques.[148]

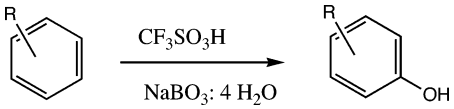
In fact, many electrophiles undergo protolytic activation in superacids.[149] Our mechanistic studies following hydrogen/deuterium exchange and theoretical studies have revealed that acetyl cation, *tert*-butyl cation, isopropyl cation and many other onium ions are indeed protolytically activated.[150−155] These observations have led George Olah to advance the concept of "superelectrophilic activation".[156,157] Since the stability of intermediates and their reactivity are opposite properties, protolytic or even Lewis acid activation[158] can lead to enormously reactive electrophiles that can efficiently react with deactivated aromatics and also C−C and C−H bonds of saturated alkanes. In many cases, we may not have a fully formed dicationic intermediates. Such electrophilic interaction, unlike solvation, enhances the reactivity of electrophiles. We have explored many such superlectrophilic reactions of practical relevance.

10. Superacid Induced Electrophilic Reactions. Apart from our studies, applications of use of superacids as a reaction media has been exploited by Jacquesy[159a] and Shudo.[159b] Trifluoromethanesulfonic acid (trflic acid) with an acidity of $H_o = -14$ (100 times stronger than 100% sulfuric acid)[5b] is an ideal nonoxidizing superacid system for the formation of reactive electrophiles. Many electrophilic reactions take place readily in triflic acid medium. We have also used $BF_3{\cdot}H_2O$ complex as an inexpensive and strong acid medium to effect electrophilic chemistry. Even typical Lewis acids such as $AlCl_3$ or $AlBr_3$ as well as $HF{:}BF_3$ and related systems have been used effectively. Just like protolytic activation of electrophiles, Lewis acid activations are also possible.[158]

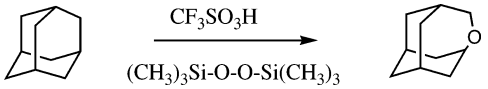
Sodium perborate hydrate in triflic acid medium functions as an excellent monohydroxylation system for aromatics in good to excellent yields, Scheme 3.[160] Typical Fridel−Crafts-type electrophilic aromatic substitution products are observed.[160] Bis-(trimethylsilyl)peroxide in triflic acid medium has been used as an efficient oxygenating system for diamondoid molecules. Adamantane is converted into oxahomoadamantane in high yield, Scheme 4.[161]

Similar to trimethylsilyl azide,[162] phenyl azides are protonated in triflic acid medium to phenylamino diazonium ions that react with aromatics to provide phenyl arylamines in high yields, Scheme 5.[163]

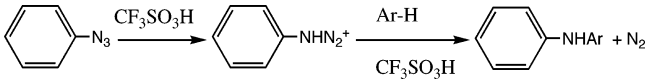
SCHEME 3



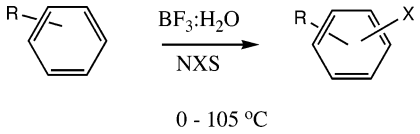
SCHEME 4



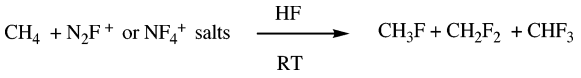
SCHEME 5



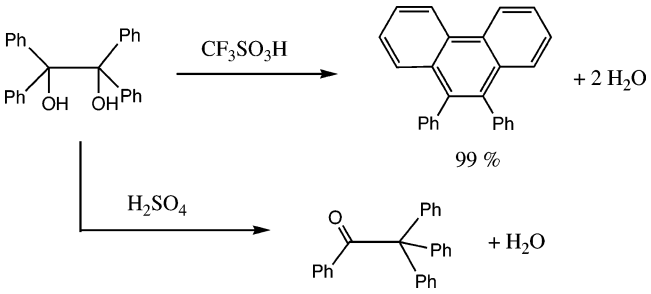
SCHEME 6



SCHEME 7



SCHEME 8



Trflic acid also activates *N*-iodosuccinimide to iodinate a series of aromatics including highly deactivated nitrobenzene in 86% yield.[164] The work has been extended to *N*-halosuccinimides using inexpensive $BF_3{\cdot}H_2O$ system, Scheme 6.[165]

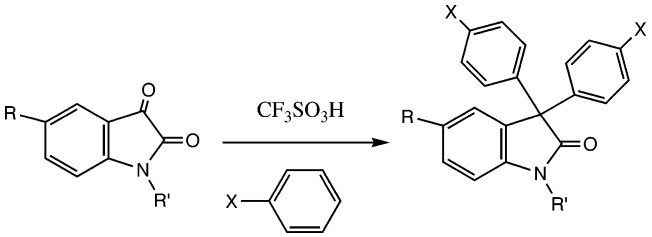
Even Selectfluor is activated in triflic acid for the electrophilic fluorination of deactivated aromatics.[166] Electrophilic fluorination of methane with N_2F^+ and NF_4^+ salts were achieved in HF solutions at low temperatures. With excess methane, methyl fluoride is formed in 63−92% relative yields with the concomitant formation of some methylene fluoride and fluoroform, Scheme 7.[167]

Unusual electrophiles such as benzaldehydes react with aromatics in superacid medim.[168] With Klumpp, we were able to convert aryl pinacols to diarylphenanthrenes in high yields in triflic acid medium. Under less acidic sulfuric acid medium, the pinacol underwent the usual pinacol−pinacolone rearrangement, Scheme 8.[169]

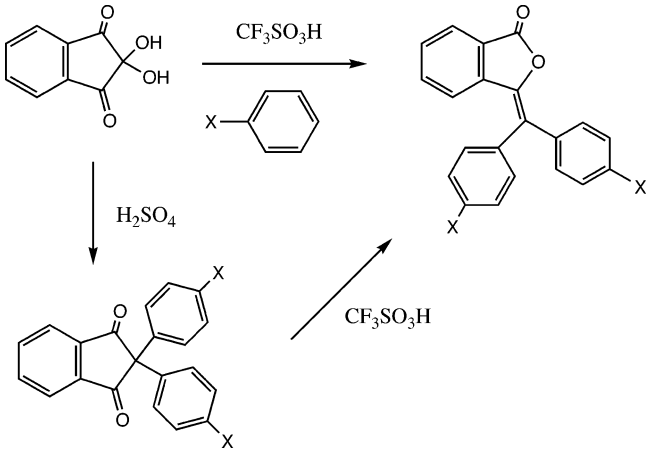
3,3-Diaryloxindoles are prepared in high yields (62−99%) by reacting isatin and substituted isatins with aromatics in triflic acid, Scheme 9. The reaction has been carried out in a combinatorial approach.[170]

Superelectrophilic Tscherniac amidomethylation of aromatics was also achieved with *N*-hydroxyphthalimide in triflic acid.[171] A new synthesis of phenyltoin and 5,5-diarylhydantoins were

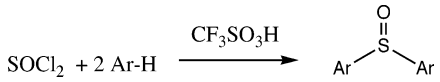
SCHEME 9



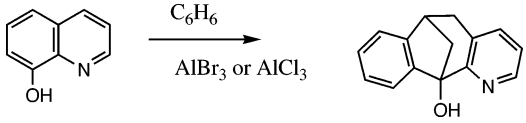
SCHEME 10



SCHEME 11



SCHEME 12



developed by the condensation of parabanic acid with aromatics in triflic acid medium.[172] Triflic acid induced reactions of ninhydrins with aromatics gave 3-(diarylmethylene)isobenzofuranones, whereas in sulfuric acid medium 2,2-diaryl-1,3-indandiones were obtained; see Scheme 10.[173]

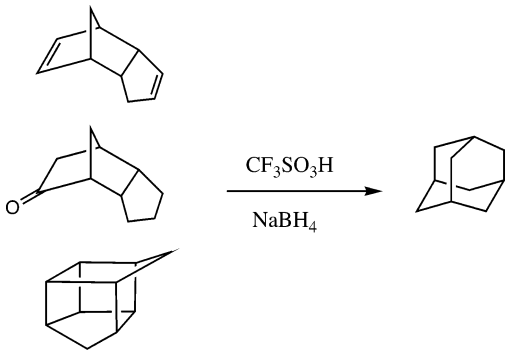
Triflic acid also activates thionyl chloride for reaction with aromatics to provide diaryl sulfoxides without any contamination from sulfones, Scheme 11.[174]

In superacids, 5-, 6-, 7-, and 8-hydroxyquinolines and 5-hydroxyisoquinolines are activated for reaction with cyclohexane and benzene.[175] With benzene, Friedel−Crafts products are obtained involving superelectrophilc intermediates; see Scheme 12. With cyclohexane ionic hydrogenation takes place. Similarly, 5-aminonaphthols,[176] 1- and 3-isoquinolinols,[177] and 2-, 3-, and 4-quinolinols[178] react with benzene and cyclohexane under superacidic conditions.

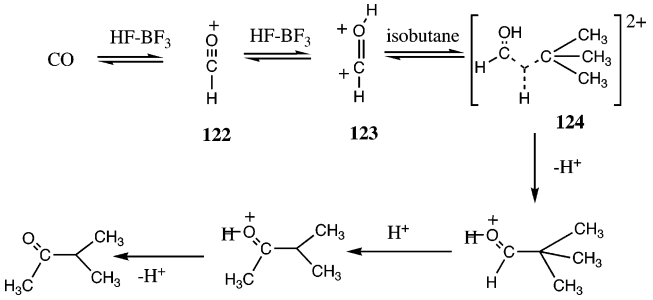
Triflic acid induced tandem alkylation−acylation of aromatics was also achieved using cinnamic acid and homocinnamic acid derivatives.[179]

Not only electrophilc aromatic substitutions but also simple alkanes undergo isomerizations in superacids.[5b] One such highly recognized reaction is the isomerization of tricyclo[5.2.1.0^{2,6}]-decane to adamantane using $AlCl_3$ catalyst, developed by Schleyer.[180] This transformation occurs more efficiently in

SCHEME 13



SCHEME 14

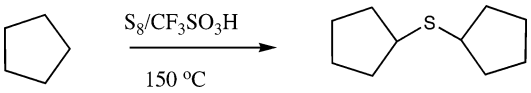


fluoroantimonic acid.[181] In a unique triflic acid−$NaBH_4$ combination, such chemistry is achieved by a reductive-isomerization protocol. A variety of C_{10} precursors are isomerized to adamantane, Scheme 13, in high yields and selectivity.[182] Similarly, C_{14} and C_{18} precursors are reductively isomerized to diamantane and triamantane, respectively.[182]

Under superacid conditions, alkylation of adamantane with olefins takes place by two mechanisms. (a) adamantylation of olefins by the adamantly cation generated via the hydride abstraction of adamantane by the alkyl cation (formed by the protonation of the olefins) and (b) direct σ-alkylation of adamantane by the alkyl cation via insertion into the bridgehead C−H bond of the adamantane through pentacoordinated carbonium ion. Both processes seem to be operational.[183]

The reactions of carbon monoxide in superacids have been of substantial interest in synthetic and mechanistic studies. Carbon monoxide can be protonated at the carbon to yield the formyl cation, **122** (HCO^+), and its direct observation has been reported in HF−SbF_5 solution using high-pressure NMR spectroscopy.[184] While the formyl cation is considered to be sufficiently electrophilic to react with arenes (Gatterman−Koch formylation), a more electrophilic protosolvated species is needed in reactions with saturated hydrocarbons (Scheme 14). For example, isobutane is converted to methyl isopropyl ketone in high yield by the reaction of carbon monoxide with HF−BF_3.[185] Since HF−BF_3 is unable to ionize isobutane to the *tert*-butyl cation directly, the results are consistent with the formation of the protosolvated formyl cation, **123**. Formylation then occurs by reaction of **123** with the tertiary carbon−hydrogen bond of isobutane (**124**) giving protonated pivaldehyde, which then rearranges to methyl isopropyl ketone. Pivalaldehyde itself has been shown to isomerize to methyl isopropyl ketone in superacids.[185] Similarly, the protosolvated formyl cation (or limiting protoformyl dication, **123**) is proposed in the conversion of adamantane to 1-adamantanecarboxaldehyde.[186]

SCHEME 15



Sulfuration of alkanes and cycloalkanes with elemental sulfur in triflic acid takes place to provide sulfides. The reaction works well with C_3 or higher hydrocarbons Scheme 15).[187]

Similarly, nitrations, methanesulfonylations, and acylations have also been carried out in superacid media.[188−190]

Epilogue. The rich and diverse electrophilic hydrocarbon chemistry that was developed over the past quarter of a century has led to our better understanding of the nature of electrophilic reactive intermediates and their reactions in superacid media. We have discussed our studies on many types of carbocations, dications, and onium ions, which in many cases are stabilized by neighboring σ-, $\pi\sigma$-, π-, and nonbonded electron pair donors. Such neighboring group participation (intra- or intermolecular), in some cases, led to multicenter bondings.[191] Such a neighboring group stabilization can be diminished in strongly acidic systems leading to superelectrophilic activation. Therefore, superacids are not just mere academic curiosities; they are indeed excellent media to perform unusual synthetic electrophilic reactions of practical significance.

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References

(1) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41 and references therein.
(2) Brown, H. C. *Acc. Chem. Res.* **1973**, *6*, 377 and references therein.
(3) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc*. **1949**, *71*, 2953; **1952**, *74*, 1147, 1159.
(4) Saunders, M.; Schleyer, P. v. R.; Olah, G. A. *J. Am. Chem. Soc*. **1964**, *86*, 5680.
(5) (a) Olah, G. A.; Tolgyeshi, W. S.; Kuhn, S. J.; Moffat, M. E.; Bastein, I. J.; Baker, E. B. *J. Am. Chem. Soc*. **1963**, *85*, 1328. (b) For a detailed discussion on superacids, see: Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985.
(6) Schleyer, P. v. R.; Watts, W. E.; Fort, R. C., Jr.; Comisarow, M. B.; Olah, G. A. *J. Am. Chem. Soc*. **1964**, *86*, 489.
(7) Olah, G. A.; White, A. M.; DeMember, J. R.; Commeyras, A.; Lui, C. Y. *J. Am. Chem. Soc*. **1970**, *92*, 4627.
(8) Olah, G. A.; Liang, G.; Mateescu, G. D.; Riemenscheider, J. L. *J. Am. Chem. Soc*. **1973**, *95*, 8698.
(9) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Anet, F. A. L. *J. Am. Chem. Soc*. **1982**, *104*, 7105.
(10) Myhre, P. C.; Yannoni, C. S. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; John Wiley and Sons: New York, 1997; Chapter 12, pp 389−431 and references therein.
(11) Schleyer, P. v. R.; Maerker, C.; Buzek, P.; Sieber, S. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; John Wiley and Sons: New York, 1997; Chapter 2, pp 19−74 and references therein.
(12) Saunders, M.; Jimenez-Vasquez.; Kronja, O. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; John Wiley and Sons: New York, 1997; Chapter 9, pp 297−347 and references therein.
(13) Saunders, M.; Kronja, O. In *Carbocation Chemistry*; Olah, G. A., Prakash, G. K. S., Eds.; John Wiley and Sons: New York, 2004; Chapter 8, pp 231−235 and references therein.
(14) (a) Arnett, E. M.; Petro, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 5402−5407. (b) Arnett, E. M.; Petro, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 5408−5416. (c) Arnett, E. M.; Pienta, N.; Petro, C. *J. Am. Chem. Soc.* **1980**, *102*, 398−400. (d) Arnett, M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 3522−3524. (e) Arnett, E. M.; Hofelich, T. *J. Am. Chem. Soc.* **1983**, *105*, 5, 2889−2895.
(15) Laube, T. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; John Wiley and Sons: New York, 1997; Chapter 14, pp 453−496 and references therein.
(16) Brown, H. C. *The Nonclassical Ion Problem*; with comments by Schleyer, P. v. R.; Plenum: New York, 1977; Chapter 5.
(17) Olah, G. A.; Prakash, G. K. S.; Saunders: M. *Acc. Chem. Res.* **1983**, *16*, 440 and references give therein.
(18) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1383.
(19) Olah, G. A. *J. Org. Chem.* **2001**, *66*, 5943.
(20) (a) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N.; Whittaker, D.; Rees, J. C. *J. Am. Chem. Soc*. **1979**, *101*, 3935. (b) Prakash, G. K. S.; Arvanaghi, M.; Olah, G. A. *J. Am. Chem. Soc*. **1985**, *107*, 6017.
(21) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.
(22) Prakash, G. K. S.; Fessner, W.-D.; Olah, G. A.; Lutz, G.; Prinzbach, H. *J. Am. Chem. Soc*. **1989**, *111*, 746.
(23) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 1545.
(24) Richie, H. G., Jr.; Nicholas, D.; Gassman, P. G.; Fentiman, A. F., Jr.; Winstein, S.; Brookhart, M.; Lustgarten, R. K. *J. Am. Chem. Soc*. **1970**, *92*, 3783.
(25) Brown, H. C.; Ravindranathan, M. *J. Am. Chem. Soc*. **1977**, *99*, 299.
(26) Coates, R. M.; Fretz, E. R. *J. Am. Chem. Soc*. **1977**, *99*, 297. Coates, R. M.; Kirkpatrick, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 4883. Coates, R. M.; Fretz, E. R. *J. Am. Chem. Soc*. **1975**, *97*, 2538.
(27) Brown, H. C.; Ravindranathan, M.; Takeuchi, K.; Peters, E. N. *J. Am. Chem. Soc*. **1975**, *97*, 2899.
(28) Farnum, D. G.; Wolf, A. D. *J. Am. Chem. Soc.* **1974**, *96*, 5166.
(29) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc*. **1977**, *99*, 5683.
(30) Prakash, G. K. S.; Iyer, P. *Rev. Chem. Int.* **1988**, *9*, 65.
(31) Olah, G. A.; Berrier, A. L.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc*. **1981**, *103*, 1122.
(32) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998.
(33) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *J. Org. Chem.* **1982**, *47*, 3903.
(34) Olah, G. A.; Prakash, G. K. S.; Farnum, D. G.; Clausen, T. P. *J. Org. Chem.* **1983**, *48*, 2146.
(35) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Am. Chem. Soc*. **1980**, *102*, 6127.
(36) Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089.
(37) Prakash, G. K. S.; Krishnamurthy, V. V.; Olah, G. A.; Farnum, D. G. *J. Am. Chem. Soc*. **1985**, *107*, 3928.
(38) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc*. **1951**, *73*, 2509.
(39) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc*. **1951**, *73*, 3542.
(40) Bartlett, P. D. *Nonclassical Ions*; Benjamin: New York, 1965; p 272.
(41) Mazur, R. H.; White, W. N.; Semenov, D. A.; Lee, C. C.; Silver, M. S,; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 1, 4390.
(42) Olah, G. A.; Juell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 146.
(43) Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah, G. A. *J. Am. Chem. Soc*. **1978**, *100*, 0, 8016.
(44) Siehl, H.-U.; Fuss, M.; Gauss, J. *J. Am. Chem. Soc*. **1995**, *117*, 7, 5983.
(45) Siehl, H.-U.; Fuss, M. *Pure Appl. Chem.* **1998**, *70*, 2015.
(46) Olah, G. A.; Buchholz, H. A.; Prakash, G. K. S.; Rasul, G.; Sosnowski, R. K.; Murray, R. K., Jr.; Kusnetsov, M. A.; Liang, G.; Meijere, A. de. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1499.
(47) Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1982**, *104*, 2600, 2605.
(48) Olah, G. A.; Donovan, D. J.; Prakash, G. K. S. *Tetrahedron Lett.* **1978**, 4779.
(49) Olah, G. A.; Prakash, G. K. S.; Nakajima, T. *J. Am. Chem. Soc.* **1982**, *104*, 1031.
(50) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Org. Chem.* **1980**, *45*, 965.
(51) Murray, R. K., Jr.; Ford, T. M.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc*. **1980**, *102*, 1865.
(52) Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69.
(53) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666.
(54) Olah, G. A.; Fung, A. P.; Rawdah, T. N.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 4646.
(55) Prakash, G. K. S.; Fung, A. P.; Olah, G. A.; Rawdah, T. N. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 5092.
(56) Olah, G. A.; Reddy, V. P.; Rasul, G.; Prakash, G. K. S. *J. Org. Chem.* **1992**, *57*, 1118.

(57) Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 762.

(58) (a) Olah, G. A.; Berrier, A. L.; Field, L. D.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 1349. (b) Olah, G. A.; Krishnamurti, R.; Prakash, G. K. S. *J. Org. Chem.* **1990**, *55*, 6061.

(59) Olah, G. A.; Reddy, V. P.; Casanova, J.; Prakash, G. K. S. *J. Org. Chem.* **1992**, *57*, 6431.

(60) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Org. Chem.* **1977**, *42*, 661.

(61) For a review, see: Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 27.

(62) (a) Olah, G. A.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *933*, 6877. (b) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6284.

(63) Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *115*, 6987.

(64) Olah, G. A.; Head, N. J.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 875.

(65) Prakash, G. K. S.; Krishnamurthy, V. V.; Arvanaghi, M.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 3985.

(66) Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1998**, *120*, 1336.

(67) Prakash, G. K. S.; Fung, A. P.; Rawdah, T. N.; Olah, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 2920.

(68) Olah, G. A.; Reddy, V. P.; Lee, G.; Casanova, J.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 1639.

(69) Olah, G. A.; Reddy, V. P.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1999**, *121*, 9994.

(70) (a) Lomas, J. S. *Nouv. J. Chim.* **1983**, *8*, 365. (b) Molle, G.; Bauer, P. *J. Am. Chem. Soc.* **1982**, *104*, 3481. (c) Dubois, J.-E.; Lomas, J. S. *Tetrahedron Lett.* **1973**, 1791. (d) Lomas, J. S.; Luong, P. K.; Dubois, J.-E. *J. Org. Chem.* **1979**, *44*, 1647.

(71) Olah, G. A.; Prakash, G. K. S.; Krishmamurti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6422.

(72) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Schleyer, P. v. R.; Graham, W. D. *J. Org. Chem.* **1982**, *47*, 1040.

(73) Bartlett, P. D.; Stiles, M. *J. Am. Chem. Soc.* **1955**, *77*, 2806.

(74) Olah, G. A.; Wu, A.; Farooq, O.; Prakash, G. K. S. *J. Org. Chem.* **1990**, *55*, 1792.

(75) Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4232.

(76) (a) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531 and references therein. (b) Buss, V.; Schleyer, P. v. R.; Allen, L. C. *Top. Stereochem.* **1973**, *7*, 253. (c) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8193. (d) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *Ibid.* **1976**, *98*, 6700. (e) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (f) Taylor, C. A.; Zerner, M. C.; Ramsey, B. *J. Organomet. Chem.* **1986**, *317*, 1.

(77) Olah, G. A.; Liang, G.; Ledlie, D. B.; Costopoulos, M. G. *J. Am. Chem. Soc.* **1977**, *99*, 4196.

(78) (a) Schleyer, P. v. R.; Bremer, M. *J. Org. Chem.* **1988**, *53*, 2362. (b) Riefling, B. Ph.D. Thesis, University of Göttingen, Germany, 1975.

(79) (a) Schöllkopf, U.; Fellenberger, K.; Patsch, M.; Schleyer, P. v. R.; Su, T.; Van Dine, G. W. *Tetrahedron Lett.* **1967**, 3639. (b) Kutzelnigg, W. *Ibid.* **1967**, 4965. (c) Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 588.

(80) (a) Creary, X. *J. Am. Chem. Soc.* **1976**, *98*, 6608. (b) Ledlie, D. B.; Swan, T.; Pile, J.; Bowers, L. *Ibid.* **1976**, *41*, 419. (c) Warner, P.; Lu, S. L. *J. Am. Chem. Soc.* **1976**, *98*, 6752 and references therein. (d) Groves, J. T.; Ma, K. W. *Tetrahedron Lett.* **1974**, 909. (e) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *J. Am. Chem. Soc.* **1978**, *100*, 7946. (f) Banert, K. *Chem. Ber.* **1985**, *118*, 1564. (g) Seebach, D.; Braun, M.; du Preez, N. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 49; *Tetrahedron Lett.* **1973**, 3509. (h) Wasserman, H. H. *Angew. Chem.* **1972**, *84*, 312. (i) Salaün, J. *J. Org. Chem.* **1978**, *43*, 2809.

(81) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985; Chapter 9.

(82) Prakash, G. K. S.; Buchholz, H.; Reddy, V. P.; de Meijere, A.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 1097.

(83) (a) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron Lett.* **1968**, 3495. (b) Cunningham, A. F., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 4864. (c) Cazlau, P.; Moulines, F.; Laporte, O.; Duboudin, F. *J. Organomet. Chem.* **1980**, *201*, C6.

(84) Gunther, H. *NMR Spectroscopy, An Introduction*; Wiley: New York, 1987.

(85) Olah, G. A.; Liang, G. *J. Org. Chem.* **1975**, *40*, 1840 and references therein. Also see: Braun, S.; Abram, T. S.; Watts, E. *J. Organomet. Chem.* **1975**, *97*, 429.

(86) Crawford, R. J.; Tokunaga, H.; Schrijver, L. M. H. C.; Goddard, J. C.; Nakashima, T. *Can. J. Chem.* **1978**, *56*, 992−997. Monti, J. P.; Faure, R.; Vincent, E. *J. Org. Magn. Reson.* **1976**, *8*, 611.

(87) (a) Fessner, W.-D.; Murty, B. A. R. C.; Worth, J.; Hunkler, D.; Fritz, H.; Prinzbach, H.; Roth, W. D.; Schleyer, P. von R.; McEwen, A. B.; Maier, W. F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 452. (b) Prinzbach, H.; Fessner, W.-D. In *Organic Synthesis: Modern Trends*; Chizhov, O., Ed.; Blackwell: Oxford, 1987; p 23.

(88) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *J. Am. Chem. Soc.* **1983**, *105*, 5446. Paquette, L. A.; Weber, J. C.; Kobayashi, T. *J. Am. Chem. Soc.* **1988**, *110*, 1303.

(89) (a) Pinkos, J.-P.; Melder, H.; Fritz, H.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 310. (b) Melder, J.-P.; Pinkos, R.; Fritz, H.; Worth, J.; Prinzbach, H. *J. Am. Chem. Soc.* **1992**, *114*, 10213. (c) Pikos, R.; Melder, J.-P.; Weber, K.; Hunkler, D.; Prinzbach, H. *J. Am. Chem. Soc.* **1993**, *115*, 7173. (d) Fessner, W.-D.; Prinzbach, H. In *Cage Hydrocarbons*; Olah, G. A., Ed.: Wiley: New York, 1990; p 353.

(90) Prakash, G. K. S.; Krishnamurthy, V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A.; Fessner, W.-D.; Prinzbach, H. *J. Am. Chem. Soc.* **1986**, *108*, 836; *J. Am. Chem. Soc.* **1988**, *110*, 7764.

(91) Prinzbach, H.; Murty, B. A. R. C.; Fessner, W.-D.; Mortensen, J.; Heinze, J.; Gescheidt, G.; Gerson, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 457.

(92) (a) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55. (b) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583. (c) Roth, H.-D.; Schilling, M. L. M.; Mukai, T.; Miyashi, T. *Tetrahedron Lett.* **1983**, *24*, 5815. Roth, H.-D.; *Acc. Chem. Res.* **1987**, *20*, 343.

(93) Fessner, W.-D.; Sedelmeier, G.; Spurr, P. R.; Rihs, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1987**, *109*, 4626.

(94) Fessner, W.-D.; Murty, B. A. R. C.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 451.

(95) Spurr, P. R.; Murty, B. A. R. C.; Fessner, W.-D.; Fritz, H.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 455. Also see: Herges, R.; Schleyer, P. v. R.; Schindler, M.; Fessner, W.-D. *J. Am. Chem. Soc.* **1991**, *113*, 3649.

(96) Murty, B. A. R. C.; Spurr, P. R.; Pinkos, R.; Grund, C.; Fessner, W.-D.; Hunkler, D.; Pritz, H.; Roth, W. R.; Prinzbach, H. *Chimia* **1987**, *41*, 32.

(97) Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193.

(98) (a) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390. (b) Child, F. R.; McGlinchey, M. J.; Varadarajan, A. *J. Am. Chem. Soc.* **1984**, *106*, 5974.

(99) (a) Cyclobutadiene dication appears to have a puckered ground-state structure: Krogh-Jespersen, K.; Schleyer, P. v. R.; Pople, J. A.; Cremer, D. *J. Am. Chem. Soc.* **1978**, *100*, 4301. (b) Hess, B. A., Jr.; Ewig, C. S.; Schaad, L. J. *J. Org. Chem.* **1985**, *50*, 5869.

(100) (a) Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Engler, E. M.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6829. (b) de Meijere, A.; Schallner, O.; Weber, W.; Schleyer, P. v. R.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 5255.

(101) Carnardi, H.; Giordano, C.; Heldeweg, R. F.; Hogeveen, H. *Isr. J. Chem.* **1981**, *22*, 229.

(102) Prakash, G. K. S.; Weber, K.; Olah, G. A.; Prinzbach, H.; Woollenweber, M.; Etzkorn, M.; Voss, T.; Herges, R. *Chem. Commun.* **1999**, 363.

(103) (a) Herges, R.; Schleyer, P. v. R.; Schindler, M.; Fessner, W.-F. *J. Am. Chem. Soc.* **1991**, *113*, 3649. (b) Prinzbach, H.; Reinbold, J.; Bertau, M.; Voss, T.; Martin, H.-D.; Mayer, B.; Heinze, J.; Neschchadin, D.; Gescheidt, G.; Prakash, G. K. S.; Olah, G. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 911.

(104) (a) Prinzbach, H.; Reinbold, J.; Bertau, M.; Voss, T.; Martin, H.-D.; Mayer, B.; Heinze, J.; Neschchadin, D.; Gescheidt, G.; Prakash, G. K. S.; Olah, G. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 911. (b).Prinzbach, H.; Reinbold, J.; Bertau, M.; Voss, T.; Martin, H.-D.; Mayer, B.; Heinze, J.; Neschchadin, D.; Gescheidt, G.; Prakash, G. K. S.; Olah, G. A. *Helv. Chim. Acta* **2001**, *84*, 1518.

(105) Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524.

(106) For reviews on homoaromaticity, see: (a) Winstein, S. Q. *Rev. Chem. Soc.* **1969**, *23*, 141. Winstein, S. *Spec. Publ. − Chem. Soc.* **1967**, No. 21, 5. (b) Story, P. R.; Clark, B. C., Jr. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, p 1007. (c) Garatt, P. J.; Sargent, M. V. In *Nonbenzenoid Aromatics*; Snyder, J. F., Ed.; Academic: New York, 1971; Vol. II, p 208. (d) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.

(107) (a) Hehre, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 5807; **1974**, *96*, 5207. (b) Haddon, R. *Tetrahedron Lett.* **1974**, *2797*, 4303. (c) Brown, R. S.; Traylor, T. G. *J. Am. Chem. Soc.* **1973**, *95*, 8025.

(108) (a) Olah, G. A.; Staral, J. S.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 6233. (b) Olah, G. A.; Staral, J. S.; Spear, R. J.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 5489.

(109) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 6803 and references therein.

(110) (a) Lustgarten, R. K.; Brookhart, M.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6350. (b) Brookhart, M.; Lustgarten, R. K.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6352. (c) Lustgarten, R. K.; Brookhart, M.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2347.

(111) (a) Masamune, S.; Sakai, M.; Jones, A. V. K.; Nakashima, T. *Can. J. Chem.* **1974**, *52*, 855. (b) Masamune, S.; Sakai, M.; Jones, A. V. K. *Can. J. Chem.* **1974**, *52*, 858. (c) Coates, R. M.; Fretz, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 2538.

(112) Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *Angew. Chem.* **1983**, *95*, 726.
(113) Prakash, G. K. S.; Farnia, M.; Keyaniyan, S.; Olah, G. A.; Kuhn, H. J.; Shaffner, H. *J. Am. Chem. Soc.* **1987**, *109*, 911.
(114) Amman, W.; Jäggi, F. J.; Ganter, C. *Helv. Chim. Acta* **1980**, *63*, 2019.
(115) (a) Scholtz, K.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 1394. (b) Ajami, D.; Oeckler, O.; Simon, A.; Herges, R. *Nature* **2003**, *426*, 819.
(116) Olah, G. A.; Prakash, G. K. S.; Kobayashi, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1988**, *110*, 1304. (b) Olah, G. A.; Prakash, G. K. S.; Fessner, W. D.; Kobayashi, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1988**, *110*, 8599.
(117) Olah, G. A.; Prakash, G. K. S.; Shih, J.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2764.
(118) Heagy, M. D.; Wang, Q.; Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1995**, *60*, 7351.
(119) Head, N. J.; Prakash, G. K. S.; Bashir-Hashemi, A.; Olah, G. A. *J. Am. Chem. Soc.* **1995**, *117*, 12005.
(120) Head, N. J.; Olah, G. A.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 11205.
(121) Olah, G. A.; Shamma, T.; Burrichter, A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3407.
(122) Olah, G. A.; Shamma, T.; Burrichter, A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 12923.
(123) (a) Olah, G. A.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8020. (b) Olah, G. A.; Rasul, G.; Yudin, A.; Burrichter, A.; Prakash, G. K. S.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Volpin, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 1446.
(124) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Krishnamurthy, V. V. *J. Am. Chem. Soc.* **1984**, *106*, 2378.
(125) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *J. Am. Chem. Soc.* **1980**, *102*, 6640.
(126) Olah, G. A.; Arvanaghi,; Prakash, G. K. S. M. *J. Am. Chem. Soc.* **1982**, *104*, 1628−1631.
(127) Sommer, J.; Bukala, J. *Acc. Chem. Res.* **1993**, *26*, 370.
(128) Mercier, H. P. A.; Moran, M. D.; Schrobilgen, G. J.; Steinberg, C.; Suontamo, R. J. *J. Am. Chem. Soc.* **2004**, *126*, 5533.
(129) Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 3076.
(130) (a) Siehl, H.-U.; Kaufmann, F.-P.; Apeloig, Y.; Braude, V.; Danovich, D.; Berndt, A.; Stamitus, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1497. (b) Siehl, H.-U.; Kaufmann, F.-P. *J. Am. Chem. Soc.* **1992**, *114*, 4937. (c) Siehl, H.-U.; Kaufmann, F.-P.; Kori, K. *J. Am. Chem. Soc.* **1992**, *114*, 9343. (d) Muller, T.; Meyer, R.; Lennartz, D.; Siehl, H.-U. *Angew. Chem., Int. Ed.* **2000**, *39*, 3074 and references therein. (e) Muller, T.; Margraf, D.; Syha, Y. *J. Am. Chem. Soc.* **2005**, *127*, 10852.
(131) Siehl, H.-U.; Muller, T. In *Chemistry of Organo Silicon Compounds, 2*; Rappoport, Z., Apeloig, Y.,Eds.; Wiley: Chichester, 1998; Part I, pp 595−701.
(132) Olah, G. A.; Laali, K. K.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley: New York, 1998.
(133) (a) Olah, G. A.; Prakash, G. K. S.; Bruce, M. R. *J. Am. Chem. Soc.* **1979**, *101*, 6463. (b) Prakash, G. K. S.; Bruce, M. R.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 2405.
(134) Head, N. J.; Rasul, G.; Mitra, A.; Bashir-Hashemi, A.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1995**, *117*, 12107.
(135) Prakash, G. K. S.; Aniszfeld, R.; Hashimoto, T.; Bausch, J.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 8726.
(136) (a) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 2373. (b) Olah, G. A.; Iyer, P. S.; Prakash, G. K. S.; Krishnamurthy, V. V. *J. Org. Chem.* **1984**, *49*, 4317.
(137) Olah, G. A.; Rasul, G.; Burrichter, A.; Hachoumy, M.; Prakash, G. K. S.; Wagner, R. I.; Christe, K. O. *J. Am. Chem. Soc.* **1997**, *119*, 9572.
(138) Olah, G. A.; Li, X.-Y.; Wang, Q.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 8962.
(139) Olah, G. A.; Li, X.-Y.; Wang, Q.; Rasul, G.; Prakash, G. K. S. *Macromolecules* **1996**, *6*, 1857.
(140) Olah, G. A.; Herges, R.; Felberg, J. D.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1985**, *107*, 5282.
(141) Olah, G. A.; Prakash, G. K. S.; Barzaghi, M.; Lammertsma, K.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1032.
(142) Schmidbauer, H.; Hofreiter, S.; Paul, M. *Nature* **1995**, *377*, 503.
(143) Prakash, G. K. S. *Nature* **1995**, *377*, 481.
(144) Olah, G. A.; Prakash, G. K. S.; Marcelli, M.; Lammertsma, K. *J. Phys. Chem.* **1988**, *92*, 878.
(145) Prakash, G. K. S.; Heiliger, L.; Olah, G. A. *Inorg. Chem.* **1990**, *29*, 4965.
(146) Olah, G. A.; Rasul, G.; Aniszfeld, R.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 5608.
(147) Prakash, G. K. S.; Rasul, G.; Burrichter, A.; Olah, G. A. *ACS Symp. Ser.* **1996**, *623*, 10.
(148) Weiske, T.; Koch, W.; Schwarz, H. *J. Am. Chem. Soc.* **1993**, *115*, 6312.
(149) Olah, G. A.; Prakash, G. K. S.; Lammertsma, K. *Res. Chem. Int.* **1989**, 141.
(150) Olah, G. A.; Burrichter, A.; Rasul, G.; Prakash, G. K. S.; Hachoumy, M.; Sommer, J. *J. Am. Chem. Soc.* **1996**, *118*, 10423.
(151) Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1993**, *115*, 6985..
(152) Olah, G. A.; Burrichter, A.; Rasul, G.; Prakash, G. K. S.; Burkhart, M.; Lammertsma, K. *J. Am. Chem. Soc.* **1994**, *116*, 6, 3187.
(153) Rasul, G.; Reddy, V. P.; Zdunek, L.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1993**, *115*, 2236.
(154) Olah, G. A.; Heiner, T.; Rasul, G.; Prakash, G. K. S. *J. Org. Chem.* **1998**, *63*, 7993.
(155) Olah, G. A.; Burrichter, A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 4594.
(156) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.
(157) Olah, G. A.; Klumpp, D. *Acc. Chem. Res.* **2004**, *37*, 211.
(158) Vol'pin, M.; Akhrem, I.; Orlinkov, A. *New J. Chem.* **1989**, *13*, 771.
(159) (a) Jacquesy, J.-C. In *Carbocation Chemistry*; Olah, G. A., Prakash, G. K. S., Eds.; John Wiley and Sons: New York, 2004; Chapter 14, p 376 and references therein. (b) Shudo, K.; Ohwada, T. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; John Wiley and Sons: New York, 1997; Chapter 16, p 525 and references cited therein.
(160) Prakash, G. K. S.; Krass, N.; Wang, Q.; Olah, G. A. *Synlett* **1991**, 39 and references therein.
(161) Olah, G. A.; Ernst, T. D.; Rao, C. B.; Prakash, G. K. S. *New J. Chem.* **1989**, *13*, 791.
(162) Olah, G. A.; Ernst, T. D. *J. Org. Chem.* **1989**, *54*, 1203.
(163) Olah, G. A.; Ramaiah, P.; Wang, Q.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 6900.
(164) Olah, G. A.; Wang, Q.; Sandford, G.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 3194.
(165) Prakash, G. K. S.; Mathew, T.; Hoole, D.; Esteves, P. M.; Wang, Q.; Rasul, G.; Olah, G. A. *J. Am. Chem. Soc.* **2004**, *126*, 15770.
(166) Shamma, T.; Buchholz, H.; Prakash, G. K. S.; Olah, G. A. *Isr. J. Chem.* **1999**, *39*, 207.
(167) Olah, G. A.; Hartz, N.; Rasul, G.; Wang, Q.; Prakash, G. K. S.; Casanova, J.; Christe, K. O. *J. Am. Chem. Soc.* **1994**, *116*, 5671.
(168) Olah, G. A.; Rasul, G.; York, C,; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *17*, 11211.
(169) (a) Klumpp, D.; Baek, D. N.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1997**, *62*, 6666. (b) Olah, G. A.; Klumpp, D. A.; Neyer, G.; Wang, Q. *Synthesis* **1996**, 321.
(170) Klumpp, D.; Yeung, K. Y.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1998**, *63*, 4481
(171) Olah, G. A.; Wang, Q.; Sandford, G.; Oxyzoglou, A. B.; Prakash, G. K. S. *Synthesis* **1993**, 1077.
(172) Klumpp, D.; Yeung, K. Y.; Prakash, G. K. S.; Olah, G. A. *Synlett* **1998**, 918.
(173) Klumpp, D. A.; Fredrick, S.; Lau, S.; Jin, K. K.; Bau, R.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1999**, *64*, 4481.
(174) Olah, G. A.; Marinez, E.; Prakash, G. K. S. *Synlett* **1999**, 1397.
(175) Koltunov, Yu. K.; Prakash, G. K. S.; Rasul, G.; Olah, G. A. *J. Org. Chem.* **2002**, *67*, 4330.
(176) Koltunov, Yu. K.; Prakash, G. K. S.; Rasul, G.; Olah, G. A. *Tetrahedron* **2002**, *58*, 5423.
(177) Koltunov, Yu. K.; Prakash, G. K. S.; Rasul, G.; Olah, G. A. *J. Org. Chem.* **2002**, *67*, 8943.
(178) Koltunov, Yu. K.; Prakash, G. K. S.; Rasul, G.; Olah, G. A. *Heterocycles* **2004**, *62*, 757.
(179) Prakash, G. K. S.; Yan, B.; Torok, B.; Olah, G. A. *Catal. Lett.* **2003**, *89*, 109.
(180) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1957**, *79*, 3292.
(181) (a) Olah, G. A.; Olah, J. A. *Synthesis* **1973**, 488.
(182) Olah, G. A.; Wu, A.-H.; Farooq, O.; Prakash, G. K. S. *J. Org. Chem.* **1989**, *54*, 1450.
(183) Olah, G. A.; Farooq, O.; Krishnamurthy, V. V.; Prakash, G. K. S.; Laali, K. *J. Am. Chem. Soc.* **1985**, *107*, 7541.
(184) (a) De Rege, P. J. F.; Galdysz, J. A.; Horvath, I. T. *Science* **1997**, *276*, 776. (b) Prakash, G. K. S. *Science* **1997**, *276*, 756.
(185) (a) Olah, G. A.; Prakash, G. K. S.; Mathew, T.; Marinez, E. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 2547. (b) Olah, G. A.; Mathew, T.; Marinez, E. R.; Esteves, M.; Etzkorn, M.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **2001**, *123*, 11556.
(186) Farooq, O.; Marcelli, M.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 864.
(187) Olah, G. A.; Wang, Q.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1988**, *110*, 864.
(188) (a) Olah, G. A, Orlinkov, A.; Oxyzoglou, A. B.; Prakash, G. K. S. *J. Org. Chem.* **1995**, *60*, 7348. (b) Olah, G. A.; Orlinkov, A.; Ramaiah, P.; Oxyzoglou, A. B.; Prakash, G. K. S. *Russ. Chem. Bull.* **1998**, *47*, 924. (c) Olah, G. A.; Ramaih, P.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 11783.
(189) Olah, G. A.; Orlinkov, A.; Ramaiah, P.; Oxyzoglou, A. B.; Prakash, G. K. S. *Zh. Org. Khim.* **1998**, *34*, 1644.
(190) Hwang, J. P.; Prakash, G. K. S.; Olah, G. A. *Tetrahedron* **2000**, *56*, 7199.
(191) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987.

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