CHAPTER 9

Carbocations

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Introduction

A recently published book on vinyl cations and related species[1] contains several relevant reviews, which will be detailed below. A comprehensive review of the interactions between carbocations and anions which take place in crystals has been published,[2] and a review commentary concerning the heterolytic bond dissociation energies of the weak carbon–carbon σ-bonds in species which dissociate to stabilized carbocations and stabilized carbanions has appeared.[3] Another review wonders whether or not acid catalysis via organic cations and electron-transfer catalysis via cation radicals are distinctive mechanisms in alkene isomerization processes, and suggests that rigorous experimental evidence be obtained before assigning one of these mechanisms.[4] A computational study suggests that interaction with π systems can considerably stabilize carbocations, for instance in the complexation of methyl cation with benzene which occurs in the gas phase.[5]

Simple Carbocations

Hydrogen–deuterium exchange processes occur during the reaction of methyl cation with methane to give ethyl cation and molecular hydrogen in the gas phase, and the exchanged products do not quite have a statistical H/D distribution.[6] The reaction of [$^3H_3$]methyl cations with *sec*-butylmethylamine in the gas phase mainly gives primary and secondary amines, but that of [^3H]butyl cations with dimethylamine mostly results in the substrate becoming labelled.[7] A high-level calculation concerning the elimination of molecular hydrogen from ethyl cation has been performed.[8] The reaction of perdeuteriated ethyl cations, formed radiolytically, with thiophene and *N*-methylpyrrole in the gas phase leads to exchanged and alkylated products, and the conclusion was reached that ethyl cations are Brønsted acids more than they are Lewis acids.[9]

   Calculations suggest that in the gas phase the 2-propyl cation forms ion pairs with FBH_3^- and LiH_2^- anions, in which the geometry of the 2-propyl cation is somewhat different from that which it adopts in the free state,[10] and that even in solution the 2-propyl cation exists mostly in the ion-paired form, as suggested by *ab initio* calculations of its ^{13}C NMR spectrum.[11] The $C_3H_9^+$ (protonated propane) cation is not an H-proponium species but has an energy-minimum structure with a proton located essentially equidistant between two carbons; however, the van der Waals complex between 2-propyl cation and molecular hydrogen is only 0.3 kcal mol^{-1} higher in energy.[12] An *ab initio* study of the rearrangements of pentacoordinated carbonium ions suggests that products formed in superacid or zeolite media result from the protonation of accessible C−H bonds rather than the inner C−C bonds of alkanes.[13]

   The gas-phase dissociation processes of the butyl cation have been the subject of an experimental and theoretical study.[14] Most butyl and isobutyl species give a mixture of *s*- and *t*-$C_4H_9^+$ in the mass spectrometer; these may decompose to methane and a $C_3H_5^+$ species with the prop-2-enyl cation structure (not allyl), but metastable $C_4H_9^+$ can give ethylene and a non-classical ethyl cation with a proton bridging the two carbons.[14] In Friedel–Crafts reactions, 2-*t*-butyl-1-tosylaziridines give a variety of products resulting from two-step 1,2-shift processes and recombinations in the intermediate carbenium ions.[15] Thermally, *N*-nitroamines apparently decompose by way of a carbocation intermediate,[16] a different mechanism from that found in the acid-catalysed solvolyses of these substrates.[17]
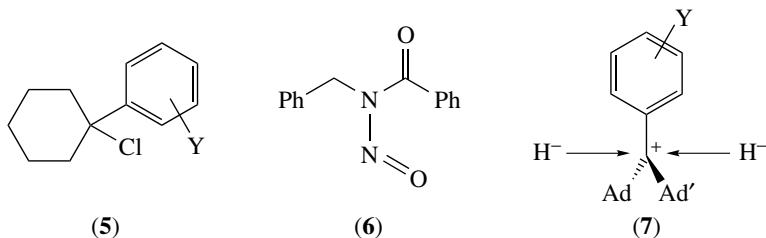
Benzyl Cations

The α-methylbenzyl cation (**1**) can be approached from the alcohol dehydration direction or the alkene protonation direction, as shown, and both of these processes have been the subject of *ab initio* molecular orbital calculations.[18] It was found that the alcohol dehydration has a transition state about half way between the two structures shown, with the transition state and the carbocation having about the same amount of π-orbital overlap. However, the alkene protonation has an earlier transition state with less effective π-orbital overlap than that in the cation. This is held to explain the different Yukawa–Tsuno r^+ values found for the two processes, 0.7–1.1 for alkene

hydrations and 1.0–1.4 for solvolyses.[18] Semiempirical studies of the α-methoxy-α-methylbenzyl cations (**2**) have enabled the twist angle between the ring and the substituents on the carbocation centre to be calculated as a measure of the resonance interaction in these species.[19] The stabilities of the *o*-, *m*-, and *p*-tolyl cations, and the tropylium ion, relative to the benzyl cation have been calculated and found to be $o < m < p$.[20] An AM1 MO study of the bond dissociation energies in a number of different benzene and toluene derivatives (R−Y, with R = Ar and ArCH$_2$) has been carried out in order to see how well the principle of maximum hardness applies to them.[21] Modern molecular mechanics calculations on a number of benzylic and cyclic delocalized cations have been shown to agree well with *ab initio* calculations on the same species.[22]

MeCHOH$_2^+$ | Ph   −H$_2$O

PhCH=CH$_2$ +H$^+$

MeCHPh$^+$

(**1**)

(**2**)

(**3**)   −Cl$^-$ (**4**)
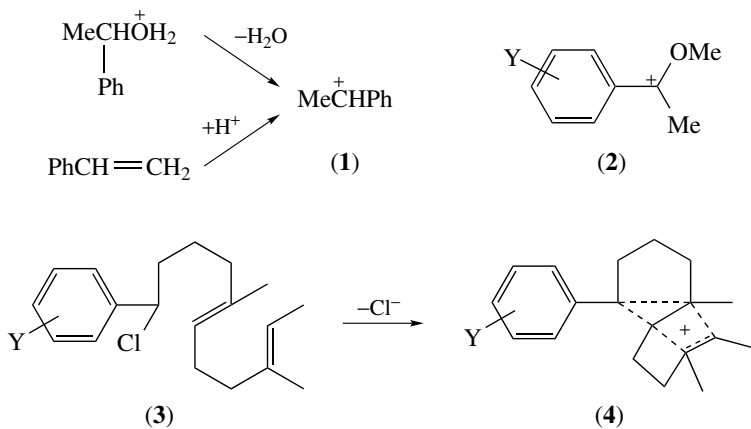
Hammett ρ^+ values referring to the formation of the intermediate (or transition state) (**4**) during the solvolysis of (**3**) have been measured to be between −1.5 and −1.8, the same as those observed for benzylic squalane derivatives; these are typical values for biomimetic cyclizations of this type.[23] Solvolysis of (**5**) in MeOH–MeCN mixtures leads to H/D isotope effects, activation parameters and ρ^+ values typical for S_N1 solvolysis processes; an observed Winstein–Grunwald *m* value of >1 is held to suggest positive charge delocalization on to the ring.[24] The decomposition of (**6**) leads to a nitrogen-separated benzyl cation–benzoate ion pair, and the benzyl cation behaves as an essentially free species, useful, for instance, in the direct alkylation of acid-sensitive heterocyclic compounds.[25] The ionization of α-chlorobenzyl alkyl ethers gives contact and solvent-separated ion pairs with great ease, as compared with the thermal decomposition to benzaldehyde and alkyl chloride that can also occur with these molecules.[26] The topomerization of these substrates was studied.[26] Hydride ion can attack the crowded cation (**7**) from either side, and the steric influence of the Y substituents on the reaction of these with hydrosilanes and sodium borohydride has been investigated.[27]
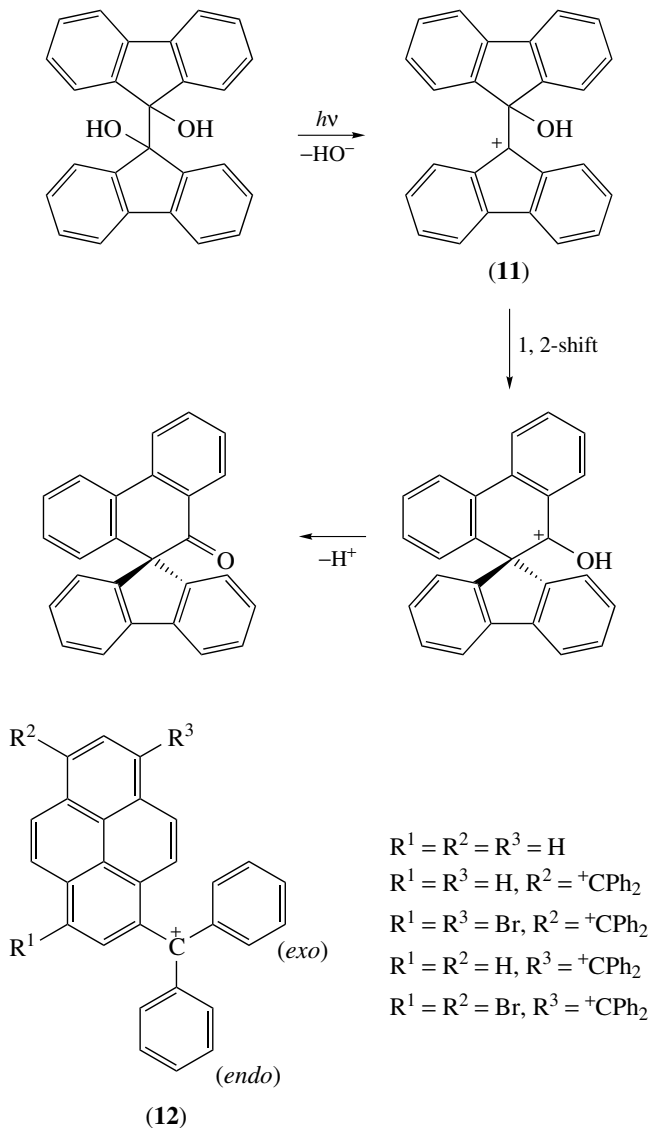
(5)   **(6)**   **(7)**

Trityl, Fluorenyl, and Related Cations

Triarylmethylamines (Ar_3CNH_2) deaminate to trityl cations in dilute aqueous perchloric acid; the rates of this process have been studied and pK values in aqueous MeCN determined.[28] The reaction was studied in more detail for the 4,4'-dimethoxytrityl cation and the kinetics of its formation, equilibria, and deuterium isotope effects were determined.[29] Ion-pair formation may occur in this system.[29] The hydride affinities of 45 trityl cations have been measured in MeCN and DMSO; the resulting free energies are a linear function of the pK_{R+} values.[30] Bis- and tris-(2,4,6-trimethoxyphenyl)carbenium ion salts (called Φ_2CHX and Φ_3CX, X being an anion) have been found to have unusual stabilities and reactivities.[31] For instance $\Phi_2CH^+ClO_4^-$ is recrystallizable from hot methanol; $\Phi_2CH^+Cl^-$ and $\Phi_2CH^+NO_3^-$ decompose to Φ_3CH in aqueous HCl or methanol, or can be reduced to Φ_2CH_2 in primary or secondary alcohol solvents. In aqueous NaOH, (**8**) is formed.[31]

(8)   **(9)**   **(10)**
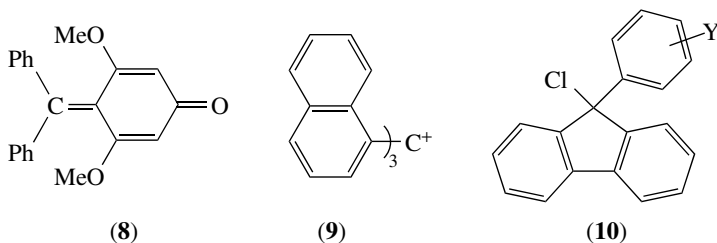
   The highly crowded tris(1-naphthyl) and tris(2-naphthyl) cations, e.g. (**9**), can be prepared by treating the alcohol precursors with $FSO_3H–SO_2ClF$ between -78 and $-20\,°C$.[32] 9-Aryl-9-chlorofluorenes (**10**) give the corresponding fluorenyl cations as solvolysis intermediates; a linear plot of the logarithm of solvolysis rate constants against σ^+ was found, but a good Winstein–Grunwald correlation was not observed.[33] The experimental evidence and the results of theoretical calculations were interpreted in favour of the fluorenyl cation behaving much like the diphenylmethyl and trityl cations.[33] An interesting photochemical pinacol rearrangement involving the fluorenyl cation (**11**) has been observed.[34]

   The reduction of xanthylium cations by BNAH apparently involves rate-determining electron transfer followed by fast hydrogen atom abstraction.[35] Conformational studies

(**11**)

1, 2-shift

−H⁺

R¹ = R² = R³ = H

R¹ = R³ = H, R² = ⁺CPh₂

R¹ = R³ = Br, R² = ⁺CPh₂

R¹ = R² = H, R³ = ⁺CPh₂

R¹ = R² = Br, R³ = ⁺CPh₂

(**12**)

on the pyrenyl carbocations (**12**) have been carried out by means of semiempirical calculations and by NMR investigation under stable-ion conditions.[36] These fairly stable crowded species are twisted, and there is a high enough barrier to rotation that *exo*- and *endo*-phenyl groups can be distinguished by NMR. The most extensive charge delocalization was found in (**12**; R¹ = R² = R³ = H).[36] Charge delocalization in the phenanthrene species (**14**) is much more extensive than it is in (**13**); some of the *O*-protonated species (**13**) do not readily undergo cisoid–transoid rotations.[37]

(13)   **(14)**

(R = Me, Ph)
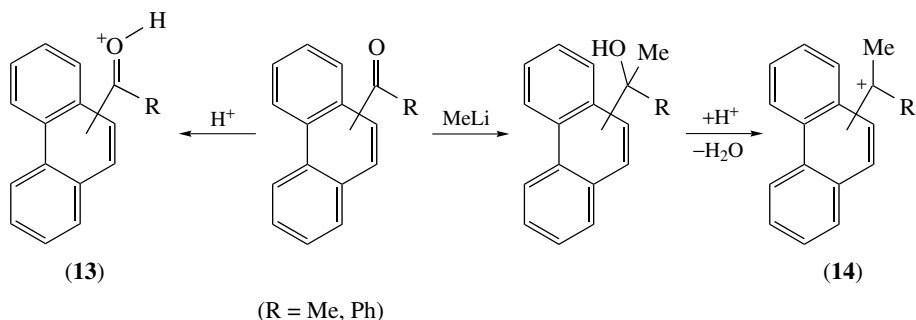
Carbocations Containing Silicon, Tin, etc.

Several review articles on different aspects of this topic have appeared. A comprehensive review covers carbenium ions stabilized by heteroatoms,[38] and the chemistry of R_3Si^+ as a bridge between organic and inorganic chemistry is discussed.[39] A more specialized article reviews attempts at the isolation and detection of silyl and germyl cations.[40] A calculational study of the tropylium, silatropylium, and germatropylium cations shows that for $C_7H_7^+$ the tropylium ion structure is the global minimum and that the benzyl cation structure is fairly close to it in energy, but that the opposite is true for $C_6H_7Ge^+$.[41] For $C_6H_7Si^+$ all of the isomeric structures were found to be very close in energy.[41] In the gas phase the relative stabilities of a series of cations **(15)** have been compared with that of the parent ion (Y = H) by being allowed to equilibrate with it.[42] The ρ and r^+ values found were significantly smaller than those found for the carbon analogue, and it is surmised that there is no significant π-delocalization of positive charge into the ring in **(15)**.[42] In a study of the γ-effect it was found that the unimolecular solvolysis of **(16)** takes place more than 10^4 times faster than does that of **(17)**, and that the C—O bond in **(16)** is lengthened with respect to that in **(17)**.[43]

(15)   M = Si, Sn; R = SO$_2$C$_6$H$_4$NO$_2$-*p*, COC$_6$H$_4$NO$_2$-*p*
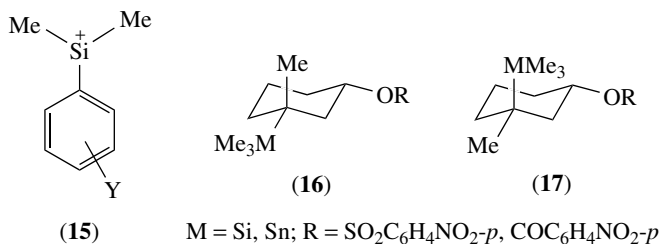
Carbocations Containing Other Heteroatoms

The recent preparation and characterization of the simple acylium systems $H-\overset{+}{C}{=}O$ and $F-\overset{+}{C}{=}O$ has been reviewed.[44] A study of the cations $R\overset{+}{C}Me_2$ (R = H, Me, Cl) has shown that α-substitution by Cl provides about as much stabilization as

does substitution by Me in these species.[45] An experimental and theoretical study of the addition of the cations and radical cations of carbon to nitriles shows that addition takes place on the nitrogen; for instance, Me^+ adds to MeCN to give $(Me-C \equiv \overset{+}{N}-Me \leftrightarrow Me-\overset{+}{C}=N-Me)$.[46] In the gas phase the 2-bromobutane cation $C_4H_9Br^+$ may lose Br to give *sec*-butyl ($C_4H_9^+$) or, at slightly lower ion energies, lose HBr to give a butenyl cation by a concerted process which may involve tunnelling.[47] Some heats of formation at 0 K were also determined.[47] Protonated carbamic acid (**18**) has been studied theoretically and by ^1H, ^{13}C and ^{15}N NMR spectroscopy.[48]

(18)   **(19)**

**(20)**   **(21)**   **(22)**
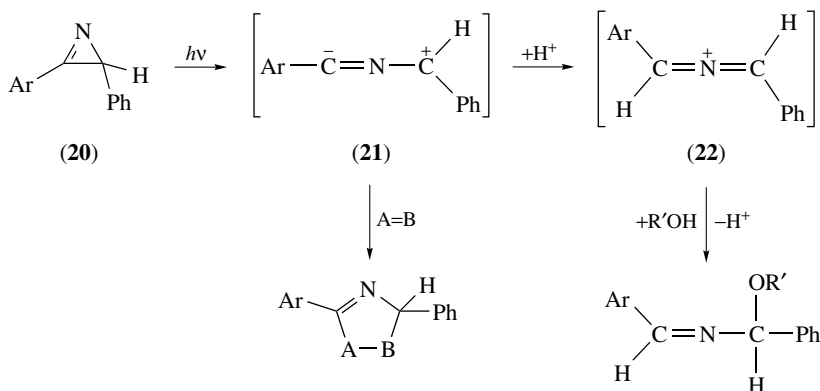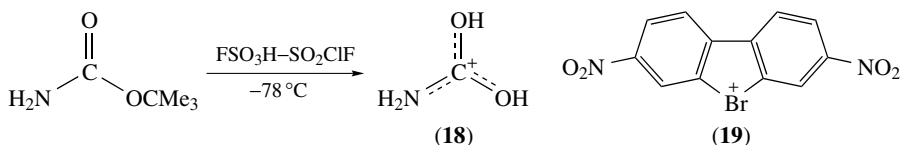
The ethylene bromonium and 1-bromoethyl cations and their neutral and anionic counterparts have been the subject of a tandem mass spectrometric study of dissociation and gas-phase redox reactions.[49] IR and Raman studies of the bioactive bromonium cation (**19**), as its hydrogensulfate salt, agree with the results of an X-ray structure determination, and theoretical calculations are also in agreement, except for the details of the NO_2 groups.[50] The azaallenium ion (**22**) is an intermediate in the photolysis of (**20**); (**21**) and (**22**) could both be seen.[51] Flash photolysis of (**23**) leads to (**24**), (**25**), and (**26**), all of which could be trapped by nucleophiles; (**27**) was not an intermediate.[52] NMR lineshape analysis of the spectrum of (**28**) leads to reaction rate constants of formation for both the intimate ion pair (**29**) and the solvent-separated ion pair (**30**).[53]

Destabilized Carbocations

These are carbocations with formally electron-withdrawing groups situated α to the positive charge centre. The presence of the α-CF_3 group in (**31**) and (**32**) causes

(23)   (24)   (25)

(26)   (27)

(28)   (29)   (30)

(31)   (32)   (33)
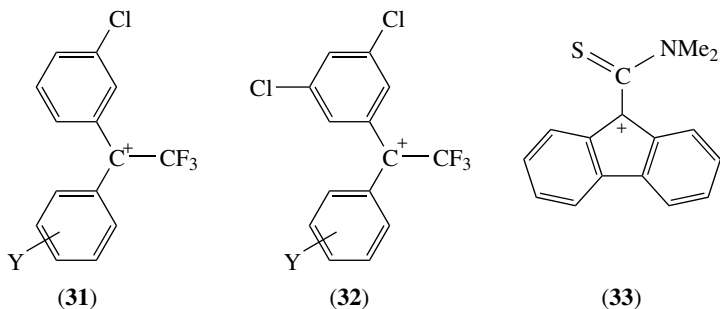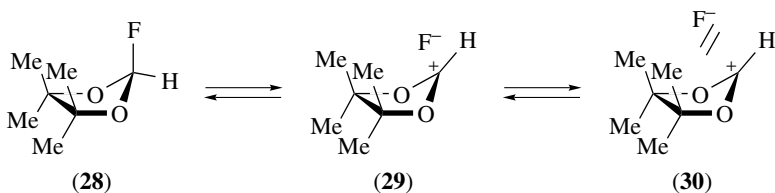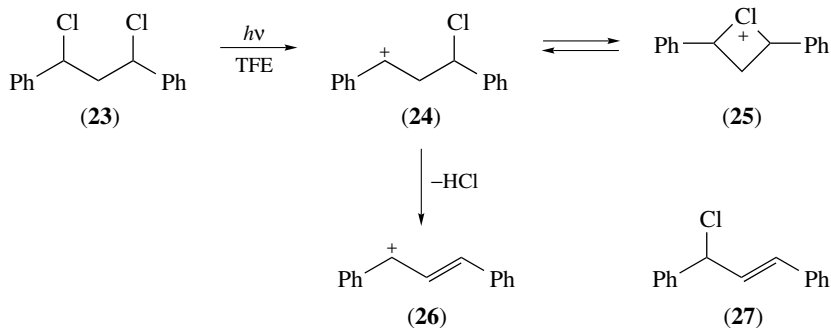
Yukawa–Tsuno plots of the logarithm of the solvolysis rate constants of the corre-
sponding tosylates (in 80% aqueous ethanol at 25 °C) to be bilinear, owing to the
changing coplanarity with substituent of the two aryl π-systems with varying elec-
tron demand.[54] The $C_2H_4NS^+$ and $C_2H_4NO^+$ potential-energy surfaces have been
compared.[55] For the thioformamidylmethyl cation an *S*-bridged species was found
to be lowest in energy, but for the formamidylmethyl cation itself the low-energy
structure is a solvated $H_2C\overset{+}{=}NH_2 \cdots CO$.[55] Benzylic α-chlorothioamides solvolyse via
intermediate carbocations such as (**33**); species such as this apparently do not have
carbonyl conjugation as a cation stabilization feature.[56] The α-thioamide-substituted
benzyl cation (**34**) has been studied under solvolysis conditions; one of the reaction
products is (**35**), and this undergoes a unique dimerization by reacting with another
(**34**) to give (**36**), the mechanism of which has been worked out.[57] In another study
(**34**) has been found to be fairly reactive, only π-nucleophiles with nucleophilicity

(34)   (35)

+
solvolysis
products

−H⁺ | dimerization

(36)
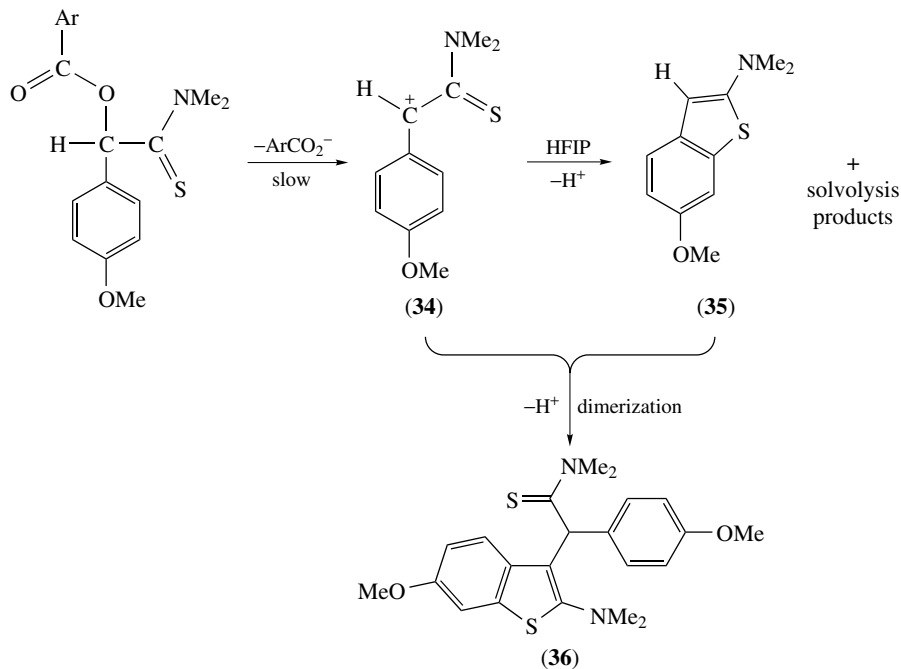
parameters >6 being able to capture it during solvolysis.[58] The presence of the α-sulfur in (37) reduces its reactivity relative to the molecule without it by a factor of $10^{-6.2}$, but the reactivity reduction for (38) is only $10^{-2.5}$.[59] This difference is attributed to stabilization by sulfur bridging as in (39), possible in the latter case but not the former.[59]

(37)   (38)   (39)
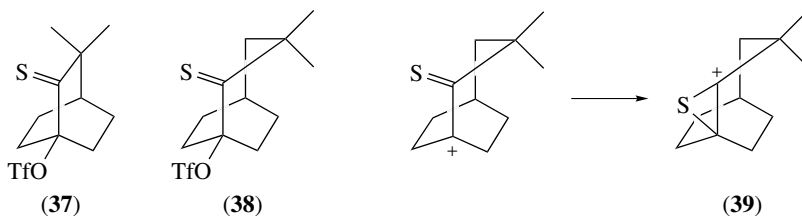
Allylic Systems

The allylic cation (40), formed in a specific acid-catalysed process, is relatively stable thermodynamically, stable enough towards trapping by nucleophiles that the reaction product obtained is almost invariably the naphthalene elimination product.[60] *cis*-Enediynes (42) are formed regiospecifically when the allylic cation (41) is trapped as shown.[61] The 'walking' of methanol around optically active 1-methyl-3-ethylallyl

(**40**)

(X = O, S; R = Bu^{t}Me$_2$Si, H)   (**41**)   (**42**)
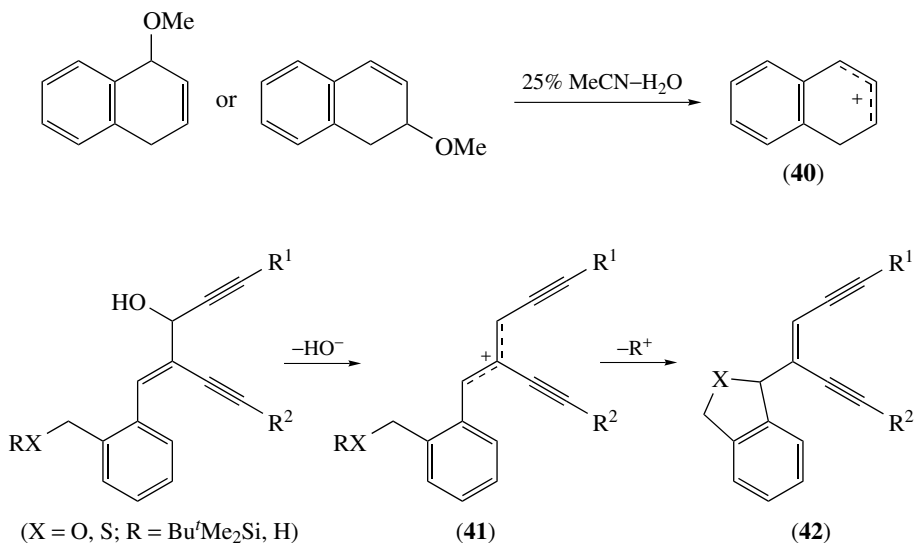
cations can be seen in the gas phase, leading to distinct hydrogen-bonded complexes; the kinetics and mechanisms of the various racemization and regio isomerization processes observable are reported.[62] The products are (*S*)-*trans*-hex-4-en-3-ol and (*R*)-*trans*-hex-3-en-2-ol.[62] Some stable allylic [60]fullerene carbocations, $C_{60}Ar_5^+$, have been observed.[63]

Vinyl, Aryl, and Related Cations

Many valuable reviews of the chemistry of these species are given in the new book *Dicoordinated Carbocations*.[1] An introduction by Grob[64] is followed by reviews of various theoretical studies of vinyl cations,[65] their gas-phase chemistry,[66] their generation by nuclear decay,[67] and their NMR spectroscopic characterization.[68] Vinyl cation production by addition to acetylenes and allenes,[69] by solvolysis,[70] and photolytically[71] are covered, together with the chemistry of the species generated in these various ways. The next chapter deals with the synthetic applications of vinyl cations,[72] and alkynyl and aryl cations are covered in the last chapter.[73] A review of the NMR spectroscopic and quantum-chemical investigation of vinyl cations in superacid media (also of dienyl and 1-cyclopropylvinyl cations) is published separately,[74] as is a review of alkynylcarbenium ions, e.g. $[R^1R^2\overset{+}{C}-C \equiv C-R^3 \leftrightarrow R^1R^2C=C=\overset{+}{C}-R^3]$, and related unsaturated species.[75] The structural sensitivity of 1,2-aryl rearrangements in triarylvinyl cations has been examined; (**44**) may be an intermediate or a transition state in the interconversion of (**43**) and (**45**), depending on the substituents present, and it may be chiral or achiral depending on the bulk of the ring substituents.[76] The gas-phase chemistry of dehydrobenzoyl cations has been examined; these are distonic ions with dual free radical and acylium ion reactivity.[77]

(**43**)   (**44**)   (**45**)
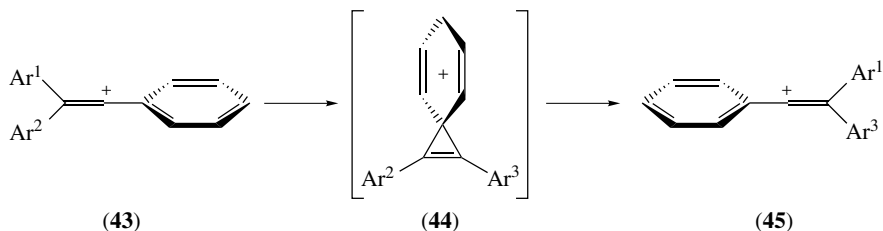
Arenium Ions

The thermodynamic stabilities of phenonium ions relative to the parent have been determined in the gas phase by measuring the position of the equilibrium between (**46**) and (**47**).[78] The results followed a Yukawa–Tsuno relationship with a ρ value of -12.6 and an r^+ value of 0.62, the general behaviour being more like benzenium ions than benzyl cations, with π-delocalization less effective than in benzyl cations.[78] A theoretical study of the elimination of molecular H_2 from the benzenium ion $C_6H_7^+$ shows that the barrier to this process appears to be very small.[79] The gas-phase Friedel–Crafts alkylation reaction of $CF_3C_6L_6^+$ (L = H or D) with C_2L_4 is accompanied by isotopic scrambling, which has been used to elucidate the mechanism of this process.[80] A theoretical calculation shows that the lifetime of triplet phenyl cation must be very short.[81]


$ArCH_2CH_2Br$ + $\xrightleftharpoons{K}$ + $PhCH_2CH_2Br$

(**46**)   (**47**)
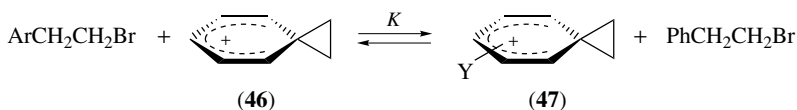
Nitrenium Ions

The nitrenium ion $^+NH_2$ has been the subject of a detailed, comprehensive calculation.[82] Calculations on (**48**) with 15 different X substituents reveal a large substituent sensitivity, and also that aqueous solvation preferentially stabilizes the singlet state.[83] This substituent sensitivity agrees with the results of a time-resolved IR study of the diphenylnitrenium ion (**49**), which shows that resonance contributors such as (**50**) and (**51**) are very important to the overall structure.[84] Substituted 4-biphenyl nitrenium ions

(**48**)   (**49**)   (**50**)   (**51**)
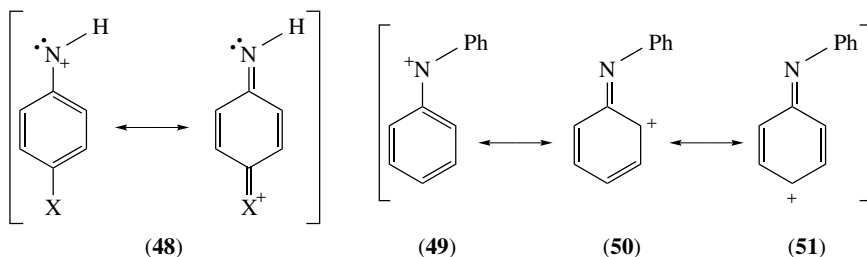
(**48**; X = C_6H_4Y) have lifetimes of 0.6 ms (Y = 4-OMe) to 26 ns (Y = 4-CF$_3$).[85] They are quenched by azide ion at the diffusion limit. The Yukawa–Tsuno r^+ value for these is 2.8, also consistent with a large amount of resonance delocalization.[85] Photolysis of (**52**) results in the *N*-methyl-*N*-phenylnitrenium ion (**53**), which presumably gives the observed products (**54**), aniline and *N*-methylaniline as shown.[86]
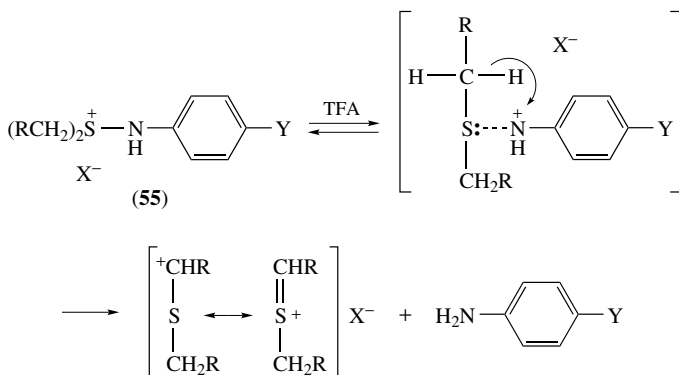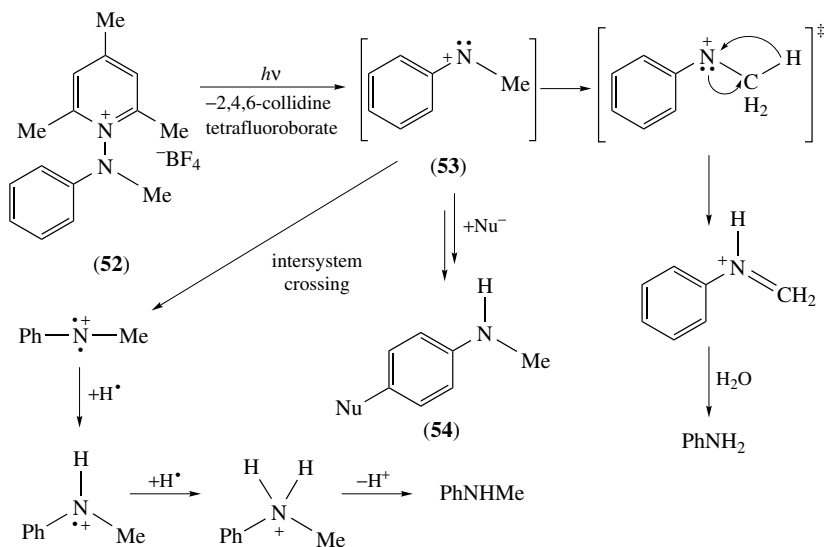
A different method of generating a nitrenium ion has been demonstrated; the sulfur–nitrogen bond in (**55**) cleaves and then a novel intramolecular hydride shift to the arylnitrenium ion centre takes place.[87] The nitrenium species (**56**) undergoes two nucleophilic additions to the double bond to give the product (**57**).[88] Two studies concerning the physiological effects of nitrenium ions *in vivo* are reported.[89,90] Products are formed from both the ion-paired nitrenium ion (**59**) and the free ion (**60**)

AcNOSO$_3^-$ NAc NAc HNAc

$\xrightarrow[\text{in water}]{\text{5\% MeCN}}$

$\xrightarrow[\substack{\text{(azide or} \\ \text{water)}}]{+Nu^-}$

$\xrightarrow[+Nu']{+H^+}$

Ph Ph Ph Ph

Nu Nu Nu'

(56) **(57)**

Me$_3$CCO$_2^-$

HNOCOCMe$_3$ HNOCOCMe$_3$ NH NH

$\underset{+H^+}{\overset{K_a}{\rightleftharpoons}}$ $\xrightarrow{h\nu}$ $\xrightarrow{k_d}$ $+$ Me$_3$CCO$_2^-$

Ph Ph Ph Ph

$^+$NH N $+$ N $+$ N

(58) **(59)** **(60)**

k_r k_{Az}

$+N_3^-$ k_s $+ H_2O$

O
‖
Me$_3$C—C—NH NH$_2$ NH$_2$ NH$_2$

OH O—C—CMe$_3$ N OH
‖
O N—N

N N N—N N

Ph Ph Ph Ph
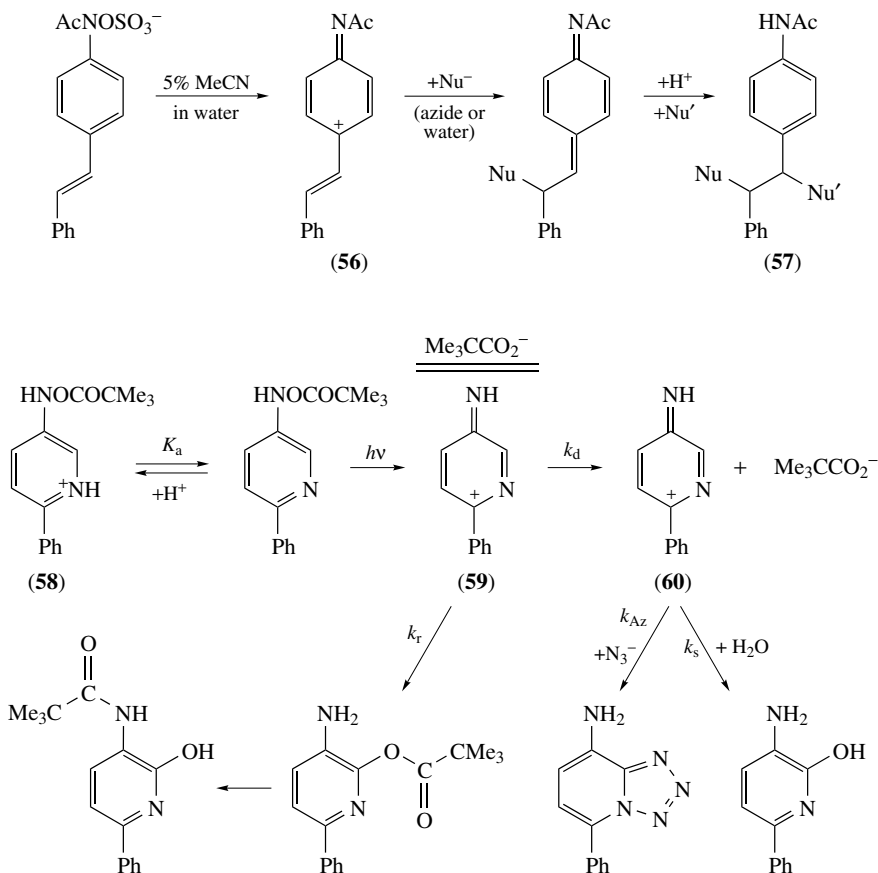
during the reaction of (**58**); the kinetics of these processes were studied.[89] The *N*-acetyl-*N*-(2-fluorenyl)nitrenium ion readily adds to monomeric 2′-deoxyguanosine.[90]
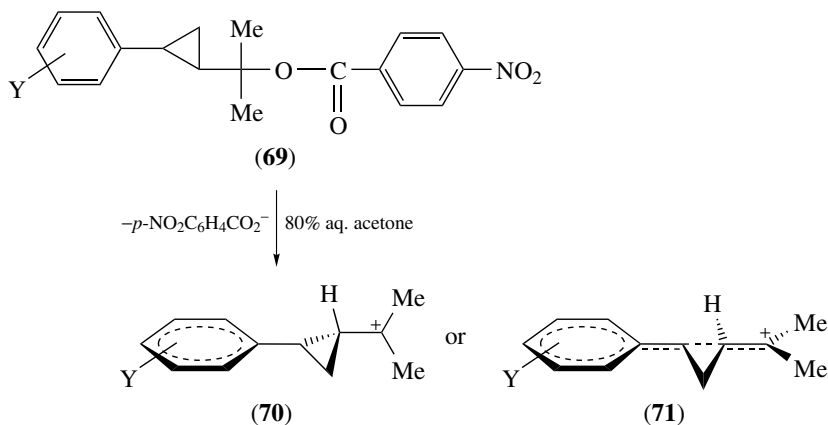
Aromatic Systems

The phosphirenylium cation (**61**) can form when the halogenated precursor is treated with liquid SO$_2$.[91] High-level theoretical calculations show that the aromatic character is due to a three-centre two-electron π-type bond; the resonance energy is fairly high at $\sim$38 kcal mol^{-1}.[91] The trichlorocyclopropyl cation (**62**) is substantially more stable than are the *t*-butyl or adamantyl cations, according to a theoretical study and some FTICR experimental measurements.[92] Trinaphthophenalenium trifluoroacetate (**63**) is a dark-violet solid; the cation represents a new $n = 7$ aromatic system.[93] The tropylium ion, C$_7$H$_7^+$, is the subject of a recent theoretical calculation; the spectral assignments were updated.[94] The substituted tropylium ion (**64**) rearranges to (**65**) on heating.[95] C$_7$Ph$_7^+$, the heptaphenyl tropylium ion (**66**), is not planar but has a seven-bladed propeller structure.[96] According to theoretical calculations (**67**) has the positive charge

(**61**)   (**62**)   (**63**)

$R^1, R^2 =$ H, Me, SiH$_3$,
        CN, NH$_2$, OH

(**64**)   (**65**)

(**66**)   (**67**)   (**68**)
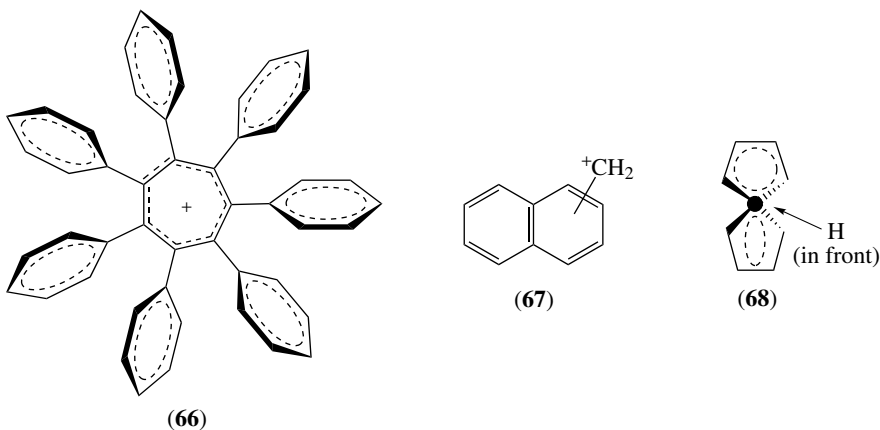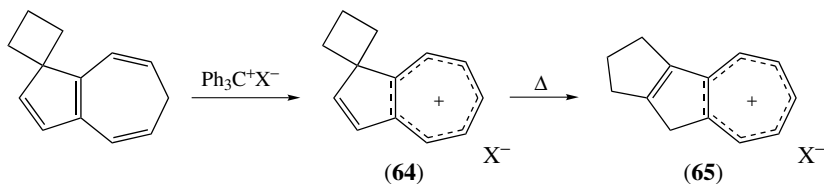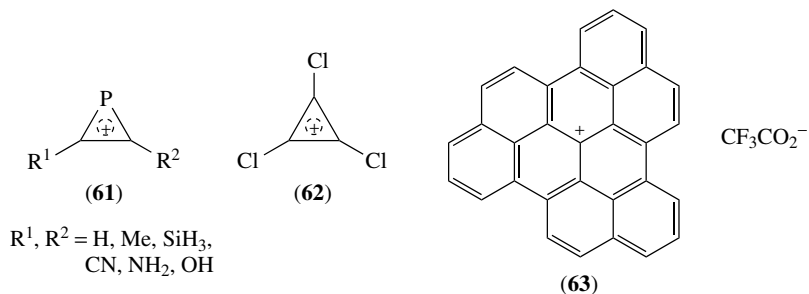
delocalized over the whole molecule if the substituent is in the 2-position, but in the 1-position delocalization is partly limited to the first ring.[97] Monocyclic (CH)$_9$$^+$, which is difficult to draw but an attempt is given as (**68**), is an aromatic Heilbronner Möbius [4n]annulene.[98]

Cyclic Systems

Molecular mechanics and *ab initio* calculations on the cyclopentadienyl cation have been carried out; an allylic structure is favoured.[99] Calculations referring to the initiation of polymerization of 1,1-disubstituted cyclopropanes by cations (also neutrals and anions) are reported.[100] Rate constants for the solvolyses of (**69**) show reasonable Yukawa–Tsuno correlations, interpreted in terms of the less reactive substituents

(69)

$-p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2^-$ | 80% aq. acetone

(70)   or   (71)

preferring the cyclopropylmethyl cation pathway (70), and the more reactive ones preferring to react by way of the allylic cation species (71).[101]

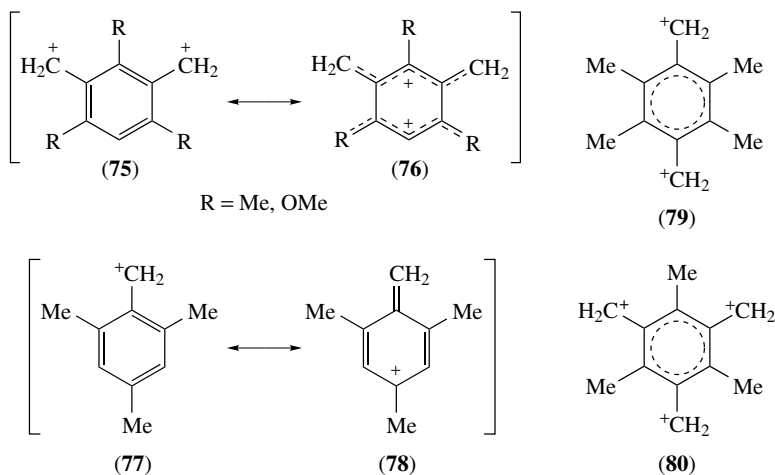The salts of the diazepines (72; $R^1 = R^3 = H$, $R^2 = Ph$) and (72; $R^2 = H$, $R^1 = R^3 = Ph$) have been compared; Ph in the 6-position has less conjugative interaction than it does in the other positions, but electrophilic substitution still occurs readily in both molecules.[102] Crystal structures of the 2,3-cyclohexano derivatives, as the picrates, are reported.[102] The crystal and molecular structures of the 2,3-dihydro derivatives have also been determined.[103] The very interesting 2,6,10-tris(dialkyl-amino)trioxatriangulenium ions (73; R = diethylamino) and (73; R = N-pyrrolidinyl) are reported.[104] The X-ray structure of the latter shows that the ion is planar, and the former is so stable that its pK_{R+} value of 19.7 is 10 orders of magnitude higher than that of any other reported carbocation, and has to be measured in strong base media.[104] Stereospecific ring opening in buffer media of the diol epoxide precursor gives the cation (74), which can be trapped as shown; the ring opening becomes reversible in more basic amine buffers.[105] The 2-deoxyglucosyl oxocarbenium ion is not solvent-equilibrated in water, hydrolysis of the α- and β-anomers not involving a common intermediate.[106]
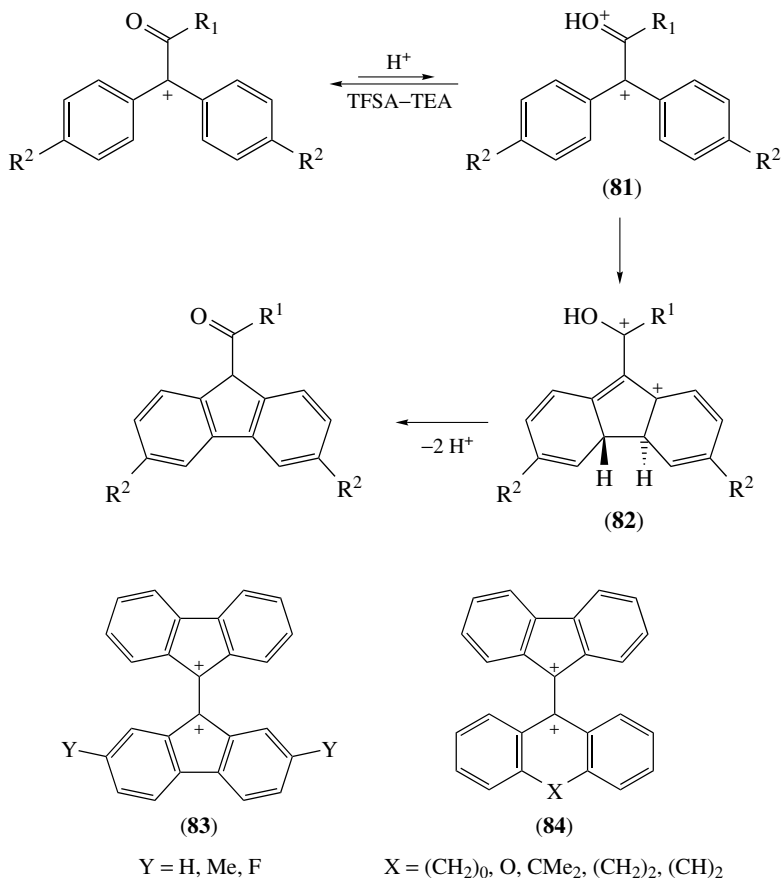

(72)

(73)

Dications

Some benzylic mono- and di-cations have been studied by the ^{13}C NMR/DFT/IGLO technique.[107] Of the stable dications, the trimethyl species (**76**; R = Me) was found to be the major resonance contributor to the structure of (**75**), and the same was found to be true for the trimethoxy derivative. In the related monocations, for (**77**) the major resonance contributor was (**78**), and this was also the case for the pentamethyl and 2,5-dimethyl-4-*t*-butyl compounds.[107] The dication (**79**) and the trication (**80**),

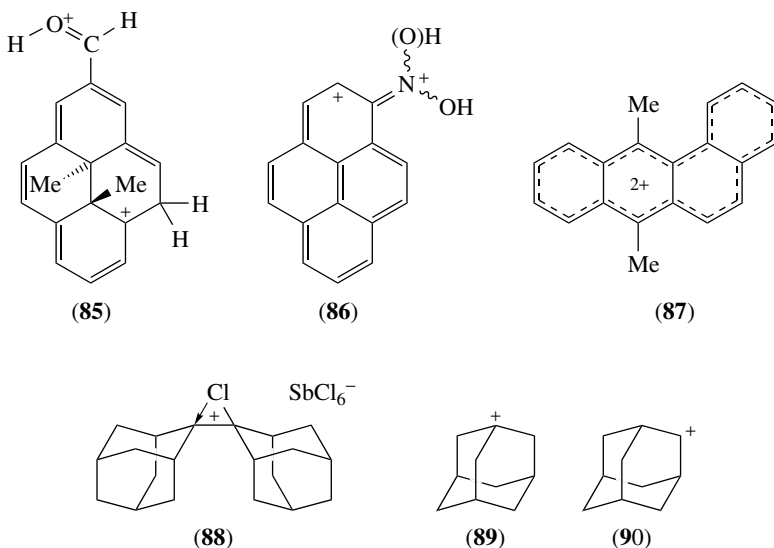however, could not be prepared.[107] Treatment of the aldehyde precursor with the strong acid system trifluoromethanesulfonic acid–trifluoroacetic acid causes a mono-cation–dication equilibrium to be set up, and (**81**) ring closes to give the fluorene via dication (**82**).[108] A strange-looking dication derived from hexakis(methylthio)benzene is proposed as a possible reaction intermediate in a Pummerer-type rearrangement.[109]
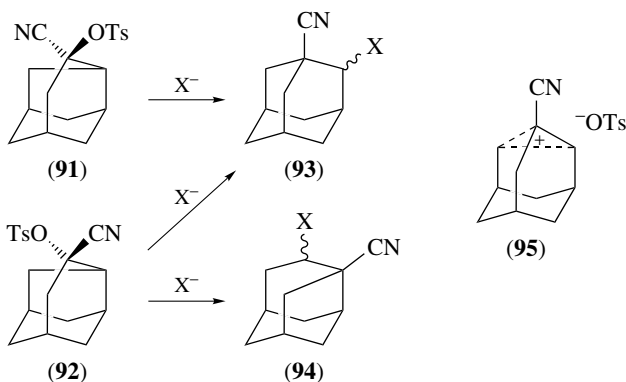
(**81**)

(**82**)

(**83**)

Y = H, Me, F

(**84**)

X = (CH₂)₀, O, CMe₂, (CH₂)₂, (CH)₂

The difluorenyl dication (**83**) results when the parent fluorenylidene is treated with SbF₅ in SO₂ClF.[110] The two ring systems are at right-angles to one another, and the significant paratropicity observed is attributed to an antiaromatic ring current.[110] The related systems (**84**) behave similarly; substituent effects are held to be transmitted by cross-hyperconjugation.[111] The parent aldehyde, with chemical shifts for the 15,16-methyl groups being −3.91 and −3.90, is monoprotonated on the carbonyl group in FSO₃H in SO₂ClF, chemical shifts −1.95 and −1.87, and diprotonated to (**85**) in FSO₃H–SbF₅ (4:1) in SO₂ClF, with methyl chemical shifts of +0.48 and +0.10.[112] This was typical of several compounds studied.[112] Similarly, nitropyrene gives (**86**) in 1:1 FSO₃H–SbF₅.[113] With SbF₅ in SO₂ClF at −30 °C several benzoanthracene derivatives give delocalized dications, e.g. (**87**).[114]
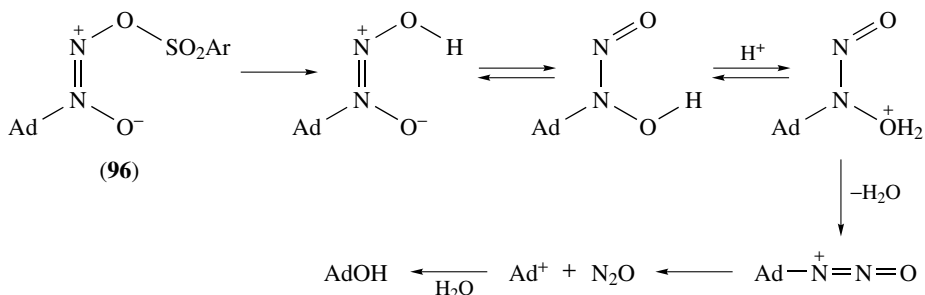
Adamantyl Systems

The X-ray structure of the bridged chloronium cation (**88**) is reported; it is described as being 'unsymmetrical' and 'non-classical.'[115] It shows distinctive electrophilic

(85)   (86)   (87)

(88)   (89)   (90)

chlorination reactivity compared with singly bonded chloroarenium cations.[115] The 1-adamantyl (**89**) and 2-adamantyl (**90**) cations have had their gas-phase heats of formation determined; they are 152 ± 3 and $171 \pm 3\,\text{kcal mol}^{-1}$, respectively.[116] The stereoselectivities of the destabilized 1-cyano-2-adamantyl and 3-cyano-4-protoada-mantyl carbocations have been examined; (**91**) gives only (**93**), but (**92**) gives both (**93**) and (**94**).[117] The *endo* selectivity found previously for (**95**) was not observed.[117] The mechanism of solvolysis of 2-adamantyl azoxytosylate (**96**) has been determined to be as shown, primarily from isotopic labelling and medium-effect studies.[118] The observed *m* value was only 0.46, one of the lowest observed for an unambiguous S_N1 mechanism.[118] Solvation effects in the heterolysis of some adamantyl and alicyclic substrates have been studied,[119] and salt effects in the S_N1 solvolysis of adamantyl tosylates have been investigated.[120]

(91)   (93)   (95)

(92)   (94)

(**96**)

$$ \text{AdOH} \xleftarrow[\text{H}_2\text{O}]{} \text{Ad}^+ + \text{N}_2\text{O} \longleftarrow \text{Ad}-\overset{+}{\text{N}}=\text{N}=\text{O} $$

Bicyclic Systems

An *ab initio* study of the 1-azabicyclo[1.1.0]butyl cation (**97**) and its isomers shows that (**98**) and (**99**) are much less stable than (**97**), and that the transition states between (**97**), (**98**), and (**99**) are too high in energy to allow (**99**) to form.[121] The 3-halobicyclo[1.1.1]pent-1-yl cation (**101**) has been shown to be an intermediate in the addition of halogens to (**100**).[122] The only product observed was (**102**); no rearranged products were detected.[122] The Diels–Alder-type reaction of (**103**) to give (**104**) is said to involve several carbenium ion intermediates.[123]

(**98**)   (**97**)   (**99**)

(**100**)   (**101**)   (**102**)

X or Y = I, Br, Cl

(**103**)

$$ \xrightarrow[\text{4 days, 20\,°C, dioxane, 51\%}]{\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}} $$

(**104**)

(**105**)   (**106**)   (**107**)

(**108**)   (**109**)

(**110**)

$R^1 = R^2 = H$, $R^3 = Me$
$R^1 = R^2 = H$, $R^3 = p\text{-ClC}_6H_4$
$R^1 = R^3 = Me$, $R^2 = H$
$R^1 = R^2 = R^3 = Me$

(**111**)

(**112**)

(**113**)

(**114**)

(**115**)

(**116**)

enantiomer of (**116**)
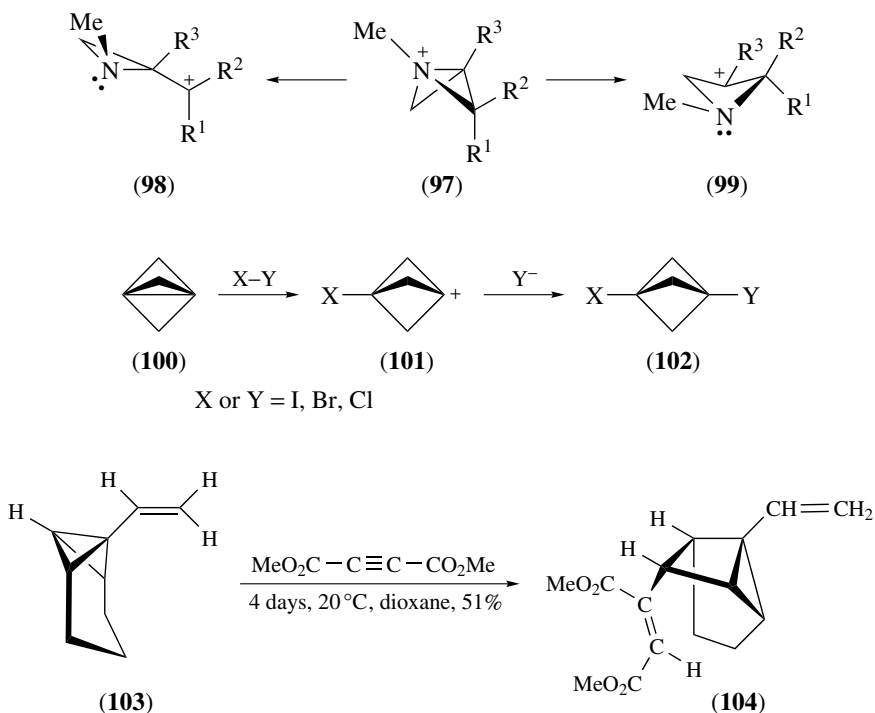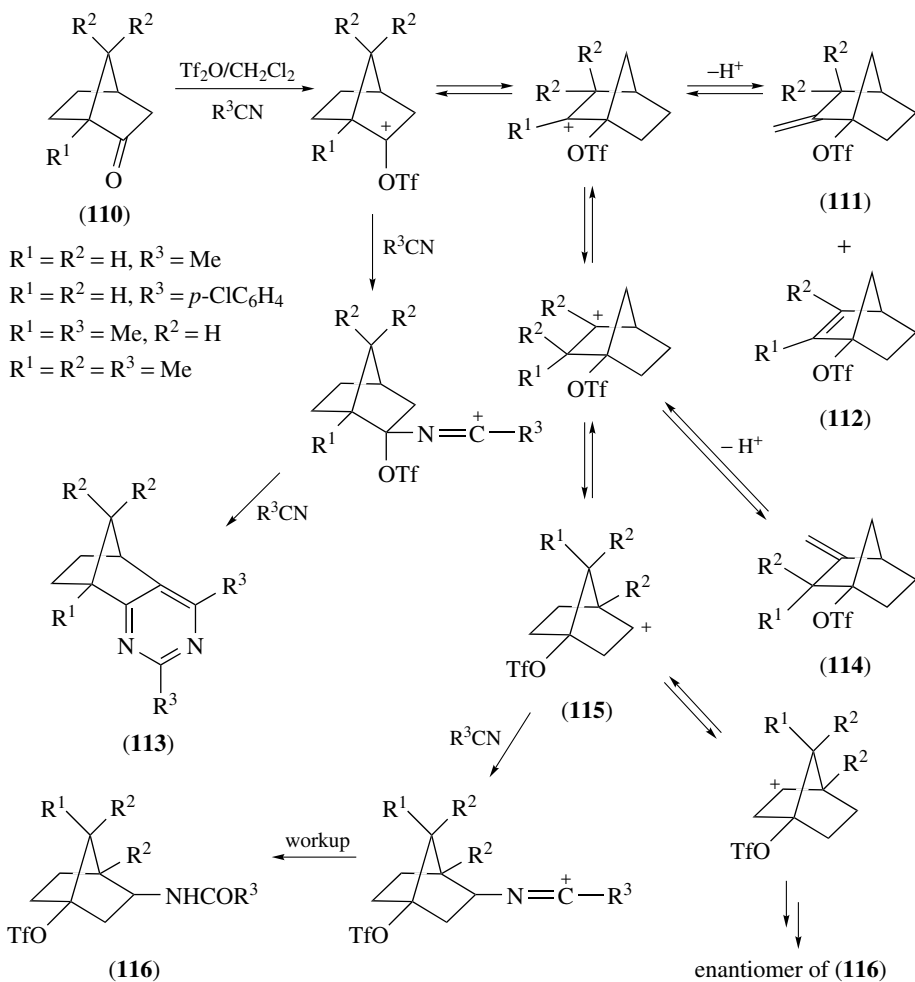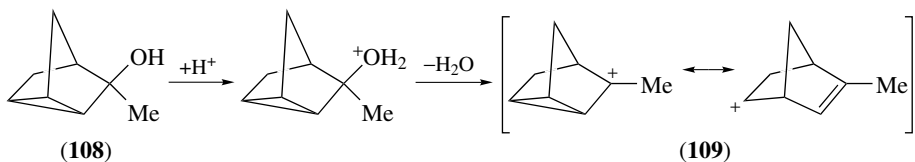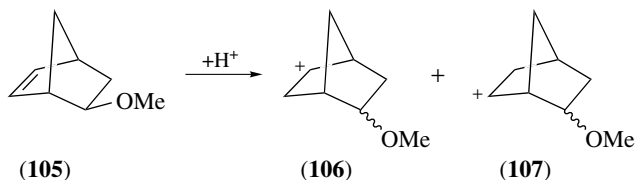
The kinetics of the hydration of *exo-* and *endo*-5-methoxy-2-norbornene and 3-methoxynortricyclane in aqueous perchloric acid have been subjected to an excess acidity analysis.[124] For instance, the hydrolysis mechanism of (**105**) probably involves the intermediacy of the cations (**106**) and (**107**).[124] A similar kinetic analysis shows that the resonance-stabilized cation (**109**) is a likely intermediate in the acid-catalysed hydrolysis of 3-methyl-2-nortricyclanol (**108**).[125] The complex series of rearrangements, hydride shifts, proton eliminations and cation trappings that take place when the norbornyl ketone (**110**) is treated with triflic anhydride in nitrile solvents has been examined.[126] The primary products are (**111**), (**112**), (**113**), (**114**) and (**116**), the last in two isomeric forms, the relative amounts formed depending on the fate of the cation (**115**). The different possibilities are in delicate balance and the product mix actually observed depends on the substitution pattern, among other factors.[126] The effect of *ortho* substituents on the direction of 1,2-migration in the rearrangement of the 2-*exo*-arylfenchyl alcohols (**117**) has been examined; cation (**118**) is the common intermediate and the observed product again depends on the substituents present.[127] Spirocyclobutane-substituted cations (**119**) and (**120**) mostly give products in which

$Z = O; R = Me$ $Z = NH, O; R = H$

(**119**)
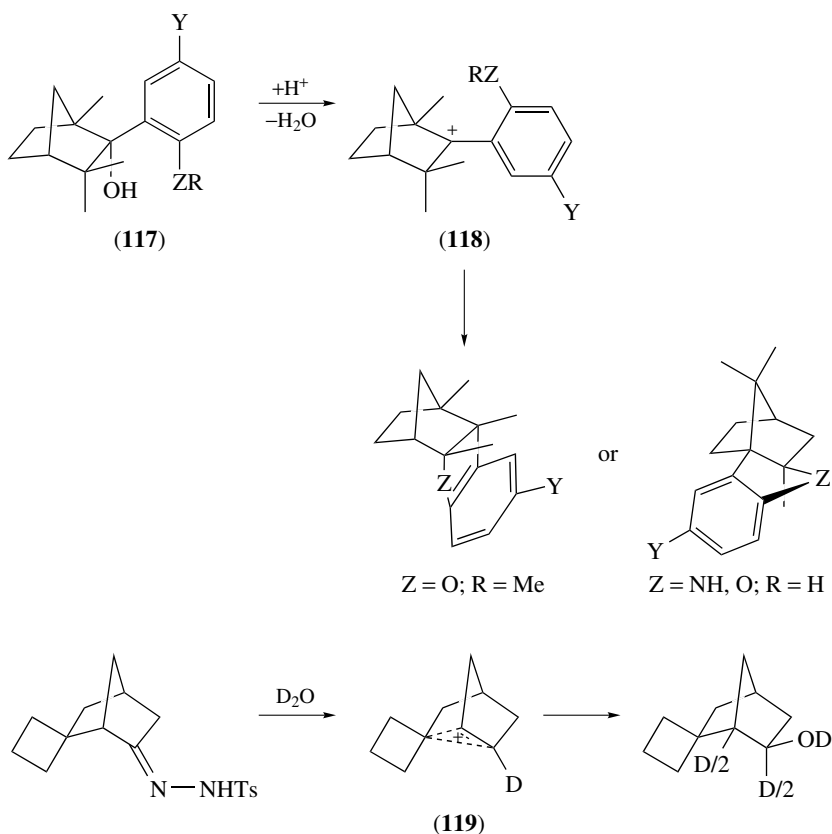
the spirocyclobutane ring is retained, much less ring expansion being observed than in the equivalent cyclopropane analogues.[128]
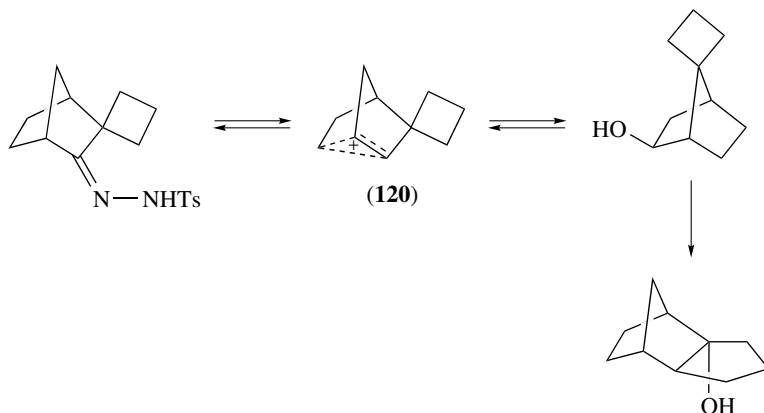
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