Chem. Rev. **2003,** *103,* 229−282

1,2-Dications in Organic Main Group Systems

Valentine G. Nenajdenko,* Nikolay E. Shevchenko, and Elizabeth S. Balenkova

Department of Chemistry, Moscow State University, 119899 Moscow, Russia

Igor V. Alabugin*

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306-4390

Received February 26, 2002

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I. Introduction

Investigations of reactive intermediates that possess high energies and unusual reactivities comprise one of the most fascinating topics of today's chemistry. Such studies push the limits of modern experimental techniques[1] and test the ability of theory for understanding complex chemical phenomena.[2] Several decades and Nobel prizes later such studies often become a part of mainstream chemistry, receive worldwide acceptance, and take their place in undergraduate textbooks. The chemistry of carbocations provides a good example of this process which is an integral part of scientific progress.[3]

This review covers the structure and chemistry of 1,2-dications—compounds with *two* cationic centers located at two *directly connected* atoms. Despite the extremely strong electrostatic repulsion of the two positive charges, 1,2-dications often possess remarkable kinetic stability. Kinetic stability makes preparation and handling of these compounds possible, while the inherent thermodynamic instability due to the strong Coulomb repulsion of the cationic centers allows use of the high chemical energy stored in 1,2-dications for a number of interesting chemical transformations.[4]

The chemistry of 1,2-dications is developing rapidly,[5] and there are several excellent reviews[6−9] and feature articles[10] dealing with small gas phase 1,2-dications as well as with certain types of organic dications containing $C^+{-}C^+$,[11] $N^+{-}N^+$,[12] and $S^+{-}S^+$ [13−15] moieties. Still, so far there has been no comprehensive review that reflects the diversity of this field and provides a unified perspective of the chemistry of 1,2-dications. This gap is especially pronounced for *organic* dications, and this is where this review is focused. Data on gas-phase dications are included as needed to illustrate general trends in 1,2-dication chemistry and to place our analysis of organic dications in proper context. We start with a brief overview of current theoretical approaches to understanding the structure and chemical properties

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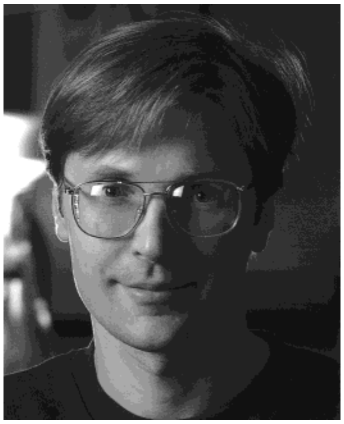
* To whom correspondence should be addressed. E-mail: Nen@acylium.chem.msu.ru; E-mail: alabugin@chem.fsu.edu.

10.1021/cr0000628 CCC: $44.00

Valentine G. Nenajdenko was born in 1967 in Ivanovo, Russia. He graduated from Moscow State University (Lomonosov) in 1991. He received his Ph.D. degree under the supervision of Professor E. S. Balenkova in 1994 researching the synthesis and application of unsaturated CF_3 ketones. In 2000, he received Doctor of Chemistry degree for his studies on chemistry of sulfonium and iminium salts. Now he is senior researcher at the Department of Chemistry of Moscow State University. The field of his scientific interest includes organic synthesis, asymmetric catalysis, chemistry of sulfur- and fluorine-containing compounds, and heterocyclic chemistry. He directed 5 Ph.D. and 14 M.Sc. students. He was the winner of the *Academiae Europeae* Award in 1997, the Russian President Award in 1996, the prize for the best scientific work at the Department of Chemistry of Moscow State University 2001, Shuvalov Award 2001.

Nikolay Shevchenko was born in Dimitrov, Ukraine, in 1974. He received M.Sc. (1996) and Ph.D. (2000) degrees at Moscow State University under the supervision of Professor E. S. Balenkova and Dr. V. G. Nenajdenko working on new synthetic applications of sulfonium salts. He is currently a senior researcher at the Department of Chemistry of Moscow State University.

Elizabeth S. Balenkova was born in Moscow in 1926. She graduated from Moscow State University in 1950 and then she was a postgraduate student of the Department of Chemistry of Moscow State University. She received her Ph.D. degree under the supervision of academician B. A. Kazansky in 1953 for research concerning medium ring hydrocarbons. Since then, she has been working at Moscow State University as a senior researcher (1959) and full professor (1986). She was a supervisor of 27 Ph.D. and 63 M.Sc. students. Her research interests are in the area of organic synthesis, electrophilic addition reactions, and the chemistry of heterocyclic and sulfur compounds.



Igor V. Alabugin was born in Novokuznetsk, Russia, in 1969 and received his Ph.D. degree in Chemistry from the Moscow State University in 1995 under the supervision of Professors N. S. Zefirov, N. V. Zyk, and V. K. Brel. After a postdoctoral study at the University of Wisconsin-Madison with Professor H. E. Zimmerman, he joined the Department of Chemistry and Biochemistry of the Florida State University as an Assistant Professor in 2000. His research interests include development of new photochemical reactions of interest for medicinal chemistry; materials science and organic synthesis; use of stereoelectronic effects in organic chemistry and materials science; chemical, electrochemical and photochemical triggering of pericyclic reactions; supramolecular control of chemical reactivity; and chemistry of main group elements.

of 1,2-dications in an attempt to merge our knowledge of gas-phase small dications and organic dications in condensed phases. In the following sections, we cover organic molecules containing dicationic moieties derived from the main group elements of Groups VIa, Va, and IVa. Our goal is to show the generality and usefulness of the dicationic function in organic chemistry, to discuss recent developments in this field, and to outline directions for future progress.

In the following short section, we will show why 1,2-dications are fascinating species to study and what unique properties they possess.

A. 1,2-Dications: Paradoxes and World Records

Noble gases do not form stable diatomic molecules, and a number of computational studies have confirmed that the binding energies of rare gas dimers are low.[16,17] For example, the $He\cdots He$ dimer is a purely van der Waals complex stable only at 0.0001 K. The energy of the $He\cdots He$ bond in the dimer is 8×10^{-6} kJ/mol, and the bond length is ca. 6.2 Å.[18] Not widely appreciated is the fact that the corresponding dication He_2^{2+} [19−23] was observed experimentally.[24] It has a large (33.2 kcal/mol) barrier to dissociation and a very short He−He distance of 0.704 Å,[25] which is shorter than both the H−H bond of the hydrogen molecule[9] and "the world's shortest bond"[26] of the H−D molecule. A number of other noble gas diatomic dications, such as $NeXe^{2+}$,[27,28] $ArXe^{2+}$,[28] $NeKr^{2+}$,[29] Ne_2^{2+}, [30] $NeAr^{2+}$,[31,32] and $HeNe^{2+}$,[33] are known. Other relevant diatomic dications in which at least one of the partners is a noble gas atom include $BeHe^{2+}$,[34] He(Ne)-B^{2+},[35] $BeNe^{2+}$,[35] CNe^{2+},[36] NNe^{2+},[37] $SiNe^{2+}$,[38,39] $MgNe^{2+}$,[40] $NeAr^{2+}$,[41] $BeAr^{2+}$,[35] BAr^{2+},[42] CAr^{2+},[38,39,42] NAr^{2+},[42] Ar_2^{2+}.[43]

Similarly, the O−O distance in the O_2^{2+} dication, 1.073 Å,[44] is, to our knowledge, the shortest O−O distance.[45,46] It is 0.134 Å shorter than the bond in molecular oxygen and is shorter than the shortest O−O distance[47] listed in the book of chemistry world records. Moreover, the O−O distance in O_2^{2+} is even shorter than the N−N distance in the isoelectronic nitrogen molecule (1.098 Å)[48] and is considered to be the shortest bond between any two heavy atoms.[45]

One might argue that transient gas phase species have no direct relevance to "the real chemistry that happens in a flask" and that this paradox of short bonds between atoms with like charges is only relevant to simple diatomic species while more complicated dications with more sophisticated internal structures will always find a low activation dissociation channel. To show that this is not necessarily so, let us consider a relatively complex organic molecule in solution. Neutral 1,6-diazabicyclo[4.4.4]-tetradecane has an N−N distance of 2.806 Å. Remarkably, upon removal of two electrons and formation of a N^+-N^+ dication, the distance between the nitrogen atoms is reduced to 1.532 Å despite the circumstance that both of the nitrogens are now positively charged![49]

These examples are quite *typical* and illustrate a *general* phenomenon of increased bonding in species that are expected to be strongly *destabilized* by Coulombic repulsion. Obviously, these examples do not mean that electrostatic repulsion does not operate in these systems but rather that structure and stability of such dications are also influenced by other factors. We analyze the nature of these factors below.

II. Structure and Stability of 1,2-Dications

A fascinating feature of many 1,2-dications is the combination of kinetic stability and thermodynamic instability, which has earned them the name "volcanic" states.[50] Kinetic stability, usually characterized by a barrier on the dissociation path, is controlled by the strength of chemical bonding in a dicationic system. Thermodynamic instability is a consequence of strong electrostatic repulsion and is usually expressed either as exothermicity of the bond cleavage or as the kinetic energy release during the fragmentation. Since these factors are important for understanding the properties of 1,2-dications, we will outline them briefly below.

Obviously, in the condensed phase (either in solution or in the solid state) dications are stabilized by counterions, by interaction with solvent molecules,[44] and/or by appropriate ligands.[51] Large polyatomic dications can also be stabilized by appropriate substituents able to accommodate the positive charge. Such "external" stabilizing factors are not present in the gas phase where the electrostatic destabilization of 1,2-dicationic moiety is developed to the fullest degree and, thus, the gas phase is the medium in which the true, unmasked stability of 1,2-dications can be investigated.

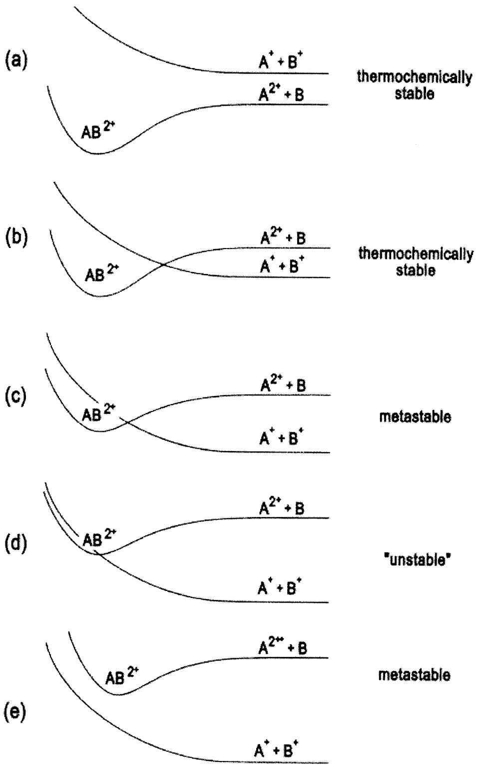


Figure 1. Schematic representation of potential energy curves for diatomic dications AB^{2+}: (a) thermochemically stable dication with $IE(A^+) < IE(B)$; (b) thermochemically stable dication with $IE(A^+) > IE(B)$; (c) metastable dication with $IE(A^+) \gg IE(B)$; (d) "unstable" dication in which the Coulomb curve crosses the charge polarization curve in the vicinity of the AB^{2+} minimum; (e) metastable dication in an electronically excited state. (Reprinted with permission from ref 10. Copyright 1999 American Chemical Society).

Surprisingly, even in the gas phase a large number of dications live long enough to allow study of their chemical and photochemical reactivity. A few of these dications are stable thermodynamically (vide infra). The majority of gas-phase small molecular dications are *metastable*. Despite their intrinsic *thermodynamic instability*, such dications possess at least one electronic state that is long-lived and separated from the dissociated state by a significantly large barrier and, thus, is stable *kinetically*.

A lucid review of factors controlling the thermodynamic stability of gas phase dications was given recently by Schröder and Schwarz (Figure 1).[10] Ultimately, the stability of a 1,2-dication AB^{2+} depends on the relative energies of the A^{2+}-B and A^+-B^+ states which, in turn, depend on the difference in electronegativity between A and B. If the lowest dissociated (asymptotic) state corresponds to A^{2+} and B, that is, IE (A^+) < IE (B), then the AB^{2+} dication is thermodynamically stable and the deepest potential minimum lies *below* any dissociation asymptote.[39,52−54,56] Several examples of such thermodynamically stable dications include AlF^{2+},[55] BeF^{2+},[56,57] MgN^{2+},[40] MgF^{2+},[40] $MgNe^{2+}$,[40] ScN^{2+},[58] SiF^{2+},[55,59] $SiNe^{2+}$,[38] PF^{2+},[38] and $XeHe^{2+}$.[52] The full list of thermodynamically stable diatomic dications is given in the feature article mentioned above.[10]

Another instance when formation of a thermodynamically stable dication is possible is when the difference in the ionization potentials of A^+ and B is smaller than the binding energy in the AB^{2+} dication (Figure 1b).

Arguably, the most typical example corresponds to a strongly bound dication which is unstable toward the charge separation but resides in a relatively deep well (Figure 1c). A good example is provided by the He_2^{2+} and O_2^{2+} dications discussed above. Since the equilibrium dicationic structure is trapped at an energy that can be substantially higher than the combined energy of the corresponding monocations, its fragmentation to a pair of singly charged ions is very exothermic. After this fragmentation ("Coulomb explosion"), two singly charged ions that possess considerable kinetic energy are formed, a typical value being 6 eV for a pair of ions formed from a diatomic dication. It is reasonable to assume that the charge on the incipient fragments at the transition state is close to unity and that the kinetic energy release is essentially the Coulombic repulsion of the two charges.[60] Such energy releases are equivalent to a reaction exothermicity of ca. 140 kcal/mol, indicating a large amount of potential energy stored in such dications, which can be consequently considered as "high energy density" materials and a possible source of propulsion energy. [50]

On the simplest level, the kinetic stability of 1,2-dications can be explained by molecular orbital (MO) theory, which predicts that loss of two electrons is favorable when electrons are removed from an antibonding molecular orbital.

As an example, let us consider formation of a homonuclear 1,2-dication derived from two atoms X that possess at least one pair of nonbonding electrons (a lone pair). When two nonbonding orbitals come into close proximity, they interact with formation of two new MOs: a bonding MO and an antibonding MO. If both of the new MOs are fully occupied, there is no gain in energy—the energy lowering due to formation of the bonding MO is more than compensated by the rise in energy due to simultaneous formation of the antibonding MO. In such a case, double oxidation (formation of a dication) removes two electrons from the antibonding MO which results in formation of a normal (two-electron/two center) chemical bond between the two atoms.

In other words, the "1,2-dication paradox" is explained by the fact that the dioxidation that produces the two positive charges on the adjacent atoms also creates a chemical bond between those atoms. The newly formed MOs can have either σ symmetry, as shown above, or π symmetry (when the two heteroatoms were already connected with a σ bond). In this approach, the barrier to the dissociation arises from the fact that a slight increase in bond lengths from the equilibrium value results in a loss of binding energy that is larger than the energy gain due to the decrease in the electrostatic repulsion.

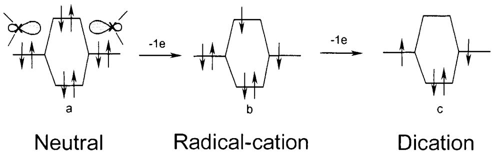


Figure 2. Chemical bond formation promoted by removal of two electrons from the antibonding orbital.

Considering the above MO analysis, it is not surprising that the first possible dication H_2^{2+} is not a minimum on the potential energy surface.[61] Since this species has no electrons, there is no electronic stabilization to overcome the Coulomb repulsion. Li_2^{2+}, which is isoelectronic with H_2^{2+}, is not an energy minimum for the same reason—there are no valence electrons to make a chemical bond. A weak one-electron two-center bond is also not sufficient to stabilize an 1,2-dication and HeH^{2+} does not correspond to an energy minimum as well. Note, however, that two valence electrons are capable of binding four alkali metal centers in Li_4^{2+} and Na_4^{2+} T_d structures.[62] Consistent with the MO explanation He_2^{2+}, which has a normal two-electron two-center chemical bond, is relatively stable, and Be_2^{2+} [63,64] and B_2^{2+} [65] are also known to be stable. The energy of a single chemical bond compensates for the electrostatic repulsion and ensures the metastability of the 1,2-dications.

The remarkable observation that the bonds of dicationic diatomics are even shorter than the corresponding bonds in isoelectronic neutrals (He_2^{2+} vs H_2, O_2^{2+} vs N_2) was explained by Dunitz and Ha.[66] They studied bond lengths in "hydrogen-like" molecules and found that a fractional increase in nuclear charge leads to stronger bonding due to reduction of the nuclear screening for the bonding electrons. This is also consistent with the well-known fact that cations are always smaller than their parent atoms.

Although the appealingly simple MO model given in Figure 2 allows qualitative discussions regarding the stability of dicationic species, it is not sufficient when quantitatively accurate description is needed. The MO energies change upon oxidation (for an illustration see Figure 7 along with the accompanying discussion) and, in any case, use of RHF MO energies to compare energies of neutral and open-shell radical-cation species is a considerable approximation by itself. In addition, although the simple MO model is able to explain the relative stability of the dication species, it does not explicitly provide information about the nature of the dissociative transition states, which is necessary for a better understanding of the kinetic stability of 1,2-dications.

There are two approaches to more accurate modeling potential energy surfaces of 1,2-dications. The first approach describes bonding in 1,2-dications as a superposition of ordinary chemical binding potential at the Coulombic repulsion of the cationic centers (Figure 3).[67−70] The second approach, first suggested by Dorman and Morrison,[71] describes the barrier for dissociation of an X^+-Y^+ dication as arising from an avoided crossing between a repulsive electronic state corresponding to $X^+ + Y^+$ and an attractive "charge-transfer" ($X + Y^{2+}$), electronic state of the same symmetry.[72]

The advantages and limitations of the above two models have been the subject of lively recent discussion.[69,70,73,74,80] The "chemical bond + Coulombic potential" approach works well for homonuclear dications. For example, Senekowitsch and ONeil[74]

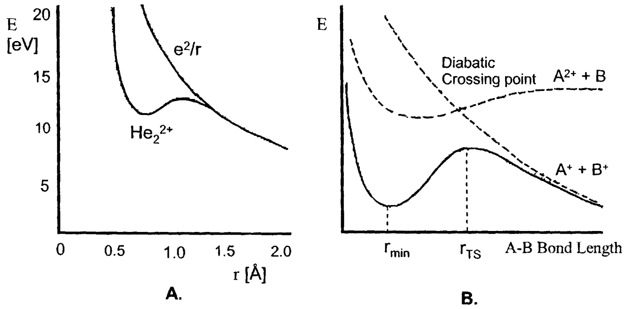


Figure 3. (A) The potential energy curve and Coulomb repulsion term (e^2/R) for He_2^{2+} (Reprinted with permission from ref 9. Copyright 1989 Wiley). (B) Schematic representation of the "avoided crossing model" with diabatic (dashed) and adiabatic (solid) potential energy curves for the ground state of a diatomic AB^{2+} dication. The kinetic energy release is T, asymptotic state separation is Δ. (Reprinted with permission from ref 76. Copyright 1988 Elsevier Science Publishers B. V.).

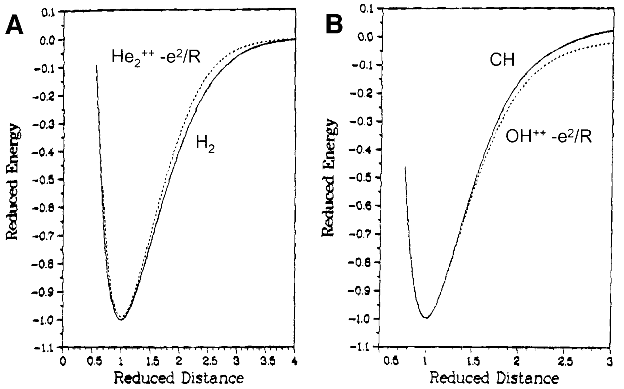


Figure 4. (Reprinted with permission from ref 69. Copyright 1992 Springer-Verlag). A. The potential energy curves for He_2^{2+} (dashed) and H_2 (solid). The authors subtracted the Coulomb repulsion term (e^2/R) from the He_2^{2+} potential at all geometries. B. Similar potential energy curves for OH^{2+} (dashed) and CH (solid).

found that the potential energy curves of F_2^{2+} are well reproduced by taking the well-established curves for the isoelectronic neutral species (O_2) and simply adding the corresponding Coulombic repulsion potential. Another impressive application of this approach was the generation of the entire manifold of N_2^{2+} excited states based on the corresponding electronic states of C_2.[69]

The "chemical bond + Coulombic repulsion" approach is illustrated in Figures 3 and 4. The similarity of the curves in Figure 4 shows that the potential energy surface (PES) of He_2^{2+} (Figure 3A), after removal of the Coulomb repulsion, is very similar to the PES for the isoelectronic H_2 molecule. The situation is analogous in the OH^{2+}/CH system, even despite the fact that the OH^{2+} dication is not an energy minimum and the chemical binding in this species is completely overcome by the electrostatic repulsion, in contrast to the metastable He_2^{2+} dication where the chemical binding "survives" the Coulomb repulsion. The main concept behind this approach is that the electrostatic repulsive component dominates at the larger distances. Thus, it accounts for the thermodynamic instability of the dication, while at the bonding distances a normal chemical bond is formed. The dication is metastable when the energy of bond formation is greater than the cost of the electrostatic repulsive component.

The second approach to description of metastable dications is the avoided crossing method (Figure 3B).[75] The original simple model of the avoided crossing approach (Figure 3B) was subsequently refined by Gill and Radom to include diabatic coupling and polarization (ACDCP method − "avoided crossing with diabatic coupling and polarization").[76] The avoided crossing description has obvious advantages for strongly polarized heteronuclear diatomics such as HCl^{2+},[77] where, at small internuclear separations, both positive charges reside on one of the atoms. Gill and Radom[72] have shown that, in general, in the case of dications of type AH^{2+} where the asymptotic energy difference between the diabatic states, Δ, is small, the beginning of the process of deprotonation (before the transition state is reached) is better described as a hydrogen atom loss than as a proton loss. In other words, at this point the fragments resemble the $A^{2+}\cdots H$ state more than the $A^{+}\cdots H^{+}$ state.

The scope and limitations of the two models were well illustrated by Radom et al. through an instructive comparison of the isoelectronic dicationic analogues of N_2, namely, O_2^{2+}, NF^{2+}, and CNe^{2+}.[78] All of the dications were predicted to be kinetically stable species lying in deep potential wells. The equilibrium bond lengths in AB^{2+} dications increase with increasing difference in electronegativities of atoms A and B. The O_2^{2+} dication was predicted to contain the shortest bond between any two heavy atoms (1.052 Å at the ST4CCD/6-311+G(2df) level of theory) and a large barrier (338 kJ mol^{-1}) to dissociation. The NF^{2+} dication was found to have a slightly longer equilibrium bond length (1.102 Å) but a larger barrier (445 kJ mol^{-1}) to dissociation. The barrier for CNe^{2+} is lower (126 kJ mol^{-1}) but much broader, while the equilibrium C−Ne bond length is quite large (1.604 Å); this has been attributed to very little π bonding in this dication.[79] It is remarkable that the pattern of dissociation energies in the above dications, $D_e(O_2^{2+}) < D_e(NF^{2+}) > D_e(CNe^{2+})$, is different than in the isoelectronic neutral species, $D_e(N_2) < D_e(CO) < D_e(BF)$. Another remarkable result was the significant barrier broadening with increasing difference in electronegativities of A and B: (r_{TS} (O_2^{2+}) = 1.58 Å, r_{TS} (NF^{2+}) = 1.97 Å, r_{TS} (CNe^{2+}) = 4.37 Å(!)).

Although the choice of isoelectronic species is not unique and can be ambiguous, this trend is not readily predicted by using the simple "isoelectronic bonding potential plus electrostatic repulsion" picture. On the other hand, the gradual evolution from a covalent bond in O_2^{2+} to a highly ionic bond in CNe^{2+} increases the contribution of the C^{2+}-Ne state in the multireference wave function. Consequently, the electronic structure at the equilibrium distance corresponds to the C^{2+}-Ne state but the dissociated asymptotic state is best described as C^{+}-Ne^{+}, in reasonable agreement with the "state-crossing" model.

Even in moderately polarized dications, the relative importance of the $A^{2+}B$ states increases when the interatomic distance is approaching the equilibrium value. For example, Polak has found that the $C^{2+}O$

valence bond (VB) configuration becomes the largest in weight (about 0.5) in five of the six states of the CO^{2+} dication.[80] This finding notwithstanding, Polak argued that the origin of the importance of $A^{2+}B$ states in the general binding paradigm differs from that proposed by the simple "two-state avoided crossing model". Instead of direct coupling between the "covalent" and "charge-transfer" states, the interaction is mediated by a number of electronically excited configurations lying between the above states.[81] On the other hand, Basch et al.[23] found that the VB coupling matrix element between the covalent (He^+-He^+) and ionic ($He^{2+}-He$) structures in a homonuclear dication such as He_2^{2+} is large and similar in magnitude to the ionic structure diagonal energy term.[82] The utility of the "avoided crossing + diabatic coupling + polarization" model of Radom[76] for dications of intermediate polarity was confirmed by the thorough study by Kolbuszewski et al.[73]

The avoided-crossing model allows estimation of r_{TS}, the transition structure bond length as the point where the two diabatic curves cross. By combining the formula of Beynon and co-workers,[83,84] which roughly equates the kinetic energy release, T_k, in the fragmentation reaction to $1/r_{TS}$, Gill and Radom found that when the energy difference between the attractive and repulsive diabatic states, Δ, is small, the kinetic energy release in the fragmentation reaction is given by approximately:

$$T_k \approx 1/r_{TS} \approx \Delta(AH^{2+}) = E(A^{2+}) + E(H) - E(A^+) - E(H^+) = IE(A^+) - IE(B) \quad (1)$$

where IE(X) is the ionization potential of X.

The model and the equation are, however, only valid for small $\Delta \leq 2-3$ eV, and for small coupling between the diabatic states. A more advanced "avoided crossing with diabatic coupling and polarization" model is more accurate.[76] According to this model, the energy of AB^{2+} can be estimated from:

$$(1 - S_{12}^2)E^2 + (2S_{12}H_{12} - \Delta + 2\alpha_B/r^4 - 1/r)E + (\Delta/r - 2\alpha_B/r^5 - H_{12}^2) = 0 \quad (2)$$

where S_{12} is the overlap between the diabatic wave functions, r is interatomic distance, Δ is the asymptotic separation between two diabatic states, H_{12} is the off-diagonal element of the CI matrix (the coupling integral), and α_B is the static electric dipole polarizability of atom B.

The thermodynamic stability of dications correlates with the electronegativity of the cationic atoms. For example, the calculated (thermodynamic) deprotonation energies of silicon dications are markedly less exothermic than those of the corresponding carbodications because of the lower electronegativity and higher polarizability of silicon.[9]

The effects of electronegativity are also manifested in the relative stability of ylide dications CH_2XH^{2+} and their conventional isomers CH_3X^{2+} (X = NH_2,[85] OH, F, PH_2, SH, Cl).[86] The barriers to fragmentation of ylide dications are substantial and such dications were predicted to be observable species. By contrast, CH_3X^{2+} dications are found to have no or little barrier to dissociation and/or to rearrangement. The relative thermodynamic stabilites of CH_2XH^{2+} and CH_3X^{2+} dications are also very different when X is a strongly electronegative element, but the difference decreases dramatically for phosphorus and, to a lesser extent, for sulfur (Table 1).

Table 1. Difference in Thermodynamic Stability between CH_2XH^{2+} and CH_3X^{2+} Dications

X	$E(CH_3X^{2+}) - E(CH_2XH^{2+})$, kJ/mol[a]
NH_2	380
OH	705
F	497
PH_2	19
SH	145
Cl	470

[a] MP3/6-31G**+ZPVE correction.

Careful control of vibrational excitation is another factor important for the treatment of metastable dications in the gas phase. For example, although it has been shown that ions of type $C_nH_2^{2+}$ are ubiquitous in mass spectra, a small fraction of such ions undergoes spontaneous dissociation 8−15 μs after formation. This observation indicates that some of the $C_nH_2^{2+}$ ions are formed in vibrationally hot states with an energy distribution sufficiently high to overcome the dissociation barrier.[87] In addition, vibrationally excited states display a larger rate of tunneling through the barrier. For example, the estimated lifetime of He_2^{2+} at its lowest vibrational level is 220 min, but it decreases to 27 ms at the next vibrational level.[50]

One approach to controlling the energy distribution involves charge-stripping mass spectroscopy. In this method, the dications are generated by oxidation of vibrationally *relaxed* monocations. It was shown that this method permits observations of dications that are not detected when direct double (vertical) ionization methods are used. One such example is the methane dication (Figure 6) where direct electron impact ionization gives an excited CH_4^{2+} that lies above the dissociation threshold.[88] In the condensed phase, if the temperature is sufficiently low, the excess of vibrational energy can be dissipated efficiently by collisions with the solvent molecules.

Another class of attractive cation−cation interactions that is important for transition metals involves interaction between d^8-d^{10}-s^2 systems and will not be discussed in this review because they are not relevant to organic dications and were recently reviewed by Pyykkö.[89]

The unusual electronic structure of 1,2-dications imposes rather stringent requirements on the computational methods used in the study of these species. It has been pointed out[69] that because a large part of the binding energy is "canceled" by electrostatic repulsion and the Coulomb repulsion part is recovered completely even by the crudest quantum-mechanical methods, only high-quality theoretical methods able to retrieve a considerable part of the correlation energy are adequate.[90,91] The requirements are increased by the inherent multiconfigurational nature of many dicationic states (especially in the vicinity of the avoided crossing). As a result,

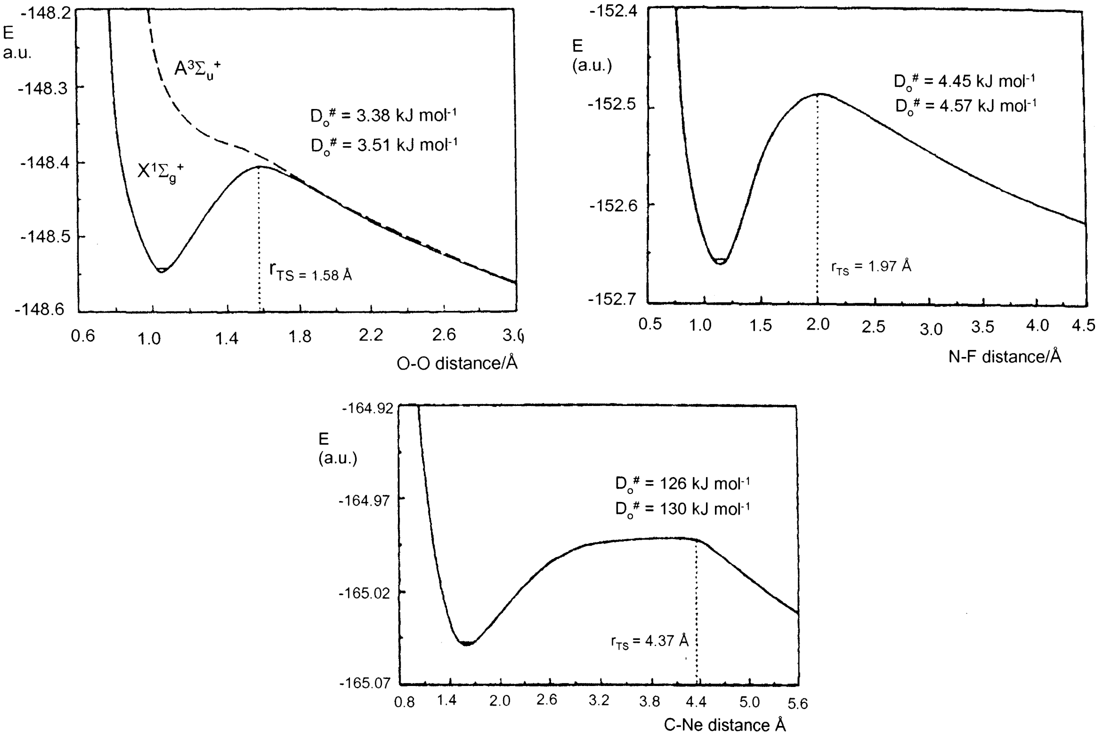


Figure 5. (Reprinted with permission from ref 78. Copyright 1989 American Institute of Physics). Potential energy surfaces for O_2^{2+}, NF^{2+}, and CNe^{2+}.

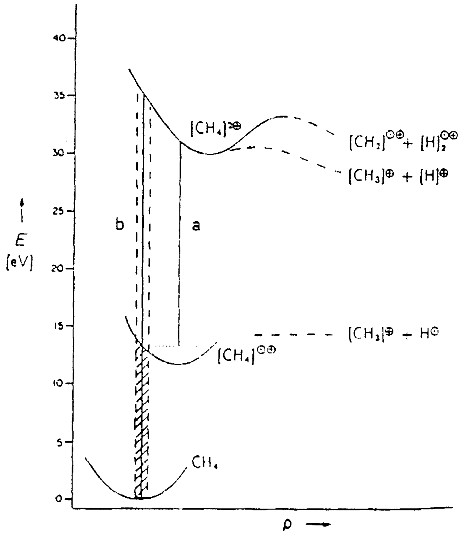


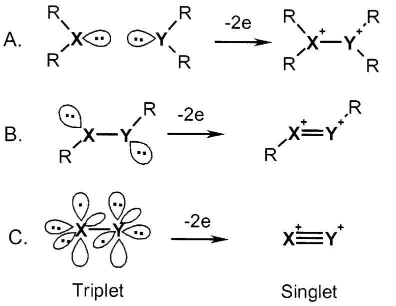
Figure 6. Calculated hypersurfaces for CH_4, $CH_4^{\bullet+}$, CH_4^{2+}. The vertical lines correspond to the Franck–Condon transitions. The charge-stripping from $CH_4^{\bullet+}$ to CH_4^{2+} is indicated by a. Direct (vertical) double ionization is shown as b. (Reprinted with permission from ref 9. Copyright 1989 VCH).

it is essential to use large basis sets, including g-functions for the first row elements and f-functions of hydrogen, GVB or MCSCF reference wave functions and extensive CI, if chemical accuracy is desired.[92]

The above short overview illustrates that the electronic structures, stabilities, and reactivities of 1,2-dications are quite diverse. At this moment, the chemistry of 1,2-dications constitutes a rather heterogeneous field, with the gas phase and the condensed phase research overlapping only rarely. However, several factors are of general importance for all 1,2-dications: (a) the way in which 1,2-dications are generated, especially if the electrons are removed from antibonding or bonding MOs, (b) the electronegativity of the atoms constituting the 1,2-dicationic moiety, (c) in the case of unsymmetric dications, the difference in electronegativities of these atoms which reflects the contribution of A^{2+}-B states to the electronic wave function, (d) the availability of delocalizing interactions (e.g., conjugation, hypercojugation, aromaticity) which play an essential role in stabilizing organic dications (e.g., carbodications). Keeping these factors in mind, we proceed to a discussion of specific types of 1,2-dications which begins with the Group VIa dications.

III. S–S Dications

Depending on the structure of a reactant, removal of two electrons from the two nonbonding orbitals of two chalcogen atoms may result in formation of a single (case A), a double (case B), or a triple (case C) bond.



The most typical case A will be discussed in detail in the next part of this review. Suprisingly, there are no experimental examples that correspond to case B,

Table 2. Equilibrium Bond Lengths (R_e), Barrier Distances (R_t), the Barrier Height Energy (E_t), and the Energy Difference between a Dication and the Asymptotic Pair of Monocations (D_e) for the XY^{2+} Systems[a]

X	Y	R_e (Å)	R_t (kcal/mol)	E_t	D_e
O	O	1.060	1.605	80.4	−103.9
S	O	1.406	2.293	86.8	−34.7
Se	O	1.563	2.546	83.2	−40.9
Te	O	1.774	3.109	67.0	−24.3
S	S	1.814	2.716	50.1	−54.1
Se	S	1.967	2.845	36.5	−62.0
Se	Se	2.115	2.962	25.4	−65.6
Te	S	2.202	3.163	28.9	−60.0
Te	Se	2.352	3.229	18.4	−67.9
Te	Te	2.603	3.396	10.4	−71.1

[a] (CAS/CEP−N11G(2d) level of theory. Parameters are defined in text.

although such species can possibly be intermediates in the monooxygenation of disulfides. The parent chalcogen dications such as O_2^{2+}, SO^{2+}, S_2^{2+} correspond to case C. These dications are isoelectronic with the triple-bonded N_2 molecule which explains their relative stability and the fact that the properties of these dications have been discussed quite extensively.[44,93−95] In the most recent comprehensive study, all 10 possible dichalcogen dications were studied computationally.[44] The most important results at the CAS/CEP−N11G(2d) level are summarized in Table 1. It was found that O_2^{2+} simultaneously exhibits the largest exothermicity and the second highest barrier to the dissociation into a pair of monocations. In other words, this dication possesses the largest thermodynamic instability together with a large kinetic stability—another paradox! Interestingly, in O_2^{2+}, SO^{2+}, SeO^{2+}, and TeO^{2+}, the exothermicity decreases faster than the barrier height. The nonoxides, in contrast, exhibit similar exothermicities but decreasing barriers as the size of the bonded atoms increases.

A description of the binding energy in 1,2-dications as the result of a balance between chemical bonding effects and electrostatic repulsion predicts that both of these effects become weaker with increasing equilibrium distance between the atoms.[44] Thus, as the atoms get bigger, the bond lengths shift to larger values due to core overlap repulsion. In addition, both the attractive bonding and cation repulsive effects decrease in parallel to give approximately the same exothermicity for the dissociation.

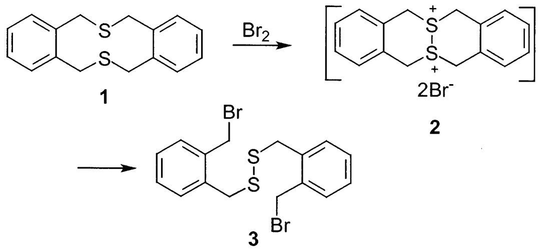
As was pointed out above, the R_e value for O_2^{2+} at 1.060 Å is probably the shortest known bond distance between two heavy atoms.[96] All of these diatomic dichalogen dications formally have a triple bond, and all of the R_e values in Table 2 are close to the shortest bond found for the given bonded pair of atoms. The triple bond character is expected to decrease in the heavier, nonoxide diatomic dications because π overlap becomes less efficient with longer bond distances. As a result, the barrier to dissociation also decreases with increase in the size of the diatomic dication.

The decrease in exothermicity observed for the dissociation of mixed dications when the difference in electronegativity between X and Y becomes larger parallels the decrease in the energy gap between the states corresponding to the dissociated asymptotes $X^{2+} + Y$ and $X^{+} = Y^{+}$. The increase in the stability of heavier and mixed dications is a general phenomenon which is also manifested in the chemistry of dichalcogenium dications (case A) (vide infra).

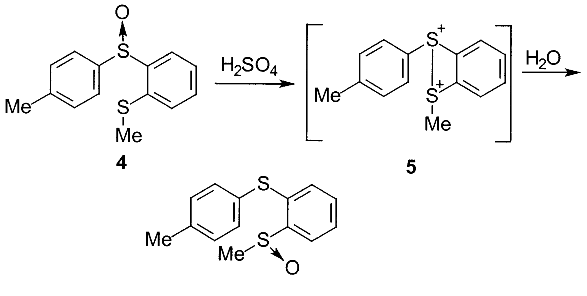
The most important of organic SS dications are disulfonium dications (also called dithioether dications)—compounds with two positively charged sulfonium atoms connected by a single bond in which the valence state of the sulfur atoms is analogous to that of ordinary sulfonium salts. Simple sulfonium salts are widely used in modern organic chemistry,[97] and formation of disulfonium salts as labile intermediates in many reactions of organic sulfides was suggested long ago. However, the formation of these compounds was firmly established, and reliable data regarding their structural features, reactivity and stability were obtained only in the last two to three decades.

A. Discovery of Disulfonium Dications

In the following, we restrict ourselves to highlights of the early history of SS dications since a detailed account has been given previously by Musker.[98] At the beginning of the last century, Bruning et al. suggested for the first time that the reaction of cyclic sulfide **1** with bromine results in formation of a disulfonium dication.[99] It was shown later that the actual reaction product is dibromodisulfide **3**.[100] However, formation of an S−S bond as the result of this reaction indeed provides a strong evidence for a reactive disulfonium dication **2** as an intermediate.[15]

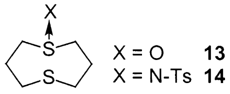


For a long time, disulfonium dications were considered only as hypothetical labile intermediates. In a typical example, Oae proposed intermediate formation of a S−S dication **5** to explain migration of the oxygen atom which occurred when (2-methylphenyl)-4-tolylsulfoxide **4** was treated with concentrated sulfuric acid.[101]



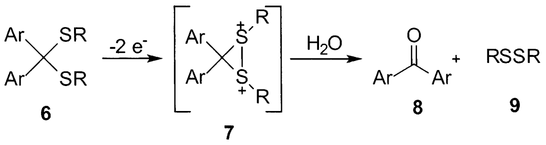
Similarly, Ruffato et al. proposed formation of a disulfonium dication as a result of intramolecular interaction during the oxygen atom transfer from arylmethylsulfoxide to dialkyl disulfide.[102] In 1974,

Table 3. Distance between the Two Sulfur Atoms in Derivatives of 1,5-Dithiacyclooctane

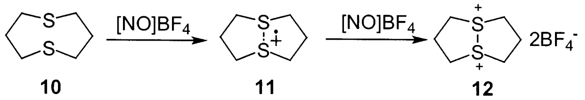


X	electron pair	O	N-Ts
S···S distance, Å	3.58	3.14	3.14

Simonet et al. suggested transient formation of an extremely unstable SS dication **7** during electrochemical oxidation of thioketals. In contrast to ordinary sulfides, electrochemical oxidation of aromatic *gem*-disulfides **6** does not lead to sulfoxides or sulfones but instead affords disulfides **9** and carbonyl compounds **8**. The key intermediate in the suggested reaction scheme is a cyclic disulfonium dication **7** whose hydrolysis results in the observed reaction products.[103]



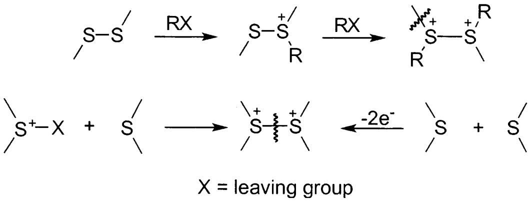
The turning point in the understanding of the chemical nature of SS dications came in 1976 when Musker reported synthesis and isolation of disulfonium dication **12** formed by the two-electron oxidation of 1,5-dithiacyclooctane **10**. The fact that the dication was stable at room temperature (!) allowed the first characterization of a dication by physical and chemical methods.[104] The researchers originally studied complexation of medium size cyclic bis-sulfides with metal ions and found that, unlike other bis-sulfides, interaction of the bis-sulfide **10** with copper (II) perchlorate results in the formation of stable 1,5-dithiacyclooctane radical cation **11**. This compound, as was established later, is also formed when sulfide **10** is treated with 1 equiv of a nitrosonium salt. Further oxidation of the radical cation results in formation of the SS dication **12**.



The unusually facile formation of a disulfonium dication from sulfide **10** is a result of stereochemical features of the eight-membered ring which favor the formation of a transannular bond.[105] According to X-ray data (Table 3), the distance between the two sulfur atoms in 1,5-dithiacyclooctane **10** is smaller than the sum of their van der Waals radii (3.75 Å) which results in a strong nonbonded interaction between the atoms. The significant transannular overlap of the sulfur atomic orbitals is also confirmed by photoelectron spectroscopy and mass-spectrometry.[106,107] This unfavorable interaction and the sulfur—sulfur distance can be decreased as a result of bond formation with an electronegative substituent as in sulfoxide **13** or sulfoximine **14**.[108,109]

B. Synthesis of Disulfonium Dications

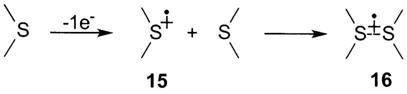
Retrosynthetic analysis provides two main approaches to the disulfonium dication functionality. The first approach is based on formation of a C—S bond and involves double alkylation of disulfides. So far, all attempts to prepare disulfonium dications by this approach have been unsuccessful, most likely because nucleophilicity of the sulfur atom in the intermediate alkylthiosulfonium salts is lowered by conjugation with the adjacent positively charged center.[110] Note, however, that double alkylation of hydrazines is known (vide infra), and, therefore, the viability of this approach to disulfonium dications is worth reinvestigating.[111]



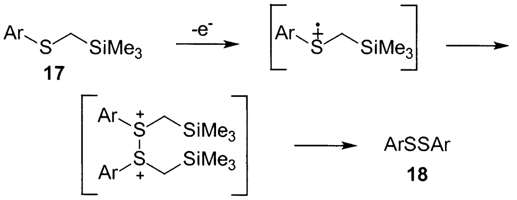
All currently known methods for synthesis of disulfonium dications involve formation of an S—S bond either by oxidative coupling of two sulfide moieties or by nucleophilic substitution at a sulfonium sulfur atom by a sulfide. Historically, the first method has been known for a longer time, and we will begin our discussion with an analysis of this approach.

1. Oxidation of Bis-Sulfides

Physical Methods. Mann has established that electrochemical oxidation of aliphatic sulfides proceeds through a relatively stable radical cation **15** localized on the sulfur atom.[112] However, the more stable configuration corresponds to a molecular complex **16** derived from two sulfide molecules.[113] Formation of this complex occurs very quickly (it is usually diffusion controlled) and is confirmed by EPR spectroscopy both in the liquid and in the solid state.[114,115]

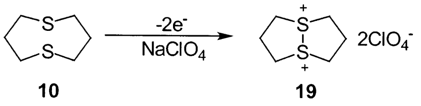


The weak bond that is formed between the interacting sulfur atoms is a two-center three-electron (2c,3e) bond. Asmus has suggested that the bond has σ/σ^* character based on the optical properties of the dimeric radical cations obtained by pulse radiolysis.[116] Further oxidation results in removal of an electron from the single-occupied antibonding σ^* orbital, and, hence, formation of an ordinary single bond between the two positively charged onium ions as discussed in the introduction. Direct formation of a disulfonium dication as the result of dimerization of the intermediate radical cations was observed only in a few instances. One such case involved electrochemical oxidation of β-silyl substituted alkyl—aryl-sulfides **17** where the radical-cation formed initially is stabilized by stereoelectronic interaction with the silyl group (β-effect).[117] Dimerization of the radical-cation leads to a labile dication which undergoes further transformations to give the disulfides **18**.[118]

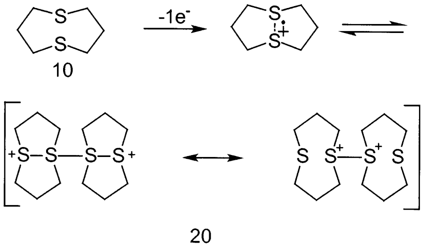


Musker and co-workers were the first to study intramolecular generation of S−S dications through oxidation of aliphatic bis-sulfides.[119] The electrochemical behavior of both cyclic and acyclic bis-sulfides containing three or four methylene units between the sulfur atoms is characterized by reversibility of the reaction and by an anomalously low oxidation potential which is almost 1 V lower than for corresponding sulfides.

The most easily oxidized 1,5-dithiacyclooctane **10** was studied in most detail by cyclic voltammetry.[120] At low concentrations (around 0.05 mM), oxidation of bis-sulfide **10** occurs at 0.34 V as a two-electron process which leads to disulfonium dication **19**.[119]



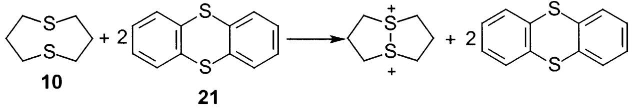
At high concentrations, the only observed anodic wave (0.34 V) corresponds to one-electron oxidation of bis-sulfide **10** and formation of radical cation **11**. The latter undergoes reversible dimerization to give a dication **20** with an intermolecular S−S bond **20**.[119]



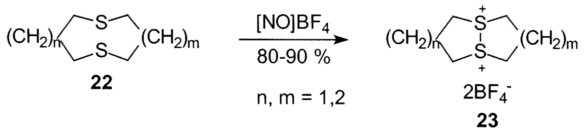
Dication **20** is directly reduced at cathode potential of −0.6 V, or, if the potential is scanned more slowly, via formation of monomeric radical cation at −0.1 V.

Subsequently, a more detailed study[121] has shown that oxidation in this case occurs as a stepwise process with the second oxidation potential 20 mV lower (!) than the first. Considering the Coulomb repulsion of the two like charged centers, one might expect that removal of the second electron to give the dicationic moiety will occur less readily than oxidation of the neutral molecule. Even in the case of two noninteracting electroactive groups, the second half-wave potential should be 36 mV more anodic.[122] Such anomalous electrochemical behavior of 1,5-dithiacyclooctane **10** presents more evidence for the formation of an ordinary chemical bond by removal of two electrons from the antibonding σ^* orbital during electrochemical synthesis of a SS dication.

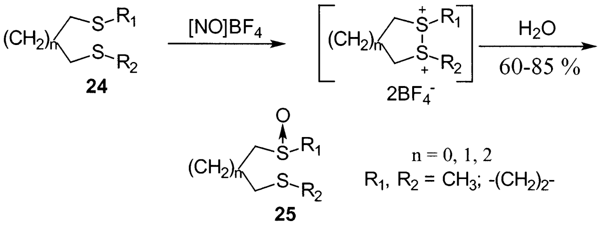
Chemical Methods. The first evidence that 1,5-dithiacyclooctane **10** can be oxidized chemically to a stable disulfonium dication was apparently obtained by Shine and co-workers.[123] While investigating the oxidative properties of the thianthrene radical cation, they found that addition of 0.5 equiv of sulfide **10** to the thianthrene radical cation **21** results in complete disappearance of the radical cation absorbance. At the same time, the expected EPR signal of 1,5-dithiacyclooctane radical cation **11** did not appear. The EPR signal along with the UV absoption at 420 nm expected for 1,5-dithiacyclooctane radical cation **11** appeared when the other 0.5 equiv of sulfide **10** was added. It is likely that at the intermediate step when the ratio of oxidant to bis-sulfide was 2 to 1, the authors observed formation of dication.



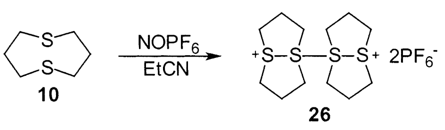
After their discovery of disulfonium dication formation upon oxidation of sulfide **10** by nitrosonium salts, Musker and co-workers carried out a systematic study of the oxidation of several cyclic and acyclic bis-sulfides using this reagent.[15] It was found that the oxidation of cyclic 8-, 9-, and 10-membered bis-sulfides **22** is especially facile.



The monocyclic dication formed from (4-methylthio)butylmethyl sulfide could also be isolated. The other bis-sulfides **24** also underwent two-electron oxidation, but reaction proceeded more slowly and the dications were relatively unstable. Therefore, the other dications were characterized as sulfoxides **25** which were formed when the reaction mixture was treated with aqueous sodium bicarbonate.



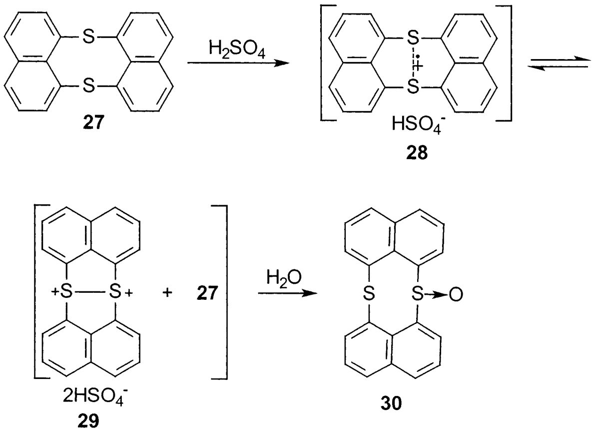
These oxidations involve stepwise transfer of two electrons from a bis-sulfide to the nitrosonium cation and the corresponding radical cation is formed as an intermediate. Radical cations of 1,5-dithiacyclooctane **10** and 1,5-dithiacyclononane are sufficiently stable to be isolated as individual compounds.[124] Interestingly, oxidation of 1,5-dithiacyclooctane **10** with 1 equiv of $NOBF_4$ in propionitrile led to the formation of paramagnetic dimeric dication solid **26** which was transformed into 1,5-dithiacyclooctane radical cation **11** when redissolved in acetonitrile.



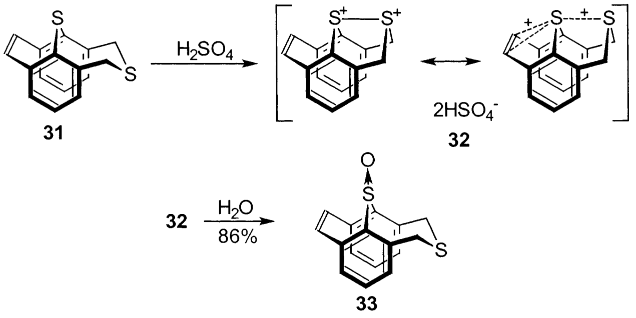
In an interesting recent finding, Clennan and Zhou[125] reported that addition of 1,5-dithiacyclooctane to zeolite CaY in the presence of molecular oxygen results in spontaneous oxidation of the bissulfide to mono- and bis-sulfoxides. The oxidation proceeds through formation of the corresponding radical cation, which was characterized by EPR and diffuse reflectance UV–Vis spectroscopy. The radical cation within the zeolite has a lifetime of more than 8 h in an argon atmosphere.

Bis-sulfides can also be oxidized to SS dications by concentrated sulfuric acid. Because sulfuric acid has lower oxidative potential than the nitrosonium cation, the dications are formed only from the most easily oxidized substrates.

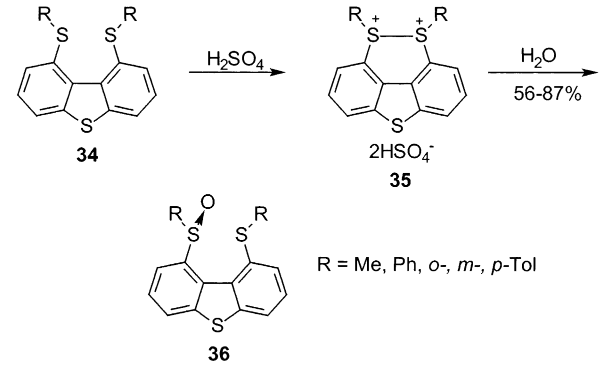
According to the EPR data, dissolving dinaphtho-[1,8-b,c]-1,5-dithiocin **27** in sulfuric acid results in formation of a radical cation **28** which affords, upon hydrolysis, an equimolar mixture of the starting sulfide **27** and monosulfoxide **30**.[126] Formation of this mixture is accounted for by an equilibrium between the starting sulfide **27**, dication **29** and radical cation **28**, which does not shift to the dication side under these conditions.[126]



Sulfuric acid easily oxidizes polycyclic bis-sulfide **31** to a dication **32**. The dication can be hydrolyzed to sulfoxide **33** in high yield.[127] Oxidation of sulfide **31** is facilitated by transannular interaction of the positively charged sulfur atom with the double bond.

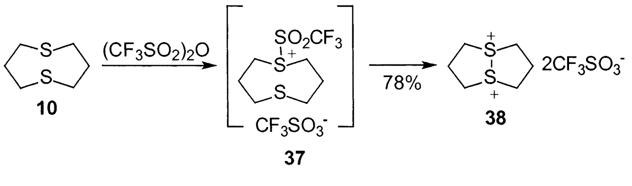


The other reactive bis-sulfides that can be successfully oxidized by sulfuric acid to dications are sterically strained 1,9-dithiosubstituted dibenzothiophenes **34**.[128] These bis-sulfides are destabilized by repulsion of the lone pairs at the transannular sufur atoms which are only 3.0 Å apart according to X-ray analysis. This repulsive interaction distorts the flat dibenzothiophene structure and facilitates oxidative formation of the disulfonium dication bond between the sulfur atoms.[129] Again, the initial product is a radical cation. If the reaction is continued for another day, further oxidation to the disulfonium dications **35** is observed. The dications can be hydrolyzed quantitatively to the corresponding monosulfoxides **36**.[130]



It is appealing to use the second oxidation potential for a bis-sulfide as a general criterion for determining if concentrated sulfuric acid can oxidize the bis-sulfide to the corresponding disulfonium dication. However, experimental limitations associated with the kinetics of the process and with the stability of the bis-sulfide under the reaction conditions complicate the situation. For example, reaction of bis-sulfide **10** with H_2SO_4 leads only to the stable radical cation **11**, notwithstanding the second oxidation potential (0.34 V) which is lower than the first oxidation potential of bis-sulfides **34**. The latter form SS dications readily when dissolved in sulfuric acid (for 1,9-bis(phenylthio)dibenzothiophene the first oxidation potential is 0.86 V).[124,126]

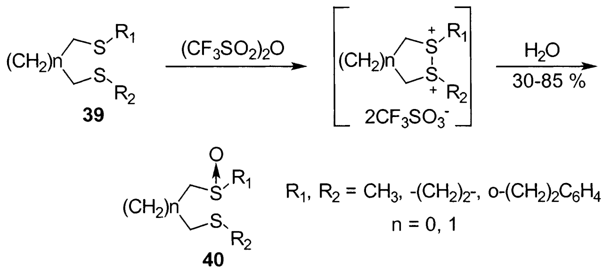
The simplest method for generating disulfonium dications is based on direct oxidation of bis-sulfides by trifluoromethanesulfonic acid anhydride (triflic anhydride) and was suggested only recently.[131] For example, treatment of 1,5-dithiacyclooctane **10** with triflic anhydride yields the corresponding dication salt **38** in high yield. As in the oxidation of monosulfides,[132] the reaction goes through formation of a sulfonyl sulfonium salt **37** which undergoes intramolecular nucleophilic substitution to give the disulfonium dication **38**.



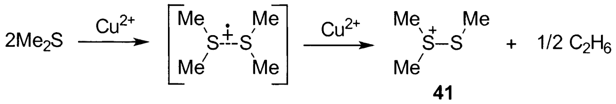
According to ^{19}F NMR, the isolated solid salt **38** has only triflate counterions. This is explained by an exchange of the trifluromethanesulfinate anion with triflic anhydride.[131]

$$CF_3SO_2^- + (CF_3SO_2)_2O \longrightarrow CF_3SO_3^- + CF_3SO_2OSOCF_3$$

A number of other cyclic and acyclic bis-sulfides **39** undergo facile oxidation to dications under these conditions.[131] The dications were treated with aqueous sodium bicarbonate to give monosulfoxides **40**. The whole procedure provides an attractive means for selective monooxidation of bis-sulfides to monosulfoxides.



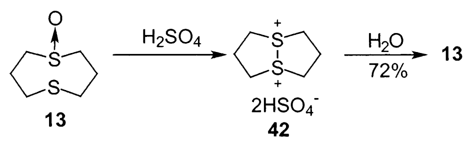
Metal ions in higher oxidation states are known to be efficient oxidizing agents for sulfides. However, the need for a large excess of sulfide due to formation of complexes with the metal ions prevents the use of these systems for oxidation to disulfonium dications. In the reaction of Cu(II) and Tl(III) complexes with five equivalents of dimethyl sulfide, the initially formed dimeric radical cation undergoes cleavage with formation of thiosulfonium salt **41** and ethane.[133]



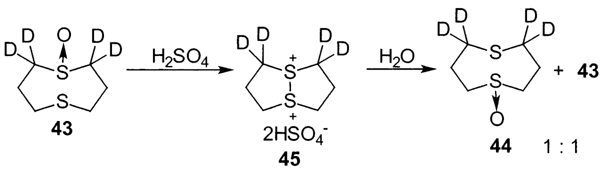
2. Interaction of H_2SO_4 with Mono-S-Oxides of Bis-Sulfides

The second main approach to disulfonium dications is based on nucleophilic substitution at sulfonium sulfur atom by a sulfide. This approach is much more efficient and versatile than the direct oxidation of sulfides. In terms of the “avoided crossing” model (see above), this can explained by the fact that, when the reactant corresponds to the $S^{2+}\cdots S$ configuration, the formation of the $S^{+}\cdots S^{+}$ moiety should be more favorable thermodynamically (see also Figures 1 and 3B),[71,72] and there is a little (if any) repulsive Coulombic contribution to the reaction barrier.

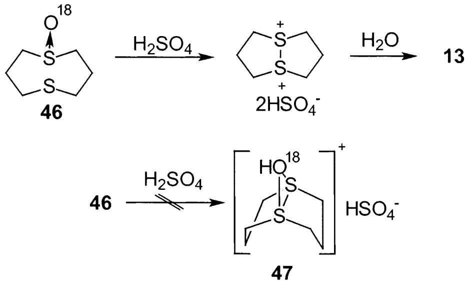
Oae[101] was the first to postulate formation of a disulfonium dication in reaction of concentrated sulfuric acid with monosulfoxide of a bis-sulfide. Later, Furukawa et al.[134] found that the crystalline hydrosulfate **42** of 1,5-dithiacyclooctane SS dication can be prepared by reaction of the corresponding monosulfoxide (or *S*-(*N*-tosyl)imide) with concentrated sulfuric acid.



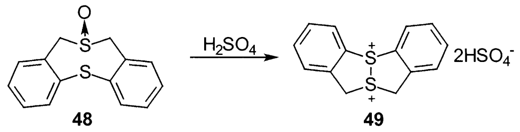
Formation of a symmetric dication **45** from 2,2,8,8-tetradeuterio-1,5-dithiacyclooctane **43** was confirmed by isolation of 1:1 mixture of deuterated sulfoxides **43** and **44** after hydrolysis.[134]

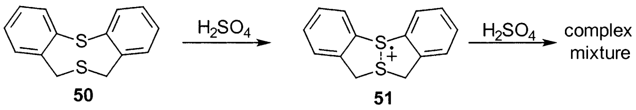


An alternative explanation for the equivalency of the sulfur atoms by assuming the formation of symmetric oxadisulfonium dication **47** was eliminated by an additional experiment in which hydrolysis of the dication obtained from O^{18}-labeled sulfoxide **46** resulted in complete loss of the isotopic label in the recovered sulfoxide.[135]

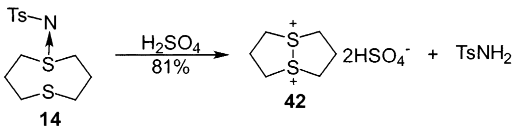


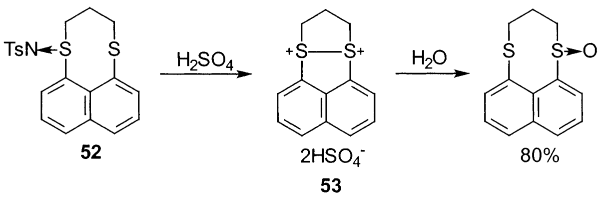
Use of monosulfoxides allows generation of dications from bis-sulfides that are not directly oxidized by concentrated sulfuric acid. The other advantage of this method is the ability to obtain such dications as **49** with benzylic substituents at sulfur. Direct treatment of bis-sulfide **50** with concentrated sulfuric acid led to a complex mixture of unidentified products, which was explained by the limited stability of radical cation **51**.[127,136]





N-Tosylimines can be used instead of sulfoxides. For example, treatment of sulfinilimines **14** and **52** with sulfuric acid yields dications **42** and **53**.[137,144]

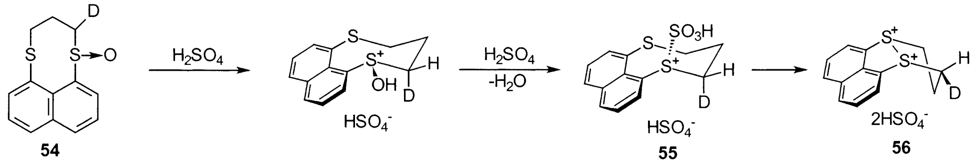




By contrast, *N*-tosylimines of simple sulfoxides give unsubstituted sulfinylimines and *p*-toluenesulfonic acid upon treatment with concentrated sulfuric acid.[138] Cleavage of the S−N bond with sulfinylimine sulfur atom but not with the sulfonylamide sulfur of the $SO_2N{=}S$ moiety is preferred under these conditions due to strong assistance to bond breaking by sulfide sulfur.

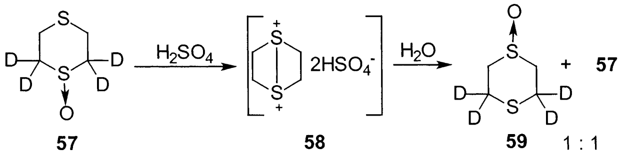
Use of concentrated sulfuric acid has certain disadvantages such as the relatively low stability of many of the resulting dications, which frequently can

Scheme 1



be characterized only spectroscopically. In addition, in some cases the reaction mechanism is more complex than just a double protonation of sulfoxide oxygen followed by an S_N2-like nucleophilic substitution of water by the second sulfur atom.[139,140] Studies of diastereomerically pure monodeuterated naphtho[1,8-bc]-1,5-dithiocin-1-oxide **54** indicated that both formation of S,S dication **56** on treatment with concentrated sulfuric acid and subsequent hydrolysis of the dication proceeded with retention of configuration at the sulfoxide sulfur. Because direct nucleophilic substitution at sulfonium sulfur is known to occur with inversion,[141] the most likely mechanism involves a double inversion which proceeds through intermediate formation of sulfonyloxysulfonium salt **55** followed by a subsequent replacement of hydrosulfate anion by the second sulfur atom and overall retention of the configuration on sulfur (Scheme 1).[142]

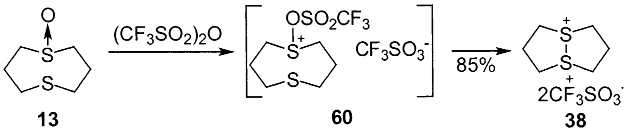
In agreement with this relatively complicated picture, the ^1H and ^{13}C NMR spectra of a SS dication formed from 1,4-dithiane by this method are more complex than expected for such a symmetric molecule.[139] This can also be explained by equilibrium of dications with intramolecular and intermolecular S−S bonds.[143] Still, hydrolysis of the tetradeuterated derivative **57** results in regeneration of the starting monosulfoxide with the isotopic label equally distributed between the α- and β-positions, which is consistent with symmetric dication **58** as an intermediate.[144]



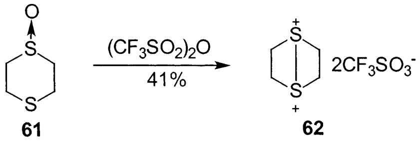
3. Interaction of Triflic Anhydride with Monosulfoxides of Bis-Sulfides

Many of the above complications can be avoided when triflic anhydride is used instead of concentrated sulfuric acid in the reaction with the monosulfoxides. This method was suggested by Furukawa and coworkers[145] in 1987.

When triflic anhydride reacts with a monosulfoxide, the initially formed trifluoromethanesulfonyloxysulfonium salt **60** undergoes clean intramolecular nucleophilic substitution of trifluoromethylsulfonate anion by the other sulfur atom with formation of the disulfonium dication **38** in a high yield and without any side products from a Pummerer rearrangement.[146]



Monosulfoxide **61** where the transannular interaction of the sulfur atoms is minimal also reacts with triflic anhydride to give a white precipitate of highly strained disulfonium dication **62** which is extremely hard to isolate when other synthetic approaches are used (see above).[145]

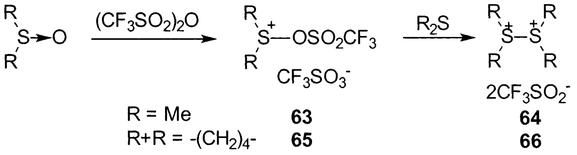


For example, the dications formed by reaction of triflic anhydride with 1,4-dithiane or by reaction of monosulfoxide **61** and sulfuric acid[144] are highly labile and their ^1H NMR spectra consititute a complex pattern of uninterpretable signals. By contrast, dication **62** obtained by reaction of monosulfoxide **61** with triflic anhydride exhibits only one ^1H NMR signal as a singlet at 3.80 ppm in agreement with a symmetric monomeric structure containing an intramolecular S−S bond.[145] The deshielding effect of the disulfonium dicationic moiety in the NMR spectra is similar to (or slightly larger than) the effect of sulfonium groups.

The large dependence of the NMR chemical shift and multiplicity on the nature of the counterions clearly shows that the nature of the counterion plays an important role in the stability and structure of dications. This role has been further illustrated by the strong interaction between sulfur atoms and oxygen atoms of the triflate counterions in the X-ray structure of dication **38**.[147] The average S···O distance (2.7 Å) is significantly shorter than the sum of van der Waals radii of the involved atoms (3.35 Å), and the $O\cdots S^+{-}S^+\cdots O$ moiety is nearly collinear, which indicates a quasisulfuranium configuration of the sulfur atoms in the crystal.

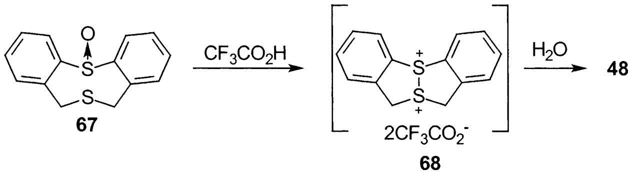
The X-ray study has also elucidated other interesting structural features of the new disulfonium dication functional group. The length of the S−S bond in dication **38** is 2.13 Å, which is slightly larger than the S−S bond length in disulfides (2.08 Å) but considerably less than the S−S distance in 1,5-dithiacyclooctane, 3.27 Å.[148] These data confirm that dication **5** is not an open eight-membered structure but a bicyclic molecule. The eight-membered ring has the chair−chair conformation with *cis*-orientation of the lone pairs at the sulfur atoms whereas the chair−boat conformation is dominant in 1-methylthionia-5-thiacyclooctane.[149] Available computational data show reasonable agreement with the experimental structure.[150,151]

More recently, this method has been extended to preparation of a variety of disulfonium dications from both acyclic and cyclic bis-sulfides, including very labile dications not observed when other methods were used.[152] Thus, simple acyclic SS dications were prepared by an *intermolecular* reaction of a monosulfide, a monosulfoxide, and triflic anhydride.[153] In the first step, reaction of triflic anhydride with dimethyl sulfoxide generates a highly electrophilic[154] complex **63** (dimethyl sulfide ditriflate).[155] The latter reacts with dimethyl sulfide to give labile tetramethyldisulfonium dication **64** identified by NMR spectroscopy.[153] In a similar manner, bis-(tetramethylene)disulfonium dication **66** is obtained from tetrahydrothiophene and its S-oxide.

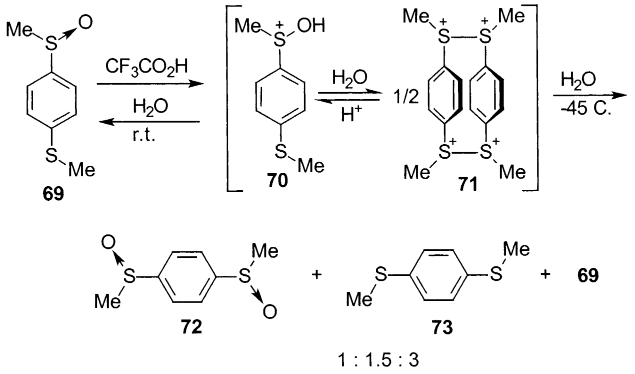


4. Reactions Involving Intermediate Formation of Disulfonium Dications

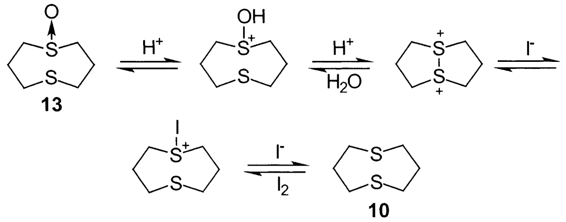
The formation of stable disulfonium dications from certain bis-sulfides provides an impetus for reevaluating the mechanisms of some old reactions. Acid-catalyzed migration of an oxygen atom from a sulfoxide to sulfide is one of the first examples in which an intermediate formation of an SS dication was proposed.[101] Recently, such intermediates were observed by physical methods. The kinetics suggested that an intramolecularly formed disulfonium dication **68** was involved in isomerization of sulfoxide **67** under influence of trifluoroacetic acid. It is possible to detect the dication in a nonnucleophilic medium such as sulfuric acid.[156]



Another example of an oxygen atom migration that proceeds through a dication is the reaction of S-oxide 1,4-dimethylthiobenzene **69** with trifluoroacetic acid. As established for the deuterated substrate, this reaction proceeeds through intermediate formation of a symmetric dimeric disulfonium dication. This dication, which was observed by NMR spectroscopy, is in rapid equilibrium with the protonated form of sulfoxide **70**. The position of the equilibrium strongly depends on temperature. At −45 °C, formation of the bis-dication **71** is strongly favored. Nucleophilic attack on this symmetric structure is possible from two directions, and as a result, hydrolysis of the reaction mixture at −45 °C affords a mixture that contains bis-sulfide **73** and bis-sulfoxide **72**, in addition to starting sulfoxide **69**.[157]

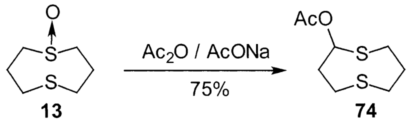


Convincing kinetic evidence for intervention of a disulfonium dication during reduction of sulfoxide **13** with iodide in aqueous acid was found by Musker and co-workers.[158] The reaction was found to proceed a million times faster than reduction of dimethyl sulfoxide under the same conditions. The rate of the reaction was almost independent of the iodine concentration but displays a second-order dependence on the acid concentration. These experiments strongly suggested formation of a disulfonium dication as the rate-limiting step.

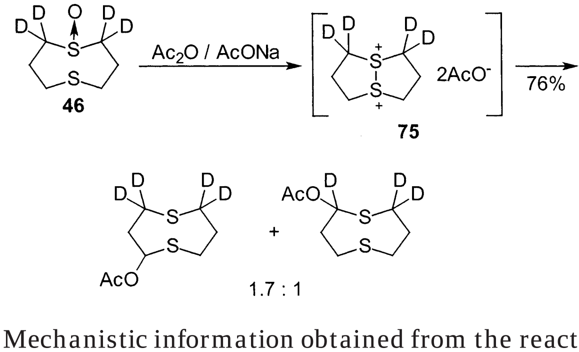


Kinetic studies of the reaction of the monosulfoxide of (3-methylthio)propylmethysulfide with iodide ions also suggest an intermediate monocyclic dication. Monosulfoxide of 1,4-dithiane behaves under these conditions as an ordinary sulfoxide.[158]

Monosulfoxide **13** undergoes the Pummerer rearrangement when treated with acetic anhydride in the presence of sodium acetate. Although the acetate **74** looks like the normal Pummerer product,[159] the experiments with tetradeuterated and ^{18}O-labeled sulfoxide confirm intermediate formation of a dication which is in rapid equilibrium with starting material.[160]

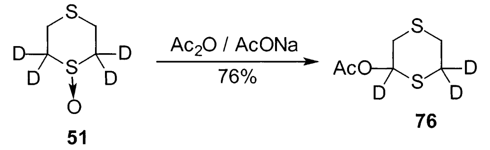


The ratio of 2,8,8-trideuterated to 4,4,6,6-tetradeuterated product **46** is equal to the intramolecular isotope effect $k_H/k_D = 1.7$.[159] This observation suggests that the rate-limiting step is associated with proton abstraction from dication **75**.



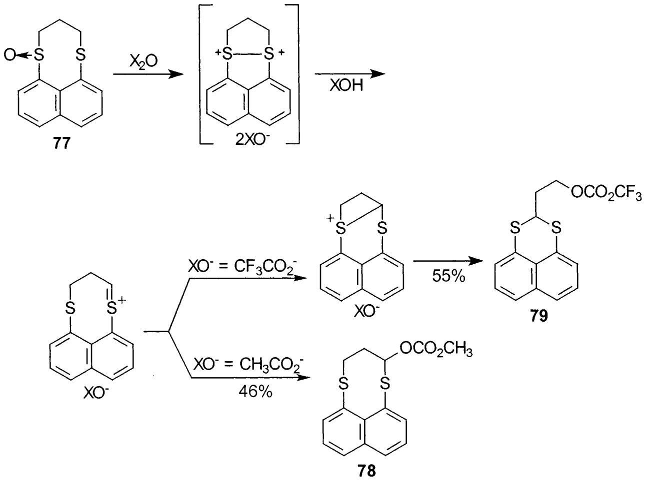
Mechanistic information obtained from the reaction with ^{18}O-labeled sulfoxide **49** suggests that the dication exists as a tight ion-pair and that the acetate counterion scrambles completely with the anhydride.[159] This contrasts the results obtained when the dication was generated in sulfuric acid and can be explained in terms of the greater nucleophilicity of acetate as compared with hydrosulfate anion.[134]

In the case of 2,2,6,6-tetradeuterated 1,4-dithiane sulfoxide **51**, only 2,6,6-trideuterated 2-acetoxy-1,4-dithiane **76** is formed.[160] Obviously, in this case formation of a dication does not occur.



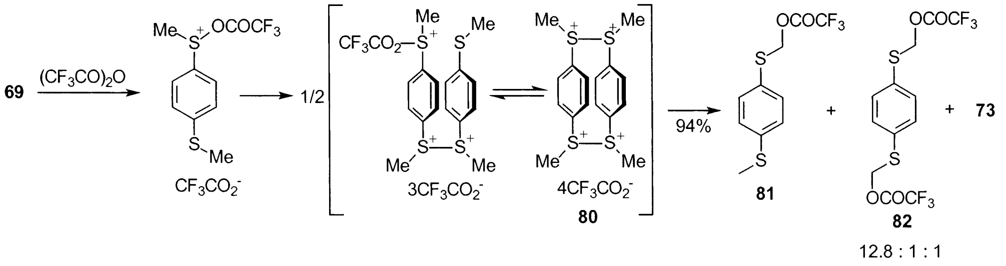
The differing nucleophilicity of acetate and trifluoroacetate anion determines the manner in which naphtho[1,8-*b*,*c*]-1,5-dithiocine **77** sulfoxide rearranges on treatment with acetic and trifluoroacetic anhydrides. In both cases, the reaction proceeds through formation of a disulfonium dication, but the final products are different. When acetic anhydride is used, the reaction affords the corresponding α-acetylsulfide **78**—a normal product of the Pummerer rearrangement, while trifluoroacetic anhydride causes isomerization with formation of dithioacetal **79** (Scheme 2).[161]

Scheme 2



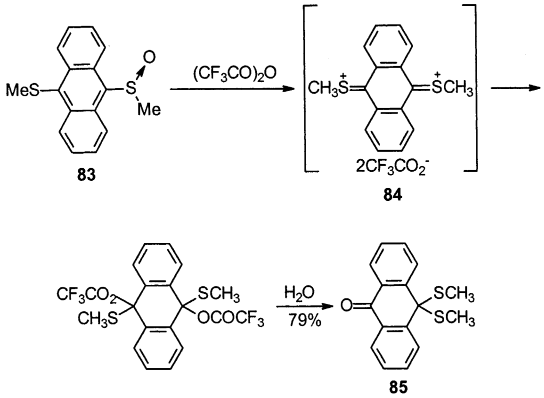
Reaction of *p*-dimethylthiobenzene sulfoxide **69** with trifluoroacetic anhydride results in a mixture of reduced sulfoxide **73** and the corresponding mono- and disubstituted products of the Pummerer rearrangement **81**, **82**.[162] In the reaction of the sulfoxide **69** with trifluoroacetic acid, the key intermediate is a bimolecular complex with two disulfonium dication bonds (Scheme 3).

Scheme 3

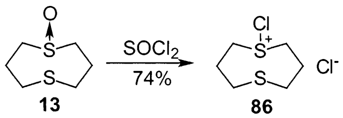


Formation of this complex is favored over a simple Pummerer rearrangement without participation of the sulfide moiety. It is also favored over formation of a quinoid structure involving conjugation of two sulfonium atoms through the aromatic system. Interestingly, in the case of polycyclic aromatic systems capable of more effective positive charge delocalization, conjugation through the aromatic moiety becomes more energetically favorable.[162] For example, reaction of 9,10-dimethylthioanthracene sulfoxide **83** with trifluoroacetic anhydride leads to 9,10-dimethylthio-10-anthraquinone **85** after hydrolysis with aqueous bicarbonate. This reaction proceeds by way of a quinoid dication **84** which gives the observed product **85** after addition of trifluoroacetate anion and hydrolysis (Scheme 4).[162]

Scheme 4

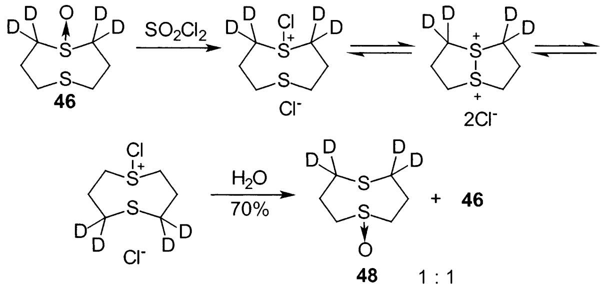


Another example that illustrates formation of a disulfonium dication as an intermediate was found in the reaction of sulfoxide **13** and thionyl chloride. Instead of a normal Pummerer product (an α-chlorosulfide), the reaction leads to stable chlorosulfonium salt **86**, stabilized by transannular interaction with the remote sulfur atom.[163]

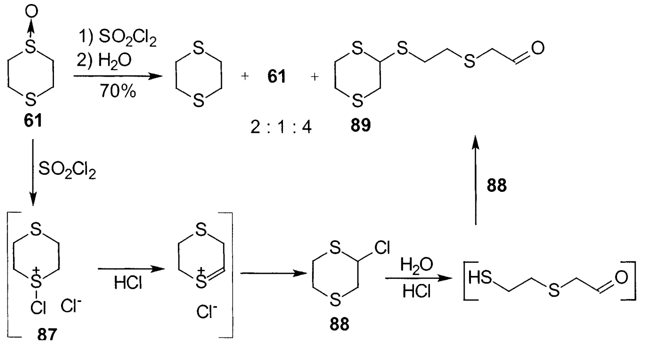


Although the two sulfur atoms are nonequivalent on the NMR time scale, hydrolysis of the salt obtained from 2,2,8,8-tetradeuterated sulfoxide **46** results in a 1:1 mixture of the two possible isomers indicating that the chlorosulfonium salt does exist in rapid equilibrium with a symmetric SS dication.

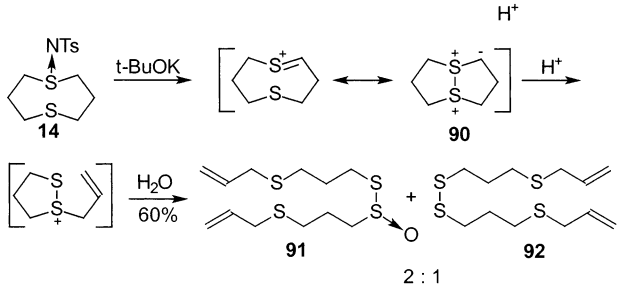
On the other hand, 1,4-dithiane monosulfoxide **61** reacts under the same conditions such as a simple aliphatic sulfide. The reaction proceeds via an un-



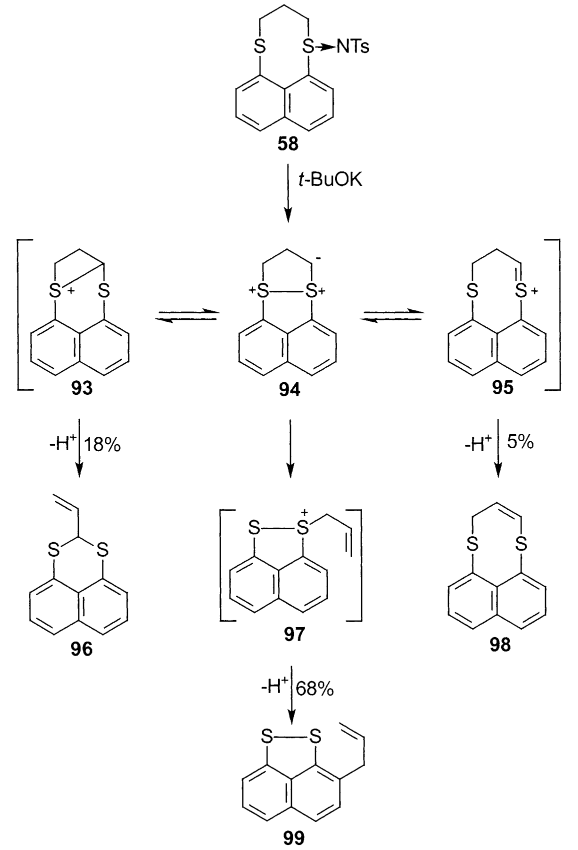
stable chlorosulfonium salt **87** which when hydrolyzed without being isolated gives rise to a mixture with aldehyde **89** as the main product. It is suggested that formation of the aldehyde proceeds through α-chlorosulfide **88**, the product of the Pummerer rearrangement.[163]



While reaction of strong bases with ordinary sulfinylimines gives Pummerer products such as *gem*-thioacetals and vinylsulfides,[164] sulfinylimines of certain bis-sulfides are converted by strong bases to ylides of the corresponding SS dications which undergo further transformations.[137] Thus, reaction of 1,5-dithianecyclooctane monosulfylimine **14** with potassium *tert*-butoxide affords a mixture of thiosulfinate **91** and disulfide **92.** Formation of the ring-opened products in this case is explained by α-deprotonation of the disulfonium-dications to give the corresponding ylide which undergoes *β*-elimination.[137]



Scheme 5



In the reaction of sulfinylimine **58** with potassium *tert*-butoxide, vinyl sulfide **98** is formed in 5% yield, while the main reaction products are disulfide **99** and dithioacetal **96** (Scheme 5).

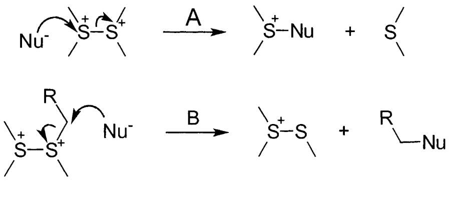
Experiments with deuterated sulfinylimine show that the reaction starts with a fast α-deprotonation, followed by elimination of the tosylamide moiety to give disulfonium dication ylide **94**. The ylide **94** is considered to be in equilibrium with two other cationic intermediates **93** and **95** which are converted to vinylsulfide **98** and dithioacetal **96** by the base present in the reaction medium. The most likely mechanism for formation of disulfide **99** involves transformation of the dication ylide **94** to allylthiosulfonium salt **97**. This salt undergoes a [3,3] sigmatropic rearrangement followed by deprotonation to give the main reaction product **99**.[137] Earlier it was shown that allylthiosulfonium salt **97** formed by thermolysis of monosulfoxide of 1,8-bis(allylthio)-naphthalene is unstable and is transformed to a disulfide **99** by a thio-Claisen rearrangement.[165]

C. Chemical Properties of Disulfonium Dications

Studies of the chemical properties of disulfonium dications were quite limited before the discovery of new convenient synthetic methods for generating these compounds. Progress in this field was especially facilitated when the disulfonium dications became readily available through the reaction of triflic anhydride with sulfoxides.[145]

1. Interaction of Disulfonium Dications with Nucleophiles

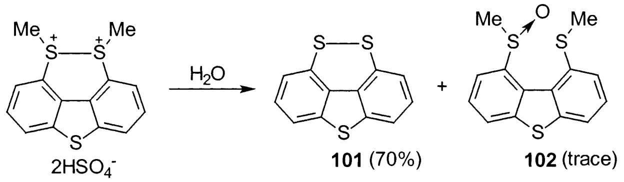
Reactions of disulfonium dications with nucleophiles can follow two pathways. Depending on the nature of the dication and nucleophile, nucleophilic substitution may occur at either the onium sulfur atom or at the α-carbon atom.



The most typical and abundant reactions involve nucleophilic substitution at the sulfonium atom (for example, hydrolysis to give monosulfoxides). This direction of attack is preferred because of the lower energy of S−S bonds, and the decreased sterical hindrance at a trisubstituted sulfur atom compared with the hindrance at a tetracoordinated carbon atom.

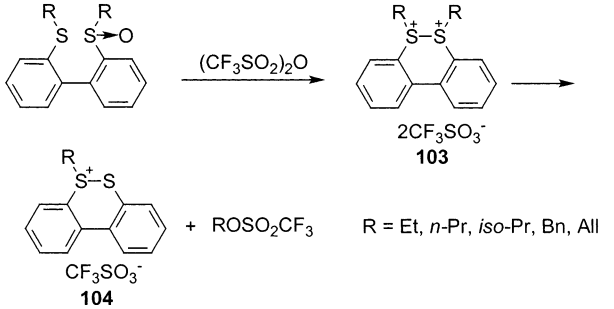
On the other hand, cleavage of the S−C bond is facile in nucleophilic substitutions involving sulfonium salts[97] and the leaving ability of the Alk_2S group compares with that of a bromide ion. As a result, there are several examples of type B substitutions in the literature. Generally, they can be classified as typical S_N2 processes.

Decomposition of some highly reactive disulfonium dications in sufficiently nucleophilic medium is accompanied by formation of disulfides. This suggests nucleophilic substitution at the α-carbon atom of the dications. For example, electrolyses of aromatic thioacetals **6**, *β*-silyl-substituted alkyl aryl sulfides **17**, and oxidation of cyclic sulfide **1** with bromine mentioned earlier are likely to proceed through dealkylation of SS dications formed as intermediates. Even hydrolysis of disulfonium dications generated from sterically rigid bis-sulfides often affords some disulfide as a byproduct in addition to the monosulfoxide main product. For example, hydrolysis of dication **100** yields sulfoxide **102** and trace amounts of heterocycle **101**.[130]



100 **101** (70%) **102** (trace)

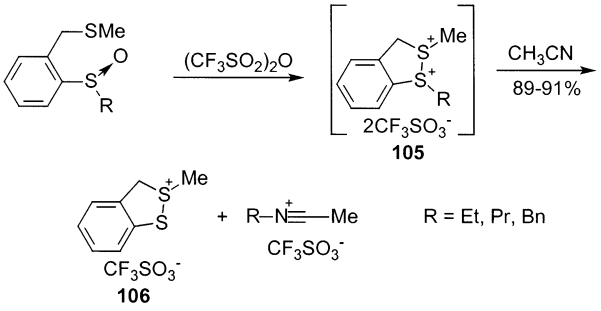
Dealkylation of labile disulfonium-dications **103** derived from 2,2′-bis(alkylthio)biphenyls, which occurs spontaneously when the reaction mixture is thawed above −45 °C, gives rise to thiosufonium salt **104.** This reaction can also be classified as a nucleophilic substitution at the α-carbon atom. The intermediate dication **103** is highly reactive but can be detected spectroscopically.[166]



103 **104**

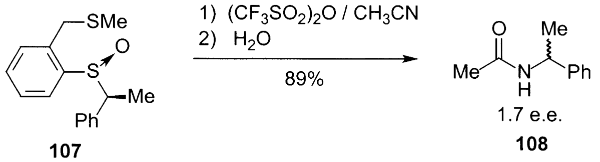
Kinetic data indicate that this reaction is an S_N1 process. One argument in favor of carbocationic character of this transformation is the extremely high reactivity of the disulfonium dication. These compounds undergo dealkylation above −45 °C in the presence of such an extremely weak nucleophile as the trifluorometanesulfonate anion. The propensity of SS dications to undergo dealkylation was studied in unsymmetrically substituted bis(alkylthio)biphenyls and was found to decrease in the order of methyl > ethyl > benzyl. This order of reactivity corresponds to an increase in the stability of the corresponding carbocations.[167]

Dealkylation of dication **105** affords thiosulfonium salt **106** in quantitative yield.[168]



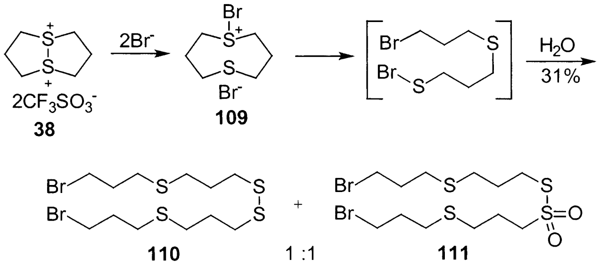
105 **106**

Kinetic studies suggest that the S_N1 mechanism of dealkylation is involved in this case as well. In addition, reaction of sulfoxide **107** with a substituent chiral at the α-carbon results in racemic nitrilium salt **108**. In the case of the 2,2-diphenylethyl substituent the reaction is accompanied by carbocationic rearrangement leading to *trans*-stilbene, which gives another indication of a S_N1 mechanism.



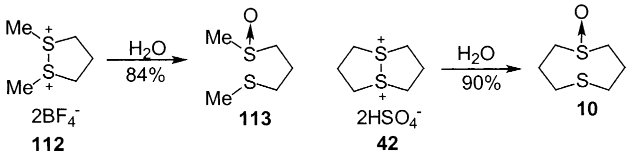
107 **108**

In the case of the most studied and stable bicyclic disulfonium dications nucleophilic substitution at the α-carbon atom does not occur.[169] Although the reaction of dication **38** with bromide ions formally leads to cleavage of S−C bond, the reaction mechanism involves initial nucleophilic substitution at the sulfonium atom by the bromide anion. The bromosulfonium salt intermediate **109** undergoes further transformations yielding disulfide **110** and thiosulfonate **111** after hydrolysis of the reaction mixture.

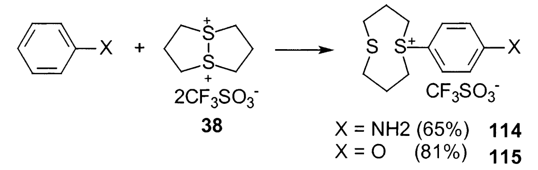


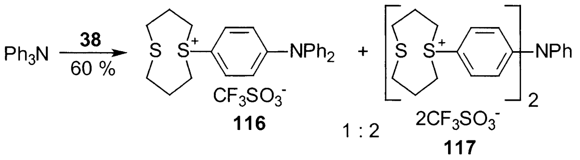
38 **109** **110** **111**

Regardless of their structure, all disulfonium dications are easily hydrolyzed to form the corresponding monosulfoxides in quantitative yield. It is suggested that the mechanism involves direct nucleophilic substitution at sulfonium sulfur.[15] Hydrolysis of SS dications represents a general way of detecting these compounds since the majority of dications are highly labile whereas their reaction with water results in stable and easily isolable compounds. For example, hydrolysis of monocyclic (**112**) and bicyclic (**42**) dications leads to sulfoxides **113** and **10** in high yield.[134]



Reaction of disulfonium dication **38** with electron donor aromatic compounds also affords products of substitution at the sulfonium atom. For example, reaction of dication **38** with aniline in acetonitrile leads to the corresponding *para*-substituted sulfonium salt **114**.[170] Phenol under these conditions gives sulfonium salt **115**. Triphenylamine also reacts with dication **38** to create a mixture of mono-**116** and disubstituted product **117**.





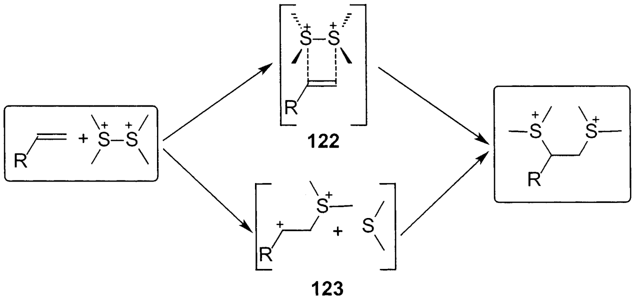
Disulfonium dications also interact with nonaromatic π bonds. This reaction is the only known example in which a 1,2-dication adds to alkenes and alkynes. The only SS dication found to participate in this reaction is the highly strained dication **62** derived from 1,4-dithiane. The reaction proceeds under mild conditions and leads to products resulting from simultaneous addition of two sulfonium groups—bicyclic disulfonium salts of bicyclo[2.2.2]octane skeleton **119** (Scheme 6).[171]

Reaction with alkenes is sensitive to steric factors; in the case of dication **62** only reaction with mono- and 1,2-disubstituted ethylenes afforded identifiable reaction products. Reaction with more substituted olefins leads to intractable mixtures. Only alkenes conjugated with aromatic or cyclopropane moiety undergo this reaction. In the case of 1,2-disubstituted alkenes, the relative configuration of substitutents at the double bond is preserved and only one diastereomer is formed.

Acyclic SS dications **64**, **66** also give 1,2-disulfonium salts **120** in reactions with olefins.[153] Formation of a mixture of diastereomers is observed in the case of 1,2-disubstituted alkenes.

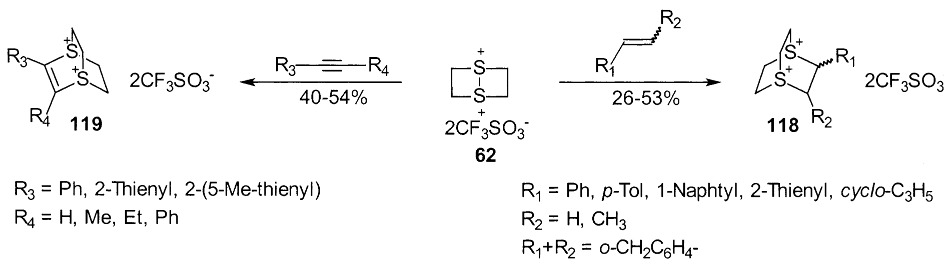
Reaction with conjugated dienes leads exclusively to the product of 1,4-addition **121**. In this instance, the addition is not highly stereoselective and leads to mixtures of E- and Z-products whose ratio depends on steric factors (Scheme 7).

Two alternative mechanisms were considered for the reaction: (a) a synchronous mechanism involving a cyclic transition state **122**, and (b) stepwise electrophilic addition proceeding through formation of a carbocation **123**.

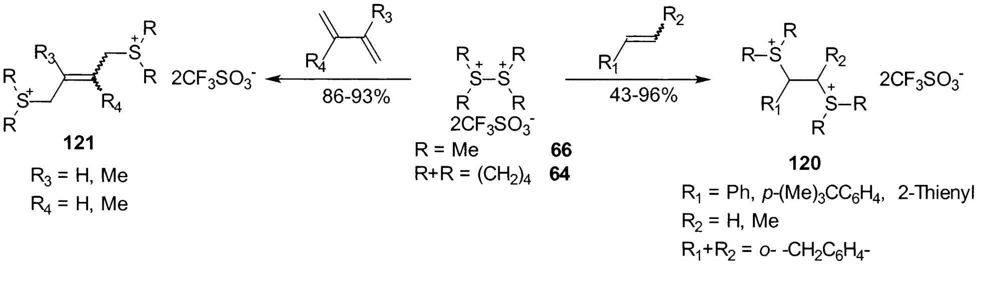


Further insight into the mechanism of this reaction was obtained with the help of molecular orbital (MO) theory and quantum mechanical calculations.[172] The following orbital diagram (Figure 7),[173,174] describes the interaction of two sulfide moieties which results in dication formation after a two electron oxidation (cases A, B, and C correspond to relative increases

Scheme 6



Scheme 7



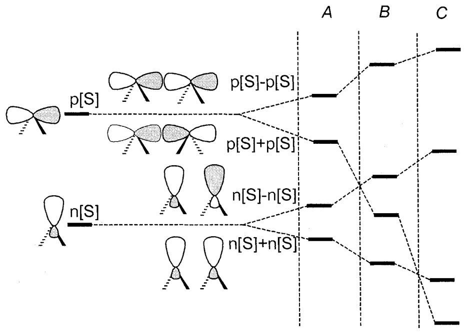


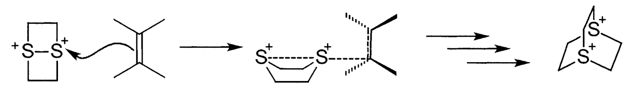
Figure 7. Bonding energy results from perturbation of the orbitals corresponding to the sulfur lone pairs. Six electrons fill three of the four molecular orbitals formed as the result of this perturbation. The LUMO of the dication corresponds to the p[S]-[S] orbital while the HOMO of the dication is an n[S]-n[S] combination except in the case of weak interaction ***A***, where the HOMO corresponds to a p[S]+p-[S] orbital.

in orbital perturbation and interaction between the sulfur atoms).

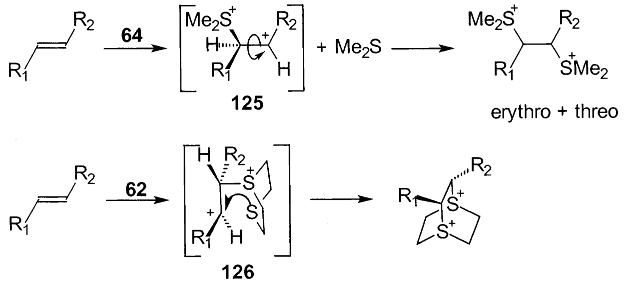
Molecular and electronic structures for the tetramethyldisulfonium dication, bicyclic 1,4-dithioniabicyclo[2.2.0]hexane, 1,5-dithioniabicyclo[3.3.0]octane, 1,4-dithioniabicyclo [3.2.0]heptane, and of 1,4- dithioniabicyclo[2.2.2]octane and the precursors of the dications—dimethyl sulfide and 1,4-dithiane (in the boat conformation) were calculated at the HF/6-31G* level,[175,172] In the electronic structure of 1,4-dithioniabicyclo[2.2.0]hexane and the *sp-sp* conformation of the tetramethyldisulfonium dication, the difference in the energy levels of n[S]-n[S] and n[S]+n[S] is significantly increased due to steric strain and the order of orbitals thus corresponds to case B. In the less strained systems, the order of orbitals corresponds to case B (1,5-dithioniabicyclo[3.3.0]octane, 1,4-dithioniabicyclo[3.2.0]heptane) or case A (*ap-ap* conformer of tetramethyldisulfonium dication). In the last two instances, the energy gain due to addition of these dications to alkenes is small due to the increase in energy of the interacting orbitals.[176]

Restricted Hartree—Fock calculations of the suprafacial addition of ethylene to 1,4-dithioniabicyclo-[2.2.0]hexane with the 6-31G* basis failed to locate the transition state for this process. Synchronous suprafacial addition should proceed through an antiaromatic transition state which is thermally forbidden according to the Woodward—Hoffmann rules.[177] At the same time, during the sidewise addition the orbital factors favor nucleophilic attack of the alkene π system on one of the sulfur atoms of disulfonium dication. This process can be described as an S_N2-like substitution at the sulfur atom (S_N2(S)) or as electrophilic addition to a double bond. The transition state was readily located at this geometry of the intermediate π complex **124**.[172] The distance between the reaction centers in complex **124** (the ethylene carbon atoms and the closest of the sulfur atoms of the dication in the episulfonium ion-type geometry) was 2.74 and 2.96 Å.

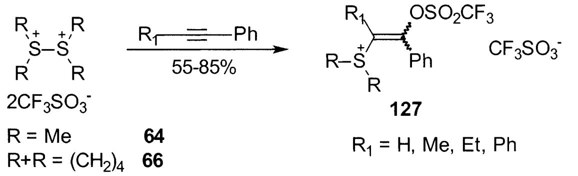
According to the stepwise electrophilic reaction mechanism, the differences in the stereochemistries of the products from the reactions of alkenes with cyclic **62** and acyclic **64** disulfonium dications can be explained by the larger rates of the intramolecular reactions. In the case of a cyclic dication, the carbocationic center in intermediate **126** which is formed as the result of initial attack by a S—S dication attack on a double C═C bond reacts with nucleophiles intramolecularly, thus conserving the configuration of the substituents at the double bond. On the other hand, an acyclic dication undergoes transformation to two kinetically independent particles (**125** and dimethyl sulfide) with a consequent loss of stereoselectivity.



124



Interaction of simple àcyclic dications with acetylenes proceeds anomalously. Reaction leads not to the unsaturated disulfonium salts but to products resulting from nonstereospecific addition of sulfonium and triflate groups—the corresponding vinyltriflates **127**.[178]

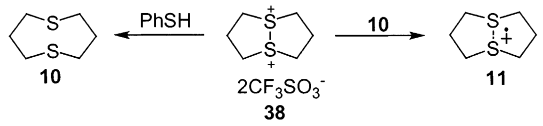


It was shown earlier[179] that the interaction of trifluoromethylsulfonyloxysulfonium triflate (the “dimethyl sulfide—ditriflate” complex) with certain acetylenes leads to analogous vinyl triflates.

The drastic differences between the reactions of cyclic and àcyclic dications with acetylenes provide another evidence for a stepwise mechanism of this process. Stabilization of the carbocationic intermediate in the case of bicyclic dication **62** is the result of intramolecular reaction where the presence of external nucleophiles is not important. In the reaction of acyclic dications **64**, **66** this step occurs intermolecularly, and there is competition between the two external nucleophiles—sulfide and trifllate anion.

2. Reduction of Disulfonium Dications: Reactions with Bases

Reduction of bicyclic disulfonium dication **38** can lead either to a bis-sulfide **10** or to a stable radical cation **11** depending on the redox potential of the reducing agent. For example, reaction of dication **38** with sulfide **10** leads to the corresponding radical cation **11**, whereas treatment with thiophenol[124] or 1,2-diphenylhydrazine[170] affords bis-sulfide **10**.



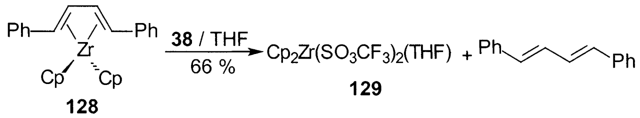
$$\mathrm{PhNH{-}NHPh} + \mathbf{38} \xrightarrow[71\%]{} \mathrm{PhN{=}NPh} + \mathbf{10}$$

Mercaptans are oxidized by disulfonium dication **38** under mild conditions with formation of disulfides. Yields for this reaction are usually high except for sterically hindered substrates such as *tert*-butylmercaptan (42%). The method is general and was successfully applied to syntheses of aliphatic, aromatic, and heteroaromatic disulfides from the corresponding thiol.[180]

$$\mathrm{RSH} + \mathbf{38} \xrightarrow[42-86\%]{} \mathrm{RS{-}SR} + \mathbf{10}$$

R = n-Bu, t-Bu, Ph, *cyclo*-C_6H_{13}, *p*-MeC_6H_4, *o*-MeC_6H_4, *p*-ClC_6H_4, *p*-Py, *o*-Py

In addition, dication **38** is a mild and selective reagent for synthesis of trifluoromethanesulfonates of transition metals. Diene complexes of zirconium and tantalum are transformed to corresponding bis-trifluoromethanesulfonate complexes **129** in good yields. Earlier these complexes were prepared in low yield and by more complex procedures.[181]

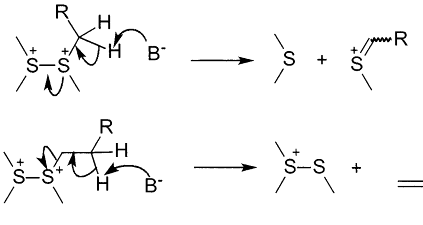


Another promising application of this reaction is the oxidation of samarium metal to samarium ditriflate. The previous approach to this salt was based on reduction of Sm (III) salts with Grignard reagents and led to a ditriflate contaminated with magnesium salts. This contamination decreased the catalytic activity of the Sm ditriflate. Oxidation with disulfide **38** eliminates this problem; ditriflate **130**, synthesized according to this procedure, acts as an active and highly diastereoselective catalyst for pinacol coupling of carbonyl compounds.[182]

$$\mathrm{Sm} \xrightarrow[66\ \%]{\mathbf{38}\ /\ \mathrm{MeCN}} 1/n[\mathrm{Sm(CF_3SO_3)_2(MeCN)_{1.5}}]_n$$

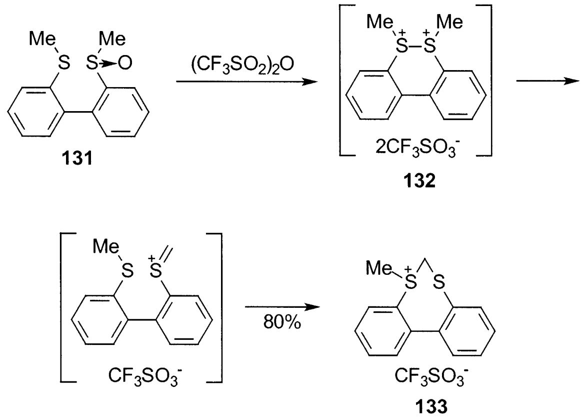
130

In analogy to the properties of ordinary sulfonium salts, reaction of disulfonium dications with bases may lead to *β*- or α-deprotonation. α-Deprotonation can result in S—S bond cleavage and formation of a sulfenium salt in a process which can be characterized as a "thia"-Hofmann cleavage.

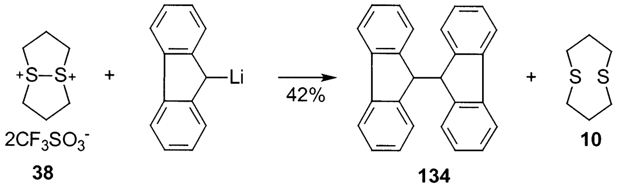


We have noted above that deprotonation of the SS dication formed during the Pummerer rearrangement of monosulfoxides of certain bis-sulfides **13**, **77**, **69** is a key step of the reaction.[159,160] Furukawa and coworkers also suggested that direct formation of disulfonium dication ylides occurred upon treatment of sulfinylimines of cyclic eight-membered bis-sulfides **14**, **58** with potassium *tert*-butoxide.[137]

Reaction of triflic anhydride with sulfoxide **131** affords sulfonium salt **133.** It has been suggested[152] that this reaction proceeds through deprotonation of the corresponding SS dication **132**. Although the dication itself would not be observed by physical methods due to its lability, experiments with deuterated derivatives ruled out the possibility of a simple Pummerer mechanism and confirmed that the dication was a key intermediate.[152]



Even more interesting is the observation that all attempts of direct deprotonation of stable dication **38** by a number of strong bases have failed. All of the investigated bases—Grignard reagents, organolithium compounds, and alkoxides—act as one-electron electron donors toward the dication thus leading to formation of the corresponding sulfide **10**.[183] One-electron oxidation transforms carbanionic reagents into radicals which undergo dimerization. For example, reaction of fluorenyllithium with dication **38** afforded the fluorenyl dimer **134**, as well as regenerated fluorene.

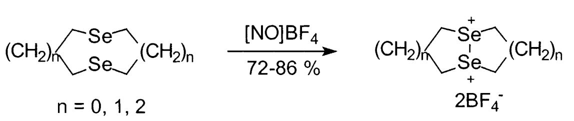


This mechanism is confirmed by generation of a stable radical from 9-mesitylfluorenyllithium.[169] Such bases as sodium methylate, potassium *tert*-butoxide, and lithium diisopropylamide reduce dication **38** to bis-sulfide **10** without any side products thus indicating that the dication is not deprotonated.[169]

IV. Se–Se, Te–Te, and Mixed Dications

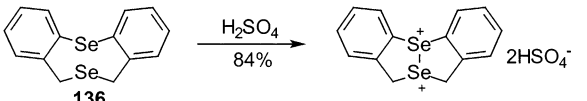
The larger atomic radius and larger polarizability of selenium and tellurium together with the lesser electronegativity of these elements results in increased stability of the corresponding dications. Similarities in chemical properties and electronic structure allow for formation of mixed dichalcogen dications as well.

Synthetic approaches to selenium, tellurium, and mixed dications are similar to the methods used for disulfonium dications. Oxidation of bis-selenides to diselenonium dications **135** with two equivalents of nitrosonium salts, $NOBF_4$, $NOPF_6$,[184] occurs more readily than the oxidation of sulfides and the corresponding dications are formed in better yields.[169,185]

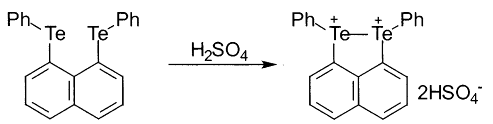


135

Because the redox potential of selenides is sufficiently low, oxidative generation of Se–Se and S–Se dications on treatment with sulfuric acid is more general than in the case of disulfonium dications, where it was efficient only for the most easily oxidizable bis-sulfides. For example, formation of dications **137** and **139** occurs readily after the corresponding bis-selenide **136** and bis-telluride **138** are dissolved in sulfuric acid.[186–188]

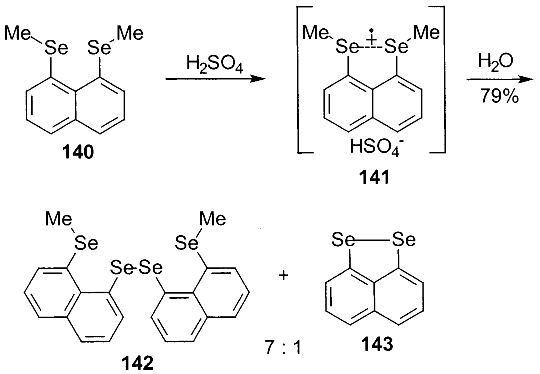


136 **137**



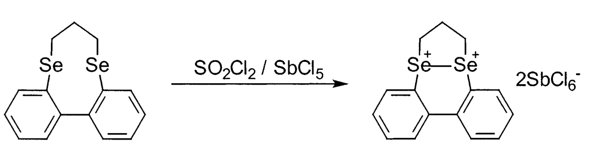
138 **139**

The only limitation of this method is the low stability of some substrates in concentrated sulfuric acid. For example, oxidation of bis-selenide **140** with H_2SO_4 followed by hydrolysis led to a mixture of diselenides **142** and **143** formed by degradation of radical cation **141.**[189]



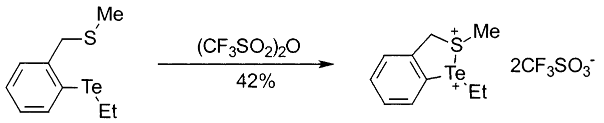
140 **141** **142** **143**

Diselenium dication **144** is also formed in the reaction of the corresponding bis-selenides with a 1:2 mixture of sulfuryl chloride and antimony pentachloride.[152]



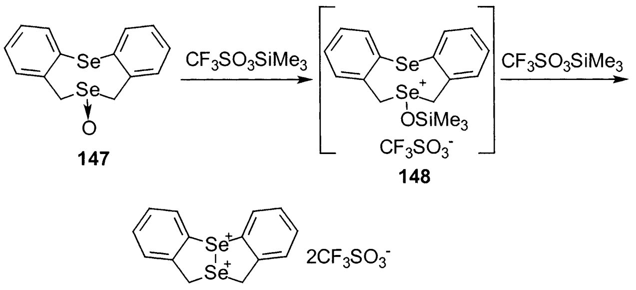
144

The possibility that selenium and tellurium containing dications may be synthesized by direct oxidation with triflic anhydride was investigated only recently.[190] An example is provided by the preparation of dication **146** from mixed bis-chalcogenide **145.**



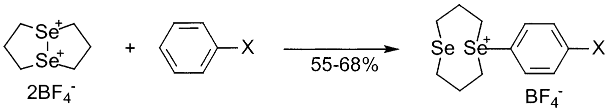
145 **146**

The most versatile approach to disulfonium dications—the reaction of triflic anhydride with monosulfoxides of bis-sulfides—has certain limitations in the case of selenium due to the lability of selenoxides which contain β-hydrogen atoms.[191–193] Trimethylsilyl triflate was used instead of triflic anhydride for synthesis of dication **149** from a selenoxide **147.**[194] In this case, the mechanism of dication formation is analogous to the reaction with triflic anhydride with the only difference that trimethylsilyloxyselenonium cation **148** is formed as an intermediate.



147 **148** **149**

Although diselenonium, ditelluronium, and mixed sulfonium–selenonium dications can exhibit either oxidative or electrophilic properties, substitution at the onium chalcogen atom is more typical in reactions with nucleophiles that proceed as typical nucleophilic substitutions at the onium atoms.[169] Due to the increased stability of heavier dichalcogenium dications, they react only with highly activated substrates such as aniline and *N*,*N*-dimethylaniline, but no reaction is observed with phenol and diphenylamine.[184] Reactions of ditelluronium dications with activated aromatics are also not known.[185]

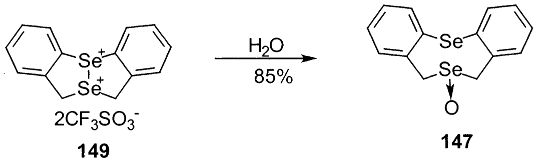


150 **151**

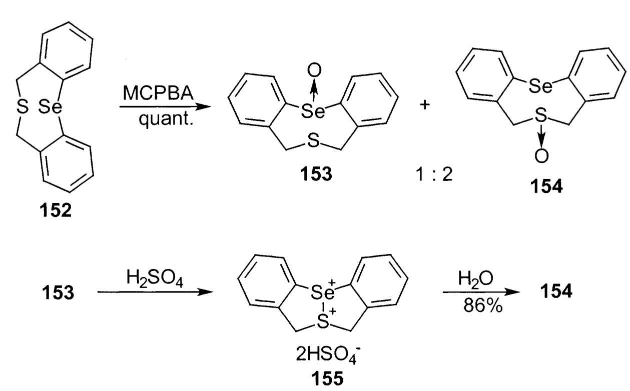
X = NH_2, NMe_2

The lesser electrophilic activity of the derivatives of selenium and tellurium is also displayed in their hydrolysis. In general, all diselenonium dications are more stable toward hydrolysis than the corresponding disulfonium dications. 1,5-Diselenoniabicyclo-

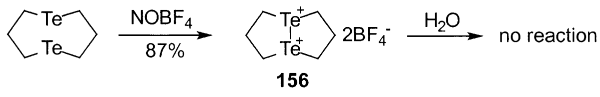
[3.3.0]octane **150**, which is expected to be hydrolyzed to an unstable selenoxide, is stable in water.[195] On the other hand, dication **149** is hydrolyzed by aqueous carbonate solution at a moderate rate to give selenoxide **147**.[194]



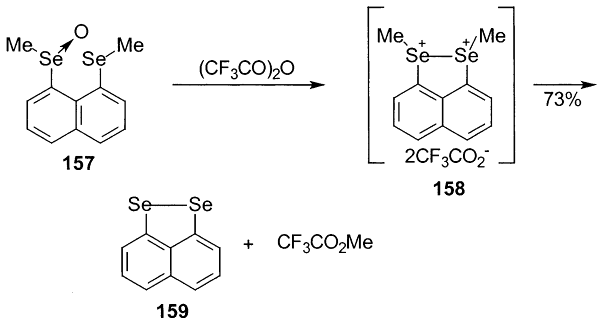
It is known that selenides are oxidized by *m*-chloroperbenzoic acid more easily and in higher yields than sulfides. Oxidation of heterocycle **152** leads to a mixture of the corresponding selenoxide **153** and sulfoxide **154**. However, hydrolysis of mixed S−Se dication **155,** prepared by treatment of selenoxide **153** with sulfuric acid, furnishes only sulfoxide **154** indicating the higher electrophilicity of sulfonium center in dication **155**.[196]



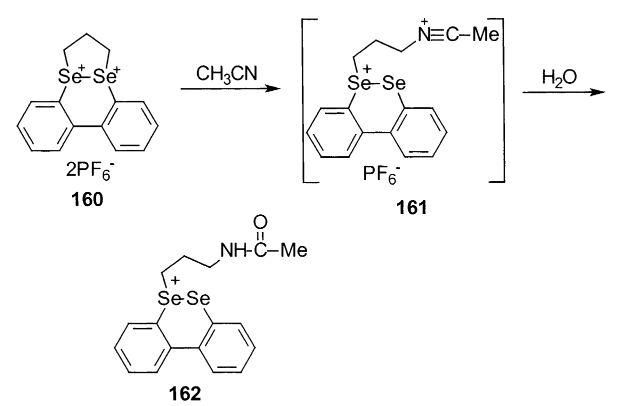
The Te−Te dication **156** is sufficiently stable toward hydrolysis, and its oxidative properties can be studied in aqueous solution.[185]



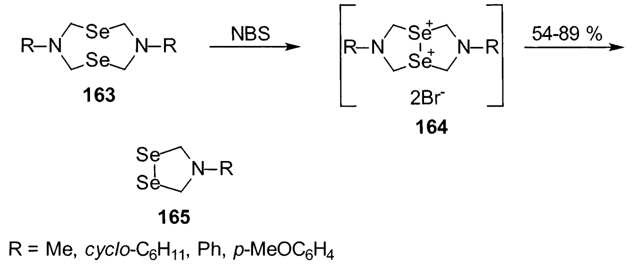
In the case of most labile compounds, substitution at the carbon atom of diselenonium and ditelluronium dications is also a possible pathway. For example, formation of diselenide **159** from selenoxide **157** was explained by demethylation of intermediate dication **158** with trifluoroacetate anion.[197]



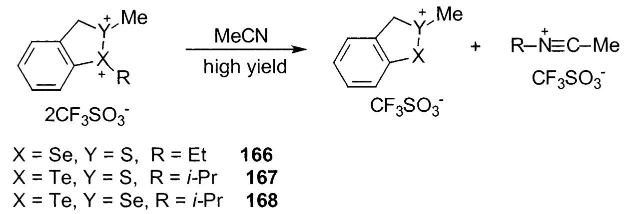
Dealkylation of salt **160**, which is stable up to −20 °C, leads to formation of a nitrilium salt **161**. The latter is transformed to amide **162** upon hydrolysis.[137]



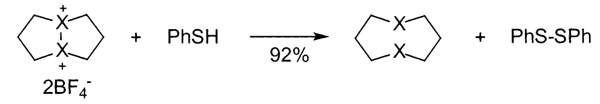
Dealkylation of intermediate diselenonium dication **164** was suggested as the key step in the oxidative synthesis of 1,2,4-diselenazolidines **165** from eight-membered heterocycles **163**.[198]



Dealkylation is the main direction in the decomposition of mixed dications **166**−**168**. Stability of these dications strongly depends on the nature of the chalcogen and substituents.[190] For example, deethylation of the Se−S dication **166** occurs at 0 °C, the corresponding Te−S dication **146** is stable even upon heating, whereas the isopropyl analogues **167** and **168** decompose at room temperature. In general, the order of stability is consistent with the difference in electronegativities and changes as follows: Te $\gg$ Se $>$ S.[190,168] Similar to the dealkylation of disulfonium dications, kinetic studies prove that all nucleophilic substitutions at the α-carbon atom of Se and Te containing dications follow the S_N1 mechanism.[152]

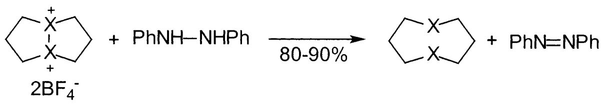


The oxidative properties of ditelluronium and diselenonium dications were studied using the same substrates used for the study of the oxidative properties of disulfonium dications. For instance, interaction of thiophenol with either the diselenonium dication **150** or the ditelluronium dication **156** leads to almost quantitative formation of diphenyl disulfide and reduced bis-chalcogenides.[184,185,195]



X = Te **156**
X = Se **150**

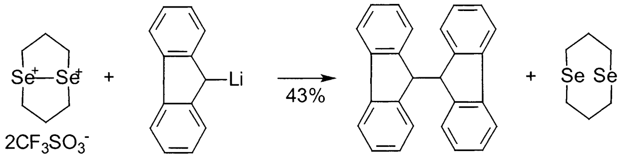
Reduction of diselenonium and ditelluronium dications with 1,2-diphenylhydrazine in the presence of diazabicyclooctane affords the corresponding bis-selenides and bis-tellurides in good yields.[184]



X = Te **156**
X = Se **150**

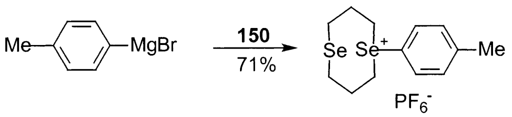
Reduction of diselenonium **150** and ditelluronium dication **156** with sodium borohydride gives the same products as above but proceeds quantitatively.[199] Reaction with $NaBD_4$ does not lead to any incorporation of deuterium at the α-carbon position, thus indicating a direct electron-transfer rather than an elimination-addition mechanism observed for a corresponding hydrazinium dication derived from bicyclo-[3.3.3]undecane.[199]

Just as disulfonium dication **38**, diselenonium **150** and ditelluronium dication **156** do not undergo deprotonation. Instead, reaction of dication **150** with fluorenyllithium affords bis-selenide and fluorene dimer **134**. The Li-organic compound serves as a one-electron donor and is transformed to fluorenyl radical intermediate which undergoes dimerization.[169]



150 **134**

Unlike organolithium compounds, a softer Lewis base such as *n*-tolylmagnesium bromide reacts with diselenonium dication **150** to give selenonium salt **169**, a product of nucleophilic substitution at the onium atom.[200]



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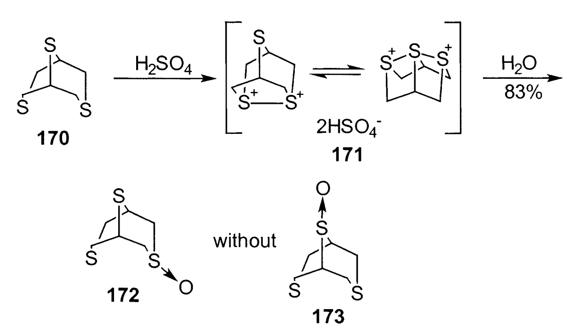
V. Trischalcogen Dications

Generation of disulfonium dications involves stabilization of the cationic centers on the sulfur atoms through formation of a new S−S bond between the two sulfonium centers. When such an interaction involves more than two chalogen atoms, it leads to formation of new interesting types of dications which contain hypervalent central atoms, such as sulfurane, selenurane, or tellururane atoms. These dications are different from similar structures in which the central chalcogen atoms are in the usual two-coordinated environment, such as the products of double alkylation of the end atoms in tri- or polychalcogenides. The most studied compounds of this class are trichalcogen dications. Methods of synthesis as well as chemical properties of these compounds are very similar to those of the corresponding dichalcogen dications.[167]

One can use the same methods for generation of trithio dications as for synthesis of disulfonium dications, i.e., oxidation of suitable tris-sulfides with concentrated sulfuric acid or with nitrosonium salts having nonnucleophilic anions, as well as reaction of a corresponding monosulfoxide with either triflic anhydride or sulfuric acid.[201]

Treatment of 3,7,9-trithiabicyclo[3.3.1]nonane **170** with concentrated sulfuric acid or 2 equiv of a nitrosonium salt leads to oxidation of the trisulfide with formation of a dication **171**, as in the case of a bis-sulfide. NMR spectra do not allow unambiguous assignment of a structure to this dication involving bonding of all three sulfur atoms.[202] Moreover, **171** yields sulfoxide **172** and does not lead to sulfoxide **173** with oxygen at the middle sulfur atom, indicating that contribution of the strained sulfurane structure to the general equilibrium is insignificant.



170 **171** **172** **173**

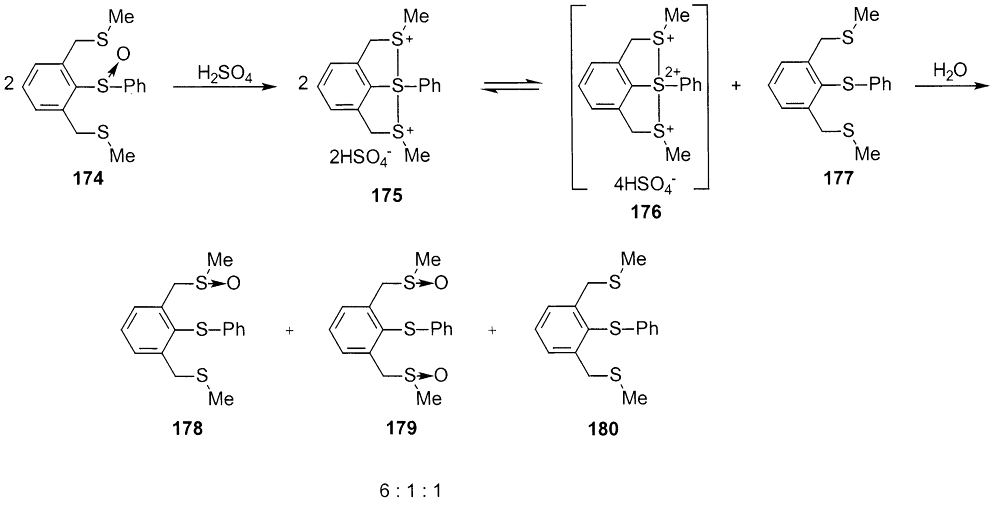
Stereochemical features of (2,6-bismethylthiomethylphenyl)phenylsulfide **174** favor formation of a sulfurane dication **175**.[203] Treatment of monosulfoxide **174** with concentrated sulfuric acid resulted in formation of the corresponding trithio dication **175** which was detected by NMR spectroscopy. Hydrolysis of this dication afforded an equimolar mixture of disulfoxide **179** and reduced tris-sulfide **180** in addition to monosulfoxide **178**. This can be explained in terms of an equilibrium involving a dication with an intermolecular S−S bond. The authors, however, suggest that this result indicates disproportionation of the dication **175** to tetracation **176** and starting tris-sulfide **177** (Scheme 8).[204]

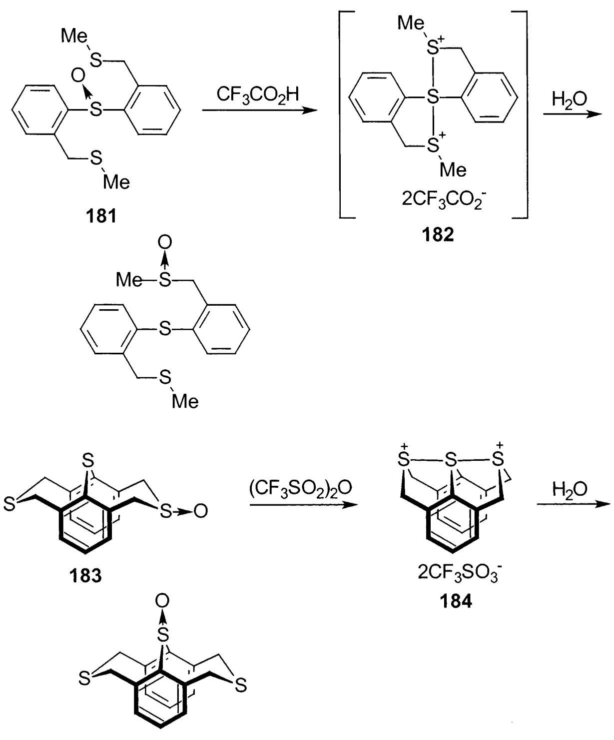
The sulfuranyl dication **182** is postulated to be involved in the 1,5-oxygen migration observed in the reaction of monosulfoxide **181** with trifluoroacetic acid. Note that in this case formation of the disulfoxide and the reduced tris-sulfide is not observed.[156]

Studies of trithia dications formed from cyclic sulfides afforded more convincing evidence for formation of these species. Crystalline dication **184** prepared by reaction of monosulfoxide **183** with triflic anhydride is sufficiently stable to be isolated and studied spectroscopically.[205]

It is interesting that sulfurane dication **184** leads only to aromatic sulfoxide **185**, while the usual acid-catalyzed oxygen transfer which is mediated by disulfonium formation of a dication occurs from aromatic sulfoxide to aliphatic sulfide.[101,102] The

Scheme 8





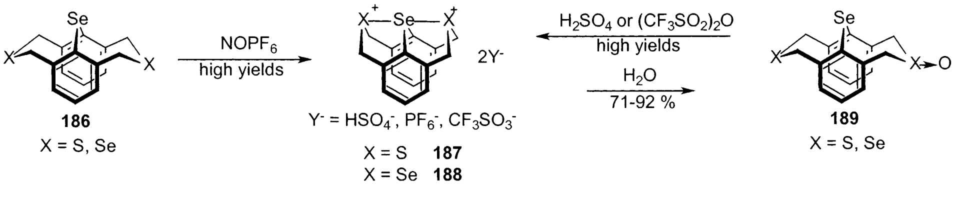
direction of hydrolysis, similar to the case of dication **32**, results from rigidity of the molecular skeleton which moves the "aromatic" sulfur atom out of conjugation with the benzene rings.[205] Additional evidence for formation of a dication sulfurane is the change in the conformation of the eight-membered ring. When the trithia dication **184** is generated, formation of the transannular bond between the three sulfur atoms leads to a boat−boat conformation, although in the starting sulfide and sulfoxide the most stable geometry corresponded to a chair−chair conformer.[205]

Other trichalcogen dications containing either one or two different chalcogen atoms were prepared and investigated starting from similar structures (Scheme 9). Selenurane dications **187**, **188** were obtained either by oxidation of a trichalcogenide **186**, or by reaction of concentrated sulfuric acid or triflic anhydride with a corresponding oxide **189**.[206]

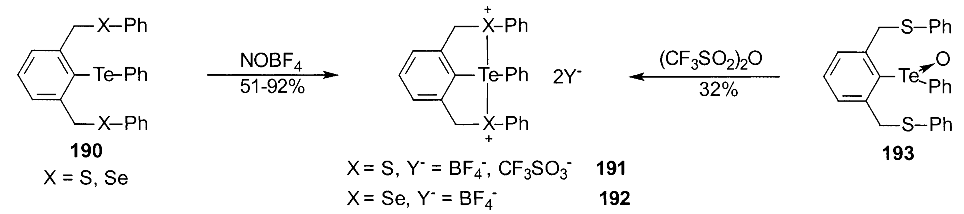
The structure of these compounds was established by NMR spectroscopy and by single-crystal X-ray analysis of a triselenium dication **188** with trifluorosulfonate counterions. A large spin−spin coupling constant (210 Hz) between the selenonium and selenurane atoms observed in ^{77}Se NMR also indicates formation of a chemical bond between these atoms.[207] Conformational changes associated with formation of selenurane dications **188** and **187** from the corresponding tris-chalcogenide **186** are analogous to those found for tris-sulfides: formation of the dication is accompanied by transition from a chair−chair to a boat−boat conformation.[206] According to the X-ray data,[208] triselenium dication **188** has a bent structure with the C(Ar)−Se−C(Ar) angle equal to 95.6°. The geometry is consistent with a selenium atom in the center of a trigonal bipyramid surrounded by the two selenonium atoms occupying the axial positions and the two Se−C bonds and the lone electron-pair being the equatorial ligands and Se···Se distances, which are 2.65 and 2.56 Å longer than a normal Se···Se bond in diselenide (2.34 Å). The Se−Se−Se angle (170°) corresponds to the angle expected for a two-electron three-center bond.

The charge distributions in triselenium dications were characterized[208] by ab initio calculations at the RHF/3-21G* level using the "Natural Population Analysis" method.[209,210] The positive charge is delocalized exclusively at the three selenium atoms without involvement of the phenyl rings. The natural charge at the central atom is +1.02, while at the end

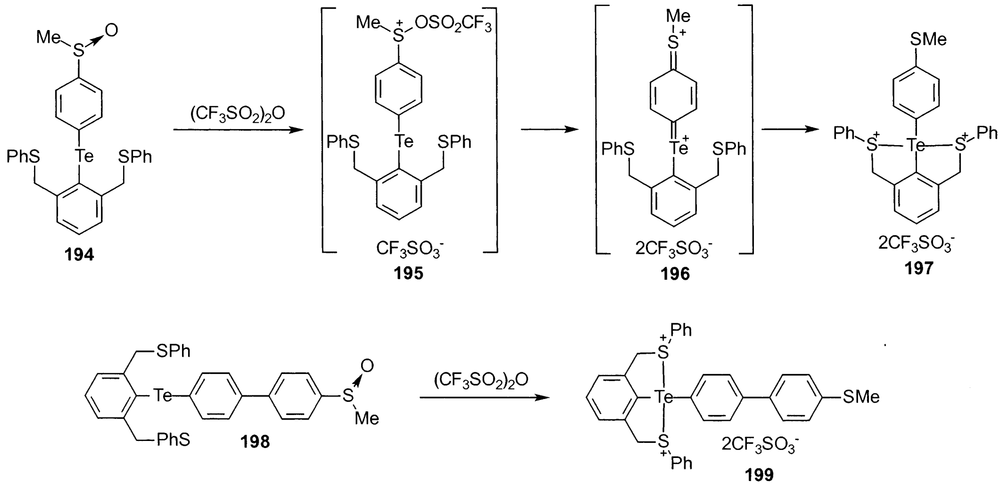
Scheme 9



Scheme 10



Scheme 11



atoms it is +0.70. The Mulliken Se···Se bond order is 0.59. [211]

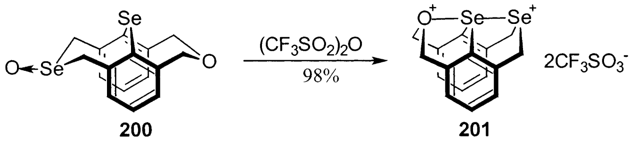
Tellururane dications **191**, **192** were obtained by oxidation of the corresponding tris-chalcogenides **190** with nitrosonium tetrafluoborate or by reaction of triflic anhydride with a telluroxide **193** (Scheme 10).[212]

These dications were characterized by NMR spectroscopy and X-ray crystallography.[167] The spin–spin coupling constant of the end selenium atoms through the central tellurane atom is 71 Hz, confirming bonding of the three chalcogen atoms. This is the first experimentally measured example of a spin–spin interaction through a three-center four-electron bond. X-ray data agree well with the tellurane structure of the dication: the central tellurium atom has the trigonal–bipyramidal configuration with the sulfur or selenium or selenium atoms in the axial positions and two Te···C bonds and the lone pair in the equatorial positions.[212] The Se···Te distance (2.78 Å) and the S···Te distance (2.67 Å) are slightly longer than the normal single Se···Te and S···Te bond lengths (2.52 and 2.36 Å, respectively). The X···Te···X angle is close to 160°, as expected for a tellurane structure.

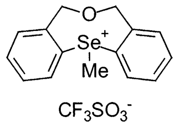
Natural atomic charges at the RHF/3-21G* level of theory indicate that the positive charge is localized at the three chalcogen atoms.[212] The tellurium atom in a sulfonium environment has the charge of +1.60, in the selenonium environment the charge is slightly lower (+1.42). The charges at the sulfur and selenium atoms are equal to +0.49 and +0.61, respectively. Thus, polarizations of bonds between chalcogens correspond well to those usually observed in hypervalent compounds.[213]

An interesting way to generate a telluronium dication involves electron transfer through a π-conjugated system to a spatially remote sulfoxide sulfur atom in a “domino” manner (Scheme 11). Treatment of substrate **194** with triflic anhydride results in reduction of the terminal sulfoxide group with simultaneous oxidation of the tellurium atom in the para position and formation of a trichalcogen dicationic moiety **197**[214] through the intermediate sulfonium salt **195** and quinoid structure **196**.

The only example of an organic dicationic system with participation of oxygen was described for the selenuranium dication **201** prepared by reaction of selenoxide **200** with triflic anhydride.[215]



The ^{1}H NMR spectrum indicates that formation of the selenurane structure **201** is accompanied by a change in the conformation of the eight-membered ring from a chair in starting material **200** to a chair–chair in product **201**. X-ray analysis of this dication confirmed the formation of a hypervalent structure with almost collinear geometry of the O–Se–Se moiety (165°) and a Se–Se bond (2.39 Å), which is only marginally longer than a Se–Se bond in diselenides (2.34 Å).[215] The distance between the central Se atom and oxygen (2.43 Å) is considerably shorter than the sum of van der Waals radii of selenium and oxygen (3.4 Å), but corresponds to a relatively weak interaction similar to the one found, for example, in the selenonium salt **202**, where the Se···O distance is 2.6 Å.[216] This indicates that resonance structure **203** with the positive charge localized at the oxygen atom is less important as a consequence of the higher electronegativity of oxygen. This can also explain the instability of dioxonium dications such as $H_4O_2^{2+}$, which have been studied only computationally.[217,218]



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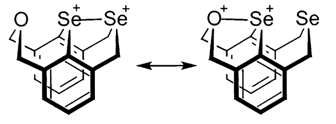
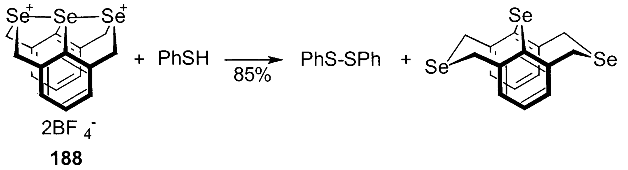
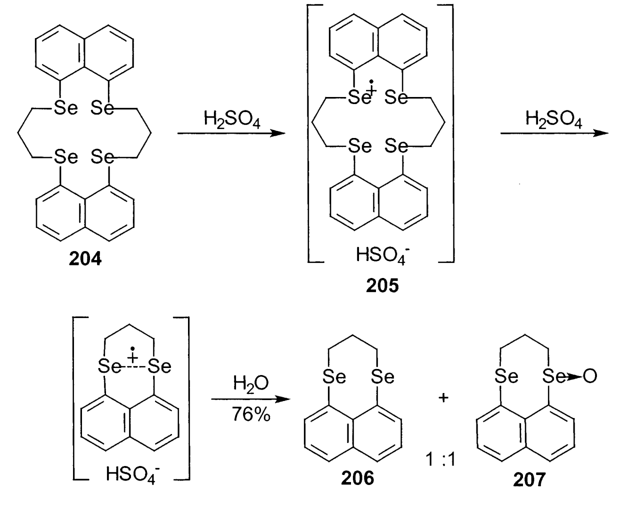


203

The chemical properties of trichalcogen dications are, in many ways, analogous to the properties of dichalcogen dications but are considerably less studied. Hydrolysis of chalcogenurane dications illustrates that nucleophilic substitution in such systems occurs preferentially at the onium chalcogen atom (Scheme 9). This rule is violated only for trithia dication **184** where substitution at the sulfurane atom is observed.[146] Similar to the usual dichalcogen dications, trichalcogen dications also display oxidative properties. For example, reduction of selenurane dication **188** is observed in reactions with Sm (II) salts, triphenylphosphine or thiophenol.[206]

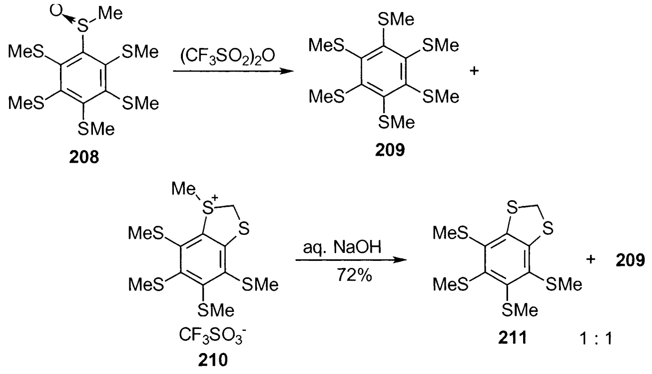


The possibility of generating a delocalized dication with four selenium atoms was studied by oxidizing tetraselenide **204** with concentrated sulfuric acid. Unfortunately, the only intermediate detected in this reaction was radical cation **205** which underwent ring-contraction instead of further oxidation. As the result, hydrolysis of the reaction mixture resulted in formation of eight-membered monoselenoxide **207** and bis-selenide **206**.[219]



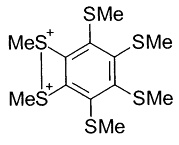
The possibility of generating a dication stabilized by interaction of six sulfur atoms was investigated in the case of hexakis(methylthio)benzene **209** (Scheme 12). Treatment of monosulfoxide **208** with triflic anhydride or with concentrated sulfuric acid led to formation of the reduced sulfide **209** and sulfonium salt **210** in a Pummerer-like reaction. Hydrolysis of this salt with aqueous base resulted in demethylation with formation of heterocycle **211**.[152]

Scheme 12



Experiments with deuterium-labeled starting material **208** have shown that all of the sulfur atoms become equivalent. This can be a consequence of either fast delocalization of the positive charge within the six sulfur atoms or by a fast equilibrium between the dicationic pairs.

Since the intermediate dication is too labile to be observed by physical methods, it was studied by DFT calculations (B3LYP/6-31G*).[220] Five different structures were considered: three with σ delocalization of the positive charge (localized disulfonium dication **212**, trithia dication **213** (3c-4e) and completely delocalized hexathia dication **214** (6c-10e)), as well as the two π-delocalized structures of quinoid **215** and anti-quinoid **216** type. The results indicate that the preferred delocalization pattern involves σ delocalization of the positive charge between the six sulfur atoms equally with formation of a cyclic six-center 10-electron system which possesses Hückel aromaticity. A similar structure was suggested for hexaiodobenzene dication, where the aromatic ring current involving the six iodine atoms was observed experimentally by ^{13}C NMR spectroscopy.[221]



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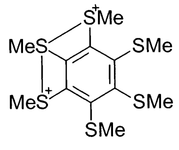

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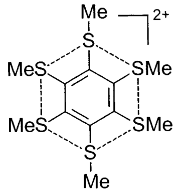

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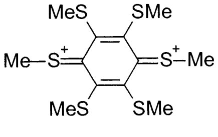

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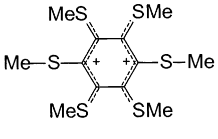

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VI. Polyatomic Chalcogen Dications

The chemistry of organic dichalcogen dications has interesting parallels to the chemistry of inorganic homo- and polynuclear chalcogen dications. Polyatomic dications of sulfur, selenium, and tellurium were discovered at the end of the 60s, before isolation of first organic disulfonium dication, during the

Table 4. Polyatomic Chalcogens Dications[a]

no. of atoms	4	6	8	10	> 10
	S_4^{2+} Se_4^{2+} Te_4^{2+}	$Te_3S_3^{2+}$ $Te_2Se_4^{2+}$ Te_6^{2+}	S_8^{2+} Se_8^{2+} Te_8^{2+} $Te_2Se_6^{2+}$	Se_{10}^{2+} $Te_2Se_8^{2+}$	S_{19}^{2+} Se_{17}^{2+}

[a] Polymeric polyatomic dications of chalcogens are not including in this table.

investigation of intensively colored solutions known for almost a century. These solutions are formed when chalcogens are dissolved in concentrated sulfuric acid or oleum.[222] Subsequent work by Gillespie, Bierrum, and Corbett showed that the color of these solutions is due to the presence of chalcogen polycations. The first dications studied by X-ray crystallography were a hydrosulfate of tetraatomic selenium dication Se_4^{2+} [223] and tetrachloroaluminates of octaatomic selenium dication Se_8^{2+} [224] and tetraatomic tellurium dication Te_4^{2+}.[225]

These results became a starting point for further studies of polyatomic chalcogen dications. Up to now, a large volume of reliable data on synthesis and structure of a number of homo- and heteropolyatomic chalcogen dications has been accumulated (Table 4).[226]

The main results of such studies has been presented in several reviews,[227−229] including some published recently.[220,236] Therefore, we will consider only selected aspects of synthesis, structure, and properties of polyatomic chalcogen dications where the analogies (or contrasts) with the chemistry of organic dichalcogenium dications are especially appealing. We have also included a few chemical transformations of inorganic chalcogen dications that were not discussed in previously published reviews.

A. Preparation

Similar to their organic counterparts, inorganic chalcogen dications are highly electrophilic. Counterions that are capable of stabilizing these reactive species are conjugate bases of very strong Lewis acids, anions such as AsF_6^-, SbF_6^-, SO_3F^-, $AlCl_4^-$. The preparation of chalcogen polycations is carried out in such nonnucleophilic media as H_2SO_4, HSO_3F, HF, AsF_3, and SO_2. Some inorganic dications are more stable thermally, which makes it possible to use melted $Na[AlCl_4]$ as the reaction medium.

There are two main approaches to polyatomic chalcogen dications. The first approach which is similar to the synthesis of disulfonium dications from bis-sulfides is based on the use of suitable one-electron (WCl_6, WF_6, PtF_6, $SO_3F^\bullet$ radical) or two-electron oxidizing agents (SbF_5, AsF_5), as in examples (3) and (4).[231]

$$4Se + S_2O_6F_2 \xrightarrow{HSO_3F} Se_4[SO_3F]_2 \tag{3}$$

$$S_8 + 3AsF_5 \xrightarrow{SO_2} S_8[AsF_6]_2 + AsF_3 \tag{4}$$

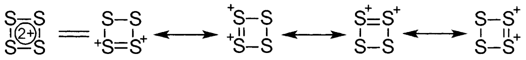
The other approach which is analogous to the generation of disulfonium dications from a sulfoxide and sulfide in the presence of a suitable Lewis acid is based on synproportionation between an elementary chalcogen and the corresponding chalcogen halogenide, with the latter being activated with a Lewis acid acceptor of the halogenide anion ($AlCl_3$, $Ag[Sb(OTeF_5)_6]$, $BiCl_3$, $NbOCl_3$). Typical examples are generations of a tellurium dication (5) and a selenium dication (6).[232]

$$7Te + TeBr_4 + 4Ag[Sb(OTeF_5)_6] \xrightarrow{SO_2} 2Te_4[Sb(OTeF_5)_6]_2 + 4AgBr \tag{5}$$

$$15Se + SeCl_4 + 4AlCl_3 \xrightarrow{Na[AlCl]_4} 3Se_8[AlCl_4]_2 \tag{6}$$

A detailed survey of these synthetic approaches is given in a recent review.[229] Recently, a new method for preparation of polyatomic chalcogen dications by solid-state synthesis, without use of any solvents, was described. This method permitted synthesis of a number of dicationic salts (Te_8^{2+}, T_6^{2+}), which were impossible to prepare by other methods. This technique has been discussed in reviews.[226,233]

The principal differences in the structures of organic and inorganic chalcogen dications are well illustrated by the tetraatomic cations Te_4^{2+}, Se_4^{2+}, and S_4^{2+}. On the basis of the octet rule and count of valence electrons, one might suggest that the dications contain chalcogen atoms of two different types—two divalent and two positively charged trivalent atoms. However, according to X-ray analyses of a number of such salts, all of the chalcogen atoms are equivalent. They are located in the corners of a square and equally participate in delocalization of the positive charge.[234−236] According to a number of quantum-mechanical studies such a dication can be represented as a typical 6π aromatic system **217** with equal contributions from four Lewis structures.[237−239] This bond order explains why the distance between the adjacent chalcogen atoms is slightly less than the length of a corresponding single bond which is equal to 2.66 Å for Te_4^{2+}, 2.28 Å for Se_4^{2+}, and 1.98 Å for S_4^{2+}.[228] This structure presents an interesting contrast to the cyclobutadienyl dication which is nonplanar (vide infra).[357]



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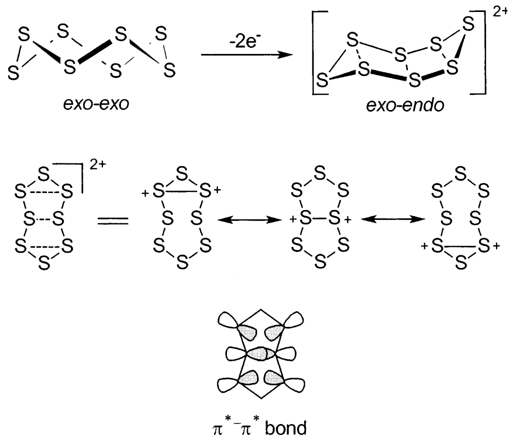
Involvement of neighboring atoms in the positive charge delocalization is a characteristic feature of polyatomic chalcogen dications. As a consequence, a description of these structures in terms of the usual localized σ bond framework with two onium chalcogen atoms is incorrect. This is a significant difference from the situation in organic disulfonium dications and their analogues. The degree of such delocalization depends on the nature of the inorganic dications, which, in general, are typical cluster compounds.

The structure of octaatomic chalcogen dications provides a good illustration of this point. According to X-ray data, initially obtained for the S_8^{2+} and Se_8^{2+} dications, their structure derives in a simple way from the well-known structure of the corresponding

Chart 1



nonoxidized free elements which exist in the form of a crown-shaped eight-membered ring.[240] Removal of a pair of electrons from the S_8 molecule leads to a change in conformation from *exo*−*exo* to *exo*−*endo* and to a decrease of the distance between the atoms in the first and fifth positions of the ring from 4.68 to 2.86 Å (Chart 1). Initially, formation of a transannular bond between the sulfur atoms 1 and 5 was invoked to explain these changes and the dication was believed to have a bicyclic [3.3.0] structure shown in the chart.[228] Such an interpretation is consistent with positive charge localization at the bridgehead sulfonium atoms and with a structure that is analogous to the structure of organic disulfonium dication **12** prepared from 1,5-dithiocyclooctane, with the methylene bridges substituted with divalent sulfur atoms.

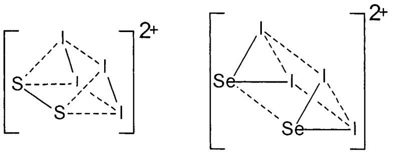
However, a closer look shows that this simple Lewis model is incorrect. The transannular contact between the sulfur atoms at positions 1 and 5 is shorter than in S_8, but it is still 0.8 Å longer than a single S−S bond. In addition, the pairs of atoms at the second and fourth positions, as well as at the eighth and six positions, are at a comparable distance, 2.92 and 3.03 Å, respectively. Modern interpretation of the chemical bonding in the S_8^{2+} dication suggests formation of a weak delocalized $\pi^*-\pi^*$ bond as a result of overlap of six 3p orbitals of the sulfur atoms located at the opposite sides of the eight-membered ring (Chart 1).[230] Formation of a bond with participation of six atomic orbitals having 10 electrons results in delocalization of the additional bonding and the positive charge between all of the six-atoms (Chart 1). Various quantum-mechanical calculations which were carried out recently confirm the existence of $\pi^*-\pi^*$ bonding in the octachalcogen dication.[241−243] Such salts as $Se_8[AlCl_4]_2$ and $Te_8[ReCl_6]$ contain the Se_8^{2+} and Te_8^{2+} ions which are, according to X-ray crystallography data, analogous in structure to the S_8^{2+} dication.[244,245]

Such dications as $S_2I_4^{2+}$ and $Se_2I_4^{2+}$[246] can also be formally classified as belonging to the general class of dications containing two directly bonded positively charged chalcogen atoms.[247] The first dication was isolated as the only characterized product from the reaction of S_4^{2+} with an excess of iodine. Alternatively, it can be prepared in quantitative yield by direct reaction of arsenic (V) fluoride, iodine, and elementary sulfur (7).[248]

$$1/4S_8 + 2I_2 + 3AsF_5 \xrightarrow{SO_2} S_2I_4[AsF_6]_2 + AsF_3 \qquad (7)$$

However, the X-ray data indicate a cluster-like character of the dication containing separate $S_2I_4^{2+}$ groups with a distorted triangular prismatic geometry. The S−S bond length is equal to 1.83 Å, which is smaller than the distance of 1.89 Å in the neutral diatomic molecule S_2 and is the shortest S−S distance in all known compounds of sulfur.[249] The structural features of this dication are explained by the very similar ionization potentials of the I_2 and S_2 molecules, 9.40 and 9.36 eV, so chemical bonding in this cluster can be explained as a weak $\pi^*-\pi^*$ interaction of partially charged molecules, $2I_2^{+0.66}$ and $S_2^{+0.66}$ (Chart 2).

Chart 2



Dication $Se_2I_4^{2+}$ was synthesized similarly to its sulfur analogue by reaction of $I_2Sb_2F_{11}$ with Se and has properties of a typical cluster compound (8).[250]

$$2I_2Sb_2F_{11} + 2Se \xrightarrow{SO_2} Se_2I_4[Sb_2F_{11}] \qquad (8)$$

Although the structure of this compound can be described as a distorted triangular prism, this compound, unlike $S_2I_4^{2+}$, has a strong Se−I bond. The length of this bond is 2.45 Å which is shorter than 2.51 Å in SeI_3^+. Bonding in this cluster dication can be described as an interaction of two SeI^{2+} radical cations by means of a weak $\pi^*-\pi^*$ bond (Chart 2).[251]

B. Chemical Properties

The chemical properties of polyatomic chalcogen dications have been studied only to a small extent and not systematically. Like organic dichalcogenium dications, the inorganic dications display electrophilic and oxidative properties but are much more reactive. As noted earlier, all cluster chalcogen dications are unstable in nucleophilic media and are rapidly hydrolyzed in the presence of traces of water with disproportionation to elementary chalcogen and its dioxide (9).[226]

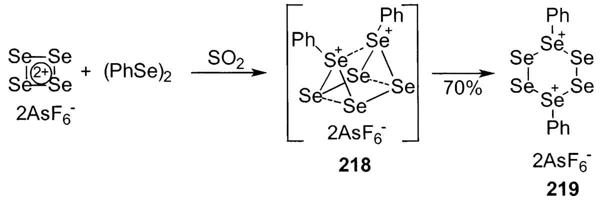
$$2Se_4^{2+} + 6H_2O \rightarrow 7Se + SeO_2 + 4H_3O^+ \qquad (9)$$

The interaction of polycations with free chalcogens leads, in some cases, to new cluster compounds. This also illustrates the electrophilic character of these polycations (10).[252]

$$Se_8[AsF_6]_2 + 2Te \xrightarrow{SO_2} Se_8Te_2[AsF_6]_2 \qquad (10)$$

Reaction of the aromatic tetraatomic selenium dication with diphenyldiselenide affords a compound

$Ph_2Se_6^{2+}$ (**219**). X-ray crystallography shows that this has a six-membered ring made of six selenium atoms in the boat conformation and two phenyl radicals at the "*para*" positions.[253]

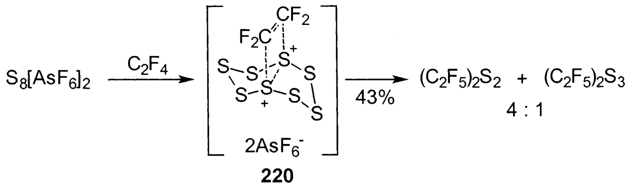


It has been suggested that this reaction proceeds through a complex which is similar to the π complex observed in electrophilic aromatic substitution and by formation of a triangular prismatic intermediate **218** in a second step.[253]

Reactions of S_8^{2+}, S_4^{2+}, Se_8^{2+}, Se_4^{2+}, and Te_4^{2+} dications with tetrafluoroethylene and hexafluoropropylene usually result in formation of a mixture of products, mainly perfluoropolychalñogenides.[254,255] For example, exposure of solid $Se_8[AsF_6]_2$ to an excess of tetrafluoroethylene led to formation of pentafluoroethyldiselenide with admixture of the corresponding triselenide in a total yield of 66%.[256]

$$Se_8[AsF_6]_2 + C_2F_4 \xrightarrow[66\%]{} (C_2F_5)_2Se_2 \underset{99:1}{+} (C_2F_5)_2Se_2 + \ldots$$

The interaction of $S_8[AsF_6]_2$ with tetrafluoroethylene proceeds analogously. It is interesting that the authors[257] suggest a reaction mechanism which involves addition of the tetrafluoroethylene π bond to the transannular bond of the S_8^{2+} dication with formation of a cyclic key intermediate **220**. This provides a very close analogy to the synchronous mechanism for the addition of organic disulfonium dication to alkenes. However, modern ideas about the nature of bonding in octachalcogen dications render actual formation of such an intermediate unlikely.



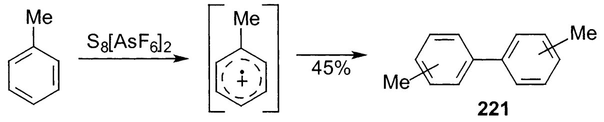
Alternatively, this transformation can be explained in terms of a free radical mechanism. An argument in favor of this mechanism is the propensity of the S_8^{2+} dication to dissociate into radical cations.

The presence of free radicals in solutions of the S_8^{2+} dication has been known for a long time. A measurable paramagnetism of different salts of this dication has also been traced to its dissociation to radical cations. The exact nature of these radicals is still a matter of debate. Initially, $S_4^{\bullet+}$ was detected by EPR, and its formation was explained by Coulombic explosion of the dication into two analogous monocations.[258] When radical cation $S_5^{\bullet+}$ was detected in solutions of S_8^{2+} it was proposed to be responsible for the color and paramagnetic properties of these solutions. Thermodynamic data shows that S_8^{2+} is unstable in the gas phase and dissociation into all stoichiometrically possible combinations of $S_n^{\bullet+}$ particles, $n = 2-7$, and that formation of $S^{2\bullet+}$, $S_5^{\bullet+}$, $S_7^{\bullet+}$ is the most favorable energetically.[230]

In general, radical transformations are typical for reactions of polyatomic chalcogen dications. Oxidation of such inert compounds as simple hydrocarbons with S_8^{2+} indicates the high oxidative potential of these salts. The reaction proceeds by a radical mechanism.[259] For example, reaction of $S_8[AsF_6]_2$ with propane leads to a mixture of isomeric sulfides and a disulfide in a total yield of 30%. An analogous oxidation is also observed for *n*-butane.

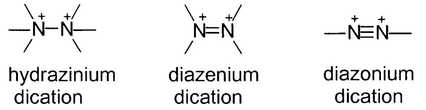
$$Se_8[AsF_6]_2 + C_3H_8 \xrightarrow[30\%]{} (iso\text{-}Pr)_2S\ (iso\text{-}Pr)_2S_2\ (iso\text{-}Pr)SPr \quad 50:56:1$$

The radical mechanism was confirmed by observation of the formation of a mixture of isomeric biphenyls **221** when toluene was oxidized with S_8^{2+}. The reaction was suggested as proceeding through an initial electron transfer from the aromatic system to the dication.



VII. N–N Dications

A particularly interesting and well-studied class of dications are N–N dications. It has been proposed that the N_2^{2+} dication participates in atmospheric processes in the ionosphere; this has been studied extensively both experimentally[260,261] and theoretically.[262,263] Recent results have been thoroughly discussed by Martin and co-workers[261] while the older research has been well reviewed by Wetmore and Boyd.[262] Depending on hybridization and substitution pattern of the positively charged nitrogen atoms, organic N–N dications, which were thoroughly studied by Nelsen and Alder, can be classified either as derivatives of hydrazine or as azo compounds. Differences in synthesis, structure, and chemical properties of hydrazinium and diazenium dications make their separate discussion worthwhile.

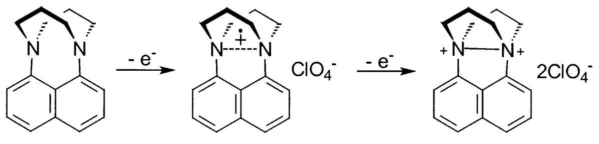


A. Hydrazinium Dications

1. Synthesis of Hydrazinium Dications

Oxidation of Cyclic Diamines. Aliphatic hydrazinium dications are formally products of exhaustive alkylation of hydrazine. Nevertheless, the first fully substituted hydrazinium dication (as well as its disulfonium analog) was prepared by oxidation of a diamine and not by alkylation of a hydrazine. 8,9,10,11-Tetrahydro-7*H*-7,11-propanonaphtho [1,8-*bc*]-

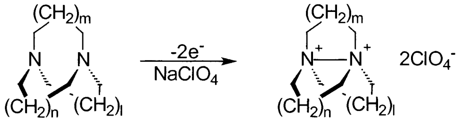
[1,5]diazocine **222** exhibited two reversible oxidation waves at 0.11 and 0.72 V vs SCE in acetonitrile. The first wave corresponds to the formation of radical cation **223,** the second wave indicates formation of dication **224**.[264] The second oxidation wave is reversible only at high scan speeds and only when a special drying technique is used. This observation is explained by the lability of dication **224** in the presence of traces of water.[265]



222 **223** **224**

Oxidation of amine **222** with SbF_5 in the nonnucleophilic solvent SO_2ClF was suggested for synthesis on a preparative scale of compound **224** as a hexafluoroantimonate salt.[264] Considerable amounts of the diprotonated form of diamine **222** were formed due to proton acid impurities present during the oxidation.[264]

The oxidation potential of diamine **222** is exceptionally low for a nonconjugated amine. Moreover, when Alder and co-workers investigated the electrochemical oxidation of a number of bicyclic diamines **225** with nitrogen atoms at the bridgehead position, they noted that formation of the corresponding hydrazinium dication **226** occurs at even lower oxidation potentials such as 0.1−0.2 V.



225 **226**

n, m, l = 1-3

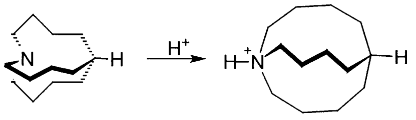
Further studies found that electrochemical reduction of mono- and bicyclic hydrazinium dications is irreversible. In other words, formation of dications due to oxidation of the corresponding linear and monocyclic amines does not occur.[266] Evidently, the unusually facile formation of tricyclic hydrazinium dications from bicyclic diamines occurs because of stereochemical features of the bicyclic compounds with medium size rings.[111]

Bicyclic compounds with small rings, common-sized rings and macrobicyclic compounds are common among organic substances and their structural features have been investigated in detail.[267] However, analogous medium size ring compounds are less well studied, despite the number of interesting properties which they exhibit. Alder has pointed out several "landmarks" of such structures:[268] (a) high strain due to steric repulsion between hydrogen atoms of the bridges; (b) *in*−*out* isomerism; (c) encapsulations of small species.

The feature that is particularly relevant to dication chemistry is that in compounds with nine and more atoms in the ring, the *in*−*out* conformation is preferred.[49] In this conformation, one of the bridgehead atoms projects inward to relieve ring strain. This process brings the bridgehead atoms closer. The energy gain in this conformation is so significant that the basicity of amine **227** (called "hiddenamine" by Alder) is about 10 orders of magnitude less than the basicity of triethylamine. Protonation of the nitrogen atom by solvent should result in its "pyramidalization" outward to form the more strained *out*−*out* conformation **228**—a highly unfavorable process.[269]

Table 5. Enthalpies of Hydrogenation of Several Propellanes

propellane	hydrogenation product	ΔH, kJ/mol
[2.2.2]propellane	bicyclo[2.2.2]octane	−280
[3.3.3]propellane	bicyclo[3.3.3]undecane	+25
[4.4.4]propellane	Bicyclo[4.4.4]tetradecane	+163



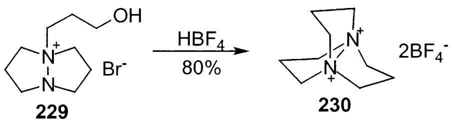
227 **228**

The stereochemical features of such bicyclic compounds facilitate formation of a bond between the bridgehead atoms ("the intra-bridgehead bond formation"). This tendency is well illustrated by the trends observed for the enthalphies of hydrogenation of propellanes (Table 5).[270]

In addition to electrochemical methods, oxidation with SbF_5 and nitrosonium salts—$[NO]BF_4$ and $[NO]PF_6$—was also used to prepare tricyclic hydrazinium dications.[271] Although yields were low, a systematic search for more suitable oxidizing agents was not conducted. This was probably due to the difficulty in synthesizing the required starting medium size bicyclic amines. In fact, many of these amines were synthesized for the first time by reduction of the corresponding tricyclic hydrazinium dications.[111]

Alkylation of Hydrazine Derivatives. Formation of doubly protonated hydrazinium dications as intermediates in rearrangements of various hydrazine derivatives is well-known.[272] However, the hydrazinium cation is a very weak base (second K_a of hydrazine ca. −1). The pentamethylhydrazinium cation is only half-protonated in 70% sulfuric acid.[273] The nucleophilicity of a hydrazinium cation is sufficiently low to prevent a second alkylation which would result in formation of a corresponding dication when ordinary alkylating agents are used. For example, an attempt to alkylate pentamethylhydrazinium cation by methylfluorosulfonate was unsuccessful.[274] In addition, hydrazinium dications are unstable under most conditions used for double alkylation of tetraalkylhydrazines.[275]

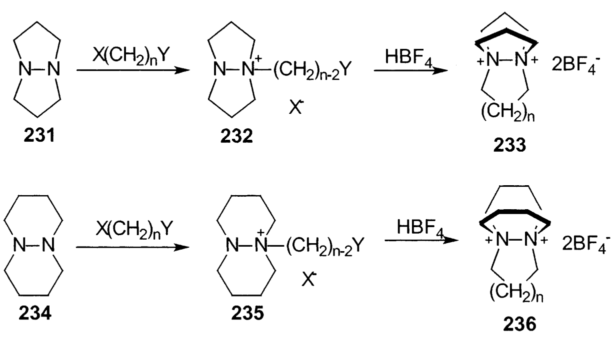
The first successful alkylation to give a hydrazinium dication was found serendipidously during an attempt to substitute bromide in ammonium salt **229** by tetrafluoroborate anion on treatment with 40% aqueous HBF_4.[111] Dication **230** was isolated instead.



229 **230**

This example provides a good illustration of the conditions necessary for preparation of hydrazinium dications. Due to the high sensitivity of these compounds to nucleophilic attack, the optimal conditions include absence of nucleophilic or basic anions in the reaction mixture and running the reaction at ambient temperature in a solvent capable of efficient solvation. Because it is impossible to maintain such conditions in the first alkylation step, the second step, preparation of the hydrazinium dication, should, when possible, be conducted separately from the alkylation.[111]

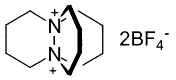
This method was used to prepare a number of hydrazinium dications from bicyclic hydrazines **231** and **234.**[275] In the first step, alkylation of the hydrazines with ω-halogen-substituted alcohols or α,ω-dihalogenides affords the corresponding hydrazinium salts **232** and **235**. These salts undergo further cyclization to give dications **233, 236** in yields up to 87% when treated with 40% HBF_4.[275]



X = Cl, Br; Y = Br, OH; n = 0-3

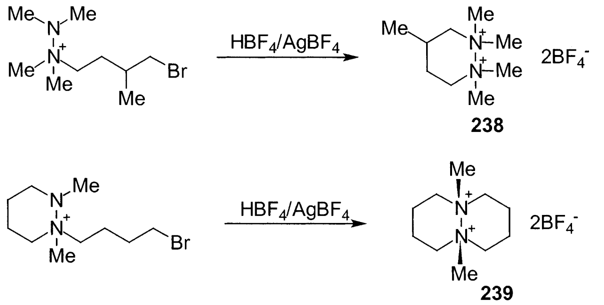
In the case of α,ω-dihalogenalkanes, both the rate of the second step and the reaction yield can be significantly improved if an equimolar amount of Ag_2O is used.[266] Yields of salts **233** are higher than in the case of salts **236**, an observation that is probably associated with the larger nucleophilicity of nitrogen in monocation **232** compared with that in **235** due to steric factors. Steric factors can also explain why it was impossible to obtain hydrazinium dication **236** when 4-bromobutanol was used. Cyclization of hydrazinium cation **234** with formation of a seven-membered ring does not occur. In the case of hydrazine **231**, the corresponding dication was obtained in 50% yield but only when the reaction was carried out in a mixture of CF_3COOH and $(CF_3CO)_2O$.[275]

X-ray analysis of salt **237** has shown that the structure of the dication is similar to the structure of [4.4.4] propellane, with all of the six-membered rings in the chair conformation.[276] The size of the C−N−C angle in the dication (109.0°) agrees with an increased inward pyramidalization compared with that in the corresponding diamine and radical cation which have C−N−C angles of 115.5° and 114.0° respectively. The N−N bond length, 1.53 Å, is significantly larger than in alkylhydrazines (1.45 Å)[277] and in diprotonated hydrazine − $N_2H_6^{2+}$ (1.44 Å, HF/6-31G* data).[278]



237

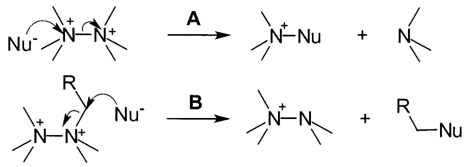
Despite all limitations, this method remains the most general up to date and allows preparation of bicyclic **239** and even monocyclic derivatives such as **238**.[279,280]



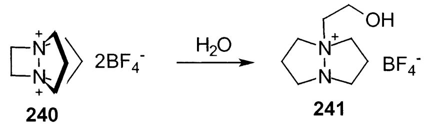
2. Properties of Hydrazinium Dications

Reactions with Nucleophiles and Bases. Although in the very first report[266] describing a hydrazinium dication, it was noted that these compounds undergo fast decomposition in the presence of traces of water, it was shown later[111] that aliphatic hydrazinium dications, and in particular tricyclic dications, are moderately stable in acidic aqueous solution. These dications are very reactive in nucleophilic substitution reactions.

Two directions for the nucleophilic attack were suggested initially: (type A) attack at the positively charged nitrogen atom or (type B) attack at the electrophilic α-carbon atom.

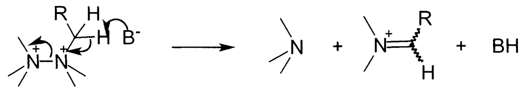


To date there are no examples of "type A" nucleophilic substitutions in hydrazinium dications, although nucleophilic substitution at the nitrogen atom in quaternary ammonium salts is known.[281] A "type B" S_N2 reaction at an α-carbon atom (typical for the disulfonium dications) was observed only in the case of dication **240** where the reaction proceeds with opening of a strained four-membered cycle.[275]

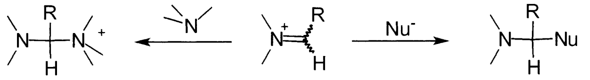


240 **241**

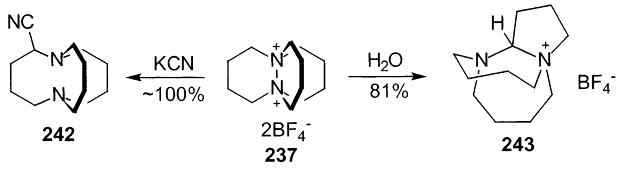
All experimental data on the chemistry of hydrazinium dications show that reactions with bases and nucleophiles, even of low basicity, proceed through initial α-deprotonation with formation of the corresponding iminium salt and concominant N−N bond cleavage.[282] This is in sharp contrast to the chemistry of disulfonium dications. Presumably, the reason for the larger acidity of α-hydrogen atoms in hydrazinium dications is the larger electronegativity of nitrogen.



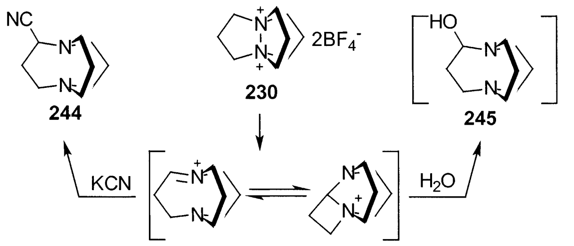
Although quaternary ammonium salts are commonly deprotonated by strong bases such as butyl- or phenyllithium, use of aqueous sodium bicarbonate is sufficient for deprotonation of hydrazinium dications.[283] Formation of the iminium salt is considered as "aza-Hofmann" fragmentation where the abstracted hydrogen which is *β* to the leaving group (the amino moiety) has increased CH acidity due to the influence of the adjacent positively charged nitrogen atom. In the next step, the iminium salt can either react with an amine to give an aminoammonium salt or react with any other nucleophile present in the reaction medium to afford α-substituted amines.



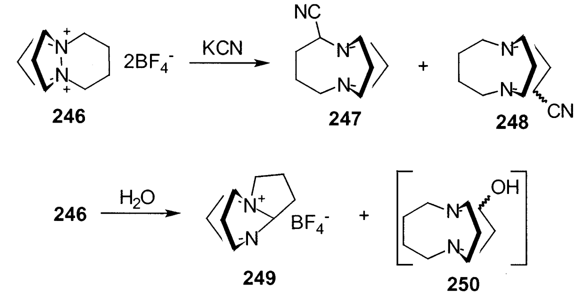
Which reaction path is observed depends on the structure of the hydrazinium dication and on the nature of the nucleophile. For example, the reaction of symmetric dication **237** with potassium cyanide leads to nitrile **242**, while hydrolysis with aqueous carbonate in the absence of strong nucleophiles leads to aminoammonium salt **243**.[266]



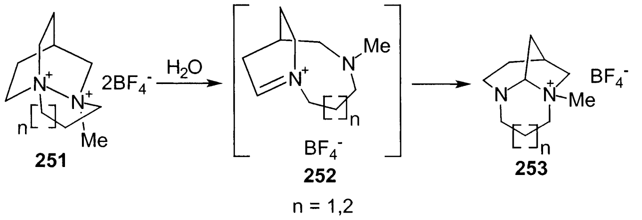
Reaction of salt **230** with potassium cyanide affords α-aminonitrile **244**. Hydrolysis of the salt, however, leads to a complex mixture due to the low stability of the intermediate aminoammonium salt containing a strained four-membered ring. *Gem*-amino alcohol **245** is a possible intermediate in this reaction.



Reactions of nonsymmetric tricyclic hydrazinium dications are not very selective. Treatment of salt **246** with potassium cyanide affords nitriles **247** and **248** in about a 1:2 ratio. Hydrolysis involves α-deprotonation at all possible positions to give a mixture of aminoammonium salt **249** and unstable *gem*-amino alcohol **250**.[284]

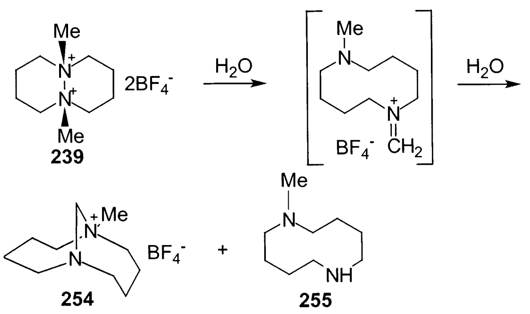


The stereochemical requirements for this process are similar to the requirements for the Hofmann elimination of ammonium salts—the C−H bond that is broken should be coplanar with the N−N bond.[282] For example, hydrolysis of dications **251** leads to aminoammonium salts **253** as a result of selective deprotonation at those methylene group which have hydrogen atoms antiperiplanar to the N−N bond.

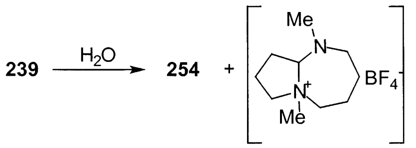


Interestingly, bases do not abstract hydrogen from the less hindered methyl group of salt **251**. Experiments with a D_3-labeled methyl group[285] eliminated the possibility that the initially formed iminium salt isomerizes by an intramolecular hydrogen transfer since no substitution of deuterium by protium was detected in the reaction product.[282]

On the other hand, hydrolysis of dication **239** was reported to give a mixture of products **254** and **255** in agreement with exclusive deprotonation at the less sterically hindered methyl group according to the Hofmann rule.[284]



However, a more recent study by different authors[282] established that hydrolysis of dication **239** under the same conditions does result in partial deprotonation of the methylene group as well. The resulting aminoammonium **256** is unstable in aqueous solution and undergoes further transformations to give nonidentifiable products. As a result the observed ratio of products derived from deprotonation of methyl vs methylene groups increases with reaction time.

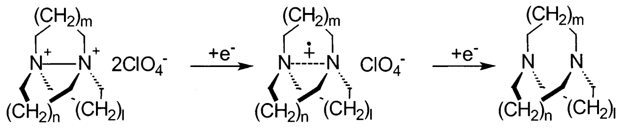


256

The basicity of a chloride anion in acetonitrile is sufficient for deprotonation of the hydrazinium dication **239**.[271]

Reduction of Hydrazinium Dications: Radical Cation. The mutual influence of two positively charged atoms in hydrazinium dications and in disulfonium dications results in moderately strong oxidative properties of these compounds. Such properties are not characteristic of monocationic ammonium and sulfonium salts.[281] Electron transfer to the doubly charged cation decreases the total Coulombic charge of the system thus alleviating repulsion of the adjacent charges.

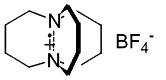
The electrochemical reduction of tricyclic hydrazinium dications has been studied by cyclic voltammetry. Two reversible reduction waves are observed that correspond to formation of radical cation **257** and neutral diamine **225**. Due to experimental difficulties, the accurate determination of the oxidation potential was not possible. The reported value is 0.1 ± 0.1 V.[111]



226 257 225

n, m, l = 1-3

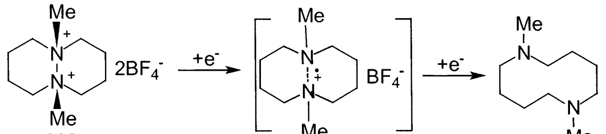
Because of the aforementioned structural features of medium size bicyclic systems such radical cations are very stable.[266] The most actively studied compound **258** is completely stable in the solid state and moderately stable in solution.[286] This stability allowed use of this radical cation for studies of the fundamental properties of three-electron two-center (3e-2c) σ bonds.[268,287]



258

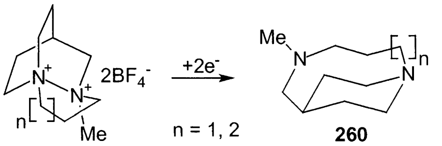
Structural parameters of radical cation **258** were established by X-ray crystallography.[276] The length of the N−N bond is 2.29 Å, which is significantly shorter than the distance between the nitrogen atoms in the corresponding diamine, 2.81 Å.[288] On the other hand, due to the characteristic features of the bicyclic skeleton, the N−N bond length is longer than in the parent hydrazinium radical cation, 2.16 Å.[284] A similar situation exists in the corresponding dications. Compound **258** is just the second example (besides He_2^+) where the length of a (3e-2c) σ bond was determined experimentally.[276]

The electrochemical reduction of other hydrazinium dications is irreversible and leads to N−N bond cleavage and formation of the corresponding diamines. The lifetime of the intermediate radical cation **259** is short compared with that of tricyclic radical cation **258**. For example, a study of the reduction of dication **239** with solvated electrons generated by pulse radiolysis has shown that the half-life of the corresponding radical cation **259** is about 5 ms.[279]



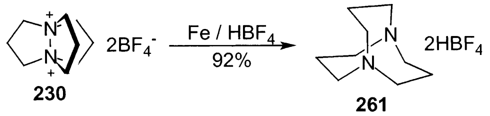
239 259

Electrochemical reduction of dications **251** leads to the isolation of tricyclic diamines **260**. The corresponding cation radical was not detected under conditions in which **259** was formed.[271]



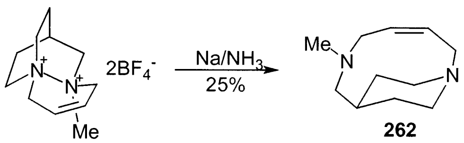
251 260

For reduction of hydrazinium dications on a preparative scale, one can use a number of reducing agents: metals in dilute solutions of acids, sodium in ammonia, sodium borohydride, and lithium aluminum hydride. The most general method is the use of iron or zinc in dilute aqueous HBF_4, which affords the corresponding diamine as a diprotonated salt **261** in quantitative yield.[275]



230 261

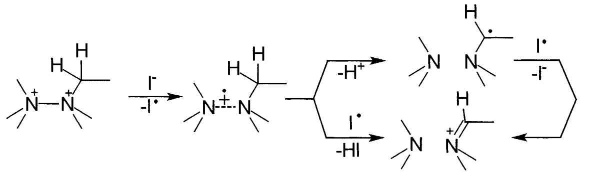
Reduction with sodium in liquid ammonia is applicable to the majority of hydrazinium dications and has the advantage of generating the corresponding diamine as a free base which is important in the case of unstable reduction products such as **262**.[289]



262

When sodium borohydride is used, formation of an aminoammonium salt as a side product is often observed. This salt is reduced more slowly, and, as a result, the yields are lower.[275]

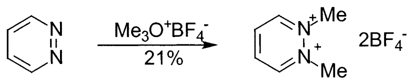
The reaction of hydrazinium dications with iodide ions is interesting. In this case, as in the reaction with bases, aminoammonium salts were isolated as products. The reaction mechanism includes electron transfer from iodide anion to hydrazinium dication with formation of an iodine radical and a nitrogen radical cation. The latter can either convert to an α-radical, which is oxidized by iodine to an iminium salt, or act as a hydrogen atom donor toward an iodine radical to give the same iminium salt.



The second mechanism is more likely since hyperconjugation of the unpaired electron and the C−H bond in the radical cation decreases the energy of the homolytic bond cleavage of this bond. It was found experimentally[290] that interaction of stable radical cation **258** with a number of organic radicals generated by pulse radiolysis leads to extremely fast hydrogen transfer. Even in the case of the stable thienyl radical the main pathway for interaction of the radical with cation radical **258** is abstraction of the α-hydrogen atom with formation of an iminium salt.[290]

3. Heteroaromatic N,N-Dications

A special class of heterocyclic compounds which can be formally classified as 1,2-dications consists of derivatives of pyridazine **263**, 1,2,4-triazole **264**, and 1,3,4-thiodiazole **265** with two adjacent quaternized nitrogen atoms. Synthesis of these compounds from the corresponding free bases is possible when very strong alkylating agents such as trialkyloxonium salts are used.[291]



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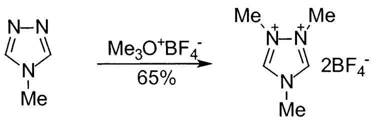

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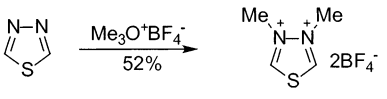

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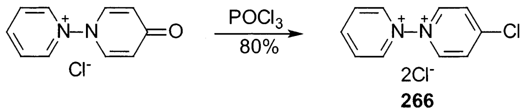
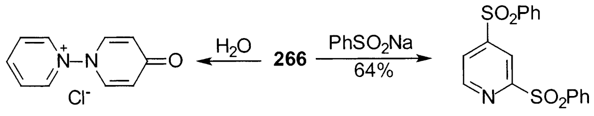
A different class of heteroaromatic 1,2-dications is represented by an *N*,*N*-bipyridinium derivative **266** where the two adjacent positively charged nitrogen atoms belong to different aromatic systems.[292]



266

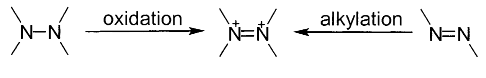
Salts of this type are highly reactive but cumbersome preparation and limited stability of these compounds prevent them from being widely used in synthesis. Chemical properties of these salts have been scarcely studied. Similar to other 1,2-dications, these compounds possess oxidative properties[291] and the electron-deficient aromatic ring in salt **266** is sensitive to nucleophilic attack.[292]



B. Diazenium and Diazonium Dications

1. Synthesis of Diazenium Dications

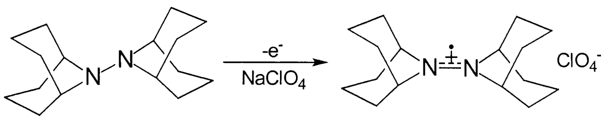
On the basis of the analogy with hydrazinium dications, one can suggest two main approaches to diazenium dications. The first approach involves formation of the N−N π bond through oxidation of tetrasubstituted hydrazines, whereas the second approach utilizes alkylation of azo compounds or diazenium salts and creation of a new C−N σ bond.



Hypothetically speaking, recombination of two nitrenium ions can also lead to formation of diazenium dications.[293] Although similar processes are known for carbenes[294] and nitrenes,[295] there are no examples of the dimerization of nitrenium ions in the literature. This absence can be explained by the presence of a high energy barrier to approach of two nitrenium cations as a result of electrostatic repulsion by the like charges.

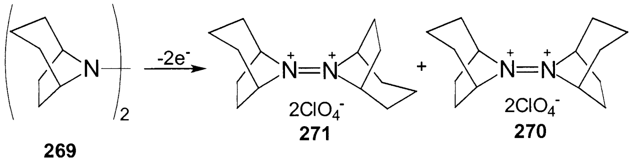
Also there are no literature data about double alkylation of diazenes, probably due to the extremely low nucleophilicity of nitrogen atoms in diazenes and diazenium cations. To prepare diazenium salts from the corresponding azo compounds, one has to use such efficient alkylating reagents as alkylfluorosulfonates or Meerwein salts.[296,297] Monoalkylation only is observed when diazenes are treated with an alkylhalogenide/$AgBF_4$ system, which allows preparation of hydrazinium dications from hydrazinium cations.[298]

Oxidation of hydrazine derivatives with N-bonded hydrogens is well studied due to its possible application to synthesis of other nitrogen-containing functional groups, and to highly reactive species able to undergo further transformations.[281] Oxidation of tetrasubstituted hydrazines has drawn a lot of theoretical interest. For example, it was found that electrochemical oxidation of these compounds leads to formation of relatively stable hydrazinium radical cations after one electron transfer.[298] Removal of an electron results in formation of an additional 3e-2c π bond between the nitrogen atoms and, as a consequence, to dramatic structural changes such as flattening at nitrogen and shortening of the N−N bond. The rotational barrier about the N−N bond is increased as well.[299] Nelsen and co-workers[300] successfully used the kinetic stabilization provided by Bredt's rule to prepare the extraoridinarily stable radical cation **268** by oxidation of hydrazine **267**.[301]



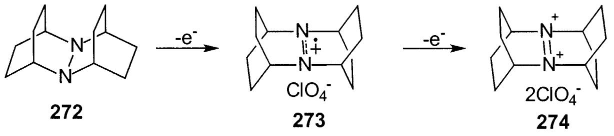
267 **268**

Nelsen and co-workers found that unlike in all previously known hydrazines the second oxidation wave of hydrazine **267** is reversible. In other words, the dication of hydrazine **267** is stable on the time scale of cyclic voltammetry (ca. 1 s).[299] Hydrazine **269** also forms a dication. Interestingly, the second oxidation wave has two maxima at 1.14 V and 1.01 V, corresponding to formation of *cis*-**270** and *trans*-**271** diazenium dications.[302]

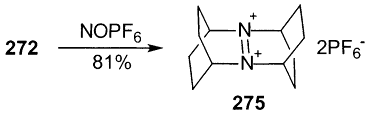


The stability of radical cations prepared from hydrazines **267** and **269** allowed the authors to study their structure by X-ray analysis. The difference in optical absorption spectra and redox properties of the two different conformers of dications of **269** also made possible the first experimental measurement of the rotational barrier around a three-electron π bond. This value can be taken as a good estimate of the energy of this bond.[299,303] The energy barrier between two conformers is 21.8 kcal/mol, which indicates that the energy of 3e,2c π bond is approximately half as strong as a 2e,2c π bond.

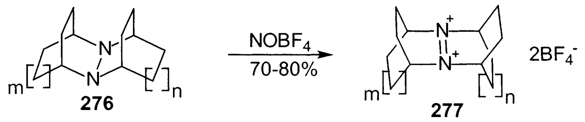
Polycyclic hydrazine **272** (structurally similar to hydrazine **267**)[304] is one of the most easily oxidized hydrazines—the first oxidation potential (corresponding to formation of stable radical cation **273**) is -0.53 V. A second oxidation also occurs fairly easy at 0.95 V to give stable diazenium dication **274**—the first diazenium dication isolated as an individual compound.



Dication **275** (as a complex with CH$_3$CN) can be prepared in 81% yield by oxidation of hydrazine **272** with NO[PF$_6$].[304] Its stability allowed an X-ray study as its hexaflurophosphate salt.[305] As expected for sp^2 hybridization, substituents at the nitrogen atoms adopt a planar arrangement. The length of the N=N bond is 1.27 Å, which is only 0.03 Å longer than the bond in the analogous neutral bicyclic azo compound 2,3-diazobicyclo[2.2.2]oct-2-ene.[306] Other structural parameters of dication **275** are also close to 2,3-diazobicyclo[2.2.2]oct-2-ene.

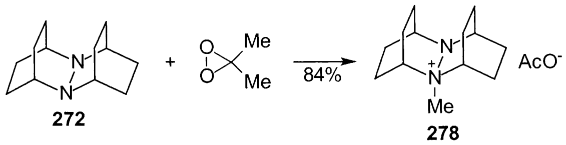


Following the first synthesis of a stable diazenium dication, a number of similar dications derived from hydrazines **276** with five- to eight-membered rings were synthesized. Low-temperature oxidation of these hydrazines with nitrosonium salts (NO[BF$_4$] and NO[PF$_6$]) leads to the corresponding dications **277**.[307]



The most efficient is the formation of dication **275**. Any changes in ring size (both decrease and increase) lead to a decrease in the stability of the diazenium dication and, as a consequence, to lower yields.[308]

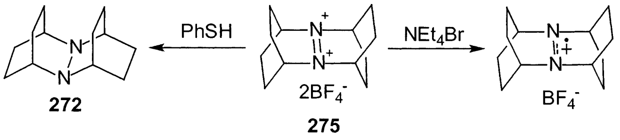
An interesting reaction of hydrazine **272** with dimethyldioxirane gives *N*-methylhydrazinium acetate **278**.[309]



It is suggested that the initial electron transfer from hydrazine **272** to dioxirane is very fast and results in formation of hydrazinium radical cation and dimethyldioxirane radical anion. Transfer of a methyl group with concominant breaking of a carbon—methyl bond is rare, but it is quite efficient under these conditions and results in formation of salt **278**.

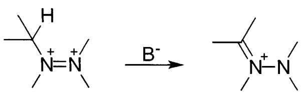
2. Reactions of Diazenium Dications

Reduction. Diazenium dications display oxidative properties. Electrochemical reduction occurs at 0.9−1.2 V, and leads to the corresponding hydrazine through intermediate formation of a radical cation. Both the radical cation and the hydrazine can be isolated depending on the redox potential of the reducing agent. For example, reaction of dication **275** with thiophenol affords hydrazine **272** and diphenyl disulfide, while weaker reducing agents such as Br$^-$, I$^-$ lead to the stable radical cation.



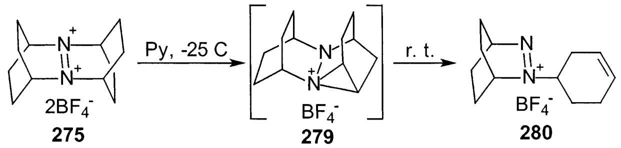
Since the only synthetic approach to diazenium dications is oxidation of the corresponding hydrazines, reduction of the dications does not present any synthetic interest and was not studied systematically.

Reactions with Nucleophiles and Bases. The instability and high reactivity of diazenium dications and hydrazinium dications stem from their high CH acidity. The majority of simple tetraalkyl derivatives undergo fast α-deprotonation to iminoalkylated hydrazones, and, hence, formation of dications is not detectable.[301]

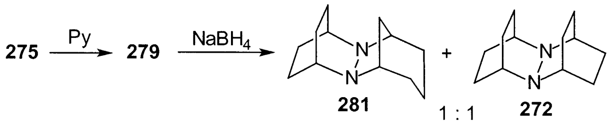


In the case of hydrazines such as **270** and **275**, where the alkyl substituents are incorporated into bicyclic rings, formation of the aminoiminium salt should lead to a strained structure violating Bredt's rule.[310] Due to the high activation energy of the deprotonation, the bicyclic diazenium dications are stabilized kinetically to the extent that allows their isolation as individual compounds.[305]

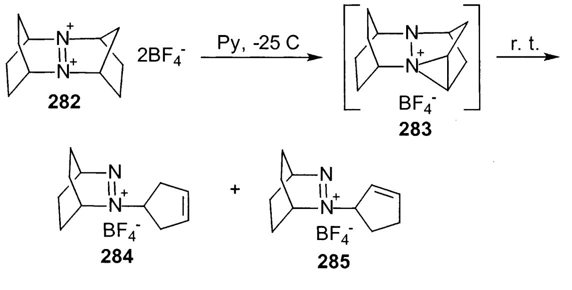
In the case of dication **275,** α-deprotonation, forbidden by Bredt's rule, is not observed. However, elimination of a *β*-proton with formation of unstable aziridinium salt **279** occurs after treatment with weak bases such as potassium carbonate, ammonium acetate, and even tetramethylammonium chloride in acetonitrile.[308] At room temperature, the reaction product is salt **280**, while at −25 °C the product is aminoaziridinium salt **279**, which rearranged quantitatively to **280** at ambient temperature. This transformation can be considered as a retroaddition of a nitrenium cation to a double bond.



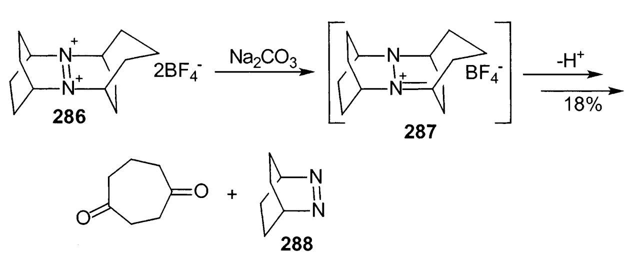
Chemical evidence for aziridinium salt **279** as an intermediate is the formation of a mixture of hydrazines **272** and **281** when dication **275** was treated with sodium borohydride in the presence of pyridine.[308]



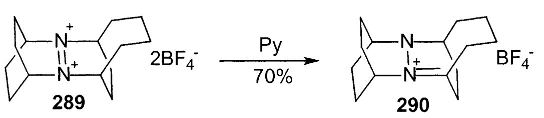
Deprotonation of dication **282** occurs mainly from the *exo*-position of the five-membered ring and also leads to the formation of aziridinium salt **283**.[307] The authors explained this selectivity by a "W-plan" overlap between the N−N orbital and *exo*-C−H bonds, which is larger for the *β*-*exo*-position of the five-membered cycle. The thermal stability of salt **283** is similar to that of salt **279**, and when the reaction mixture is warmed to the room temperature, alkenes **284** and **285** are formed in quantitative yield.[307]



An unusual result was observed in the reaction of base with salt **286**, with a seven-membered ring. The two products isolated in low yields result from hydrolysis of the initially formed iminium salt **287.** Formation of 1,4-cycloheptanedione can be explained either by oxidation of initially formed 4-hydroxycycloheptanone or by deprotonation at the bridgehead position of cation **287** with concomitant N−N bond cleavage followed by hydrolysis of two C═N bonds.[311]

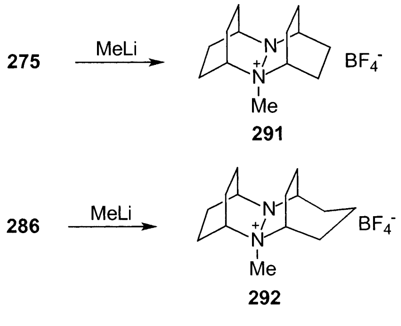


α-Deprotonation of diazenium dication **289** with an eight-membered ring using pyridine gave stable iminium salt **290**.[311]



Computational data[307] suggest that the distortions of normal double bond geometry in the product of α-deprotonation of diazenium dications **279** and **287** are similar. The twist angle of the C═N$^+$ bond in salt **287** is equal to 27°, which is 12° smaller than in the case of compound **279**. *β*-Deprotonation is thermodynamically preferred in the case of dications **275** and **286**. Only for eight-membered compound **290** is the iminium salt more stable (by 16 kcal/mol) than the aziridinium cation.[307] Hence, deprotonation of salt **287** is determined by kinetic factors. This is confirmed by computational data which show that the positive charge in **287** is +0.23 for the α-hydrogen but only +0.12 for the *β*-hydrogen.[312]

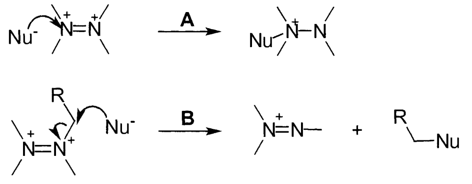
When diazenium dications were treated with organometallic compounds, no products of deprotonation were found.[307] The only transformation observed in the reaction of salts **275** or **286** with methyllithium is a redox reaction proceeding through intermediate formation of a hydrazinium radical cation and methyl radical. Recombination of these radicals results in formation of methylhydrazinium salts **291** or **292**.



The direction of this reaction is explained by the low activation energy for an electron transfer in such systems which occurs, unlike the deprotonation, with only slight change in molecular geometry.[307]

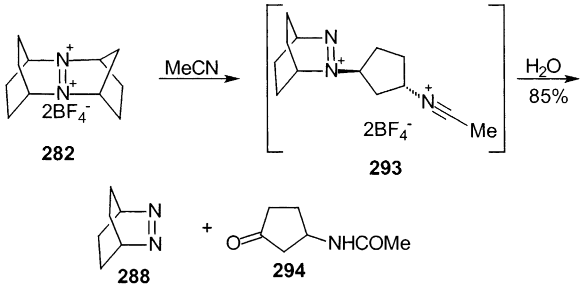
In theory, interaction of diazenium dications with nucleophiles can lead to hydrazinium ions, the products of addition to the N═N double bond (type A**)**, as well as to diazenium salts in an S$_N$2-type reaction (type B).

According to computational data, the very low energy of the LUMO (*π** for diazenium dications), ca. (10.9 eV), favors nucleophilic addition to the N═N *π* bond.[312] Surprisingly, such examples are absent from



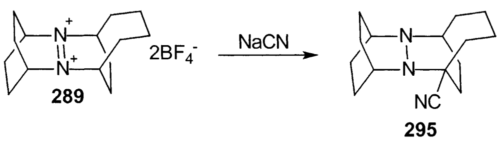
the literature which can be explained by the increased sensitivity of dications to basic and reducing properties of nucleophilic reagents, as well as by the steric hindrance created by the hydrocarbon skeleton of polycyclic dications. Reaction of salt **275** with methyllithium results in a product formally resulting from addition of methyl anion to the N=N double bond. However, it was established by EPR spectroscopy that the reaction follows a mechanism involving reduction of the diazenium moiety.[307]

The high CH acidity of diazenium dications accounts for the low number of reported examples of direct “type B” nucleophilic substitution, despite the fact that the leaving ability of diazenium dicationic group should be comparable to the leaving ability of diazonium salts.[307] Salt **282** and acetonitrile react with a half-life of about 5 min at room temperature to lead to nitrilium salt **293**. Hydrolysis of this salt affords amide **294** and azo compound **288**.[307]

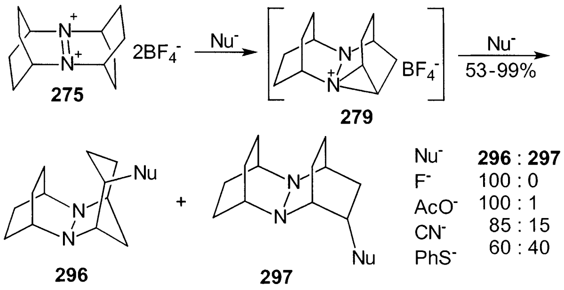


Formation of nitrilium salt **293** indicates that diazenium dication **282** is a strong alkylating agent. The *trans*-configuration of salt **293** suggests that acetonitrile attacks from the less hindered direction and corresponds to the stereochemistry expected for S_N2 substitution.

Reactions of seven- and eight-membered diazenium dications with all studied nucleophiles proceed as elimination/addition reactions via aminoiminium salts and afford substituted hydrazines. For example, reaction of salt **289** with sodium cyanide leads to nitrile **295**.[307]



Reaction of dication **275** with six-membered rings also occurs through initial deprotonation. Nucleophilic opening of the intermediate aziridinium salt results, depending on the nature of the nucleophiles, in formation of substituted hydrazines **296** and **297**.[313]

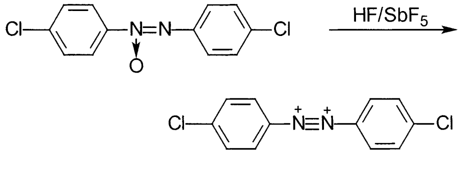


Nu⁻	**296** : **297**
F⁻	100 : 0
AcO⁻	100 : 1
CN⁻	85 : 15
PhS⁻	60 : 40

Each of the polycyclic hydrazines **296** and **297** is formed as the single diastereomer expected upon S_N2 cleavage of **279**. The amount of hydrazine **297** is larger in the case of the soft nucleophiles PhS⁻ and CN ⁻.[307]

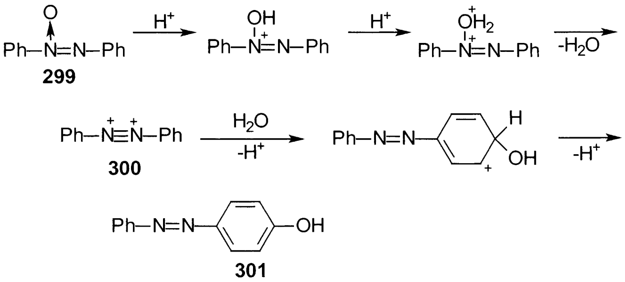
3. Diazonium Dications

Aryldiazonium salts have a long history and have been studied in detail.[314] Many of these compounds are quite stable in the presence of an appropriate counterion. The diazonium dication moiety carrying two aryl rings is sufficiently stable only in superacidic media at low temperatures. For example, formation of dication **298** was detected by NMR spectroscopy when 4,4′-dichloroazoxybenzene was treated with $HSbF_6$.[315]



298

These data provide an argument in favor of a diazonium dicationic mechanism for the Wallach rearrangement of azoxybenzene **299** to 4-hydroxyazobenzene **301**, a reaction that has been known for a long time. Formation of a doubly protonated intermediate in this reaction is also confirmed by kinetic studies and by the need to have a reaction medium that is significantly more acidic than required for monoprotonation of the substrate (pK_a −9−10). Formation of diazonium dication **300** was suggested as the rate-limiting step of the Wallach rearrangement.[316]

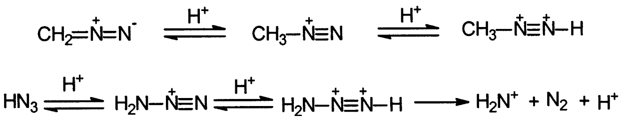


This reaction is the only nitrogen analogue to the most general synthetic approach to disulfonium dications through acid-catalyzed sulfide/sulfoxide comproportionation.

Olah et al.[317] suggested that the monoprotonated nitrogen molecule undergoes fast disproportionation in superacidic media with formation of a protodiazonium dication and a neutral nitrogen molecule (11).

$$2\mathrm{H{-}N^{+}{\equiv}N} \rightarrow \mathrm{H{-}N^{+}{\equiv}N^{+}{-}H} + \mathrm{N{\equiv}N} \quad (11)$$

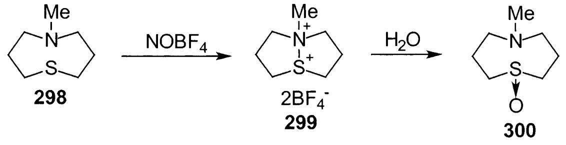
Formation of methyldiazonium dication in a very low equilibrium concentration was suggested to occur as the result of double protonation of diazomethane in HF−SbF_5.[318] Dissolving HN_3 in superacidic media results in decomposition with liberation of nitrogen. This process was also suggested to occur through double protonation and formation of an aminodiazonium dication.[319]



4. Mixed Dications

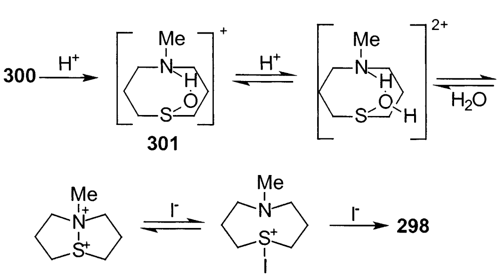
Two electron oxidation of chalcogenides, which possess a suitably positioned electron donor nitrogen group, may lead to mixed dications with onium atoms from different groups of the periodic system. Only a few examples of such dications are described in the literature.

When 2 equiv of a nitrosonium salt are used for oxidation of aminosulfide **298** which has amine and a sulfide groups in close proximity, a salt-like product is formed. The ^{1}H and ^{13}C NMR spectra of the product agree well with the N−S dication structure **299**.[320]



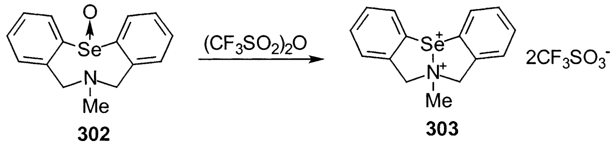
298 **299** **300**

Kinetic data on reduction of aminosulfoxide **300** with hydrogen iodide also agree with intermediate formation of a N−S dication. In addition to an increase in the reduction rate compared with the reduction of simple sulfoxides, this reaction is first order in hydrogen ions, second order in iodide ions and first order in the substrate. These data suggest initial protonation of the substrate with formation of relatively stable salt **301**.[320]



301

A Se−N dication with a single bond between nitrogen and selenium atoms was prepared by treatment of selenoxide **302** with triflic anhydride. In addition to characteristic chemical shifts in the ^{1}H, ^{13}C, and ^{77}Se NMR spectra, the presence of a transannular interaction between the Se and N atoms is confirmed by stereochemical changes in the molecule, namely, by adoption of the boat conformation in dication **303**.[321]



302 **303**

Chemical properties of S−N and Se−N dications are likely to be similar to the properties of dichalcogenium and hydrazinium dications. For example, reduction of dication **299** by iodide ions indicates its oxidative properties.[201]

VIII. P−P Dications

Phosphorus is less likely to form multiple bonds than carbon or nitrogen.[322] This is possibly a reason P−P dications corresponding to diazenium dications are not known.

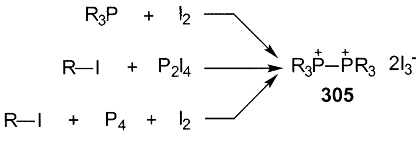
Diphosphonium dications with two directly bonded positively charged phosphorus atoms are structurally similar to hydrazinium dications. Nevertheless, the larger atomic radius and the possibility of covalent coordination of more than four ligands have consequences in synthesis and properties of P−P dications.

A. Synthesis of Diphosphonium Dications

Formation of a diphosphonium dication was suggested for the first time in a study dealing with decomposition of the triphenylphosphine−bromocyane adduct.[323] On heating this compound eliminates unstable hexaphenyldiphosphonium dibromide **304** which upon further heating disproportionates to triphenylphosphine and triphenylphosphine dibromide.

$$\mathrm{Ph_3P} \rightarrow \mathrm{BrCN} \xrightarrow{\Delta} \underset{\mathbf{304}}{\underset{2\mathrm{Br}^-}{\mathrm{Ph_3P^{+}{-}P^{+}Ph_3}}} \xrightarrow{\Delta} \mathrm{Ph_3P} + \mathrm{Ph_3P} \rightarrow \mathrm{Br_2}$$

Equally facile is the formation of a P−P bond during alkylation of phosphorus diiodide with cyclohexyliodide. The redox reduction yields a dimeric phosphonium salt. The latter was found to dissociate in acetonitrile to give symmetric hexaalkyldiphosphonium cation.[324] Further studies established that the analogous diphosphonium salt **305** is also formed during the reaction of red phosphorus with alkyl iodides in the presence of iodine[325] or as a result of oxidation of trialkylphosphines by iodine in acetonitrile.[326] Chemical yields for the above reactions vary from 60% to quantitative.



305

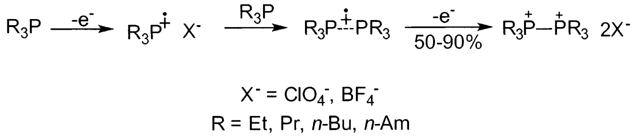
R = Me, Et, *cyclo*-C_6H_{11}, *n*-$C_{16}H_{33}$

Formation of diphosphonium dications occurs more easily than for other 1,2-dications and many oxidants can be utilized. For example, in contrast to the nitrogen analogue, oxidation of trimethylphosphine by Cu(II) and Tl(III) salts resulted in quantitative formation of hexadimethyldiphosphonium dication (eq 12).[133]

$$2Me_3P + 2Cu[PF_6]_2 \rightarrow Me_3P^+\text{-}P^+Me_3\ 2PF_6^- + Cu_2[PF_6]_2 \quad (12)$$

Electrochemical oxidation of phosphine derivatives leads to oxidative dimerization with formation of dicationic compounds. Initially, this process was discovered in the case of triamidophosphites.[327] Later, it was discovered that electrolysis of trialkylphosphine solutions in the presence of nonnucleophilic salts as electrolytes also results in formation of diphosphonium dications.[328]

The reaction mechanism involves intermediate formation of a phosphonium radical cation and reaction of the latter with a neutral phosphine molecule to give a dimeric radical cation which is rapidly oxidized to the dication at the same potential.



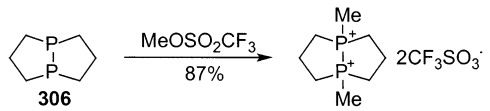
$$R_3P \xrightarrow{-e^-} R_3P^{+\bullet}\ X^- \xrightarrow{R_3P} R_3P\overset{+\bullet}{\cdots}PR_3 \xrightarrow[50\text{-}90\%]{-e^-} R_3\overset{+}{P}\text{—}\overset{+}{P}R_3\ 2X^-$$

$X^- = ClO_4^-, BF_4^-$

R = Et, Pr, *n*-Bu, *n*-Am

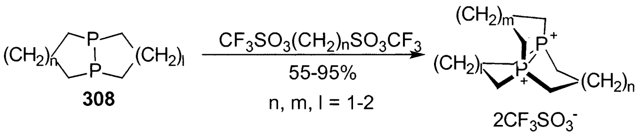
Preparative electrolysis of alkylphosphines yields 50−90% of the salts. The yields are lower when tetrafluoroborate anion is used which is likely due to decreased stability of phosphonium derivatives in the presence of fluoride anion.[328]

The other synthetic approach to diphosphonium dications is based on alkylation of tetraalkyldiphosphines which is analogous to the synthesis of hydrazinium dications from the corresponding alkylhydrazines. The nucleophilicity of the neutral phosphorus atom in the intermediate monophosphonium salt is low due to the presence of the adjacent cationic center. Nevertheless, the fact that the electron shells of phosphorus are more diffuse compared to those of nitrogen permits milder conditions for the alkylation than in the case of hydrazinium salts. For instance, methylation of cyclic diphosphine **306** by methyl triflate proceeds rapidly at the room temperature to give diphosphonium dication **307**.[329]



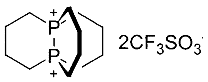
306 **307**

This method was used to prepare several propellane diphosphosphonium salts **309** from cyclic diphosphines **308** and bis-triflates of α,ω-alkanediols.[330] The reaction proceeds readily in a polar solvent (nitromethane) but stops at the first alkylation step when dichloromethane is used as a solvent. The yields vary from 55 to 95% depending on ring size. Unlike the case of polycyclic hydrazines the cyclization is the most efficient when a six-membered ring is formed.



308 **309**

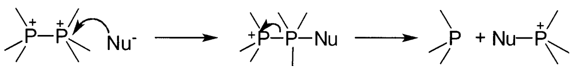
X-ray analysis of salt **310** synthesized by this method showed that the structure of this dication was similar to the structure of [4.4.4]propellane.[331] All of the rings adopt the chair conformation slightly distorted due to the presence of long P−P bonds. The P−P distance in the dication is shorter (2.17 Å) than in the starting diphosphine (2.19 Å).[332]



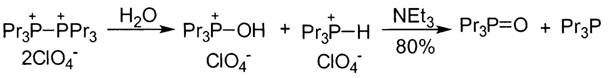
310

B. Reactions of Diphosphonium Dications: Nucleophilic Substitution

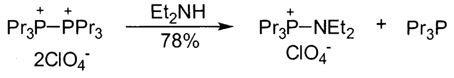
The special properties of phosphorus atoms lead to the result that, unlike the hydrazinium dications, deprotonation of the α-carbon atoms was never observed in reactions of diphosphonium dications with nucleophiles and bases. The only observed reactions are nucleophilic substitutions at the onium phosphorus atom which can proceed through an addition−elimination mechanism.[328]



Initially, the reactions of diphosphonium dications with nucleophiles were studied in the case of acyclic derivatives. The latter easily undergo hydrolysis due to even a trace amount of water present in commercially available solvents. The reaction leads to equimolar amount of phosphonium and hydroxyphosphonium salts. When treated with a base, these salts are converted to trialkylphosphine and trialkylphosphine oxide.[328] Reactions with amines follow an analogous scheme.

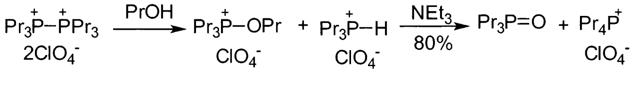


$$\underset{2ClO_4^-}{Pr_3\overset{+}{P}\text{–}\overset{+}{P}Pr_3} \xrightarrow{H_2O} \underset{ClO_4^-}{Pr_3\overset{+}{P}\text{–}OH} + \underset{ClO_4^-}{Pr_3\overset{+}{P}\text{–}H} \xrightarrow[80\%]{NEt_3} Pr_3P{=}O + Pr_3P$$



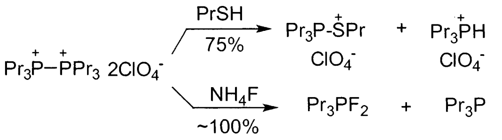
$$\underset{2ClO_4^-}{Pr_3\overset{+}{P}\text{–}\overset{+}{P}Pr_3} \xrightarrow[78\%]{Et_2NH} \underset{ClO_4^-}{Pr_3\overset{+}{P}\text{–}NEt_2} + Pr_3P$$

It was found that reaction with alcohols results in initial formation of protonated trialkylphosphonium and trialkylalkoxyphosphonium salts. The latter are known to alkylate many nucleophilic compounds including phosphines.[322] As a result, treatment of the reaction mixture with a base affords tetraalkylphosphonium salts and a phosphine oxide.

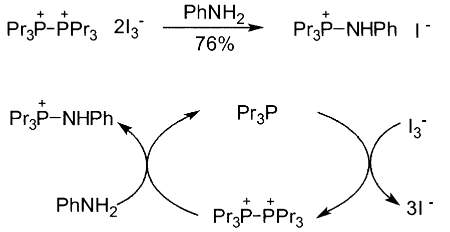


$$\underset{2ClO_4^-}{Pr_3\overset{+}{P}\text{–}\overset{+}{P}Pr_3} \xrightarrow{PrOH} \underset{ClO_4^-}{Pr_3\overset{+}{P}\text{–}OPr} + \underset{ClO_4^-}{Pr_3\overset{+}{P}\text{–}H} \xrightarrow[80\%]{NEt_3} Pr_3P{=}O + \underset{ClO_4^-}{Pr_4P^+}$$

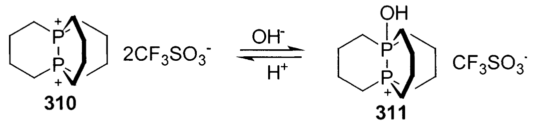
The most rapid P−P bond cleavage occurs in nucleophilic substitution with fluoride and alkylthiolate anions.[328]



Diphosphonium dications formed by reaction of alkyl iodides with phosphorus diiodides or by oxidation of trialkylphosphines with iodine undergo fast nucleophilic substitution at the onium phosphorus atom.[333] Yields of aminophosphonium salts are higher than expected when the reaction stoichiometry is considered. This is most likely due to oxidation of trialkylphosphine, the second reaction product, to diphosphonium dication under the reaction conditions.

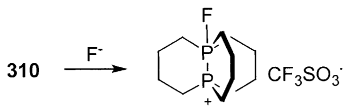


Nucleophilic substitution in tricyclic diphosphonium dications with a propellane structure takes an unusual course. The ability of medium size rings to stabilize weak bonds between bridgehead atoms and the possibility of formation of up to five covalent bonds on phosphorus due to the availability of d orbitals results in formation of stable adducts. These adducts have a P−P bond and a pentasubstituted phosphorus atom.[334] The presence of a strong P−P interaction in these adducts is confirmed by large spin−spin coupling constants between the phosphorus atoms in the ^{31}P NMR spectra. For example, hydrolysis of dication **310** leads to salt **311**. This reaction is reversible despite the formation of a strong P−O bond. Strong acids regenerate the starting dication **310**.[335]



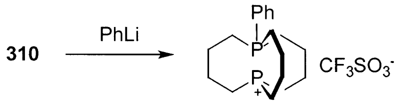
310 **311**

Reaction of dication **310** with fluoride anion proceeds in a manner similar to give the fluoride-containing adduct **312**.[334] This result is in sharp contrast to the reaction of hexapropyldiphosphonium dication.



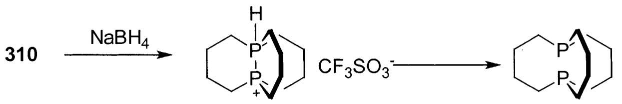
312

Dication **310** reacts with Grignard reagents and organolithium reagents to give products in which one alkyl or aryl group has been added to a phosphorus atom in a process that can be considered as an ordinary nucleophilic substitution at the onium phosphorus atom.[330] Treatment of salt **310** with phenyllithium leads to phosphonium salt **313** where, unlike in compound **312**, the P−P bond is absent due to the possibility of additional conjugation of the phosphonium center with a phenyl ring.



313

Unexpectedly and in contrast to the case of hydrazinium dications, electrochemical reduction of dication **310** does not lead to P−P bond cleavage. The authors concluded that radical cations produced by reduction of **310** ("indefinitely stable" in the case of the nitrogen analogue **258**) cannot have a lifetime more than 1 μs at ambient temperature. Electrochemical reduction of **310** is irreversible even at −80.[334] Dication **310** can be reduced on a preparative scale by sodium borohydride.



314 **314a**

Protonated phosphine **314** is a very weak acid which is impossible to deprotonate by ordinary bases.[332] Treatment with butyllithium leads to isomerization with formation of 1-[4-(1-phospholanyl)butyl]-phospholane **314a**. This reaction is most likely to start with initial deprotonation at the α-carbon atom.

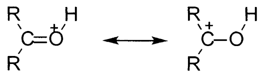
IX. Carbodications

As it has probably become obvious from material discussed in the previous pages, the most stable dications are produced by removal of electrons from an antibonding combination of nonbonding orbitals at the central atoms. This approach is not applicable to carbodications because stable carbon compounds do not have nonbonding orbitals. As a result, carbodications are produced exclusively by removal of electrons from bonding orbitals and the energy penalty for this transformation is intrinsically much higher than for oxidative formation of disulfonium or hydrazinium dications. On the other hand, the diversity of delocalizing interactions available to organic structures provides many ways to overcome this intrinsic instability, and, in a way, carbodications can be considered as a testing ground for discovery of generally efficient ways of manipulating reactivity and stability of other dicationic functions.

Studies on carbodications have benefited from the fact that monocarbocations represent an extremely important, well-studied, and ubiquitous class of organic reactive intermediates whose importance for the understanding of chemical reactivity and reaction mechanisms has been recognized for a long time going back to the work of Baeyer, Meerwein, and Ingold among others. Later, the chemistry of carbocations was spectacularly developed by Olah and co-workers who found that in *superacidic* media carbocations are so stable[336,337] that this field was called "stable ion chemistry".[338] It is interesting that although carbodications were first prepared in solution in the beginning of the 60s[339,340] and gas phase multiply charged organic cations were detected three decades earlier,[341] carbodications remained for a long time a rare curiosity without direct relevance to mainstream organic chemistry.

During the last two decades, the chemistry of carbenium and carbonium dications has experienced a period of fast growth in two different directions.[342] On one hand, the gas-phase studies were stimulated by the development of new mass spectrometric techniques for generation of dications. Although mass spectrometric methods do not provide direct information on the structure of dications, they provide important data about energetic properties of these species. A comparison of these properties with results of ab initio calculations provides a way for evaluating the quality of theoretical approaches and their ability to provide accurate information about the structure and chemical bonding in these species. These aspects of the chemistry of small carbodications are well covered in an excellent review.[343] On the other hand, a large volume of recent experimental data confirms that dications play an important role as real intermediates in a number of electrophilic reactions in superacidic media. The results of these studies are summarized in several reviews.[11,344,345] In this review, we have concentrated on unique chemical transformations involving participation of organic carbon 1,2-dications that were not covered separately in any of the other, previously published reviews. We believe that these data illustrate the enormous synthetic potential of organic dications and their increasing significance in organic chemistry.

In classifying the material, we have simplified the coverage by not taking into account the fact that electron distribution in carbodications can be described by use of several Lewis structures of similar importance. For example, we have used both hydrocarbenium **316** and carboxonium **315** structures to represent protonated carbonyl compounds.

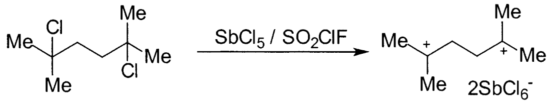


315 **316**

A. Dicarbenium Dications

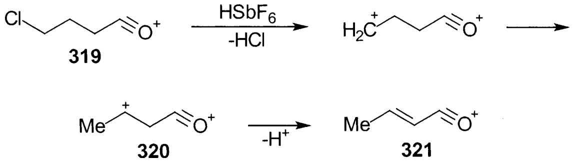
The stability of dicarbenium dications depends on a number of factors such as the proximity of the positive charges and the efficiency of stabilizing delocalizing interactions such as conjugation, hyperconjugation, and aromaticity. Conjugation with π orbitals and lone pairs provides the most efficient approach to stabilization of dications. In the absence of π-donating substituents, the role of hyperconjugation becomes increasingly important. Finally, some dications have extremely interesting properties related to their aromaticity or antiaromaticity.

Organic 1,4-dications are relatively readily available. For example, simple dication **318** can be prepared by ionization of the corresponding dichloride **317** and is sufficiently stable to be detected in solution.[346]



317 **318**

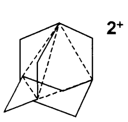
The proximity of two positively charged centers in 1,3- and 1,2-dications containing only σ donor substituents results in extreme instability of these compounds as a consequence of strong Coulombic repulsion. For a long time, 1,3-dicarbenium dications without n or π donor groups escaped detection by physical methods,[347] although indirect data pointed to the possibility of their involvement in some reactions in superacidic media,[348] e.g., the formation of stable cation **321** from acyl cation **319**.[349,350]



319 **320** **321**

Recently, Olah and co-workers reported that cyclopropyl groups are highly efficient in stabilizing a 1,3-dicationic moiety and ionization of 1,1,3,3-tetracyclopropyl-1,3-propanediol in SbF_5/SO_2Cl F gives the stable 1,1,3,3-tetracyclopropyl-1,3-propanediyl dication.[347] Interestingly. 1,1,3,3-tetraphenyl-1,3-propanediol yielded only the 1,1,3,3-tetraphenyl allyl cation at −130 °C and products of disproportionation/fragmentation at the higher temperatures.

A remarkable example of an exceptionally stable 1,3-dication **322** without n- or π-donating groups was observed by Schleyer and co-workers.[351] The 1,3-dehydro-5,7-adamantanediyl dication, formed by ionization of 1,3-dehydro-5,7-difluoroadamantane, owes its stability to three-dimensional aromaticity due to the overlap of four p orbitals in a tetrahedral fashion. Another interesting 1,3-dication **323** has been prepared by Olah to probe aromaticity in a two-electron Y-conjugated p system.[352]



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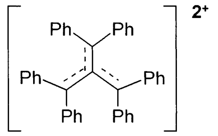
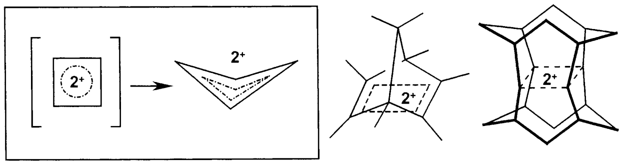


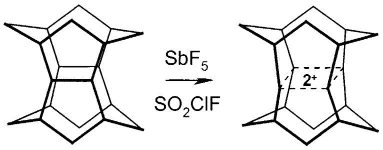
323

Aromaticity in a set of theoretically important four-electrons two-center delocalized systems such as the dications of cyclobutadiene,[353] norbornadiene,[354] and pagodane[355,356] was a subject of several elegant studies. In contrast to the planar S_4^{2+} dication **217**, the cyclobutadiene dication is puckered. The energies of the π MOs are lowered by orbital mixing in the nonplanar form and the whole π system "strives to achieve the three-dimensional aromaticity exemplified by the 1,3-dehydro-5,7-adamantanediyl dication".[357] On the other hand, the rigid molecular framework enforces the D_{2h} symmetry in pagodane dication **324**. The latter can be considered as the frozen aromatic transition state formed in the reaction of two ethylene radical cations.[355,358]

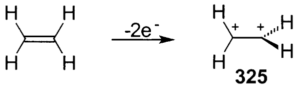


324

Another unique feature of pagodane dications that were studied extentsively by Prinzbach, Olah, and co-workers is that these compounds are the only known stable dications that can be prepared by removal of two electrons from *a σ bond*. The only other dication prepared by removal of two σ electrons is the D_2^{2+} dication which dissociates immediately upon its formation.[61]



Oxidation of π bonds is a much more common approach to 1,2-carbodications such as the ethylene dication **325**. This dication is thermodynamically unstable with respect to its fragmentation into a pair of positive ions but has a relatively high activation barrier for this dissociation because the process involves breaking of a C−C σ bond.[360] According to numerous calculations,[343] the only energetically favorable configuration of this simplest unsubstituted dicarbenium dication[359] corresponds to perpendicular structure **325** where the vacant p orbitals, corresponding to cationic centers, are mutually orthogonal and hyperconjugated with the adjacent CH_2 moieties. This conjugation shortens the C−C bond by 0.14 Å relative to an ordinary carbon−carbon bond (MP3/6-31G**).[360] The flat structure which corresponds to the transition state is 28 kcal/mol higher in energy than **325**.

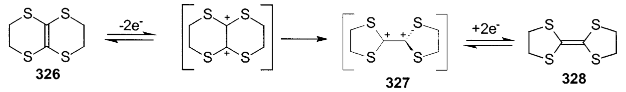


325

The high energy required for removal of two electrons from an ethylene molecule (the second ionization potential for ethylene is about 20 eV),[361] along with the high chemical reactivity of the dication makes its preparation in the condensed phase unlikely. Because the hyperconjugative donor abilities of C−H and C−C bonds are not significantly different,[362] the ethylene dication is not stabilized by alkyl substitution, and all attempts to obtain the tetramethylethylene dication in the condensed phase have been unsuccessful.[363]

The presence of π and n donors provides a much more efficient way to stabilize a dicationic moiety and to delocalize the positive charge toward remote atoms of the donor substituents. As a result, the energy of the flat conformation decreases proportionally to the combined energy of the conjugative interactions. MP2/6-31G(d) computations predict the flat structure for a number of hydroxy- and amino-substituted ethylene dications such as $C_2(OH)_4^{2+}$, *gem*- and *vic*-$C_2H_2(NH_2)_2^{2+}$, $C_2(OH)_2(NH_2)_2^{2+}$, and even $C_2F_4^{2+}$.[364] The ability of fluorine to serve as a quite efficient donor toward cationic centers is also consistent with the observation that the second ionization energy of ethylene does not increase with the introduction of fluorine atoms. The experimental values for the second ionization are as follows[364] (the theoretical values are given in parentheses[9]): 20.4 eV for H_2CCH_2, 18.7 (18.4 eV) for $FHCCF_2$, and 19.0 (18.2 eV) for F_2CCF_2.

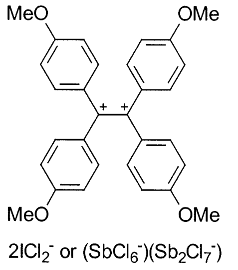
On the other hand, the perpendicular structure is favored by 9.3 kcal/mol in the mercaptosubstituted dication $C_2(SH)_4^{2+}$ due to the lesser efficiency of mesomeric conjugation for sulfur and the larger hyperconjugative donor ability of C−S bonds.[365] The greater stability of the perpendicular structure in the tetrathioethylene dication is illustrated by the known electrochemical isomerization of sulfide **326** to tetrathiofulvalene **328**.[366] The driving force for this rearrangement is formation of the more favorable perpendicular structure **327** in the intermediate dication, which is impossible for the dication containing an endocyclic double bond.



326 **327** **328**

Even in the case of efficient π donors, the difference in energies between the flat and perpendicular structures is not large (e.g., 2.8 kcal/mol for $C_2F_4^{2+}$ 364). Steric factors were used to explain why the gauche conformation of the tetraaminoethylene dication is 11.2 kcal/mol (MP2/6-31G*) lower in energy than the eclipsed flat conformation.[365] The geometry of phenyl-substituted ethylene dications is also intermediate between the flat and perpendicular structures.[367]

The stability of ethylene dication derivatives possessing two strong mesomeric electron donor substituents is sufficiently high to allow direct X-ray studies. Torsion angles in the dicarbenium dication moieties of **329** and **330** (41−76°) vary to some extent depending on the nature of the counterions. The distances between the carbon atoms in the ethylene dication moiety of tetra-(4-methoxyphenyl)ethylene dication **329**[368,369] and tetrakis(dimethylamino)ethylene dication **330**[370] are significantly increased compared with the parent neutral compounds. These distances are close to the typical single C−C bond lengths. In a very detailed structural study, Kochi and co-workers demonstrated that successful electron removal from tetraanisylethylene led to a progressive elongation of the central C−C bond from 1.359 Å in tetraanisylethylene itself to 1.417 Å in the radical cation and to 1.503 Å in the dication.[369] This bond elongation is consistent with the fact that the electrons are removed from a bonding MO and provides a contrast to the shortened bond observed in those dications which are formed by removal of electrons from antibonding MOs (He_2^{2+}, O_2^{2+}, disulfonium and hydrazinium dications, etc.).



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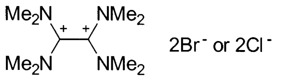
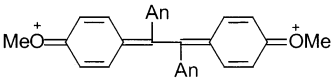


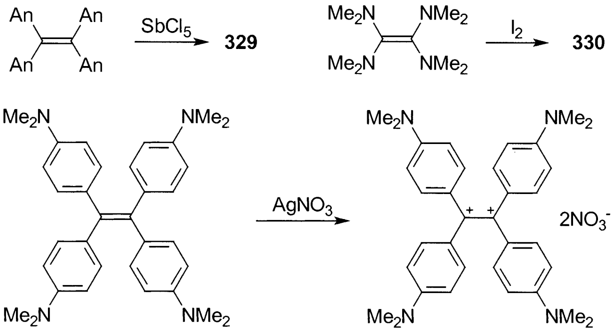
330

An interesting structural feature of dication **329** is the presence of two types of anisyl substituents at one carbenium center. One pair of approximately coplanar vicinal anisyl groups is more involved in positive charge delocalization than the other vicinal pair and, hence, undergoes significantly larger quinoidal distortion as illustrated by the oxonium structure **331**.[369]



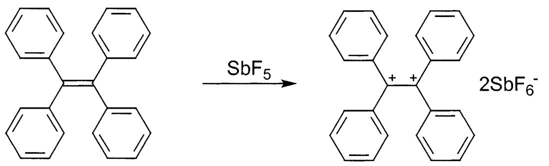
331

A variety of oxidation agents including halogens,[368,371] $SbCl_5$,[346] silver salts,[372] and bis(trifluoromethyl) disulfide[373] can be used for oxidative generation of 1,2-dicarbenium ions from electron-rich ethylenes.



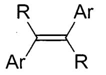
332

A stronger oxidizing agent, SbF_5, has to be used instead of $SbCl_5$ for the oxidation of less reactive alkenes such as tetraphenylethylene.[374,346]

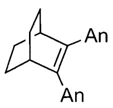


333

Electrochemical oxidation of electron donor ethylenes to dications is also well studied.[369,375,376] Whereas the oxidation potential for formation of a dication is ca. 1 V for 1,2-dianisylethylene and ca. 1.4 V for tetratolylethylene, oxidation of a 1,1-dianisylethylene to the corresponding dication occurs irreversibly only at 1.6 V. This agrees well with the above finding that only one of the geminal pair of aryl substituents efficiently participates in delocalization of the positive charge.[369]



R = Ar = 4-An **334a**
R = Ar = 4-Tol **334b**
Ar = 4-An, R = 4-Tol **334c**
Ar = 4-An, R = Et **334d**



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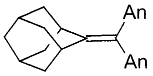
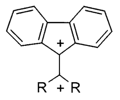


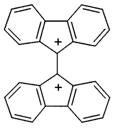
336

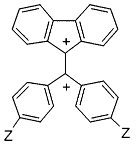
Ethylene	**334a**	**334b**	**334c**	**334d**	**335**	**336**
Eox (II)	0.91	1.37	1.02	1.11	1.15	1.61*

*irreversible oxidation

An unusual suite of interesting antiaromatic dications has been reported recently by Mills et al.[377–382] Chemical oxidation of a variety of fluorenylidenes by SbF_5/SO_2ClF results in a fluorenyl cation with a cationic substituent, **337**. The protons of the fluorenyl system exhibit substantial paratropic shifts in the NMR spectrum, with an average shift of 3.34 ppm for **338** when compared to the tetraphenylethylene dication.[381] The magnitude of the paratropic shift is affected by electronic and steric[378] changes in R, with the more electron-poor substituent causing the larger paratropic shift.[379]





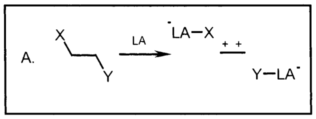


337 **338** **339** Z=OCH_3, CH_3,H, F, Cl, Br, CF_3

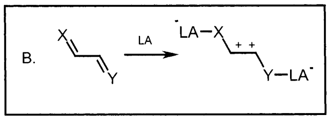
Aromaticity/antiaromaticity of these dications was also evaluated by consideration of other magnetic properties, most importantly, magnetic susceptibility exaltation,[383] and nucleus independent chemical shift, NICS.[384] Dication **338** and the substituted diphenylmethylidenefluorene dications **339** have large positive NICS values, indicating an appreciable degree of antiaromaticity,[381,382] particularly in comparison to the fluorenyl monocation. The calculated magnetic susceptibility exaltation, Λ, also indicates appreciable antiaromaticity for **338**. Interestingly, the stability of dications **339**, as estimated from their redox potential, does not indicate an extraordinary degree of instability, when compared with the redox potentials of other substituted tetraphenylethylenes.[382]

Finally, the acetylene dication can be formed by removal of two electrons from acetylene π bonds by different gas-phase ionization techniques.[385] According to numerous calculations, the most stable structure of this dication corresponds to linear geometry with a triplet electronic configuration.[386] The calculated C−C bond length corresponds to the value expected for a carbon−carbon double bond (1.34 Å at CASSCF/ TZP level of theory).[387] This dication is relatively unstable: its dissociation in the gas phase has five reaction channels leading to three molecular fragments. Several of the processes are faster than fragment rotation and one possibly involving dissociation of CH^+ to H^+ occurs within 25 fs.[388]

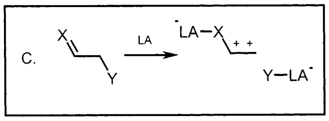
Substituted 1,2-dicarbenium dications can also be generated by ionization of halogenides, alcohols, and other substrates with unshared electron pairs or π bonds under the influence of strong Lewis or Brönsted acids. Depending on the structure of the substrate, the ionization is accompanied by cleavage of either σ (case A)[344,345] or π C−X bonds (case B). This approach to 1,2-dications is energetically more favorable than oxidation of an alkene since the energetically unfavorable bond breaking is partially compensated by the energy gain due to formation of new bonds.



X,Y=Hal, OH



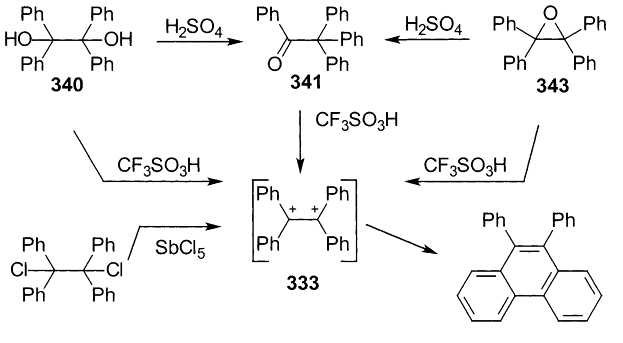
X,Y=O, N



X=O, Y=OH, Hal (LA =Lewis Acid)

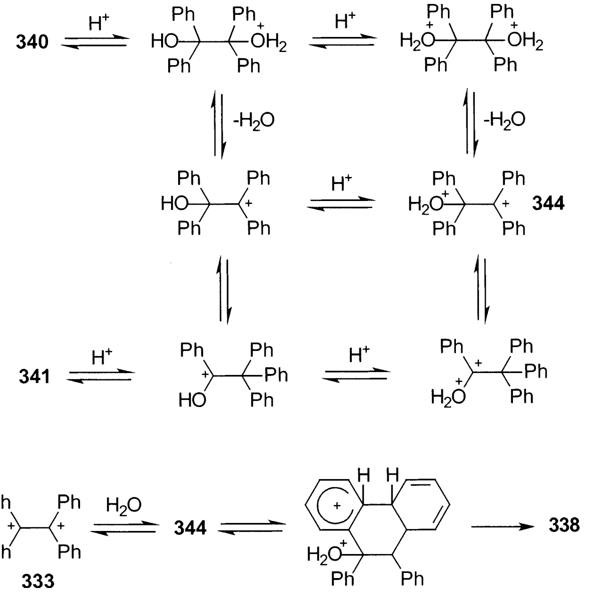
This approach can be considered as an additional activation of electrophiles through coordination with a Lewis acid. This concept is extremely important for synthesis of substituted 1,2-dicarbenium dications and their application in organic chemistry. Since this field was thoroughly discussed a decade ago,[11] we will only outline recent developments, which are associated mainly with the work of Olah and Shudo.

Rearrangement of benzopinacol to benzopinacolone **341** by treatment with sulfuric acid is the well-known pinacol rearrangement. In contrast, reaction with triflic acid leads to diphenylphenanthrene.[389] Analogous results were found for the cyclization of benzopinacolone **341**, tetraphenylethyleneoxide **343**,[390] and 1,1,2,2-tetraphenyl-1,2-dichloroethane.[391]



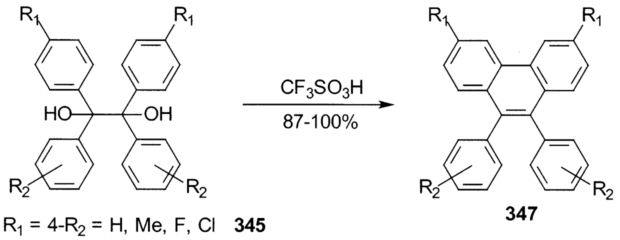
It has been suggested[389] that tetraphenyl substituted ethylene dication **333** (or its hydrate **344**) is a key intermediate in this reaction and that the mechanism can be represented by the following scheme (Scheme 13).

Scheme 13



Formation of the intermediate dication **344** is supported by indirect data.[390] Ketone **341** is sufficiently basic to be completely protonated in media with acidity $H_0 = -9$, and, hence, any further increase in the acidity is not expected to increase the reaction rate. However, the cyclization occurs only when the acidity function H_0 is below −11. This clearly indicates that a second protonation is necessary.

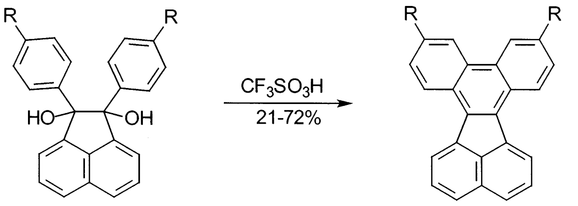
Other substituted phenylpinacols **345** and **346** are converted quantitatively into the corresponding phenanthrenes **347**. In the case of unsymmetrical diols **346**, the regioselectivity of the cyclization is sensitive to the deactivating influence of acceptor substituents and cyclization occurs with participation of the less electron-poor unsubstituted phenyl rings.[389]



$R_1 = 4\text{-}R_2$ = H, Me, F, Cl **345**

R_1 = H; R_2 = 4-Cl, 4-Br, 2-Cl, 3,4-Br_2 **346**

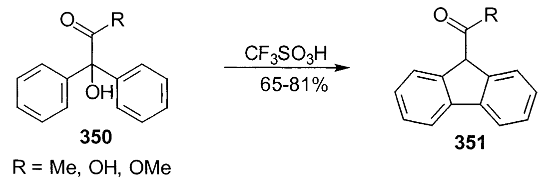
Cyclization of the acenaphthene diols **348** occurs only when the acidity of the reaction medium is higher than $H_0 = -12$ and leads to polycyclic aromatic compounds **349**.[390]



348 **349**

R = H, Me, F

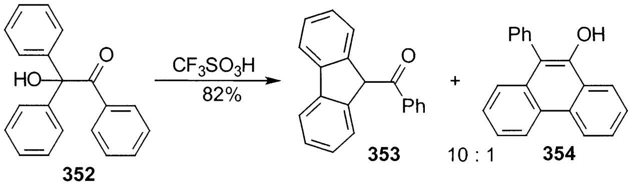
Diphenylhydroxycarbonyl compounds **350** also undergo cyclization with formation of fluorenes **351** when treated with triflic acid at −50°. Formation of small amounts of phenanthrene **354** was observed in the cyclization of triphenyl-substituted substrate **352** in addition to fluorene **353**.[392]



350

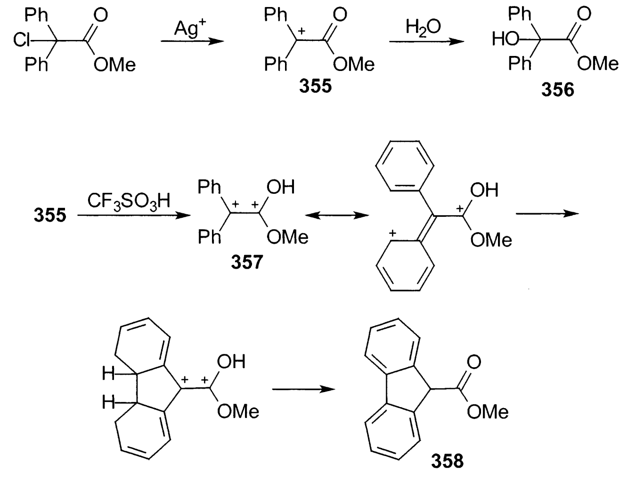
R = Me, OH, OMe

351



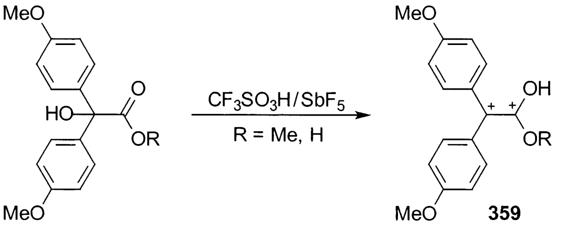
352 **353** **354**

The intermediacy of a dicationic intermediate in such electrophilic cyclizations was elegantly illustrated by a control experiment in which the monocation **355** was generated in an inert solvent. Addition of water to carbocation **355**, which is stable even at 0 °C, results in formation of hydroxycarbonyl compound **356**, while use of excess of triflic acid leads to cyclization product **358**. Thus, it was suggested that the rate-limiting step of the cyclization involves protonation of cation **355** at the oxygen atom to give 1,2-dicarbenium dication **357**.[392]



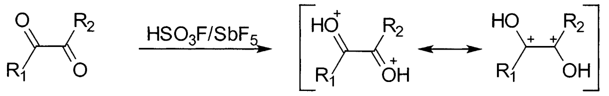
355 **356** **357** **358**

This mechanism gained support when similar stable ethylene dications **359** were prepared in superacidic media and their spectral characteristics were found to be consistent with the proposed structure.[392]



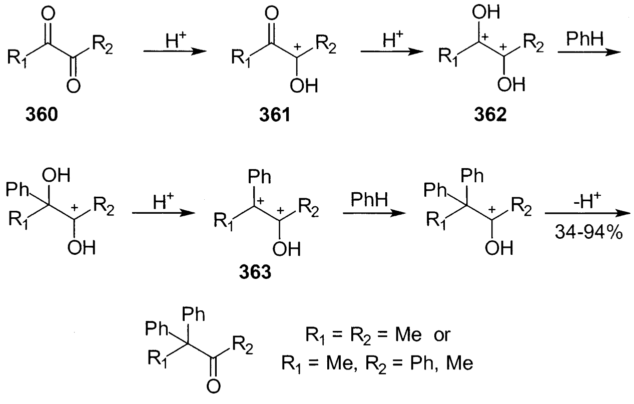
359

Double protonation of dicarbonyl compounds in superacidic medium is the most common example of generation of 1,2-dicarbenium dications by addition of positively charged electrophiles to substrates with two double bonds.[393] Spectroscopic methods indicate that a number of 1,2-dicarbonyl compounds undergo double protonation in "magic acid" (HSO_3F/SbF_5) with formation of hydroxy-substituted ethylene dications.[394,395]



R_1, R_2 = Ph, Me

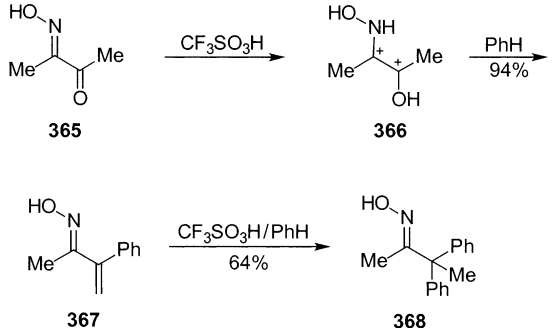
Unlike hydroxycarbenium cations, 1,2-dihydroxydicarbenium dications **362** which are generated from 1,2-dicarbonyl compounds in superacidic medium are sufficiently electrophilic to react with nonactivated aromatic compounds such as benzene. Although no reaction is observed at acidities where diketones **360** are mainly monoprotonated ($H_0 = -8$), a further increase of acidity results in formation of diphenyl substituted ketones **364**.[396] NMR spectroscopy confirmed that the active electrophilic species in this Friedel−Crafts-type transformation is a diprotonated dicarbonyl compound which can be classified as a *vic*-dihydroxysubstituted ethylene dication **362**.[397] The intermediate monophenylated dicarbenium-dication **363** was not detected due to its high reactivity.



360 **361** **362** **363** **364**

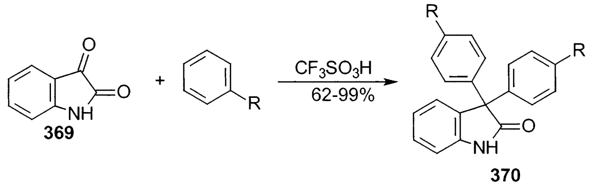
$R_1 = R_2$ = Me or
R_1 = Me, R_2 = Ph, Me

The electrophilic activity of dication **366** formed from monooxime **365** is moderated by the stabilizing mesomeric effect of the hydroxylamino group, and the reaction conditions can be controlled in a way that allows for formation of products of either mono- or diarylation.[397]



365 **366** **367** **368**

Formation of 3,3-diaryloxoindenes **370** in reaction of isatin **369** with relatively electron-poor aromatic compounds such as chloro- and fluorobenzene in triflic acid proceeds only when the acidity of reaction medium is below $H_0 = -11.5$, which confirms that formation of the reaction product occurs only from dicationic intermediates. Although the regiochemistry of protonation was not studied, the most likely dicationic intermediate is a dihydroxysubstituted dicarbenium dication (O,O-diprotonated isatin).[398]

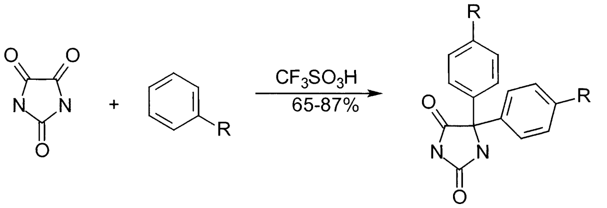


369

370

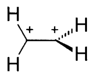
R = H, Me, Cl, F, n-Nonyl

Arylation of parabanic acid in the presence of triflic acid proceeds in a similar manner and only when a 1,2-dicarbenium dication is formed.[399]



R = H, Me, Cl, F, n-Nonyl

In addition to dications containing two directly connected classic carbenium centers, there are other, even more exotic, types of 1,2-dicarbodications. A cationic center in an organic molecule can be formed by two different ways: (a) by removal of a substituent with a bonding electron pair from a tetrasubstituted carbon atom with formation of a classic trivalent carbenium center, or (b) by addition of a cationic particle to a tetrasubstituted carbon atom with formation of a carbonium pentacoordinated cationic center. Considering all possible combinations, one can suggest two more types of carbon 1,2-dications in addition to the already discussed dicarbenium dication (ethylene dication) **325**: a carbenium carbonium dication **371** and a dicarbonium dication **372**.



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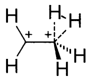

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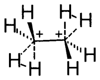
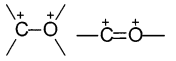


372

Dications **371** and **372**, as well as their derivatives, have not been detected directly by physical methods in the condensed phase. Indirect data confirming participation of these species in organic transformations are scarce. However, some of them can be generated in the gas phase by ionization of suitable precursors.[343] For example, the ethane dication $C_2H_6^{2+}$, detected in the course of a number of mass spectroscopic experiments in the gas phase,[400] indeed has the carbenium–carbonium structure **371** as the most stable configuration according to quantum mechanical calculations (MP2/6-311G*).[401] In principle, dicarbonium dication **372** can be formed by double protonation of ethane, but, as of this moment, this dication has not been observed even in the gas phase and has been studied only theoretically.[401]

B. Carbenium Heteroonium Dications

The presence of an atom with an unshared electron pair close to a carbenium center leads to substantial stabilization of the positively charged species due to donor interaction of the substituent electron pair with the vacant p orbital of the cationic center. As a result, the positive charge is partially transferred to the donor atom and the cation attains relative stability but becomes less reactive, which can be undesirable when these species are generated for use as electrophilic agents. Coordination of the nonbonding electron pair in the n donor substituent with a Lewis acid inverts the electronic properties of this substituent and leads to a dramatic increase in reactivity. Despite the unfavorable interaction of the proximal cationic centers, such activation is possible in superacidic media.[402] The resulting 1,2-carbenium–heteroonium dications are called gitonic dications as opposed to distonic dications where the positive charges are far apart. These dipositively charged, highly electrophilic and extremely reactive species have properties that are so drastically different from the well-known monocationic reagents that Olah introduced the new term "*superelectrophiles*" for these compounds.[403] 1,2-Dicationic superelectrophiles can be classified by the type of heteroatom adjacent to the carbenium center. Current literature examples include the carbenium oxonium **373**, carbenium ammonium **374**, and carbenium sulfonium **375** dications.



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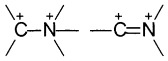

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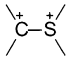
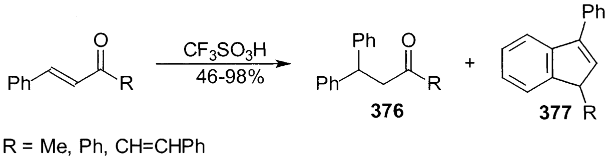


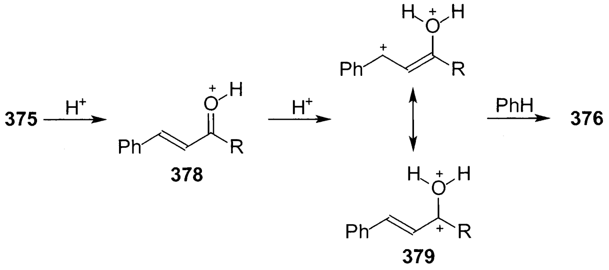
375

The literature dealing with dications **373** and **374** was recently reviewed,[343] and an interested reader is referred to this paper for additional information. The reinterpretation of many previously known electrophilic reactions in superacidic media (Friedel–Crafts acylations, Houben-Hoesch and Gatterman reactions, etc.) in terms of carbenium–heteronium dications as intermediates has also been discussed in a recent review.[404] These excellent reviews allow us to concentrate only on the most recent data concerning chemical transformations involving participation of dications **373** and **374**.

Despite the fact that unsaturated ketones are fully protonated in trifluoroacetic acid to give monocationic species **378**, they do not react with benzene under these conditions. On the other hand, when the reaction is carried out in triflic acid, a Friedel–Crafts-like alkylation of benzene with formation of ketones **376** along with indenes **377** is observed.[405]

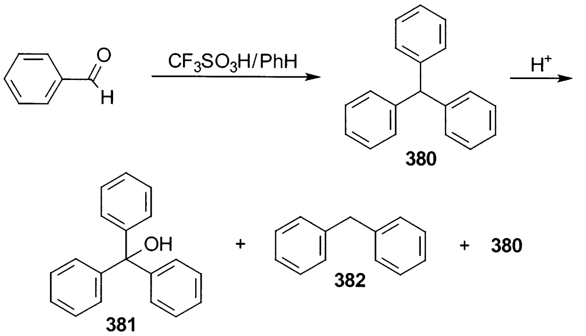
The necessity for using a superacidic medium for this reaction is consistent with intermediate formation of a doubly protonated substrate **379**. The oxonium carbenium structure suggested for the latter was based on the absence of deuterium exchange in





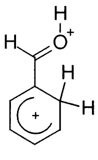
deuterated triflic acid and on the results of MP2/6-31G* calculations.[405]

The reaction of benzaldehyde with benzene in triflic acid was also suggested to proceed through a dication.[406] Because all attempts to characterize the dication spectroscopically were unsuccessful and that several groups arrived at different opinions about the nature of the intermediate, this deceptively simple reaction was studied in detail.[407] Initially, it was suggested that formation of triphenylcarbinol **381** and diphenylmethane **382** occurs directly as a result of transformylation.[408] However, recent data suggest that the reaction products are formed as the result of further transformations of triphenylmethane **380**.[409]



Computational data (MP2/6-31G*) suggest the dications **383** and **384** generated by the second protonation of benzaldehyde at the *ortho*- and *meta*-positions of the benzene ring are 5 kcal/mol lower in energy than the product of *para*-protonation **385**. The O,O-diprotonated structure **387** and the *ipso*-protonation product **386** are even less favorable (by 21 and 13 kcal/mol, respectively).[406]

On the other hand, the experimental data do not agree with the computations since the absence of deuterium exchange in the benzaldehyde/[^{2}H]-triflic acid makes a second protonation of benzaldehyde and formation of such structures as **383**−**385** unlikely.[407] On the basis of the available data, it is not possible to choose unambiguously from the two lower structures **386** and **387**; however, indirect data indicate that carbenium oxonium dication **387** is preferred. For example, the O,*ipso*-C diprotonated pentamethylacetylbenzene **388** readily loses an acetyl cation at very low temperature.[410]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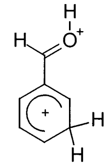
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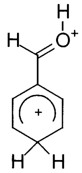
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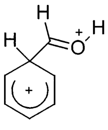
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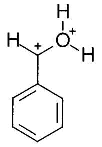
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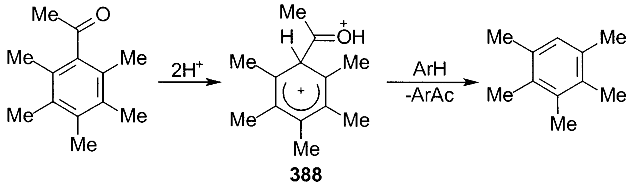
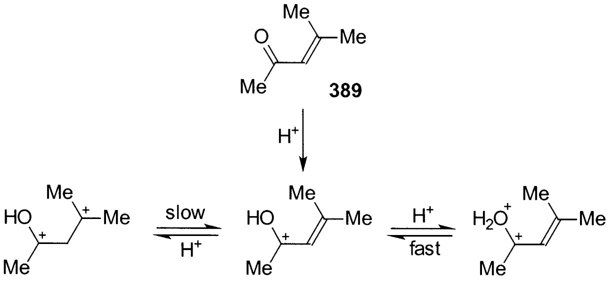
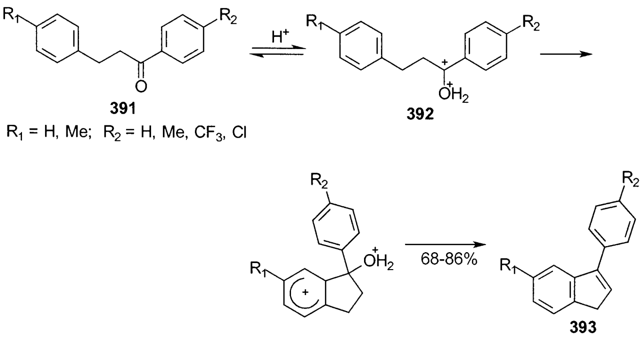


The probability of the O,O-diprotonation is also consistent with the data obtained for the protonation of mesitylene oxide **389** in superacids in which O,O-diprotonation was found to be kinetically favored over C,O-diprotonation.[411]

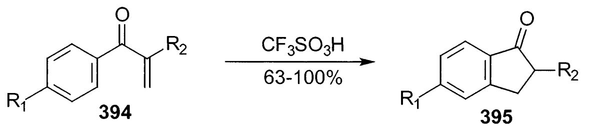


Kinetic data on intramolecular cyclization of ketones **391** in triflic acid to substituted indenes **393** also suggest involvement of oxonium carbenium intermediates **392** (Scheme 14)[412] because there is a direct dependence of the reaction rate on the acidity of the medium (H_0) in the region where the acidity is higher than the one sufficient for complete monoprotonation of substrate **391**.

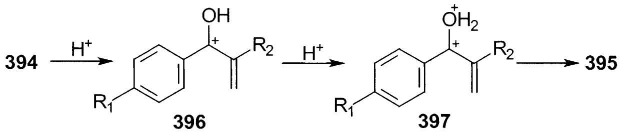
Scheme 14



Another example of an intermolecular cyclization with participation of an oxonium carbenium 1,2-dication in the rate-limiting step is the formation of indanones **395** when propenones **394** are treated with triflic acid.[413]

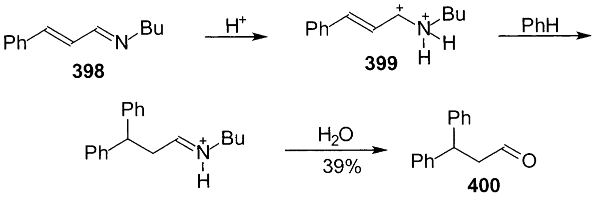


R_1 = H, CF_3; R_2 = H, Me, Et, Ph, 4-$CF_3C_6H_4$

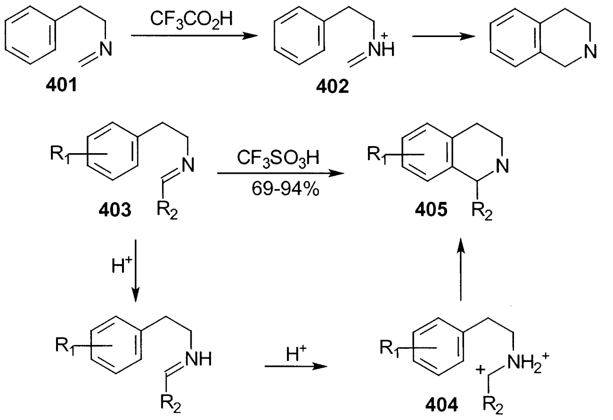


Formation of oxonium carbenium intermediates **397** was confirmed by the absence of deuterium exchange in the starting material in deuterated triflic acid.[413] According to B3LYP/6-31G computations, the preferred pathway involves O,O-diprotonation of the substrate[414] with formation of oxonium carbenium dication **397** which exists in dynamic equilibrium of its *s-cis* and *s-trans* conformations. Electrocyclization of the dication with formation of indanones has a relatively low activation barrier of 9 kcal/mol, unlike the cyclization of carboxonium ion **396** where the activation energy is 25 kcal/mol.

As expected carbenium−ammonium dications are generally more stable than the corresponding carbenium−oxonium dications. Sometimes, this has synthetic advantages. For example, arylation of imine **398** with benzene in triflic acid leads, after hydrolysis, to diphenyl propanal **400** in 39% yield, while the free aldehyde gives only 6% of this product.[405]

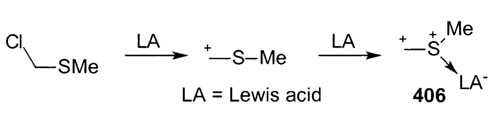


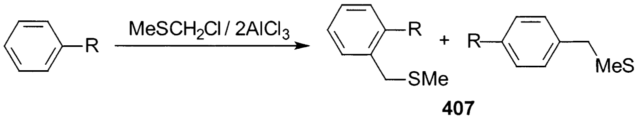
Unlike the well-known Pictet−Spengler cyclization of unsubstituted *N*-methylenephenylethylamine **401** in trifluoroacetic acid, which proceeds through a monocation **402**, cyclization of imines **403** to isoquinolines **405** requires use of a stronger proton donor such as triflic acid.[415] Participation of a doubly protonated substrate in the rate-limiting step is confirmed by a linear dependence of the reaction rate on acidity in the region where the substrate is known to be doubly protonated. An indirect proof that the diprotonated intermediate corresponds to a carbenium−ammonium dication **404** is given by studies of deuterium exchange in the reaction with deuterated triflic acid.



R_1 = H, 3-Me, 3,5-Me_2, 3,4-$(MeO)_2$
R_2 = H, *iso*-Pr, 4-ClC_6H_4, Ph

Methylthiomethylation with an equimolar complex formed from chloromethylmethyl sulfide and Lewis acids is applicable only to electron-rich aromatic substrates. Use of 2 equiv of aluminum chloride leads to a dramatic increase in the activity of the reagent. This increase is attributed to additional coordination of the Lewis acid at the sulfur atom in the intermediate monocation to give carbenium−sulfonium dication **406** which has been detected by NMR spectroscopy. The resulting superelectrophilic reagents are sufficiently reactive to alkylate chloro- and bromo-substituted benzenes.[416]





R = H, Me, Et, F, Cl, Br

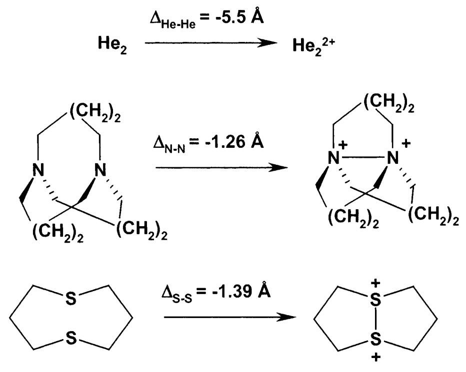
X. Conclusions

Structures, reactivities, and other properties of 1,2-dications are diverse. We will conclude this review with a summary of the structural changes associated with formation of a 1,2-dicationic moiety. These changes illustrate how stability and reactivity of dications depend on their molecular structure and the method by which these dications are generated.

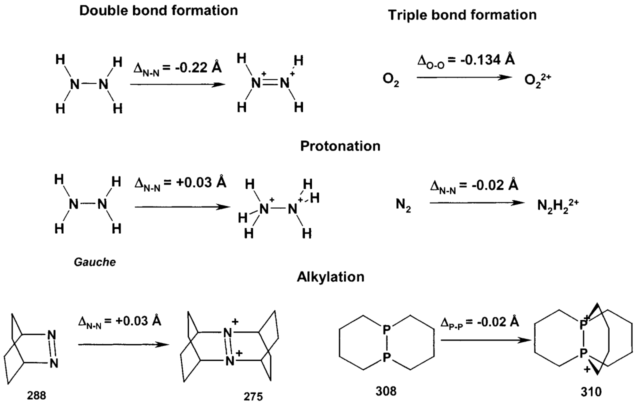
There are three approaches to 1,2-dications. 1,2-Dications can be created either by forming a new bond or by breaking an existing bond between two atoms. In the first case, two electrons are removed from an antibonding MO (usually an antibonding combination of nonbonding orbitals). In the second case, two electrons are removed from a bonding MO. Finally, the third approach involves formation of two σ bonds with electrophilic species which can either coordinate at a lone pair or add to a π system. Obviously, the electronic and structural consequences of these three processes are drastically different.

Among the two possible ways of the oxidative formation of a new $X^+{-}Y^+$ bond, comproportionation of X^{2+} and Y is generally preferred over sequential removal of electrons from both atoms. This finding, which has been first applied to gas-phase dications, was later confirmed by the results for organic disulfonium dications in solution. This is one of the first examples of fruitful cross-pollination between gas phase and solution studies of 1,2-dications—the fields that have been almost completely mutually exclusive so far.

Formation of a new bond results in significant stabilization of a dication with a concomitant dramatic decrease in the interatomic distance, especially when a σ bond is formed.

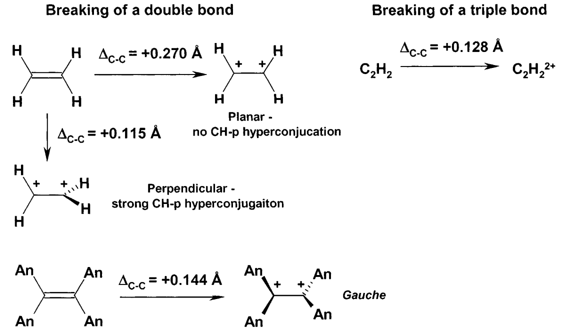


Formation of a double or a triple bond results in progressively smaller decreases in the distance and imparts smaller (but still considerable) stabilization to these dications.



It is harder to estimate the influence of two positive charges per se. For example, double protonation of hydrazine results in a small increase in the N–N distance, but this can be attributed to removal of the gauche effect which shortens the N–N bond in hydrazine. Diprotonated nitrogen seems to be a better model and it shows that the N–N distance decreases upon protonation when hyperconjugative effects do not mask the effect which the introduction of positive charge produces. This result is consistent with the difference in the bond lengths between the isoelectronic H_2 and He_2^{2+} species and observations of Dunitz and Ha.[20] The driving force for formation of such dications as hydrazinium dication and $N_2H_2^{2+}$ is the formation of two new σ bonds. Double alkylation has a similar effect, and, again, the observed changes in bond lengths depend on the interplay of several factors.

When electrons are lost from bonding orbitals, only removal of π electrons results in metastable dications. Removal of electrons from a σ orbital leads to spontaneous dissociation of a dication with the pagodane dication as the only known exception. As far as oxidation of π bonds is concerned, C–C bond elongation in the acetylene dication is considerably smaller than in the planar ethylene dication. Note, however, that the C–C bond length in the more stable perpendicular conformer of the ethylene dication is much shorter due to hyperconjugation of the cationic center with C–H orbitals. This provides another good indication of the intimate connection between the factors that stabilize dicationic moieties and interatomic distance between the two cationic centers.



The experimental and theoretical data reviewed in this paper illustrate that even intrinsically unstable dicationic moieties (such as carbodications and dications formed by removal of bonding σ electrons) can be stabilized to an extent that their formation becomes important in many organic and inorganic processes. As a result, 1,2-dications which have been considered for a long time as hypothetical or ephemeral intermediates finally have come to the forefront of chemical research. The unusual structures of these compounds render their reactivities remarkably different from other classic organic intermediates. The large structural changes associated with formation of certain dications can be used in a variety of interesting practical applications and we foresee rapid development of this field in the future.

XI. Acknowledgments

Financial support from the Russian Fundamental Investigation Foundation (Grant N 00-03-32763a) is gratefully acknowledged. A. I. thanks Florida State University for First Year Assistant Professor Award, Professors J. Saltiel, S. Nelsen, W. Herz, and N. Mills for helpful discussions, and Mr. B. Breiner and Ms. M. Naiman for proofreading this manuscript. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research (to A.I.).

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(61) Note, however, that this fact does not preclude the use of D_2^{2+} dication as a probe of spatial alignment of D_2 molecules with intense laser light. See Mathur, D. Bhardwaj, V. R.; Safvan, C. P.; Rajgara, F. A. *Int. J. Mass Spectrom.* **1999**, *192*, 367.

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