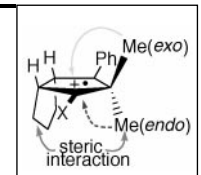
Regio- and diastereoselective rearrangement of cyclopentane-1,3-diyl radical cations generated by electron transfer



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Cyclopentane-1,3-diyl radical cations are readily available from azoalkanes or bicyclo[2.2.0]pentanes (housanes) by electron transfer. These short-lived intermediates may stabilize by numerous chemical processes, predominantly by 1,2-migration to form the corresponding cyclopentene derivatives after back electron transfer. This review focuses on the regio- and diastereoselectivities in the rearrangement of the strained cyclopentane-1,3-diyl radical cations and explores the mechanism of this novel 1,2-migration. This highly selective transformation offers attractive opportunities for the convenient and efficient synthesis of complex polycyclic structures.

1 Introduction

Radical cations are mechanistically versatile intermediates in numerous chemical transformations (Scheme 1), which include isomerization, rearrangement, cycloreversion, fragmentation, Diels–Alder cycloadditions, nucleophilic capture and dimerization.[1] For the cyclopentane-1,3-diyl radical cations generated from azoalkanes or bicyclo[2.2.0]pentanes (housanes), 1,2-migration represents the dominant reaction path to yield the corresponding cyclopentene derivatives (path A) after back electron transfer (BET).[2–5] Nevertheless, on appropriate substitution, other stabilization processes may be triggered to compete with the 1,2-shift. Thus, urazol annelation significantly alters the reactivity of the intermediary radical cations through the hetereoatom substitution. Instead of the 1,2-alkyl shift observed for the carbocyclic analogs, these nitrogen-substituted radical cations prefer to deprotonate (path B).[6] Furthermore, such urazol-annelated 1,3-radical cations are efficiently trapped by methanol to afford hemiaminal products (path C).[6] The cyclobutene-annelated cyclopentane-1,3-diyl radical cation is intramolecularly trapped by the juxtaposed double bond to afford bicycloheptadiene and norbornadiene derivatives (path D).[7] In the case of norbornadiene annelation, fragmentation to cyclopentadienes competes with the 1,2-shift (path E).[8]

The chemical reactivity of cyclopropane radical cations, the parent structures for the more strained cyclopentane-1,3-diyl radical cations, has been extensively explored in recent years.[9–17] The rich array of chemical transformations for cyclopropane radical cations are particularly well manifested for the strained cyclopentane-1,3-diyl derivatives (Scheme 1), which are the subject of the present review. These short-lived intermediates are readily generated from azoalkanes and housanes by photochemical and chemical electron transfer, of which the latter process is more convenient. Their existence is established by means of spectral methods, most definitively through EPR spectroscopy, and chemical trapping. Of the chemical transformations in Scheme 1, we shall focus on the rearrangement process (path A) since it is the most abundant reaction, for which the regio- and diastereoselectivities are now well understood and which illustrate the most characteristic transformation of these unusual transient species.

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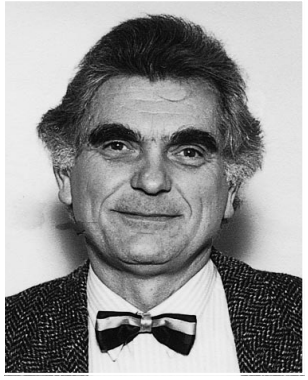
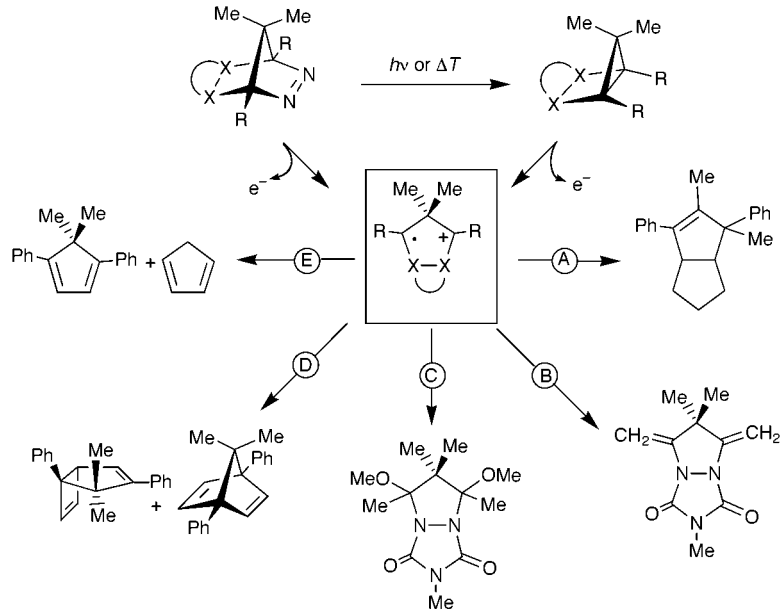


Waldemar Adam

Thomas Heidenfelder, born in 1970 in Germany, commenced his chemistry studies in 1989 at the University of Würzburg and joined Professor Adam's group in 1995 (Diplom 1995, Doctorate 1998). His doctoral work was concerned with the regio- and diastereoselectivity of the rearrangement of cyclopentane-1,3-diyl radical cations.

Thomas Heidenfelder



Scheme 1

2 Generation of radical cations

A vide variety of chemical and physical methods, which range from chemical electron transfer (CET), electrochemical oxidation, γ radiolysis, electron-impact ionization and photoinduced electron transfer (PET), have been used for the generation of radical cations. For mechanistic studies in solution, the desired radical cations are most conveniently produced chemically[18] or photochemically.[19]

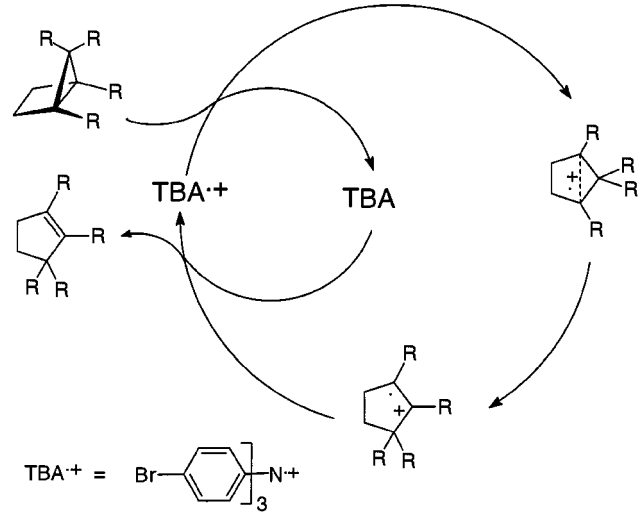
In the case of photosensitized electron transfer, a set of suitable sensitizers has become available[20] for the selective generation of radical cations through appropriate matching of the energies of the excited states to allow exothermic electron transfer between the electron-accepting sensitizer and electron-donating substrate. Alternatively, chemical electron transfer with persistent and isolable radical cation salts may be used, *e.g.* the well-known trisarylaminium salts.[21,22] Such aminium salts serve as one-electron oxidants, whose oxidation potential is conveniently tunable by the type, degree and pattern of substitution of the three aryl rings.

An extensive comparative study of the PET and CET processes has revealed that the CET mode is particularly advantageous for the oxidation of azoalkanes and housanes. Specifically, the CET oxidations proceed catalytically in a clean manner to afford the rearranged olefins in high yields (Scheme 2), while in the PET mode side reactions with the reduced photooxidant lead to by-products and low mass balances. Even when the aminium salt possesses a lower oxidation potential than the azoalkanes or housanes, complete conversion of the substrate may be achieved due to the driving force that originates from the irreversible exothermic rearrangement step after the endothermic electron transfer. The catalytic cycle is completed by BET from the amine Ar_3N to the cyclopentene radical cation to form the cyclopentene product and regenerate the aminium salt $Ar_3N^{\cdot+}$.

For most of the applications presented herein, the CET mode has been utilized to generate the radical cations, except in the EPR-spectral studies. Since these must be conducted under matrix isolation at cryogenic temperatures, neither CET nor PET is feasible and γ radiolysis constitutes the most expedient method.

3 Evidence for transient radical cations

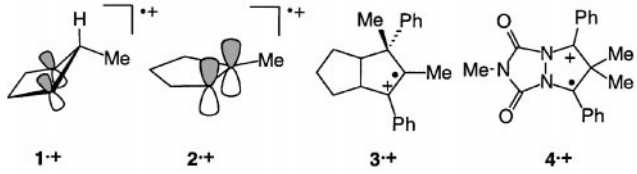
Besides EPR spectroscopy under matrix-isolation conditions[23,24] and pulse-radiolysis[25,26] studies, also chemical trapping[7,27] proved helpful in detecting and characterizing the transient radical cations derived from azoalkanes and housanes. Thereby valuable mechanistic insight has been gained into the chemical behavior of these short-lived reactive intermediates.



Scheme 2 Note that the radical cations, as drawn, are structurally not to be construed to constitute closed cyclopropane-type radical cations; they are planar, open 1,3-diyl radical cations, with the unpaired electron located either on the H- or the R-bearing terminus and the two possible limiting structures are represented for convenience and economy by means of the dashed line.

EPR spectroscopy under matrix isolation is the most direct and structurally informative method to detect radical cations. For example, the cyclopentane-1,3-diyl radical cation **1**$^{\cdot+}$ derived from the corresponding housane by γ radiolysis at 80–90 K was shown to possess a puckered conformation.[23] On warm-up to *ca.* 105 K, the relatively labile radical cation **1**$^{\cdot+}$

rearranged diastereoselectively to the olefin radical cation **2**$^{\cdot+}$ by a 1,2-shift of the axial hydrogen.



For the spectral characterization of the phenyl-substituted radical cations **3**$^{\cdot+}$ and **4**$^{\cdot+}$, EPR was inconclusive because of unresolved hyperfine structure. However, time-resolved optical absorption spectroscopy allowed the detection and characterization of such transients, generated from the corresponding housanes or azoalkanes by pulse radiolysis.[25,26] Unfortunately, for the cyclopentane-annelated case only the corresponding 1,2-radical cation species **3**$^{\cdot+}$ was observed, because the initially formed 1,3-radical cation was too short-lived to be detected at the time resolution of the pulse radiolysis (*ca.* 1 μs). Nevertheless, for the corresponding urazole-annelated derivative, the initial 1,3-radical cation **4**$^{\cdot+}$ was detected.[25,26]

Chemical trapping provides indirect evidence through product analysis for the detection and characterization of the cyclopentane-1,3-diyl radical cations in solution. While for cyclopentane-1,3-diyl diradicals, trapping experiments with dioxygen or aminoxyls as scavengers serve as a valuable mechanistic tool,[28–30] such trapping studies are not feasible for the corresponding 1,3-diyl radical cations because the rates are too slow. However, numerous studies on intermolecular and intramolecular nucleophilic trapping of 1,2-radical cations through reactions with alcohol,[31,32] amine,[31] and nitrile[31] functionalities are known.

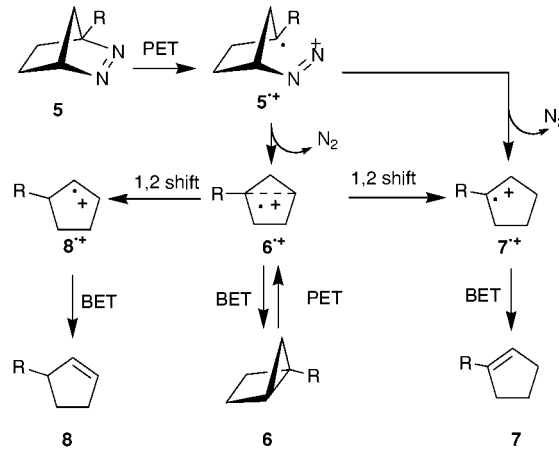
4 Rearrangement of cyclopentane-1,3-diyl radical cations

4.1 Regioselectivity[2–5]

As already mentioned, cyclopentane-1,3-diyl radical cations derived from diazabicyclo[2.2.1]heptene (DBH) derivatives or housanes exhibit a high propensity to rearrange by a 1,2-shift to the corresponding 1,2-radical cations, which after back electron transfer yield substituted cyclopentenes. For an unsymmetrical substrate, regioisomeric products are expected due to the relative stabilization of the cation and radical sites in the oxidized 1,3-diyl species. Indeed, the one-electron oxidation of the unsymmetrical methyl-substituted housane **6a** yielded exclusively 3-methylcyclopentene (**8a**), whereas its phenyl analog **6b** gave mainly 1-phenylcyclopentene (**7b**) as rearrangement product (Scheme 3).[4,24]

Moreover, the distinctly different product distributions in the PET reactions of the azoalkanes **5** and the corresponding housanes **6** provide strong evidence for the involvement of diazenyl radical cations in the denitrogenation of the oxidized azoalkanes **5**. This was already documented by the matrix EPR studies in the radiolytic oxidation of housanes and azoalkanes. Thus, like the diazenyl diradicals, the corresponding radical cations **5**$^{\cdot+}$ expel N_2 with a concomitant 1,2-hydrogen shift through backside attack on the remaining C–N bond.[24,33]

Recent *ab initio* calculations furnished a detailed mechanistic trajectory for the 1,2-shift in the methyl-substituted cyclopentanediyl radical cation **6**$^{\cdot+}$ (Fig. 1).[34] Thus, the 1,3-radical cation **6**$^{\cdot+}$ possesses a stable puckered conformation due to population of a bonding orbital by the unpaired electron. The puckered species requires *ca.* 3 kcal mol^{-1} of activation to form the twisted conformer, which lies in an energy well of *ca.* 2.6 kcal mol^{-1} due to methyl stabilization of the localized positive



5a: R = Me	53	40	7
5b: R = Ph	0	78	22
6a: R = Me	>99		<1
6b: R = Ph	22		78

Scheme 3 Note that in this Scheme, the product distributions in the PET reactions of the azoalkanes **5a**,**b** (the first two rows) and the housanes **6a**,**b** (last two rows) are shown.

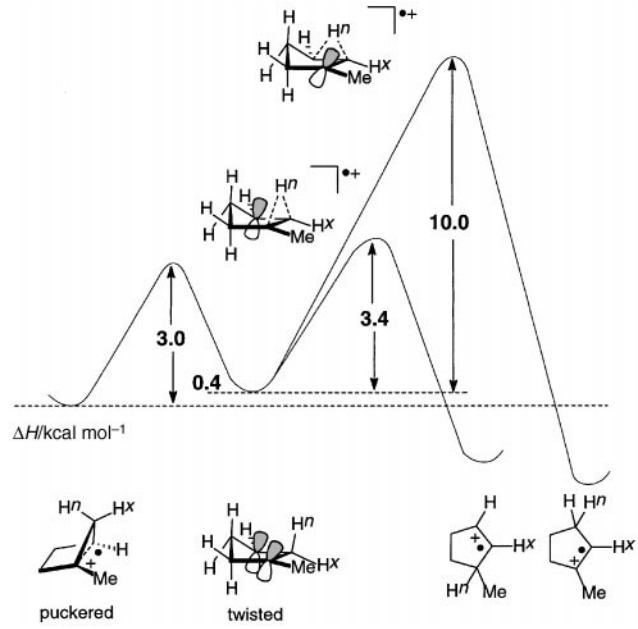
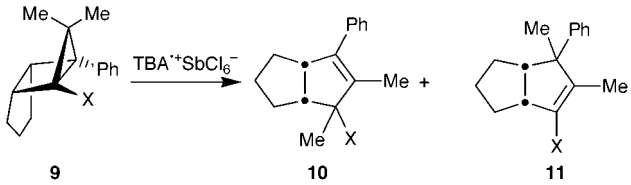


Fig. 1 QCISD//MP2-631G* reaction coordinate for the 1,2-H shift of the bridgehead methyl-substituted housane (energies in kcal mol^{-1}); *n* stands for *endo* and *x* for *exo*.

charge. Subsequently, the twisted conformer needs about 3.4 kcal mol^{-1} for the Wagner–Meerwein-type hydrogen shift to the methyl-substituted cation site. The migration to the unsubstituted radical site lies, with *ca.* 10 kcal mol^{-1}, much higher. The reason for this substantial difference (*ca.* 6 kcal mol^{-1}) in energy barrier of these two modes of hydrogen migration is due to the fact that for the shift to the cationic center a favorable two-electron/two-orbital interaction applies, while the shift to the radical site requires an unfavorable three-electron/two-orbital interaction. As a consequence, 1,2-hydrogen migrations in cations are facile, but in radicals are reluctant.[35,36]

The low energy barrier of *ca.* 3 kcal mol^{-1} for the hydrogen shift is corroborated by the EPR findings in that the 1,3-radical cation **6**$^{\cdot+}$ does not persist even at 77 K.[24] The alternative 1,2-shift through a puckered transition-state structure (not shown in Fig. 1) requires a prohibitive activation barrier of *ca.* 40 kcal mol^{-1}.[34]

To assess the relative stabilization of the cation and radical sites in the cyclopentane-1,3-diyl radical cations, the readily accessible cyclopentane-annelated housanes **9** were prepared and the regioselectivity of the CET-induced 1,2-methyl rearrangement determined.[2,3] The CET reactions that afford the olefinic products **10** and **11** are displayed in Scheme 4. A



9 **10** **11**

X= CH_3, CH_2F, CH_2CN, CH_2OH, CH_2OMe, CHO, COMe, C_6H_4-*p*-Me, C_6H_4-*p*-Cl, C_6H_4-*p*-CO_2Me, C_6H_4-*p*-CN

Scheme 4

complete reversal in the regioselectivity of the 1,2-shift was observed: for the CH_3, CH_2OH, CH_2OCH_3, CH_2F, and C_6H_4-*p*-Me derivatives the regioisomer **10** is preferred (migration to the X-substituted terminus), but for the CH_2CN, CHO, $COCH_3$, C_6H_4-*p*-Cl, C_6H_4-*p*-CO_2CH_3 and C_6H_4-*p*-CN cases the regioisomer **11** is favored (migration to the Ph-substituted terminus).[2,3]

These regioselectivities reflect a profound electronic effect of the X substituent at the migration terminus in the intermediary cyclopentane-1,3-diyl radical cations. The relevant orbital interaction for the 1,2-methyl shift engages the LUMO(σ*) of the cyclopentane-1,3-diyl radical cations **9**$^{\cdot+}$ and the HOMO(σ) of the migrating C–Me σ bond. The required relative LUMO(σ*) energies may be assembled in a qualitative manner through the interaction of the orbitals for the fragments R–CMe_2 and Ph–CMe_2 in the 1,3-radical cation. This is shown in Fig. 2 for two extreme cases, namely complete methyl migration to the X or to the Ph terminus.

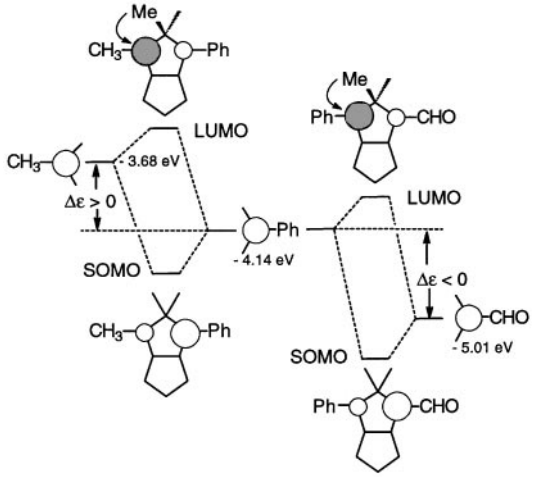
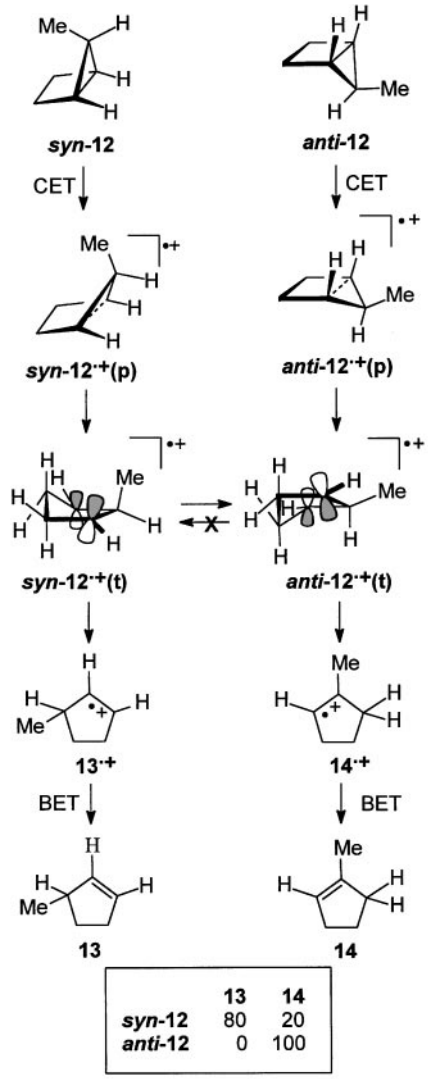


Fig. 2 Schematic orbital-interaction diagram of the radical fragments.

The relative ordering of the orbital fragments is given by the corresponding ε_{SOMO} orbital energies, which are readily accessible through AM1 calculations. For convenience, the $\Delta\varepsilon$ quantity is defined, for which positive values ($\Delta\varepsilon > 0$) apply when the ε_{SOMO} of the X-substituted fragment lies above the cumyl one (the phenyl substituent is taken as reference point), while negative values ($\Delta\varepsilon < 0$) are observed when the ε_{SOMO} of the X-substituted fragment lies below the cumyl one. As a consequence, for $\Delta\varepsilon > 0$, the LUMO in the radical cation **9**$^{\cdot+}$ will be in energy more similar to the X-substituted fragment and also carry the larger coefficient at this site (Fig. 2). Hence, the 1,2-shift will take place preferentially to the X site to yield the regioisomer **10**. In contrast, for $\Delta\varepsilon < 0$, the LUMO of the 1,3-radical cation **9**$^{\cdot+}$ lies closer in energy to the cumyl fragment and the phenyl terminus (Fig. 2) bears the larger coefficient such that the regioisomer **11** is preferred. Indeed, a plot of the logarithm of the regioisomeric ratios [ln(**10**/**11**)] *versus* the semiempirical orbital energy differences ($\Delta\varepsilon$) displays an excellent linear correlation (r^2 = 0.989). This linear correlation substantiates that electronic and not steric effects of the X substituent control the observed regioselectivities in the radical cations **9**$^{\cdot+}$.[2,3]

4.2 Stereochemical memory effect of the migrating group

A remarkable stereochemical memory effect was disclosed in the PET chemistry of the stereolabeled *syn*- and *anti*-5-methylbicyclo[2.1.0]pentanes ***syn/anti*-12**: the *anti* stereoisomer furnished only 1-methylcyclopentene as the rearrangement product, while the *syn* one afforded predominantly 3-methylcyclopentene (Scheme 5).[24] On the basis of this diastereoselectivity, combined with EPR spectroscopy[24] and *ab initio* calculations,[34] the mechanism in Scheme 5 was deduced.

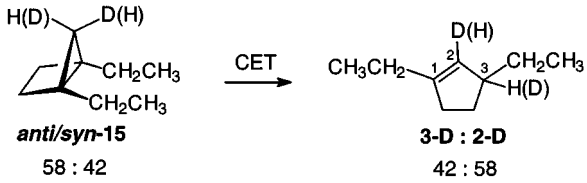


	13	14
***syn*-12**	80	20
***anti*-12**	0	100

Scheme 5

Oxidation of the housanes ***anti,syn*-12** affords the persistent, puckered 1,3-radical cations ***anti,syn*-12**$^{\cdot+}$**(p)**, as confirmed by EPR spectroscopy under matrix isolation. Breakage of the one-electron bond generates the twisted conformers ***anti,syn*-12**$^{\cdot+}$**(t)**, which on Wagner–Meerwein rearrangement leads to the respective olefin radical cations **13**$^{\cdot+}$ and **14**$^{\cdot+}$, and final BET produces the corresponding cyclopentenes. The ring-flip

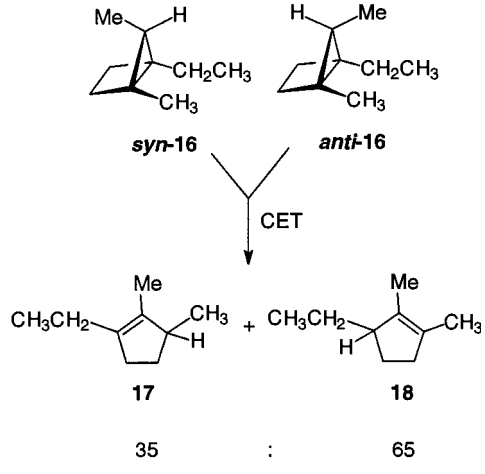
in the ***syn*-12$^{\cdot+}$(t)** isomer competes with a 1,2-shift; presumably, methyl migration leads to the thermodynamically less stable dialkylated olefin radical cation **13**$^{\cdot+}$, whereas hydrogen migration for the ***anti*-12$^{\cdot+}$(t)** isomer results in the more stable trialkylated one **14**$^{\cdot+}$. Also in the CET reaction of the deuterium-labeled housanes ***syn/anti*-15** the initial *syn/anti* deuterium distribution was conserved quantitatively within the experimental error (*ca.* 3%) in the rearrangement to the corresponding cyclopentene products **2-D** and **3-D** (Scheme 6).[4]



Scheme 6

These labeling results confirm the already mentioned stereochemical memory effect also for the more persistent disubstituted 1,3-diyl radical cations ***syn/anti*-15**$^{\cdot+}$. Evidently, analogously to the twisted conformation of the radical cation ***syn/anti*-11**$^{\cdot+}$**(t)**, the original *syn* substituent acquires a pseudo-axial orientation in almost perfect coplanar alignment with the 2p orbital at the bridgehead position, while the pseudo-equatorial substituent is located essentially parallel to the nodal plane of the 2p orbitals. Clearly, migration of the pseudo-axial substituent is favored, and this stereoelectronic control accounts for the diastereoselective migration in the CET-induced rearrangement of the deuterium-labeled housanes in Scheme 6.

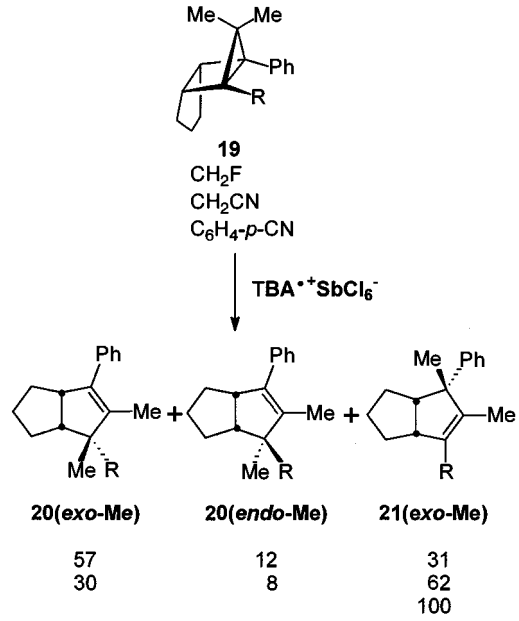
In contrast, for the methyl-stereolabeled ***syn/anti*-16** housanes (Scheme 7),[4] only a 1,2-hydrogen shift had occurred for both the *anti* and the *syn* isomer. AM1 calculations reveal that the resulting tetraalkylated olefin radical cations (H migration) **17**$^{\cdot+}$ and **18**$^{\cdot+}$ possess *ca.* 12 kcal mol^{-1} less energy than the corresponding trialkylated ones (Me migration). Presumably, a common planar radical cation intermediate is involved in this rearrangement, in which hydrogen migration results in the thermodynamically favored product.



Scheme 7

4.3 Diastereoselectivity

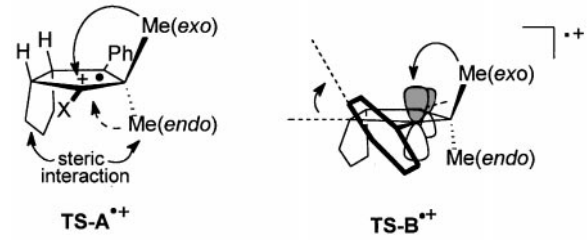
Cyclopentane annelation, as in the bicyclo[3.3.0]octane skeleton, provides an inherent stereochemical label to assess the diastereoselectivity of the rearrangement process in cyclopentane-1,3-diyl radical cations (Scheme 8).[2–5] The product data show that the diastereoselectivity in the CET-induced



Scheme 8

rearrangement of these cyclopentane-annelated housanes **19** depends on the type of substitution at the bridgehead positions. Thus, also some **20(*endo*-Me)** product is observed when the rearrangement terminus bears alkyl groups, *i.e.* CH_2OH, CH_2OMe, CH_2F or CH_2CN, whereas exclusively the *exo* product is obtained when this site carries an aryl substituent. The formation of both the *exo*-Me and *endo*-Me diastereomers **20** as olefinic products suggests a planar radical cation geometry in the rearrangement step. If a twisted conformation analogous to **12**$^{\cdot+}$**(t)** were to be involved, only the **20(*exo*-Me)** diastereomer should have been formed.

The preference for the *exo*-Me diastereomer of the regioisomer **20** results from the larger steric interaction with the annelated cyclopentane ring in the **TS-A**$^{\cdot+}$ transition state during the transposition of the *endo*-methyl group. Also steric effects are responsible for why aryl substitution at the rearrangement terminus suppresses *endo*-methyl product completely for the regioisomer **21** (Scheme 8), as displayed in the transition-state structure **TS-B**. Inspection of molecular models

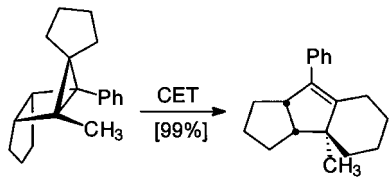


reveals that severe repulsive interactions between the aryl group and the annelated cyclopentane ring in the radical cation oblige the phenyl ring to align conformationally in a skewed orientation with respect to the planar cyclopentane-1,3-diyl ring. As a consequence, the *endo*-methyl group is sterically blocked by the skew aryl substituent and exclusively the **21(*exo*-Me)** diastereomer is produced (Scheme 8). Thus, the diastereoselectivity of the 1,2-shift is controlled by steric factors in the intermediary planar 1,3-radical cations **TS-A**$^{\cdot+}$ derived from the cyclopentane-annelated housanes **19**.[2,3]

4.4 Synthetic potential

The high degree of stereoselectivity and the control of regioselectivity through appropriate bridgehead substitution in

the housane offer an opportunity to employ the rearrangement of cyclopentane-annelated cyclopentane-1,3-diyl radical cations (path A in Scheme 1) for the synthesis of complex ring systems, *e.g.* the wide-spread diquinanes (Scheme 8).[37] In particular the CET methodology with trisarylaminium salts constitutes an effective method for this purpose. On one hand, back electron transfer to the cyclopentane-1,3-diyl radical cations is minimized and, on the other hand, this reaction may be run on a preparative scale.[37] Moreover, when the methylene bridge of the housane is spiro-substituted, this oxidative rearrangement allows the preparation of polycyclic structures through stereocontrolled ring expansion. For instance, the triquinane-related olefin **23** in Scheme 9 was obtained in excellent yield upon oxidation of the spiro-substituted tricyclooctane **22** with catalytic amounts of $TBA^{\cdot+}$, in which the quarternary center is perfectly diastereo- and regioselectively introduced. Surely, this novel synthetic methodology provides an efficent and convenient access to unusual cyclopentanoid derivatives.[37]



22 **23**

Scheme 9

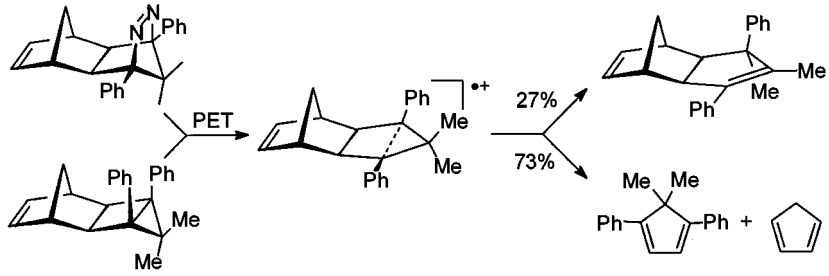
5 Perspectives

Of the various transformations for the distonic cyclopentane-1,3-diyl radical cations displayed in Scheme 1, the product studies establish that the rearrangement by a 1,2-shift (path A) is the prominent stabilization channel. The driving force originates from the energy-favored formation of the proximate cyclopentene-1,2-diyl radical cation (olefin radical cation), *ab initio* computations disclose a relatively low (*ca.* 3 kcal mol^{-1}) activation barrier for the 1,2-H migration. It is, thus, not surprising that low-temperature (*ca.* 80 K) matrix isolation is essential for direct EPR-spectral detection of these elusive species, while unequivocal trapping is reserved for a few specialized cases, *e.g.* intermolecularly by methanol for the nitrogen-substituted derivative (path C) or intramolecularly for the cyclobutene-annelated system (path D) in Scheme 1.

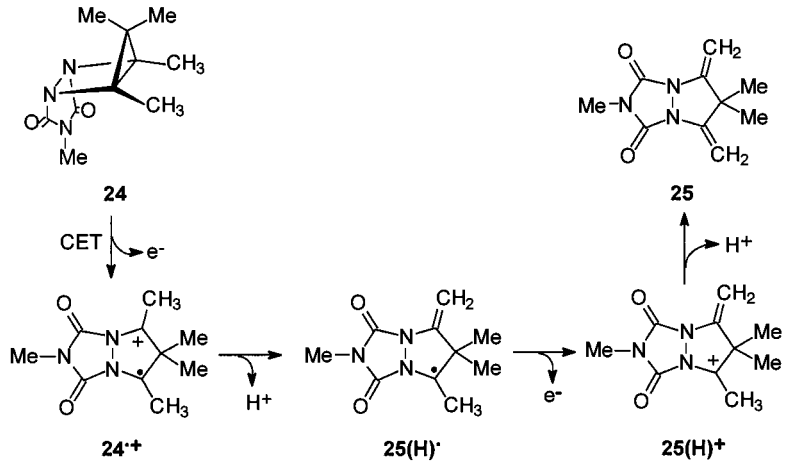
To date, very few other transformations are known to compete with the facile rearrangement process (path A) in Scheme 1, and then only under special circumstances. One of these is fragmentation (path E), which is detailed in Scheme 10 for the norbornene-annelated derivative; in fact, cycloreversion into the two cyclopentadienes dominates over the diastereoselective 1,2-methyl migration.[8,27] The mechanistic reasons for this reactivity preference are yet to be elucidated, but presumably the rigidity of the annelated bicyclic ring encumbers the proper conformational alignment for the methyl shift (*cf.* the twisted conformation in Fig. 1) such that the annelating σ bonds are cleaved preferentially. Of course, considerable impetus for fragmentation derives from the formation of the diphenyl-substituted cyclopentadiene radical cation, stabilized through conjugation.

A dramatic example constitutes the deprotonation (path B, Scheme 1) of the diaza-substituted 1,3-radical cation $\mathbf{24}^{\cdot+}$, which offers exclusively the bisolefin **25** (Scheme 11), without even traces of rearrangement product.[6,25] It was shown that the monoradical $\mathbf{25(H)}^{\cdot}$ intervenes, derived from the 1,3-radical cation $\mathbf{24}^{\cdot+}$ on proton loss. Subsequently, $\mathbf{25(H)}^{\cdot}$ is oxidized by a second equivalent of $Ar_3N^{\cdot+}$ to yield the corresponding cation $\mathbf{25(H)}^{+}$ and a second deprotonation affords finally the bisolefin **25**. Evidently, the two nitrogen atoms in the urazole-bridged radical cation stabilize it by conjugation, while the juxtaposed carbonyl group facilitates proton loss such that 1,2-methyl migration is completely suppressed.[6,25]

The profound differences in the chemical behavior of cyclopentane-, norbornene- and urazole-annelated 1,3-radical



Scheme 10



Scheme 11

cations illustrate that on appropriate substitution, other stabilization processes may be triggered to compete with the 1,2-shift. Now that we understand quite well the regio- and diastereocontrolled rearrangement process (path A), a future goal of the research should be to uncover competitive chemical reactivity of cyclopentane-1,3-diyl radical cations and elucidate the structural and electronic features that steer it. For instance, a worthwhile task would be the exploration of methylene-bridge substitution (the intervening carbon center between the radical sites) and how it dictates reactivity modes. Poorly migrating groups should enhance alternative reaction channels of the cyclopentane-1,3-diyl radical cations as preferred stabilization process (Scheme 1). Little if anything is known about this mechanistic query even for carbocations and the readily accessible housane-derived 1,3-radical cations offer challenging opportunities.

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