Generation of 4,5-Diazacyclopentane-1,3-diyl Radical Cations by Chemical Electron Transfer (CET) Oxidation of Urazole-Bridged Bicyclic Housanes (Bicyclo[2.1.0]pentanes) and Their Chemical Transformations

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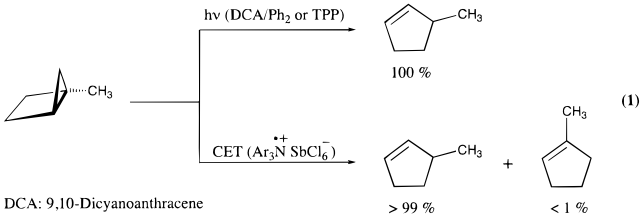
4,5-Diazacyclopentane-1,3-diyl radical cations $\mathbf{3}^{\bullet+}$ were generated from urazole-bridged bicyclic housanes **3** through chemical oxidation by using tris(4-bromophenyl)aminium hexachloroantimonate as oxidant to afford the two olefinic products **4** and **5**. Product studies establish that the bisolefins **5** are the result of double oxidation of the housanes **3**, whereas the monoolefins **4** are formed by acid-catalyzed rearrangement, which can be suppressed by excess of base (2,6-di-*tert*-butylpyridine). In the case of dibenzyl substitution (**3c**), disproportionation of two monoradical species **5(H)c**• serves as an alternative pathway to the corresponding olefins **4** and **5** because higher amounts of double oxidation product were isolated in the absence of base than expected if only a stoichiometric reaction were operating. Semiempirical MO calculations suggest that ionization takes place from one of the nitrogen lone pairs rather than from the strained central C−C bond as implied by the significantly lower (by ca. 0.5 eV) ionization potential. Furthermore, in the initially puckered radical cation, the positive charge is mainly located at the two nitrogen atoms, while after relaxation to the planar geometry, the charge shifts essentially entirely to the radical cation carbon atoms. The trapping reaction with methanol leads to the hemiaminal-type products **6** and **7**, which establish the involvement of the cationic intermediates $\mathbf{3(H)}^+$ and $\mathbf{5(H)}^+$. In addition, ^{13}C NMR spectroscopy confirmed these cationic intermediates [$\mathbf{3(H)}^+$ and $\mathbf{5(H)}^+$] by detection of the characteristic signals below δ 250 for carbenium ions. Unquestionably, the urazole ring significantly influences the radical cation reactivity of the housanes **3**. Thus, in contrast to the corresponding homocyclic tricyclooctane derivatives, stoichiometric instead of catalytic amounts of CET oxidant are needed, the two nitrogen atoms of the hydrazino bridge stabilize the radical cation $\mathbf{3}^{\bullet+}$ by conjugation, and the carbonyl groups of the urazole moiety assist the deprotonation to the exocyclic double bonds to prevent 1,2 alkyl migration.

Introduction

The discovery of fast deazatation of 1,1′-azadamantane upon one-electron oxidation[1] promoted the general interest in exploring the nature of azoalkane radical cations, their fragmentation mechanism, and their importance as precursors for radicals, diradicals, cations, and radical cations.[1−4] Cyclic derivatives, particularly the 2,3-diazabicyclo[2.2.1]hept-2-enes and their corresponding bicyclo[2.1.0]pentanes (housanes), serve as precursors for 1,3 diradicals, which have been comprehensively examined,[5] as well as for 1,3-diyl radical cations.[6] The latter exhibit a high tendency to rearrange by 1,2 alkyl or hydrogen shift to the corresponding 1,2 radical cations, which after electron back-transfer yield substituted cyclopentenes.[6] This stabilization process is closely related to the exothermic cyclopropane−propene rearrangement.[7] The generation of the cyclic 1,3 radical cations can either occur photochemically[6a,b] or chemically[6c] (eq 1), the latter by using one-electron oxidants like aryl aminium salts,



(1)

DCA: 9,10-Dicyanoanthracene
TPP: Triphenylpyrylium tetrafluoroborate
Ph_2: Biphenyl

which are readily available by the reported synthesis.[8]

In the late 1960s, the photochemistry of heteroatom-substituted cyclic azoalkanes was examined.[9] For ex-

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(1) (a) Bai, D. H.; Engel, P. S; Hoque, A. K. M. M.; Keys, D. E.; Lee, W.-K.; Shaw, R. W.; Shine, H. J. *J. Am. Chem. Soc.* **1985**, *107*, 2561−2562. (b) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964−4975. (c) Engel, P. S.; Kitamura, A.; Keys, D. E. *J. Org. Chem.* **1987**, *52*, 5015−5021.

(2) (a) Mendicino, M. E.; Blackstock, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 713−715. (b) Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2484−2496.

(3) (a) Adam, W.; Casado, A.; Miranda, M. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 797−798. (b) Adam, W.; Dörr, M. *J. Am. Chem. Soc.* **1987**, *109*, 1570−1572. (c) Adam, W.; Grabowski, S.; Miranda, M. A.; Rübenacker, M. *J. Chem. Soc., Chem. Commun.* **1988**, 142−143.

(4) (a) Williams, F.; Guo, Q.-X.; Petillo, P. A.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 7887−7888. (b) Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1498−1501. (c) Gerson, F. *Acc. Chem. Res.* **1994**, *27*, 63−69.

(5) (a) Adam, W.; Denninger, U.; Finzel, R.; Kita, F.; Platsch, H.; Walter, H.; Zang, G. *J. Am. Chem. Soc.* **1992**, *114*, 5027−5035. (b) Engel, P. S.; Culotta, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 2686−2696. (c) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165−172. (c) Adam, W.; DeLucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762−779. (d) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99−150.

(6) (a) Adam, W.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007−3014. (b) Adam, W.; Sahin, C.; Sendelbach, J.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1994**, *116*, 2576−2584. (c) Adam, W.; Sahin, C. *Tetrahedron Lett.* **1994**, *35*, 9027−9030.

(7) (a) Boche, G.; Walborsky, H. M. in *Updates from the Chemistry of Functional Groups: Cyclopropane-derived Reactive Intermediates*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1990; pp 207−236. (b) Qin, X.-Z.; Snow, L. D.; Williams, F. *Chem. Phys. Lett.* **1985**, *117*, 383−385. (c) Qin, X.-Z.; Williams, F. *Chem. Phys. Lett.* **1984**, *112*, 79−83.

(8) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577−585.

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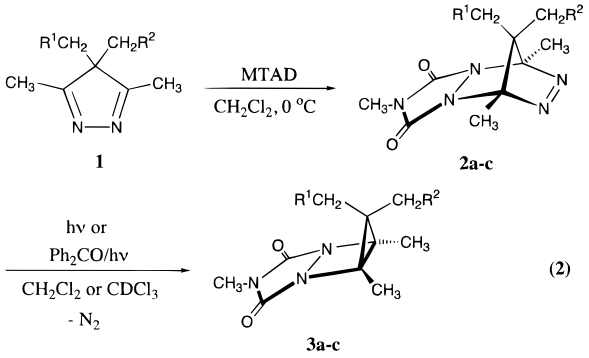
ample, the urazole-bridged azoalkanes were prepared in high yields by Diels−Alder reaction of isopyrazoles with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD).[9] The direct photolysis of these heteroatom-substituted azoalkanes led on denitrogenation to the corresponding housanes through the intermediary 1,3 diradicals, whose triplet states were EPR-spectrally detected under matrix isolation. The poor solubility of the PTAD cycloadducts can be conveniently circumvented by using 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) derivatives,[10] which does not alter the direct or sensitized photolytic properties (eq 2) of these azoalkanes **2** and housanes **3**.



1 **2a-c** **3a-c** (2)

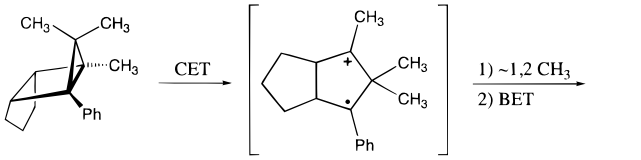
$R^1 = R^2 =$ H (**2a**, **3a**)

$R^1 =$ H, $R^2 =$ Ph (*syn*-**2b**, *anti*-**3b**)

$R^1 =$ Ph, $R^2 =$ H (*anti*-**2b**, *syn*-**3b**)

$R^1 = R^2 =$ Ph (**2c**, **3c**)

On the basis of the knowledge about the electron transfer chemistry of carbocyclic bicycles, it was our interest to assess whether N-heteroatom substitution would alter the behavior and reactivity of the transient 1,3 radical cations derived by one-electron oxidation of the urazole-bridged housanes **3**. To date, little if anything is known about such heteroatom-substituted radical cation intermediates. A suitable system for comparison is the analogous carbocyclic housanes, namely the tricyclo[3.3.0.0^{2,4}]octanes, which rearrange on treatment with tris(4-bromophenyl)aminium hexachloroantimonate quantitatively to substituted diquinanes (eq 3).[11] The latter are formed by 1,2 alkyl migration, a rearrangement which proceeds catalytically and highly regio- and diastereoselectively to generate complex ring structures.[11] These homocyclic 1,3-cyclopentanediyl radical cations may serve as reference system to verify the influence of heteroatoms on the reactivity and persistence of 1,3 radical cations. In addition, it is known from the work of Nelsen *et al.*[12] on substituted hydrazine derivatives that they easily form stable radical cations and dications by oxidation at the nitrogen atoms, which either are stable enough to be isolated as their corresponding salts or undergo rearrangement or deprotonation.



(3)

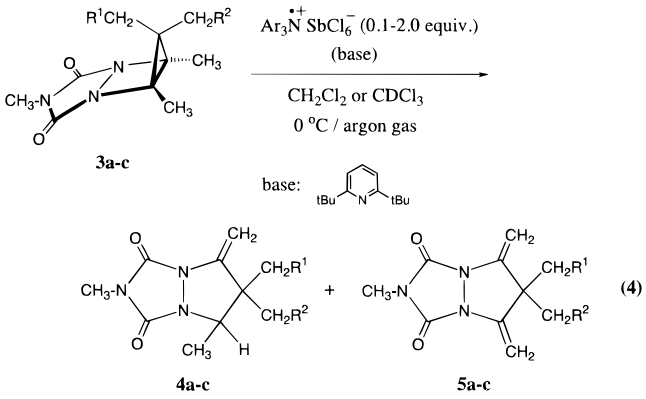
100 %

Herein we present our results, in which we demonstrate that the annelated urazole ring significantly alters the reactivity of the intermediary radical cations **3**$^{\bullet+}$ through the heteroatom substitution. Instead of the 1,2 alkyl shift[13] observed for the carbocyclic analogs (eq 3), the nitrogen-substituted radical cations **3**$^{\bullet+}$ prefer to deprotonate, a chemical behavior dictated by the N acyl groups adjacent to the radical cation sites.

Results

The synthetic route (eq 2) for the preparation of the urazole-bridged housanes **3** started from the corresponding diketones, which gave in a four-step synthesis the bicyclo[2.1.0]pentane derivatives.[9,10] Either direct or sensitized photolysis (benzophenone as sensitizer) led to the corresponding housanes **3**. Due to their thermal lability, the CET reactions with tris(4-bromophenyl)-aminium hexachloroantimonate were performed at 0 °C to avoid any product formation by thermal decomposition.[10] The CET oxidant tris(4-bromophenyl)aminium hexachloroantimonate (TBA$^{\bullet+}$SbCl$_6^-$) was prepared by following Steckhan's synthesis.[8]

The electron transfer reaction was either performed in the absence or presence of base (2,6-di-*tert*-butylpyridine), cf. eq 4. Without base, the two olefinic products **4** and **5** were isolable after flash chromatography on silica



3a-c

(4)

4a-c **5a-c**

gel, e.g. 48% of the monoolefin **4a** and 33% of bisolefin **5a** (Table 1, entry 1), if 0.75 molar equivalent of CET oxidant was used. In the presence of an excess of base (entries 2 and 3), the only product isolated was the bisolefin **5a**. The bis-olefinic products **5** are the double oxidation products of the housanes **3**, as could be clearly shown for the parent substance **3a** (entries 1−3) and for

(9) (a) Evnin, A. B.; Arnold, D. R.; Karnischky, L. A.; Strom, E. *J. Am. Chem. Soc.* **1970**, *92*, 6218−6231. (b) Evnin, A. B.; Arnold, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 5330−5332. (c) Arnold, D. R.; Evnin, A. B.; Kasai, P. H. *J. Am. Chem. Soc.* **1969**, *91*, 784−785. (d) Arnold, D. R.; Evnin, A. B.; Karnischky, L. A. *Pure Appl. Chem.* **1970**, *24*, 523−530.

(10) Adam, W.; Goller, K.; Kammel, T.; Peters, K. *J. Org. Chem.* **1995**, *60*, 308−316.

(11) Adam, W.; Heidenfelder, T.; Sahin, C. *Synthesis* **1995**, 1163−1170.

(12) (a) Nelsen, S. F.; Wang, Y. *J. Org. Chem.* **1994**, *59*, 3082−3090. (b) Nelsen, S. F. In *Acyclic Organonitrogen Stereodynamics*; Lambert, J. B., Takeuchi, Y., Eds.; VCH: Weinheim, Germany, 1992; pp 89−121. (c) Nelsen, S. F.; Kim, Y.; Neugebauer, F. A.; Krieger, C.; Siegel, R.; Kaftory, M. *J. Org. Chem.* **1991**, *56*, 1045−1051.

(13) The thermolysis of either azoalkane **2c** or housane **3c** led by a 1,2 benzyl shift to the corresponding olefin analogous to the carbocyclic derivative shown in eq 3. Besides this rearrangement process, retrocleavage to the isopyrazole **1c** and the dimer of 4-methyl-1,2,4-triazoline-3,5-dione were observed.

Table 1. Product Studies in Chemical Electron Transfer Oxidation of Bicyclopentanes 3 with Tris(4-Bromophenyl)aminium Hexachloroantimonate ($TBA^{\bullet+}SbCl_6^-$)

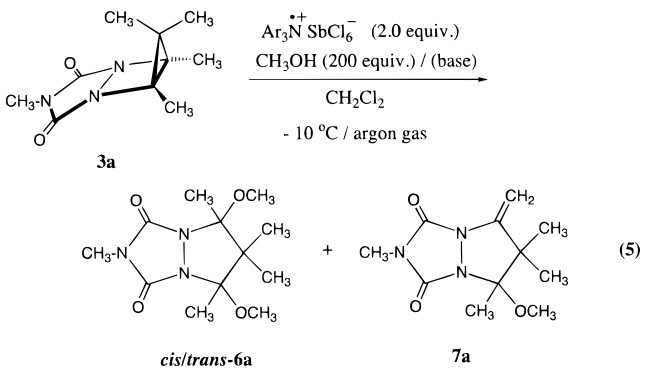
			reagents (equiv)[a]		product distribution[b,c]	
entry	substrate	solvent[d]	$TBA^{\bullet+}SbCl_6^-$	base[e]	**4** [%]	**5** [%]
1	**3a**	$CDCl_3$	0.75	–	48	33 (37.5)
2	**3a**	$CDCl_3$	1.0	2.0	–	43 (50)
3	**3a**	CH_2Cl_2	2.0	4.0	–	85 (100)
4	**3b**	$CDCl_3$	0.5	–	<5	24 (25)
5	**3b**	$CDCl_3$	1.0	2.0	11	49 (50)
6	**3c**	$CDCl_3$	0.1	–	25	13 (5)
7	**3c**	$CDCl_3$	0.2	–	52	20 (10)
8	**3c**	$CDCl_3$	0.5	–	41	24 (25)
9	**3c**	$CDCl_3$	0.5	2.0	–	21 (25)
10	**3c**	$CDCl_3$	1.0	2.0	–	39 (50)
11	**3c**	CH_2Cl_2	1.5	4.0	–	69 (75)
12	**3c**	CH_2Cl_2	2.0	4.0	–	76 (100)

[a] Molar equivalents are given relative to the amount of housane used. [b] In all cases complete conversion; yields of isolated material after flash chromatography on silica gel. [c] In parentheses are given the maximum yields of bisolefin **5** based on 2 equiv of CET reagent used. [d] Dry, acid-free solvents were used, which were passed through a short basic alumina oxide column. [e] 2,6-Di-*tert*-butylpyridine was used as base.

the monobenzyl-substituted derivative *syn*-**3b** (entries 4 and 5). It was unnecessary to examine the CET chemistry of the individual stereoisomers *syn*/*anti*-**3b** because tris(4-bromophenyl)aminium hexachloroantimonate catalyzed efficiently the *anti* → *syn* isomerization and this process was faster than the CET reaction to the olefinic products **4b** and **5b**. Thus, only the chemical oxidation of the *syn* isomer **3b** (entries 4 and 5), which is the thermodynamically more stable product (*syn*/*anti* ratio = 94:6 at ca. 20 °C),[10] was examined.

When less than molar amounts of CET oxidant were applied to the dibenzyl system **3c** in the absence of base (entries 6 and 7), higher yields of bisolefin **5c** were isolated than expected if only a stoichiometric reaction was operating. If higher amounts of oxidant were used (entry 8), the double oxidation product **5c** was obtained in stoichiometric amounts besides the monoolefin **4c**. In the presence of base (entries 9−12) only the bisolefin **5c** was observed at all concentrations of $TBA^{\bullet+}SbCl_6^-$ employed.

When the CET reaction of housane **3a** was executed in the presence of a large excess of cation scavenger such as methanol, the cationic intermediates $\mathbf{3a}^{\bullet+}$ and $\mathbf{7(H)a}^+$ were efficiently trapped in form of the *cis*/*trans*-**6a** bishemiaminals, which were isolated by flash chromatography (eq 5). The major product was the double trapping product *cis*-**6a**, which could be clearly distinguished from



(5)

the minor product *trans*-**6a** by NMR spectroscopy. The latter possesses C_2 symmetry and, thus, the two methyl

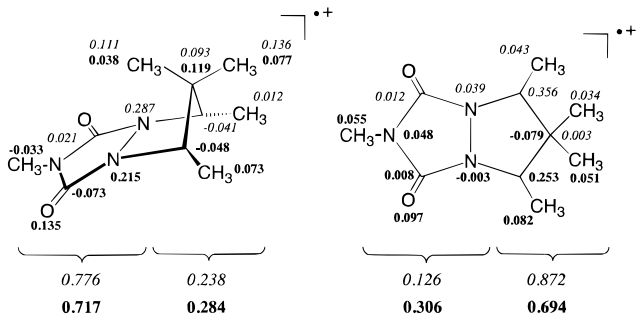


Figure 1. PM3-calculated **charge** (q_i) and *spin* densities (ρ_i) of the puckered and planar radical cations $\mathbf{3a}^{\bullet+}$.

groups at the C-2 position exhibit only one resonance in the ^1H NMR. Because of the lability of these trapping products toward acids, the reaction had to be run in the presence of an excess of 2,6-di-*tert*-butylpyridine.

By means of NMR spectroscopy, it was possible to detect in the crude product mixture of the CET reaction of housane **3a** not only the two olefinic products **4a** and **5a**, but also their cation precursors $\mathbf{3(H)a}^+$ and $\mathbf{5(H)a}^+$ as their corresponding hexachloroantimonate salts. Thus, ^{13}C NMR spectroscopy revealed two signals below δ 250, a region where carbenium ions show characteristic resonances.[14] These resonances were assigned to the two cationic intermediates $\mathbf{3(H)a}^+$ and $\mathbf{5(H)a}^+$ (Scheme 1). When the crude product was filtered through basic alumina oxide, these intermediates were converted to the olefins **4a** and **5a**, as confirmed by NMR spectroscopy.

Control experiments established that the olefins **4** were not only the products of thermal decomposition,[10] but also of acid catalysis. Possible oxidation of the monoolefinic products **4** to the bisolefins **5** by tris(4-bromophenyl)-aminium hexachloroantimonate was excluded by control experiments, which clearly established that the olefins **5** were not secondary products of olefin **4**.

The charge densities (q_i), calculated by the PM3 method for the puckered and planar conformations of the radical cation $\mathbf{3a}^{\bullet+}$, are displayed in Figure 1.[15−17] For the puckered structure most of the positive charge resides on the two nitrogen atoms, whereas in the planar case most of the charge is located at the C-1 and C-3 positions of the cyclopentane ring. Furthermore, the semiempirical MO calculations on the housane **3a** suggest that ionization takes place from one of the nitrogen lone pairs to generate the radical cation $\mathbf{3a}^{\bullet+}$, because they have the lowest ionization potential (10.1 eV). To confirm this, photoelectron spectroscopy (PE)[18] on the housane **3a** was

(14) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 2378−2383.

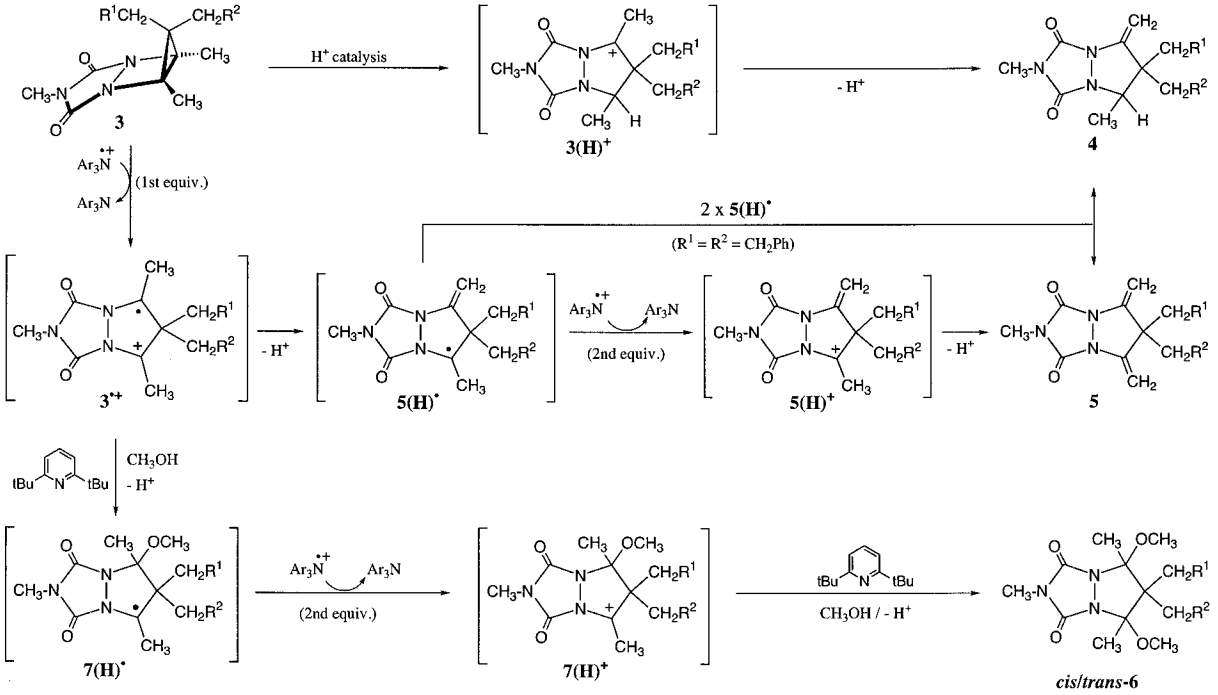
(15) We are grateful to H. M. Harrer for performing these MO calculations using the PM3[16]-method on a Silicon Graphics Iris Indigo workstation under the program VAMP 5.0 provided by Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T., University of Erlangen-Nürnberg. For the puckered radical cation conformation the housane configuration was taken as model whereas the planar triplet diradical[17] was chosen for the planar radical cation. The ionized structures of these model species were not energy minimized. The planar conformation was found to possess a lower heat of formation (ca. 50 kcal/mol) than the puckered one. This energy difference is surely exaggerated and only the relative trend is applicable.

(16) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221−264. (c) Stewart, J. J. P. *J. Comput. Chem.* **1991**, *12*, 320−341.

(17) (a) Sherrill, C. D.; Seidl, E. T.; Schaefer, H. F., III. *J. Phys. Chem.* **1992**, *96*, 3712−3716. (b) Pranata, J.; Dougherty, D. A. *J. Phys. Org. Chem.* **1989**, *2*, 161−176.

(18) The PE experiment was performed in Prof. R. Gleiter's research group at the University of Heidelberg, whom we thank for assistance.

Scheme 1. Mechanism of the CET Reaction of Urazole-Bridged Housanes 3 with Tris(4-bromophenyl)aminium Hexachloroantimonate



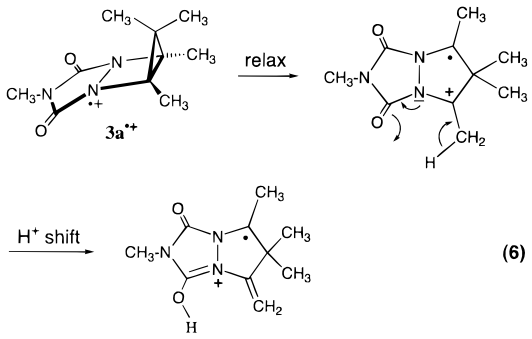
performed; unfortunately, the PE spectrum was severely contaminated by the thermal rearrangement of the labile housane **3a** to the olefin **4a**. Thus, a definitive spectral confirmation whether electron loss proceeds from the nitrogen lone pair or the strained central C−C bond of the housane **3** could not be made.[19]

Discussion

As already mentioned, the CET reaction of tricyclooctane derivatives[11] with tris(4-bromophenyl)aminium hexachloroantimonate leads to rearranged olefins (eq 3). The intermediary 1,3 radical cations transform by 1,2 alkyl migration to the corresponding 1,2 radical cations, which after electron back-transfer (BET) afford the substituted diquinanes. In contrast, replacement of the annelated cyclopentane by a urazole ring changes the reaction pathway decisively. Instead of the catalytic activity observed for the carbocyclic derivative, 2 equiv of the CET oxidant are required to drive the reaction to completion under basic conditions. Furthermore, the 1,3 radical cation $\mathbf{3}^{\bullet+}$ does not rearrange by an 1,2 alkyl shift; instead, on proton loss an exocyclic double bond (Scheme 1, path $\mathbf{3}^{\bullet+} \rightarrow \mathbf{5(H)}^{\bullet}$) is formed. The resulting monoradical $\mathbf{5(H)}^{\bullet}$ is oxidized again by the second equivalent of tris(4-bromophenyl)aminium hexachloroantimonate to yield the cation $\mathbf{5(H)}^{+}$, which analogous to the first oxidation step, loses a proton to give the stable bisolefin **5**.

The monoolefins **4** are the result of acid-induced rearrangement, except **4c**, which is the product of the disproportionation of two $\mathbf{3c}^{\bullet+}$ radical cations (see below). This acid-catalyzed catalytic process occurs exclusively as monitored by ^{1}H NMR spectroscopy (mass balances above 80%). The efficiency of product formation is a function of substitution at the methano bridge of the housanes **3**, i.e. increased steric hindrance by bulky substituents such as the benzyl group leads to a significant decrease in the conversion rate.

Heteroatom substitution has, thus, a strong influence on the chemical reactivity of the transient 1,3 radical cations. First, as shown in eq 6, the nitrogen atoms at the hydrazino bridge stabilize the positive charge due to



(6)

lone pair conjugation. Second, we speculate that one of the adjacent carbonyl functionalities facilitates intramolecular proton transfer from the methyl group at the cationic site to afford a stabilized enol-type cation. These two stabilization modes are sufficiently favorable to circumvent the 1,2 alkyl shift, the usual pathway for carbocyclic 1,3 radical cations.[6,11]

In the case of the dibenzyl-substituted housane **3c**, the CET reaction in the absence of base and 0.1−0.2 mol equiv of oxidant (Table 1, entries 6 and 7) led to higher amounts of the double-oxidation product **5c** than expected if only a stoichiometric reaction was to operate. For example, if 0.2 mol equiv of oxidant were added, the maximum theoretical yield of **5c** would be 0.1 molar equivalents based on a 2:1 stoichiometry of oxidant to

(19) Cyclic voltammetry provided additional evidence for this interpretation. Either housane **3a** or its precursor, the azoalkane **2a**, show similar irreversible oxidation potentials, which indicate that the first electron is removed from the urazole moiety. Furthermore, whereas CET oxidation of housane **3a** with tris(4-bromophenyl)-aminium hexachloroantimonate led to the observed products, the corresponding azoalkane **2a** did not. The cyclovoltammetric measurements were either performed in Prof. M. Schmittel's or in Prof. S. Hünig's research group and we are grateful to H. Trenkle for technical assistance.

substrate. Instead, twice as much bisolefin **5c** was isolated (entry 7). Thus, the stoichiometric process does not apply; rather, disproportionation of two **5(H)**$^{\bullet}$ should be considered, wherein only 1 equiv of oxidant is needed for each bisolefin **5c** formed. CET-induced transformation of the monoolefins **4** to the corresponding bisolefins **5**, which would be a second alternative, could be excluded by control experiments. The monoolefins **4** are stable toward tris(4-bromophenyl)aminium hexachloroantimonate, i.e. only the protonated species **3(H)**$^{+}$ could be detected. In addition, the bisolefins **5** do not decompose in the presence of CET oxidant under the reaction conditions applied.

Shono[20] and Schäfer[21] were able to trap the cationic intermediates of the anodic oxidation of substituted cyclopropanes with methanol and Gassman *et al.*[22] extended such studies to strained polycyclic molecules. Thus, trapping of the cationic intermediates in the chemically induced oxidation of the housane **3a** in the presence of a nucleophile was successful. Nevertheless, it was necessary to execute the trapping reaction with the nucleophilic scavenger (methanol) in the presence of an excess of 2,6-di-*tert*-butylpyridine because of the acid lability of the hemiaminal-type products **6** and **7**. Since a 100-fold excess of methanol (based on the amount of starting material used and a stoichiometric ratio of 2:1 between nucleophile and housane) was applied, nucleophilic trapping efficiently competed with proton loss, i.e. the formation of the exocyclic double bond must be at least by a factor of 100 slower than trapping by methanol. Consequently, none of the olefinic products **4** and **5** were detected, and the involvement of the cationic intermediates **3(H)**$^{+}$ and **5(H)**$^{+}$ was confirmed by successful trapping. In addition, these intermediates were also detected by NMR spectroscopy. First, two resonances below δ 250 were observed by ^{13}C NMR spectroscopy of the crude product mixture, which are characteristic for carbenium ions.[14] Second, not only the two olefinic products **4** and **5** but also their cationic precursors **3(H)**$^{+}$ and **5(H)**$^{+}$, as their hexachloroantimonate derivatives, could be observed by direct ^{1}H NMR analysis of the reaction mixture. After workup, the cations **3(H)**$^{+}$ and **5(H)**$^{+}$ are converted to the corresponding olefins **4** and **5** by deprotonation. Thus, spectral as well as chemical evidence substantiate the intervention of the above cationic intermediates.

MO calculations, namely PM3,[16] a method which is well suited for molecules with nitrogen heteroatoms, were conducted to assess the influence of the urazole ring on the chemical behavior of the radical cation **3a**$^{\bullet+}$ (Figure 1). They suggest that most probably the CET oxidant abstracts an electron from one of the lone pairs of the two nitrogen atoms of the hydrazino bridge of the housane **3a** because the ionization potential for these electrons was calculated to be significantly lower (by ca. 0.5 eV) than that of the housane central bond. In addition, the calculations on the radical cation intermediates reveal that in the puckered conformation most of the positive charge is located on these two nitrogen atoms (Figure 1), whereas in the planar conformation most of the charge is located at the C-1 and C-3 atoms of the diyl moiety. Thus, as the semiempirical calculations suggest and analogous to the results Nelsen[12] obtained for hydrazine derivatives, the electron is most probably abstracted from one of the lone pairs of the nitrogen atoms, and the ionized molecule flattens out by cleavage of the housane central bond to result the distonic 1,3 radical cation. Since the calculations also predict a lower heat of formation[15] for the planar compared to the puckered conformation, it is tempting to propose that the deprotonation takes place in the planar structure (presumably proton transfer to the carbonyl group of the urazole moiety) in preference to the alkyl shift, which requires a puckered conformation.[6,11]

Photoelectron spectroscopy would provide direct spectral evidence on the preferred ionization process of the urazole-annelated housane **3**, i.e. housane central bond *versus* nitrogen lone pair. Unfortunately, it was not possible to observe a definitive photoelectron spectrum for the housane **3a** in view of its thermal lability.[18] Nevertheless, cyclic voltammetry provided experimental support for this interpretation.[19]

In conclusion, the two nitrogen atoms in the urazole-bridged radical cations **3**$^{\bullet+}$ stabilize the radical cation **3**$^{\bullet+}$ by conjugation. Subsequently, the adjacent carbonyl group presumably facilitates proton loss to such a degree that exclusively exocyclic double bonds are formed and no products derived from 1,2 alkyl migration can be observed. Consequently, *N*-acyl substitution on the radical cation sites has a profound influence on the product formation and is responsible for the significant difference in the reaction mechanism (Scheme 1) compared to the carbocyclic derivatives (eq 3) previously examined.[11]

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Supporting Information Available: Experimental data (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(20) Shono, T.; Matsumara, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2861−2864.
(21) Klehr, M.; Schäfer, H. J. *Angew. Chem.* **1975**, *87*, 173−174.
(22) Gassman, P. G.; Yamaguchi, R. *Tetrahedron* **1982**, *38*, 1113−1122.