Regioselective Rearrangement of Bridgehead-Methyl-Substituted Radical Cations Derived from Bicyclo[2.1.0]pentanes and 2,3-Diazabicyclo[2.2.1]hept-2-enes through Photoinduced Electron Transfer and Radiolytic Oxidation: Product Distribution and Matrix ESR Studies

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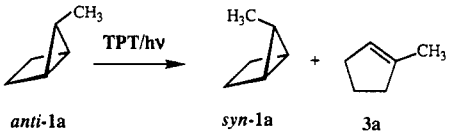
Abstract: Cyclopentane-1,3-diyl radical cations were generated from the 1-methyl- and 1,4-dimethyl substituted bicyclo-[2.1.0]pentanes **1b,c** through photoinduced electron transfer (PET) and radiolytic oxidation. The unsymmetrical bridgehead-substituted bicyclopentane **1b** rearranged spontaneously and exclusively to the 3-methylcyclopentene **3b** under PET conditions. ESR studies showed similarly that **3b**$^{\bullet+}$ was the only final oxidation product of **1b**; the initial radical cation **1b**$^{\bullet+}$ was not detected because it rearranges rapidly and stereoselectively by a 1,2-hydrogen shift to **3b**$^{\bullet+}$, even at 80 K, and no trace of the more stable 1-methylcyclopentene radical cation **3a**$^{\bullet+}$ was observed. This contra--thermodynamic regioselectivity is rationalized in terms of essential localization of positive charge at the tertiary center as the reaction proceeds in the 1,3-diyl radical cation **1b**$^{\bullet+}$. The symmetrical dimethyl derivative **1c** rearranged much more reluctantly than **1b** despite its lower oxidation potential, and this is attributed to the greater persistence of radical cation **1c**$^{\bullet+}$ through its reluctance to undergo a 1,2-H shift. This was confirmed by direct ESR observation, which also showed that the rearrangement of **1c**$^{\bullet+}$ is much slower than that of the parent cyclopentane-1,3-diyl radical cation **1**$^{\bullet+}$. This difference is attributed to a larger effect of methyl stabilization on the reactant than on the product, leading to a decrease in exothermicity and an increase in the activation energy for the rearrangement of **1c**$^{\bullet+}$ relative to that of **1**$^{\bullet+}$. The 1-methyl and 1,4-dimethyl substituted 2,3-diazabicyclo[2.2.1]hept-2-enes **2b,c** on PET reaction also yielded evidence for the intermediacy of 1,3-diyl radical cations; however, the product distributions suggest that denitrogenation can also be accompanied by concomitant 1,2-H shifts at the stage of the intermediate diazenyl radical cations, albeit with lower efficiency. ESR studies on the oxidation of **2c** failed to detect the very stable **1c**$^{\bullet+}$ species on the pathway to the 1,3-dimethylcyclopentene radical cation **3c**$^{\bullet+}$, indicating that denitrogenation of **2c**$^{\bullet+}$ results in a rapid rearrangement to **3c**$^{\bullet+}$ even under matrix-isolation conditions at 77 K. Consequently, the oxidation of these azoalkanes generates highly reactive transients, presumably diazenyl radical cations, which readily denitrogenate and undergo 1,2-H shifts in either a consecutive or concerted manner to form olefin radical cations.

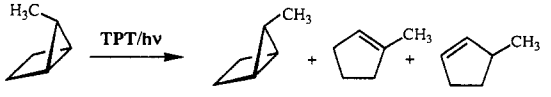
Recent investigations[1] have shown that 2,3-diazabicyclo[2.2.1]-hept-2-enes (DBH)[2] and bicyclo[2.1.0]pentanes serve as precursors not only for the well-examined 1,3 biradicals[1a,3] but also for 1,3-diyl radical cations in single electron transfer (SET) reactions[1b] (Scheme 1). While the 1,3-cyclopentanediyls, if not thermally activated or photochemically excited,[1a] cyclize to yield the bicyclo[2.1.0]pentanes, the corresponding 1,3-diyl radical cations exhibit a high propensity to rearrange by 1,2-alkyl or hydrogen shifts.[1b] This is closely related to the radical cation rearrangment of cyclopropane to propene, which is exothermic by ca. 13 kcal/mol.[4]

The SET reactions are strongly affected by changes in the substitution of the housane and azoalkane substrates. Even diastereomers, e.g. the housanes *anti*-**1a** and *syn*-**1a**, show profound changes in the product composition. Thus, the housane *anti*-**1a** on photoinduced electron transfer (PET)[5] with the sensitizer triphenylpyrylium tetrafluoroborate (TPT) yielded only 1-methylcyclopentene **3a** (eq 1a) as the rearrangement product,



(1a)

anti-**1a** *syn*-**1a** **3a**



(1b)

syn-**1a** *anti*-**1a** **3a** **3b**

whereas the housane *syn*-**1a** yielded both the 1-methyl- and

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(4) (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) It may be noted, however, that the radical cation rearrangement of the parent cyclopropane to propene has not been observed by matrix ESR spectroscopy at low temperatures: Qin, X.-Z.; Snow, L. D.; Williams, F. *Chem. Phys. Lett.* **1985**, *117*, 383–385. Qin, X.-Z.; Williams, F. *Chem. Phys. Lett.* **1984**, *112*, 79–83.

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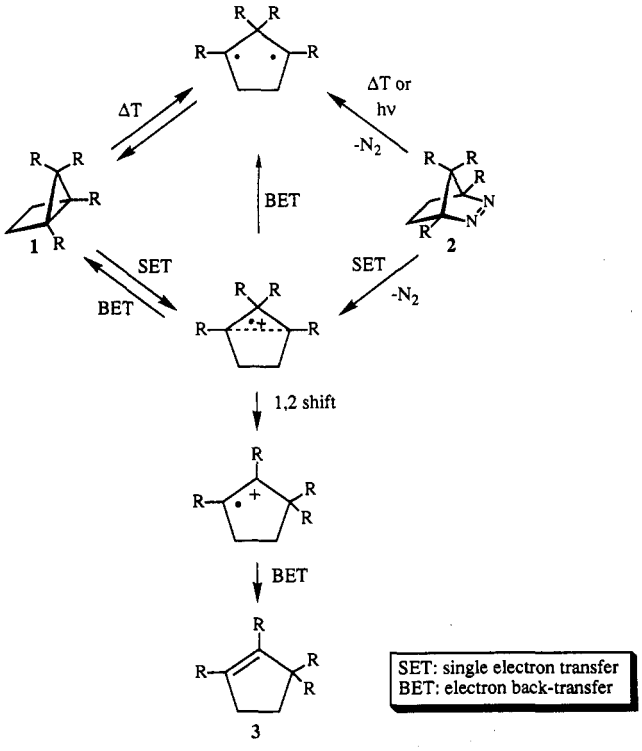
Table 1. Product Studies of the PET Reactions[a] of Housanes **1b,c** and Azoalkanes **2b,c** in Acetonitrile

						product distribution[b,c] (%)				
entry	substrate	sensitizer	time (min)	conversion[b,c] (%)	mb[b,c] (%)	1'[e]	3a	3b	3c	4c
1	**1b**	TPT	5	20	15	*f*	*g*	100		
2	**1b**	DCA	60	22	36	*f*	*g*	100		
3	**1b**	DCA/Ph_2	10	18	48	*f*	*g*	100		
4	**2b**	TPT	5	22	48	11	12	77		
5	**2b**	DCA	25	20	70	46	12	42		
6	**2b**	DCA/Ph_2	20	15	80	3	16	81		
7	**1c**	TPT	20	30	40	*f*			100	*g*
8	**1c**	DCA	120	5	0	*f*			*g*	*g*
9	**1c**	DCA/Ph_2	10	15	60	*f*			95	5
10	**2c**	TPT	5	66	75	18			74	8
11	**2c**	DCA	25	75	99	46			54	*g*
12	**2c**	DCA/Ph_2	15	22	60	19			78	3

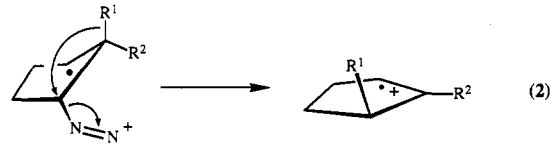
[a] See Experimental Section for details; at −5 °C. [b] Determined by quantitative capillary GC; mb = mass balance. [c] Error ca. 5–10% of stated value. [d] Relative yields normalized to 100%; error ca. ±2%. [e] **1'** is **1b** or **1c** if starting material is **2b** or **2c**. [f] Starting material. [g] Not detected by capillary GC.

Scheme 1



3-methylcyclopentenes **3a,b** (eq 1b) under identical conditions.[1b] These product studies, combined with direct information on the radical cations from ESR data, allowed valuable mechanistic conclusions to be drawn about the conformational behavior and reactivity of cyclopentane-derived 1,3-diyl radical cations.

Similar results were obtained when the *syn*- and *anti*-7-methyl-substituted DBH served as starting materials in PET reactions.[1b] As one possible pathway, it was proposed that the primary radical cation intermediates extrude molecular nitrogen by stepwise cleavage of both C–N bonds to yield carbon-centered radical cations, which is analogous to the well-accepted fact[1a,6] that extrusion of dinitrogen from neutral bicyclic azoalkanes takes place by a two-step mechanism with diazenyl biradicals as bona fide intermediates. However, again like the diazenyl biradicals,[1] the corresponding radical cations may expel N_2 with concomitant hydrogen and/or alkyl-1,2 shift through backside attack on the remaining C–N bond (eq 2).



(2)

Since experimental evidence for diazenyl radical cations of DBH derivatives is scant, comparative studies on the PET and radiolytic oxidation behavior of the methyl-substituted housanes **1b,c** (1-methyl- and 1,4-dimethylbicyclo[2.1.0]pentane) and azoalkanes **2b,c** (1-methyl- and 1,4-dimethyl-2,3-diazabicyclo-[2.2.1]hept-2-ene) have been undertaken. It was of particular mechanistic relevance to assess the effects of bridgehead substitution on the stabilities of $\mathbf{1b}^{\bullet+}$ and $\mathbf{1c}^{\bullet+}$ and on the ease of denitrogenation of the diazenyl radical cations generated through PET chemistry of azoalkanes **2b,c**. Also, the importance of the 1,2-shift and the regiochemistry in the rearrangement of the 1,3-diyl radical cations derived from **2b,c** and the corresponding housanes **1b,c** has been examined by both ESR and PET studies.

Results

PET Reactions. The product data are summarized in Table 1. Thus, oxidation of bicyclopentane **1b** by photoinduced electron transfer yielded the cyclopentene **3b** as the only product detected by GC (entries 1–3, Table 1). With excited 9,10-dicyanoanthracene (DCA) as electron acceptor, the conversion of bicyclopentane **1b** was rather sluggish (entry 2, Table 1). Addition of biphenyl (Ph_2) as cosensitizer[7] enhanced the rate of conversion significantly (entry 3, Table 1). The low mass balances for the housanes **1b** and analogously **1c** are due to undefined products of higher molecular weight[2a] which go undetected by GC analysis.

The azoalkanes **2b,c**, which exhibited higher mass balances, readily extrude molecular nitrogen on TPT- or DCA-sensitized electron transfer. Azoalkane **2b** yielded housane **1b** and both cyclopentenes **3a,b** as rearrangement products, with **3b** as the major regioisomer. Interestingly, the relative yield of regioisomer **3a** is very similar in all runs, while the relative yields of housane **1b** and cyclopentene **3b** depend strongly on the choice of sensitizer (entries 4–6, Table 1). Replacement of the sensitizer TPT by DCA increased the relative yield of housane **1b** at the expense of cyclopentene **3b** (entry 4 versus entry 5, Table 1). With biphenyl as cosensitizer, the ratio of housane **1b** versus cyclopentene **3b** changed drastically, in that the formation of **1b** was suppressed almost completely but the relative yield of cyclopentene **3a** was altered only marginally (entry 6, Table 1). Control

(6) (a) Adam, W.; Simpson, C. J. S.M.; Wilson, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 4728–4732. (b) Adams, J.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 9115–9121. (c) Sheridan, R. S.; Reedich, D. E. *J. Am. Chem. Soc.* **1988**, *110*, 3697–3698. (d) Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3303–3312.

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experiments confirmed that the cyclopentenes **3a,b** do not interconvert into each other in the TPT- and DCA-sensitized reactions.[1b]

In the TPT-sensitized reaction, bicyclopentane **1c** underwent rearrangement to cyclopentene **3c** (entry 7, Table 1). With DCA, however, the conversion was low and no volatile products were detected, even after prolonged irradiation (entry 8, Table 1). After addition of biphenyl, conversion to cyclopentene **3c** took place readily and minor amounts of a new product were observed, which was identified by GC-MS as cyclopentadiene **4c** (entry 9, Table 1).

The PET reaction of azoalkane **2c** yielded housane **1c** and cyclopentene **3c** in all cases (entries 10–12, Table 1). The nature of sensitizer affected the ratio of housane (cyclization) versus cyclopentenes (rearrangement) in the same manner as observed for azoalkane **2b** (see above). Highest yields of rearrangement product were again achieved with biphenyl as cosensitizer (entry 12, Table 1); however, formation of housane **1c** was not as strongly suppressed as in the case of azoalkane **2b**. Additionally, minor amounts of cyclopentadiene **4c** were detected.

Control experiments by monitoring the product distributions of the photolyses as a function of time revealed that no secondary oxidation of the housanes took place up to the conversions stated in Table 1. The possible involvement of an acid-catalyzed rearrangement of the housanes **1b,c** was probed by allowing the photolysates to stand for up to 24 h after photolyses; in all DCA-sensitized reactions, no acid catalysis took place.

With TPT as sensitizer, however, the acid-catalyzed rearrangement of housanes **1b,c** to cyclopentenes **3a,c** was observed;[1b,8] a control experiment for **1b** showed that this acid-catalyzed rearrangement was suppressed by the addition of 2,6-di-*tert*-butylpyridine. As further control experiments, some of the DCA-sensitized photolyses were conducted in the presence of the above base, and the unaltered product distributions confirmed that this hindered pyridine does not interfere in the PET reactions. For the azoalkanes **2b,c** no acid catalysis was observed in the PET processes, which established that these azoalkanes themselves are strong enough bases[9] to neutralize any traces of acid produced through photodecomposition of TPT.

ESR Studies of the Radiolytic Oxidation of Methyl-Substituted Bicycloalkanes 1b,c and 2b,c and Cyclopentenes 3a,c in Freon Matrices. The oxidations were carried out by γ-irradiation of dilute solutions of the substrates in various Freons. Subsequent ESR measurements were made in a variable-temperature cryostat from 80 K up to the softening point of the particular matrix, usually close to 150 K, at which point the ESR signals decayed.

(a) Monomethyl-Substituted Derivatives 1b, 2b, 3a, and 3b. In previous work[1b] on the radiolytic oxidation of the epimers of the 5-methylbicyclo[2.1.0]pentane (*anti*- and *syn*-**1a**) in the haloethane matrices $CF_2ClCFCl_2$ and CF_3CCl_3, the corresponding radical cations were detected by ESR spectroscopy at 80–90 K and shown to retain the stereochemical integrity of the parent molecules despite the considerable weakening of the bond between the bridgehead carbons. These relatively labile *anti*-**1a**$^{\bullet+}$ and *syn*-**1a**$^{\bullet+}$ intermediates were then found to rearrange stereoselectively at 105 K into the olefin radical cations **3a**$^{\bullet+}$ and **3b**$^{\bullet+}$, by 1,2-hydrogen or 1,2-methyl transfer from the *endo* (*syn*) position at C-5, the isothermal rates of both these rearrangements in the range between 90 and 110 K being very similar to that observed for the parent radical cation **1**$^{\bullet+}$ derived from the oxidation of bicyclo[2.1.0]pentane (**1**).[10] However, under exactly the same experimental conditions of radical cation generation and ESR observation as in the previous study,[1b] the radiolytic oxidation of the bridgehead-substituted methylhousane **1b** in $CF_2ClCFCl_2$ at 85 K gave rise initially to the spectrum of the olefin radical cation **3b**$^{\bullet+}$ without any evidence for the putative precursor radical cation **1b**$^{\bullet+}$. Similarly, no evidence was obtained for **1b**$^{\bullet+}$ when the oxidation of **1b** was carried out in the CF_3CCl_3 matrix; in this case, the spectral resolution was of inferior quality below about 100 K, but at 108 K the ESR spectrum was essentially indistinguishable from that of **3b**$^{\bullet+}$ obtained by the direct oxidation of **3b** in this matrix. Therefore, the oxidation of **1b** in Freon at 77 K apparently does not produce a stable **1b**$^{\bullet+}$ species on the pathway to the olefin radical cation. Nonetheless, as described below, the ESR results show that the overall rearrangement proceeds stereoselectively to **3b**$^{\bullet+}$.

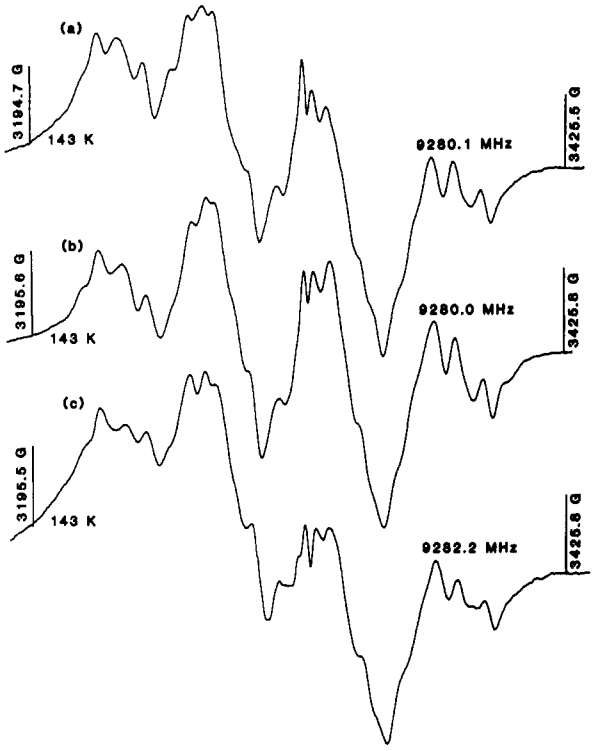

Figure 1. ESR spectra at 143 K of the 3-methylcyclopent-1-ene radical cation **3b**$^{\bullet+}$ generated by the radiolytic oxidation of **1b** (a), **3b** (b), and **2b** (c). The $CFCl_3$ solid solutions (0.01 M in substrate) were γ-irradiated (dose, 0.2 Mrad) at 77 K and then annealed to 143 K before recording the ESR spectra; the resolution was optimal at this latter temperature.

Analogous regioselectivity in olefin radical cation formation without the observation of any specific precursor (azoalkane or 1,3-diyl) radical cation species was also found in the oxidation of the azoalkane **2b**. Thus, the spectrum in this case was again dominated by the 3-methylcyclopentene radical cation **3b**$^{\bullet+}$, and no clearly recognizable contribution from its regioisomer **3a**$^{\bullet+}$ was present. Thus, Figure 1 shows a comparison of the ESR spectra obtained from the oxidation of **1b**, **3b**, and **2b** in $CFCl_3$. These spectra are almost exactly superimposable on each other, with only slight differences in the resolution of the substructures. As described previously,[1b] the ESR spectra of **3a**$^{\bullet+}$ and **3b**$^{\bullet+}$ consist of quite different patterns which thereby allow for a high degree of spectral discrimination between these two signal carriers. Hence, on a semiquantitative basis, it seems reasonable to estimate from the ESR spectra a and c in Figure 1 that the ratio of **3b**$^{\bullet+}$ to **3a**$^{\bullet+}$ formation in the respective oxidations of **1b** and **2b** is at least 50:1 in each case under matrix conditions at low temperature. This clearly signifies a high degree of stereoselectivity in both of these rearrangements.

(b) Dimethyl-Substituted Derivatives 1c, 2c, and 3c. In contrast to the apparent instability of **1b**$^{\bullet+}$, the exceedingly stable 1,3-

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Table 2. ESR Parameters for the Methyl-Substituted Radical Cations Derived from Bicyclo[2.1.0]pentanes and 2,3-Diazabicyclo[2.2.1]hept-2-enes

radical cation	neutral precursor	matrix	T (K)	g_{iso}	hyperfine coupling constants (G)
1$^{\bullet+}$ [a]	**1** [a]	CF_3CCl_3	90	2.0033(5)	44.9 (1H), 33.5 (2H), 11.7 (2H)
	1 [a]	$CF_2ClCFCl_2$	80	2.0032(5)	44.8 (1H), 32.4 (2H), 12.0 (2H)
1c$^{\bullet+}$	**1c**	CF_3CCl_3	125	2.0028(5)	43.2 (1H), 27.1 (2H), 17.0 (6H)
	1c	$CF_2ClCFCl_2$	84	2.0030(5)	44.4 (1H), 27.2 (2H), 16.5 (6H)
	1c	$CFCl_3$	86	2.0028(5)	44.2 (1H), 27.3 (2H), 16.5 (6H)
3b$^{\bullet+}$	**1b**	$CFCl_3$	143	2.0032(5)	49.3 (2H), 45.7 (1H), 20.5 (1H), 7.6 (2H)
	2b	$CFCl_3$	141	2.0035(5)	49.6 (2H), 45.5 (1H), 20.3 (1H), 7.8 (2H)
	3b	$CFCl_3$	143	2.0036(5)	49.6 (2H), 46.0 (1H), 20.5 (1H), 7.4 (2H)
3c$^{\bullet+}$	**2c**	CF_3CCl_3	142	2.0028(5)	45.0 (1H), 24.2 (1H), 22.1 (1H), 16.3 (3H), 10.6 (1H), 4.0 (1H)
	3c	CF_3CCl_3	143	2.0028(5)	44.1 (1H), 24.4 (1H), 22.1 (1H), 16.5 (3H), 10.6 (1H), 4.2 (1H)
8c$^{\bullet+}$ or **8c**$^{\bullet}$ (see text)	**1c**	$CF_2ClCFCl_2$	113	2.0032(5)	67.7 (1H), 35.4 (2H), 22.2 (3H), 2.6 (1H)
	2c	$CF_2ClCFCl_2$	114	2.0028(5)	67.4 (1H), 34.9 (2H), 22.4 (3H), 2.6 (1H) [b]

[a] **1**$^{\bullet+}$ and **1** are cyclopentane-1,3-diyl$^{\bullet+}$ and bicyclo[2.1.0]pentane, respectively; the data are taken from ref 10. [b] Not well resolved.

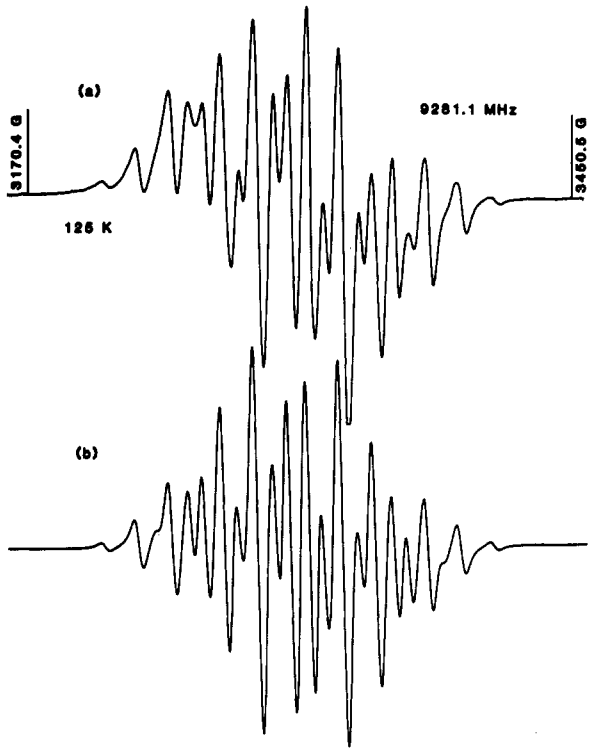


Figure 2. ESR spectrum of **1c**$^{\bullet+}$ (a) from a γ-irradiated (dose, 0.2 Mrad) solid solution (ca. 0.01 M) of 1,4-dimethylbicyclo[2.1.0]pentane (**1c**) in CF_3CCl_3. The spectrum was recorded with optimal resolution after annealing the γ-irradiated sample from 77 to 125 K. Spectrum b was simulated by using the coupling constants for **1c**$^{\bullet+}$ given in Table 2.

dimethylcyclopentane-1,3-diyl radical cation (**1c**$^{\bullet+}$) was observed as the oxidation product of **1c**. Evidently, the substitution of two methyl groups at the bridgehead positions of the housane endows greatly increased persistence to the unrearranged radical cation, whereas the introduction of only one such group has just the opposite effect.

The well-defined ESR spectrum of **1c**$^{\bullet+}$ in CF_3CCl_3 is shown in Figure 2(a); the same characteristic well-resolved pattern was observed after the oxidation of **1c** in the $CFCl_3$ and $CF_2ClCFCl_2$ matrices. The pattern was readily analyzed by inspection as a multiplet derived from hyperfine interactions with 6H, 2H, and 1H in the order of increasing couplings (Table 2), and the analysis was confirmed by the good fit with the computer-simulated spectrum shown in Figure 2b. This distribution of hyperfine interactions establishes a symmetrical (C_s) puckered structure for **1c**$^{\bullet+}$. The largest coupling constant of 43–44 G (1H), which can be assigned to the pseudoaxial (*endo*) hydrogen at C-5,[1b] is almost unchanged from the corresponding values reported for the isostructural parent housane radical cation[10] **1**$^{\bullet+}$ and for the *anti*-**1a**$^{\bullet+}$ species[1b]. On the other hand, the coupling assigned to the two pseudoaxial hydrogens on the dimethylene bridge is lowered from ca. 33 G in the parent radical cation and its 5-methyl derivatives[1b,10] to 27 G in **1c**$^{\bullet+}$, which suggests that for the latter there is a slight reduction in the dihedral angle between the p orbital on C-1 (also on C-4) and the pseudoaxial hydrogen on C-2 (also on C-3). However, part of this decrease in hyperfine coupling can also come about by the delocalization of spin into the two methyl groups at the spin-bearing carbons.

Evidence for this methyl hyperconjugation is provided by the fact that the 17-G hyperfine coupling to the six equivalent methyl hydrogens in **1c**$^{\bullet+}$ is intermediate in value between the 15-G coupling for the twelve equivalent hydrogens of the four methyl groups in the 1,1,2,2-tetramethylcyclopropane radical cation and the ca. 21-G value for the six equivalent hydrogens in the radical cations of *cis*- and *trans*-1,2-dimethylcyclopropane.[11] Because of the structural similarity of **1c**$^{\bullet+}$ to these cyclopropane radical cations in which the spin is also concentrated at the two methyl-substituted carbons,[11] these comparisons serve to reinforce the spectral assignment for **1c**$^{\bullet+}$.

The thermal stability of **1c**$^{\bullet+}$ was revealed by its persistence on annealing the irradiated solid solutions of $CFCl_3$ and CF_3CCl_3 up to 130 and 150 K, respectively. In both cases the signals from **1c**$^{\bullet+}$ decayed quite slowly until the above temperatures close to the softening points of the matrices were reached. Moreover, no significant growth of a daughter signal carrier accompanied the decay of **1c**$^{\bullet+}$, although some very weak residual signals from **3c**$^{\bullet+}$ were detected in CF_3CCl_3 samples during the decay of **1c**$^{\bullet+}$ on annealing.

Whereas the rearrangement of **1c**$^{\bullet+}$ to **3c**$^{\bullet+}$ is evidently quite sluggish in the temperature range (80–150 K) of these matrix experiments, the oxidation of the corresponding azoalkane **2c** resulted in the formation of strong signals from **3c**$^{\bullet+}$ without the detection of a possible precursor such as **1c**$^{\bullet+}$ (Figure 3). Although there are minor differences in the fine structure of the patterns (a) and (b) obtained from the oxidation of **2c** and **3c**, the spectral profiles are essentially the same with almost identical total widths. The ESR parameters of **3c**$^{\bullet+}$ (Table 2) were determined by simulation of these experimental spectra; the computer-generated matching spectrum is shown as the lower trace (c) of Figure 3.

Additionally, ESR evidence was obtained for a product of the bimolecular reactions in the annealing of γ-irradiated $CF_2ClCFCl_2$ solutions of **1c** and **2c**. It is well-known[12] that such "ion–molecule" reactions can occur above ca. 110 K in the $CF_2ClCFCl_2$ matrix due to the increased mobility of the solute molecules (and of the derived intermediate species) in the region above this matrix transition temperature. Remarkably, the ESR pattern (Figure 4) of interest was observed at ca. 120 K from irradiated solutions of both **1c** and **2c** (but not from **3c**) despite the fact that not only the neutral solute but also the antecedent radical cation species (**1c**$^{\bullet+}$ and **3c**$^{\bullet+}$) present at lower temper-

(11) Qin, X.-Z.; Williams, F. *Tetrahedron* **1986**, *42*, No. 22, 6301–6314.
(12) (a) Williams, F.; Qin, X.-Z. *Radiat. Phys. Chem.* **1988**, *32*, No. 2, 299–308. (b) Williams, F. *J. Am. Chem. Soc.* **1964**, *86*, 3954–3957.

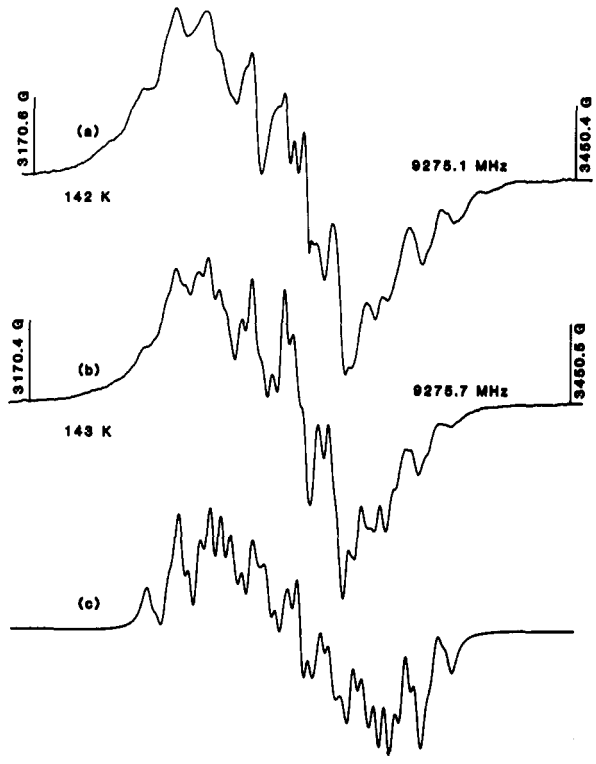


Figure 3. ESR spectra of the 1,3-dimethylcyclopent-1-ene radical cation $3c^{\bullet+}$ generated by the radiolytic oxidation of **2c** (a) and **3c** (b). The CF_3CCl_3 solid solutions (0.01 M in substrate) were γ-irradiated (dose, 0.2 Mrad) at 77 K and then annealed to the temperature shown on the figure, at which the ESR spectra were recorded. Spectrum c was simulated using the coupling constants for $3c^{\bullet+}$ given in Table 2.

atures in these solutions differed from each other. Analysis of the spectrum was facilitated by the presence of well-resolved 1:3:3:1 quartet components in the wings, and the derived ESR parameters given in the last two rows of Table 2 can be reasonably assigned to a neutral radical with a basic 1-methylcyclopent-1-yl structure. Thus, the 22.3-G coupling to the three equivalent hydrogens clearly points to an α-methyl group at the radical site, while the couplings to the four other hydrogens are formally consistent with β-hydrogen interactions in a cyclopentyl radical. These latter couplings are unusual, however, insofar as they are equivalent for two of the β-hydrogens (32.5 G) while the other two are not only nonequivalent (Table 2) but extremely disparate (67.5 and 2.6 G).

A more specific assignment of this cyclopentyl signal carrier can now be sought by considering the possible ion–molecule reactions that can occur in the case of $1^{\bullet+}$ (Scheme 2). First, proton loss from the radical cation to the neutral molecule can take place in three different ways, leading to **5c**$^{\bullet}$, **6c**$^{\bullet}$, and **7c**$^{\bullet}$ as possible products. However, the 1,3-dimethylcyclopent-2-en-1-yl radical **6c**$^{\bullet}$ can definitely be ruled out, since its allylic character with two equivalent methyl groups would give rise to a quite different hyperfine pattern with an ca. 14.5-G septet substructure. The possible assignment of the spectrum to radical **5c**$^{\bullet}$ or **7c**$^{\bullet}$ also presents problems, since it is difficult to understand why only one pair of β-hydrogens should be equivalent in either case. Indeed, the cyclopent-3-en-1-yl radical, which is the unsubstituted form of **5c**$^{\bullet}$, possesses four equivalent β-hydrogens,[10] and substitution at the γ-position would not be expected to bring about the drastic conformational change needed to accord with the β-hydrogen couplings of the present spectrum (Table 2).

An alternate assignment that is not inconsistent with the conformational requirements can be made either to the distonic radical cation $8c^{\bullet+}$ formed by oligomerization (Scheme 2) or to the neutral radical **8c**$^{\bullet}$ resulting from the loss of a proton from $8c^{\bullet+}$. Although the ESR characterization only pertains to the

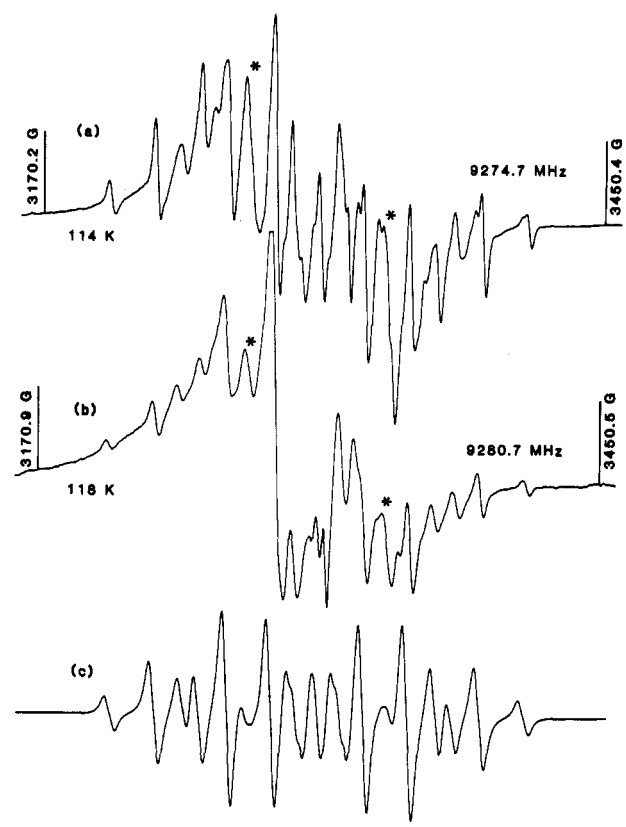


Figure 4. ESR spectra of γ-irradiated (dose, 0.2 Mrad) $CF_2ClCFCl_2$ solutions containing ca. 0.01 M of **1c** (a) and ca. 0.01 M of **2c** (b) recorded after annealing the samples from 77 K to the indicated temperatures. The spectra are both assigned to a neutral 1-methylcyclopent-1-yl radical center in a distonic dimer radical cation such as $8c^{\bullet+}$ or **8c**$^{\bullet}$ (see text) formed by a bimolecular reaction of the parent (or rearranged) radical cation with the neutral substrate molecule (see text). Spectrum c was simulated using the ESR parameters given for $8c^{\bullet+}$ in Table 2. Extraneous lines in spectra a and b are marked by asterisks.

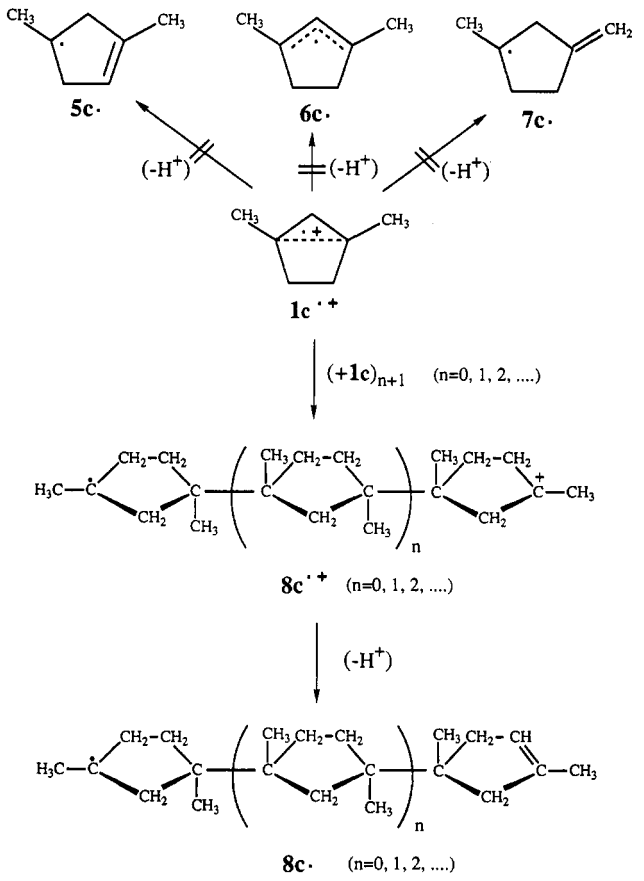
radical center, $8c^{\bullet+}$ can be postulated as resulting from the ring-opening addition of $1c^{\bullet+}$ to **1c**, with possible subsequent addition reactions. This process is analogous to the propagation reaction in cycloolefin epoxide polymerization,[13] except that the attack in the present case would have to occur at a bridgehead position. A similar attack of the radical cation $3c^{\bullet+}$ directly on the azoalkane **2c** to form a 1-methylcyclopent-1-yl radical center and elimination of molecular nitrogen from the resulting adduct appears somewhat less plausible.

Discussion

As illustrated by the previous work on the epimers of **1a** and the corresponding azoalkanes,[1b] matrix ESR studies nicely complement the investigation of PET processes in solution. In particular, the spectroscopic results can provide critical information about the key role of radical cations in overall rearrangement reactions. However, it must be appreciated that the temporal properties of the radical cations studied by these investigative methods represent two extremes: in particular, the matrix radiolysis technique is generally concerned with comparatively long-lived species that do not undergo back electron transfer because the oxidation step is accompanied by *irreversible* electron attachment to the halide matrix, while the PET process of course concerns transient ions in solution. Moreover, the reaction conditions attainable in the matrix and solution regimes

(13) (a) Aikins, J. A.; Williams, F. In *Ring-Opening Polymerization*; McGrath, J.E., Ed.; ACS Symposium Series 286; American Chemical Society: Washington, DC, 1985; Chapter 24, pp 335–359. (b) Williams, F. In *Fundamental Processes in Radiation Chemistry*; Ausloos, P., Ed.; Wiley: New York, 1968; Chapter 8, pp 515–598.

Scheme 2

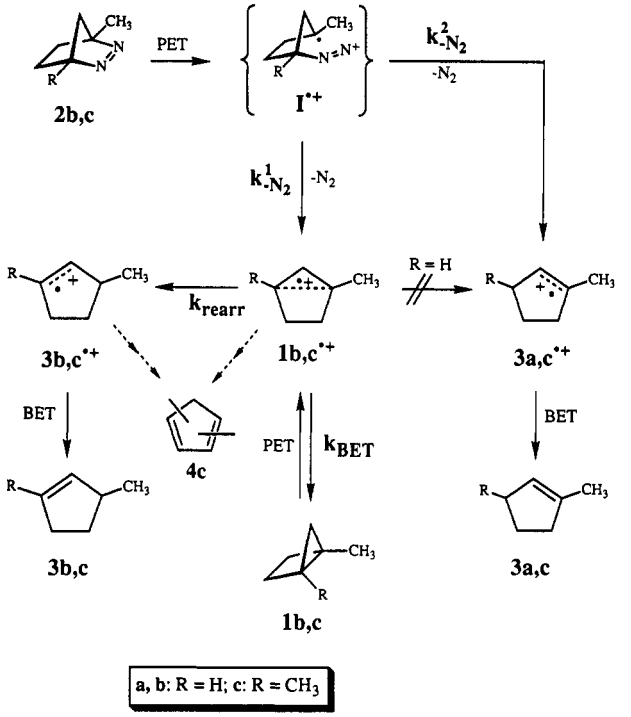


are usually confined to different temperature ranges. These limitations must be borne in mind when comparing the two sets of experimental data. It seems appropriate, therefore, to summarize the main conclusions of the ESR studies first and then to discuss the chemistry of the PET results in the light of these findings on the intermediate radical cations.

The ESR results for the oxidation of **1b** imply that **1b**$^{\bullet+}$ rearranges almost instantaneously to **3b**$^{\bullet+}$ on the time scale of the matrix experiments, even below 100 K. The failure to detect **1b**$^{\bullet+}$ contrasts with the previous observation of *anti*- and *syn*-**1a**$^{\bullet+}$ under comparable conditions. Thus, for these housane radical cations, methyl substitution at the bridgehead position confers much greater reactivity than it does at the C-5 position. Moreover, since the reactivities of *anti*- and *syn*-**1a**$^{\bullet+}$ [1b] are quite similar to that of the unsubstituted cyclopentane-1,3-diyl radical cation,[10] this tendency of **1b**$^{\bullet+}$ to rearrange more rapidly than the parent species and its regioisomers is almost certainly attributable to the bias introduced by the methyl group in the structure of the 1,3-diyl radical cation. In its extreme form, which is probably only reached well along the reaction coordinate, **1b**$^{\bullet+}$ can be considered as a distonic radical cation species with the radical center at the unsubstituted bridgehead carbon and the cationic center at the methyl-substituted site. Rearrangement by hydride ion transfer from C-5[1b] to this carbocation center (vide infra) would then naturally account for the observed stereoselective formation of **3b**$^{\bullet+}$ (Figure 1a).

In view of the results for **1b**, it is striking that the oxidation of **1c** produces the unrearranged radical cation **1c**$^{\bullet+}$, which in fact is considerably more stable than the parent species[10] (vide infra and especially Figure 6) as well as *anti*- and *syn*-**1a**$^{\bullet+}$.[1b] Clearly, the substitution of a methyl group at each of the diyl radical cation sites inhibits rearrangement to the olefin radical cation **3c**$^{\bullet+}$. This confirms the idea expressed above that it is structural bias at the diyl radical cation sites (unsymmetrical substitution of the radical cation) which enhances the propensity

Scheme 3



for rearrangement rather than the electronic effects of methyl substitution per se.

Regarding the oxidation of the azoalkanes **2b,c**, the ESR results provide evidence for the stereoselective formation of **3b**$^{\bullet+}$ in the former case as well as of **3c**$^{\bullet+}$ in the latter but do not reveal the detailed pathway by which these rearrangements occur. The stereospecificity of **3b**$^{\bullet+}$ formation from the oxidation of **2b** would be consistent with an intermediate role for **1b**$^{\bullet+}$ produced by nitrogen extrusion. However, the failure to detect the very stable **1c**$^{\bullet+}$ from the oxidation of **2c** implies that either the diyl radical cations are already produced in a highly reactive (hot) state from their azoalkane precursors or another reaction channel is available for the rearrangement to olefin radical cations, such as that potentially offered by the extremely labile diazenyl radical cations (vide infra). These latter species are not sufficiently persistent to be detected by matrix ESR, however, and presumably the rearranged olefin radical cations are already produced immediately at very low temperatures during the oxidation of azoalkanes.

Turning now to the PET results, the observation that housane **1b** rearranges exclusively to cyclopentene **3b** but that azoalkane **2b** under identical conditions yields both regioisomeric cyclopentenes **3a,b** as rearrangment products is accounted for by the mechanism outlined in Scheme 3. Since the rearrangement of a 1,3-radical cation is likely to be of the Wagner–Meerwein type,[1,2c,14] the regioselective formation of cyclopentene **3b** requires in accord with the ESR studies that the positive charge be largely centered on the tertiary carbon as the reaction proceeds in the intermediate radical cation **1b**$^{\bullet+}$. This preference can be attributed to the avoidance of the SOMO destabilization at the radical center. Thus, although a *net* stabilization is achieved by methyl substitution in each case, a larger stabilization is obtained when the cationic center is located at the methyl-substituted postition. Accordingly, this essential localization of spin and charge leads, on rearrangement by hydride transfer from C-5, to the thermodynamically less favored 1,2-radical cation **3b**$^{\bullet+}$ (Figure 5), which in the gas phase has been estimated to be between 9 and 12 kcal/mol less stable than its regioisomer **3a**$^{\bullet+}$.[15] The formation of **3a**$^{\bullet+}$ by the alternative process of hydrogen atom

(14) Mattes, S. L.; Farid, S. *Org. Photochem.* **1983**, *6*, 233–326.

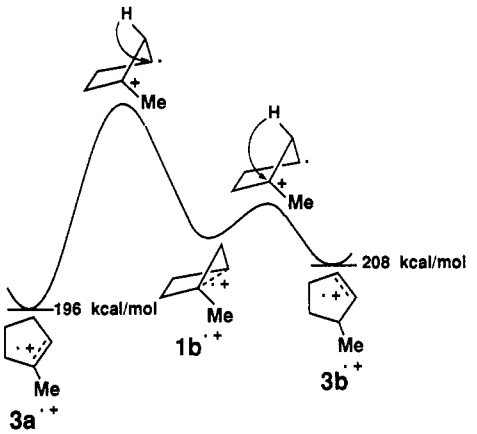


Figure 5. Schematic potential energy curves depicting the two possible reaction pathways from the distonic 1,3-diyl radical cation **1b**$^{\bullet+}$ to the 1-methylcyclopent-1-ene and 3-methylcyclopent-1-ene radical cations (**3a**$^{\bullet+}$ and **3b**$^{\bullet+}$, respectively). The pathway to **3b**$^{\bullet+}$ is favored by the lower activation barrier for hydride transfer compared to that for hydrogen atom transfer, resulting in kinetic rather than thermodynamic control of the reaction product.

transfer to the radical center (Figure 5) must presumably require a much larger activation energy, since neither **3a**$^{\bullet+}$ nor **3a** was observed in the respective ESR and PET experiments. These results strongly imply that, in terms of reactivity, the 1,3-radical cation **1b**$^{\bullet+}$ should more appropriately be considered as being distonic, i.e. as localized, rather than possessing a widened, one-electron bond, as proposed for cyclopropane and bicyclo[1.1.0]-butane radical cations.[4,11,17] However, as mentioned earlier, we emphasize that this distonicity may only become fully developed as the rearrangement reaction proceeds. Thus, no contradiction is involved with the recent finding[17c] that the oxidation of 1-methylbicyclo[1.1.0]butane gives a delocalized 1,3-diyl radical cation, since in this latter case[17c] there appears to be no driving force for rearrangement to a cyclobutene species.[1b]

Due to the low mass balance (formation of undefined products of higher molecular weight) of the PET reactions of housane **1b**, the possibly very minor intervention of the radical cation **3a**$^{\bullet+}$ and its reaction channels could not be rigorously assessed.

The PET reactions of azoalkane **2b** yield both regioisomeric cyclopentenes **3a,b** as final products. The detection of housane **1b** provides evidence for the intermediacy of the 1,3-radical cation **1b**$^{\bullet+}$ (Scheme 3). The ratio of housane **1b** (cyclization) versus cyclopentene **3b** (rearrangement) varies strongly with sensitizer type (entries 4–6, Table 1). The latter results presumably originate from differing rates of back electron transfer (k_{BET}). Fast BET is expected to lead to an increased amount of housane **1b** because rearrangement of radical cation **1b**$^{\bullet+}$ to cyclopentene **3b** must compete with its cyclization to housane **1b** ($k_{BET} > k_{rearr}$, Scheme 3), most likely through a biradical intermediate.

If this is the case, then according to eq 3, which applies to the normal Marcus region,[1b,7a] it can be estimated that, for the sensitizer DCA, k_{BET} should be distinctly larger than that for TPT, since k_{BET} increases with the exergonicity of the BET process.[18a] Thus, with DCA as sensitizer more housane **1b** and

$$\Delta G_{BET} = E_{red}(\text{acceptor}) - E_{ox}(\text{donor}) \quad (3)$$

Acceptor: sensitizers DCA (E_{red} = –0.89 V/SCE[5b])
or TPT (E_{red} = –0.29 V/SCE[5b])

less rearrangement product **3b** are obtained than with TPT. Cosensitization with Ph_2 represents a special case (entry 6, Table 1), in which free and, consequently, longer lived radical cations intervene.[7] This leads to almost complete rearrangement of the 1,3-radical cation **1b**$^{\bullet+}$.

Since the PET reactions with the housane **1b** as starting material showed that cyclopentene **3a** cannot be derived from the radical cation **1b**$^{\bullet+}$, an alternative reaction pathway has to be at play to account for the formation of cyclopentene **3a** from azoalkane **2b**. We postulate that cyclopentene **3a** derives from the direct rearrangement of the diazenyl radical cation **Ib**$^{\bullet+}$ (Scheme 3).[18b,c]

As suggested previously,[1a,b] denitrogenation of the intermediate **Ib**$^{\bullet+}$ may be accompanied by a simultaneous 1,2-shift (see eq 2). Thus, the diazenyl radical cation **Ib**$^{\bullet+}$ gives rise not only to 1,3-radical cation **1b**$^{\bullet+}$ by cleavage of the remaining C–N bond ($k^1_{-N_2}$, Scheme 3) but, in a competing process, also directly to the 1,2-radical cation **3a**$^{\bullet+}$ through C–N bond cleavage with a *concerted* 1,2-H shift ($k^2_{-N_2}$, Scheme 3).[18] Due to the short lifetime of diazenyl intermediates,[6] it can be expected that these two latter processes ($k^1_{-N_2}$, $k^2_{-N_2}$) are faster than back electron transfer. If this is the case, the relative yield of cyclopentene **3a** should not vary with the sensitizer used. Indeed, as entries 4–6 (Table 1) show, the yield of cyclopentene **3a** is independent of the sensitizer employed and is not even affected by cosensitization. This finding is further evidence for the involvement of diazenyl radical cation **Ib**$^{\bullet+}$.

The reluctance of the radical cation **1c**$^{\bullet+}$ to rearrange is also manifested in the PET chemistry of the dimethylhousane **1c**, since with excited DCA as electron acceptor almost no conversion is observed even after prolonged irradiation (entry 8, Table 1). Under these PET conditions the unsymmetrical housane **1b** rearranged, albeit slowly, to cyclopentene **3b** (entry 2, Table 1), although it should be less readily oxidized than the higher substituted housane **1c**. For example, the oxidation potentials of bicyclo[1.1.0]butanes decrease regularly with an increasing number of methyl substituents.[19] Thus, if electron transfer from excited DCA to housane **1b** is energetically feasible, it should be even more facile for housane **1c**. However, in the liquid phase at –5 °C, rearrangement of housane **1c** was only observed on PET activation when the stronger oxidant TPT or cosensitization with Ph_2 was employed (entries 7 and 9, Table 1). As discussed above, under these conditions lower k_{BET} values apply, which render the 1,2-H shift as more competitive.

These PET results therefore strongly reinforce the ESR observations (vide supra) on the remarkable kinetic stability of **1c**$^{\bullet+}$ to rearrangement. A comparison of the reactivity of **1c**$^{\bullet+}$ with that of the parent cyclopentane-1,3-diyl radical cation **1**$^{\bullet+}$ therefore becomes of particular interest because these two radical cations are isostructural. As is revealed by examination of their ESR hyperfine parameters in Table 2, both species belong to the C_s point group with a mirror plane bisecting the one-electron bond such that the diyl radical cation centers are equivalent in

(15) (a) Wolkoff, P.; Holmes, J. L. *Can. J. Chem.* **1979**, *57*, 348–354. (b) *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1, p 253. (c) The cyclopentene **3a** is 2.7 kcal/mol more stable than its regioisomer **3b**; see ref 16. (d) An alternate explanation for the stereoselective formation of **3b**$^{\bullet+}$ from **1b**$^{\bullet+}$ would demand that the spin be localized at the methyl-substituted site in **1b**$^{\bullet+}$ in the course of the reaction and that the subsequent rate of hydrogen atom transfer from C-5 to this site greatly exceed that of the corresponding hydride transfer to the cationic site. Since both of these requirements would be in contradiction with a considerable body of experimental evidence amassed from reactivity studies on other systems, this alternative explanation can be dismissed as intrinsically improbable.

(16) DeTar, D. F. *J. Org. Chem.* **1991**, *56*, 1470–1474.

(17) (a) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405–3412. (b) Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 3283–3289. (c) Arnold, A.; Burger, U.; Gerson, F.; Kloster-Jensen, E.; Schmidlin, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 4271–4281.

(18) (a) Distinctly different correlations of k_{BET} with the energy gap apply for charge recombination (DCA-derived geminate pair) and charge shift (TPT-derived geminate ion pair).[7a] (b) In Scheme 3 only the diazenyl radical cation **Ib**$^{\bullet+}$ (R = H) is presented, in which the more highly substituted C–N bond is broken. Cleavage of the H-substituted C–N bond cannot be excluded, but then simultaneous 1,2-H shift would lead to the 1,2 radical cation **3b**$^{\bullet+}$. Since **3b**$^{\bullet+}$ is also derived from the regioisomeric radical cation **1b**$^{\bullet+}$, the intervention of the regioisomeric diazenyl radical cation, which is omitted in Scheme 3 for purposes of clarity, cannot be assessed. (c) We thank one of the reviewers for suggesting that the different product distributions observed for the housanes and azoalkanes originate in part from different intermediate radical cations in the two cases (cf. Schemes 1 and 3).

(19) Gassman, P. G.; Yamaguchi, R. *Tetrahedron* **1982**, *38*, 1113–1122.

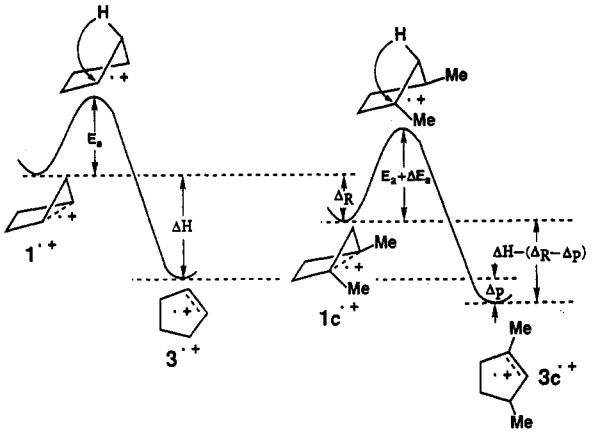


Figure 6. Diagrammatic representation of the effect of 1,3-dimethyl substitution on the reaction profile for the radical cation rearrangement of cyclopentane-1,3-diyl to cyclopentene. The difference between the heats of formation of the reactants is denoted by Δ_R, and the corresponding difference for the products is Δ_P. The increase in the barrier height ΔE_a on 1,3-dimethyl substitution is attributed to the net reduction in reaction exothermicity by $\Delta_R - \Delta_P$ (see text).

each case. This simplifies the ensuing analysis, since only one reaction path has to be considered, in contrast to the potentially dual situation for **1b**$^{\cdot+}$ (Figure 5).

In the previous studies,[1b,10] it was found that the reaction rates for the rearrangement of *syn*-**1a**$^{\cdot+}$, *anti*-**1a**$^{\cdot+}$, and **1**$^{\cdot+}$ in solid matrices were comparable in the temperature range between 90 and 110 K, and the activation energy E_a was estimated to be ca. 6.9 kcal/mol. By contrast, the persistence of **1c**$^{\cdot+}$ up to 150 K in the present work suggests a value of at least 10 kcal/mol for the E_a of its rearrangement, assuming the same frequency factor of 6×10^{11} s^{-1}.[1b] The problem therefore reduces to explaining how this increase in activation energy comes about on dimethyl substitution.

Figure 6 indicates how the reaction path profile is likely to be modified by methyl substitution at the diyl radical cation sites. The difference Δ_R between the heats of formation of the reactants **1c**$^{\cdot+}$ and **1**$^{\cdot+}$ includes a significant term for the effect of dimethyl stabilization in the former. Similarly, the corresponding Δ_P between the products **3c**$^{\cdot+}$ and **3**$^{\cdot+}$ embodies a similar term for the effect of dimethyl stabilization in **3c**$^{\cdot+}$. The essential feature of the argument is that this stabilization in the reactant is likely to exceed that in the product because both methyl groups interact with the π-system in the former (**1c**$^{\cdot+}$) whereas only one methyl group is directly attached in the latter (**3c**$^{\cdot+}$). Since the other quantities relating to bond strengths that contribute to both Δ_R and Δ_P will largely cancel in the difference $\Delta_R - \Delta_P$, the net effect of the methyl substitution is to make Δ_R more negative than Δ_P, leading to a reduction in the reaction exothermicity ΔH by the subtraction of $\Delta_R - \Delta_P$. Consequently, as illustrated in Figure 6, the activation energy is expected to increase by ΔE_a on dimethyl substitution, thereby accounting for the greatly increased kinetic stability of **1c**$^{\cdot+}$ relative to **1**$^{\cdot+}$.

In contrast to housane **1c**, azoalkane **2c** yields in the DCA-sensitized reaction cyclopentene **3c** as rearranged product (entry 11, Table 1). Again, rearrangement at the stage of the diazenyl radical cation **1c**$^{\cdot+}$ accounts for the different PET behavior of the azoalkane **2c** versus that of housane **1c**. Additionally, the extruded molecular nitrogen in the solvent cage of the geminate ion pair **2c**$^{\cdot+}$/DCA$^{\cdot-}$ might promote spatial separation between the ions, and consequently, a lower k_{BET} value[5,20] would apply with more rearrangement in the PET chemistry of azoalkane **2c** compared to housane **1c**.

The formation of the cyclopentadiene **4c** derives probably from allyl cations or allyl radicals by abstraction either of H$^{\cdot}$ or of H^{+}, as reported for other cases.[21] That the dimethyl substrates **1c** and **2c** yield minor amounts of cyclopentadiene, whereas the monomethyl derivatives **1b** and **2b** do not, is probably due to the longer lifetime of the radical cation **1c**$^{\cdot+}$, as established by ESR measurements.

Finally, the apparent observation of the putative distonic species **8c**$^{\cdot+}$ or its conjugate base **8c**$^{\cdot}$ in the present ESR studies under matrix conditions suitable for the occurrence of bimolecular reactions[12] points to one likely reason for oligomer formation and poor mass balances under PET conditions. Since such ion–molecule addition reactions are generally characterized by exceedingly large rate constants similar to those encountered in cationic polymerization studies,[13] it is probable that such bimolecular reactions can proceed during geminate recombination in the presence of high substrate concentration. The kinetic situation is comparable to that encountered in the radiation chemistry of organic liquids where "scavengers" have been routinely employed to probe the geminate ion recombination process.[12]

Conclusions

The present ESR and PET results firmly establish that methyl substitution at both bridgehead carbons in bicyclo[2.1.0]pentane leads to a significantly more persistent 1,3-diyl radical cation than for the parent or monosubstituted cases. On the other hand, the monomethyl 1,3-diyl radical cation substituted at the bridgehead position rapidly and regioselectively rearranges by hydride transfer to the thermodynamically less stable cyclopentene, thereby providing evidence for the development of a pronounced localization of spin and charge in the reaction of this unsymmetrical 1,3-diyl radical cation. Comparison of the ESR and PET results for the housanes **1b** and **1c** with those of the azoalkanes **2b** and **2c** reveals that nitrogen-free 1,3-diyl radical cations are generated from DBH derivatives to a significantly smaller extent. The distinctly different product distributions in the PET reactions of housane **1b** and azoalkane **2b** are interpreted as strong evidence for the involvement of a diazenyl radical cation in the denitrogenation of oxidized azoalkane **2b**. Although the latter does not persist sufficiently even under matrix isolation at low temperatures to allow the acquisition of direct ESR spectral evidence for these labile nitrogen-containing transients, the lack of formation of the very stable **1c**$^{\cdot+}$ in corresponding matrix studies on **2c** confirms that the oxidation path to **3c**$^{\cdot+}$ does not proceed exclusively through the 1,3-diyl radical cation **1c**$^{\cdot+}$.

Experimental Section

Instrumentation. The preparative GC separations were performed on a Carlo Erba Strumentazione 4200, equipped with a flame ionization detector (FID). Glass columns (5-mm i.d.) were used, and these were packed according to standard procedures. The GC analyses were performed on a Fractovap 2900 Series capillary GC instrument from Carlo Erba, equipped with a FID and a Shimadzu C-R1B electronic integrator. All capillary columns had an internal diameter of 0.25 mm and a film thickness of 0.25 mm. GC-MS analyses were performed at the Institute of Organic Chemistry by Dr. G. Lange (8200 Finnigan MAT mass spectrometer coupled with a Varian 3700 gas chromatograph).

Conversions, relative yields, and mass balances were determined by GC and corrected for the response factors of the starting material and the products. As quantitative measures, the integrated peak areas of the chromatograms were used. The mass balances (mb) were determined according to eq 4, where A_t = peak area after reaction time t, A_0 = peak

$$\% \text{ mb} = 100[\sum A_t(\text{P})/A_t(\text{IS})]/[A_0(\text{S})/A_0(\text{IS}) - A_t(\text{S})/A_t(\text{IS})] \quad (4)$$

area before the reaction, S = substrate, IS = internal standard, and P = product. The amount of unreacted starting material is not included

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in the mass balance. The entries in Table 1 refer to conversions at which no secondary photolysis, i.e. change in product distribution, was observed.

Synthesis of Starting Materials. Azoalkanes **2b,c** were prepared as reported.[22] The bicyclopentanes **1b,c**[8] were obtained by vacuum flash pyrolysis (ca. 230 °C/100 Torr) of the azoalkanes **2b,c** and separated by preparative gas chromatography on a 1.5-m column packed with 10% SE 30 (100% methyl silicone gum) on Volaspher A2. The column was operated at 30 °C with nitrogen as the carrier gas at a pressure of 1.2 bar and the injector and detector temperatures both at 150 °C.

3-Methylcyclopent-1-ene (**3b**) was prepared from 1-bromocyclopent-2-ene[23] and CH_3MgI by analogy to the literature procedure[24] and purified by preparative GC on a 1.5-m column packed with 10% SE 30 on Chromosorb WHP support. The column was operated at column/injector/detector temperatures of 50/125/125 °C with nitrogen as the carrier gas at a pressure of 1.6 bar.

1-Methylcyclopent-1-ene (**3a**) was obtained from the Aldrich Chemical Company in 98% purity. 1,3-Dimethylcyclopent-1-ene (**3c**)[25] was obtained by vacuum flash pyrolysis (ca. 520 °C/20 Torr) of bicyclopentane **1c** and separated by preparative gas chromatography as described above for housanes **1b,c**.

General Procedure for PET Reactions. CH_3CN was purified and dried by standard procedures and stored under an argon gas atmosphere. All photolyses were carried out on a 5-mL scale in a closed system, provided with a gas inlet, a sampling inlet, and a cold finger. The solutions were ca. 0.015 M in substrate and contained as GC standards *n*-heptane for housane **1b** and azoalkane **2b** and *n*-nonane (both Merck-Schuchardt) for housane **1c** and azoalkane **2c**. The sensitizers 9,10-dicyanoanthracene (DCA) or 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) were added (ca. 10 mol %) and the solutions purged with argon gas for 15 min prior to photolysis. In the case of DCA, which is only partially soluble (ca. 0.01–5 M), saturated solutions were employed and the photolyses were run in the presence of undissolved material. The cosensitizer biphenyl was used in tenfold excess (0.15 M).

The irradiations were performed at −5 °C and $\lambda > 400$ nm by using an external light source (150-W Heraeus TQ 150 high-pressure mercury arc with a Schott GG 400 glass filter) while stirring magnetically. The progress of the photolyses was monitored at appropriate intervals by capillary GC on a 30-m OV 1 fused silica column, typically operated at 15 °C for 10 min and then raised within 5 min to 150 °C for 15 min at injector/detector temperatures of 150/175 °C and a carrier gas (He) pressure of 0.7 bar.

The identity of the products was confirmed by coinjection of authentic material on two capillary columns [30-m OV 1, at the above operating conditions; additionally, a 30-m CW 20M fused-silica column was used and operated at 15 °C for 10 min and then raised within 3 min to 80 °C for 15 min at injector/detector temperatures of 150/175 °C by using a carrier gas (He) pressure of 0.6 bar]. Cyclopentadiene **4c** was identified by GC-MS, which showed a molecular ion peak of $m/z = 94$. In the PET reactions of the azoalkanes **2b,c**, the mass balances were corrected for the different GC response factors of the starting materials and the products.

Radiolytic Oxidation in Freon Matrices and ESR Measurements. The same general procedure was employed as in the previous investigation.[1b] Oxidation of the bicycloalkane or cycloolefin substrate was accomplished by the γ-irradiation of samples which contained an ca. 0.01 M solution in $CFCl_3$, $CF_2ClCFCl_2$, or CF_3CCl_3 at 77 K in a Cobalt-60 source. The total dose was usually in the range of 0.2–0.3 Mrad (1 Mrad = 10 kGy and 1 Gy = 1 J/kg), and the dose rate was ca. 30 krad/h with exposure times of 6–10 h. The samples were prepared in 3-mm (i.d.) Spectrosil quartz tubes on a vacuum line and the tubes sealed off after several freeze–pump–thaw degassing cycles.

After γ-irradiation, the sample tube was transferred into the variable-temperature Dewar insert within the cavity of a Bruker ER 200 D SRC spectrometer at an initial temperature of ca. 80 K. ESR spectra were then recorded at 10-deg intervals over the range from 80 K up to the softening points of the matrices in the region of 150 K. Spectral changes on sample annealing were monitored and always checked for reversibility by recycling to the lower temperature. In this way it was possible to differentiate between an irreversible radical cation (or neutral radical) reaction and a reversible change due only to an improvement in the spectral resolution of the radical cation at higher temperature.

Measurements of hyperfine coupling constants and *g* factors were made from spectra recorded with magnetic field calibration markers by using the Bruker ER 035 M microprocessor-controlled NMR gaussmeter. The microwave frequency was measured with a Systron Donner Model 6054 B counter and monitored during the recording of the spectra. Computer-simulated ESR spectra were generated by interfacing the recorder to a Bruker ER 144 data-handling system served by an ASPECT 2000 dedicated minicomputer.

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