*J. Am. Chem. Soc.* **1992**, *114*, 3007–3014

1 H), 1.25–1.96 (m, 6 H), 1.93 (s, 3 H), 2.04–2.07 (m, 1 H), 2.23–2.28 (m, 2 H), 2.64–2.74 (m, 2 H), 2.86–2.92 (m, 1 H), 3.39–3.43 (m, 1 H), 3.46–3.51 (m, 1 H), 3.83–3.86 (m, 2 H), 4.22–4.26 (m, 1 H), 5.01 (dd, $J = 10.7$, 10.6 Hz, 1 H), 5.43 (m, 1 H), 5.62 (s, 1 H), 5.69 (s, 1 H), 5.74 (dt, $J = 15.3$, 5.7 Hz, 1 H), 5.97 (dd, $J = 10.7$, 10.7 Hz, 1 H), 6.40 (dd, $J = 14.5$, 11.4 Hz, 1 H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 21.6, 24.5, 28.7, 29.2, 30.4, 31.0, 31.4, 31.8, 32.7, 34.9, 61.3, 62.3, 68.2, 97.3, 117.3, 126.0, 127.2, 131.8, 136.5, 158.4, 165.3, 174.6; high-resolution mass spectrum (Cl, $NH_3$) $m/z$ 439.2267 [(M + $NH_4^+$), calcd for $C_{22}H_{35}N_2O_5S$ 439.2223].

**Acknowledgment.** We are pleased to acknowledge support of this investigation by the National Institutes of Health (Institute of General Medical Sciences) through Grant GM-33833 and by Merck Sharp and Dohme Research Laboratories. In addition, we thank Dr. George Furst, Dr. Patrick J. Carroll, and Mr. John Dykins of the University of Pennsylvania Spectroscopic Service Centers for their assistance in securing and interpreting high-field NMR spectra, X-ray crystallographic data, and mass spectra, respectively. The technical assistance of Mr. Michael Becker is also gratefully acknowledged. Dr. Christopher S. Shiner provided helpful suggestions and critical comments.

**Supplementary Material Available:** Tables of experimental details, positional parameters, and thermal parameters for the X-ray analyses of (−)-**21**, (+)-**42**, (+)-**46**, and (−)-**ii** (31 pages). Ordering information is given on any current masthead page.

---

# Photochemical and ESR Spectral Evidence for a Stereoselective Rearrangement of Radical Cations Derived from Azoalkanes and Bicyclopentanes

**Waldemar Adam,*,[†] Herbert Walter,[†] Guo-Fei Chen,[‡] and Ffrancon Williams*,[‡]**

*Contribution from the Institute of Organic Chemistry, University of Würzburg, D-8700 Würzburg, Germany, and Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600.*

*Received April 8, 1991.*
*Revised Manuscript Received November 12, 1991*

**Abstract:** Studies of the photosensitized electron transfer (PET) reactions of *anti*/*syn*-5-methylbicyclo[2.1.0]pentane (**1a,b**) and *syn*/*anti*-7-methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**2a,b**) have revealed a remarkable *stereochemical memory effect.* Thus, **1a** and **2a** furnished only 1-methylcyclopentene (**3a**) as the rearrangement product, while their isomers **1b** and **2b** afforded predominantly 3-methylcyclopentene (**3b**). The pathway responsible for the stereoselective olefin formation can be assigned to a radical cation rearrangement. This was established on the basis of direct ESR evidence showing that the 1,3-diyl radical cations $\mathbf{1a,b}^{\bullet+}$ detected initially at 80–90 K following the radiolytic oxidation of **1a,b** in $CF_3CCl_3$ rearranged stereoselectively into the olefin radical cations $\mathbf{3a,b}^{\bullet+}$ at 105 K. The ESR results further establish that, in the puckered conformations of $\mathbf{1a,b}^{\bullet+}$, the pseudo-axial substituent on the methylene bridge is in almost perfect coplanar alignment with the radical cation 2p orbital lobes, thus facilitating its stereoselective migration. Also, in agreement with PET results, matrix ESR studies demonstrated that, on radiolytic oxidation of the azoalkanes **2a,b**, the olefin radical cations $\mathbf{3a,b}^{\bullet+}$ were formed with high selectivity, although no precursor radical cations were detected in this case.

Azoalkanes[1] and strained hydrocarbons[2] serve as suitable electron donors in photosensitized electron transfer (PET) reactions carried out in liquid media at ambient temperature, and there is a considerable body of evidence which indicates that their transient radical cations can undergo fragmentation, rearrangement, or addition reactions.[1,2] A valuable underpinning in the rationalization of this diverse reactivity comes from direct studies of radical cations by matrix ESR spectroscopy.[1c,3] Thus, the chair cyclohexane-1,4-diyl and puckered cyclopentane-1,3-diyl radical cations formed by the respective oxidations of bicyclo[2.2.0]hexane[3d] and bicyclo[2.1.0]pentane[3c] were found to rearrange smoothly to the corresponding cyclohexene and cyclopentene radical cations by intramolecular hydrogen transfer at 90–100 K. In contrast, the structurally similar bicyclo[1.1.0]butane radical cation[3e] did not isomerize to the cyclobutene radical cation up to 160 K, the softening point of the matrix.

Taken at face value, these differing results would appear to suggest that the radical cation isomerization of cycloalkanediyls to the more stable cycloalkenes is facilitated by a 1,3- rather than a 1,2-hydrogen transfer since only the former process is excluded for the cyclobutane-1,3-diyl radical cation. However, the present work demonstrates inter alia that this quite reasonable conjecture[3c] is *incorrect*, at least for the cyclopentane-1,3-diyl radical cation, thereby illustrating the pitfalls of mechanistic conclusions based only on comparative studies of different reactants, even when these are done within the same family!

The dearth of information regarding the actual mechanism of

---

[†] University of Würzburg.

[‡] University of Tennessee.

(1) (a) Adam, W.; Dörr, M. *J. Am. Chem. Soc.* **1987**, *109*, 1570–1572. (b) Engel, P. S.; Kitamura, A.; Keys, D. E. *J. Org. Chem.* **1987**, *52*, 5015–5021. (c) Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2484–2496.

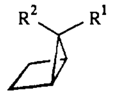
(2) (a) Gassman, P. G. In *Photoinduced Electron Transfer Part C. Photoinduced Electron Transfer Reactions: Organic Substrates*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; pp 70–87. (b) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343–350. (c) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401–449. (d) Fox, M. A. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Gollnick, K., Eds.; Wiley: New York, 1986; Vol. 13, pp 237–327. (e) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, pp 233–326. (f) Tsuji, T.; Miura, T.; Sugiura, K.; Nishida, S. *J. Am. Chem. Soc.* **1990**, *112*, 1998–1999. (g) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462–2464. (h) Gollnick, K.; Paulmann, U. *J. Org. Chem.* **1990**, *55*, 5954–5966. (i) Miyashi, T.; Takahashi, Y.; Ohaku, H.; Yokogawa, K.; Morishima, S.; Mukai, T. *Tetrahedron Lett.* **1990**, *31*, 2411–2414. (j) Boche, G.; Walborsky, H. M. In *Cyclopropane Derived Reactive Intermediates*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1990; pp 207–236.

(3) (a) Mendicino, M. E.; Blackstock, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 713–715. (b) Rhodes, C. J. *J. Chem. Soc., Chem. Commun.* **1990**, 799–801. (c) Williams, F.; Guo, Q.-X.; Kolb, T. M.; Nelsen, S. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1835–1837. (d) Williams, F.; Guo, Q.-X.; Bebout, D. C.; Carpenter, B. K. *J. Am. Chem. Soc.* **1989**, *111*, 4133–4134. (e) Gerson, F.; Qin, X.-Z.; Ess, C.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1989**, *111*, 6456–6457. (f) Williams, F.; Guo, Q.-X.; Petillo, P. A.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 7887–7888. (g) Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1498–1501. (h) Qin, X.-Z.; Williams, F. *Tetrahedron* **1986**, *42*, 6301–6314. (i) Ushida, K.; Shida, T.; Walton, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2805–2807. (j) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180–186.

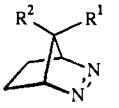
0002-7863/92/1514-3007$03.00/0

this simple but unprecedented cycloalkanediyl to cycloalkene radical cation rearrangement, as well as our continuing interest in these unusual reactive intermediates, prompted us to try to elucidate the precise nature of the hydrogen shift by means of suitable stereochemical labeling. In making this attempt, we recognized that the matrix ESR studies already hinted at a relatively high degree of conformational stability in these radical cations, as evidenced by the absence of line-broadening and coalescence effects resulting from rapid ring inversion or chair–chair interconversion, as the case may be. Thus, hydrogen migration appeared to be faster than stereomutation for the radical cations of cyclopentane-1,3-diyl and cyclohexane-1,4-diyl in Freon matrices at 90–100 K. These observations held out the promise that, at least under these conditions, the integrity of the stereochemical label would be preserved prior to reaction, as required to obtain meaningful mechanistic information.

Whether the above requirement would also apply to the reactions of these flexible species in solution at ambient temperature, however, remained an open question at the start of this work. Moreover, yet another stringent requirement of the labeling experiment which applies specifically to PET reactions in solution is that either the rate of radical cation rearrangement or the rate of separation of the geminate pair should compete favorably with back electron transfer. As it turns out, our results show that these requirements were met, and we report here a detailed study on the rearrangement of the radical cations derived from the one-electron oxidation of the bicyclo[2.1.0]pentane stereoisomers **1a,b**[4] and the corresponding azoalkanes **2a,b**[5] by using both PET and radiolytic methods.



1a,b



2a,b

a: $R^1 = CH_3$, $R^2 = H$, b: $R^1 = H$, $R^2 = CH_3$

## Experimental Section

**Gas Chromatography 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 an 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 μm.

**Synthesis of Starting Materials.** The preparation of the azoalkanes **2a,b** was modeled after the published procedure.[5] Substitution of MTAD (4-methyl-1,2,4-triazoline-3,5-dione) for PTAD (4-phenyl-1,2,4-triazoline-3,5-dione) in the Diels–Alder reaction with 5-methylcyclopenta-1,3-diene allowed the separation of the two diastereomeric adducts. An X-ray analysis on the stereoisomer produced in the lesser amount revealed that the methyl group in this case possessed the anti configuration with respect to the urazole moiety. This is contrary to the literature assignment, which assumes that the epimer produced in excess has the anti configuration.[5] This was based on the false presumption that attack of the dienophile should proceed with greater ease to give this isomer.

The bicyclopentanes **1a,b**[4] were obtained by vacuum flash pyrolysis (ca. 230 °C/100 Torr) of the azoalkanes **2a,b** and separated by preparative gas chromatography on a 3-m column packed with 20% β,β-ODPN (oxydipropionitrile) on Volaspher A2. The column was operated at 30 °C with nitrogen as the carrier gas at a pressure of 0.65 kg/cm², the injector and detector temperatures being 130 °C.

**Other Materials.** 3-Methylcyclopent-1-ene (**3b**) was prepared from 1-bromocyclopent-2-ene[6] and $CH_3MgI$ by analogy to the literature procedure[7] and purified by preparative GC on a 1.5-m column packed with 10% SE30 (100% methyl silicone gum) on a 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 kg/cm².

1-Methylcyclopent-1-ene (**3a**) was obtained from Aldrich Chemical Co. in 98% purity. Methylene chloride and acetonitrile were also obtained from commercial sources.

**General Procedure for Carrying Out PET Reactions.** Solvents ($CH_2Cl_2$ and $CH_3CN$) were 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 device for internal cooling. The solutions were made up ca. 0.02 M in substrate and contained cycloheptane (Merck-Schuchardt) as a GC standard. They were either saturated with 9,10-dicyanoanthracene (Kodak) or 10 mol % 2,4,6-triphenylpyrylium tetrafluoroborate (Merck-Schuchardt) was added and then deaerated prior to photolysis.

The irradiations were performed at −5 °C with $\lambda > 400$ nm using an external light source (150-W Hereaus TQ 150 high-pressure mercury arc with a Schott GG 400 glass filter) while the solutions were stirred magnetically. The progress of the photolyses was monitored at appropriate intervals by capillary GC on a 30-m OV 1 fused-silica column. This was operated at 20 °C for 10 min and then raised within 3 min to 80 °C for 15 min using injector/detector temperatures of 150/175 °C and a carrier gas ($N_2$) pressure of 0.7 kg/cm². Irradiations of 5–20-min duration were generally sufficient to achieve the desired 8–15% conversions of the substrate.

The identity of the products was confirmed by coinjection of authentic materials on two capillary columns (30-m OV 1, operating conditions as above; additionally, a 30-m CW 20M fused-silica column was operated at 20 °C for 8 min and then raised within 3 min to 80 °C for 15 min with injector/detector temperatures of 150/175 °C using a carrier gas ($N_2$) pressure of 0.6 kg/cm²). In studies on the PET reactions of the azoalkanes **2a,b**, the mass balances were corrected for the different response factors of the starting materials and the products.

**Radiolytic Oxidation in Freon Matrices.** This technique was first employed by Shida and Kato[8a] to obtain well-resolved ESR spectra of organic radical cations in $CFCl_3$.[8] Typically, a 0.01 M solution of the substrate to be oxidized was prepared in a Freon solvent and γ irradiated in the solid state at 77 K for a dose of 0.2–0.3 Mrad (1 Mrad = $10^4$ J/kg). Irradiations were carried out in a cobalt-60 γ source (Atomic Energy of Canada Gammacell 200) at a dose rate of ca. 38 krad/h. The ESR signal intensity of the radical cation generated on γ irradiation was generally independent of the substrate concentration over at least a 10-fold change (0.1–0.01 M), provided the concentration was not excessive (vide infra). This is consistent with the widely-held view[8c] that the oxidation process occurs *indirectly* through the efficient mediation of the positive holes that are generated almost exclusively in the Freon solvent at these dilutions (<0.1 M) by the high-energy radiation. In fact, substrate concentrations higher than 0.1 M often produced broader and more complicated ESR spectra, especially in $CF_3CCl_3$, suggesting that secondary reactions had occurred after substrate oxidation. High substrate concentrations were therefore avoided.

The Freon solvents used in this study were $CFCl_3$, $CF_3CCl_3$, and $CF_2ClCFCl_2$, all supplied by Aldrich. These materials were degassed by several freeze–pump–thaw cycles and stored in portable glass vessels fitted with greaseless valves. Solutions of the particular substrate (**1a,b**, **2a,b**, **3a,b**) were prepared on a vacuum line in Spectrosil ESR sample tubes (3-mm i.d.) as described previously.[9]

**ESR Measurements.** After γ irradiation at 77 K, the sample tube was quickly transferred into a variable-temperature Dewar insert, which was already mounted in the cavity of an ESR spectrometer (Bruker ER 200D SRC) and held initially at ca. 80 K. Spectra were recorded at several temperatures, usually at intervals of 10 K, as the sample was progressively annealed up to the softening point of the particular matrix. During this annealing process, the sample was often recycled to a lower temperature to determine whether any spectral changes induced on warming were reversible or irreversible. The microwave frequency was measured

---

(4) (a) White, D. H.; Condit, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7931–7933. (b) Wiberg, K. B.; Kass, S. R.; Bishop, K. C., III *J. Am. Chem. Soc.* **1985**, *107*, 996–1002. (c) Baldwin, J. E.; Ollerenshaw, J. *J. Org. Chem.* **1981**, *46*, 2116–2119.

(5) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688–4694.

(6) Bordwell, F. G.; Kern, R. J. *J. Am. Chem. Soc.* **1955**, *77*, 1141–1144.

(7) (a) Descoins, C.; Julia, M.; van Sang, H. *Bull. Soc. Chim. Fr.* **1971**, 4087–4093. (b) Ohbe, Y.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2389–2390.

(8) (a) Shida, T.; Kato, T. *Chem. Phys. Lett.* **1979**, *68*, 106–110. (b) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963–5970. (c) Shida, T. *Annu. Rev. Phys. Chem.* **1991**, *42*, 55–81.

(9) Snow, L. D.; Williams, F. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 57–69.

Table I. Product Studies of the Photosensitized Electron Transfer Reactions[a] of Bicyclopentanes **1a,b** and Azoalkanes **2a,b**

| substrate | sensitizer | solvent | time (min) | conversion[b,c] (%) | mass balance of product formation[b,c] (%) | product distribution (%)[b,d] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **1a** | **1b** | **3a** | **3b** |
| **1a** | TPT | $CH_2Cl_2$ | 5 | 15 | 22 | *e* | 59 | 41 | *f* |
| **1b** | TPT | $CH_2Cl_2$ | 5 | 13 | 30 | 80 | *e* | 4 | 16 |
| **2a** | TPT | $CH_3CN$ | 10 | 14 | 46 | 4 | 2 | 94 | *f* |
| **2a** | DCA | $CH_3CN$ | 20 | 10 | 78 | 13 | 8 | 79 | *f* |
| **2b** | TPT[g] | $CH_3CN$ | 10 | 15 | 10 | 6 | 3 | 14 | 77 |
| **2b** | DCA | $CH_3CN$ | 30 | 8 | 30 | 17 | 23 | 14 | 46 |

[a] See the Experimental Section for reaction conditions. [b] Determined by quantitative capillary GC. [c] Error 5–10% of stated value. [d] Relative yields normalized to 100%; error ca. ±1%. [e] Starting bicyclopentanes **1a,b**. [f] Not detected by capillary GC; detection limit ca. 1% relative yield. [g] Additional hydrocarbon products were detected which due to their similar retention times complicated the product analysis of **1a** and **3a**. Bicyclopentanes **1a,b** and olefins **3a,b** account for ca. 84% of the total product composition.

Table II. ESR Parameters for the Radical Cations of Cyclopentane-1,3-diyl, Cyclopentene, and Their Selected Methyl Derivatives

| radical cation | neutral precursor | matrix | *T* (K) | $g_{iso}$ | hyperfine couplings (G) |
|---|---|---|---|---|---|
| cyclopentane-1,3-diyl$^{\bullet+}$[a] | *a* | $CF_3CCl_3$ | 90 | 2.0033 (5) | 44.9 ($1H_{a1}$),[b] 33.5 ($2H_{a2}$),[c] 11.7 ($2H_b$)[d] |
| | | $CFCl_2CFCl_2$ | 80 | 2.0032 (5) | 44.8 ($1H_{a1}$), 32.5 ($2H_{a2}$), 12.0 ($2H_b$) |
| **1a**$^{\bullet+}$ | **1a** | $CF_3CCl_3$ | 83 | 2.0037 (5) | 43.9 ($1H_{a1}$), 32.8 ($2H_{a2}$), 11.7 ($2H_b$) |
| | | $CF_2ClCFCl_2$ | 91 | 2.0034 (5) | 44.7 ($1H_{a1}$), 32.6 ($2H_{a2}$), 12.6 ($2H_b$) |
| **1b**$^{\bullet+}$ | **1b** | $CF_3CCl_3$ | 86 | 2.0040 (5) | 32.5 ($2H_{a2}$), 11.9 ($2H_b$) |
| | | $CF_2ClCFCl_2$ | 89 | 2.0040 (5) | 32.5 ($2H_{a2}$), 12.6 ($2H_b$) |
| cyclopentene$^{\bullet+}$[a] | *a* | $CFCl_3$ | 140 | 2.0028 (5) | 49.7 ($4H_\beta$), 8.8 (4H)[e] |
| | | $CF_3CCl_3$ | 110 | 2.0039 (5) | 49.6 ($4H_\beta$), 10.5 ($2H_\alpha$), 7.0 ($2H_\gamma$) |
| **3a**$^{\bullet+}$ | **3a** | $CFCl_3$ | 133 | 2.0040 (5) | 51.4 ($2H_{\beta1}$), 32.8 ($2H_{\beta2}$), 15.8 ($3H_{Me}$), 8.3 ($1H_\alpha$) |
| | **2a** | $CFCl_3$ | 132 | 2.0038 (5) | 50.9 ($2H_{\beta1}$), 33.1 ($2H_{\beta2}$), 15.9 ($3H_{Me}$), 8.2 ($1H_\alpha$) |
| | **1a** | $CFCl_3$ | 130 | 2.0035 (5) | 51.9 ($2H_{\beta1}$), 32.8 ($2H_{\beta2}$), 15.8 ($3H_{Me}$), 8.3 ($1H_\alpha$) |
| | **3a** | $CF_3CCl_3$ | 146 | 2.0037 (5) | 49.0 ($2H_{\beta1}$), 32.1 ($2H_{\beta2}$), 16.5 ($3H_{Me}$), 10.9 ($1H_\alpha$), 4.0 ($2H_\gamma$) |
| | **1a** | $CF_3CCl_3$ | 140 | 2.0037 (5) | 50.1 ($2H_{\beta1}$), 32.8 ($2H_{\beta2}$), 15.8 ($3H_{Me}$), 10.8 ($1H_\alpha$), 4.1 ($2H_\gamma$) |
| **3b**$^{\bullet+}$ | **3b** | $CFCl_3$ | 153 | 2.0033 (5) | 50.5 ($2H_{\beta1}$), 45.6 ($1H_{\beta2}$), 20.1 (1H),[f] 6.7 ($2H_\alpha$) |
| | **2b**[g] | $CFCl_3$ | 153 | 2.0038 (5) | 50.6 ($2H_{\beta1}$), 45.8 ($1H_{\beta2}$), 20.0 (1H),[f] 6.6 ($2H_\alpha$) |
| | **1b** | $CFCl_3$ | 150 | 2.0029 (5) | 50.6 ($2H_{\beta1}$), 44.9 ($1H_{\beta2}$), 19.8 (1H),[f] 7.0 ($2H_\alpha$) |
| | **3b** | $CF_3CCl_3$[h] | 143 | 2.0039 (5) | 45.6 ($2H_{\beta1}$), 28.1 ($1H_{\beta2}$), 10.0 (3H)[i] |
| | **1b** | $CF_3CCl_3$[h] | 140 | 2.0040 (5) | 47.3 ($2H_{\beta1}$), 31.7 ($1H_{\beta2}$), 10.0 (3H)[i] |

[a] Reference 3c; the neutral precursor was the parent bicyclo[2.1.0]pentane. [b] Pseudo-axial hydrogen on methylene bridge. [c] Pseudo-axial hydrogens on dimethylene bridge. [d] Bridgehead hydrogens. [e] Separate couplings to $2H_\alpha$ and $2H_\gamma$ cannot be distinguished. [f] This apparent doublet may represent the sum of couplings due to some of the five $\gamma$ hydrogens. [g] The spectrum of **3b**$^{\bullet+}$ from the oxidation of **2b** in $CFCl_3$ at lower temperatures (ca. 115 K) gave different couplings associated with an unrelaxed form of this radical cation. A similar anomalous spectrum was obtained from the oxidation of **2b** in $CF_3CCl_3$, but it did not undergo an irreversible change at higher temperature as was observed in the $CFCl_3$ matrix. The problem of unrelaxed olefin radical cations seems most acute for the generation of **3a,b**$^{\bullet+}$ from **2a,b** in the $CF_3CCl_3$ matrix, and the ESR parameters are omitted for these cases. [h] The coupling to one of the $\beta$-hydrogens ($1H_{\beta2}$) of **3b**$^{\bullet+}$ is much reduced in $CF_3CCl_3$ relative to the value in $CFCl_3$, suggesting a matrix-dependent conformation for this radical cation. [i] The approximate quartet substructure is assigned to nearly equal couplings for $2H_\alpha$ and a single effective $H_\gamma$.

with a Systron-Donner counter (Model 6054 B), and markers were recorded during the magnetic-field sweep by means of a microprocessor-controlled NMR gaussmeter (Bruker ER 035 M).

## Results

**PET Reactions.** On 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) sensitized electron transfer, the bicyclopentanes **1a,b** underwent interconversion and rearrangement into cyclopentenes (Table I); however, bicyclopentane **1a** afforded only 1-methylcyclopent-1-ene (**3a**) as the rearrangement product, while in the case of bicyclopentane **1b** the rearrangement into the isomeric 3-methylcyclopent-1-ene (**3b**) was preferred over **3a**. The reactions were monitored at low conversion of the starting materials to ensure that secondary oxidation of the hydrocarbon products did not encumber and therefore distort the product distribution. Additionally, careful monitoring of the product composition as a function of time after photolysis revealed that adventitious proton catalysis did not intervene at conversions of **1a,b** lower than 30%.[4b]

The PET reactions of azoalkanes **2a,b** by employing either TPT or 9,10-dicyanoanthracene (DCA) as the photosensitizer displayed analogous results at partial conversion (up to 15%). Thus, **2a** yielded only **3a** while **2b** gave predominantly **3b** as the rearrangement products. Also, for both azoalkanes **2a,b**, the stereoisomeric bicyclopentanes **1a,b** were formed (Table I), the proportions of these products depending on the sensitizer employed. Lower mass balances were observed for azoalkane **2b** compared to **2a**, irrespective of whether TPT or DCA was used. As in the case of **1a,b**, material of higher molecular weight was presumably formed, which went undetected by the GC analyses.

Control experiments confirmed that cyclopentene **3b** does not isomerize into **3a** in the TPT- or DCA-sensitized reactions. Again, mainly high molecular weight material was formed.

**ESR Studies.** Following the radiolytic oxidation of **1a,b** in Freon matrices, the initial spectra at 80–90 K revealed signals from the corresponding 1,3-diyl radical cations **1a,b**$^{\bullet+}$. However, as previously observed for the oxidation of the parent bicyclo[2.1.0]pentane,[3c] the initial signal intensity of the diyl radical cation relative to that of the rearranged product (olefin radical cation) before the annealing depended strongly on the matrix. This ratio was smallest for $CFCl_3$, making this matrix very unsuitable for the characterization of these diyl radical cations.[3c,i] Accordingly, we directed our attention to haloethane matrices which had provided such clear results in the case of the parent compound.[3c]

Figure 1 shows the low-temperature spectra (a and b) obtained from the respective oxidations of **1a** and **1b** in $CF_2ClCFCl_2$. These spectra are of such clarity that they allow immediate analysis by inspection according to the hyperfine patterns given in the stick diagrams and can be assigned to the corresponding radical cations **1a,b**$^{\bullet+}$ by analogy to the structure deduced for the parent species;[3c] the measured ESR parameters are listed in Table II. As might be expected in the absence of ring inversion, the spectrum of **1a**$^{\bullet+}$ (Figure 1a) closely resembles that of the parent cyclopentane-1,3-diyl radical cation,[3c] while the spectrum of **1b**$^{\bullet+}$ (Figure 1b) differs predictably from this common pattern by the omission of the ca. 44-G coupling previously assigned to a pseudo-axial (flagpole) hydrogen ($H_{a1}$) on the methylene bridge (Table II) since the methyl group now occupies this pseudo-endo position. These ESR results for **1a,b**$^{\bullet+}$ therefore verify the original assignment

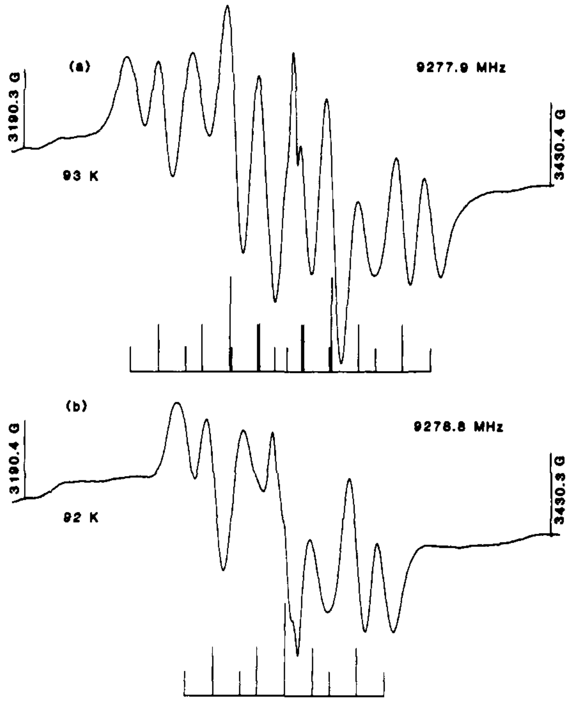


**Figure 1.** ESR spectra of $\gamma$ irradiated (dose, 0.2 Mrad) solid solutions containing ca. 0.01 M *anti*-5-methylbicyclo[2.1.0]pentane (**1a**) in $CF_2ClCFCl_2$ (a) and ca. 0.01 M *syn*-5-methylbicyclo[2.1.0]pentane (**1b**) in $CF_2ClCFCl_2$ (b). Both spectra were recorded after annealing the $\gamma$ irradiated sample from 77 to 92–93 K. Stick diagram reconstructions of the hyperfine patterns for **1a**$^{\bullet+}$ and **1b**$^{\bullet+}$ are shown below spectra a and b, respectively.

of the largest hyperfine coupling in the parent species[3c] to the pseudo-axial hydrogen on the methylene bridge. This finding assumes particular importance for the mechanism of the hydrogen shift in the rearrangement to the olefin cation, as will be discussed later. A more subtle point that is only established by the present results is the virtual absence of stereorandomization in the formation of the diyl radical cation. Considering that excess vibrational energy may be present as the parent species relaxes to its equilibrium structure, the persistence of the stereochemical label intact is noteworthy for such a flexible radical cation.

The oxidation of **1a,b** in $CF_3CCl_3$ gave very similar spectra at 80–90 K to those shown for **1a,b**$^{\bullet+}$ in $CF_2ClCFCl_2$ (Figure 1), except for some admixture of weak signals from the corresponding olefin radical cations **3a,b**$^{\bullet+}$ (vide infra). Despite this minor complication, the thermal rearrangements of **1a,b**$^{\bullet+}$ to **3a,b**$^{\bullet+}$ on subsequent annealing could be followed much more clearly in $CF_3CCl_3$ than in the less-rigid $CF_2ClCFCl_2$ because the onset of bimolecular ion–molecule reactions[10] in the latter matrix at ca. 110 K, as evidenced by the growth of strong signals from the neutral 2-methylcyclopent-3-en-1-yl radical in each case, competed with the unimolecular process. Thus, measurements on the formation of **3a,b**$^{\bullet+}$ were confined to $CF_3CCl_3$, and the radical cation rearrangements were observed to take place very rapidly on annealing above 110 K ($t_{1/2}$ ca. 5 min at 105 K in each case).

Evidence for the stereoselectivity of these thermal rearrangements is presented in Figure 2, where the upper spectra (a, a′), recorded after the complete conversion of **1a,b**$^{\bullet+}$ in $CF_3CCl_3$, are seen to pair up precisely with the lower spectra (b, b′) of **3a,b**$^{\bullet+}$ generated by the direct oxidation of **3a,b** in the same matrix.[11] It was also found that **3b**$^{\bullet+}$ isomerizes to **3a**$^{\bullet+}$ on photobleaching with visible light under matrix-isolation conditions, strongly suggesting that **3a**$^{\bullet+}$ is thermodynamically more stable than **3b**$^{\bullet+}$.[12] Accordingly, a pathway exists for the consecutive formation of **3b**$^{\bullet+}$ and **3a**$^{\bullet+}$ starting only from **1b**$^{\bullet+}$, and as illustrated in Figure 3, the spectra (a and b) taken before and after photobleaching show virtually no common features. This proved that the photoisomerization of **3b**$^{\bullet+}$ to **3a**$^{\bullet+}$ was essentially complete, as might be expected. More importantly, however, the result also demonstrates reciprocally that **3b**$^{\bullet+}$, the less stable of the two olefin radical cation isomers, was originally produced from **1b**$^{\bullet+}$ with a very high degree of stereoselectivity. Thus, to all intents and purposes, the thermal rearrangements of **1a,b**$^{\bullet+}$ to **3a,b**$^{\bullet+}$ are stereospecific at ca. 110 K.

Turning to the oxidation of the azoalkanes **2a,b**, neither the parent species **2a,b**$^{\bullet+}$ nor the putative diyl radical cations **1a,b**$^{\bullet+}$ were observed as precursors to the olefin radical cations **3a,b**$^{\bullet+}$, irrespective of the Freon used as the matrix. Similarly, only the cyclopentene radical cation was previously detected in the oxidation of the parent 2,3-diazabicyclo[2.2.1]hept-2-ene in $CFCl_3$.[1c] Since the spectra derived from the oxidation of **2a,b** were generally of poor resolution below 100 K, measurements were made after annealing to higher temperatures. The $CFCl_3$ matrix proves to be the most suitable for the observation of **3a,b**$^{\bullet+}$ from different precursors, and Figure 4 shows a comparison of the spectra derived from the oxidations of **1a,b** (upper traces), **3a,b** (middle traces), and **2a,b** (lower traces). There is a good match between the three fingerprint spectra in each set, demonstrating that **3a,b**$^{\bullet+}$ are generated stereospecifically from the oxidation of **2a,b** as well as from **1a,b** (vide infra). The ESR parameters of **3a,b**$^{\bullet+}$ obtained from the three different precursors in several matrices are collected in Table II.

## Discussion

The pathway responsible for the stereoselectivity of cyclopentene formation in the PET reactions of **1a,b** can be assigned to a radical cation rearrangement on the basis of the direct ESR evidence presented above. Evidently, the puckered conformation of the radical cations **1a,b**$^{\bullet+}$ (Scheme I) places the original syn substituent into a pseudo-axial orientation in almost perfect coplanar alignment with the 2p orbital lobes at the bridgehead positions, while the pseudo-equatorial substituent is located essentially in the nodal plane of the 2p orbitals. The migration of the pseudo-axial substituent should, therefore, be favored, which accounts for the stereoselective formation of **3a**$^{\bullet+}$ from **1a**$^{\bullet+}$ and of **3b**$^{\bullet+}$ from **1b**$^{\bullet+}$.[13] In this context, it is interesting to note that the ESR measurements indicate that the absolute rate of rearrangement at 100–110 K does not depend on the nature of the migrating group; i.e., the hydrogen or methyl substituent migrates with equal facility, provided it possesses a coplanar arrangement with each of the p orbitals at the diyl radical cation centers. Unfortunately, the limited temperature range in which this rearrangement can be followed by standard ESR techniques does not allow the Arrhenius parameters to be determined with the desired degree of accuracy.[14]

---

(10) Qin, X.-Z.; Williams, F. *Radiat. Phys. Chem.* **1988**, *32*, 299–308.

(11) Careful comparison of spectra a′ and b′ in Figure 2 reveals a slight disparity in the total widths [$(a')_w > (b')_w$], although the patterns are the same. This is because the sum of the $\beta$-hydrogen hyperfine couplings for **3b**$^{\bullet+}$ in $CF_3CCl_3$ is marginally greater when this species is formed by the rearrangement of **1b**$^{\bullet+}$ rather than by the oxidation of **3b** (Table II). These minor differences in coupling constants are attributed to a matrix effect resulting from incomplete relaxation of the rearranged radical cation to its equilibrium geometry at the prevailing temperature.

(12) (a) Under liquid-phase PET conditions, the limited lifetime of **3b**$^{\bullet+}$ essentially precludes its direct photoisomerization to **3a**$^{\bullet+}$. (b) In agreement with this experimental order of stability in matrices, the heats of formation of **3a**$^{\bullet+}$ and **3b**$^{\bullet+}$ as determined in the gas phase are 196 and 208 kcal/mol, respectively: *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1, p 253. See also: Wolkoff, P.; Holmes, J. L. *Can. J. Chem.* **1979**, *57*, 348–354. Lossing, F. P.; Traeger, J. C. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 9–22. (c) The radical cation photoisomerization of 1-butene to the more stable 2-butene species has been previously demonstrated in Freon matrices using visible light.[8b] See also: Toriyama, K.; Nunome, K.; Iwasaki, M.; Shida, T.; Ushida, K. *Chem. Phys. Lett.* **1985**, *122*, 118–123.

(13) Although the observed stereoselectivity is attributed primarily here to the better orbital overlap for the migration of the pseudo-axial (endo) group and the concomitant formation of the one-electron $\pi$ bond, a related factor may be an intrinsically lower energy barrier for the expected stereoinversion at the bridgehead carbon atom undergoing substitution by the migrating endo group. In this latter connection, Dinnocenzo and his co-workers have shown that for the intermolecular attack of nucleophiles on cyclopropane radical cations,[2g] the ring-opening cleavage of the one-electron $\sigma$ bond proceeds with almost complete inversion of configuration. Also, theoretical considerations predict that the energy barrier for inversion of stereochemistry is likely to be lower than that for retention in nucleophilic displacements on one-electron bonds: Shaik, S. S.; Dinnocenzo, J. P. *J. Org. Chem.* **1990**, *55*, 3434–3436.

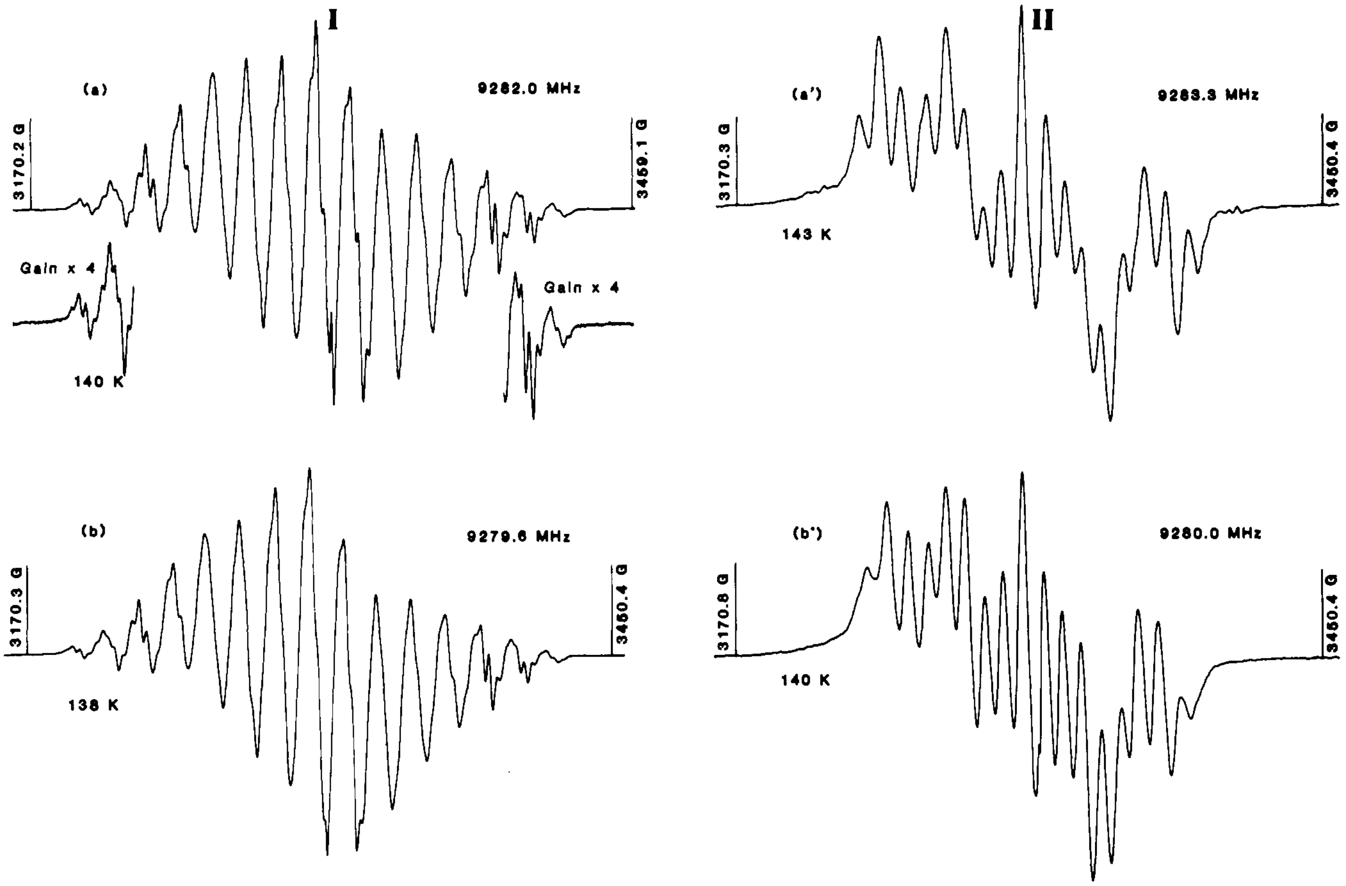
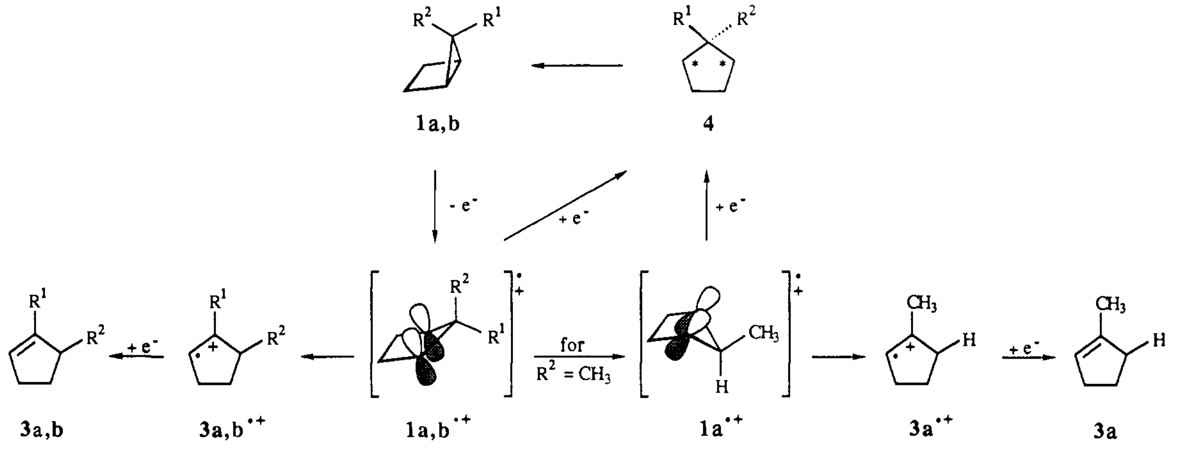


**Figure 2.** I: ESR spectra of the 1-methylcyclopent-1-ene radical cation ($3a^{\bullet+}$) generated in $CF_3CCl_3$ by the thermal rearrangement of the radiolytically-produced precursor $1a^{\bullet+}$ (a) and by the radiolytic oxidation of **3a** (b). II: ESR spectra of the 3-methylcyclopent-1-ene radical cation ($3b^{\bullet+}$) generated in $CF_3CCl_3$ by the thermal rearrangement of the radiolytically-produced precursor $1b^{\bullet+}$ (a') and by the radiolytic oxidation of **3b** (b'). The $CF_3CCl_3$ solid solutions (ca. 0.01 M substrate) of **1a,b** and **3a,b** were $\gamma$ irradiated (dose, 0.2 Mrad) at 77 K to produce $1a,b^{\bullet+}$ and $3a,b^{\bullet+}$, respectively, and then annealed as described in the text to the indicated temperatures (ca. 140 K), at which the featured ESR spectra were recorded.

**Scheme I**



a: $R^1$ = $CH_3$, $R^2$ = H, b: $R^1$ = H, $R^2$ = $CH_3$

For the PET reactions in solution, the degree of stereoselectivity of cyclopentene formation depended on the starting bicyclopentane stereoisomer. Thus, while bicyclopentane **1a** yielded the olefin **3a** virtually without any **3b**, bicyclopentane **1b** gave small amounts of **3a** in addition to the rearrangement product **3b**. This observation indicates that a fraction of $1b^{\bullet+}$ suffers a ring flip to yield $1a^{\bullet+}$ (Scheme I), whereas the reverse process is excluded on the time scale that applies (vide infra). Since the methyl substituent in $1a^{\bullet+}$ occupies the thermodynamically more favorable pseudoequatorial position, the unidirectional character of this ring inversion is understandable, as the reverse process from $1a^{\bullet+}$ to $1b^{\bullet+}$

---

(14) (a) Assuming an Arrhenius pre-exponential factor of $6 \times 10^{11}$ $s^{-1}$, which applies for some 1,2-aryl shifts in neutral radical rearrangements,[14b] the rate constant of $2.3 \times 10^{-3}$ $s^{-1}$ at 105 K ($t_{1/2}$ ca. 5 min) corresponds to an activation energy of 6.9 kcal/mol. (b) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Essay 4, pp 161–310, and especially Table 1, p 171.

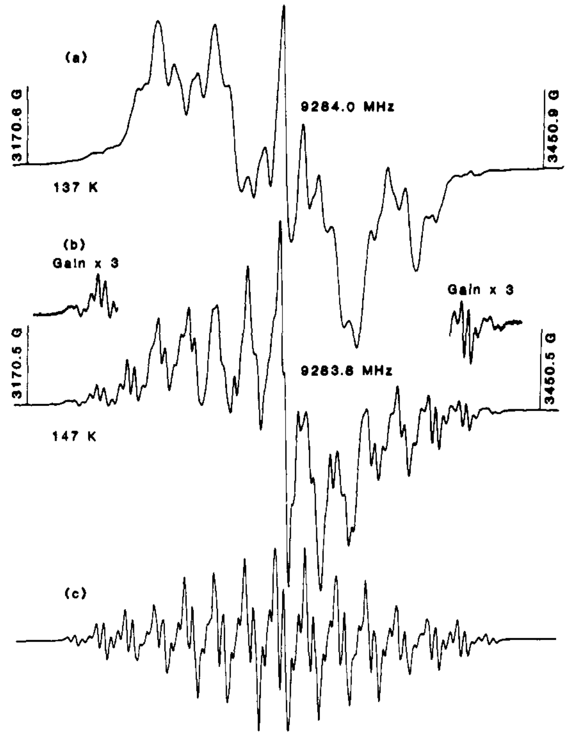


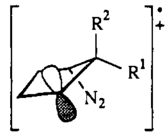
**Figure 3.** ESR spectrum at 137 K of the 3-methylcyclopent-1-ene radical cation (**3b**$^{\bullet+}$) produced by the thermal rearrangement of **1b**$^{\bullet+}$ following the radiolytic oxidation at 77 K of a solid solution containing 0.01 M of **1b** in $CF_3CCl_3$ (dose, 0.2 Mrad) (a). ESR spectrum of the 1-methylcyclopent-1-ene radical cation (**3a**$^{\bullet+}$) produced by visible light photobleaching of the **3b**$^{\bullet+}$ sample which gave spectrum a above, a slightly higher recording temperature (147 K) being used to improve the resolution (b). Simulated ESR spectrum using the hyperfine parameters of **3a**$^{\bullet+}$ in the $CF_3CCl_3$ matrix (Table II) (c).

has a higher activation energy so that it cannot compete with back electron transfer (i.e., within the lifetime of the geminate pair) or the rearrangement of **1a**$^{\bullet+}$ to **3a**$^{\bullet+}$. It may be added that, had this reverse process been competitive, **3b** should certainly have been formed from **1a** because the rates of hydrogen and methyl migration for **1a**$^{\bullet+}$ and **1b**$^{\bullet+}$, respectively, are comparable according to the ESR results.

Accordingly, the lower stereoselectivity of the rearrangement from **1b** to **3b** as compared to that from **1a** to **3a** in the PET experiments at 268 K (Table I) is attributed to the competing effect of the thermodynamically favorable **1b**$^{\bullet+}$ to **1a**$^{\bullet+}$ ring flip on the **1b**$^{\bullet+}$ to **3b**$^{\bullet+}$ rearrangement (Scheme I). It must be stressed that this interpretation is not incompatible with the very high selectivity of the **1b**$^{\bullet+}$ to **3b**$^{\bullet+}$ rearrangement observed in the ESR studies at ca. 110 K (Figure 2, set II). The integrity of the stereochemical label in **1b**$^{\bullet+}$ is clearly maintained at this low reaction temperature, and this strongly suggests that the activation energy for ring flip is higher than that for the rearrangement. It therefore follows that the **1b**$^{\bullet+}$ to **1a**$^{\bullet+}$ ring flip is expected to become more competitive with the **1b**$^{\bullet+}$ to **3b**$^{\bullet+}$ rearrangement at the much higher temperature used for the PET studies, as observed.

The PET reaction products from **1a,b** include the isomerized bicyclopentanes **1b,a** as well as the olefins **3a,b**. Since we have already ruled out stereomutation of **1a,b**$^{\bullet+}$ on the basis of the ESR measurements and, even more pertinently, the PET results analyzed above, an additional intermediate presumably intervenes to account for the stereorandomization of **1a,b** under PET reaction conditions. It is, therefore, proposed that back electron transfer to **1a,b**$^{\bullet+}$ furnishes 2-methylcyclopentane-1,3-diyl (**4**),[15] which can then collapse into *both* **1a** and **1b** (Scheme I).

Although the mechanistic picture is less clear-cut for the azoalkanes **2a,b**, the product compositions observed in the PET reactions (Table I) resemble those obtained for the bicyclopentanes **1a,b**, suggesting that the radical cations **1a,b**$^{\bullet+}$ again play a major role (Scheme I). In this case, however, the matrix ESR experiments failed to detect either **2a,b**$^{\bullet+}$ or **1a,b**$^{\bullet+}$ following the radiolytic oxidation of **2a,b**, with only the corresponding olefin radical cations **3a,b**$^{\bullet+}$ being observed.[16] Nonetheless, the stereospecificity of olefin radical cation formation is fully maintained (Figure 4). Thus, the stereochemical memory effect observed in the radiolytic oxidation of **2a,b** may be attributed either to the one-step loss of $N_2$ from **2a,b**$^{\bullet+}$ with concomitant migration of the substituent anti to the azo linkage or possibly to a two-step process that involves intermediate diazenyl radical cations **5a,b**$^{\bullet+}$, which undergo facile denitrogenation with concomitant migration of the antiperiplanar substituent.[17] Such diazenyl radical cations may be too short-lived to be detected under the conditions of the ESR experiments.



5a,b$^{\bullet+}$

Similar radical cation mechanisms are also expected to apply for the stereoselective conversion of **2a,b** to **3a,b** by means of the PET reactions conducted in solution, but it is difficult to distinguish between them experimentally. On the subject of the lower mass balances for azoalkane **2b** compared to **2a**, it should be pointed out that this is not due to the formation of significant amounts of unidentified volatile products from **2b** but rather to the formation of nonvolatile materials with higher molecular weights. This complication seems to have little to do, however, with the stereoselectivity of the transformation to olefin, which is the main subject of this paper.

It is noteworthy that the use of DCA instead of TPT as the sensitizer in the PET reactions of **2a,b** furnishes better mass balances; also, more significantly, increased amounts of bicyclopentanes **1a,b** are observed (Table I). This latter result may be expected for two reasons. First, for back electron transfer in the *normal* Marcus region,[18] the greater exothermicity of this process in the case of DCA should result in a shorter lifetime and therefore less rearrangement of the derived **1a,b**$^{\bullet+}$ radical cations, although distinctly different correlations of the rate of back electron transfer with the energy gap apply for charge recombination (DCA-derived geminate pair) and charge shift (TPT-derived geminate pair) processes.[19,20] Secondly, the ease of diffusive separation into free ions is expected to be considerably greater for a TPT-derived geminate pair, since for a radical cation and neutral radical pair there is no Coulombic attraction to overcome as in the case of the radical cation and radical anion pair associated with the use of DCA.[20,21] Therefore, in the TPT-sensitized PET reactions, a larger proportion of **1a,b**$^{\bullet+}$ can diffuse apart to afford *free* radical cation species. Under these conditions, the diffusive reencounter

---

[15] There is an ongoing debate in the literature on the depth of the local energy minimum of the parent species, singlet cyclopentane-1,3-diyl; see: ref 4a and Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 2681–2683.

[16] Similarly, the cyclohexane-1,4-diyl radical cation has not been detected as an intermediate in the photofragmentation of the 2,3-diazabicyclo[2.2.2]oct-2-ene radical cation to the cyclohexene radical cation.[3f] However, this latter result is probably attributable to the consecutive photoisomerization of the diyl radical cation under the prevailing photobleaching conditions.

[17] For an analogous migration concomitant with denitrogenation in diazenyl diradicals, see: Adam, W.; De Lucchi, O.; Dörr, M. *J. Am. Chem. Soc.* **1989**, *111*, 5209–5213.

[18] (a) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79–185. (b) Julliard, M. In *Photoinduced Electron Transfer Part B. Photoinduced Electron Transfer Reactions: Experimental Techniques and Medium Effects*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; pp 216–313.

[19] (a) Kakitani, T.; Mataga, N. *J. Phys. Chem.* **1985**, *89*, 4752–4757. (b) Kakitani, T.; Mataga, N. *J. Phys. Chem.* **1986**, *90*, 993–995. (c) Kakitani, T.; Mataga, N. *J. Phys. Chem.* **1987**, *91*, 6277–6285.

[20] Gould, I. R.; Moser, J. E.; Armitage, B.; Farid, S.; Goodman, J. L.; Herman, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 1917–1919.

[21] Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 3601–3602.

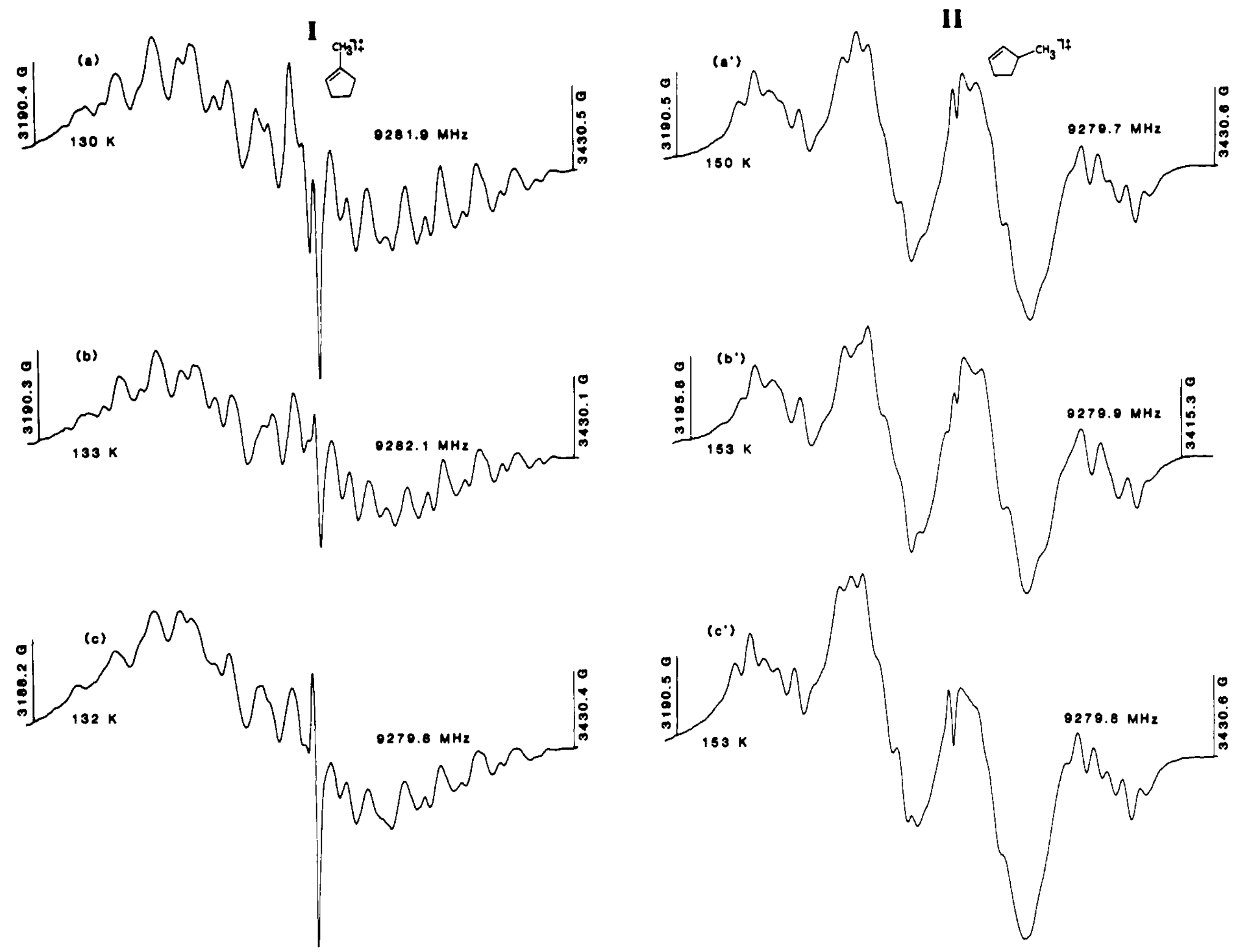


**Figure 4.** I: ESR spectra of the 1-methylcyclopent-1-ene radical cation ($3a^{\bullet+}$) generated in $CFCl_3$ by the radiolytic oxidation of **1a** (a), **3a** (b), and **2a** (c). II: ESR spectra of the 3-methylcyclopent-1-ene radical cation ($3b^{\bullet+}$) generated in $CFCl_3$ by the radiolytic oxidation of **1b** (a′), **3b** (b′), and **2b** (c′). The $CFCl_3$ solid solutions (ca. 0.01 M substrate) were $\gamma$ irradiated (dose, ca. 0.2 Mrad) at 77 K and then annealed to the temperatures at which the ESR spectra were recorded. These temperatures were 130–133 K for set I and 150–153 K for set II, as shown on the figure.

cannot compete with the rearrangement of $\mathbf{1a,b}^{\bullet+}$ into $\mathbf{3a,b}^{\bullet+}$ and, consequently, less **1a,b** should be formed with the TPT sensitizer, as observed.

Expanding on earlier remarks, the migration of the pseudo-axial substituent in the rearrangement of $\mathbf{1a,b}^{\bullet+}$ to $\mathbf{3a,b}^{\bullet+}$ corresponds to an ideal starting geometry for this 1,2-shift. First, the bond to the migrating pseudo-axial group is coplanar with the axis of the 2p orbital at the diyl center which serves as the substitution site, thereby facilitating the migration. Second, the bond to the pseudo-equatorial substituent is already almost coplanar with the carbon–hydrogen bond at the other diyl center, so that formation of the singly occupied $\pi$ orbital as the reaction proceeds requires very little torsional adjustment. Thus, *both* the substitution and the olefin-forming elimination character of the rearrangement are nicely synchronized in a favorable mode when the pseudo-axial substituent migrates, whereas migration of the pseudo-equatorial substituent would clearly correspond to the least favorable initial orientation for both processes and therefore for the entire rearrangement. The *principle of least motion*[22a] is therefore well exemplified in this rearrangement.

Another aspect of this reaction which deserves brief comment is that the suprafacial 1,2-sigmatropic shift is predicted by the favorable orbital interaction[22b] between the symmetric SOMO of the diyl radical cation and the $\sigma$ bonding orbital of the migrating group, which allows the unpaired electron to go into the $\pi$ orbital of the olefin radical cation product. To illustrate this point, a corresponding positive overlap between an antisymmetric SOMO of the diyl radical cation and the $\sigma$ bonding orbital of the migrating group has the effect of forcing the unpaired electron into the $\pi^*$ orbital of the product and therefore makes the reaction path unfavorable in such a case. Hence, the symmetry of the diyl radical cation SOMO seems to be critical for this rearrangement.

Although the observed selectivity of pseudo-axial substituent migration vicinal to the carbon radical center is in full accordance with chemical expectation, it is remarkable to find no precedent for this finding. Of course, one obvious difficulty in studying radicals is that the stereochemical nonequivalence must be retained for the duration of the chemical reaction in the face of rapid conformational inversion. Yet another requirement which applies to neutral radicals is that the reaction must generally be bimolecular, since another radical center must necessarily be involved in bringing about the migration.[22] In a singular previous report on this topic, Livant and Lawler[23] cleverly used the indirect CIDNP technique to overcome the problem of conformational inversion by studying the NMR signals produced by the very rapid disproportionation of a pair of cyclohexyl radicals ($10^{-9}$–$10^{-10}$ s)

---

[22] (a) The unimolecular rearrangement of a 1,3-biradical to an olefin represents the neutral counterpart of the radical cation rearrangement described in this paper. Clearly, the stereochemical integrity of a label at C-2 is lost if the 1,3-diyl adopts a planar conformation.[15] For an excellent review of biradical rearrangements, see: Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Essay 5, pp 311–390. (b) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57–64. (c) Whereas 2-methylcyclopentane-1,3-diyl produced in the singlet manifold isomerizes to 1-methylcyclopentene,[4a] its triplet counterpart does not rearrange into olefin and gives only **1a,b**: Walter, H., Ph.D. Thesis, University of Würzburg, Würzburg, Germany, in preparation.

[23] Livant, P.; Lawler, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 6044–6045.

within a solvent cage. However, this experiment apparently indicated a preference for the migration (abstraction) of the pseudo-equatorial $\beta$-hydrogen, a finding which the authors recognized as surprising. This unexpected result was then explained[23] as the consequence either of the steric bulk of the abstracting radical or of the imposition of a severely distorted cyclohexyl ring conformation in the transition state, factors which could well have reversed the natural preference. On the other hand, the present work is free from any possible ambiguities of this kind. Moreover, the spectroscopic and chemical methods used here with stereochemically-labeled precursors give direct information[24] on the reaction selectivity without recourse to theoretical models of the type needed to simulate CIDNP patterns. Thus, there seems no reason to doubt that the least-motion migration of the pseudo-axial substituent will ordinarily be preferred in radical reactions.

We now return to the problem raised in the Introduction as to why the radical cation isomerization of bicyclo[1.1.0]butane to cyclobutene is not observed.[3c] In the light of our present findings, the proper question is the following: why does 1,2-hydrogen transfer[25] from the pseudo-axial position on the methylene bridge occur for the bicyclo[2.1.0]pentane radical cation, but not for the structurally similar bicyclo[1.1.0]butane radical cation[3c] under parallel matrix-isolation conditions? We suggest that the answer lies not in mechanistic diversity but in the much smaller thermodynamic driving force, if any, for the reaction in the latter case. Thus, the experimental enthalpy of isomerization in the gas phase is −22 kcal/mol for the bicyclo[2.1.0]pentane radical cation, whereas the value for the bicyclo[1.1.0]butane radical cation is +2 kcal/mol.[26] Clearly, the much less favorable energetics for the isomerization of the bicyclo[1.1.0]butane radical cation to the highly strained cyclobutene radical cation is likely to translate into a considerably higher barrier for reaction.

There also remains the question of the precise nature of the migrating entity in this radical cation rearrangement; namely, for the case of methyl group transfer, is it a methyl radical or a methide ion? In terms of the previous discussion in which both substitution and elimination are regarded as the interlocking and synchronous component steps of the rearrangement, methyl group and methide ion transfer correspond to radical and nucleophilic substitution mechanisms. Although the present results cannot distinguish between these mechanisms, methide ion transfer would appear to be the more likely because methyl group rearrangements—contrary to hydrogen atom transfers[4a,27]—are not commonly encountered in the chemistry of cyclopentane-1,3-diyl derivatives.[28] This mechanism would also be consistent with the known facility of nucleophilic reagent attack on cyclopropane radical cations.[2g,13]

Finally, it is of interest to inquire as to the reason for the similar rates of hydrogen and methyl migration in this rearrangement,[29] bearing in mind that methyl migrations are generally much faster than hydrogen migrations in carbocation rearrangements. The explanation probably lies in the fact that methyl migration in the rearrangement of **1b**$^{\bullet+}$ leads to the thermodynamically less stable dialkyl olefin cation **3b**$^{\bullet+}$, whereas the hydrogen migration in **1a**$^{\bullet+}$ results in the more stable trialkyl olefin cation **3a**$^{\bullet+}$. Consequently, the expected larger rate of methyl migration (all other things being equal) is compensated here by the greater thermodynamic driving force of the hydrogen migration. These opposing tendencies then appear to cancel each other, resulting in the observation of commensurate rates for the **1a,b**$^{\bullet+}$ rearrangements.

**Conclusion.** For the first time, stereoselective rearrangements of the radical cations derived from bicyclopentanes **1a,b** and azoalkanes **2a,b** have been demonstrated by PET and ESR studies. Experimental evidence is provided that the matrix-isolated bicyclopentane radical cations **1a,b**$^{\bullet+}$ possess puckered conformations in which the pseudo-axial substituent originally in the syn position on the methylene bridge migrates stereoselectively to a bridgehead position so as to form the corresponding methylcyclopentene radical cations **3a,b**$^{\bullet+}$.

**Acknowledgment**. We thank Professor J. P. Dinnocenzo for his comments on an earlier version of this paper. The research at the University of Tennessee was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy (Grant No. DE-FG05-88ER13852). The authors at Würzburg thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Stifterverband for generous financial support of this work. H.W. is grateful to the University of Würzburg for a doctoral fellowship (1989–1991). We express appreciation for spectral services to Dr. G. Lange (MS) and Dr. D. Scheutzow (NMR).

**Registry No. 1a**, 76898-65-2; **1a**$^{\bullet+}$, 139240-46-3; **1b**, 50338-79-9; **1b**$^{\bullet+}$, 139240-47-4; **2a**, 71805-59-9; **2b**, 71805-62-4; **3a**, 693-89-0; **3a**$^{\bullet+}$, 70104-64-2; **3b**, 1120-62-3; **3b**$^{\bullet+}$, 70144-49-9; TPT, 448-61-3; DCA, 1217-45-4.

---

(24) The possibility of using labeling methods to detect the steric preference for hydrogen atom migration from the cyclohexyl radical was broached,[23] but we are unaware of any actual studies.

(25) In addition to providing direct evidence for the 1,2-shift of the pseudo-axial substituent on the methylene bridge of **1a,b**$^{\bullet+}$, the present work rules out a 1,3-hydrogen migration since this would generate **3b**$^{\bullet+}$, irrespective of the starting **1a,b**$^{\bullet+}$ stereoisomer. Also, a 1,2-hydrogen migration from either of the two pseudo-axial hydrogens on the dimethylene bridge of **1b**$^{\bullet+}$ would furnish the 4-methylcyclopentane-1,3-diyl radical cation whose ESR splitting pattern should closely resemble those of the parent cyclopentane-1,3-diyl radical cation[3c] and **1a**$^{\bullet+}$ (Figure 1a and Table II). However, no such transformation from **1b**$^{\bullet+}$ was observed in competition with the rearrangement to **3b**$^{\bullet+}$.

(26) *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1, pp 147, 192. The listed heats of formation for the bicyclo[1.1.0]butane and cyclobutene radical cations are 253 and 255 kcal/mol, respectively, while the corresponding values for the bicyclo[2.1.0]pentane and cyclopentene radical cations are ca. 238 and 216 kcal/mol.

(27) Baldwin, J. E.; Andrews, G. D. *J. Org. Chem.* **1973**, *38*, 1063–1064.

(28) (a) Roth, W. R.; Klörner, F.-G.; Grimme, W.; Köser, H. G.; Busch, R.; Muskulus, B.; Breuckmann, R.; Scholz, B. P.; Lennarts, H.-W. *Chem. Ber.* **1983**, *116*, 2717–2737. (b) Zang, G., Ph.D. Thesis, University of Würzburg, Würzburg, Germany, 1990.

(29) We thank a reviewer for raising this point.