Articles

Photosensitized Electron Transfer from Azoalkanes: Generation, Fragmentation, and Rearrangement of Radical Cations Structurally Related to Dicyclopentadiene

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Received April 27, 1993•

The azoalkanes **1a–c** extrude nitrogen upon photosensitized electron transfer (PET) to yield 1,3-radical cation intermediates $\mathbf{2}^{\bullet+}$, which undergo interesting transformations. Electron back transfer (BET) affords the unrearranged housanes **2**, but significant rearrangement to dicyclopentadiene derivatives **3** occurs prior to BET. In some cases, fragmentation to cyclopentadienes **4** is observed, a cycloreversion that occurs at the 1,3-radial cation stage rather than through the corresponding 1,3-biradical intermediates. The diphenyl-substituted azoalkane **1a** affords high yields of the symmetric cyclopentadiene **4a**, while the alkyl-substituted **1b** produces only small amounts of a rearranged cyclopentadiene **4'b**. The housanes **2a,b** are also oxidized by PET, but are more reluctant to rearrange. Strong electron acceptors such as triphenylpyrylium tetrafluoroborate (TPT) or cosensitization with biphenyl (Ph_2) must be utilized to induce rearrangement to **3a,b** and fragmentation to **4** and **4'**.

Introduction

Previously it was reported that ground state azoalkanes can serve as electron donors and thereby be converted to radical cations.[1–7] A method frequently used to induce electron transfer is photosensitization (PET),[8] because a set of well-characterized sensitizers is available. Selective excitation and appropriate matching of the energies of the excited states allow exothermic electron transfer, by using azoalkanes as donors.[4–7] While some azoalkane radical cations have been observed by ESR spectroscopy directly under matrix isolation, e.g. 2,3-diazabicyclo[2.2.2]-oct-2-ene,[1] and in solution, e.g. *trans-N,N'*-di(1-norbornyl)-diazene,[2] other azoalkanes experience rapid loss of nitrogen upon one-electron oxidation.[3–7] Well-known for their rapid N_2 extrusion upon direct and triplet-sensitized photolysis,[9] 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and its derivatives denitrogenate effectively upon electron transfer to yield carbon-centered radical cations.[5–7] Large amounts of products with rearranged carbon skeletons and products which arise from nucleophilic cyclization were found.[10]

A number of intriguing mechanistic features were revealed. Rearrangement takes place not only at the 1,3 radical cation stage, but also at the diazenyl radical cation stage.[6] One class of DBH derivatives, namely the azoalkanes **1a–c**, looked promising for the study of fragmentation reactions (cycloreversion) of radical cations. The PET reactions of azoalkanes **1** and the corresponding housane derivatives **2**,[11] which possess a strained cyclopropane moiety and are prone to oxidation,[12] would provide access to 1,3- and 1,2-radical cations (Scheme I).

Radical cations derived from dicyclopentadienes have attracted considerable interest.[13,14] For example, the term "nonvertical" radical cations was coined to describe the intriguing structure of those intermediates, which are distinctly different from the diamagnetic starting material. Interconversions into other isomers and cycloreversion were studied to show that such reactions are sensitive to the conformation and the substituents of the starting

• Abstract published in *Advance ACS Abstracts*, August 15, 1993.

(1) (a) Williams, F.; Guo, Q.-X.; Petillo, P. A.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 7887. (b) Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1498.

(2) (a) Blackstock, S. C.; Mendicino, M. E. *J. Am. Chem. Soc.* **1991**, *113*, 713. (b) Gescheidt, G.; Lamprecht, A.; Rüchardt, C.; Schmittel, M. *Helv. Chim. Acta* **1992**, *75*, 351.

(3) (a) Engel, P. S.; Kitamura, A.; Keys, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 4964. (b) Engel, P. S.; Kitamura, A.; Keys, D. E. *J. Org. Chem.* **1987**, *52*, 5015. (c) Engel, P. S.; Lee, W. K.; Marschke, G. E.; Shine, H. J. *J. Org. Chem.* **1987**, *52*, 2813. (d) Engel, P. S., Robertson, D. M., Scholz, J. N., Shine, H. J. *J. Org. Chem.* **1992**, *57*, 6178. (e) Adam, W.; Grabowski, S.; Miranda, M. A.; Rübenacker, M. *J. Chem. Soc. Chem. Commun.* **1988**, 142.

(4) (a) Kitamura, A.; Karatsu, T.; Hotta, H. *J. Chem. Soc. Chem. Commun.* **1991**, 1451. (b) Goodman, J. L.; Zona, T. A. *Tetrahedron Lett.* **1992**, 6093–6096.

(5) (a) Adam, W.; Dörr, M. *J. Am. Chem. Soc.* **1987**, *109*, 1570. (b) Adam, W.; Miranda, M. A. *J. Org. Chem.* **1987**, *52*, 5498.

(6) Adam, W.; Chen, G.-F.; Walter, H.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007.

(7) Adam, W.; Denninger, U.; Finzel, R.; Kita, F.; Platsch, H.; Walter, H.; Zang, G. *J. Am. Chem. Soc.* **1992**, *114*, 5027.

(8) (a) Turro, N. J.; Kavarnos, G. J. *Chem. Rev.* **1986**, *86*, 401. (b) Fox, M. A.; Chanon, M., Eds. *Photoinduced Electron Transfer, Part C*; Elsevier: Amsterdam, 1988. (c) Kavarnos, G. J. *Top. Curr. Chem.* **1990**, *156*, 20.

(9) (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (b) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165.

(10) Sendelbach, J. Ph.D. Dissertation, University of Würzburg, 1993.

(11) (a) Beck, K.; Höhn, A.; Hünig, S.; Prokschy, F. *Chem. Ber.* **1984**, *117*, 517. (b) Beck, K.; Hünig, S. *Chem. Ber.* **1987**, *120*, 477. (c) Hünig, S.; Kraft, P. *J. Prakt. Chem.* **1990**, *332*, 133.

(12) (a) Gassman, P. G. In *Photoinduced Electron Transfer, Part C*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 70. (b) Boche, G.; Walborsky, H. M. In *Updates from the Chemistry of Functional Groups: Cyclopropane Derived Reactive Intermediates*; Patai, S., Rappoport, Z., Eds.; J. Wiley: Chichester, 1990; p 207.

(13) (a) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *Tetrahedron* **1986**, *42*, 6157. (b) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343. (c) Roth, H. D. *Pure Appl. Chem.* **1988**, *60*, 933.

(14) Shida, T.; Momose, T.; Ono, N. *J. Phys. Chem.* **1985**, *89*, 815.

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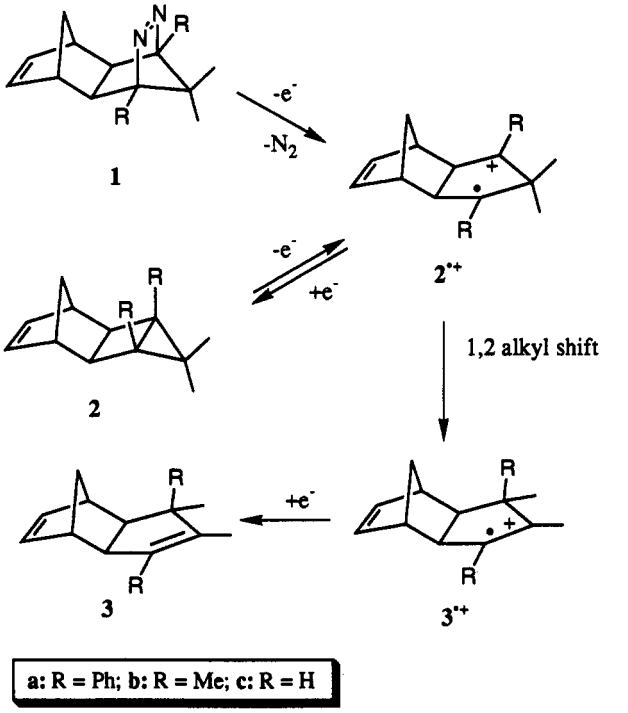
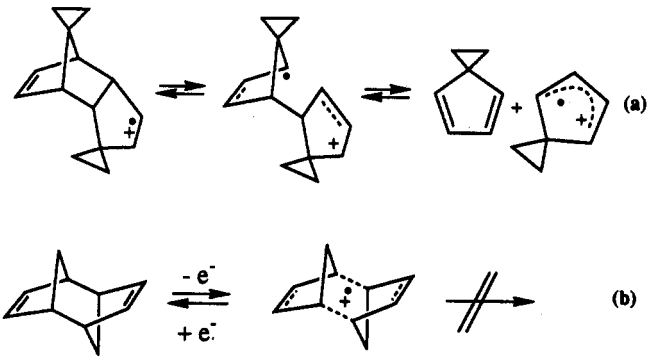
Scheme I



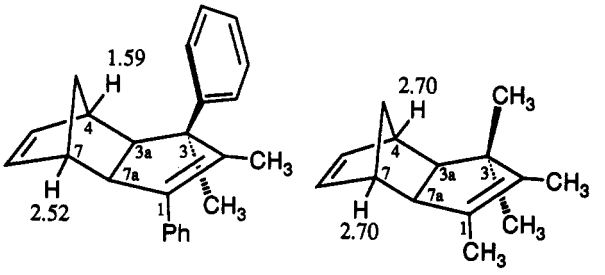
Scheme II



material.[13] While *endo/exo*-dicyclopentadiene does not fragment after electron transfer in spite of the fact that its radical cation possesses one cleaved C–C bond,[13,14] dispiroheptadiene suffers rapid cycloreversion (Scheme IIa).[15] In contrast, the *anti*[4 + 4] dimer (Scheme IIb) undergoes no C–C bond cleavage at all.[13a] Therefore, the chemical behavior of the intermediates outlined in Scheme I cannot be predicted *a priori*, and detailed product studies are essential to gain mechanistic insight. We describe the results of this investigation herein.

Results

In PET reactions of azoalkane **1a** as an electron donor, rapid denitrogenation occurred to yield the housane derivative **2a**, rearranged product **3a**, and, in some cases, cyclopentadiene and its derivative **4a** (Table I, entries 1–3). Due to the high volatility of cyclopentadiene, its propensity to dimerize, and its difficult distinction from the solvent by GC, only the cyclopentadiene derivative **4a** was analyzed in order to quantify the extent of cycloreversion. With 9,10-dicyanoanthracene (DCA)[16] as PET sensitizer, no cycloreversion was observed, but minor amounts of rearrangement product **3a** were observed (Table I, entry 1). GC, HPLC, and NMR analysis proved that the rearrangement product consisted in all cases (Table I, entries 1–3, 9, 10) of only one diastereomer, **3a**. Unfortunately, its configuration could not be established by nuclear Overhauser experiments due to the overlap of relevant NMR signals, but the pronounced high-field shift of the 4-H bridgehead proton (cf. **3b**) suggests that **3a** is of the *R** configuration. Molecular models show that in this configuration the 4-H bridgehead proton is effectively



3a **3b**

shielded by the phenyl group, which is rotationally fixed by interaction with the methano bridge.

When electronically excited 2,4,6-triphenylpyrylium tetrafluoroborate (TPT)[16] was utilized as an electron acceptor, a greater amount of rearrangement product **3a** was observed and, more importantly, fragmentation yielded the symmetric cyclopentadiene **4a** (Table I, entry 2). As observed earlier,[10] the addition of biphenyl (Ph_2) as cosensitizer[17] to the PET reactions of these azoalkanes caused important changes in the relative product yields. While DCA alone gave no fragmentation (Table I, entry 1), with Ph_2 as cosensitizer (Table I, entry 3), fragmentation was the major pathway and significant rearrangement occurred. The mass balances were close to 100% in all runs, making insignificant any other reaction paths such as oligomerization or coupling with the reduced sensitizer, as was observed for sterically less hindered azoalkanes.[6,7]

Hydrocarbon **2a** is prone to photosensitized oxidation, as was confirmed by the PET reaction with TPT (Table I, entry 9); however, with DCA as electron acceptor, even after prolonged irradiation only very low conversion was achieved and no products were detected by GC or HPLC analysis (Table I, entry 8). Again, addition of the cosensitizer Ph_2 changed the reaction drastically. Rapid conversion to rearranged product **3a** and cycloreversion to **4a** was the primary reaction course.

Under the same PET conditions as above, azoalkane **1b** experienced rapid nitrogen loss to yield the corresponding tetracycle **2b**, the dicyclopentadiene **3b**, and, in some cases, small amounts of cyclopentadiene **4'b** (Table I, entries 4–6). Interestingly, in this case the fragmentation product is a rearranged cyclopentadiene and none of the symmetrical product **4b** was detected, this having been unambiguously established by GC coinjection with au-

(15) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 6098.

(16) The ground state reduction potential E^{red} and singlet excitation energy E_S are −0.89 V/SCE and 2.86 eV for DCA and −0.29V/SCE and 2.82 eV for TPT.[8a]

(17) (a) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. (b) Julliard, M. In *Photoinduced Electron Transfer, Part B*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 216.

Table I. Product Studies of the Photosensitized Electron Transfer Reaction[a] of Azoalkanes 1a–c and Tetracyclodecenes 2a,b in Acetonitrile

						product distribution (%)[b,e]			
entry	substrate	sensitizer	time (min)	conv[b,c] (%)	mb[b–d] (%)	2	3	4	4′
1	**1a**	DCA	3	25	100	86	14	–	–
2	**1a**	TPT	3	38	98	67	21	12	–
3	**1a**	DCA/Ph_2	3	42	99	10	42	47	–
4	**1b**	DCA	7	15	90	70	30	–	–
5	**1b**	TPT	7	28	75	24	73	–	3
6	**1b**	DCA/Ph_2	7	36	85	9	89	–	2
7	**1c**	DCA	10	20	12	~50	*f*	–	–
8	**2a**	DCA	40	15	0	*h*	–	–	–
9	**2a**	TPT[g]	3	47	88	*h*	42	58	–
10	**2a**	DCA/Ph_2	3	70	85	*h*	27	73	–
11	**2b**	DCA	40	20	0	*h*	–	–	–
12	**2b**	TPT[g]	4	40	63	*h*	94	–	6
13	**2b**	DCA/Ph_2	4	55	80	*h*	92	–	8
14	**3b**	DCA/Ph_2	120	5	0	–	*h*	–	–

[a] See Experimental Section for reaction conditions. [b] Determined by quantitative capillary GC, except for **1a** (HPLC). [c] Error 5–10% of stated value. [d] The amount of unreacted starting material is *not* included in the mass balance (mb). [e] Relative yields normalized to 100%, error ca. 2%. [f] The remainder is made up of several volatile products, which were not characterized. [g] 10 mol% of 2,6-di-*tert*-butylpyridine were added as base. [h] Starting material.

thentic material. Under PET conditions, no isomerization of cyclopentadiene **4b** to **4′b** was observed.

The strained hydrocarbon **2b** with TPT and DCA/Ph_2 also yielded some unsymmetrical cyclopentadiene **4′b** and, as the major component, the rearrangement product **3b** (Table I, entries 12, 13). As for **2a**, with DCA alone no reaction was observed (Table I, entry 11). In a control experiment, dicyclopentadiene derivative **3b** gave no cycloreversion to **4′b** with TPT or DCA/Ph_2 as PET sensitizer. No significant conversion was observed even after prolonged irradiation (120 min).

Azoalkane **1c** decomposed upon DCA-sensitized photolysis to yield housane **2c** and as many as five volatile products of similar retention time as **2c** (Table I, entry 7). No cyclopentadiene or its dimethyl derivatives were detected. Due to the very low mass balance and the low yield of separable material, the new products were not isolated and characterized except for housane **2c**. Direct[11] and benzophenone-sensitized photolysis of the azoalkanes **1b,c** gave no fragmentation and, for **1a**, only insignificant amounts (<1%). All three azoalkanes **1a–c** yielded, after denitrogenation through PET, direct or triplet-sensitized photolysis and thermolysis, the isomers **2a–c** exclusively with retention. This is due to steric repulsion of the *gem*-dimethyl group and the methano bridge in the intermediates $2^{\bullet\bullet}$ and $2^{\bullet+}$.

Mechanistic Discussion

To explain the above PET results, we propose the mechanism displayed in Scheme III. The significant amount of cyclopentadiene **4a**, which was formed on PET photolysis of azoalkane **1a** (Table I, entries 2–3) or the housane derivative **2a** (Table I, entries 9–10), constitutes unambiguous evidence that the corresponding 1,3-radical cation $\mathbf{2a}^{\bullet+}$ undergoes not only rearrangement but also cycloreversion. Since no 1,5-dimethyl-2,5-diphenylcyclopentadiene (**4′a**) was found, cycloreversion does not take place at the stage of the rearranged radical cation $\mathbf{3a}^{\bullet+}$, i.e. that of the dicyclopentadiene.

PET reactions of azoalkane **1a** and housane **2a** with TPT (Table I, entries 2,9) and with DCA in the presence of cosensitizer Ph_2 (Table I, entries 3,10) show that fragmentation can compete well with rearrangement, but sensitization with DCA alone (Table I, entries 1, 8) yields no fragmentation products. Housane **2a** gives no significant conversion at all (Table I, entry 8), in spite of the fact that an exergonic electron transfer is expected with DCA as acceptor, as the run in the presence of the cosensitizer Ph_2 (Table I, entry 10) implies.

Presumably, the addition of the cosensitizer Ph_2 affects the degree of solvation of the radical ion pairs and, thus, the rate of electron back transfer (k_{BET})[20] but not the exergonicity of the electron transfer itself.[17a] Furthermore, since housane derivatives such as 2-methylbicyclo[2.1.0]-pentane[18] rearrange upon DCA-sensitized photolysis,[6] we postulate that hydrocarbon **2a** is, indeed, oxidized to radical cation $\mathbf{2a}^{\bullet+}$, but that the latter is prevented from rearranging by stabilization due to benzylic conjugation. BET, which is most rapid for DCA,[21] then yields starting material **2a** again. By retarding BET via addition of the cosensitizer Ph_2 or the use of the cationic sensitizer TPT, which affords a radical cation/neutral radical pair with lower coulombic interactions,[6] rearrangement and fragmentation can compete with the formation of housane **2a**.

The minor amount of rearranged product **3a** that is formed in the PET reaction of azoalkane **1a** on DCA photosensitization (Table I, entry 1) could arise from rearrangement at the stage of a diazenyl radical cation $\mathbf{1a}^{\bullet+}$, in which nitrogen expulsion is facilitated by backside attack of the pseudoaxial methyl group[6] (Scheme III). Such a reaction pathway is not available for the cycloreversion and, therefore, not observed in the short-lived $\mathbf{2}^{\bullet+}/DCA^{\bullet-}$ radical ion pair.

The same holds true also for the tetramethyl derivatives **1b** and **2b**. Fragmentation of the radical cations of these substrates, which took place to a small extent with the sensitizers TPT and DCA/Ph_2 (Table I, entries 5, 6 and 12, 13), did not occur at all with DCA as sole sensitizer (Table I, entries 4,11). As was the case for derivative **2a**, housane **2b** yielded no volatile products. It has been shown before that 1,4-dialkyl substitution in bicyclo[2.1.0]-

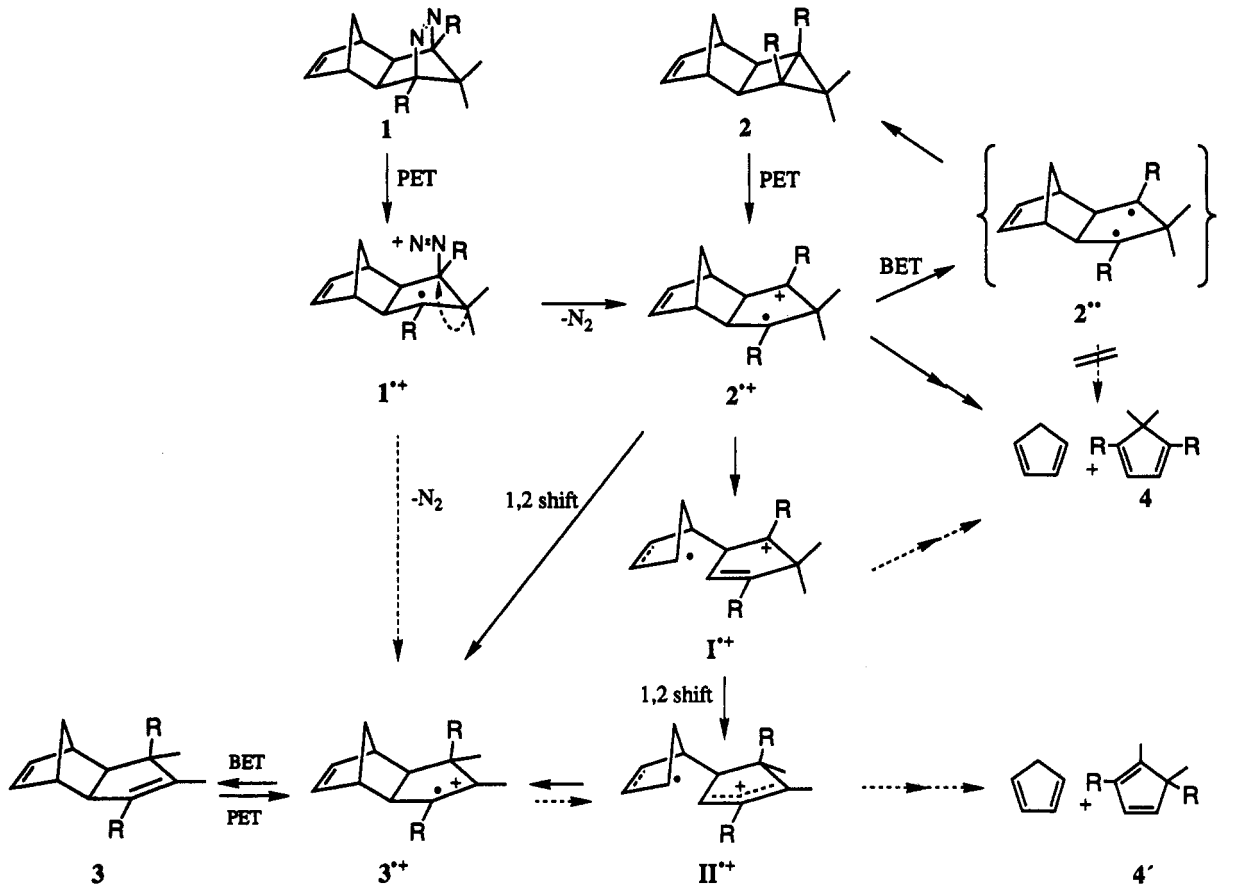
(18) For bicyclo[1.1.0]butane it was found[19] that the oxidation potential decreases with an increasing number of alkyl substituents; this trend should also hold true for housane derivatives.

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

(20) (a) Suppan, P. *Chimia* **1988**, *42*, 320. (b) Mattay, J.; Vondenhof, M. *Top. Curr. Chem.* **1991**, *159*, 219.

(21) In the *normal* Marcus region, k_{BET} increases with the exergonicity of BET ($\Delta G_{BET} < 0$), which can be approximated by $\Delta G_{BET} = E^{red}(\text{acceptor}) - E^{ox}(\text{donor})$[8,17a]. Thus, the lower the reduction potential of the sensitizer, the faster is BET in the radical ion pair.

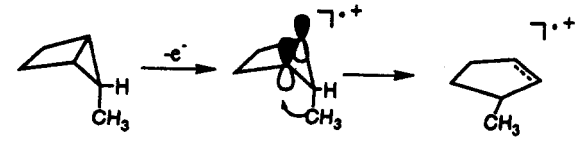
Scheme III



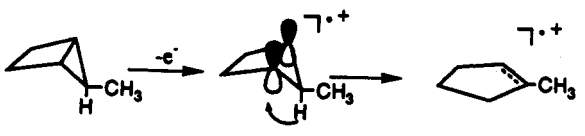
a: R = Ph; b: R = Me; c: R = H

pentane derivatives exerts a stabilizing effect on the corresponding 1,3-radical cation and that the extent of rearrangement is less.[7,10]

It is noteworthy to mention that with azoalkane **1a** and housane **2a** as starting materials, only one diastereomer of the rearrangement product **3a** is formed. This can be accounted for either by steric hindrance, which may evolve from migration of a methyl group *syn* to the methano bridge or by the migratory preference of a pseudoaxial methyl group. The latter possibility was thoroughly investigated in the case of *anti,syn*-7-methyl-2,3-diazabicyclo[2.2.1]hept-2-ene and the corresponding housane. Due to the puckered conformation of the latter radical cations, which was established by ESR studies, favorable orbital overlap facilitates the migration of the pseudoaxial substituent (eq 1).[6] It is expected that due to the extensive



(1a)



(1b)

conjugation which arises during the cleavage of intermediate $2a^{\bullet+}$, cycloreversion is energetically more favorable than in the case of $2b^{\bullet+}$. It is intriguing however that $2b^{\bullet+}$ gives rise to significant amounts of unsymmetrical cyclopentadiene **4'b** (Table I, entries 12, 13). The most obvious pathway, namely cycloreversion after rearrangement of the dicyclopentadiene radical cation $3b^{\bullet+}$, is excluded on the grounds that dicyclopentadiene **3b** did not give fragmentation products under PET conditions (Table I, entry 14), although tetraalkyl-substituted double bonds possess a low-enough oxidation potential to be oxidized by TPT* or DCA*.[22] No isomerization of cyclopentadiene **4b** to **4'b** was observed.

We have no experimental evidence for the ring-opened, nonvertical intermediate $II^{\bullet+}$ (Scheme III), but in view of the results obtained for other dicyclopentadiene derivatives,[13,14] it is feasible that the radical cation $3b^{\bullet+}$ undergoes ring-opening to the nonvertical intermediate $IIb^{\bullet+}$. It is difficult to rationalize the formation of the cycloreversion product **4'b** without involving intermediates $3b^{\bullet+}$ or $IIb^{\bullet+}$. Presumably, during the 1,2-methyl shift in intermediate $2b^{\bullet+}$ or $Ib^{\bullet+}$ that leads to rearranged product **3b**, a transition state is traversed from which minor amounts of $2b^{\bullet+}$ or $Ib^{\bullet+}$ are diverted to the cycloreversion product **4'b**.

It is of mechanistic interest to assess whether the radical cations $2^{\bullet+}$ undergo C–C bond cleavage to afford nonvertical intermediates $I^{\bullet+}$ (Scheme III) as observed for radical cations of dicyclopentadienes.[13,14] The driving force

(22) 1-Methylcyclohexene, with a less-substituted double bond than in **3b**, has an oxidation potential E^{ox} of 1.77 V/SCE.[23]

(23) Gassman, P. G.; Bottorff, K. J. *Tetrahedron Lett.* **1987**, 5449.

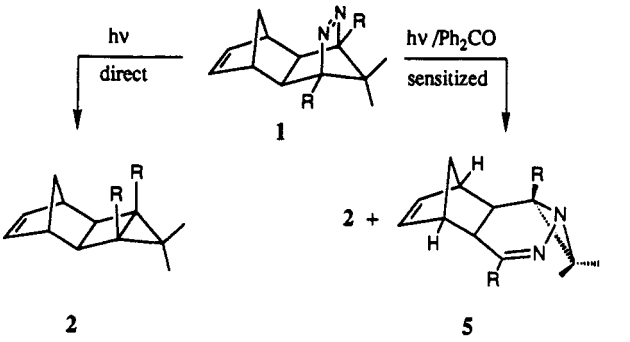
for the bond cleavage in dicyclopentadiene radical cations $3^{\bullet+}$ is the generation of intermediate $II^{\bullet+}$, in which the radical as well as the cation sites are stabilized by allylic conjugation.[13] Similar energy advantages are at play for the 1,3-radical cation $2a^{\bullet+}$. One-bond cleavage would yield radical cation $Ia^{\bullet+}$, in which the radical site is stabilized by allylic and the cation center by benzylic conjugation ($Ia^{\bullet+}$, Scheme III).[24] For an unpaired spin, stabilization by allylic conjugation is favored by ca. 4 kcal/mol over benzylic conjugation.[25]

Similarly, for radical cation $2b^{\bullet+}$ which has tertiary radical and cation sites, the transformation to the allylic radical/tertiary cation $Ib^{\bullet+}$ is also energetically favorable.[26] Intermediate $I^{\bullet+}$ may subsequently rearrange by 1,2-methyl shift to the even more stable open radical cation $II^{\bullet+}$. Recyclization of the latter would give $3^{\bullet+}$ and, on BET, dicyclopentadiene **3**. The pathway $2^{\bullet+} \rightarrow I^{\bullet+} \rightarrow II^{\bullet+} \rightarrow 3^{\bullet+}$ constitutes a stepwise rearrangement process (Scheme III). Alternatively, further fragmentation of $I^{\bullet+}$ would result in cyclopentadiene **4** and that of $II^{\bullet+}$ would result in the rearranged cyclopentadiene **4'**, which represents stepwise cycloreversion.

In contrast to azoalkanes **1a,b**, which undergo clean PET reactions with high mass balances, azoalkane **1c** gives only low yields of products, from which only hydrocarbon **2c** was identified. No cycloreversion products were detected. The sterically less hindered, unstabilized radical cations are clearly more prone to oligomerization reactions, which yield products of higher molecular weight and are not accounted for by our gas chromatographic analysis. This is in keeping with the low mass balances reported for 7,7-dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene and the corresponding housane.[7,27]

It is important to note that the biradicals $2^{\bullet\bullet}$, which result from BET to the radical cations $2^{\bullet+}$ (Scheme III), are not the precursors of the cycloreversion products **4** and **4'** nor of the rearrangement products **3**. This was established by direct photolysis of the azoalkanes **1**, which gave exclusively the housanes **2** by cyclization,[11] and upon triplet sensitization, the heterocycles **5** also (eq 2).[28] For the singlet biradicals, the lowest energy path is cyclization, so they are too short-lived to undergo fragmentation. On the other hand, cycloreversion of the longer-lived triplet biradicals would lead to excited triplet cyclopentadienes. Such limitations are not imposed on the radical cations $2^{\bullet+}$.

In conclusion, it is noted that the PET reactions of azoalkanes **1a,b** and the corresponding housane derivatives **2a,b** offer an entry to the interesting chemistry of the 1,3-radical cations $2a,b^{\bullet+}$, which behave quite differently



(2)

than the related 1,2-radical cations $3a,b^{\bullet+}$. While the latter undergo, at most, cleavage of one C–C bond to yield a nonvertical intermediate $II^{\bullet+}$, the 1,3-radical cation $2a^{\bullet+}$ fragments to cyclopentadiene **4a**. Derivative $2b^{\bullet+}$ is less prone to cycloreversion, but when it occurs, it yields the rearranged cyclopentadiene **4'b**, which is not accessible through the corresponding dicyclopentadiene radical cation $3b^{\bullet+}$. This further illustrates the intriguing chemical fate of radical cations derived from dicyclopentadienes and their isomers.

Experimental Section

General Aspects. Gas chromatographic analyses were conducted on capillary GC instruments, equipped with a flame ionization detector (FID). OV-1 and OV-1701 30-m fused silica columns with an internal diameter of 0.25 mm and a film thickness of 0.25 μm were used. IR data are given in cm^{-1}. The PET reactions were carried out by irradiating with a 150-W high-pressure mercury lamp and a Schott GG 400 glass filter to block all light below λ = 400 nm.[29]

Solvents and commercially available chemicals were purified by standard procedures. Column chromatography was carried out on silica gel (0.032–0.063 μm). Conversions, relative yields, and mass balances were determined by GC and HPLC (for **1a**) and corrected for the response factors of the starting material and the products. As a quantitative measure, the integrated peak areas of the chromatograms were used. The mass balances (mb) were determined according to eq 3, where A_t = peak area

$$\%\,\mathrm{mb} = [\sum A_t(\mathrm{P})/A_t(\mathrm{IS})]/[A_o(\mathrm{S})/A_o(\mathrm{IS}) - A_t(\mathrm{S})/A_t(\mathrm{IS})] \times 100 \quad (3)$$

after reaction time t, A_o = peak area before the reaction, S = substrate, IS = internal standard, and P = product. Thus, the amount of unreacted starting material is *not* included in the mass balance.

Preparation of the Starting Materials. Azoalkanes **1a-c**,[11] the housanes **2a**,[11b] **2b**,[11c] and 5,5-dimethyl-1,4-diphenylcyclopenta-1,3-diene (**4a**)[30,31] were prepared according to the literature procedures. 1,4,5,5-Tetramethylcyclopenta-1,3-diene (**4b**)[32] and 1,2,5,5-tetramethylcyclopenta-1,3-diene (**4'b**)[33] were obtained as a 9:1 mixture (NMR) when distilling the housane **2b** at 100 °C/0.1 Torr through a 30-cm quartz tube heated to 400 °C. Capillary GC (for conditions cf. PET reactions of **1b**, **2b**) revealed the same ratio of the two isomers as on NMR analysis, which allowed an assignment of the peaks in the gas chromatogram.

(1*S,2*S**,3*R**)-4,4-Dimethyltetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-ene (2c).** By volatalizing 110 mg (0.585 mmol) of the azoalkane

(24) (a) The question was raised by a reviewer whether the energy gain by allylic conjugation and release of ring strain in the open structure $I^{\bullet+}$ compensates for the σ to π bond change. Similar considerations should apply to the ring opening of the dicyclopentadiene radical cation, which was observed directly by CIDNP.[13] In the latter case the significantly more stable 1,2-radical cation[24b] is transformed into a nonvertical radical cation by C–C σ bond cleavage and consequently such a fragmentation would be expected for a 1,3-radical cation. (b) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405. Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 3283.

(25) Baldwin, J. E. *J. Chem. Soc. Chem. Commun.* **1988**, 31.

(26) March, J. *Advanced Organic Chemistry*, 4th ed.; J. Wiley: Chichester, 1992; pp 171.

(27) Walter, H. Ph.D. Dissertation, University of Würzburg, 1992.

(28) (a) Adam, W.; DeLucchi, O. *J. Am. Chem. Soc.* **1980**, *102*, 2109. (b) Adam, W.; Hill, K. *J. Am. Chem. Soc.* **1985**, *107*, 3686. (c) Adam, W.; Dörr, M.; Hill, K.; Peters, E. M.; Peters, K.; von Schnering, H. G. *J. Org. Chem.* **1985**, *50*, 587. (d) Padwa, A.; Kumagai, T.; Tohidi, M. *J. Org. Chem.* **1983**, *48*, 1834. (e) Dougherty, D. A.; Chang, M. H. *J. Am. Chem. Soc.* **1982**, *104*, 2333.

(29) The azoalkanes **1** have an absorption band at *ca.* 330–370 nm (n→π* excitation) with maxima at 355–365 nm.

(30) Adam, W.; Reinhard, G.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1990**, *112*, 4570.

(31) Paquette, L. A.; Leichter, L. M. *J. Org. Chem.* **1974**, *39*, 461.

(32) Descotes, G.; Fournier, M.; Mugnier, R. *Bull. Soc. Chim. Fr.* **1968**, 382.

(33) Bentley, T. W.; Irrgang, B.; Mayr, H., von Ragué Schleyer, P. *J. Org. Chem.* **1988**, *53*, 3492.

1c at 80 °C/0.1 Torr into a 30-cm quartz tube heated at 350 °C, the colorless oil of **2c** was collected (80%). An analytical sample was obtained by preparative GC (1.5-m glass column packed with 10% SE-30 on Volaspher A2; N_2 flow of 1.8 bar; operated isothermally at 120 °C at injector and detector temperatures of 150 °C and 160 °C): IR (CCl_4) 3050, 2995, 2950, 2905, 2860, 1530, 1455, 1445, 1365, 1330; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (s, 3H), 1.06 (br s, 2H), 1.15 (s, 3H), 1.23 (d, J = 8.4 Hz, 1H), 1.48 (br s, 2H), 2.23 (d, J = 8.4 Hz, 1H), 2.63 s, 2H), 6.02 (ps t, J = 1.7 Hz, 2H); ^{13}H NMR (50 MHz, $CDCl_3$) δ 14.8 (q), 24.9 (2 × d), 30.9 (q), 39.6 (2 × d), 41.8 (t), 43.8 (2 × d), 51.2 (s), 136.0 (2 × d). Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.58; H, 10.36.

General Procedure for PET Reactions. All photolyses were carried out on 5-mL samples in a closed system, which was provided with a gas inlet, a sampling inlet, and a water-cooled finger. The acetonitrile solutions were ca. 0.015 M in substrate and contained *n*-dodecane as internal GC standard. These stock solutions were either saturated with DCA (ca. 10^{-5} M) or 10 mol% TPT was added and then purged with argon gas for 15 min prior to photolysis. The cosensitizer biphenyl (Ph_2) was used in 10 molar excess (0.15 M). The progress of the photolyses was monitored at appropriate intervals by capillary GC and HPLC (for **1a**).

PET Reactions with 1a, 2a. The capillary GC analyses were conducted on a 30-m, OV-1701 column operated at 50 °C for 5 min, raised at 10 °C/min to 200 °C, and held there for 30 min with a He flow of 0.8 bar at injector and detector temperatures of 210 °C and 220 °C; t_R (**2a**) = 28.4 min, t_R (**3a**) = 32.2 min, t_R (**4a**) = 19.1 min. The HPLC analyses were performed on a C-18 reversed-phase column with methanol/water (8/2) as eluent at a flow of 0.8 mL/min and UV detection at 215 nm; t_R (**1a**) = 6.3 min, t_R (**2a**) = 27.4 min, t_R (**3a**) = 29.5 min, t_R (**4a**) = 9.5 min. For the characterization of the unknown dicyclopentadiene derivative **3a**, a preparative run was conducted, in which a sample of 200 mg of the azoalkane **1a** (0.588 mmol) in 30 mL of acetonitrile was irradiated ($\lambda > 400$ nm) for 3–4 h in the presence of DCA (30 mg, 0.114 mmol). The reaction mixture was concentrated and separated through preparative GC on a 1.5-m glass column, which was packed with 1% SE-30 on Volaspher A2 and heated from 160 °C to 200 °C at 4 °C/min at a N_2 flow of 1.9 bar with injector and detector temperatures of 210 °C and 230 °C.

(3aα,3α,4β,7β,7aα)-1,3-Diphenyl-2,3-dimethyl-3a,4,7,7a-tetrahydro-4,7-methanoindene (3a): IR (CCl_4) 3042, 3018, 2980, 2924, 2880, 1573, 1470, 1418, 1305, 1290; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (d, J = 6.6 Hz, 1H), 0.92 (dt, J = 6.6, 1.6 Hz, 1H), 1.58 (br s, 1H), 1.59 (s, 3H), 1.73 (d, J = 2.0 Hz, 3H), 2.08 (dd, J = 7.4, 1.6 Hz, 1H), 2.52 (br s, 1H), 3.24 (br d, J = 7.4 Hz, 1H), 6.01 (br s, 2H), 7.18–7.39 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.5 (q), 29.4 (q), 41.4 (t), 42.7 (d), 43.1 (d), 50.3 (s), 55.1 (d), 56.4 (d), 126.4 (d), 126.9 (d), 127.2 (d), 128.1 (d), 128.8 (d), 128.9 (d), 129.0 (d), 129.1 (d), 129.8 (d), 130.6 (d), 138.4 (s), 139.2 (s), 139.6 (d), 139.8 (d), 141.8 (s), 142.9 (s). Anal. Calcd for $C_{24}H_{24}$: C, 92.24; H, 7.76. Found: C, 91.94; H, 7.97.

PET Reactions with 1b, 2b, and 1c. The capillary GC analyses were conducted on a 30-m OV-1 column operated at 40 °C for 5 min, raised at 25 °C/min to 100 °C and then at 5 °C/min to 180 °C, and held there for 15 min. A He flow of 0.8 kp/cm^2 was employed at an injector and detector temperature of 180 °C and 200 °C; t_R (**1b**) = 23.9 min, t_R (**2b**) = 17.7 min, t_R (**3b**) = 18.2 min, t_R (**4'b**) = 7.8, t_R (**4b**) = 7.6 min; t_R (**1c**) = 19.8 min, t_R (**2c**) = 15.2 min. For the characterization of the unknown dicyclopentadiene derivative **3b**, a preparative run was conducted in which 200 mg of the azoalkane **1b** (0.925 mmol) in 30 mL of acetonitrile was irradiated for 4 h in the presence of DCA (60 mg, 0.227 mmol), and the products were separated by preparative GC on a 1.5-m glass column, which was packed with 10% SE-30 on Volaspher A2 and operated at 120 °C at a N_2 flow of 1.7 bar with injector and detector temperature of 170 °C and 190 °C.

(3aα,3α,4β,7β,7aα)-1,2,3,3-Tetramethyl-3a,4,7,7a-tetrahydro-4,7-methanoindene (3b): IR (CCl_4) 3020, 2920, 2882, 2820, 1550, 1522, 1425, 1355, 1307, 1240; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.98 (s, 3H), 1.13 (dt, J = 8.3, 1.6 Hz, 1H), 1.29 (d, J = 8.3 Hz, 1H), 1.48 (m_c, 3H), 1.55 (m_c, 3H), 1.62 (dd, J = 7.2, 1.6 Hz, 1H), 2.51 (br d, J = 7.2 Hz, 1H), 2.70 (br s, 2H), 6.07 (br s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.9 (q), 12.4 (q), 21.2 (q), 31.5 (q), 42.3 (t), 42.4 (d), 43.9 (s), 44.9 (d), 52.7 (d), 55.5 (d), 130.1 (s), 137.2 (d), 138.4 (d), 140.7 (s). Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.09; H, 10.45.

Acknowledgment. We are most grateful for financial support by the Deutsche Forschungs-gemeinschaft and the Fonds der Chemischen Industrie for a doctoral fellowship to J.S.