Rearrangements of Free Radicals, XIII[1]

Thermal and Photochemical Rearrangements of Cyclic C_8H_9 Radicals in Adamantane Matrix

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Received March 14, 1993

Key Words: Free radicals / Rearrangement / ESR spectroscopy / Adamantane matrix / Molecular orbital calculations

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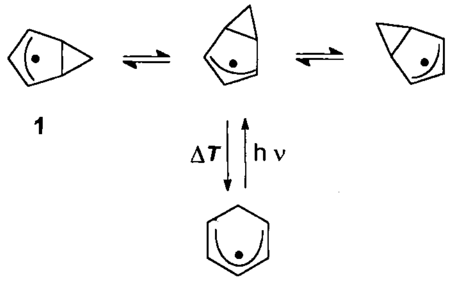
The ESR spectra observed after X-irradiation of bicyclo[5.1.0]octa-2,5-diene (homotropylidene) (**12**) in a [D_{16}]adamantane matrix at 210 K have been identified to be mainly due to the cyclooctatrienyl radical (**8**), formed by thermal ring opening of the initial bicyclo[5.1.0]octa-2,5-diene-4-yl (homotropylidenyl) radical (**7**). The same spectrum has also been observed in X-irradiation of bromocyclooctatriene and a mixture of bromocyclooctatriene and 7-bromobicyclo[4.2.0]cycloocta-2,4-diene in a [D_{16}]adamantane matrix. In all cases, UV irradiation of the matrix caused an irreversible transformation of radical **8** (and probably **7**) into the bicyclo[3.3.0]octa-2,6-diene-4-yl radical (**17**). Tricyclo[3.3.0.0^{2,4}]oct-6-en-7-yl radical (**19**), generated by X-irradiation of tricyclo[3.3.0.0^{2,4}]oct-2-ene (**20**) in adamantane, is thermally stable up to 370 K, but also undergoes a facile rearrangement to the radical **17** on UV irradiation. This process is reasonably explained to occur stepwise via radicals **7** and **8**. The postulated reaction paths and the spectral assignments are supported by semiempirical (AM1, PM3), ab-initio (UHF/3-21G*), and molecular mechanics (MM2ERW) calculations, which are in accord with the finding that **8** is energetically more stable than **7**. The quantum mechanical calculations predict that a degenerate sigmatropic circumambulation of the cyclopropane ring in radical **7** should favorably compete with its ring opening.

During the past two decades the adamantane matrix isolation technique[2] has been established as a useful tool for the ESR investigation of rearrangement reactions of free radicals which, due to competing fast bimolecular decay reactions, cannot be observed in low-viscous fluid solution[1,3,4]. An intriguing example of that kind was the identification of a "walk" rearrangement (circumambulation) of the cyclopropyl group in the (deuterated) bicyclo[3.1.0]hexenyl radical (**1**)[3a,b] from the observation of a statistical distribution of deuterium in the cyclohexadienyl radical (**2**) which is formed by electrocyclic ring opening of **1** at temperatures above 210 K. This ring opening is photochemically reversible[3a,b].



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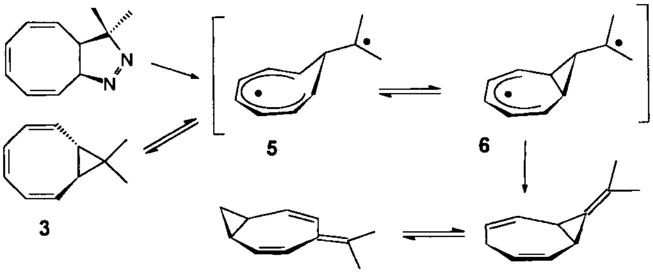
In order to explain the thermally induced reactions of *trans*-bicyclo[6.1.0]nona-2,4,6-triene (**3**) – the degenerate cyclopropane walk rearrangement and the isomerization to homoheptafulvene (**4**) – an electrocyclic ring closure in the intermediate cyclooctatrienyl diradical **5** to the bicyclo[5.2.1]octadienyl (homotropylidenyl) diradical (**6**) was postulated[5].



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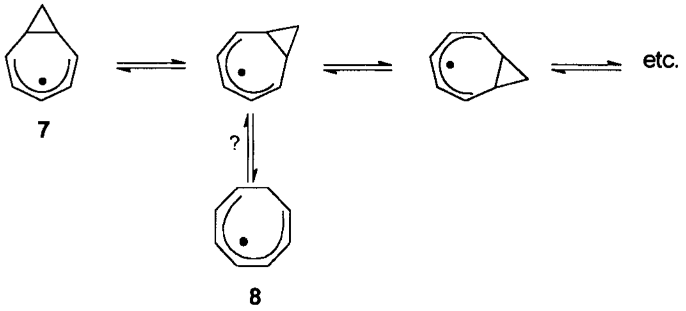
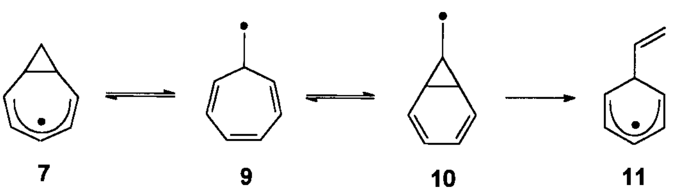
Similarly, in the dimerization of cyclooctatetraene leading to a pentacyclic precursor of bullvalene an electrocyclic ring closure of an intermediate cyclooctatrienyl diradical to a homotropylidenyl diradical was assumed as a key step[6].

According to these observations the electrocyclic ring opening of the bicyclo[5.1.0]octa-2,5-diene-4-yl (homotropylidenyl) radical (**7**) and the ring closure of the cyclooctatrienyl radical (**8**) are expected to proceed exceedingly faster than the corresponding reaction **1**→**2**. Therefore, it would be of interest to learn if radical **7** undergoes a mutual interconversion with radical **8** and if this isomerization is competitive with a potential degenerate cyclopropane walk rearrangement in 7.



The migration of the cyclopropyl group may occur in a concerted (pericyclic) or nonconcerted fashion; for the latter process the cycloheptatrienylmethyl radical (9) should be the intermediate. This would allow a third mode of rearrangement in which via a cycloheptatriene-norcaradiene-like rearrangement of 9 intermediate 10 will be formed, which further would open to the vinylcyclohexadienyl radical (11). Products supporting the intermediate formation of 8 and 11 have been found by Walton et al.[7] in bromination studies of bicyclo[5.1.0]octa-2,5-diene (12) at 350 K. The same authors[7] have also observed by ESR spectroscopy radical 7 and its 8-carboxylated derivative in solution; here, no indication of a rearrangement has been reported for temperatures up to 320 K. Thus, ring opening in these systems must occur at rates $<10^3\ s^{-1}$[8]. However, since the "walk" migration of the cyclopropyl group in 7 is a degenerate process it would only be observable from a specifically substituted homotropylidenyl radical.

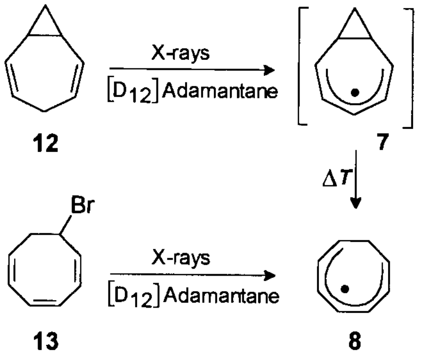


In this paper we report on the ESR investigation of the C_8H_9 radicals produced by X-irradiation of bicyclo-[5.1.0]octa-2,5-diene (12) and some related precursors in adamantane and [D_{16}]adamantane matrices and their thermally and photochemically initiated transformations. The structures and rearrangement reactions of these radicals are also investigated by semiempirical (AM1 and PM3), ab-initio (UHF/3-21G*), and molecular mechanics (MM2ERW) calculations.

Results and Discussion

ESR Experiments

When a [D_{16}]adamantane pellet containing some 12 was exposed to X-irradiation for 30 min at 210 K a multiline ESR spectrum of ca. 60 G overall width was observed in the temperature range from 200 to 315 K (Figure 1a). This spectrum could not be analyzed in terms of the corresponding homotropylidenyl radical (7). Spectral simulations using the hyperfine splittings (hfs) as given in ref.[7] for 7 (Table 1) showed a similar multitude of lines but did not satisfactorily reproduce the experimental spectrum. Furthermore, the overall width of ca. 50 G expected for 7 (by comparison with other cycloheptatrienyl radicals[9], see Table 1, and the results of the semiempirical calculations, see below) is significantly smaller than that of our spectrum. With the aid of an autocorrelation method[10] we were able to evaluate from the digitized experimental spectrum a set of hfs constants (Table 1) which satisfactorily could reproduce the spectrum (Figure 1b). We attribute the spectrum to the cyclooctatrienyl radical (8)[11] on the basis of the results (Table 1) of the semiempirical calculations and the results of the experiments described below. The formation of 8 can easily be explained by a thermally induced ring opening of the initially formed homotropylidenyl radical (7).



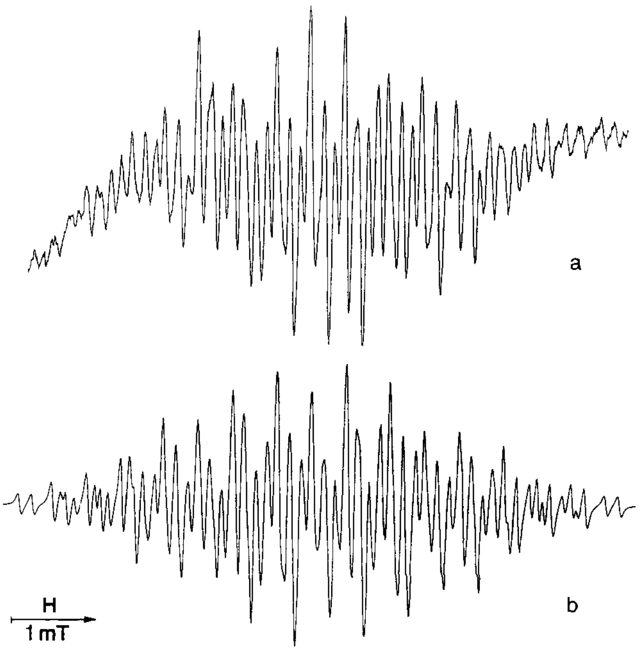
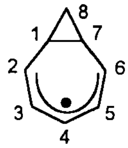
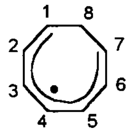
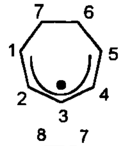
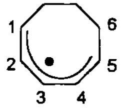
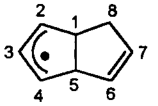
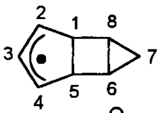
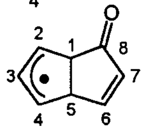
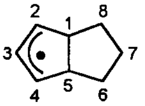


Figure 1. (a) ESR spectrum at 240 K of radical 8, generated by X-irradiation of 12 in [D_{16}]adamantane matrix at 210 K. (b) Computer simulation

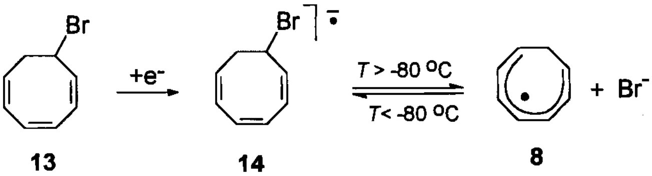
In order to generate 8 by an independent route we also subjected bromocyclooctatriene (13) in [D_{16}]adamantane to X-irradiation at 77 K. In this experiment we first observed

Table 1. Experimental and calculated ESR hyperfine splittings [G] of C_8H_9 and some related radicals

Radical		T [°C]	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
	**7**		3.4	10.2	7.8	11.4	7.8	10.2	3.4	1.4; 1.0[a]
			5.8	9.5	6.0	12.4	6.0	9.3	5.2	1.6; 5.6[b]
			8.3	9.3	6.2	12.9	6.2	9.3	8.3	1.1; 3.3[c]
		-130	5.8	8.7	2.9	12.4	2.9	8.7	5.8	1.7; 0.9[d]
	**8**		6.5	9.2	9.1	6.4	9.1	9.1	6.5	6.2; 2.4[a]
			8.9	15.6	14.8	7.6	14.6	17.0	8.2	12.7; 4.9[b]
			7.4	9.3	9.9	6.5	9.9	9.3	7.4	21.0; 10.5[e]
		-40	6.83	3.35	11.35	4.21	11.35	3.35	6.83	11.1; 1.33[f]
			10.5	6.65	13.6	8.1	10.4	28.9	32.9	
								3.7	8.0[b]	
		-109	9.78	3.67	12.84	3.67	9.78	15.0	15.0	
								5.2	5.2[g]	
		-91	9.80	3.67	13.17	3.67	9.80	9.25	0.63	9.25
								6.33	0.63	6.33[g]
	**17**	-30	14.90	14.33	2.66	14.25	19.60	-	-	1.87; 0.60[f]
	**19**	-30	15.7	14.1	2.8	14.1	15.7	0.7	-	0.7[f]
		-27	21.9	14.25	2.8	14.25	19.1[h]			
		-40	17.6	14.1	2.6	14.1	17.6	1.5; 1.8	-	1.5; 1.8[i]

[a] AM1/UHFQ data on UHF/3-21G* geometry; this work. – [b] INDO data on AM1/UHF geometry; this work. – [c] INDO data on MNDO/UHF geometry; ref.[7] – [d] Exp. data in solution; ref.[7] – [e] "Adjusted" INDO data; ref.[11] – [f] Exp. data; this work. – [g] Exp. data in solution; ref.[9b] – [h] Exp. data; ref.[3d] – [i] Exp. data; ref.[3f]

at temperatures below 190 K an ESR signal showing just three broad lines (ΔH_{pp} ca. 1.5 G) with a line separation of ca. 3.5 G. At higher temperatures this spectrum slowly converted into a well-resolved multiline spectrum. The ESR spectrum recorded above 200 K (Figure 2) appeared to be virtually identical to that obtained from **12**, providing strong support for the above interpretation. Interestingly, on cooling the matrix back to 180 K the spectrum of **8** was replaced by the broad signals observed initially. The three-line spectrum again diminished on raising the temperature, and the spectrum of **8** reappeared. This process could be repeated several times. Because the broad low-temperature ESR signal did not match the spectral features of the 2-adamantyl radical (which is frequently observed in this type of experiments[3e,4]) we tentatively attribute the initial spectrum to the bromocyclooctatriene radical anion (**14**). It is commonly believed that in adamantane matrices the radiation-induced formation of neutral free radicals from halogenated compounds occurs by trapping of free electrons followed by elimination of a halide ion (dissociative electron capture)[12]. Thus, the observed reversible temperature-dependent spectral changes might be due to the elimination-association process of the bromide ion which is kept in close proximity



13 **14** **8**

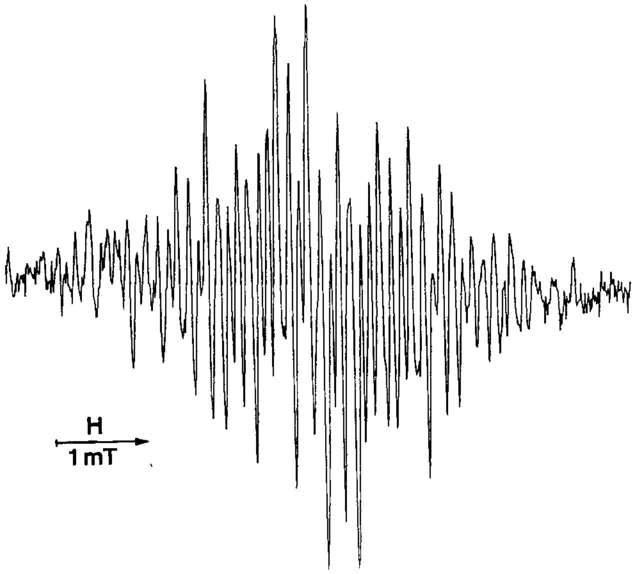
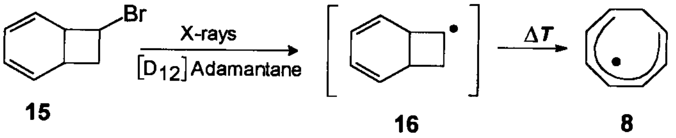


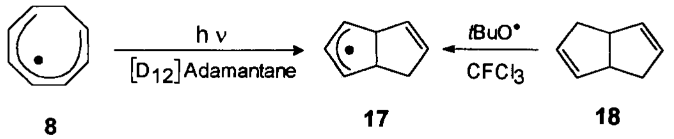
Figure 2. ESR spectrum at 210 K of radical **8**, generated by X-irradiation of **13** in [D_{16}]adamantane at 77 K

to radical **8** by the matrix cage[13]. We made no effort to elucidate further the true nature of this interesting phenomenon as it is outside the scope of our study.

X-irradiation of a mixture of **13** and 7-bromobicyclo-[4.2.0]octa-2,4-diene (**15**) in [D_{16}]adamantane at 77 K yielded the same ESR spectrum as before, even at temperatures as low as 180 K. It is worth mentioning that no primary radical **16** could be detected from **15**. This indicates that either compound **15** is inert towards radical formation under the applied conditions, or, more likely, radical **16** easily isomerizes to **8**.



Although there can be no doubt that the major part of the experimental spectra from all three sources is due to radical **8**, discrepancies in some of the line intensities of the calculated and experimental spectra as well as the slight asymmetry of the latter indicated the presence of additional radical species. Careful inspection of the spectra obtained from **12** implied that in this case the minor component should have an overall width of ca. 55 G. Trial simulations in which **8** and varying relative amounts of the unrearranged radical **7** (using the data of ref.[7]) were superimposed did not lead to improved fits to the experimental spectra[14]. Thus, we cannot assign the additional species with some certainty to **7**. If **7** indeed were present in the spectrum then



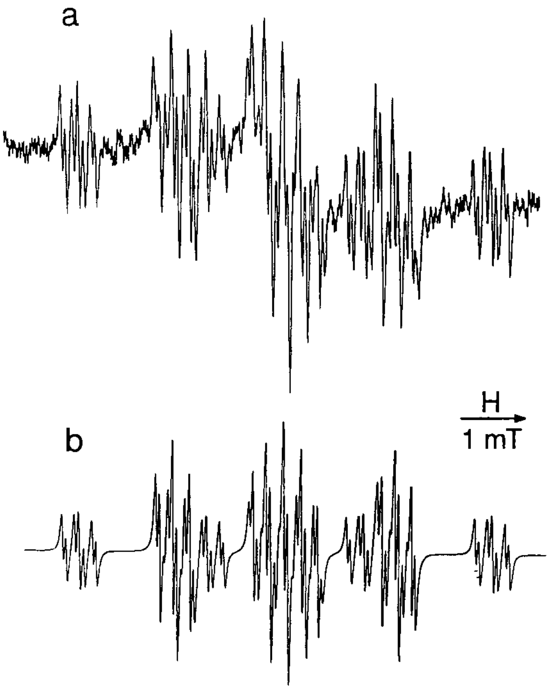


Figure 3. (a) ESR spectrum of radical **17**, obtained after a 4-min photolysis of **8** in [D_{16}]adamantane at 240 K. (b) Computer simulation

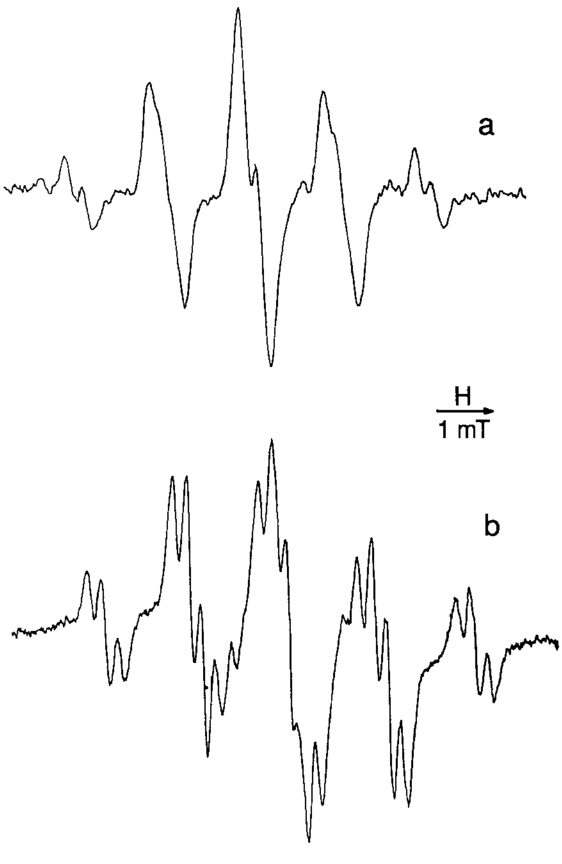
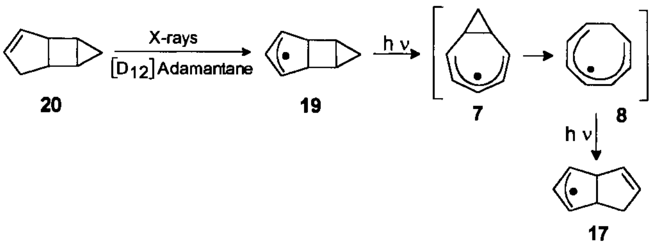


Figure 4. (a) ESR spectrum of radical **19** in adamantane matrix at 230 K. (b) Spectrum obtained from a) after 5 min photolysis

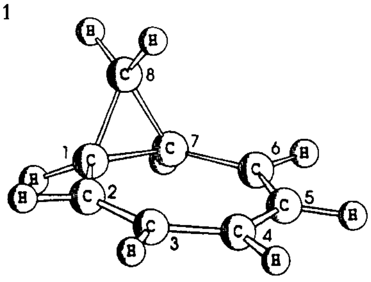
it should exhibit hfs constants markedly different from those in the liquid phase. In view of the fairly rigid structure of **7** this seems very unlikely[15]. In addition, temperature variation between 200 and 340 K revealed no general changes in the spectra as would have been expected for a thermal equilibrium between **7** and **8**. Also, the presence of other C_8H_9 radicals, e.g. **9**, **10**, **11**, or **16**, which might have been formed in a reasonable manner by other rearrangement processes, can safely be excluded on the basis of the expected hfs constants. Therefore, the additional ESR signals very likely derive from some side products formed in the X-irradiation procedure. In particular, the addition of hydrogen (deuterium) atoms to unsaturated systems is a common process in the application of this technique[3c–3f].

When the $[D_{16}]$adamantane matrices containing radical **8** were irradiated with UV light (230–360 nm) the ESR signals of **8** disappeared almost completely within ca. 4 min and a new, well-resolved ESR spectrum was observed (Figure 3). This spectrum was easily identified to be due to the allylic-type bicyclo[3.3.0]octa-2,6-diene-4-yl radical (**17**) by a comparison with literature data[3d,3f] (Table 1) and independent generation by hydrogen abstraction from bicyclo[3.3.0]octa-2,6-diene (**18**) in Freon solution. Thus, a 1,5 ring closure reaction of **8** has been photolytically induced.

Consequently, if some **7** initially might have been present in the matrices it also should have been finally transformed into **17** by initial β-scission of the interring bond in **7**. The formation of **17** was thermally and photochemically irreversible in the temperature range from 230 to 350 K which indicated **17** to be the thermodynamically most stable isomer in our series of C_8H_9 radicals.



Scheme 1



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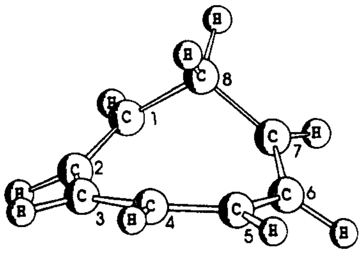

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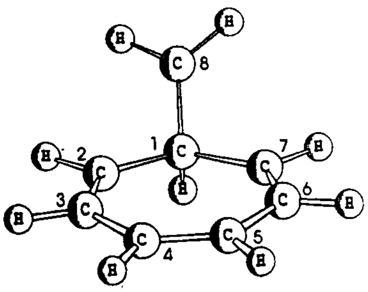

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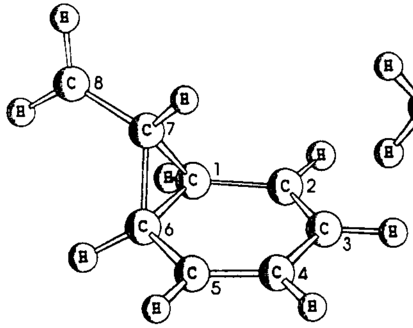

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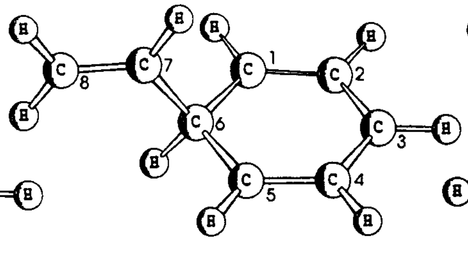

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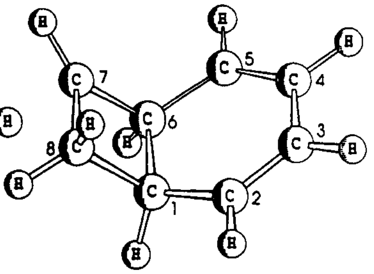

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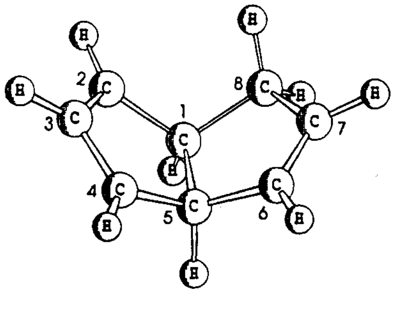

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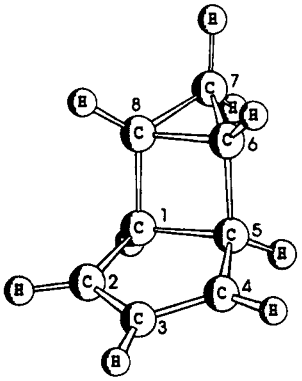

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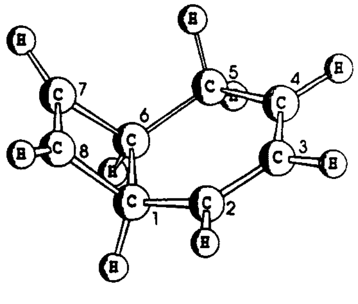

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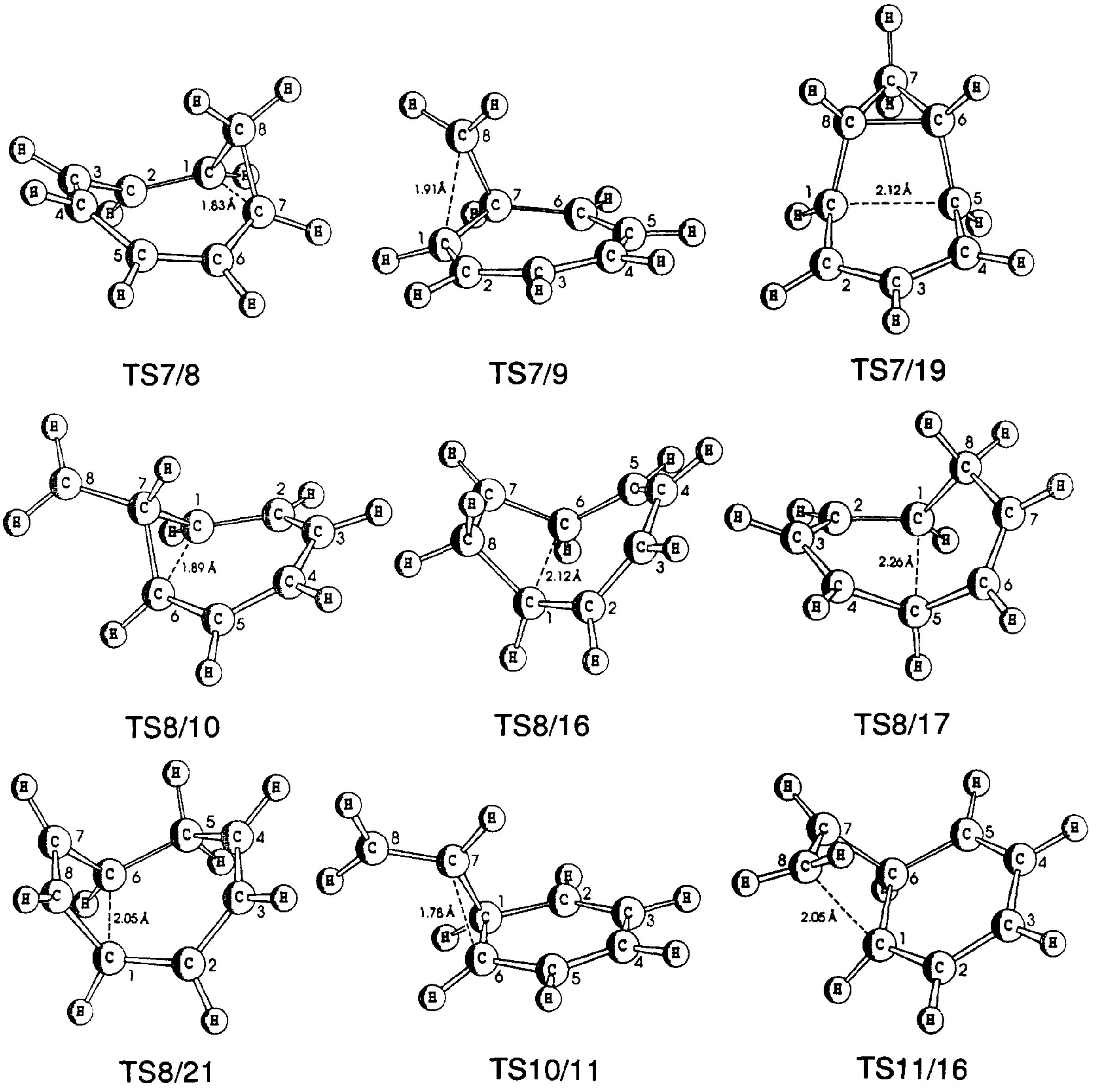
Since the release of ring strain can be assumed to provide a major part of the driving force for the above rearrangements, we also expected the tricyclo[3.3.0.$0^{2,4}$]oct-6-en-7-yl radical (**19**) to undergo rearrangement to **8** by consecutive rupture of the interring bonds in the cyclobutane and cyclopropane rings, respectively. X-irradiation at 77 K of tricyclo[3.3.0.$0^{2,4}$]oct-6-ene (**20**) incorporated in adamantane led to an ESR spectrum (Figure 4a) displaying the spectral characteristics of an anellated cyclopentenyl radical[3] (Table 1). We assign this spectrum to the corresponding radical **19**. No significant changes in the ESR spectrum could be detected at temperatures up to 360 K within an hour; thus, thermal C1–C5 ring opening to give primarily **7** is energetically not a favorable process under these conditions. However, when the adamantane matrix was exposed to UV light at 293 K smooth conversion to **17** was monitored (Figure 4b), confirming that the above sequence of ring openings has been followed.

Molecular Orbital Calculations

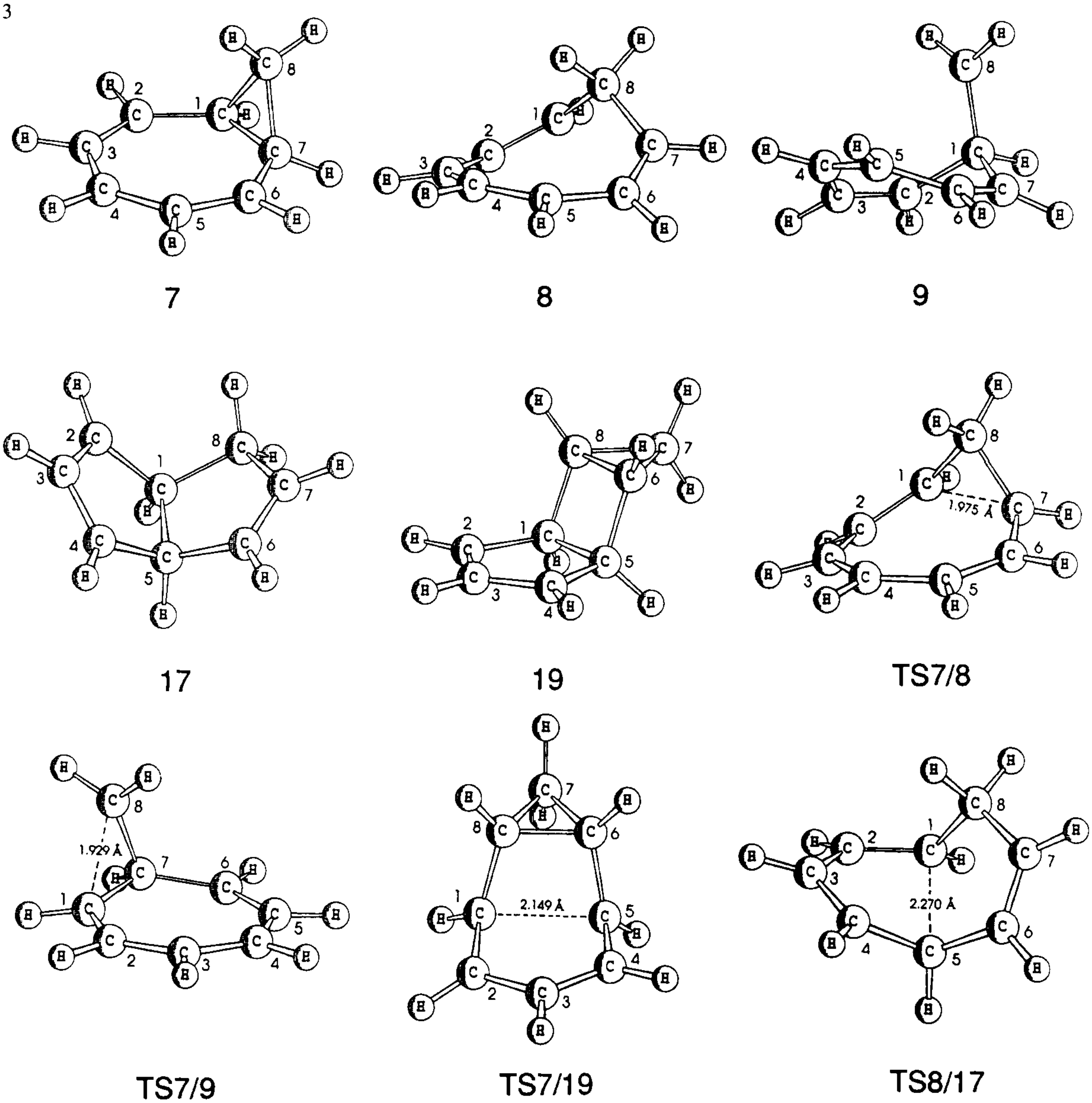
In order to get further insight into the energetics of the C_8H_9 radical hypersurface we carried out semiempirical AM1/UHF[16] and PM3/UHF[17] calculations on the above mentioned radicals and the transition states of their mutual interconversions. For the more important species of this study ab-initio calculations on the UHF/3-21G*[18] level of theory were also performed. The fully optimized structures are displayed in Schemes 1, 2 (PM3), and 3 (ab initio).

In terms of geometrical parameters the semiempirical and the ab-initio calculations gave very similar results[19]. As expected, the seven-membered ring in radical **7** appears to be almost completely planar, the angle with the plane of the cyclopropane ring is estimated to about 108° by all three methods. Likewise, for the C1–C7 bond, which is the one to be broken in the 7 → 8 rearrangement, all calculations yield a standard cyclopropane bond length of about 151 pm.

Scheme 2



Scheme 3



Correspondingly, the semiempirical and the ab-initio calculations predict the cyclooctatrienyl radical (**8**) to adopt a (slightly twisted) boat-like minimum conformation in which carbon atoms C2–C3–C5–C6 are almost in plane. The interplane angle with the approximate plane formed by carbon atoms C1–C2–C6–C7 amounts to about 153 (AM1, UHF/3-21G*) and 150°(PM3), respectively. Relative to this "plane" the CH_2 (C8) group is bent by about 64 (AM1, UHF/3-21G*) and 67°(PM3), i.e. the CH_2 group is oriented almost perpendicular to the C2–C3–C5–C6 plane. C4 is slightly (PM3: 12°; AM1: 8.5°, UHF/3-21G*: 10°) bent out of the C2–C1–C5–C6 plane. The C1–C7 distance is calculated to be 243 and 241 pm by the AM1 and PM3 methods, respectively, but somewhat wider (251 pm) by the ab-initio procedure.

The transition structure (**TS7/8**) for the **7**→**8** interconversion resembles largely the boat-like structure of **8**, with the central C1–C7 bond being more elongated in the AM1 (200 pm) and the ab-initio structure (198 pm) than in the PM3 (185 pm) structure. In terms of molecular orbital correlations the **7** → **8** ring opening is a symmetry-forbidden electrocyclic process, leading to an excited state of the product if the rearrangement proceeds through a pathway conserving the symmetry plane bisecting the interring C1–C7 bond[20]. Such a process seems to be in contradiction with the fact that the ring opening already occurs at temperatures as low as 200 K. The structural asymmetry of **TS7/8** thus may reflect the breakdown of the initial geometry during the reaction, by which the correlation between the ground states becomes feasible.

The AM1/UHF and the UHF/3-21G* geometries were used as input structures for the calculation of the ESR hyperfine splittings of radicals **7** and **8**. We employed the AM1/UHFQ method[21] to the UHF/3-21G* geometry, and on the AM1/UHF geometry an INDO calculation was performed (Table 1). For **7** the results are in qualitative agreement with the experimental data[7]. However, as generally found with delocalized radicals, the hfs constants (a_3, a_5) at the positions carrying a negative spin density are overestimated[21,22]. As demonstrated by the scatter of the data for **8** (Table 1), the hfs constants of this radical are strongly dependent on small changes in the geometry of the radical. Therefore, the calculations are not extremely useful for the assignment of the experimental values. Because radical **8** should be much more flexible than **7**, an influence of the matrix on the conformation of **8** cannot be excluded. Thus, the hfs parameters obtained in this study may differ from those to be observed in solution. In any case, however, the hfs parameters for the methylene hydrogens at C8 can safely be assumed to be considerably smaller than reported in ref.[11], where an ideal envelope-type geometry with a planar arrangement of carbon atoms C1 to C7 was assumed for **8**.

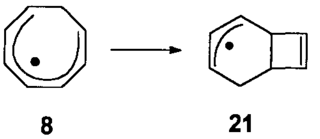
The calculations provide no indication that a possible circumambulatory migration of the cyclopropane ring in radical **7** should be a concerted sigmatropic process. Instead, the cycloheptatrienylmethyl radical (**9**) was found to be a distinct intermediate (see below). In the transition structure (**TS7/9**) for its formation one of the peripheral cyclopropane bonds in **7** is calculated to be elongated to about 191 pm (AM1, PM3) and 193 pm (UHF/3-21G*).

The boat-like conformation of **8** already represents a favorable structure for a thermal ring closure to the bicyclic radical **17**. (We assume that the photochemically induced reaction proceeds via a transition structure identical or similar to that of the thermal reaction.) The semiempirical and the ab-initio methods predict a similar, twisted boat conformation for the transition state (**TS8/17**) of the **8** ⟶ **17** ring closure, with a C1—C5 distance of 226 and 227 pm, respectively.

As expected, the conversion of the tricyclic radical **19** into radical **17** is confirmed by the calculations to be a stepwise process, beginning with the cleavage of the C1—C5 interring bond to give **7** as the first intermediate. The only remarkable geometrical change in reaching the transition state (**TS7/19**) for this step is the elongation of the C1—C5 distance from ca. 159 in **19** to about 206 (AM1), 212 (PM3), and 215 pm (UHF/3-21G*).

In addition to the foregoing C_8H_9 rearrangement reactions we also calculated by the semiempirical methods the ring opening of the cyclobutyl-type radical **16** (which might have been formed in the experiment where we used a mixture of **13** and **15** as starting material, see above) to give either **8** by C1—C6 bond cleavage or the vinyl-substituted cyclohexadienyl radical **11** by C1—C8 bond cleavage.

A third mode of a single-step ring closure reaction of the cyclooctatrienyl radical (**8**) would be a C1—C6 interaction to give the bicyclic radical **21**. This reaction, as well as the rearrangement sequence **9** ⟶ **10** ⟶ **11** mentioned in the introduction, were also calculated for the sake of completeness.



8 **21**

In view of the experimental observations, the energetic relationships of the above radicals are the focal point of our calculations (Tables 2, 3). The semiempirically calculated heats of formation (Table 2) and the relative (to **7**) ab-initio energies (Table 3) are graphically displayed in Figures 5 and 6, respectively.

Qualitatively, the data are in agreement with the experimental observations. Radical **17** appears to be the thermodynamically most stable radical of our series, in full accord with its final photolytical formation from the three sources employed in this study. Most satisfying, the calculations also show that the cyclooctatrienyl radical (**8**) indeed is more stable than the homotropylidenyl radical (**7**); the energy differences of 12.1 (AM1), 8.4 (PM3), and 12.6 kcal mol^{-1} (UHF/3-21G*), respectively, account for the fact that we could not detect **7** with some certainty in our ESR spectra. The calculated activation energies of 19.8 (AM1), 19.3 (PM3), and 23.3 kcal mol^{-1} (UHF/3-21G*) for the **7** ⟶ **8** interconversion (**TS7/8**) certainly are too high, because this

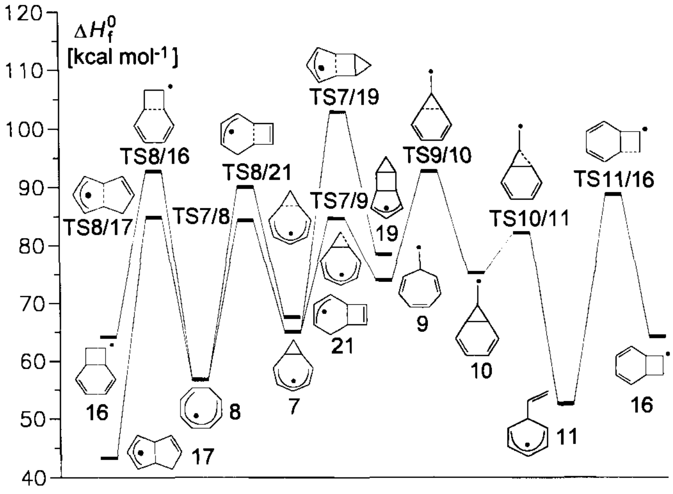


Figure 5. PM3 energy scheme for C_8H_9 radicals

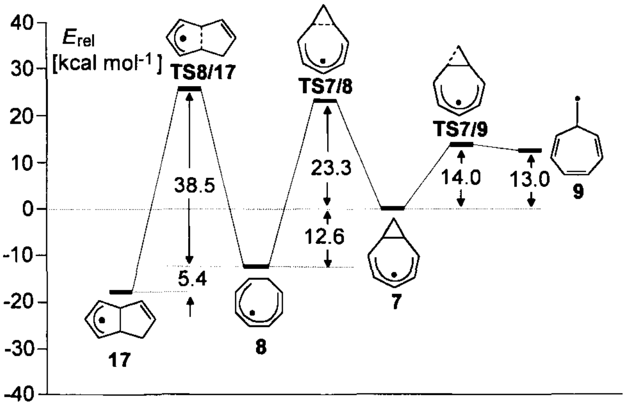


Figure 6. UHF/3-21G* energy scheme for C_8H_9 radicals

Table 2. AM1-, PM3-, and MM2ERW-calculated heats of formation [kcal mol^{-1}]

	7	**8**	**9**	**10**	**11**	**16**	**17**	**19**	**21**
AM1	62.5	50.4	69.2	76.3	51.0	69.8	47.7	91.1	74.3
PM3	65.1	56.7	74.0	75.3	52.8	64.2	43.3	78.5	67.6
MM2ERW	79.5	(70.8)[a]	90.6	(95.6)[a]	68.6	(91.0)[a]	64.8	90.4	86.1

	TS7/8	**TS7/9**	**TS7/19**	**TS8/16**	**TS8/17**	**TS8/21**	**TS9/10**	**TS10/11**	**TS11/16**
AM1	82.3	82.1	109.1	93.5	81.9	93.8	93.0	82.4	92.0
PM3	84.4	84.7	103.3	92.8	84.9	90.3	92.8	82.3	89.0

[a] Calculation not possible with current version of MM2ERW; estimated by the isodesmic reaction of the parent hydrocarbon with a suitable carbon radical, taking into account the difference of resonance stabilization of the pentadienyl and the heptatrienyl radical (W. v. E. Doering, T. Sarma, *J. Am. Chem. Soc.* **1992**, *114*, 6038–6043).

reaction occurred already at temperatures as low as 210 K[23]. It is known that the energies of radical-type transition structures generally are overestimated by the semiempirical as well as the ab-initio UHF methods[18]. For a sufficiently accurate estimation of the transition-state energies, in particular for "forbidden" reactions, an extensive electron correlation has to be taken into account[18,24]. Such calculations are beyond the objective of this study.

Table 3. Total UHF/3-21G* energies [hartrees][a]

7	**8**	**9**	**17**	**19**
-306.3892074 (0)	-306.4093092 (-12.6)	-306.3684531 (13.0)	-306.417968 (-18.0)	-306.359421 (18.7)
TS7/8	**TS7/9**	**TS8/17**	**TS7/19**	
-306.351997 (23.3)	-306.3669087 (14.0)	-306.3478731 (25.9)	-306.315219 (46.4)	

[a] Relative energies (kcal mol^{-1}) in parentheses.

Interestingly, the transition structure **TS8/17** for the ring closure of **8** to radical **17** [activation barriers: 31.5 (AM1), 28.2 (PM3), and 38.5 (UHF/3-21G*) kcal mol^{-1}] almost lies on the same energy level as the transition structure **TS7/8**, i.e. the ring closure **8** → **7** exhibits similar activation barriers of 31.9 (AM1), 27.7 (PM3), and 27.9 kcal mol^{-1} (UHF/3-21G*). From the fact that we did not observe a *thermal* ring closure **8** → **17**, we have to conclude that due to the relative stabilization of **8**, compared to **7**, this activation barrier is too high to be overcome at a sufficient rate at the maximum temperature (310 K) at which we were able to record the spectrum of **8**. Provided that the calculated energy differences between **7** and **8** are close to the "real" values it should, in principle, be possible to induce a thermal reaction **8** → **17** at temperatures not far above 310 K. In this connection it is interesting to note that the radical cation of cyclooctatetraene – which in terms of the π system is isoelectronic to **8** – also undergoes a similar, photolytically induced ring closure to the bicyclo[3.3.0]octa-2,6-diene radical cation[25].

Both the semiempirical and the ab-initio methods predict the degenerate walk rearrangement of the cyclopropyl group in **7** via intermediate **9** to be a feasible process in competition with the ring opening to **8**. The AM1 and PM3 methods estimate the activation barrier for the cleavage of a peripheral cyclopropane bond in **7** (**TS7/9**) to be of almost the same value (19.6 and 19.5 kcal mol^{-1}, respectively) as the barrier (**TS7/8**) for the rupture of the interring bond (19.8 and 19.3 kcal mol^{-1}). Since the cycloheptatrienylmethyl radical **9** is calculated by AM1 to be 6.7 and by PM3 to be 8.8 kcal mol^{-1} less stable than **7** a (partial) migration of the cyclopropyl ring should occur in competition with the irreversible ring opening to **8**. The situation appears even more favorable when calculated by the UHF/3-21G* method. Here, the transition structure **TS7/9** is considerably lower in energy (activation barrier 13.2 kcal mol^{-1}) than the transition structure **TS7/8** (activation barrier 23.3 kcal mol^{-1}). Furthermore, intermediate **9** lies just 1 kcal mol^{-1} below the transition structure **TS7/9**, i.e. a circumambulatory migration is predicted to be strongly favored over ring opening.

Experience shows that heats of formation of free radicals are notoriously underestimated by the AM1 and PM3 methods. Therefore, we also calculated ΔH_f values for some of our radicals by the recently developed MM2ERW force field[26] (Table 2). This molecular mechanics procedure can be expected to reproduce the "true" heats of formation within ±1 kcal mol^{-1}. For the structures for which MM2ERW is parametrized the data (Table 2) agree with the relative order of stability of the radicals as calculated by the MO methods. Particularly, the ground-state energy differences of **7**, **8**, **9**, and **17** are close to the UHF/3-21G* values. This gives us further confidence in the general validity of our energy scheme.

The endothermicity of the formation of **9** explains why this intermediate could not be observed by ESR spectroscopy. Unfortunately, the high number of hyperfine lines and the relatively poor quality of the ESR spectra we were able to produce from **12** (see Figure 1) make an experimental proof of the walk migration by ESR spectroscopy (e.g. by specific deuteration of **12**, compare **1**[3a,b]) under these conditions a hopeless venture.

The structural characteristics and the energetics of the analogous rearrangement reactions of the bicyclic radical **1**[3a,3b] (see above) have been theoretically examined recently by ab-initio multiconfiguration calculations[27]. These calculations confirm the early hypothesis[3a,3b] that the circumambulatory migration of the cyclopropyl ring in **1** is not truly a pericyclic process but rather involves the intermediate cyclopentadienylmethyl radical, in correspondence with the present situation. Similar to our results for radical **7**, the transition structure for the exothermic ring opening of **1** to the cyclohexadienyl radical (**2**) ($\Delta G^{\ddagger}_{exp} = 14.5$ kcal mol^{-1} at 223 K[3a]) was also found to lie above the transition structure leading to the cyclopentadienylmethyl radical. Thus, **1** and **7** show a parallel rearrangemental behavior.

Because of the higher ring strain one expects the tricyclic radical **19** to be the least stable radical of our study. This is confirmed by all calculations. Interestingly, the barrier for its conversion to **7** (**TS7/19**) is estimated to be relatively high, having values of 36.3 (AM1), 24.8 (PM3), and 27.7 kcal mol^{-1} (UHF/3-21G*), in reasonable agreement with the experimental observation that **19** is stable in the adamantane matrix up to ca. 360 K.

In accord with expectation, a 1,4-ring closure of the cyclooctatrienyl radical (**8**) to give the bicyclic radical **21** can be excluded on the basis of the AM1 and PM3 results for this reaction. Not only is **21** calculated to have a 23.9 (AM1) or 11 (PM3) kcal mol^{-1} higher heat of formation, but also the ring closure affords a fairly high activation enthalpy of 43.4 (AM1) or 33.6 (PM3) kcal mol^{-1}, respectively. The reverse reaction, ring opening of **21**, however, might be detectable by the ESR/adamantane matrix technique, provided that **21** can be generated independently.

The 43.1- (AM1) or 36.1- (PM3) kcal mol^{-1} activation enthalpy for the rupture of the interring bond in the cyclobutyl-type radical **16** implies that this radical should be observable in adamantane matrix at low temperatures. Our failure to detect **16** thus might be interpreted in a way that this radical has not been produced to some extent by X-irradiation of the mixture of **13** and **15**.

The cycloheptatriene-norcaradiene-like ring closure **9** → **10**, as discussed by Walton et al.[7], is not expected to occur under our conditions on the basis of the AM1 and PM3 results. **10** appears to be slightly less stable than **9**, and the activation barrier **TS9/10** for this rearrangement is ca. 9–10 kcal mol^{-1} higher than that for the recyclization to **7**. However, the overall exothermicities of the **7** → **8** and **9** → **10** rearrangements are identical to within the computational error. In view of the known weakness of the semiempirical calculations to predict reasonably reliable activation barriers, the difference of about 10 kcal mol^{-1} is rather small. In reality, the two pathways may be energetically very similar. For such a situation, the influence of the matrix cannot be neglected, i.e. compared with the liquid phase, the other pathway may be favored, e.g. because of geometrical constraints. It might be that our system represents a genuine case where small effects from the matrix indeed tips the balance in favor of one route.

We thank the *Höchstleistungsrechenzentrum (HLRZ) Jülich* for generous allocation of computing resources, the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support.

Experimental

^{1}H and ^{13}C NMR (internal standard TMS): Varian XL 200 and Bruker AMX-300. – ESR: Bruker ER-420. – GC: Varian 2000, 50 m OV-101.

Bicyclo[5.1.0]octa-2,5-diene (**12**) was prepared by the reaction of cycloheptatriene with diazomethane[28] and purified by preparative GLC.

7-Bromo-1,3,5-cyclooctatriene (**13**) and *7-bromocyclo[4.2.0]octa-2,4-diene* (**15**) were prepared by the reaction of cyclooctatetraene with HBr according to ref.[29] **13** was separated from **15** by treatment of the mixture with tetracyanoethylene as described in ref.[29]

Bicyclo[3.3.0]octa-2,6-diene (**18**) was produced from **12** by thermal isomerization at 300°C according to ref.[28]

Tricyclo[3.3.0.0^{2,4}]oct-6-ene (**20**) was prepared by 1,3-dipolar cycloaddition of diazomethane to bicyclo[3.2.0]hepta-2,6-diene[30] followed by photochemically induced N_2 elimination[31].

Adamantane and [D_{16}]adamantane matrices were prepared by cocrystallization of the matrix material (60 mg) and the substrate (5 mg) from a *n*-pentane solution (5 ml) by slow evaporation of the solvent at 0°C. The crystallized material was pressed to pellets (5 mm diameter) by using a standard IR pressing tool. X-irradiation and ESR experiments were carried out as described previously[3,4]. ESR data acquisition and spectral simulation, using an extended version of ESRSPEC2 (QCPE No 210, author P. J. Krusic), were performed on a PDP11/34 minicomputer. For the AM1/PM3 calculations the SCAMP 4.20 package[32] was used on a MicroVax GPX-II workstation. Ab-initio calculations were performed with the GAUSSIAN-90 program[33] on a CRAY Y-MP at the Höchstleistungsrechenzentrum Jülich, Germany. Graphical output was produced with the PERGRA program[34].

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