J. Am. Chem. Soc. 1994, 116, 9795–9796 9795

Excited State Reactivity as a Function of Diradical Structure. Evidence for Two Triplet Cyclopropyldicarbinyl Diradical Intermediates with Differing Reactivity[1]

Howard E. Zimmerman,* Andrei G. Kutateladze,
Yasunari Maekawa, and John E. Mangette

*Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706*

Received June 28, 1994

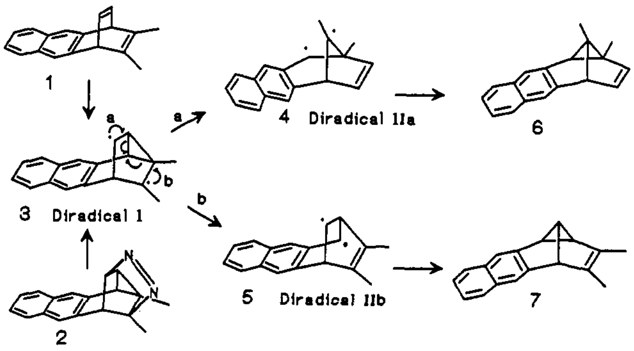
Photochemical reactivity is subject to two types of control: (*i*) by barriers on the excited state hypersurface and (ii) by radiationless decay to alternative ground state species.[2] The Di-π-methane rearrangement provides a good test of these two factors. Relevant to this issue are two, sequential diradicals which are triplets in the case of bicyclic reactants. While the reactivity of diradical I, the first formed species, has been well characterized,[3] evidence for its electronic makeup has been sparse.

We now report (a) the existence of two nonequilibrating naphthobarrelene "diradicals I" (i.e., T_1 and T_2); (b) generation of T_1 and T_2 specifically; (c) two independent routes to each diradical I; (d) differing regioselectivity for T_1 versus T_2; (e) that diradicals I and II are energy minima on the reaction hypersurface, with diradical I being thermally equilibrated, as already known[2] for diradical II; (f) Jahn–Teller stretching of one vinyl bond of T_1 of barrelene, benzobarrelene, and naphthobarrelene; and (g) experimental and theoretical evidence that spin–orbit coupling leads to preferential intersystem crossing via the second sequential diradical ("diradical II") of the mechanism.

We first dealt with the rearrangement of dimethylnaphthobarrelene **1**, whose basic mechanism is shown in Scheme 1. Our strategy utilized the premise that the regioselectivity of three-ring opening of any diradical I would be characteristic of the structure and state of this diradical if it is a thermally equilibrated intermediate. Xanthone-sensitized (E_T = 74 kcal/mol) photolysis of dimethylnaphthobarrelene **1** led to the two semibullvalenes **6** and **7** in an 8.2:1 ratio.[4] An independent route to diradical I was found in the benzil-sensitized (E_T = 53 kcal/mol) photolysis of the azo precursor **2**. Strikingly, semibullvalenes **6** and **7** were formed in a ratio (i.e., 8.3:1) identical within experimental error with that from the naphthobarrelene. In agreement with our previous generalization,[5] the preferred regioselectivity involved dissipation of odd-electron density from the secondary carbon rather than from the more stabilized tertiary one.

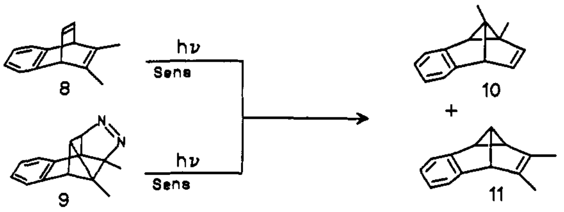
It is clear that the mechanism in Scheme 1 and any conclusions rely on the di-π-methane rearrangement proceeding as shown with vinyl–vinyl bridging rather than naphtho–vinyl bridging. While this has precedent in our earlier studies of the unsubstituted naphthobarrelene,[6] it seemed prudent to check this point in the present instance. Using the approach described in the earlier studies[2,6,7] dependent on the fate of deuterium in the reactant labeled with deuterium on the vinyl group, we found no vinyl deuterium at the benzylic positions of the semibullvalene photoproducts, thus establishing vinyl–vinyl bridging as the reaction mechanism.

Scheme 1. Two Photochemical Approaches to Diradical I of the Naphthobarrelene to Naphthosemibullvalene Triplet Mechanism



If diradical I were a transition state or a mere point on the triplet hypersurface, the direction of approach to such a point would control the subsequent travel on the surface as understood in a trajectory analysis.[8] Conversely, a thermally equilibrated diradical I as an intermediate would give the same regioselectivity independent of its source. Since the regioselectivity was independent of the diradical's source, we can conclude that diradical I is indeed a thermally equilibrated intermediate.

In order to check the generality of the di-π-methane behavior, we investigated the corresponding dimethylbenzobarrelene **8** and its azo relative **9**; **8** has been studied previously in elegant studies by C. O. Bender.[9] At 0 °C the ratio of semibullvalene **10** to its isomer **11** was 12.2 (±0.6):1 independent of the source of diradical I. The direction of the preference is seen (note eq 1) to be the same as in the naphthobarrelene case. For the benzobarrelene rearrangement, we can again conclude that diradical I is a thermally equilibrated species. The two benzosemibullvalenes **10** and **11** were formed in a 6:1 ratio at 50 °C, suggesting a 2.45 kcal/mol difference in enthalpic activation barriers for alternative modes of diradical I three-ring opening. Our conclusion that diradical I is a thermally equilibrated and real species is in agreement with a different approach to the same question provided in a study based on the regioselectivity exhibited at this point along the reaction coordinate and also with ab initio computations.[10,11]



(1)

A remarkable observation was that, with higher energy sensitizers, the naphtho azo compound **2** led to a totally different regioisomer ratio, a ratio closer to that of the direct irradiation of the naphthobarrelene **1**. With xanthone (74 kcal/mol) or thioxanthone (65 kcal/mol), the naphtho azo diradical precursor **2** afforded a 2.6:1 ratio of semibullvalenes **6** and **7**. Direct irradiation of naphthobarrelene **1** led to a 4.2:1 ratio of the two

---

[1] This is paper 172 of our photochemical series and 236 of our general papers.

[2] Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933.

[3] Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680–7689.

[4] All new compounds gave acceptable analytical data.

[5] Zimmerman, H. E.; Pratt, H. E. *J. Am. Chem. Soc.* **1970**, *92*, 6259–6267.

[6] (a) Zimmerman, H. E.; Bender, C. O. *J. Am. Chem. Soc.* **1969**, *91*, 7516–7518. (b) Zimmerman, H. E.; Bender, C. O. *J. Am. Chem. Soc.* **1970**, *92*, 4366–4376.

[7] Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3316–3323.

[8] Lyons, B. A.; Pfeifer, J.; Peterson, T. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1993**, *115*, 2427–2437.

[9] Bender, C. O.; Bengtson, D. L.; Dolman, D.; Herle, C. E. L.; O'Shea, S. F. *Can. J. Chem.* **1982**, *60*, 1942–1952.

[10] Zimmerman, H. E.; Sulzbach, H. M.; Tollefson, M. B. *J. Am. Chem. Soc.* **1993**, *115*, 6548–6556.

[11] Note recent corresponding computations. (a) On a singlet: Reguero, M.; Bernardi, F.; Jones, H.; Olivucci, M.; Ragazos, I. N.; Robb, M. *J. Am. Chem. Soc.* **1993**, *115*, 2073–2074. (b) On a triplet: Quenemoen, K.; Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1985**, *107*, 5054.

0002-7863/94/1516-9795$04.50/0

regioisomers. A reasonable interpretation is that the azo route in this case affords a T_2 diradical I while the direct naphthobarrelene irradiation leads largely to this triplet but with minor leakage to T_1.

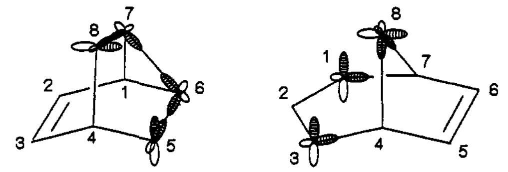
We needed to consider the electronic structure of T_1. A fascinating result arose from ab initio geometry optimization [CASSCF(6,6)/6-31G* or 3-21G] of the lowest barrelene, benzobarrelene, and naphthobarrelene triplets. A common feature encountered was the presence of one stretched double bond (1.51 Å) in each along with the remaining double bond(s) being normal (1.34 Å). Hence we can conclude that the triplet excitation is largely localized in the barrelene moiety in benzo- and naphthobarrelene. In the case of barrelene itself, the 3-fold symmetry leads to a degenerate antibonding pair of MOs only singly occupied in the triplet; and this is responsible for the molecular distortion. The benzo and naphtho cases distort due to promotion from a degenerate pair in a fashion carried over from the barrelene situation.

Even ROHF/STO-3G afforded the "stretched bond" phenomenon, although the energies were more approximate. Interestingly, in the case of naphthobarrelene, ROHF/3-21G led to two triplets. One corresponded in geometry to the CASSCF T_1 with the barrelene stretched double bond. The other had perfectly normal double-bond lengths (i.e., ca. 1.34 Å) but a distorted naphtho group with four naphthalene bonds elongated as anticipated for odd electrons being concentrated at the remote α carbons. The energy difference of 17 kcal/mol (ROHF/3-21G) suggested a lack of thermal equilibration.

Our previous computations[10] for T_1 of barrelene used ROHF while our present study improved these with CASSCF(6,6)/6-31G*. However, in both we obtained energy minima corresponding to diradicals I and II. Both minima cross S_0 by ca. 1.5 kcal/mol. Thus, the question arises concerning where intersystem crossing (ISC) takes place to afford the ground state. We know that diradical I on ISC will lead to the (S_0) 1,4-singlet diradical, which is known[3,12] to revert to the corresponding barrelene. The known quantum yields are ca. 0.5.[6b,9] Hence ISC must occur preferentially at the diradical II reaction stage. To understand the preferential ISC at this point, we have considered not only the energy gap but also spin–orbit coupling. To this end, we employed spin–orbit coupling computations as formulated in GAMESS[13] using a multiconfiguration MCSCF singlet interacting with the three components of the triplet. Strikingly, as outlined in Table 1 spin–orbit coupling in diradical I is less than $^1/_4$ that for diradical II, rationalizing greater decay for diradical II. Interestingly, diradical II has its "diradical orbitals" closer to perpendicular than does diradical I. NBO[14] analysis led to an 11° angle between the two odd-electron-containing orbitals in diradical I contrasted with an 86° angle for diradical II. We note the suggestion[15] that a 90° orientation is optimum for spin–orbit coupling.

Table 1. Spin–Orbit Coupling in Barrelene Diradicals I and II (cm^{-1})

	L_x	L_y	L_z
Diradical I. RMS Spin–Orbit Coupling: 0.758			
$\langle(S=0.0,MS=0.0)//(S=1.0,MS=1.0)\rangle$	0.5360	–0.0001	0.0000
$\langle(S=0.0,MS=0.0)//(S=1.0,MS=0.0)\rangle$	0.0000	0.0000	–0.0001
$\langle(S=0.0,MS=0.0)//(S=1.0,MS=-1.0)\rangle$	–0.5360	0.0001	0.0000
Diradical II. RMS Spin–Orbit Coupling: 3.264			
$\langle(S=0.0,MS=0.0)//(S=1.0,MS=1.0)\rangle$	–0.8079	–0.0887	0.0000
$\langle(S=0.0,MS=0.0)//(S=1.0,MS=0.0)\rangle$	0.0000	0.0000	3.0544
$\langle(S=0.0,MS=0.0)//(S=1.0,MS=-1.0)\rangle$	0.8079	0.0887	0.0000



HYBRID 1	: HYBRID 2	SOC Contrib.
π8	: σ8-C7	0.227558 X
π5	: σ5-C6	0.227507 X
π5	: σ6-C7	-0.127316 Z
π8	: σ7-C6	0.127303 Z

HYBRID 1	: HYBRID 2	SOC Contrib.
π8	: σ8-C7	1.51B466 Z
π8	: σ8-C4	1.463247 Z
π3	: σ3-C4	-1.638605 Y
π1	: σ1-C7	1.485929 Y

Figure 1. Four largest contributions for diradicals I and II, respectively. The *X*, *Y*, *Z*, and *MS* components here and in Table 1 are coordinate system dependent.

However, we have taken a new approach to dealing with spin–orbit coupling. This involved dissection of the entirety into local hybrid orbital–orbital contributions. Figure 1 shows the hybrids contributing most heavily to spin–orbit coupling for each of the diradicals. It was found[16] that the main contributions come from interaction of the odd-electron-containing p orbitals with the hybrid orbitals at the same centers.

Hence, while the direction taken on the excited state reaction hypersurface is known to be controlled by energy barriers[10] presented to the vertical excited state, the present example provides evidence that radiationless decay may be an additional and equally important factor.

Acknowledgment. Support of this research by the NSF is gratefully acknowledged.

Supplementary Material Available: Spectral and analytical data for various compounds and tables of computed bond distances and angles and dihedral angles for naphthobarrelene, benzobarrelene, and barrelene (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(12) Zimmerman, H. E.; Carpenter, C. W. *J. Org. Chem.* **1988**, *53*, 3298–3305.

(13) Schmidt, M. W.; et al. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

(14) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

(15) Carlacci, L.; Doubleday, C.; Furlani, T. R.; King, H. F.; McIver, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 5323–5329.

(16) Complete details of our spin–orbit coupling dissection will be published.