tion effects involving these two molecules.

Table IV lists $\bar{I}_{S,\min}$ and pK_a's[17,20,21] for a group of oxygen acids. As mentioned earlier, the lowest value of $\bar{I}(\mathbf{r})$ on the molecular surface of the nitrite ion is found near the nitrogen, even though the proton was lost by an oxygen. However the difference between the oxygen and nitrogen $\bar{I}_{S,\min}$ values is only 0.02 eV. There is an excellent linear relationship between $\bar{I}_{S,\min}$ and pK_a, with a correlation coefficient of 0.99. This is noteworthy in that the group contains a rather diverse set of molecules and considerable differences in solvent effects might be anticipated.

While the discussion so far has treated different families of acids separately, it is gratifying that all of the 25 included in Tables I–V do satisfy a single $\bar{I}_{S,\min}$ vs pK_a relationship, with a correlation coefficient of 0.97 (Figure 4). This general correlation includes the nitrogen acids NH_3, NH_2CONH_2, and NH_2NO_2, the pK_a's of which are listed in Table V. The relationship shown in Figure 4 provides a capability for predicting the pK_a's of a wide range of molecules (carbon, oxygen, and nitrogen acids). For example, we predict the pK_a of $HN(NO_2)_2$ to be −5.6, comparable to that of the very strong acid $CH(NO_2)_2CN$.

Summary

Good linear correlations have been found between the aqueous acidities of four groups of carbon and oxygen acids and the $\bar{I}_{S,\min}$ values of their conjugate bases. A single linear relationship between pK_a and $\bar{I}_{S,\min}$ that includes all of the systems studied also exists; the correlation coefficient is 0.97. This provides a means for predicting the pK_a's of a large variety of carbon, oxygen, and nitrogen acids.

Acknowledgment. We appreciate the support of this work by the U.S. Army Research Office.

---

(20) Williard, H. L.; Merrit, L. L.; Dean, A. D.; Settle, A. S. *Instrumental Methods of Analysis*, 6th ed.; Litton Educational Publishing: Belmont, CA, 1981.

(21) Ricci, J. E. *J. Am. Chem. Soc.* **1948**, *70*, 109.

(22) Huheey, J. E. *Inorganic Chemistry*, 2nd Ed.; Harper and Row, New York, 1978.

(23) Arrowsmith, C. H.; Awwal, A.; Ester, B. A.; Kresge, A. J.; Lau, P. P. T.; Onwood, D. P.; Tang, Y. C.; Young, E. C. *J. Am. Chem. Soc.* **1991**, *113*, 172.

Photochemistry of 4-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene†

Christopher Owen Bender,* Douglas Dolman, and Noah Tu

Department of Chemistry, University of Lethbridge, Lethbridge, Alberta, T1K 3M4 Canada

Received January 31, 1991

4-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (**11**) was found to be thermally and photochemically reactive. Heating solutions of **11** at 150 °C for 2 h gave 5-cyanobenzocyclooctatetraene (**10**) quantitatively. The direct irradiation of triene **11** gave 2-cyanobenzosemibullvalene (i.e., SB **12**, 63%, $\Phi = 0.067$), COT **10** (28%, $\Phi = 0.031$), and 1-cyanonaphthalene (ca. 0.5%, $\Phi = 0.0005$). Upon sensitization with *p*-(dimethylamino)benzophenone, **11** gave **12** (30%, $\Phi = 0.028$), COT **10** (9%, $\Phi = 0.0093$), and 1-cyanonaphthalene (2%, $\Phi = 0.0018$). Studies with deuterium-labeled triene (**11a**) revealed that the semibullavene produced from direct irradiation possessed a different label distribution to that obtained from sensitized irradiation, and hence state-dependent pathways operate in the SB formation. The mechanism proposed for the SB formation from S_1 of **11** involves a 1,2-shift with cleavage of the cyclobutene C_1–C_6 bond of the triene, while SB formation from T_1 results from a Zimmerman di-π-methane rearrangement.

Introduction

Semibullvalene derivatives have been shown to be useful starting materials in the synthesis of cyclopentanoid natural products.[1] Recently, we[2-6] and others[7] have reported on the photochemical formation of semibullvalenes (i.e., SB's) from several 2,3-benzobicyclo[4.2.0]octa-2,4,7-trienes (e.g., **1** and **6**). One of our interests in the topic was to determine the effect of varying the site of cyano substitution throughout the aliphatic framework of the triene. To date we have reported on five of the six possible monocyano derivatives, and in all cases SB's have been identified as primary products of the sensitized and/or direct irradiations of the trienes (e.g., **1** → **4**[2]).

Interestingly, the SB's are not produced by a single mechanistic pathway. The results of deuterium-labeling experiments indicate that at least three routes can operate in their formation, the most common of which is a Zimmerman di-π-methane (i.e., DPM) rearrangement[8] involving the two vinyl portions of the triene system (e.g., **1** → **4**, route i, Scheme I[2]). The mechanisms proposed for the less observed pathways involve either a 1,2-shift, with initial cleavage of the cyclobutene C_1–C_6 bond (e.g., **1** → **4**, route ii, Scheme I), or initial bridging between the distal carbons (C-4 and C-8) of the vinyl groups (e.g., **6** → **9**, route iii, Scheme I[3]). We now report on the photochemistry of the remaining cyano derivative **11** and provide evidence for a dramatic excited-state multiplicity dependency on

---

† Dedicated to Howard E. Zimmerman on the occasion of his 65th birthday.

(1) (a) Demuth, M. *Mod. Synth. Methods* **1986**, *4*, 89; (b) *Pure Appl. Chem.* **1986**, *58*, 1233. (c) Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820. (d) Schaffner, K.; Demuth, M. *Synth. Methods* **1986**, *4*, 61.

(2) Bender, C. O.; Clyne, D. S.; Dolman, D. *Can. J. Chem.* **1991**, *69*, 70.

(3) Bender, C. O.; Dolman, D. *Can. J. Chem.* **1989**, *67*, 82.

(4) Bender, C. O.; Dolman, D.; Murphy, G. K. *Can. J. Chem.* **1988**, *66*, 1556.

(5) Bender, C. O.; Bengtson, D. L.; Dolman, D.; O'Shea, S. F. *Can. J. Chem.* **1986**, *64*, 237.

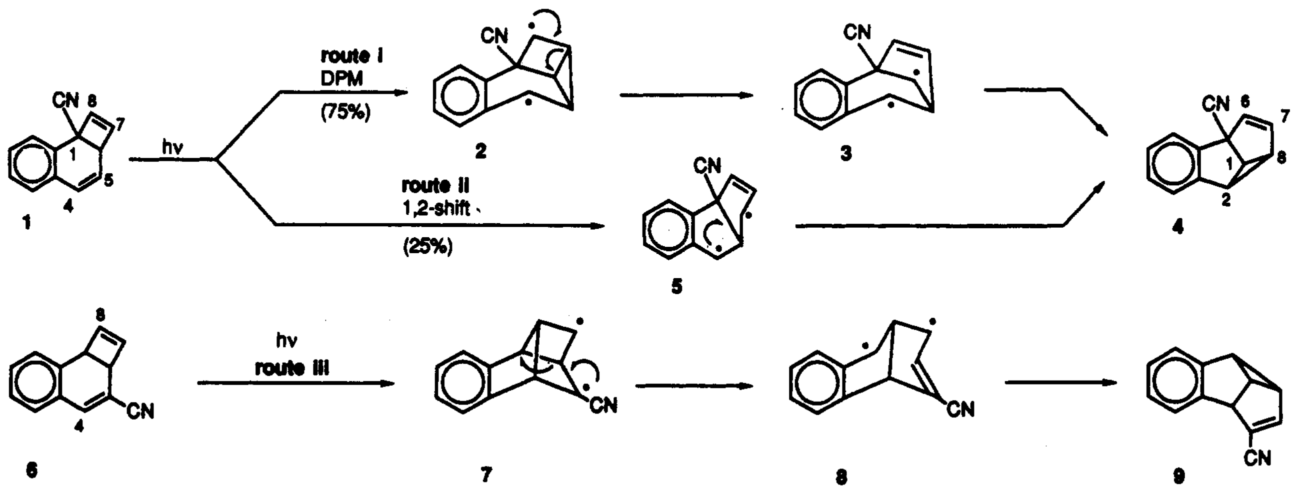
(6) Bender, C. O.; Cassis, I. M.; Dolman, D.; Heerze, L. D.; Schultz, F. L. *Can. J. Chem.* **1984**, *62*, 2769.

(7) Scheffer, J. R.; Yap, M. *J. Org. Chem.* **1989**, *54*, 2561.

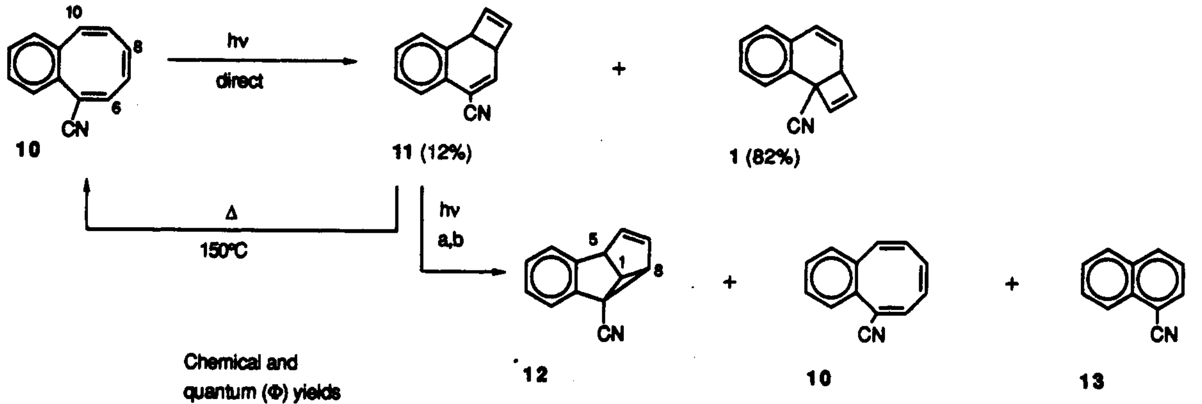
(8) For reviews of the di-π-methane rearrangement, see: (a) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Essay 16, pp 131–166; (b) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

0022-3263/91/1956-5015$02.50/0

Scheme I



Scheme II



Chemical and quantum (Φ) yields	12	10	13
a, Direct	63 % (0.067)	28 % (0.031)	ca. 0.5 % (0.0005)
b, Sensitized	30 % (0.028)	9 % (0.0093)	2 % (0.0018)

the pathways competing in the SB formation.

Results

4-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (11) was obtained as previously described[2] as the minor product from the direct irradiation of 5-cyanobenzocyclooctatetraene (10; Scheme II). Like the other[2-5] monocyano derivatives of the triene system, 11 is thermally labile and reverts to the starting COT. The rearrangement of 11 → 10 is noticeable on GC columns at all useful working conditions and is quantitative at column temperatures >185 °C or on heating solutions of 11 to 150 °C for 2 h.

Upon direct ($\lambda \geq 295$ nm) and sensitized ($\lambda \geq 360$ nm; *p*-(dimethylamino)benzophenone) irradiations 11 gave 2-cyanobenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (12) as the major product along with minor amounts of COT 10 and 1-cyanonaphthalene (13). The chemical yields (GC/NMR analysis) and quantum yields (Φ's) are given in Scheme II. In the case of sensitization, the mass balance for the photoproducts 10, 12, and 13 is poor (ca. 40%) due to the formation of polymeric or other higher molecular weight materials that precipitated in the preparative runs at the high conversion levels used (ca. 70%).

The characterization of SB 12 was not straightforward since like several other cyano SB's (e.g., 15[3]) it undergoes rapid polymerization upon solvent removal. The structure determination rests on spectroscopic evidence and reduction results.

The mass spectrum (via GC/MS) established that 12 was isomeric with triene 11 (molecular ion at $m/e = 179$), and the NMR spectrum revealed proton chemical shifts and coupling constants characteristic of the rigid benzosemibullvalene framework. The NMR data for 12 are compared with those of the related benzosemibullvalenes 15[3] and 17[9] in Table I (note structures given in Scheme III). Further structural support for 12 was obtained from diimide reduction, which gave 2-cyanobenzotricyclo[3.3.0.0^{2,8}]oct-3-ene (14) as the unique product (GC evidence). The identity of 14 is based on comparison of its NMR spectral details with those of the positional isomers 16[3] and 18[10] (see Table II); the *W* coupling constant between H-5 and H-7 is 1.5 Hz in 14, as it is in 16 and 18,

Table I. ^{1}H NMR Data of Semibullvalenes 12, 15, and 17

	description and signal positions,[a] δ		
assignment	12	15	17
aromatics	7.05–7.56, m	7.09–7.47, m	7.00–7.44, m
H-1	3.80, t	3.78, t	
H-2		3.74, d	3.66, d
H-5	4.07, dd	4.09, dd	4.22, d
H-6	5.73, dd	5.72, dd	5.70, dd
H-7	5.26, dd	5.17, d	5.20, dd
H-8	3.43, dd		3.33, dd

[a] Coupling constants for 12 are $J_{1,8} = J_{1,5} = 6$ Hz, $J_{5,6} = J_{7,8} = 2.5$ Hz, and $J_{6,7} = 5$ Hz; corresponding coupling constants for 15 and 17 are within 0.5 Hz.

---

(9) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* 1968, *90*, 6096.

(10) Bender, C. O.; O'Shea, S. F. *Can. J. Chem.* 1979, *57*, 2804.

Scheme III

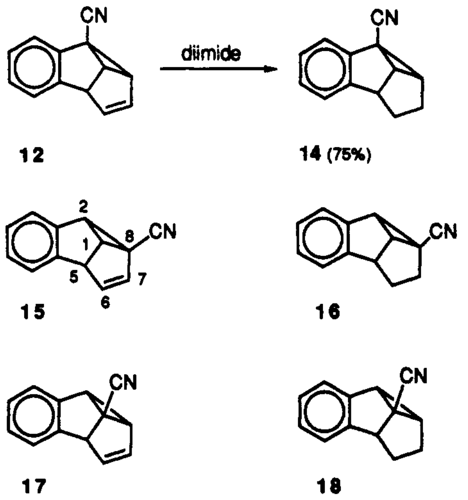


Table II. ^{1}H NMR Data of the Dihydrosemibullvalenes 14, 16, and 18

	description and signal positions,^{a,b} δ		
assignment	14	16	18
aromatics	7.03–7.42, m	7.00–7.33, m	7.02–7.20, m
H-1	3.44, dd	3.36, dd	
H-2		3.09, dd	3.18, dd
H-5	3.73, br t	3.76, br t	3.87, br t
H-6	2.21, m	2.45, m	2.45, m
H-6′	1.63, dd	1.68, br dd	1.76, br dd
H-7	1.98, m	2.10, ddd	2.01, m
H-7′	1.24, m	1.38, ddd	1.19, m
H-8	2.59, ddd		2.60, ddd

^{a}Run in $CDCl_3$ solvent with TMS as internal standard. ^{b}Coupling constants for 14 are $J_{1,8} = 7.5$, $J_{1,5} = J_{5,6} = 5.0$, $J_{5,7} = J_{7',8} = 1.5$, $J_{5,6'} = J_{6',7} = 0$, $J_{6',7'} = 6.0$, $J_{7,8} = 6.5$, $J_{6,7} = 9$, $J_{6,6'} = J_{6,7'} = 11.5$, $J_{7,7'} = 14$; corresponding coupling constants for 16 and 18 are within 1.0 Hz.

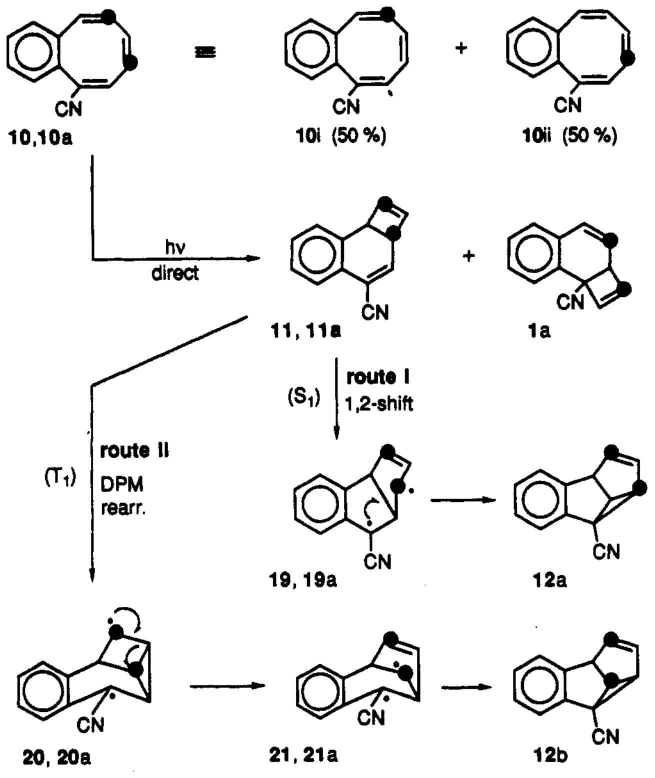
and this feature appears to be characteristic of the dihydrosemibullvalene system.

Next, the photochemistry of SB 12 was examined to ascertain if it was featured in secondary interconversions during irradiations of triene 11. Under either the direct ($\lambda \geq 295$ nm) or sensitized ($\lambda \geq 360$ nm; *p*-(dimethylamino)benzophenone) conditions used for 11, SB 12 was found to be essentially inert with only the slow loss of starting materials being evident; COT 10 was not produced in the photolysates (GC monitoring).

Mechanistic Considerations. A priori, the formation of SB 12 from triene 11 can be rationalized by two of the three mechanisms previously encountered in bicyclo[4.2.0]octa-2,4,7-triene photochemistry, i.e., by the Zimmerman DPM rearrangement depicted as route ii in Scheme IV or by the 1,2-shift pathway shown as route i. The two processes are skeletally distinct and the extent to which they participate in the semibullvalene formation was determined by examining the photoproducts from the deuterated triene material 11a. The structure designated as 11a (Scheme IV) is a 50:50 mixture of two label isomers, one deuterated at C-6 (ca. 90%-d_1) and the other at C-8 (ca. 90%-d_1). This label mixture was obtained from the direct irradiation of the known[11] deuterated material COT 10a, which was composed of equal amounts of COT 10i (ca. 90%-d_1 at C-9) and 10ii (ca. 90%-d_1 at C-7).

Most unexpectedly, the deuterium distribution found in the SB product isolated from the direct irradiation of 11a differed strikingly from that of the SB material produced from sensitized runs, as determined by proton NMR analyses (note Experimental Section). The label in the SB from direct irradiation was located in equal amounts at C-6 and C-8 in agreement with the label distribution designated by 12a, within experimental error. By contrast, the SB produced from sensitization possessed deuterium in equal amounts at C-1 and at C-6, corresponding to structure 12b. Thus, whereas the DPM rearrangement (route ii, Scheme IV) alone accounts for the conversion of triplet excited 11 to 12, it is the 1,2-shift pathway (i.e., route i, Scheme IV) that is utilized in the formation of SB 12 from direct irradiations of 11.

Scheme IV^a



^{a}Structures denoted by a or b represent a 50:50 mixture of two components, each singly labeled with 90%-d_1 at positions marked by ●; e.g., the structure designated as 10a represents a mixture of 50% 10i and 50% 10ii. For structures denoted by a number only (e.g., 10), ● = H.

Of additional interest in connection with the present labeling studies is the formation of COT 10 from 11. Mechanistically, the isomerization can be rationalized by two literature-precedented pathways. One involves a DPM rearrangement via initial bridging between C-5 and C-7, with the formation of octavalene 24a and subsequent thermal reorganization to COT 10b (route i, Scheme V). A similar mechanistic proposal was invoked by us to account for the generation of 6- and 7-cyano BCOT from 8-cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene,[4] and it is known that independently generated 1,3-cyclobutanediyls like the proposed intermediate 23a do close at the radical centers to give bicyclobutanes.[12]

The second pathway is via the well-established[13] $2\sigma_s + 2\pi_s$ electrocyclic opening of the cyclobutene ring of the

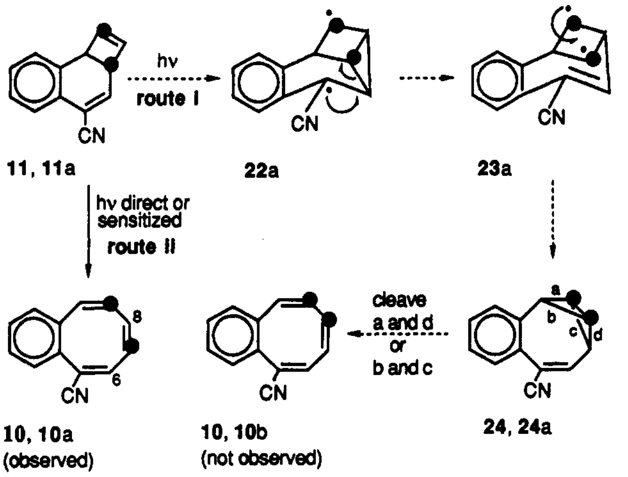
---

[11] Bender, C. O.; Brooks, D. W.; Cheng, W.; Dolman, D.; O'Shea, S. F.; Shugarman, S. S. *Can. J. Chem.* **1978**, *56*, 3027.

[12] Adam, W.; Dörr, M.; Kron, J.; Rosenthal, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 7074.

[13] Woodward, R. B.; Hoffmann, R. In *The Conservation of Orbital Symmetry*. Verlag Chemie; Weinheim and Academic Press: New York, 1970; p 63.

Scheme V[a]



[a] Structures denoted by a or b represent a 50:50 mixture of two components, each singly labeled with 90%-d_1 at positions marked by ●; e.g., the structure designated as 10a represents a mixture of 50% COT labeled with deuterium at C-7 and 50% COT labeled with deuterium at C-9. For structures denoted by a number only (e.g., 10) ● = H.

triene (route ii, Scheme V). These two mechanistic options (i.e., routes i and ii, Scheme V) would lead to the differently labeled COT products designated as 10b and 10a, respectively. It was found that the COT product isolated from both the direct and sensitized irradiations of triene 11a gave NMR proton integrations corresponding to the presence of 10a only (i.e., no deuterium at C-8; note Experimental Section). Thus, the DPM mechanism depicted as route i (Scheme V) does not participate in the generation of COT 10 from triene 11.

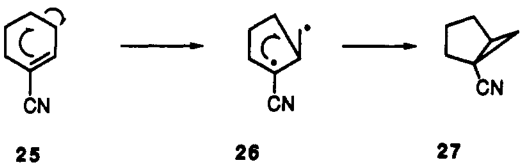
Discussion

The experiments with the deuterium-labeled material 11a have uncovered two pathways that lead to SB 12. Each operates to the exclusion of the other and is accessed by a different mode of excitation. This mechanistic switch in the SB formation is unprecedented in bicyclo[4.2.0]octa-2,4,7-triene photochemistry and is attributed to reactions from different excited states of triene 11. The only previous[2] example of a triene → SB conversion occurring via dual mechanisms is that of 1 → 4 (Scheme I). In that case the bifurcation was interpreted as being exclusively from S_1 since the semibullvalene was a product of direct, but not sensitized, irradiations of triene 1.

With triplet sensitization, the production of SB 12 can be accounted for in terms of a DPM rearrangement from T_1 of 11 (note route ii, Scheme IV). The operation of the mechanism here falls in line with two of the generalizations delineated by Zimmerman concerning DPM reactivity:[8] (i) that the rearrangement in rigid systems shows a preference for triplet initiation and (ii) that substitution by electron-delocalizing groups at the radical centers of the 1,4-carbodiyl intermediate promotes the transformation (note species 20, in which one center is both benzylic and attached to a cyano group).

In the case of direct irradiations of the triene, the labeling studies showed an absence of deuterium at C-1 of the SB product. Thus, the DPM rearrangement does not occur, and hence intersystem crossing to the reactive T_1 state of 11 is essentially zero. We therefore conclude that SB 12 and the other two products from the direct irradiation of 11 are singlet derived and that the quantum yields for process a (direct) in Scheme II correspond to efficiencies of S_1.

Scheme VI



A possible explanation[14] for the differential singlet and triplet photoreactivity of triene 11 may be found in a qualitative approach developed by Michl.[15] According to this method the T_1 state of a diradical prefers a "loose" geometry while the S_1 state prefers a "tight" geometry. A parallel view proposed by Zimmerman and Epling is that odd electron separation is ideal for facile triplet reactivity but spacial overlap of the two electrons optimizes singlet processes.[16] Thus, in the present case, S_1 follows a pathway (route i, Scheme IV) involving the tight geometry of the 1,3-diradical 19, while T_1 follows the pathway (route ii, Scheme IV) involving the loose geometry of the 1,4-diradical 20. However, this rationale may have only limited utility in bicyclo[4.2.0]octa-2,4,7-triene photochemistry, since it does not account for the excited-state reactivity of the 8-cyano derivative in which both S_1 and T_1 appear to undergo the same DPM rearrangement to give 6-cyanobenzosemibullvalene as the major product.[4]

Lastly, we note that the stepwise[17] 1,2-shift mechanism depicted as route i (Scheme IV) is closely analogous to that invoked by McCullough and Manning[20] to rationalize the photoformation of 1-cyanobicyclo[3.1.0]hexane (27) from 1-cyanocyclohexene (25; Scheme VI). Favorable stabilization of a radical center by the cyano group in intermediate 26 appears to be a key factor in facilitating the rearrangement. The radical centers in the corresponding intermediate 19 in the case of triene 11 enjoy considerably more stabilization: one is allylic while the other is benzylic and attached to a cyano group.

Experimental Section

Instrumentation and Materials. The NMR spectra were recorded on either Bruker 250- or 400-MHz instruments, with TMS as internal standard. The chemical shifts are in δ units and the coupling constants (J) in Hz. The abbreviations br, s, d, t, q, and m refer to broad, singlet, doublet triplet, quartet, and multiplet, respectively. The GC/MS was recorded on an HP 5890 (GC)/5970 (MS) instrument fitted with a DB-5 fused silica capillary column, 15 m × 0.25 μm. The IR spectra were recorded on a Bomem MB 102 FT spectrometer. The UV spectra were measured on a Varian DMS 100S spectrometer; maxima are given in nm, with λ_{max} values in parentheses; sh = shoulder. Melting points are uncorrected. Elemental analyses were performed by Galbraith Labs, Inc., Knoxville, TN. Unless stated otherwise, column chromatography was carried out on silica gel 60 (Merck; 230–400 mesh) mixed with Sylvania 2282 phosphor and slurry packed into quartz columns permitting monitoring by a hand UV lamp or on Lobar columns (Merck; size B, LiChroprep Si 60). The GC analyses were made on a Varian 3700 instrument (FID), coupled to a Varian CDS 111 computing integrator, and fitted with an SE-30 fused silica capillary column 30 m × 0.32 mm. Analytical high-performance liquid chromatography was carried out on a Waters 501 HPLC pump with detection by a Waters

---

(14) Discussion of the topic of this paragraph was at the request of a reviewer.

(15) Michl, J. *Mol. Photochemistry* **1972**, *4*, 243; **1972**, *4*, 257.

(16) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 8749.

(17) The available evidence does not rule out the possible operation of a concerted pathway involving a 4-electron Hückel cyclic array with zero nontrivial sign inversions[18] (i.e., a $2\sigma_a + 2\pi_a$ process[19]).

(18) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1565; **1966**, *88*, 1566; *Acc. Chem. Res.* **1972**, *4*, 272.

(19) Reference 13, p 97.

(20) McCullough, J. J.; Manning, C. *J. Org. Chem.* **1978**, *43*, 2839.

Model 481 LC spectrophotometer. Cyclohexane solvent for photolyses was prepared by scrubbing with 20% fuming sulfuric acid followed by washing with 10% aqueous sodium hydroxide, drying ($MgSO_4$), and finally distilling from calcium hydride. The sensitizer *p*-(dimethylamino)benzophenone was recrystallized (after sublimation) prior to use.

General Procedures for Preparative Photolyses. The apparatus consisted of a 450-W Hanovia medium-pressure mercury arc surrounded by a water-cooled quartz immersion well. Unless otherwise stated, the light was filtered through either a cylindrical sleeve of Pyrex, or Corex, or an aqueous lead nitrate solution (1 g of $Pb(NO_3)_2$ and 100 g of NaBr in 1 L of water; transmittance was 0% below 318 nm) contained in a concentric filter jacket (10-mm path length). Three types of sample cell were used. Cell A (200-mL sample volume) consisted of a cylindrical collar (Pyrex) that surrounded the aqueous filter jacket. Cell A was fitted with gas inlet and exit ports, and sample solutions were purged with argon prior to and during irradiations. Cell B (35-mL sample volume) and cell C (3.5 mL) were a quartz test-tube-like vessel and a quartz cuvette, respectively; sample solutions contained therein were deoxygenated by flushing with argon and sealed under a positive pressure; the solutions were magnetically stirred throughout the course of the irradiations.

Preparation of Triene 11. 4-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (11) was made by a modification of the previously described method.[2] A solution of 178.9 mg (1.00 mmol) of COT **10**[11] in 200 mL of cyclohexane was photolyzed at >318 nm for 14 h in Cell A. The photolysate was concentrated and chromatographed on a Lobar column (2% ether–hexane). Three bands were observed. The first band contained 1.5 mg (7%) of triene 11: mp 74–76 °C (from hexane; lit.[2] mp 74–76 °C); ^1H NMR (400 MHz; $CDCl_3$) δ 7.52 (m, 1 H, 1 aromatic), 7.27 (m, 2 H, 2 aromatics), 7.13 (m, 1 H, 1 aromatic), 6.76 (d, 1 H, H-5, $J_{5,6}$ = 4.5), 6.11 (br d, 1 H, H-7, $J_{7,8}$ = 2.5), 6.07 (br d, 1 H, H-8, $J_{8,7}$ = 2.5), 4.17 (d, 1 H, H-1, $J_{1,6}$ = 4.5), and 3.79 (t, 1 H, H-6, $J_{6,5}$ = $J_{6,1}$ = 4.5); note that the assignments of H-7 and H-8 have been reversed from the original designations.[2] The second band contained 60.8 mg (34%) of recovered COT **10**. The third band gave 87.7 mg (49%) of triene 1, mp 65–67 °C (from hexane; lit.[2] mp 65–67 °C).

Thermolysis of Triene 11. A solution of 13.9 mg (0.078 mmol) of 11 in 3 mL of *n*-nonane was refluxed (ca. 150 °C) for 2 h. The thermolysis product was chromatographed on silica gel 60 (0.9 cm × 10 cm; 5% ether–cyclohexane). Crystallization of the main band from hexane gave 1.9 mg (93%) of COT 10; mp 66–68 °C (lit.[11] mp 66–68 °C); ^1H NMR (400 MHz; $CDCl_3$) δ 7.24–7.37 (m, 3 H, aromatics), 6.99–7.05 (m, 1 H, aromatic), 6.90 (d, 1 H, H-6, $J_{6,7}$ = 4.5), 6.65 (d, 1 H, H-10, $J_{10,9}$ = 11.5), 6.03–6.09 (m, 2 H, H-8 and H-9), and 5.91 (dd, 1 H, H-7, $J_{7,6}$ = 4.5, $J_{7,8}$ = 11.5); previously the NMR spectrum was reported[11] at 100 MHz in CCl_4.

Direct Irradiation of Triene 11. A solution of 24.6 mg (0.14 mmol) of 11 and 4.6 mg of tetradecane (GC standard) in 25 mL of cyclohexane was irradiated (Pyrex filter) for 2 h in Cell B. Analytical yields for the photolysate components were ca. 0.1 mg (ca. 0.5%) of 1-cyanonaphthalene, 5.3 mg (22%) of COT 10, 11.8 mg (48%) of SB 12, and 5.8 mg (24%) of triene 11, as determined by GC (and NMR) peak areas relative to those of the calibrated tetradecane internal standard. The photolysate was concentrated and chromatographed on silica gel 60 (0.9 cm × 22 cm; 2% ether–hexane). The first band eluted was a trace of 1-cyanonaphthalene (identified by GC and TLC comparison with an authentic sample). The second band was a mixture of COT 10 and triene 11. The third band contained SB 12 of GC purity >98% (note: SB 12 rapidly polymerizes when solvent free): mass spectrum (from GC/MS) showed *m/e* at 179 (65, M^+), 178 (base peak); $C_{13}H_9N$ requires 179; ^1H NMR (250 MHz; $CDCl_3$) see Table I; the proton assignments were confirmed by spin decoupling experiments; ^{13}C NMR (62.9 MHz; $CDCl_3$) δ 50.0, 51.9, 54.02, 53.97, 119.2, 120.1, 121.7, 125.1, 127.3, 127.3, 139.0, and 148.6 (one C missing).

The second band was rechromatographed on a Lobar column (2% ether–hexane) to give 4.2 mg (17%) of recovered triene 11 and 4.3 mg (17%) of COT 10, mp 66–68 °C (from hexane).

Diimide Reduction of SB 12. To a stirred mixture of ca. 12 mg (0.067 mmol) of 12 and 584 mg (3.04 mmol) of potassium azodicarboxylate in 10 mL of dioxane at room temperature was added a 0.25-mL quantity of acetic acid in one portion. The mixture was stirred during 2.5 h and then added to 40 mL of toluene and washed with 10% sodium carbonate solution (20 mL) followed by water (2 × 75 mL). The toluene extract was dried ($MgSO_4$) and concentrated and the residue chromatographed on a Lobar column (1% ethyl acetate–79% hexane–20% toluene). Short-path distillation (60 °C (0.1 Torr)) of the contents of the main band gave 9.1 mg (76%) of 2-cyanobenzotricyclo[3.3.0.0^{2,8}]oct-3-ene (14) as a colorless oil: IR (film) 2236 cm^{-1} (C≡N); UV (hexane): 257 sh (340), 253 (520), 270 (750), and 277 (810); ^1H NMR (400 MHz, $CDCl_3$) see Table II; the proton assignments were confirmed by spin decoupling experiments; ^{13}C NMR (62.9 MHz; $CDCl_3$) δ 22.8, 29.1, 39.4, 43.1, 46.9, 48.5, 119.9, 123.4, 123.5, 126.3, 127.6, 136.1, and 147.2; mass spectrum showed *m/e* at 181.0886 (100, M^+); $C_{13}H_{11}N$ requires 181.0892. Anal. Calcd for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73. Found: C, 85.78; H, 6.12; N, 7.69.

Sensitized Irradiation of Triene 11. A solution of 21.6 mg (0.120 mmol) of 10, 8.0 mg of tetradecane (GC standard), and 9.4 mg (0.042 mmol) of *p*-(dimethylamino)benzophenone in 20 mL of cyclohexane was irradiated for 10 min in Cell B, with light filtered through a WG 360 glass (Schott) filter. Analytical yields for the photolysate components were 0.33 mg (1.5%) of 1-cyanonaphthalene, 1.4 mg (6.5%) of COT 10, 4.6 mg (21%) of SB 12, and 6.5 mg (30%) of unreacted triene 11, as determined by GC (and NMR) peak areas relative to those of the calibrated tetradecane internal standard. The photolysate was concentrated to ca. 5 mL and chromatographed on silica gel 60 (0.9 cm × 22 cm; 2% ether–hexane). The first band eluted was a trace of 1-cyanonaphthalene (identified by GC and TLC comparison with an authentic sample). The second band was a mixture of COT 10 and triene 11. The third band contained the SB 12 (GC purity >98%).

The second band was rechromatographed on a Lobar column (2% ether–hexane) to give 5.1 mg (24%) of recovered triene 11 and 0.9 mg (4%) of COT 10, mp 65–67 °C (from hexane).

Labeled COT 10a. Deuterated COT 10a, a mixture consisting of an equal amount of two singly labeled isomers, one incorporating ca. 90%-d_1 at C-9 (COT 10i) and other ca. 90%-d_1 at C-7 (COT 10ii), was obtained as previously described:[11] ^1H NMR (400 MHz; $CDCl_3$) δ 7.24–7.36 (m, 3.90 H, 3 aromatics + residual $CHCl_3$), 6.99–7.04 (m, 1.00 H, 1 aromatic), 6.89–6.92 (m, 0.96 H, H-6), 6.65 (overlapping s and d, 0.98 H, H-10; $J_{10,9}$ = 11.5), 6.03–6.09 (m, 1.52 H, H-8 and residual H-9), and 5.91 (dd, 0.53 H, residual H-7; $J_{7,6}$ = 4.5, $J_{7,8}$ = 11.5). Integrations for 10a and for all subsequent deuterium-labeled compounds were normalized by assigning integer values to one or more aromatic proton signals, unless otherwise stated; integration errors are estimated to be within ca. ±0.05 H.

Labeled Triene 11a from COT 10a. A solution of 145.7 mg (0.81 mmol) of COT 10a in 200 mL of cyclohexane was photolyzed at >318 nm for 12 h in Cell A. The photolysate was worked up as in the case of the direct irradiation of unlabeled COT 10 to give 8.7 mg (6%) of triene 11a: ^1H NMR (400 MHz; $CDCl_3$) δ 7.52 (m, 1.00 H, 1 aromatic), 7.27 (m, 5.17 H, 2 aromatics + residual $CHCl_3$), 7.13 (m, 1.00 H, 1 aromatic), 6.76 (m, 1.00 H, H-5), 6.11 (m, 1.00 H, H-7), 6.07 (br d, 0.54 H, H-8; $J_{7,8}$ = 2.5), 4.17 (m, 1.03 H, H-1), and 3.79 (t, 0.56 H, H-6, $J_{6,5}$ = $J_{6,1}$ = 4.5).

Direct Irradiation of Triene 11a. A solution of 14.3 mg (0.080 mmol) of triene 11a and 4.1 mg of tetradecane (GC standard) in 10 mL of cyclohexane was divided into three equal volumes, and each was separately irradiated (Pyrex filter) for 5 h in Cell C (67% conversion by GC/NMR). The photolysates were worked up as in the case of the direct irradiation of unlabeled triene 11 to give 1.9 mg (13%) of COT 10a [^1H NMR (400 MHz; $CDCl_3$) δ 7.24–7.36 (m, integration not determined, 3 aromatics + residual $CHCl_3$), 6.99–7.04 (m, 1.00 H, 1 aromatic), 6.89–6.92 (m, 0.97 H, H-6), 6.65 (overlapping s and d, 1.01 H, H-10; $J_{10,9}$ = 11.5), 6.03–6.09 (m, 1.50 H, H-8 and residual H-9), and 5.91 (dd, 0.59 H, residual H-7; $J_{7,6}$ = 4.5, $J_{7,8}$ = 11.5)], 3.5 mg (24%) of recovered triene 11a [^1H NMR (400 MHz; $CDCl_3$) δ 7.52 (m, 1.00 H, 1 aromatic), 7.27 (m, 3.34 H, 2 aromatics + residual $CHCl_3$), 7.13 (m, 1.00 H, 1 aromatic), 6.76 (m, 0.98 H, H-5), 6.11 (m, 0.99 H, H-7), 6.07 (br d, 0.51 H, H-8; $J_{7,8}$ = 2.5), 4.17 (m, 1.01 H, H-1), and 3.79 (t, 0.52 H, H-6, $J_{6,5}$ = $J_{6,1}$ = 4.5)], and SB 12a (a residue of 4.5 mg of material was recovered from NMR sample) [^1H NMR (250 MHz; $CDCl_3$)

δ 7.10–7.56 (m, integration not determined, 3 aromatics + residual $CHCl_3$), 7.05–7.10 (m, 1.00 H, 1 aromatic), 5.73 (dd, 0.53 H, H-6, $J_{6,5} = 2.5$, $J_{6,7} = 5$), 5.26 (m, 0.95 H, H-7), 4.07 (m, 1.00 H, H-5), 3.80 (m, 0.99 H, H-1), 3.43 (dd, 0.59 H, H-8, $J_{8,1} = 6$, $J_{8,7} = 2.5$).

Sensitized Irradiation of Triene 11a. A solution of 21.0 mg (0.12 mmol) of **11a**, 12.7 mg (0.055 mmol) of *p*-(dimethylamino)benzophenone, and 4.0 mg of tetradecane (GC standard) in 20 mL of cyclohexane was divided into two equal portions, and each was separately irradiated for 10 min in Cell B with light filtered through a WG-360 glass (Schott) filter (70% conversion by GC/NMR). The photolysates were worked up as in the case of the sensitized irradiation of unlabeled triene **11** to give 1.1 mg (5%) of COT **10a** [^1H NMR (400 MHz; $CDCl_3$) δ 7.24–7.36 (m, integration not determined, 3 aromatics + residual $CHCl_3$), 6.99–7.05 (m, 1.00 H, 1 aromatic), 6.89–6.92 (m, 0.99 H, H-6), 6.65 (overlapping s and d, 0.95 H, H-10; $J_{10,9} = 11.5$), 6.03–6.09 (m, 1.51 H, H-8 and residual H-9), and 5.91 (dd, 0.55 H, residual H-7, $J_{7,6} = 4.5$, $J_{7,8} = 11.5$)], 6.1 mg (28%) of recovered triene **11a** [^1H NMR (400 MHz; $CDCl_3$) δ 7.52 (m, 1.00 H, 1 aromatic), 7.27 (m, integration not determined, 2 aromatics + residual $CHCl_3$), 7.13 (m, 1.00 H, 1 aromatic), 6.76 (m, 0.95 H, H-5), 6.11 (m, 0.96 H, H-7), 6.07 (br d, 0.49 H, H-8; $J_{7,8} = 2.5$), 4.17 (m, 0.99 H, H-1), and 3.79 (t, 0.53 H, H-6, $J_{6,5} = J_{6,1} = 4.5$)], and SB **12a** (a residue of 3.2 mg of material was recovered from NMR sample) [^1H NMR (250 MHz; $CDCl_3$) δ 7.10–7.56 (m, 3.90 H, 3 aromatics + residual $CHCl_3$), 7.05–7.10 (m, 1.00 H, 1 aromatic), 5.73 (dd, 0.52 H, H-6, $J_{6,5} = 2.5$, $J_{6,7} = 5$), 5.26 (m, 0.96 H, H-7), 4.07 (m, 1.01 H, H-5), 3.80 (t, 0.52 H, H-1, $J_{1,5} = J_{1,8} = 6$), 3.43 (m, 1.01 H, H-8).

Quantum Yield Determinations. Quantum yields were performed on an apparatus previously described,[21] which includes an optical bench arranged for beam splitting into a ferrioxalate actinometer.[22] Cyclohexane solutions (3.5 mL) of reactants (ca. (4.5–6.5) × 10^{-3} M) and sensitizer, if any (*p*-(dimethylamino)benzophenone, ca. 1.0 × 10^{-3} M), were deoxygenated prior to irradiation by flushing with argon. A positive pressure of argon was maintained over the stirred solutions throughout the course of the irradiations. The quantum yields (Φ's) were obtained from several runs extrapolated to zero conversion. Product analyses were determined by a combination of GC (internal tetradecane standard) and HPLC (for the determination of relative amounts of COT **10** and triene **11**). The HPLC analyses were performed on a normal-phase 16-μm silica column (Waters, μ Porasil, 3.9 mm × 300 mm). The eluting solvent system was 1% ethyl acetate in hexane. Photometric detection was carried out at 300 nm, chromatograms were integrated using a Waters 740 Data Module, and relative detector responses were calibrated against known mixtures of COT **10** and triene **11**. For the direct irradiation of triene **11**, light of wavelength 280 nm was used. For sensitized runs with *p*-(dimethylamino)benzophenone, the sensitizer absorbed >95% of the incident light (366 nm) employed.

Acknowledgment. We thank the Spectroscopic Services Laboratory of the University of Alberta (U. of A.) and the Agriculture Canada Research Station at Lethbridge for the 400-MHz NMR. The U. of A. is also thanked for the precision mass spectra. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

---

(21) Bender, C. O.; Bengtson, D. L.; Dolman, D.; Herle, C. E. L.; O'Shea, S. F. *Can. J. Chem.* **1982**, *60*, 1942.

(22) (a) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London*, **1956**, Ser. A, 235, 518. (b) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2334.

Stereochemistry of Photocycloaddition of (*E*)-1,2-Dicyano- and (*Z*)-1,2-Diethoxyethylene to 5-Substituted Adamantanones

Wen-Sheng Chung,[†,‡] Nicholas J. Turro,[*,‡] Sushil Srivastava,[§] and William J. le Noble[*,§]

Department of Chemistry, Columbia University, New York, New York 10027, and State University of New York, Stony Brook, New York 11794

Received February 26, 1991

The photocycloaddition of olefins to 5-substituted adamantanones produces two geometrically isomeric oxetanes in which the oxygen atom and the 5-substituent are in anti or syn positions. The substituent was varied from fluoro, chloro, bromo, hydroxyl, and phenyl to *tert*-butyl. Although the mechanisms of the reaction with electron-rich and electron-poor olefins are quite different, the product ratios are similar (~60:40) in all instances. The preference of product formation from the attack on the *zu* face is discussed in terms of transition-state hyperconjugation.

Introduction

5-Substituted adamantanones **1-X** and their derivatives have proved to be useful probes in research aimed at understanding the electronic factors in face selection. The advantages to their use include the presence of two virtually isosteric faces, the absence of conformational uncertainty, the possibility of forming only two geometrically isomeric products, and the ease of handling the (usually) solid products. Almost any reaction involving interconversions between trigonal and tetragonal carbon can be examined by means of them,[1] and a generalization has emerged that the new bond preferentially forms at that face that leaves it antiperiplanar to the most electron-rich vicinal bond(s). This notion, that delocalization of the electrons comprising these bonds into the σ* component of the incipient one stabilizes the transition state, was first proposed by Cieplak[2] in 1981 to account for the well-known propensity of nucleophiles to attack the axial face of cyclohexanones.

We reported[3] recently in a preliminary paper that the concerted (if not synchronous) photocycloaddition of the electron-poor olefin (*E*)-1,2-dicyanoethylene (**2**) to 5-sub-

---

[†] Present address: Department of Chemistry, Yale University, New Haven, CT 06511.

[‡] Columbia University.

[§] State University of New York.

(1) For a summary of earlier studies and references, see: Bodepudi, V.; le Noble, W. J. *J. Org. Chem.* **1991**, *56*, 2001.

(2) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.

(3) Chung, W.-S.; Turro, N. J.; Srivastava, S.; Li, H.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7882.