iodide (100 μL, 1.606 mmol). After 60 min at 0 °C, hydrogen peroxide (30%, 0.5 mL) and aqueous sodium hydroxide (3 M, 0.5 mL) were added, and stirring was continued for 15 min prior to dilution with ether and water. The aqueous phase was extracted with ether, and the combined organic layers were washed with 10% hydrochloric acid and saturated sodium bicarbonate solution prior to drying. Concentration left an oil that was purified by MPLC on silica gel (elution with 3% ethyl acetate in petroleum ether) to give 81 mg (56%) of **10b** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.12–2.05 (m, 1 H), 1.86–1.18 (series of m, 12 H), 1.05 (d, J = 7.1 Hz, 3 H), 1.032 (s, 3 H), 0.97 (d, J = 6.1 Hz, 3 H); m/z calcd (M^+) 206.1671, obsd 206.1674; $[\alpha]^{24}_D$ +23.6° (c 4.9, $CHCl_3$).

(−)-Silphiperfol-6-ene (1). Methyllithium (330 μL of 1.19 M in ether, 0.39 mmol) was added to a solution of **10b** (54 mg, 0.262 mmol) in dry tetrahydrofuran (10 mL) at −78 °C. After 1 h, saturated ammonium chloride solution (2 mL) was added, and the resulting mixture was allowed to warm to room temperature. Concentration in vacuo afforded a residue that was diluted with water and extracted with ethyl acetate. The combined extracts were washed with brine, dried, and evaporated to furnish 55 mg (94%) of the tertiary alcohol: ^{1}H NMR ($CDCl_3$) δ 2.06–1.03 (series of m, 14 H), 1.03 (s, 3 H), 0.99 (d, J = 6.6 Hz, 3 H), 0.98 (s, 3 H), 0.87 (d, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) ppm 82.6, 69.9, 55.6, 47.3, 46.2, 44.0, 42.7, 42.1, 35.7, 31.0, 28.8, 25.9, 20.3, 19.2, 13.6; m/z calcd (M^+) 222.1984, obsd 222.1955; $[\alpha]^{27}_D$ −7.2° (c 16.0, $CHCl_3$).

Freshly distilled phosphorus oxychloride (41 μL, 0.440 mmol) was added to a solution of the above alcohol (73 mg, 0.328 mmol) in dry pyridine (2 mL), and the resulting mixture was stirred at room temperature for 3 days. Ice water (50 mL) was added, and the product was extracted into pentane (4 × 25 mL). The combined extracts were washed with 10% hydrochloric acid (3 × 15 mL), saturated sodium bicarbonate solution (15 mL), and brine (15 mL) prior to drying. Concentration in vacuo gave a yellow oil, which was purified by chromatography on silica gel (pentane elution). There was isolated 45 mg (67%) of (−)-**1**. Elution with ethyl acetate returned 16 mg of unreacted alcohol. The corrected yield of silphiperfol-6-ene is therefore 86%: IR ($CDCl_3$, cm^{-1}) 1450, 1380; ^{1}H NMR ($CDCl_3$) δ 2.20 and 1.95 (ABd, J = 16 Hz, 2 H), 1.9–1.1 (series of m, 12 H), 1.54 (m, 3 H), 1.52 (m, 3 H), 0.99 (s, 3 H), 0.96 (d, J = 6.5 Hz, 3 H); m/z calcd (M^+) 204.1878, obsd 204.1903; $[\alpha]^{23}_D$ −34.2° (c 3.05, $CHCl_3$).

Acknowledgment. We are pleased to acknowledge the support of this investigation by the National Institutes of Health through Grant GM-28468.

Registry No. 1, 74284-56-3; **2**, 77887-60-6; **4a**, 92269-51-7; **4b**, 92269-52-8; **5** (isomer 1), 92269-53-9; **5** (isomer 2), 92269-54-0; **6** (isomer 1), 92269-55-1; **6** (isomer 2), 92418-26-3; **7**, 92269-56-2; **8**, 92269-57-3; **9**, 92269-58-4; **10a**, 92269-59-5; **10b**, 92269-60-8; $CH_3CH_2C(=CH_2)CH_2OTs$, 92269-61-9; 2-(2-bromoethyl)-1,3-dioxane, 33884-43-4; 2-ethyl-2-propen-1-ol, 4435-54-5; methyl 2,4,5,6-tetrahydro-1,4-dimethyl-2-oxo-3a(3*H*)-pentalenecarboxylate, 92269-62-0; 1,3a,4,6a-octahydro-1,4-dimethylpentalene, 92269-63-1.

Effective Control of Regioselectivity by a Bridgehead Substituent in the Di-π-methane Rearrangement of Dibenzobarrelenes and Benzonorbornadienes

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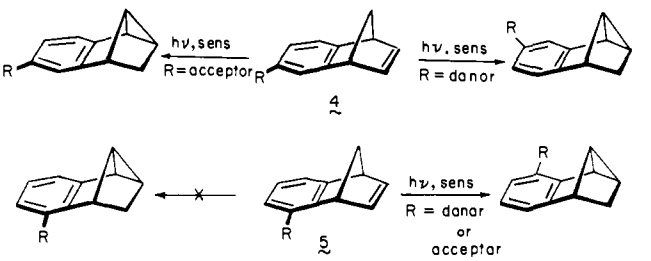
Abstract: The triplet-state photoisomerizations of eight bridgehead monosubstituted benzonorbornadienes are described. Six of the examples underwent di-π-methane rearrangement with a highly regioselective or fully regiospecific preference for proximal bond reorganization. In the bromo example, a 50:50 distribution of the two possible photoisomers was observed. When the substituent group was deuterium, a substantial preference for distal rebonding was encountered (k_H/k_D = 1.27). This finding prompted a companion investigation of two benzobarrelenes isotopically substituted at one of their bridgehead sites. The k_H/k_D values noted for the last two substrates are of comparable magnitude and in the same direction. A synopsis of the regiochemical consequences of bridgehead substitution in various doubly channeled di-π-methane substrates reveals the existence of two entirely different preferred reaction modes. This is taken to be a reflection of the operation of two different mechanistic pathways involving product-determinative aryl–vinyl bridging on the one hand and direct 1,2-aryl migration on the other.

The present investigation was initiated with the idea of studying the role of a functional group on the bridgehead carbon of benzonorbornadiene where this substituent is varied in its effective ability to withdraw or donate electron density. Because the ring system is a dual-channel di-π-methane substrate having two competitive isomerization pathways open to fit, the controlling effect of the R group in **1** following triplet sensitization can be easily determined by simple ^{1}H analysis of the **2**/**3** ratio.

1 **2** **3**

This interest was prompted by previous investigations involving meta- (**4**)[1] and ortho-substituted derivatives (**5**)[2] which revealed that electronic perturbation of aryl sites exerts a major impact on the product-forming steps of the rearrangement. Dramatic



4 **5**

regioselectivities have also been noted when the vinyl double bond is forced to carry a cyano[3] or methyl group.[4] Because of its role

(1) (a) Paquette, L. A.; Cottrell, D. M.; Snow, R. A.; Gifkins, K. B.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 3275. (b) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *Ibid.* **1977**, *99*, 3723. (c) Hahn, R. C.; Johnson, R. P. *Ibid.* **1977**, *99*, 1508.

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as a moderate controller of excited-state regioselectivity, vinyl methyl has proven to be a useful probe of these reactions and has allowed additivity effects to surface in a number of examples.[4]

Whereas the regioselectivities encountered in our earlier work conform in direction to vacant orbital energies and shapes existing in the starting material, as calculated by STO-3G procedures,[2,3,5] a comparable analysis cannot be applied to **1** because the R group is too remote from and orthogonal to the π clouds of the aromatic ring and norbornene double bond to exert a significant impact.

Eight 1-substituted benzonorbornadienes were chosen for study. Additionally, the observation of a substantial excited-state deuterium isotope effect with the 1-deuterio derivative prompted a companion investigation of two benzobarrelenes isotopically substituted at one of their bridgehead sites. It quickly became apparent that the k_H/k_D values for these systems were of comparable magnitude and in the same direction, and therefore pertinent.[6]

Results

Synthetic Considerations. 1-Methyl- (**1f**) and 1-(trimethylsilyl)benzonorbornadiene (**1d**) were prepared by adding benzyne to the appropriate cyclopentadiene.[7] Access to the remaining substrates was conveniently achieved by conversion of the known 1-bromo derivative (**1g**)[8] to its Grignard reagent followed by reaction with a suitable electrophile. Addition of cyanogen[9] and *tert*-butyl perbenzoate[10] resulted in direct formation of **1a** and **1c**, respectively. The carbomethoxy derivative **1b** was obtained by sequential addition of gaseous carbon dioxide and ethereal diazomethane. To arrive at **1e**, advantage was taken of amination with methoxyamine followed by acetylation.[11] Quenching of a tetrahydrofuran-d_8 solution of the Grignard with 100% deuterium oxide resulted in 80% d_1 incorporation (^{1}H NMR integration). When the same reaction was performed in unlabeled solvent, the extent of isotope incorporation dropped to 25%.

By use of literature precedent concerned with the all-protio example,[12] Diels–Alder cycloaddition of dimethyl acetylenedicarboxylate to anthracene-*9-d* (**6**) delivered **7**. Dibenzobarrelene **10** was prepared by analogous cycloaddition to *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene to **6** and subsequent treatment of the adduct mixture (**8**/**9**) with tetra-*n*-butylammonium fluoride in hot tetrahydrofuran.[13]

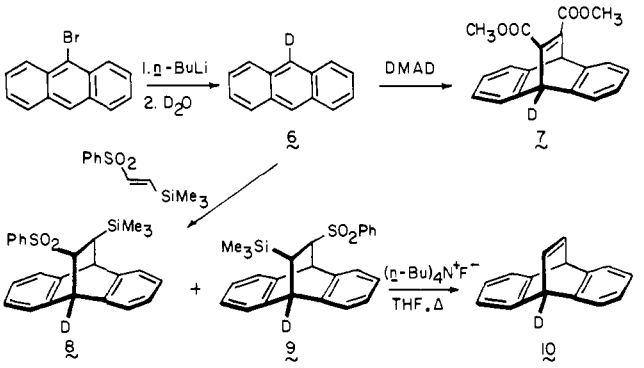

Table I. Photorearrangement Product Ratios for 1-Substituted Benzonorbornadienes (**1**)

R	2,[a] %	3,[a] %
1a, CN	100	0
1b, $COOCH_3$	100	0
1c, $OC(CH_3)_3$	100	0
1d, $Si(CH_3)_3$	100	0
1e, $NHCOCH_3$[b]	100	0
1f, CH_3	90	10
1g, Br	50	50
1h, D	44	56

[a] The limits of detection are considered to be ±3% except in the case of **1h** where it is ±0.4%. [b] An unidentified byproduct is formed in this instance (see text).

Photoisomerization of the Benzonorbornadienes. For the sake of standardization and to guarantee reaction via the respective T_1 states,[14] recourse was again made to irradiation of dilute benzene solutions containing acetophenone (E_T 73.6 kcal/mol) with a 3500-Å light source. These conditions proved adequate to discount absorption by starting material and photoproduct(s) of most of the incident radiation. In all cases, the isomerizations were rapid (complete within 20–40 min) and essentially quantitative.

When the 1-cyano derivative **1a** was treated under these conditions, a single photoproduct resulted. The conformationally rigid network of multiply fused three-, four-, five-, and six-membered rings that comprises the tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1-(7),8,10-triene ring system generates well-defined dihedral angle relationships among the aliphatic protons. Additionally, very characteristic chemical shifts are exhibited by each tetrahedrally bound proton. In the present circumstances, the cyano group must be located at C-4 as in **2** or at C-6 as in **3**. One or the other of these easily distinguished protons must therefore be lacking. That **2a** was indeed formed follows from the absence of H-4 while all the other anticipated coupling constants persist (see Experimental Section).

When **1b**, **1c**, and **1d** were comparably irradiated, the photoisomerizations were again noted to be regiospecific (Table I). ^{1}H NMR spectral data revealed clearly that the carbomethoxy, *tert*-butoxy, and trimethylsilyl substituents were uniformly bonded to the C-4 cyclopropane carbon. Further substantiation of the common structural relationship to **2a** was derived from the ^{13}C NMR spectra.

Turning attention to **1e**, we noted that **2e** formed as rapidly as in the preceding examples. However, a second substance, which at times constituted as much as 25% of the reaction mixture, was formed concurrently. Unfortunately, chromatographic separation could not be achieved. In the ^{1}H NMR spectrum, the superimposed signals attributable to this byproduct revealed it to be structurally allied to **2e**. However, we have avoided categorizing the compound as **3e** because at least one proton absorption anticipated for this photoisomer is unquestionably lacking. Therefore, its structure remains yet an open question.

Sensitized irradiation of 1-methylbenzonorbornadiene (**1f**) afforded a product mixture which could not be separated gas chromatographically. However, its ^{1}H NMR spectrum clearly revealed the presence of two photoisomers. By relative integration of the well-separated (except for the aryl region) pairs of signals, the product composition was determined to be 90:10, the major component being **2f**. Once again, the reduced capability of a methyl group to control regioselectivity was made evident, although a substantial propensity for proceeding to the 4-isomer still persists.

The excited-state bonding preference for the 1-bromo derivative **1g** was next assessed. In this instance, the two possible products were formed in equal amounts. Although separation was again

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not achieved, unequivocal assignment was possible by virtue of the exceptional clarity of the ^1H NMR spectrum (see Experimental Section). We consider the lack of regioselectivity to arise from the heavy atom effect of the bromine substituent or its intrinsic inability to stabilize carbon-centered radicals.

Excited-State Deuterium Isotope Effects. The first of the monodeuterated examples to be studied was **1h**. Here product formation is controlled only by the direct involvement of the D- or H-substituted bridgehead carbon atoms as the aryl ring undergoes migration. If one reaction channel is preferred and this fractionation occurs at or before the rate-determining step, isotope effects differing from unity can be expected. Following standard irradiation of this hydrocarbon, intact photoisomerization mixtures from several runs were individually analyzed by proton-decoupled ^2H NMR spectroscopy. Repeated integration showed the signal at 2.21 ppm due to **2h** to dominate over that due to **3h** at 3.58 ppm by the ratio of 56:44 (±0.4%).

The photoinduced rearrangement of **1h** was also performed in a 10000-G magnetic field in order to investigate possible magnetic effects[15] on the regioselectivity of this di-π-methane reaction. From the outset, we anticipated the possibility of observing an effect to be small. This is because the magnitude of the $^1S_0 \rightarrow {}^1T_0$ gap in diradicals that might be generated from **1h**, although unknown, should be large, at least several times the hyperfine splitting available at this field strength. Consequently, hyperfine-induced intersystem crossing should be minimal. In line with this analysis, no alteration in the k_H/k_D value of 1.27 was observed.

A 1.15:1 mixture of **11a** and **12a** resulted from acetone-sensitized irradiation of dibenzobarrelene **7**. Once again, the distribution of photoisomers was neatly unraveled by appropriate integration of the two deuterium signals at 4.3, and 3.73 ppm, respectively. Analogous handling of **10** was seen to produce **11b** (3.78 ppm) and **12b** in a ratio of 1.11:1.

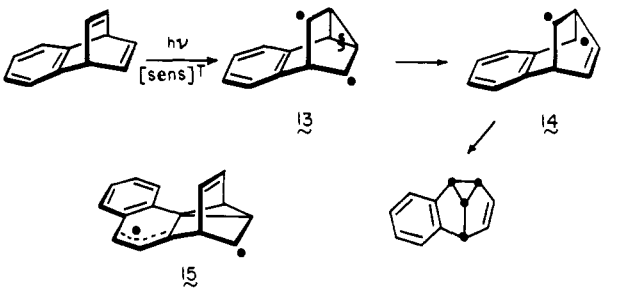
11 **12**

a, R = $COOCH_3$ b, R = H

Discussion

Our results reveal the importance of considering the environment of the central carbon, more specifically here the bridgehead carbon, of a di-π-methane moiety and point to the existence of several controlling factors in addition to those previously considered to contribute to the regioselectivity of these photoisomerizations.[16]

Mechanistic Options in Doubly Connected Di-π-methane Systems. By means of a series of elegant deuterium labeling studies, Zimmerman and his co-workers showed that, like the parent barrelene molecule itself,[17] benzobarrelene,[18] 2,3-naphthobarrelene,[19] 2,3-anthrabarrelene,[20] and 5,12-dihydro-2,3-naphthacenobarrelene[21] uniformly undergo triplet-sensitized di-π-methane photorearrangement via initial vinyl–vinyl bridging. Arrival at the semibullvalene product was formulated as proceeding via a stepwise mechanism involving rearrangement of first-formed biradical **13** to **14** prior to carbon–carbon bond formation. The preferential generation of **13** and like cyclopropyldicarbinyl diradicals was explained in terms of the greater

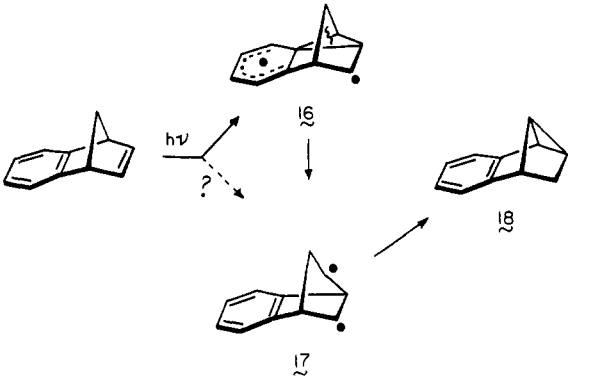


13 **14** **15**

energy minimization realized upon interaction between the pair of vinyl chromophores. Thus, while the original excitation energy resides most heavily in the aryl group of the starting material, this segment of the molecule has no further involvement in the bond reorganization.

An exception to this general phenomenon was noted in the case of 1,2-naphthobarrelene.[19] A priori, this unsymmetrical substrate in its triplet excited state can partition itself among three reaction channels. Of these, 1-naphtho to vinyl migration is followed preferentially. It was assumed that bridging as in **15** was involved. The intermediacy of **15** adapted itself well to the hypothetical energetic arguments advanced at the time.

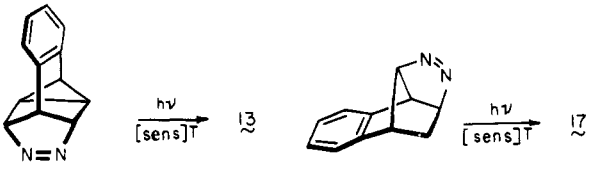
A few years earlier, Edman disclosed that benzonorbornadiene similarly rearranges from its triplet state to give **18**.[14] Invoking



16 **18** **17**

analogy, he advanced biradicals **16** and **17** as sequential precursors of **18**. Benzonorbornadiene has no vinyl–vinyl bridging option open to it. However, neither the possibility of direct 1,2-aryl migration nor of reversibility at any step was considered.

Independent Generation of the More Advanced Cyclopropyldicarbinyl Diradicals. In the mid-1970s, Zimmerman demonstrated that the denitrogenation of azoalkanes such as **19** provides an alternative entry point into the diradical manifold of barrelene photochemistry.[22] Similar observations were made by Adam and DeLucchi[23] who also demonstrated that **20** serves as a mechanistic



19 **13** **20** **17**

probe of the potentially more complex photochemistry of benzonorbornadiene.[24] Upon excitation of either the (n,π*) azo chromophore or the (π,π*) benzene chromophore of **20**, only 1–4% of so-called di-π-methane reversion was noted. Speculation followed that the quite small levels of benzonorbornadiene that

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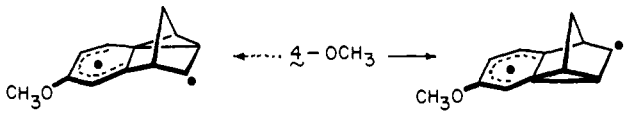
were produced arose from a vibrationally excited ("hot") singlet state form of **17**. For all practical purposes, therefore, arrival at **17** very likely constitutes an irreversible commitment to photoproduct generation.

We hasten to point out that the valuable information garnered about the chemical reactivity of **17** has revealed essentially nothing concerning the possible involvement of **16**. Is **16** a necessary prerequisite to **17** on the excited state manifold interconnecting benzonorbornadiene with **18**, or may the latter result from a direct 1,2-aryl migration? If **16** is indeed the first-formed diradical, is it capable of readily equilibrating with its progenitor molecule?

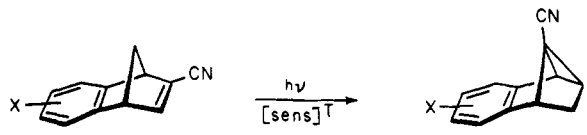
Regiochemical Consequences of Aryl and Vinyl Substitution of the Benzonorbornadiene Nucleus. The preceding mechanistic concerns caused us first to examine the role of polar substituent influence on the regiochemical outcome of triplet-state benzonorbornadiene photoisomerizations. Dramatic changes in preferred rearrangement pathways were immediately noted when meta substituents were appended as in **4**.[1] Perhaps the most significant observation was that the anisole derivative (**4**-OCH_3) proceeds to give only that product having the aryl group para to the cyclopropane moiety. Adherence to the Zimmerman mechanistic hypothesis would consequently necessitate that the less stable meta-bridged benzo vinyl diradical (viz., **22**) be formed preferentially. Ortho substituents exerted similarly large directive effects, although all were now in the *same* direction.[2]



21 22

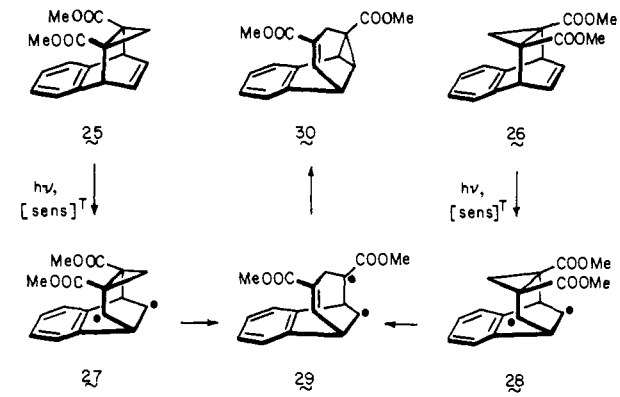
Although bond-making and bond-breaking steps necessarily operate in these processes, it must be recognized that only the overall result can be directly evaluated. Hahn and Johnson[1c] concluded in their later study of **4**-NO_2 that the aryl bridging step is the source of the regiospecific involvement of the para carbon. No quantitative support was offered for this opinion which is also shared by Zimmerman.[16] A qualitative molecular orbital model for bridging regioselectivity was introduced at roughly the same time by Santiago and Houk,[5] supported by photoelectron spectroscopic data,[25] and subsequently applied rather broadly.[2,3]

When a vinyl cyano substituent was observed to overhelm the directionality of the di-π-methane rearrangement of **23** irrespective of the nature of X,[13,26] the controlling influence of a vinyl methyl group was next examined.[4] In many though not all cases, the product ratios fell within experimental error of those calculated on the basis of perfect substituent additivity effects culled from the unsubstituted 2-methyl derivative, **4**, and **5**. These findings lent added credence to the theoretical notion that donor–acceptor interactions in the relevant frontier orbital may be important to the overall regiochemistry picture. Zimmerman has previously state that "it is necessary to note that the structures drawn are approximations of species along the reaction coordinate and are not necessarily intermediates (i.e., energy minima). These may simply be points on the energy hypersurface leading from excited state of reactant to product ground state, and each case must be considered separately."[16,17] Despite this disclaimer, however, bridged biradicals have been repeatedly invoked as central intermediates in the di-π-methane process.



23 24

From our viewpoint, more explicit unraveling of the detailed mechanistic picture remained to be achieved. It bears repeating here that little doubt surrounds the involvement of **17** and related biradicals. The azo work discussed earlier[28] and the more recent report report of Hemetsberger and Holstein concerning **25** and **26**[29] convincingly implicate this type of intermediate. Where the homobenzobarrelene diesters are concerned, arrival at **27** and **28** is followed in each instance by cyclopropylcarbinyl–homoallyl isomerization. Once **29** has evolved, it leads irreversibly to the lone photoproduct **30**.

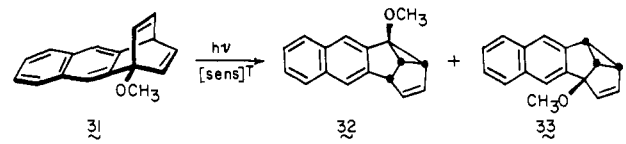


25 30 26

27 29 28

Regiocontrol by Bridgehead Substituents in Naphthobarrelene and Dibenzobarrelene. When a 1,4-diene carries a substituent at C-3, direct perturbation of the diene frontier orbitals by this functionality is greatly diminished. This is particularly true when R is fixed in a conformationally orthogonal relationship to the flanking π bonds as in **1**. Thus, the HOMO-LUMO treatment devised by Houk[5] cannot be applied to examples of this type and a unique opportunity for investigating regioselectivity from a more expansive perspective presents itself.

Isolated earlier reports relating to bridgehead functionalized di-π-methane substrates can be found in the literature. Bender and coworkers observed that benzophenone sensitized irradiation of naphthobarrelene **31** gives rise to **32** and **33** in 22 and 51% yield, respectively.[30] The marked positional substituent effect translates into a 2.3-fold *less facile* migration of vinyl away from the methoxy-substituted center.



31 32 33

Ciganek uncovered the fact that irradiation of **34a** leads efficiently to a 67:33 mixture of **35a** and **36a**.[31] When R is methyl,

(25) Santiago, C.; McAlduff, E. J.; Houk, K. N.; Snow, R. A.; Paquette, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 6149.

(26) Bender and his co-workers have made similar observations in the benzo- and naphthobarrelene area: (a) Bender, C. O.; Burgess, H. D. *Can. J. Chem.* **1973**, *51*, 3486. (b) Bender, C. O.; Shugarman, S. S. *J. Chem. Soc., Chem. Commun.* **1974**, 934. (c) Bender, C. O.; Brooks, D. W. *Can. J. Chem.* **1975**, *53*, 1684. (d) Bender, C. O.; Wilson, J. *Helv. Chim. Acta* **1976**, *59*, 1469. (e) Bender, C. O.; King-Brown, E. H. *J. Chem. Soc., Chem. Commun.* **1976**, 878.

(27) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, **1980**; Vol. 42, Part 3, Essay 16, pp 131–164.

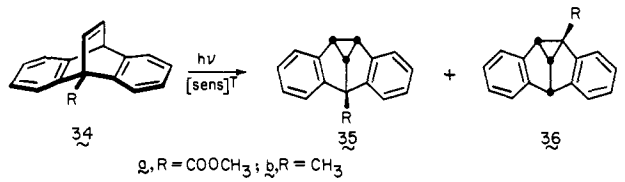
(28) Recent work dealing with the thermal decomposition of optically active azo compounds of general formulae i and ii has shown the dihydro-

i ii

semibullvalene and semibullvalene products to retain optical activity ((a) Sheridan, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5140. (b) Askani, R.; Hornykiewytsch, T.; Müller, K. M. *Tetrahedron Lett.* **1983**, 5513). A concerned [σ^2s + σ^2s + π^2s] cycloreversion is believed to operate since the presence of the allylic double bond is required for the nitrogen expulsion. Certainly, the intermediacy of a symmetrical allylic radical can be dismissed.

(29) Hemetsberger, H.; Holstein, W. *Tetrahedron* **1982**, *38*, 3309.

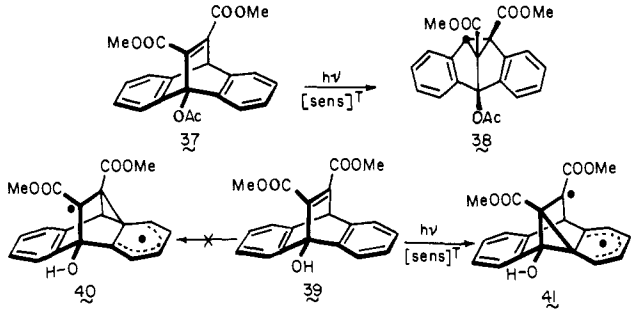
(30) Bender, C. O.; Elder, J. L. M.; Herbst, A. J.; Miller, L. E. *Can. J. Chem.* **1972**, *50*, 395.



34 35 36

a, R = $COOCH_3$; b, R = CH_3

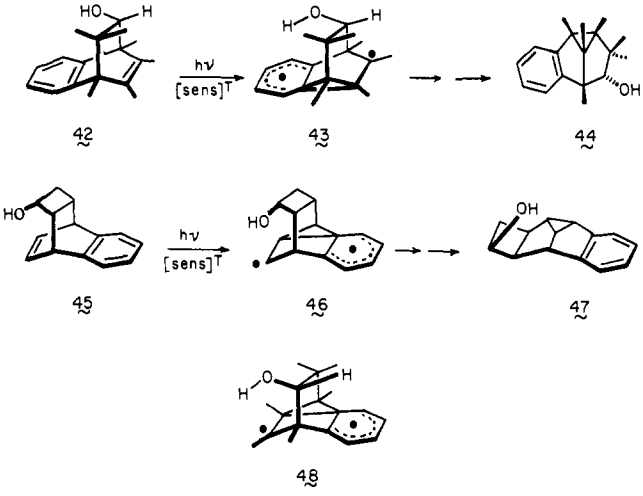
Cristol has determined that triplet sensitization leads to a 40:60 mixture of **35b** and **36b**.[32] The somewhat more ornate dibenzobarrelenes **37** and **39** constitute an interesting contrast.[33] Whereas the acetoxy derivative isomerizes regiospecifically to **38** under triplet conditions, its hydroxy counterpart chooses to follow the alternative pathway exclusively.



37 38 40 39 41

The behavior of **34a** has been interpreted in terms of a reluctance on the part of the rearranging molecule to position the electronegative carbomethoxy group at an incipient cyclopropyl site that is gaining substantial s character.[16] On this basis, the methyl group in **34b** can be expected to exert a stabilizing influence when cyclopropyl bound; however, its impact in this instance is relatively small. The control exerted by the acetoxy group in **37** has also been attributed largely to electronegativity considerations.[33] The nonconformist behavior of **39** was deemed by Richards and co-workers to reflect an overriding of the electronegativity effect by hydrogen-bonding considerations. In their opinion, favored reaction via. **41** instead of **40** is due to the intrinsic inability of a hydrogen-bonded carbomethoxy to delocalize an odd electron as well as one that is not so coordinated.

The concept of regiochemical control by virtue of hydrogen bonding is not new, having been advanced earlier by Hart to explain the exclusive formation of **44** from **42** (the 7-anti alcohol provides a mixture of both positionally isomeric photoproducts)[34] and by Murata to account for the exclusive formation of **47** from **45**.[35] These dramatic perferences were attributed to stabilization



42 43 44 45 46 47 48

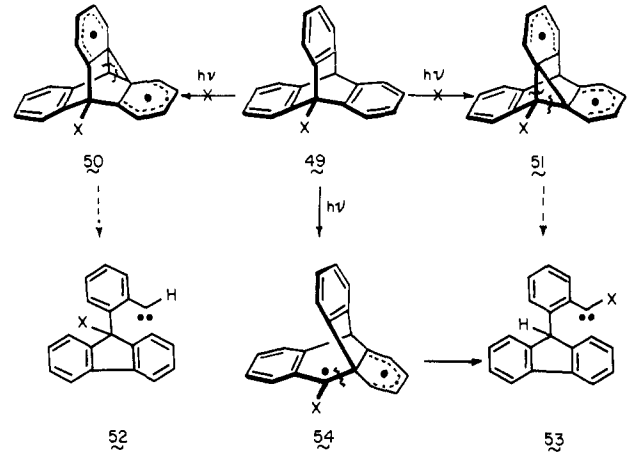
of putative intermediates **43** and **46**, respectively, by internal coordination of the hydroxyl group to a free radical locus or by charge-transfer interaction with the proximate oxygen atom. Why **48**, the intermediate analogously derivable from Hart's 7-anti alcohol, should not enjoy a level of stabilization comparable to that in **46** has not been explained.

Table II. Regioselectivities for Bridgehead-Substituted 9,10-Dicarbomethoxydibenzobarrelenes (e.g., **37**, **39**) and Triptycenes (**49**)[36]

substituent	dibenzobarrelenes		triptycenes	
	proximal rebonding	distal rebonding	proximal rebonding	distal rebonding
OCH_3	0	100	100	0
OCOPh	0	100	100	0
CH_3	29	71	21	79
$(CH_3)_2CH$	23	77		
$(CH_3)_3C$	0	100	0	100
Br	0	100	100	0
Ph	100	0	100	0
CH_3CO	29	71	100	0
CHO	12	88	100	0
NO_2	0	100		

Comparative Analysis of Regioselectivity in Bridgehead-Substituted Dibenzobarrelenes and Triptycenes. The excited-state behavior of a broader range of 1-substituted dibenzobarrelenes of type **39** was examined by Iwamura and co-workers.[36] Their results, which are compiled in Table II, show a number of revealing trends. Thus, atoms having nonbonded electron pairs such as oxygen and bromine discourage rearrangement from occurring near to them as in **41**. Acetoxy derivative **37** was previously shown to behave in this manner. Whereas carbonyl functionalities are moderately selective for proximal bond reorganization, other π-acceptor groups exhibit less consistency. For example, a phenyl group is seen to accelerate nearby aryl migration, while nitro is strongly retardive of this process. Also, while simple alkyl groups favor a reaction course analogous to **40**, an increase in their steric bulk acts to inhibit channeling toward **41**. these various regioselectivities were intrepreted in terms of the standard aryl–vinyl bridging mechanism.

Iwamura's intent was to compare the above results with those realized from irradiation of bridgehead-substituted triptycenes. It has been estabished previously that triptycene (**49**, X = H) is transformed by light into a carbene (**53**, X = H) which undergoes



50 49 51 52 54 53

intramolecular addition to a nearby aromatic π bond.[37] Once again, the original assumption was that aryl–aryl bridging operated

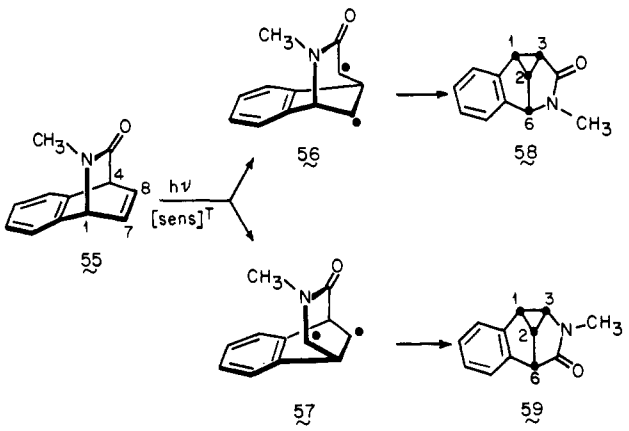
(31) Ciganek, E. *J. Am. Chem. Soc.* **1966**, *88*, 2882.
(32) Cristol, S. J.;Kaufman, R. L.; Opitz, S. M.; Szalecki, W.; Bindel, T. H. *J. Am. Chem. Soc.* **1983**, *105*, 3226.
(33) Richards, K. E.; Tillman, R. W.; Wright, G. J. *Aust. J. Chem.* **1975**, *28*, 1289.
(34) (a) Hart, H.; Murray, R. K., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 2182. (b) Hart, H.; Love, G. M. *Ibid.* **1973**, *95*, 4592.
(35) Murata, I.; Sugihara, Y. *Tetrahedron Lett.* **1980**, 3785.
(36) Iwamura, M.; Tukada, H.; Iwamura, H. *Tetrahedron Lett.* **1980**, 4865.
(37) (a) Iwamura, H. *Chem. Lett.* **1974**, *1205*. (b) Iwamura, H.; Hoshimura, K. *J. Am. Chem. Soc.* **1974**, *96*, 2652. (c) Iwamura, H.; Tukada, H. *J. Chem. Soc., Chem. Commun.* **1975**, 969. (d) Iwamura, H.; Tukada, H. *Tetrahedron Lett.* **1978**, 3451. (e) Kawada, Y.; Tukada, H.; Iwamura, H. *Ibid.* **1980**, 181.

Table III. Product Distributions in the Triplet-Sensitized Photoisomerizations of **55**[38]

substrate	product composition, %	
	58	**59**
55	75	25
1-Me-**55**	6-Me-**58**, 82	3-Me-**59**, 18
4-Me-**55**	3-Me-**58**, 82	6-Me-59, 18
7-Me-**55**	2-Me-**58**, 91	1-Me-**59**, 9
8-Me-**55**	1-Me-**58**, 59	2-Me-**59**, 41

at the outset to give **50** or **51** which subsequently experiences two-bond fragmentation. However, it is to be noted that photorearrangement occurs in **49** (X ≠ H) with a marked preference for conversion to **53** except for the methyl and *tert*-butyl examples (Table II).[36] The observed regioselectivity contrasts strikingly with that operative within the dibenzobarrelenes. Iwamura concluded that the product-developing step in triptycene photochemistry cannot be associated with cyclopropyldicarbinyl diradicals **50** and **51** but with a different intermediate on the excited state energy surface. Since most of the substituents can stabilize the radical and carbenic centers when directly attached, the Japanese workers were forced to invoke intervention of diradical **54** as being *directly* responsible for ultimate conversion to **53**. As far as we are aware, this 1980 paper was the first to give explicit recognition to a nonbridging 1,2-aryl migration pathway for the di-π-methane rearrangement.

Excited-State Behavior of Aza Systems. Before proceeding to place our benzonorbornadiene results in proper perspective, an overview of the regiocontrolling effect of heteroatom-containing bridges is warranted. Systems of this type are of interest because they too offer more than one di-π-methane pathway to product. Paquette and Meisinger were the first to recognize that 5,6-benzo-2-azabicyclo[2.2.2]octadienones **55** exhibit a decided preference for formation of **58** irrespective of the presence of an

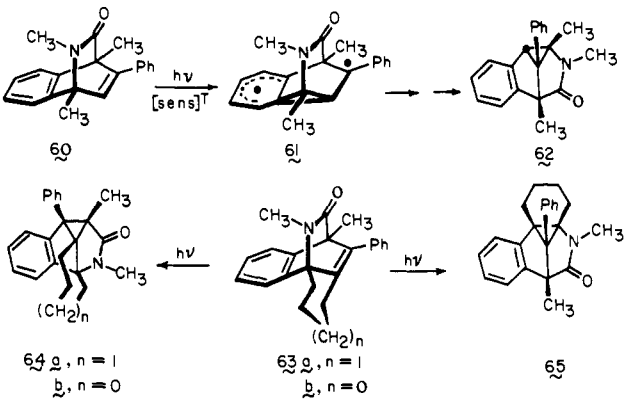


55 **56** **57** **58** **59**

additional methyl group at the various possible sites (Table III).[38] The presence of a cyano or a methoxyl substituent on the aromatic ring does not dampen this regioselectivity,[39] which can be further enhanced by increasing solvent polarity.[40]

Expectedly, a properly positioned olefinic phenyl substituent as in **60** can cleanly reverse the reaction course.[39] Less anticipated was the controlling effect of ring size in **63**. Whereas fusion of a six-membered ring leads to formation of **64** and **65** in a 55:45 ratio, similar photoisomerization of the cyclopentane analogue **63b** delivers only **64b**. In the case of **63a**, aryl substituents do affect the product composition (contrast **55**).

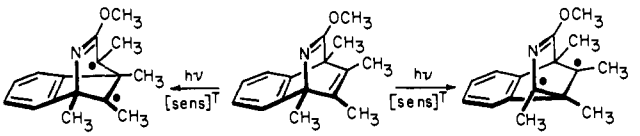
Since the odd electron on the unssubstituted bridge in **56** and **57** are in essentially identical environments, the radical-delocalizing capability of the amide carbonyl in **56** appears responsible for the



60 **61** **62** **63** a, n = 1 b, n = 0 **64** a, n = 1 b, n = 0 **65**

preferential formation of **58**.[41] This influence can be overshadowed by benzylic radical stabilization as in **61** but not by substituents positioned on the fused benzene ring. The need to include the bridgehead carbon in another ring induces a strong dependency on ring size which in turn obviously affects the regioselectivity of product formation.

Acetone-sensitized irradiation of methyl imidate **66** leads preferentially (85%) via **67** to product.[42] This strong directional



67 **66** **68**

influence, which differs from that observed in lactams **55**, is a clear reflection of the greater conjugative ability of the N=C-$(OCH_3)\dot{C}R_2$ moiety relative to the reverse arrangement C-(OCH_3)=N$\dot{C}R_2$.[41,43]

Dependency of Rearrangement Mechanism on Structure. The crucial question being raised is whether the sextet of pπ electrons in an aryl-fused doubly channeled di-π-methane system is disrupted by engaging one of the aromatic carbons in direct through-space cyclopropane bond formation. This so-called 1,3-bridging transforms the migrating center into a tetracoordinate carbon atom while simultaneously shortening the original distance to the bridge. (A referee has emphasized that little doubt surrounds the fact that migrating aryl groups utilize their sextet of π electrons during migration even if a bridged species is not an intermediate. Were only the σ electrons involved, it was stated, then aryl ought to migrate slower than alkyl or hydrogen since an sp^2–sp^3 σ bond is stronger than an sp^3–sp^3 σ bond. Several studies were alluded to (not referenced) where this ordering apparently prevails. While we have no difficulty with some admixing of π-electron character during the 1,2-shift, the level cannot be adequately high to result in spirocyclopropane formation. This distinction in the actual end use of the π involvement is the paramount one at issue. Second, it is unclear that the earlier processes referred to are ground state or photochemical in nature. In this connection, it is important to keep in mind that the original triplet excitation energy initially resides almost totally in the aryl

(38) Paquette, L. A.; Meisinger, R. H. *Tetrahedron Lett.* **1970**, 1479.
(39) Kusuya, M.; Mano, E.; Ishikawa, M.; Okuda, T.; Hart, H. *Tetrahedron Lett.* **1981**, 1613.
(40) Kusuya, M.; Ishikawa, M.; Okuda, T.; Hart, H. *Tetrahedron Lett.* **1979**, 523.
(41) For related excited-state behavior of additional bicyclic lactams, see: Paquette, L. A.; Malpass, J. R.; Krow, G. R. *J. Am. Chem. Soc.* **1970**, *92*, 1980. Paquette, L. A.; Malpass, J. R. *J. Am. Chem. Soc.* **1968**, *90*, 7151. Paquette, L. A.; Malpass, J. R.; Krow, G. R.; Barton, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 5296.
(42) Kusuya, M.; Adachi, M.; Noguichi, A.; Okuda, T. *Tetrahedron Lett.* **1983**, 2271.
(43) (a) Paquette, L. A.; Barton, T. J. *J. Am. Chem. Soc.* **1967**, *89*, 5480. (b) Paquette, L. A.; Barton, T. J.; Whipple, E. B. *Ibid.* **1967**, *89*, 5481. (c) Paquette, L. A. *Tetrahedron Lett.* **1968**, 2139. (d) Paquette, L. A.; Know, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 6107. (e) Paquette, L. A. Kakihana, T.; Hansen, J. F. *Tetrahedron Lett.* **1970**, 529. (f) Paquette, L. A.; Hansen, J. F.; Kakihana, T. *J. Am. Chem. Soc.* **1971**, *93*, 168. (g) Paquette, L. A.; Kakihana, T. *Ibid.* **1971**, *93*, 174. (h) Paquette, L. A.; Ewing, G. D. *Ibid.* **1978**, *100*, 2908. (i) Ewing, G. D.; Ley, S. V.; Paquette, L. A. *Ibid.* **1978**, *100*, 2909.

chromophore. As a result, direct comparisons to ground-state behavior need not be completely warranted.)

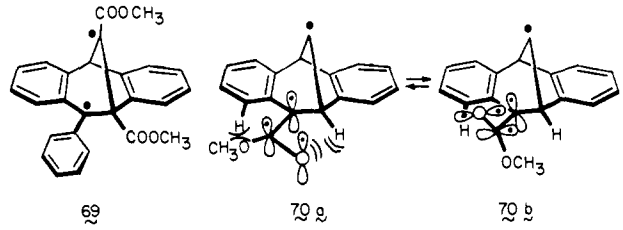
In simple benzobarrelenes, the aryl–vinyl bridging mechanism has been shown to be too energy demanding.[18,26] Instead, vinyl–vinyl bridging takes place in order to bypass the need to interfere with aromatic delocalization. However, the cyclopropyldicarbinyl diradical (e.g., **13**) which is produced is not particularly stabilized. Accordingly, if a better alternative for internal odd-electron delocalization can be found, this particular option should become dominant. The particular phenomenon in question has been uncovered in the case of 1,2-naphthobarrelene, which photoisomerizes via **15**. The important distinction here is that less aromatic character is sacrificed while a substantial gain in stabilization occurs at one of the free radical centers.

Consideration of the total biradical energy picture requires that due attention also be paid to the second odd-electron center. Should enhanced stabilization become possible at that site because of the presence of an acceptor substituent such as carbomethoxy, cyano, or phenyl, the substrate might well respond mechanistically to take advantage of this effect. In our opinion, this principle is at work when 9,10-dicarbomethoxydibenzobarrelenes of type **37** and **39** (see also the listing in Table II) are photochemically energized. Although 1,3-aryl bridging as in **40** and **41** necessarily results in transitory cyclohexadienyl radical formation, the energetic price which must be paid at this end is more than offset by the stabilization which accrues α to the carbomethoxy group. Entirely comparable arguments apply to **23** and **60** where the vinyl cyano and phenyl functionalities, respectively, fully control the regioselectivity of product formation independent of additional peripheral substitution.

How do bridgehead substituents affect the direction of rearrangement in the above systems? In **31**, a greater than 2:1 preference for bridging away from the methoxyl group is seen. Where 9,10-dicarbomethoxydibenzobarrelenes are concerned (Table II), distal rebonding again operates and the effects are more pronounced. Only when a phenyl group is present at the central carbon does proximal rebonding take place. The probable cause of this exceptional behavior is discussed below. This collection of data conforms plausibly to the hypothesis that bridging occurs to generate a cyclopropane intermediate. Those substituents having lone pairs of electrons or strong inductive affects are expected[44] to discourage attachment to a three-membered ring. While alkyl groups are the least influential in either context, they are without doubt sensitive to steric compression. It is likely that distal bridging is preferred for this reason. The powerful controlling influence of *tert*-butyl is particularly notable in this connection.

The preceding findings emphasize the importance of free radical stabilization on the di-π-methane rearrangement. What is the mechanistic fate of processes that lack these influences? Iwamura has already made it clear that triptycenes **49** avoid progressing toward either bridged intermediate (**50** and **51**) because of the need to perturb delocalization in two phenyl rings. The better energetic alternative is direct 1,2-aryl migration. This pathway enjoys the advantage of benzylic stabilization at one radical center and rehybridization of only one aromatic ring carbon atom. The direct involvement of X with one free radical center in **54** will induce product regioselectivity, particularly if X is capable of strong interaction with the odd electron. Although proximal bond relocation occurs predominantly, a reversal in regiocontrol has been noted with methyl and *tert*-butyl. This crossover presumably arises because these substituents are more sensitive to the enhanced steric compression of their environment in **54** (relative to the distal migrated intermediate) than to possible stabilization of the flanking free radical center which already enjoys benzylic status.

Placement of a phenyl group at a bridgehead position in 9,10-dicarbomethoxydibenzobarrelene also has a profound crossover effect on product formation. This distinction is thought to surface because of the capacity of this substituent to stabilize the promixal odd electron in **69**.



69 70a 70b

The effect of positioning a bridgehead substituent on the benzonorbornadiene framework is to promote the formation of photoproducts with a regioselectivity comparable to that found for the triptycenes (Table I). Can we construe this to mean that the energy surfaces interconnecting the triplet state of **1** with its photoisomers contain no minima corresponding to a cyclopropyldicarbinyl diradical? While the data concur with this conclusion, it must be pointed out that the product distributions that we have found also conform in principle to a scheme in which reversible 1,3-aryl bridging is operative. Since reversible bridging can relate to two different phenomena, it is important at this point to become more precise. With reference to the diagram dealing with biradicals **16** and **17**, the options are to return from **16** to **1**-H in either its excited or ground state. Reversible bonding in the first sense lacks precedent. No examples of real reversibility between a triplet and a biradical are known, despite many opportunities where such a scheme could operate. Excited-state reactions that proceed with the rapidity of the present examples go downhill energetically. We therefore join the many investigators who would find it difficult to envision the rapid equilibration of two triplet species that differ so significantly in geometry.

It is more difficult to rule out reversible bridging in the second sense. The known quantum yield ($\sim$0.5) for the rearrangement of benzonorbornadiene may well be an indicator that the process is relatively unimportant. However, bridgehead substitution could exert a meaningful energy dissipative influence. Our projected determination of quantum yields and lifetimes for **1a–g** is expected to shed additional light on this question at a later date.

A second key issue is whether the substrate chooses to take total advantage of the radical-stabilizing properties of bridgehead R without sacrificing aromatic stability or prefers to bridge first and progress less directly toward the penultimate 1,3-biradical. Since analogous criteria apply to dibenzobarrelenes of type **34** and lactams such as **55**, the issues just formulated pertain as well to these series. Does **55** progress directly to **56** from its triplet excited state in order to take immediate advantage of the stabilizing influence of the amide carbonyl?

The unusual regioselectivity associated with **34a** is particularly deserving of comment. Should direct 1,2-aryl migration operate, proximal rebonding leading ultimately to **36**a should be favored. However, **35a** predominates by a factor of 2:1. While this result has been used to argue in favor of the bridging mechanism, at least one additional factor must be seriously considered. As illustrated in **70a**, proximal aryl migration positions the carbomethoxy group between a pair of peri hydrogens. Because of this sterically crowded situation, overlap of the carbonyl π network with the adjacent free radical center as in **70a** might be duly inhibited. Since rotamer **70b** presents no particular delocalization advantage, the substrate could respond by preferentially following the less sterically encumbered distal bond relocation pathway to product. However, this argument is hardly ironclad.

Secondary Deuterium Isotope Effects. The k_H/k_D values for **1h**, **7**, and **10** were shown to be positive. Following completion of our work, Hemetsberger and Neustern reported that triptycene-*9-d* (**49**, X = D) undergoes direct and sensitized photoisomerization with a somewhat larger isotope effect (k_H/k_D = 2.2–2.4).[45] Consequently, all of the available fractionation factors indicate that the heavier isotope prefers to avoid positioning itself at a cyclopropyl (if a stepwise pathway is followed) or free radical

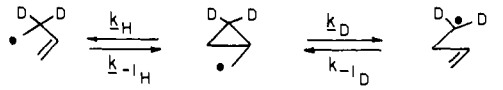
(44) Durmaz, S.; Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 6942 and relevant references cited therein.

(45) Hemtesberger, H.; Neustern, F.-U. *Tetrahedron* **1982**, *38*, 1175.

site (if the 1,2-aryl shift is concerted).

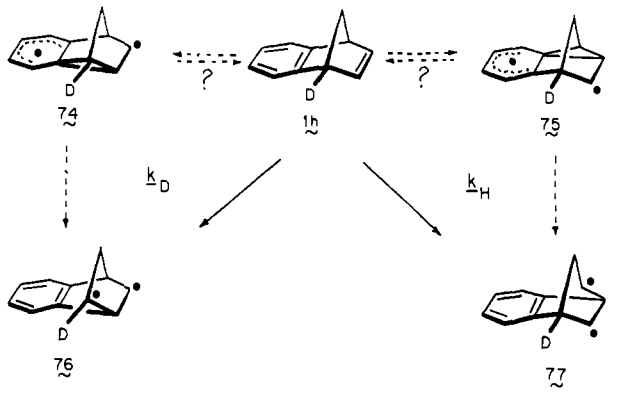
One must now inquire whether the heavier isotope might be expected to exert secondary *kinetic* isotope effects of this magnitude in this direction. Since deuterium is well-known to exhibit a preference for sites richer in s character under equilibrium conditions,[46] the existence of an *equilibrium* isotope effect does not alone explain the above findings. The source of the observed k_H/k_D values must consequently lie elsewhere.

Some insight into this question has seemingly been provided by the research groups of Montgomery[47] and Ingold.[48] These workers have independently examined the interconversion of allylcarbinyl-d_2 radicals **71** and **72** via **73** and have implicated the



71 **73** **72**

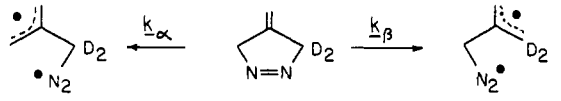
ratio of **71** and **72** to be greater than unity, although unlikely to be larger than 1.22–1.3. The important point here is the fact that ring-deuterated cyclopropylcarbinyl radicals prefer to undergo cleavage of that bond positioned between the unlabeled carbon centers. This being the case, an intermediate such as **74** would



74 **1h** **75** **76** **77**

be expected to return more often to ground state starting material than **75** if reversibility did prevail. The projected faster rate of conversion of the latter biradical to **77** could explain the predominance of **3**-D.

Analysis based on the concerted 1,2-aryl shift pathway is simpler and more direct. The observed isotope effects conform to observations by Crawford and Chang involving thermolysis reactions of various deterium-labeled 4-methylene-1-pyrazolines including **78**.[49] When heated, **78** appears to fracture the N–CH_2 bond more



78

rapidly than the N–CD_2 bond (k_α/k_β = 1.02). Thus, the heavier isotope prefers to avoid the free radical site. Presumably, comparable effects could be at play in discouraging the conversion of **1h** to **76**.

The structurally varied nature of the monodeuterated substrates examined and the relatively narrow range of their excited-state isotope effects must be construed to be an indication that this probe may not be as capable of distinguishing different mechanistic pathways as polar substituents. The accompanying paper examines the competitive state of affairs which arises when both bridgehead sites carry pendant functional groups.[50]

Experimental Section

1-Cyanobenzonorbornadiene (1a). The Grignard derivative of 1-bromobenzonorbornadiene[8] (1.0 g, 4.53 mmol) was prepared by reaction with magnesium turnings (120 mg, 4.94 mmol) in tetrahydrofuran (5 mL). Initiation with ethylene dibromide preceded a 2-h reflux period. The reaction mixture was cooled to −25 °C and treated with excess cyanogen. The cooling bath was removed and the mixture was allowed to boil (−21 °C) for 30 min. The residual cyanogen was allowed to evaporate, and water was cautiously added. The product was extracted into ether, and the combined organic layers were washed with water, dried, and evaporated. Molecular distillation (160 °C, 0.3 torr) followed by MPLC (silica gel, elution with ethyl acetate–petroleum 1:9) afforded 170 mg (22%) of **1a** as a colorless liquid: IR (film, cm^{-1}) 3060, 2223, 1450, 1300, 755, 725, 690; ^1H NMR ($CDCl_3$) δ 7.5–6.6 (series of m, 6 H), 3.91 (s, 1 H), 2.72 (dd, J = 6 and 2 Hz, 1 H), 2.56 (d, J = 6 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 148.46, 146.98, 144.14, 140.60, 126.03, 125.21, 122.34, 120.74, 119.24, 74.06, 49.67; mass spectrum, m/z (M^+) calcd 167.1073, obsd 167.0740.

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43. Found: C, 86.12; H, 5.50.

Methyl Benzonorbornadiene-1-carboxylate (1b). Benzonorbornadiene-1-carboxylic acid[8] (200 mg, 1.08 mmol) was dissolved in ether (10 mL) and treated dropwise with ethereal diazomethane until the yellow color persisted. One drop of acetic acid was added and the solution was concentrated to leave 200 mg (93%) of **1b**: IR (film, cm^{-1}) 3060, 2980, 2940, 1735, 1450, 1430, 1320, 1290, 1215, 1160, 1095, 1035, 750, 720, 690; ^1H NMR ($CDCl_3$) δ 7.35–6.75 (m, 6 H), 3.85 (br s, 4 H), 2.55 (br s, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 172.41, 150.74, 149.41, 143.52, 141.88, 124.95, 124.53, 121.80, 121.25, 72.03, 64.81, 52.01, 49.94; mass spectrum, m/z (M^+) calcd 200.0837, obsd 200.0833.

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.81; H, 6.05.

1-*tert*-Butoxybenzonorbornadiene (1c). (1-Benzonorbornadiene)-magnesium bromide [from **1g** (3.0 g, 13.6 mmol), magnesium turnings (360 mg, 14.8 mmol), and tetrahydrofuran (15 mL)] was cooled to 0 °C and neat *tert*-butyl perbenzoate (2.65 g, 13.6 mmol) was introduced slowly via syringe. The reaction mixture was stirred for 2 h at 0 °C, cautiously treated with 2 N hydrochloric acid, and extracted with ether. The combined organic layers were washed with water and saturated sodium bicarbonate solution prior to drying and solvent evaporation. MPLC of the residual oil on silica gel (elution with petroleum ether) furnished 1.6 g (55%) of pure **1c**: IR (film, cm^{-1}) 3030, 2990, 2970, 1765, 1450, 1365, 1310, 1235, 1190, 1050, 760, 700; ^1H NMR ($CDCl_3$) δ 7.3–6.75 (m, 4 H), 6.6 (br s, 2 H), 3.7 (br s, 1 H), 2.8 (dd, J = 7 and 2 Hz, 1 H), 2.41 (d, J = 7 Hz, 1 H), 1.38 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 153.17, 149.43, 146.81, 140.31, 124.38, 124.19, 120.98, 120.26, 92.68, 75.15, 46.90, 30.49; mass spectrum, m/z ($M^+ - C_4H_8$) calcd 158.0732, obsd 158.0736.

1-Acetamidobenzonorbornadiene (1e). (1-Benzonorbornadiene)magnesium bromide [from **1g** (2.0 g, 9.05 mmol), magnesium turnings (240 mg, 9.88 mmol), and tetrahydrofuran (10 mL)] was cooled to 0 °C and treated dropwise with a solution of methoxyamine[51] (320 mg, 6.81 mmol) in tetrahydrofuran (5 mL). The reaction mixture was stirred at 0 °C for 30 min, allowed to warm to room temperature, and heated at reflux for 2 h. After cooling, an excess of 1 N hydrochloric acid was cautiously added, and the solvent was removed in vacuo. The resulting aqueous emulsion was extracted with ether and made basic with sodium hydroxide. The product amine was now extracted into ether, dried, and concentrated. MPLC purification on silica gel (elution with ethyl acetate) furnished 350 mg (21%) of the amine: IR (film, cm^{-1}) 3360, 3060, 2960, 2920, 2850, 1450, 1320, 755, 735, 725, 690; ^1H NMR ($CDCl_3$) δ 7.3–6.4 (m, 6 H), 3.75 (br s, 1 H), 2.38 (dd, J = 8 and 2 Hz, 1 H), 2.21 (d, J = 8 Hz, 1 H), 1.95 (br s, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 152.40, 151.47, 145.84, 143.27, 124.33, 121.37, 118.75, 77.87, 72.87, 48.55; mass spectrum, m/z (M^+) calcd 157.0891, obsd 157.0895.

A solution of the amine (300 mg, 1.91 mmol) and triethylamine (300 mg, 2.97 mmol) in benzene (5 mL) was treated dropwise with acetyl chloride (200 mg, 2.55 mmol). After 5 min of stirring, the volatiles were removed on a rotary evaporator, water was added, and the product was extracted into ether. After it was dried and concentrated, the residue was purified by MPLC on silica gel (elution with petroleum ether–ethyl acetate 1:1). There was isolated 210 mg (55%) of **1e** as a colorless crystalline solid: mp 132–134 °C; IR (Nujol, cm^{-1}) 3280, 3060, 2990,

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2920, 1655, 1545, 1450, 1180, 1170, 745, 720, 690; ^{1}H NMR ($CDCl_3$) δ 7.4–6.5 (m, 6 H), 3.74 (br s, 1 H), 2.60 (dd, J = 5 and 2 Hz, 1 H), 2.47 (d, J = 5 Hz, 1 H), 2.00 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 170.65, 150.38, 149.53, 143.40, 141.83, 124.71, 124.35, 121.62, 119.67, 73.61, 72.16, 47.88, 23.61; mass spectrum, m/z (M^+) calcd 199.0997, obsd 199.1003.

1-Benzonorbornadiene-*1*-*d* (1h). Into a round-bottom three-necked flask fitted with a condenser, rubber septum, and three-way stopcock was placed 120 mg (4.94 mmol) of magnesium turnings. The apparatus and magnesium were flame dried under vacuum and flushed with argon. After several cycles, approximately 100 μL of deuterium oxide was syringed into a flask and the evacuation–argon flush procedure was repeated 5 additional times. A solution of **1g** (1.0g, 4.53 mmol) in tetrahydrofuran-d_8 (5 mL) was introduced and heated at reflux for 2 h. The Grignard solution was cooled to 0 °C and quenched with 100% deuterium oxide (150 μL). The precipitated salts were removed by filtration and the product was collected from the filtrate by preparative VPC (5 ft × 0.25 in. 10% SE-30 on Chromosorb W, 120 °C). The hydrocarbon so obtained (350 mg, 54%) proved to be 80% monodeuterated: ^{1}H NMR ($CDCl_3$) δ 7.25–6.65 (m, 6 H), 3.85 (br s, 1 H), 2.25 (br s, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 151.67, 142.86, 124.16, 121.47, 69.88, 51.15, 50.32, 50.01, 48.86; mass spectrum, m/z (M^+) calcd 143.0845, obsd 143.0849.

General Benzonorbornadiene Photoisomerization Procedure. The substrate (ca. 100 mg) was dissolved in benzene (50 mL) containing 2–3 drops of acetophenone and the solution was deoxygenated by bubbling nitrogen through the sample for 20 min. The reaction mixture was maintained under a nitrogen atmosphere while it was irradiated with a bank of 3500-Å lamps in a Rayonet reactor until starting material was consumed as indicated by VPC analysis. Reaction times varied from 20 to 40 min. The solvent was evaporated and the residue was purified as indicated.

1a. The single product which was produced was separated from sensitizer by MPLC on silica gel (elution with petroleum ether–ethyl acetate 9:1). There was isolated 65% of **2a**: IR (film, cm^{-1}) 3030, 2940, 2020, 1470, 1245, 1015, 990, 750; ^{1}H NMR ($CDCl_3$) δ 7.5–7.0 (7, 4 H), 3.85 (ddd, J = 5.6, 2.9, and 1.8 Hz, 1 H), 3.44 (dd, J = 7.7 and 2.9 Hz, 1 H), 3.18 (d, J = 5.6 Hz, 1 H), 3.06 (dd, J = 8.4 and 7.7 Hz, 1 H), 1.07 (dd, J = 8.4 and 1.8 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 147.47, 138.15, 126.86, 124.29, 120.55, 120.23, 50.86, 41.58, 37.58, 31.51, 12.45; mass spectrum, m/z (M^+) calcd 167.0735, obsd 167.0732.

1b. Irradiation of **1b** afforded a single compound, **2b**, which was purified by preparative VPC (2 ft × 0.25 in. 10% SE-30 on Chromosorb G, 180 °C) and isolated in 95% yield: IR (film, cm^{-1}) 3030, 3000, 2980, 1730, 1470, 1440, 1385, 1330, 1250, 1215, 1120, 945, 750, 740; ^{1}H NMR ($CDCl_3$) δ 7.45–7.05 (m, 4 H), 3.80 (ddd, J = 5.4, 3.4, and 1.8 Hz, 1 H), 3.71 (s, 3 H), 3.34 (dd, J = 7.8 and 3.4 Hz, 1 H), 3.32 (d, J = 5.4 Hz, 1 H), 3.02 (dd, J = 9.2 and 7.8 Hz, 1 H), 1.02 (dd, J = 9.2 and 1.8 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 172.25, 148.85, 140.36, 126.13, 125.89, 123.75, 120,30, 53.65, 51.66, 40.83, 38.35, 30.20, 28.84; mass spectrum, m/z (M^+) calcd 200.0837, obsd 200.0831.

1c. The single product identified as **2c** that was obtained proved to be sensitive to both VPC and MPLC: ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 4 H), 3.64 (ddd, J = 5.6, 3.9, and 2.2 Hz, 1 H), 3.28 (dd, J = 8.2 and 3.9 Hz, 1 H), 2.92 (dd, J = 8.2 and 8.2 Hz, 1 H), 2.52 (d, J = 5.6 Hz, 1 H), 1.39 (dd, J = 8.2 and 2.2 Hz, 1 H), 1.28 (s, 9 H).

1d. The lone photoisomer produced (**2d**) was purified by preparative VPC (5 ft × 0.25 in 10% SE-30 on Chromosorb W, 180 °C) and isolated in 94% yield: IR (film, cm^{-1}) 3020, 2970, 1465, 1240, 1075, 975, 845, 825, 740; ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 4 H), 3.33 (dd, J = 7.4 and 2.7 Hz, 1 H), 3.15 (ddd, J = 4.8, 2.7, and 2.7 Hz, 1 H), 2.75 (dd, J = 8.9 and 7.4 Hz, 1 H), 2.52 (d, J = 4.8 Hz, 1 H), 0.61 (dd, J = 8.9 and 2.7 Hz, 1 H), 0.04 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 149.32, 142.35, 125.69, 123.07, 119.77, 48.16, 43.35, 33.01, 30.39, 19.57, 2.62; mass spectrum, m/z (M^+) calcd 214.1178 obsd. 214.1181.

1e. Irradiation of **1e** in the usual manner led to the formation of **2e** (82–75%) which was admixed with an inseparable byproduct: ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 4 H), 6.14 (br s, 1 H), 2.88 (ddd, J = 5.5, 3.4, and 2.4 Hz, 1 H), 3.43 (dd, J = 7.9 and 4.3 Hz, 1 H), 3.20 (dd, J = 8.2 and 7.9 Hz, 1 H), 2.59 (d, J = 5.5 Hz, 1 H), 1.98 (s, 3 H), 1.1m (dd, J = 8.2 and 2.4 Hz, 1 H). Those spectral features apparent for the minor product are δ 7.41 (dd, J = 5.0 and 4.2 Hz, 1 H), 7.06 (m, 3 H), 6.23 (br m, 1 H), 3.80 (ddd, J = 5.5, 2.9, and 2.4 Hz, 1 H), 3.48 (dd, signal is too far downfield to be H_4, 1 H), 2.79 (dd, J = 8.6 and 7.9 Hz, 1 H), 2.65 (d, J = 5.5 Hz, 1 H), 2.12 (s, 3 H), and 1.35 (dd, J = 8.7 and 2.7 Hz, 1 H).

1f. The photolysate in this instance was comprised of two products in a 9:1 ratio. This mixture of isomers could not be separated by preparative VPC (5 ft × 0.25 in. 10% SE-30, 170 °C). The purified **2f/3f** was isolated in 83% yield. **2f**: ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 4 H), 3.28 (dd, J = 8.3 and 2.9 Hz, 1 H), 3.18 (ddd, J = 4.9, 2.9, and 2.9 Hz, 1 H), 2.54 (dd, J = 8.8 and 8.3 Hz, 1 H), 2.24 (d, J = 4.9 Hz, 1 H), 1.39 (s, 3 H), 0.92 (dd, J = 8.8 and 2.9 Hz, 1 H). **3f**: ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 4 H), 3.06 (ddd, J = 5.4, 4.4, and 2.8 Hz, 1 H), 2.50 (dd, J = 5.4 and 5.4 Hz, 1 H), 2.39 (dd, J = 8.8 and 3.4 Hz, 1 H), 1.95 (ddd, J = 5.4, 4.4, and 3.4 Hz, 1 H), 1.49 (d, 3 H), 0.90 (dd, J = 8.8 and 2.8 Hz, 1 H).

1g. In this case, **2g** and **3g** were formed in a 1:1 ratio. Preparative VPC (5 ft × 0.25 in. 10% SE-30, 150 °C) did not separate the isomers but gave pure mixture in 90% yield. **2g**: ^{1}H NMR ($CDCl_3$) δ 7.45–7.0 (m, 4 H), 3.75 (ddd, J = 5.6, 3.8, and 2.4 Hz, 1 H), 3.51 (dd, J = 7.8 and 3.8 Hz, 1 H), 3.04, (dd, J = 8.9 and 7.8 Hz, 1 H), 2.89 (d, J = 5.6 Hz, 1 H), 1.42 (dd, J = 8.9 and 2.4 Hz, 1 H). **3g**: ^{1}H NMR ($CDCl_3$) δ 7.45–7.0 (m, 4 H), 3.75 (ddd, J = 5.4, 4.8, and 2.4 Hz, 1 H), 3.14 (dd, J = 9.4 and 3.8 Hz, 1 H), 2.55 (dd, J = 5.4 and 5.4 Hz, 1 H), 2.18 (ddd, J = 5.4, 4.8 and 3.8 Hz, 1 H), 1.49 (dd, J = 9.4 and 2.4 Hz, 1 H).

1h. Irradiation produced **2h** (44%) and **3h** (56%). The mixture was isolated in 80% yield following preparative VPC (5 ft × 0.25 in. 10% SE-30, 120 °C) and characterized by ^{2}H NMR spectroscopy as discussed in the text.

Anthracene-*9*-*d* (6). 9-Bromoanthracene (10 g, 38.9 mmol) and ether (200 mL) were admixed under nitrogen in a flame-dried flask fitted with a serum cap. The solution was stirred magnetically at 0 °C while *n*-butyllithium was slowly introduced from a syringe. After 30 min, deuterium oxide (840 mg, 1 equiv) was added. After an additional 30 min, more D_2O (2 mL) was introduced and the reaction mixture was concentrated on a rotary evaporator. The resultant crystals were washed thoroughly with water and dried under vacuum. Recrystallization from ethanol gave 4.6 g (66%) of **6**, mp 214–216 °C, determined to be 68% d_1 by ^{1}H NMR integration.

Diels–Alder Reaction of 6 with Dimethyl Acetylenedicarboxylate. A magnetically stirred mixture of **6** (1.5 g, 8.38 mmol) and dimethyl acetylenedicarboxylate (1.5 mL) was heated under nitrogen at 180 °C for 10 min. The vigorousness of the reaction was controlled by removal of the oil bath as required. Recrystallization of the cooled reaction mixture from methanol afforded 2.3 g (86%) of **7**, mass spectrum, m/z (M^+) calcd 321.1111, obsd 321.1099.

Diels–Alder Reaction of 6 with *trans*-1-(Benzylsulfonyl)-2-(trimethylsilyl)ethylene. A slurry of **6** (1.79 g, 10 mmol) and silyl sulfone[13] (1.67 g, 6.96 mmol) in toluene (5 mL) was heated in a sealed tube at 165 °C for 10 days. The cooled dark brown reaction mixture was filtered to remove unreacted **6** and the filtrate was concentrated. Chromatography of the residue on silica gel proceeded with elution of additional unreacted **6** (petroleum ether) followed by **8/9** (ethyl acetate–petroleum ether, 1:9). After recrystallization of the product from petroleum ether–ethyl acetate (9:1), there was obtained 2.35 g (81%) of the **8/9** mixture (1:1).

9,10-Dihydro-9,10-ethenoanthracene-*9*-*d* (10). A 1.0-g (2.39 mmol) sample of **8/9** (1:1) in tetrahydrofuran (10 mL) containing tetra-*n*-butylammonium fluoride (6 mL of 1.0 M in water) was heated at reflux for 1 h. The solution was cooled, poured into water, and extracted with dichloromethane. The combined organic extracts were washed with water, dried, and concentrated. Chromatographic purification on silica gel (elution with petroleum ether) afforded 320 mg (65%) of **10** as colorless crystals, mass spectrum, m/z (M^+) calcd 205.1002, obsd 205.0995.

Photoisomerization of 7. A deoxygenated solution of **7** (100 mg, 0.31 mmol) in acetone (50 mL) was irradiated under nitrogen with a bank of 3000-Å lamps in a Rayonet reactor for 30 min. The solvent was removed in vacuo to leave a mixture of two photoisomers (100%). Direct ^{2}H NMR analysis (acetone, proton dcoupling, δ) with repeated integration showed the ratio of **11a** (4.38) to **12a** (0.73) to be 1.15:1.

Photoisomerization of 10. Under the predescribed conditions, **10** was also converted quantitatively to a mixture of **11b** (3.78) and **12b** (2.40) in a ratio of 1.11:1.

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Registry No. 1a, 83399-17-1; **1b**, 5890-14-2; **1c**, 83399-18-2; **1d**, 31862-26-7; **1e**, 83399-19-3; **1f**, 31893-12-6; **1g**, 23537-80-6; **1h**, 83399-20-6; **2a**, 83399-21-7; **2b**, 83399-22-8; **2c**, 83399-23-9; **2d**, 83399-24-0; **2e**, 83399-25-1; **2f**, 83399-26-2; **2g**, 83399-27-3; **2h**, 83399-28-4; **3f**, 83399-29-5; **3g**, 83399-30-8; **3h**, 83399-31-9; **7**, 83399-11-5; **8**, 91898-06-5; **9**, 91898-07-6; **10**, 83399-12-6; **11a**, 83399-13-7; **11b**, 83399-14-8; **12a**, 83399-15-9; **12b**, 83399-16-0; benzonorbornadiene-1-carboxylic acid, 5890-15-3; 1-aminobenzonorbornadiene, 91879-72-0; *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene, 64489-06-1; *tert*-butyl perbenzoate, 614-45-9; methoxyamine, 67-62-9; 9-bromoanthracene, 1564-64-3; anthracene-*9*-*d*, 4485-03-4; dimethyl acetylenedicarboxylate, 762-42-5; D_2, 7782-39-0.