Organic Photochemistry with 6.7-eV Photons. The Divergent Photobehavior of *exo*- and *endo*-7-Methyl-2-norcarene

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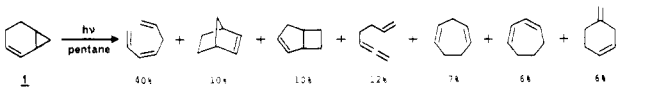
The photochemistry of *exo*- and *endo*-7-methylbicyclo[4.1.0]hept-2-ene (7-methyl-2-norcarene) upon direct and toluene-sensitized photolysis has been investigated. Direct photolysis of the two isomers in hydrocarbon solution with monochromatic 214-nm light leads to widely divergent photobehavior. Ring opening, yielding *cis*-5-methyl-1,3,6-heptatriene (via a formal $[2\pi + 2w + 2\sigma]$ process), and exo–endo isomerization are major decomposition pathways in both cases, accounting for 30–45% of the observed products. The formation of 7-methylnorbornene and 4-methylbicyclo[3.2.0]hept-2-ene is observed to proceed stereospecifically in each case, while the formation of cyclopropyl ring opening/hydrogen migration products appears to depend strongly on the orientation of the methyl group in the starting isomer. Common biradical intermediates are thus believed not to be involved in the direct photolyses of **2** and **3**. Toluene-sensitized photolysis of the two isomers leads to formation of *exo*-4-methylbicyclo[3.2.0]hept-2-ene (the photochemical vinylcyclopropane rearrangement) and exo–endo isomerization. These results are rationalized in terms of the expected behavior of two common biradical intermediates, which are formed with different efficiencies from the isomeric **2** and **3** upon triplet sensitization.

Introduction

In contrast to the singlet photobehavior generally observed in aliphatic cyclopropanes,[1] or even other vinylcyclopropane derivatives,[2] the product mixture observed upon direct irradiation (214 nm, pentane solution) of 2-norcarene (**1**, eq 1) reveals that this system is unusual in

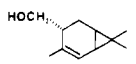


(1)

many respects.[3] In particular, as deuterium-labeling studies demonstrate,[3] the dominant photoproduct, *cis*-1,3,6-heptatriene, is formed via *formal* electrocyclic $[2\pi + 2w + 2\sigma]$ ring opening of the bicyclo[4.1.0]hept-2-ene ring system[4] in a manner analogous to the 1,3-cyclohexadiene/1,3,5-hexatriene interconversion (the "w" refers to the cyclopropane Walsh orbitals[5]). In response to several questions that were raised by this study,[3] it seemed important to investigate further the photochemistry of this system in substituted derivatives from which stereochemical information on the photoreactivity of **1** could be gained. We report here the results of a study of the direct and toluene-sensitized photolyses of the isomeric *exo*- and *endo*-7-methyl-2-norcarenes (**2** and **3**).

Although all of the products in eq 1 can be rationalized in terms of concerted pathways, it is perhaps more economical to consider their formation to be the result of secondary reactions of the two biradical intermediates (**4** and **5**) formed by competitive cleavage of the two cyclopropane bonds in conjugation with the olefinic double bond.[3] There is, however, evidence that suggests that *discrete* biradical intermediates such as these cannot be responsible for the observed products from **1**. For example, both the thermolysis and the photolysis of the bicyclic azo compound **6**, which is presumed to involve the intermediacy of the biradical **5**,[6a] yield only 2-norcarene (**1**) and, apparently, no norbornene and/or 4-methylenecyclohexene.[6b] Similarly, the thermolysis of the tricyclic azo compound **7** yields open-chain and bicyclic products, which suggests the intermediacy of the eight-membered (1,4)-biradical counterpart to **4**;[7] the product ratio, however, is totally different from the ratio of *cis*-1,3,6-heptatriene/bicyclo[3.2.0]hept-2-ene that is formed upon direct irradiation of **1**.[3] However, aside from eliminating the possibility of the involvement of discrete, ground-state biradical intermediates in the photolysis of **1**, our previous study (or, for that matter, the above examples[6a]) offers no *conclusive* evidence in favor of either concerted or biradical pathways.

The formation of *cis*-1,3,6-heptatriene in both the direct and triplet-sensitized photolyses of **1** is worthy of further note in that the analogous product was not found (in significant yield) in a previous study of a related system (**8**), although its formation was, in fact, anticipated.[8] A



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(1) (a) Srinivasan, R.; Ors, J. A. *J. Org. Chem.* **1979**, *44*, 3246–3248. (b) Srinivasan, R.; Ors, J. A.; Baum, T. H. *Ibid.* **1981**, *46*, 1950–1951. (c) Srinivasan, R.; Baum, T.; Brown, K.; Ors, J. A.; White, L. S.; Rossi, A. R.; Epling, G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 973–974. (d) Srinivasan, R.; Ors, J. A.; Baum, T. *Tetrahedron Lett.* **1981**, *22*, 4795–4798.
(2) For a recent review, see: Hixson, S. S. "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol. 4, pp 218–260.
(3) Leigh, W. J.; Srinivasan, R. *J. Am. Chem. Soc.* **1983**, *105*, 514–519.
(4) Ishii, K.; Frei, B.; Wolf, H. R.; Jeger, O. *Helv. Chim. Acta* **1981**, *64*, 1235–1246.
(5) Hoffmann, R.; Stohrer, W.-D. *J. Am. Chem. Soc.* **1971**, *93*, 6941–6948.
(6) (a) It may be difficult to compare the behavior of the biradicals from **6** and **7**, which are probably ground-state biradicals, to the behavior of **4** and **5**, which may represent biradicaloid excited states. (b) Schneider, M.; Erben, A.; Merz, I. *Chem. Ber.* **1975**, *108*, 1271–1284.
(7) Olsen, H.; Snyder, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 285–287.

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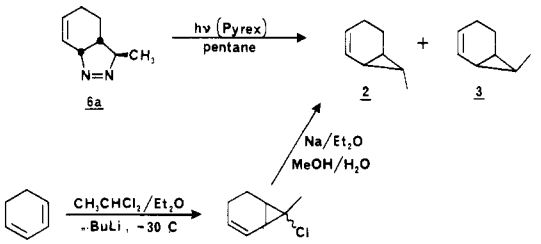
Scheme I. Preparation of *exo*- and *endo*-7-Methyl-2-norcarene (2 and 3)



possible reason for this interesting result is that the C_1–C_6 bond is somewhat stronger in **8** than it is in **1**, as is suggested by a recent theoretical study of ground- and excited-state cyclopropane C–C bond strengths as a function of alkyl substitution.[9] Thus, the C_2–C_3 bond in 1,1-dimethylcyclopropane is estimated to be ~5 kcal/mol^{-1} stronger than in cyclopropane itself in the lowest singlet excited state.

Finally, the rather low quantum yield for total product formation in the direct photolysis of **1** (ϕ = 0.26, 185-nm excitation) indicates the presence of other, nonproductive pathway(s) that are effective in excited-state deactivation in this system. It is known that cyclopropane cis–trans isomerization is an important deactivation pathway in both direct and triplet-sensitized photolyses of related, appropriately substituted systems[2] and, furthermore, that this process is predominantly the result of activation of the external (conjugated) cyclopropyl C–C bond.

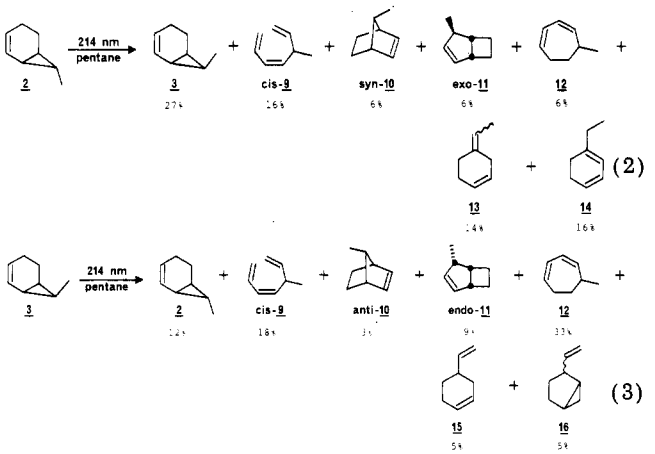
As is reported below, the photochemical behavior of the isomeric **2** and **3** sheds some light on the various questions presented above.

Results

exo- and *endo*-7-methyl-2-norcarene (**2** and **3**) were prepared by the photolysis of *exo*-9-methyl-7,8-diazabicyclo[4.3.0]nona-4,7-diene (**6a**)[6b] and in large quantities by the addition of 1-chloroethylidene to 1,3-cyclohexadiene,[10a] followed by reductive dechlorination with sodium and wet methanol[10b] (Scheme I). The isomers were separated and purified by preparative VPC.

Ultraviolet absorption spectra of **2** and **3** (not shown) were measured in pentane. The spectra of the two isomers are indistinguishable (λ_{max} 200 nm, ϵ_{max} 5000) and are similar in all respects to that of the parent compound, 2-norcarene.[3]

Irradiation of stirred, deoxygenated 0.015 M pentane solutions of **2** and **3** (separately) with a zinc resonance lamp (λ 214 nm) produced the product mixtures summarized in eq 2 and 3 and Scheme III (Discussion). The products were isolated by preparative VPC from runs carried to 30–50% conversion and were identified by comparison of their spectral data (IR, ^{1}H NMR, MS) and GC retention times with those of authentic samples and/or literature data (see below and Experimental Section). In both cases, the photolysates contained other products for which quantities adequate to enable positive identification could not be obtained. The total yield of these unidentified products was ca. 9% from **3** and ca. 12% from **2**. Progress of the reactions was followed by GC, and product yields were calculated from the slopes of concentration vs. time plots, which were linear for all products and starting materials up to at least 8% conversion. The material balances



(total products vs. consumed starting material, from the slopes of the concentration vs. time plots) were at least 80%.

In no case did the product mixtures contain >3% of *trans*-**9** in addition to the cis isomer, even at conversions as high as 20%. *endo*-**11** and *syn*-**10** could not be detected as products in the photolysates from **2** and **3**, respectively, at low conversions (<20%); these products were clearly resolvable from *exo*-**11**, *anti*-**10**, and all other components of the mixtures under the GC conditions employed for the analyses. An upper limit of ca. 1% can be estimated for the yields of these products that would have gone undetected under our conditions. *anti*-**10** and *exo*-**11** could not be resolved under these conditions. These were collected in higher conversion runs (ca. 30%) and subjected to further analysis with use of different GC conditions. Thus, *anti*-**10** could not be detected as a product of the photolysis of **2** and, similarly, *exo*-**11** was not detected as a photoproduct of **3**. Thus a lower limit of ~80% can be placed on the degree of stereospecificity with which *syn*-**10**/*exo*-**11** and *anti*-**10**/*endo*-**11** are formed upon photolysis of **2** and **3**, respectively.

Similarly, **13** could not be detected as a photoproduct from **3** (estimated upper limit of ~2%). No indication of the isomeric composition (i.e., *cis*/*trans*-**13**) of this component was obtained. 1-Ethyl-1,3-cyclohexadiene (**14**) could not be resolved from **2** under the analytical conditions. Therefore, it was isolated by subsequent GC analysis of samples of **2** collected from the photolysates. In this manner, **14** was shown not to be present in the photolysate of **3** in >1% yield. Compounds **15** and **16** could not be detected as products of photolysis of **2**. The stereochemistry of **16** could not be determined.

Quantum yields for total product formation from **2** and **3** at 214 nm (pentane solution) were determined relative to 2-norcarene under the same conditions and are summarized in eq 4 and 5.

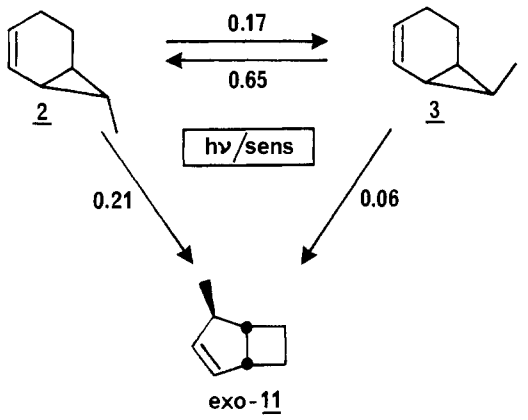
$$\phi^2_{prod} = (1.4 \pm 0.2)\phi_{2\text{-norcarene}} \quad (4)$$

$$\phi^3_{prod} = (1.4 \pm 0.2)\phi_{2\text{-norcarene}} \quad (5)$$

Irradiation of 0.032 M solutions of **2** and **3** in pentane containing 0.004 M toluene at 254 nm produced the product mixtures summarized in Scheme II. Also included in the scheme are the measured rates (min^{-1}) of formation of the volatile products. *cis*- and *trans*-**9** were also evident as products in the toluene-sensitized photolysis of **2** at low (<5%) conversions, with the cis isomer predominating. Instrumental problems prevented a quantitative determination of their yields. These products appeared to be extremely susceptible to photosensitized degradation, as was the case for the corresponding products in the sen-

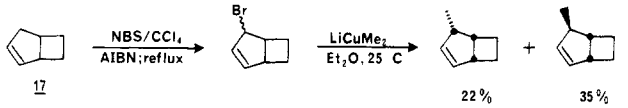
(8) Kropp, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 1126–1134.
(9) Rossi, A. R. *J. Phys. Chem.* **1979**, *83*, 2554–2556.
(10) (a) Arora, S.; Binger, P. *Synthesis* **1974**, 801–803. (b) Winstein, S.; Sonnenberg, J. *J. Am. Chem. Soc.* **1961**, *83*, 3235–3244.

Scheme II. Toluene-Sensitized Photolysis of 2 and 3 (Pentane Solution)



sitized irradiation of 1,[3] so that their apparent yields dropped off very quickly at conversions higher than ~ 5%.[11] *endo*-11 could not be detected as a product from 2 or 3, under GC conditions that were shown to resolve clearly this compound from the other components of the photolysates. The photostationary state (2/3 = 2.55 ± 0.15) was determined after extended irradiation of the two solutions.

exo- and *endo*-11 were synthesized by methylation of 4-bromobicyclo[3.2.0]hept-2-ene[12] with lithium dimethylcuprate (eq 6). The isomers were separated by



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VPC and their structures assigned on the basis of their IR, 300-MHz ^{1}H NMR (Figure 1), 90-MHz ^{13}C NMR (Table I), and mass spectra and spectral comparisons with bicyclo[3.2.0]hept-2-ene (17). The 300-MHz ^{1}H NMR spectra of these three compounds are summarized in Table I along with the ^{13}C NMR spectra and assignments.

The mass and infrared spectra of *exo*- and *endo*-11 and their comparison to those of 17 identify the bicyclo[3.2.0]hept-2-ene ring system as the basic skeletal structure of the two isomers. The mass spectra of *exo*- and *endo*-11 are very similar to each other and to those of the isomeric 7-methylnorbornenes (10). This similarity to the mass spectrum of the isomeric norbornene derivative exists for the parent compound 17 as well. The infrared spectra of the three compounds are perhaps more conclusive; all three show absorption at 920 cm^{-1} (cyclobutane ring vibration[13]) and in the 630–670- and 1050-1070-cm^{-1} regions (cyclopentene ring[14]).

The ^{13}C NMR spectra of the three derivatives were most helpful in identifying *exo*- and *endo*-11, and the basic similarities in the spectra provide further support for the gross structures of the two isomers (see Table I). The resonances due to the methyl group and the C_6,C_7 carbons, which are found in the 13–27-ppm range, are particularly

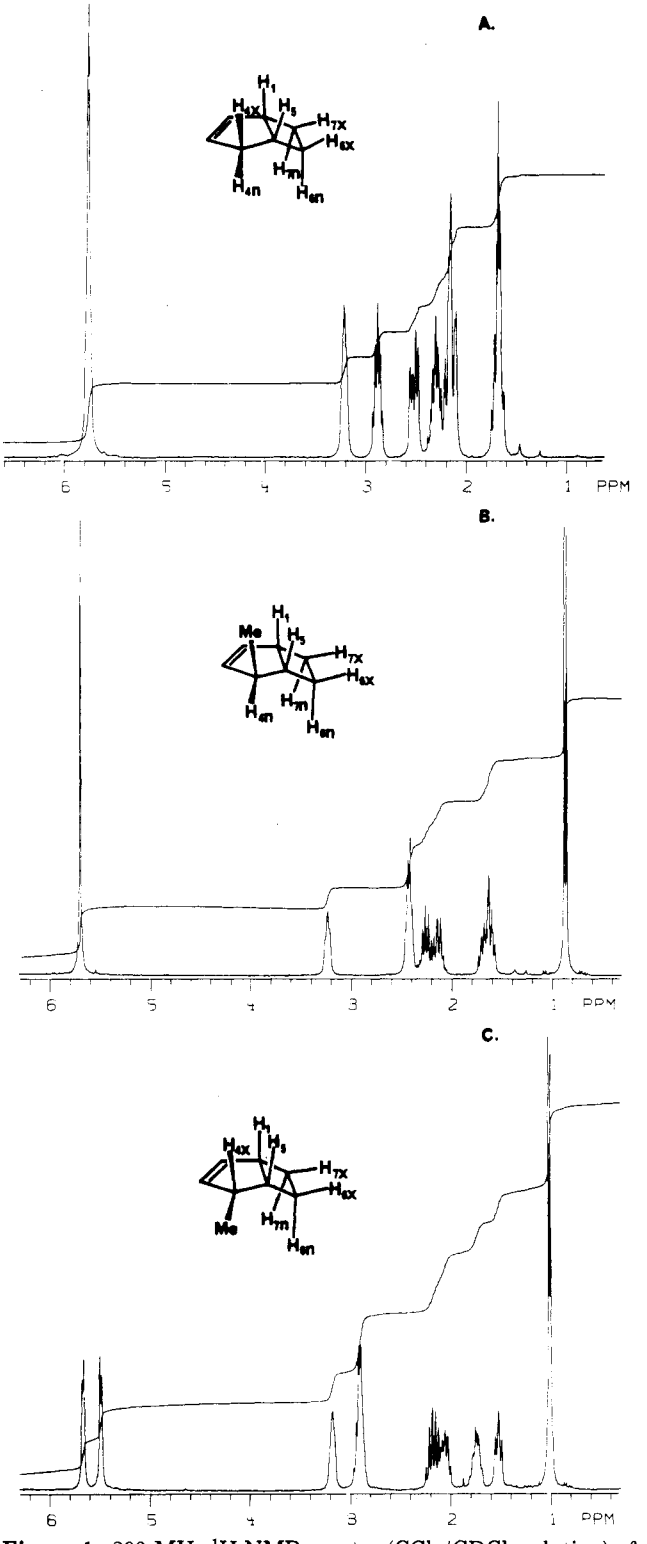


Figure 1. 300-MHz ^{1}H NMR spectra (CCl_4/$CDCl_3$ solution) of (a) bicyclo[3.2.0]hept-2-ene (17), (b) *exo*-11, and (c) *endo*-11.

useful in the stereochemical assignment. Examination of molecular models indicates that these carbons should be most profoundly affected by the stereochemistry at C_4. While exo substitution is expected to lead to little change in the positions of the C_6,C_7 resonances from their positions in the spectrum of 17, endo substitution should produce a marked upfield shift of the C_6 carbon as a result of steric interactions between the methyl group and the endo proton on C_6. A similar upfield shift would be expected for the methyl resonance. Thus, the spectrum with triplets at δ 26.1 and 26.2 and a quartet at δ 21.1 is assigned to

(11) Extended irradiation of these solutions results in the buildup of several high-boiling products (as evidenced by their GC retention times), which were not isolated. This presumably accounts for the rapid disappearance of *cis*- and *trans*-9 upon extended photolysis. Material balances were generally 70–80% in these experiments.

(12) Hamer, N. K.; Stubbs, M. E. *Tetrahedron Lett.* **1972**, 3531–3534.

(13) Bellamy, L. J. "The Infrared spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, 1975; p 33.

(14) Pouchert, C. J. "The Aldrich Library of Infrared Spectra"; Aldrich Chemical Co.: Milwaukee, WI, 1981.

Table I. 300-MHz ^{1}H NMR and 90-MHz ^{13}C NMR Spectral Data of 17, *exo*-11, and *endo*-11[a]

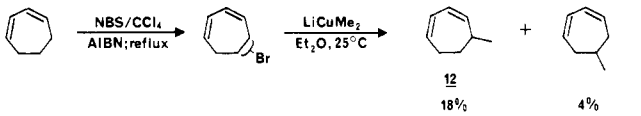
	^{1}H NMR			^{13}C NMR		
position	17	*exo*-11	*endo*-11	17	*exo*-11	*endo*-11
1	3.20	3.23	3.17	46.0 (d)	45.1 (d)	46.5 (d)
2, 3	5.75	5.70	5.48	134.2 (d)	136.3 (d)	136.4 (d)
			5.67	130.1 (d)	133.0 (d)	132.9 (d)
4 endo	2.15	2.43		40.8 (t)	48.1 (d)	42.5 (d)
4 exo	2.51		2.91			
5	2.87	2.43	2.91	35.7 (d)	43.5 (d)	40.9 (d)
6 endo	1.68	1.62	1.52	27.1 (t)	26.1 (t)	19.3 (t)
6 exo	2.15	2.15	2.05			
7 endo	1.68	1.62	1.75	27.1 (t)	26.2 (t)	24.6 (t)
7 exo	2.29	2.25	2.16			
Me		0.86	1.00		21.1 (q)	13.4 (q)

[a] All spectra were measured in $CCl_4/CDCl_3$ (1:1). Chemical shifts are in ppm vs. Me_4Si.

exo-11, while that with triplets at δ 19.3 and 24.6 and a quartet at δ 13.4 is assigned to *endo*-11. The C_6,C_7 carbon resonances occur together at δ 27.1 in the spectrum of the parent compound 17.

The ^{1}H NMR spectral assignments collected in Table I are rationalized in detail in the Experimental Section. In particular, the relative positions of the methyl doublets in *exo*- and *endo*-11 as they are assigned[15] is consistent with those observed for the two corresponding saturated derivatives, *exo*- and *endo*-4-methylbicyclo[3.2.0]heptane.[16]

The structure of 5-methyl-1,3-cycloheptadiene[12] was assigned by comparison to an authentic sample, which was prepared by the methylation of 5-bromo-1,3-cycloheptadiene with lithium dimethylcuprate as outlined in eq 7. Although the ^{1}H NMR spectrum of the bromide



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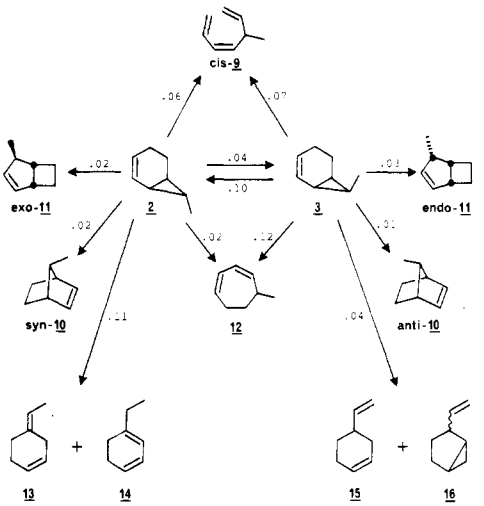
obtained from NBS bromination of 1,3-cycloheptadiene indicated that it consisted of predominantly the 5-bromo isomer, methylation of the crude, distilled product produced two isomeric methylcycloheptadienes in a 4:1 ratio. Their straightforward ^{1}H NMR spectra indicate that the major product is the desired 5-methyl derivative, while the minor product is 6-methyl-1,3-cycloheptadiene.

Discussion

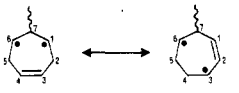
The products observed upon direct irradiation (214 nm, pentane solution) of **2** and **3** can be viewed within the framework of three formal reaction types, viz., "electrocyclic" ring opening, external bond (C_1–C_7) cleavage, and internal bond (C_1–C_6) cleavage. The discussion of the direct irradiation results has thus been divided into these three areas: the partitioning of the singlet excited states of **2** and **3** among the three pathways is summarized in Scheme III. As was concluded to be the case for the parent molecule 1,[3] the products observed upon direct irradiation are presumed to be entirely singlet derived, since the photobehavior of the isomeric **2** and **3** is completely different in the toluene-sensitized reaction. Quenching studies were not carried out in the direct photolysis.

Ring opening of the bicyclo[4.1.0]hept-2-ene ring system to yield *cis*-**9** occurs with the same regiospecificity as was

Scheme III. Direct Irradiation (214 nm, Pentane Solution) of *exo*- and *endo*-7-Methyl-2-norcarene (2 and 3)



observed to be the case for 1-7,7-d_2.[3] This rearrangement can be formally viewed as a ($2\pi + 2w + 2\sigma$) electrocyclic process, analogous to the 1,3-cyclohexadiene/1,3,5-hexatriene interconversion.[3,4] While the stereochemical information that can be derived from the present study still offers no conclusive evidence for the concerted pathway, the stereospecificity with which *exo*- and *endo*-**11** are formed from **2** and **3**, respectively, does rule out the possibility that *cis*-**9** and **11** are formed by secondary reaction of a *common* [1,3] ↔ [1,4] biradical intermediate **18**, which is sufficiently long lived to lose its stereochemical integrity at C_7. It might be alternatively proposed that the biradical



18

18 does indeed exist on the singlet excited-state surface(s) of **2** and **3**, and that it simply undergoes C_4–C_5 bond cleavage, leading to *cis*-**9**, in preference to coupling to give **11**. While this alternative can not be discounted, it seems unlikely that there would be any barrier to coupling in a singlet 1,4-biradical, even in the excited state.

In order to rationalize the apparent absence of the analogous *cis*-1,3,6-heptatriene derivative as a major product from direct irradiation of 2-carene-4α-methanol (**8**),[8] it was suggested that the C_1–C_6 bond might be somewhat stronger in **8** than in **1**.[3] Support for this suggestion comes from a recent theoretical study of C–C bond strengths in the ground- and excited-states of alkylcyclo-

(15) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", International Series of Monographs in Organic Chemistry, 2nd ed.; Pergamon Press: London, 1969; Vol. 5, Chapter 3.
(16) Schimpf, R.; Heimbach, P. *Chem. Ber.* **1970**, *103*, 2122–2137.

propanes.[9] If this were the case, then one might expect to find that the efficiency of this reaction in **2** and **3** is considerably reduced relative to that observed in the parent compound **1**, all other factors being equal. The quantum yield study suggests that this is not the case. Formation of *cis*-**9** from **2** and **3** occurs with a calculated quantum yield of ca. 0.07 in either case, while formation of *cis*-1,3,6-heptatriene from **1** occurs with a quantum yield of ca. 0.1;[3] the difference is probably not significant. The earlier study of **8** employed a medium-pressure mercury vapor lamp as an excitation source;[8] under these conditions, it has been shown that *cis*- and *trans*-1,3,6-heptatriene are particularly susceptible to secondary, degenerative photolysis.[3]

Exo–endo isomerization has been shown to occur predominantly via external bond cleavage in related bicyclic vinylcyclopropane derivatives[2] in both the singlet[17] and triplet excited states,[17,18] and we assume that it is this bond that is involved in this process in **2** and **3**. There are few examples of cyclopropane cis–trans isomerization upon direct excitation of aliphatic systems, and in the one case reported, this process accounts for less than 9% of the observed products.[1a] On the other hand, the process is ubiquitous in phenylcyclopropanes,[2] and its predominance in these systems may be the result of the lowest singlet excited state being both considerably lower in energy and more delocalized, so that higher energy processes such as two-bond cleavage (leading to a carbene and an olefin[1]) are not able to compete effectively.

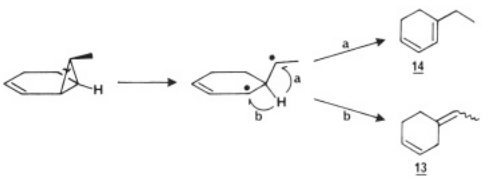
The situation with respect to **2** and **3** is intermediate between these two extremes, as might be expected, accounting for 12–25% of the observed products in this system. Thus, while (formal) external bond cleavage/reclosure does indeed account for some of the inefficiency inherent in the photolysis of **1** ($\phi_{prod} = 0.26$[3]), it can only account for an additional 10–15% of the absorbed energy. Clearly, the majority of singlet excited states in this system decay via nonproductive routes.

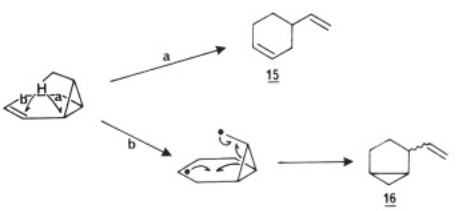
Formation of the isomeric 7-methylnorbornenes occurs with a high degree of stereospecificity in the case of both **2** and **3**, proceeding to yield *syn*-**10** from **2** and the anti isomer from **3**. This provides strong support for a concerted, suprafacial [1,3] migration (eq 8) as the mechanism


(8)

for this rearrangement. Molecular models reveal that the C_1–C_7 bond in **2** and **3** is almost exactly coplanar with the π-orbitals of the adjacent double bond, allowing for good overlap in the transition state with a minimum amount of molecular distortion.

The products of formal external bond cleavage/hydrogen migration are of particular interest, since **2** and **3** give widely divergent results with respect to these products. In both cases, the C_1–C_7 bond (which is best able to interact with the adjacent π-orbitals) is the only framework bond that appears to be involved. The difference between the two isomers is in the hydrogen atom that undergoes migration. While in the *exo*-methyl isomer **2** the cyclopropyl (C_6) hydrogen undergoes migration to C_1 and C_7, which with concomitant ring opening leads to **13** and **14**, respectively, in the *endo*-methyl isomer **3** the preferred modes of hydrogen migration appear to involve the *methyl group*. These rearrangements are formally depicted in eq 9 and 10. The H migrations in eq 9 are depicted for the


(9)


(10)

sake of simplicity as formally involving a biradical intermediate, but this is not meant to imply its necessary involvement. Indeed, the failure of **6** to afford 4-methylenecyclohexene[6b] would seem to indicate otherwise. The result that **16** is formed only from **3** might be explained by noting that in this isomer the methyl hydrogens are in close proximity to the π-orbital at C_2. However, hydrogen abstraction is not a particularly common singlet reaction of alkenes in solution, although it is known to occur in minor amounts in some cases,[18] in the gas phase upon triplet sensitization,[19] and upon direct irradiation of alkynes.[20] One might also expect to find products of abstraction from solvent in the cases of **2** and **1**; no product corresponding to either reduction or solvent addition could be conclusively identified in these cases, although the possibility of their being formed in minor yield (≤3%) cannot be excluded.[21]

It is not clear why migration of H_6 (leading to **13** and **14** from **2**) is apparently promoted by a cis arrangement of the adjacent methyl group and completely suppressed when it is oriented trans to the methyl; behavior of this type has not, as far as we know, been observed previously. The reason for the specific formation of **15** from **3** is similarly elusive.

The products that can be formally viewed as involving cleavage of the internal (C_1–C_6) bond in **2** and **3** are the stereoisomeric 4-methylbicyclo[3.2.0]hept-2-enes (**11**) and 5-methyl-1,3-cycloheptadiene (**12**). As was found to be the case for the 7-methylnorbornenes (**10**), the formation of **11** proceeds with a high degree of stereospecificity, *exo*-**11** being formed solely from **2** and *endo*-**11** solely from **3**. This again suggests a concerted mechanism for this process, possibly involving disrotatory bonding of the cyclopropyl Walsh orbital at C_6 with the π-orbitals at C_2. This is depicted in eq 11 for the formation of *exo*-**11** from **2**.


(11)

5-Methyl-1,3-cycloheptadiene (**12**) is an unexpected product from both **2** and **3**. Deuterium-labeling studies have previously demonstrated that the 1,3-cycloheptadiene

(17) (a) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 8749–8761. (b) Garin, D. L.; Cooke, D. J. *J. Chem. Soc., Chem. Commun.* **1972**, 33–34. (c) Kaplan, L.; Rausch, D. J.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1972**, *94*, 8638–8640.

(18) Kropp, P. J. "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol 4, pp 1–142.

(19) (a) Inoue, Y.; Takamuku, S.; Sakurai, H. *Can. J. Chem.* **1976**, *54*, 3117–3124. (b) Inoue, Y.; Mukai, T.; Hakushi, T. *Chem. Lett.* **1982**, 1045–1048.

(20) Inoue, Y.; Ueda, Y.; Hakushi, T. *J. Am. Chem. Soc.* **1981**, *103*, 1806–1808.

(21) A completely saturated C_7H_{12} isomer was, in fact, isolated in ca. 2% yield in the direct 185- (+254) nm irradiation of **1** but in insufficient quantities to enable its identification.[22b]

(as well as the 1,4-isomer) formed in the photolysis of **1** arises from [1,2] migration of hydrogen from C_7 to C_1 (or C_6 in the case of 1,4-cycloheptadiene). The corresponding product from **2** and **3** would thus be 1-methyl-1,3-cycloheptadiene (**19**), which was not found among the product

19

mixtures in either case.[22] Discounting the unlikely possibility[23] that **19** rearranges quantitatively to **12** under our GC conditions, two possible mechanisms for the formation of **12** remain, viz., [1,5] hydrogen migration ($C_4 \rightarrow C_6$) or [1,2] methyl migration from C_7 to C_6. Photochemically allowed antarafacial [1,5] hydrogen migration is expected to be extremely difficult in this system owing to the rigidity of the molecular framework, and should such a process occur,[24] it would be expected to do so with about equal facility from **2** and **3**; this is clearly not the case. We thus favor the [1,2] methyl shift, since one might expect some difference in efficiency for the isomeric **2** and **3**, and this is more in line with the known behavior of 1-7,7-d_2.[3] This reaction is, however, without precedent in cyclopropane photochemistry. Furthermore, it is difficult to understand the apparent preference for [1,2] methyl migration over [1,2] hydrogen migration, leading to **19**, in the direct irradiation of **2** and **3**, unless it reflects a propensity for migration of the endo-oriented substituent, be it methyl or hydrogen, in this system.

The results of toluene-sensitized photolysis of **2** and **3**, as depicted in Scheme II, are more straightforward than those of the direct irradiations, since the product mixtures are simpler. Since the relative rates of product formation (Scheme II) were measured under identical conditions for **2** and **3**, they are proportional to the product quantum yields. As is well-known,[2] cyclopropane cis–trans isomerization is important in the triplet state of these compounds and accounts for almost 95% of observed product formation in the case of **3**. Since it is well-established that this process occurs almost exclusively via formal external bond cleavage/reclosure in the triplet state of closely related systems,[17] it is assumed for the purpose of discussion that it does so as well in **2** and **3**, though there is no evidence to substantiate this assumption.

Analogous to the triplet-state behavior of **1**,[3] it was determined that at low (<2%) conversions, both the bicyclo[3.2.0]hept-2-ene (**11**) and *cis*-1,3,6-heptatriene (**9**) derivatives are formed (in the case of **2**, at least; this was difficult to confirm for **3**), although formation of the latter (**9**) was not quantitatively analyzed. The apparent yields of *cis*- and *trans*-**9** dropped off very quickly upon further irradiation.[11]

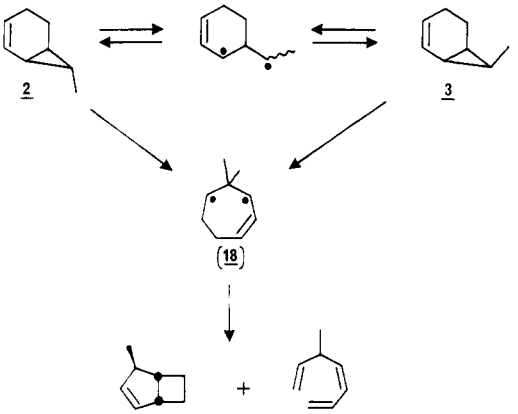
It is interesting to note that only *exo*-**11** is formed upon toluene-sensitized photolysis of both **2** and **3**. This is consistent with the intermediacy of the triplet biradical **18**, which must be sufficiently long lived to lose its stereochemical integrity at C_7 and which undergoes closure to give only *exo*-**11**. The preferred formation of this isomer of **11** is reasonable on steric grounds, since closure to the endo isomer would necessarily proceed through a transition state in which the methyl group at C_7 is brought into close contact with the developing cyclobutane ring.

Table II. Relative Rates of External vs. Internal Bond Cleavage in the Direct and Toluene-Sensitized Photolysis of 2 and 3

compd	excited state	k_{ext}/k_{int}[a]
1	singlet	2.0
	triplet	
2	singlet[b]	3.4–5.5
	triplet[c]	0.8
3	singlet[b]	0.5–0.9
	triplet[c]	10.8

[a] Determined from product yields, ignoring undetectable excited-state relaxation to starting material in each case. [b] Range in relative rates reflects the uncertainty owing to the yields of unidentified products in the direct photolyses. [c] Ignores the yields of *cis*- and *trans*-**9** (not determined).

Scheme IV. Intermediates in the Triplet-Sensitized Isomerizations of 2 and 3



With our assumption that exo–endo isomerization proceeds only via external bond cleavage (i.e, that **18** does not close to regenerate **2** and **3**), it is concluded from the observed relative rates of isomerization and *exo*-**11** formation that external bond cleavage is considerably more facile (or internal bond cleavage is much *less* facile) in the triplet state of **3** than in that of **2**. This is summarized in Table II; the mechanistic implication that the triplet states of **2** and **3** decay to two distinct biradical species[8] is summarized in Scheme IV. Provided that C_6–C_7 bond rotation is faster than reclosure to **2** and **3**, then the relative rates of isomerization should be related to the photostationary-state composition (**2**/**3**) by eq 12. The photostationary-state ratio was determined to be **2**/**3** = 2.6 ± 0.2; this compares favorably with the value of 2.5 calculated with use of eq 12 and the measured rates of formation of **2**, **3**, and *exo*-**11** (see Scheme II). The large difference in k_{ext}/k_{int} for **2** and **3** in Table II is the result of the combined effect of a threefold reduction in k_{int} and a threefold increase in k_{ext} for **3** relative to **2**. If **2** and **3** are viewed as cis,cis,trans- and cis,cis,cis-substituted cyclopropanes, respectively, then the greater propensity for **3** to undergo external bond cleavage can be understood by noting that external bond cleavage does more to relieve repulsive steric interactions in **3** than it does in **2**. Similarly, **2** has probably more to gain in the way of steric relief than does **3**

$$(2/3)_e = \frac{2k_{3\rightarrow 2} + k_{3\rightarrow 11}}{2k_{2\rightarrow 3} + k_{2\rightarrow 11}} \qquad (12)$$

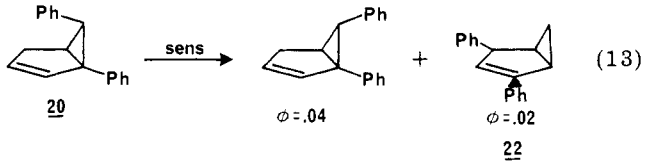
(22) (a) A product was isolated in low (<4%) yield in a preliminary 185- (+254) nm photolysis of **2** and tentatively identified as 1-methylbicyclo[3.2.0]hept--6-ene,[22b] which presumably must arise from secondary photolysis of 1-methyl-1,3-cycloheptadiene (**19**).[22c] This implies that this isomer may indeed be formed in the 214-nm photolyses of **2** and **3**, though no product with consistent spectral characteristics was isolated. (b) Leigh, W. J.; Srinivasan, R., unpublished results. (c) Chapman, O. L.; Pasto, D. J.; Borden, G. W.; Griswold, A. A. *J. Am. Chem. Soc.* **1962**, *84*, 1220–1224.

(23) Mironov, V. A.; Akhrem, A. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1972**, *1582*–1583.

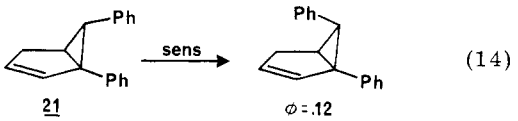
(24) Kiefer, E. F.; Tanna, C. H. *J. Am. Chem. Soc.* **1969**, *91*, 4478–4480.

upon cleavage of the internal (C_1–C_6) bond. However, quite the opposite behavior is observed in the singlet states of **2** and **3** (Table II). This may be simply a reflection of the greater propensity of the singlet states of **2** and **3** to react via concerted processes that depend on the relative conformation of the methyl group as opposed to relaxation processes that might relieve steric stress in the Franck–Condon excited states.

Quite the opposite behavior has been noted for the triplet-sensitized photolysis of the isomeric 5,6-diphenylbicyclo[3.1.0]hex-2-enes, **20** and **21** (eq 13 and 14),[17] for



(13)



(14)

which it was demonstrated that exo–endo isomerization proceeds predominantly via external bond cleavage and rearrangement to **22** involves the internal (C_1–C_5) bond.[17] The very much larger value of k_{ext}/k_{int} found for the *exo*-phenyl isomer **21** relative to that found for the endo isomer can be explained by noting that the dominant steric interaction in this system is presumably that between the phenyl groups; i.e., external bond cleavage is preponderant in **21** because it relieves a *cis*-phenyl–phenyl interaction.

Summary and Conclusions

The behavior of *exo*- and *endo*-7-methyl-2-norcarene (as well as 2-norcarene itself) in their lowest singlet excited states can be classified according to three basic reaction types. The first, corresponding to simultaneous or stepwise cleavage of two of the C–C bonds in this system, has been shown by its regio- and stereospecificity to involve formal ($2\pi + 2w + 2\sigma$) electrocyclic ring opening, although sufficient stereochemical labeling to firmly establish the concerted nature of this process has not, as yet, been provided. This reaction is a predominant one ($\phi \sim 0.1$) in each case.

The second class involves the external cyclopropane C–C bond that is in conjugation with the olefinic π-system and includes exo–endo isomerization, norbornene formation, and hydrogen migration to yield monocyclic dienes. Exo–endo isomerization provides an important, though by no means dominant, mode of excited-state decay. Norbornene formation is observed to occur stereospecifically, with retention of configuration at the migrating carbon, and is thus viewed as a photochemically allowed, suprafacial [1,3] shift. The isomeric **2** and **3** behave differently with respect to external bond cleavage/hydrogen migration: the exo isomer **2** gives products corresponding to [1,2] migration of the C_6 cyclopropyl proton, while the endo isomer **3** gives products corresponding to migration of one of the methyl hydrogens.

The third class of singlet reaction in this system involves formal cleavage of the internal cyclopropyl C–C bond and includes 4-methylbicyclo[3.2.0]hept-2-ene formation and formal [1,2] methyl migration leading to 5-methyl-1,3-cycloheptadiene (**12**). 4-Methylbicyclo[3.2.0]hept-2-ene formation occurs with retention of configuration at C_7 ($\rightarrow C_4$) and is viewed as a concerted [1,3] migration. The formation of **12** is proposed to involve [1,2] methyl migration on the basis of the known behavior of 2-norcarene-7,7-d_2 with respect to the placement of deuterium in the cycloheptadiene products.[3] Preferential migration of the substituent in the endo position at C_7 might be proposed to account for the much higher yield of **12** that is observed in the case of **3**.

While "electrocyclic" ring opening occurs with roughly equal facility in **1–3**, the relative yield of external/internal bond cleavage products is a factor of ca. 5 greater upon direct irradiation of **2** relative to **3**.

The triplet state behavior of **1–3** is much simpler than that of the singlet states. Toluene-sensitized photolysis of **2** and **3** leads to exo–endo isomerization (presumed to involve external bond cleavage) and stereospecific formation of *exo*-**11** as well as *cis*-**9**, which could be detected only at low conversions. In this case, the ratio of external/internal bond cleavage is observed to be a factor of ca. 10 greater in **3** than in **2**. This behavior is rationalized in terms of decay of two common, stereochemically equilibrated biradical intermediates; external bond cleavage is favored in **3** since it allows for more complete relief of steric stress in the Franck–Condon triplet of **3** than it does in that of **2**. The stereospecific formation of *exo*-**11** in each case is ascribed to the lesser steric interactions that are present in the transition state for closure of the seven-membered cyclic [1,3] $\leftrightarrow$ [1,4] biradical intermediate to this isomer relative to that for closure to *endo*-**11**.

Experimental Section

Infrared spectra were recorded in carbon tetrachloride solution on a Beckman Acculab 6 spectrometer and are reported in wavenumbers. ^{1}H NMR (80 MHz) and 25-MHz ^{13}C NMR spectra were recorded in carbon tetrachloride or deuteriochloroform solution (unless otherwise noted) on an IBM Instruments NR80 spectrometer and are reported in parts per million downfield from Me_4Si. Benzene-d_6 was used as both internal lock and reference for spectra run in CCl_4 solution. ^{1}H NMR (300 MHz) and 90-MHz ^{13}C NMR spectra were recorded on a Nicolet spectrometer in deuteriochloroform solution and are reported in parts per millions downfield from Me_4Si. Ultraviolet absorption spectra were recorded in pentane solution on a Cary 17D spectrometer and are reported in nanometers. Mass spectra were recorded on a Hewlett-Packard 5995 gas chromatograph/mass spectrometer equipped with a 3% OV-101 on 80/100 Supelcoport glass column (12 ft × 0.25 in.). Parent ion exact masses were determined on a AEI MS-902 mass spectrometer.

Analytical and preparative gas chromatographic separations were carried out on a Hewlett-Packard 5750B gas chromatograph (injector temperature = 155 °C) equipped with flame ionization and thermal conductivity detectors (TC detector temperature = 160 °C) and the following columns: (a) 3.8% UC W982 on 80/100 Supelcoport, 24 ft × 0.25 in., (b) 29% ODPN on 80/100 Chromosorb PNAW, 24 ft × 0.25 in., (c) 4% QF-1 on 80/100 Supelcoport, 14 ft × 0.25 in. Quantitative runs were carried out with the FID and generally column a. GC response factors were assumed to be identical for all products and starting material.

Samples of *exo*- and *endo*-7-methylbicyclo[4.1.0]hept-2-ene (**2** and **3**) for the initial, exploratory study were prepared by photolysis of *exo*-9-methyl-7,8-diazabicyclo[4.3.0]nona-4,7-diene (**6a**) in pentane solution with a 450-W medium-pressure mercury vapor lamp and Pyrex filter. **2** and **3** were isolated and purifed by preparative VPC (columns a and b) after evaporation of solvent and column chromatography (alumina, isopentane eluant) of the crude photolysate. This method afforded a ca. 50:50 mixture of **2** and **3** in nearly quantitative yield, as has been reported.[6]

Larger quantities of **2** and **3** were prepared by reductive dechlorination with sodium and wet methanol[3,10b] of 7-chloro-7-methylbicyclo[4.1.0]hept-2-ene (bp 61–62 °C (10 torr)), which was prepared in 60% yield from 1,3-cyclohexadiene, 1,1-dichloroethane, and *n*-butyllithium in anhydrous ether at −40 °C.[10a] The crude, distilled (bp 75–76 °C (200 torr)) mixture so obtained (**2**/**3** ~ 65:35, 35% overall yield) was separated by preparative VPC (column a); final VPC purification using columns a or b afforded samples of **2** and **3** of >98% purity, the only significant contam-

inant being the other isomer. The ^{1}H NMR spectra of the two isomers agreed with those reported,[25] and their IR, UV, and mass spectra are as follows. **2**: IR 3020 (s), 2915 (s), 1630 (m), 1445 (br, m), 1045 (s), 935 (w), 675 (s) cm^{-1}; UV λ_{max} 199 nm (ϵ 5040); MS, *m/e* 27 (100), 39 (98), 79 (90), 77 (60), 41 (46), 91 (36), 93 (32), 51 (30), 78 (24), 53 (22), 108 (20). **3**: IR 3020 (s), 2915 (s), 1630 (m), 1445 (br, m), 1120 (m), 1060 (m), 875 (m), 685 (s), 590 cm^{-1} (m); UV λ_{max} 199 (ϵ 5000); MS, *m/e* 79 (100), 39 (73), 27 (66), 77 (61), 93 (40), 91 (40), 41 (29), 78 (26), 51 (25), 108 (24).

***syn*- and *anti*-7-methylnorbornene (10)** were prepared by reductive dehalogenation of 7-bromo-7-methylnorbornene[26] with sodium and wet methanol[11] in 58% yield. The crude mixture was bulb-to-bulb distilled under reduced pressure, and the isomers were separated and purified by preparative VPC (columns a and (c). Identification of the two was based on comparison of their 25-MHz ^{13}C NMR spectra in carbon disulfide to those previously reported;[27] the syn isomer elutes first on both VPC columns a and c. The ^{1}H NMR spectra of *syn*- and *anti*-**10** are indistinguishable on our spectrometer and show δ 5.80–5.90 (br s, 2 H), 2.4–2.5 (br s, 2 H), 1.60 (m, 3 H), 1.20 (m, 1 H), 0.65–0.95 (m, 4 H, including the methyl doublet). Infrared and mass spectral data are as follows. *syn*-**10**: IR 3060 (m), 2975 (br, s), 2885 (s), 1460 (br, m), 1380 (m), 1340 (s), 1130 (m), 910 (w), 870 (w), 685 (w) cm^{-1}; MS, *m/e* 80 (100), 39 (81), 27 (80), 79 (79), 77 (30), 41 (30), 51 (22), 108 (10). *anti*-**10**: IR 3060 (m), 2975 (br, s), 2882 (s), 1470 (m), 1445 (m), 1380 (m), 1330 (m), 1120 (w), 910 (w), 880 (w), 865 (w), 685 (s) cm^{-1}; MS, *m/e* 80 (100), 79 (90), 39 (81), 27 (79), 77 (35), 41 (28), 51 (23), 91 (18), 93 (17), 108 (12).

4-Bromobicyclo[3.2.0]hept-2-ene was prepared by NBS bromination of bicyclo[3.2.0]hept-2-ene (**17**).[3,28] In a 15-mL round-bottom flask fitted with reflux condenser and magnetic stirrer were placed **17** (0.72 g, 7.7 mmol), *N*-bromosuccinimide (1.42 g, 8.0 mmol), azobis(isobutyronitrile) (0.1 g), and carbon tetrachloride (6 mL). The stirred mixture was brought to reflux with a heating mantile, which resulted in an extremely exothermic reaction. The mixture was stirred for a further 5 min, cooled, and added to pentane. The mixture was then filtered and the solvent evaporated to afford a slightly yellow liquid (1.3 g) whose ^{1}H NMR spectrum coincided with that previously reported for 4-bromobicyclo[3.2.0]hept-2-ene.[12] IR (neat) 3020 (w), 2970 (s), 2925 (s), 2850 (m), 1590 (m), 1355 (m), 1230 (m), 785 (m), 765 (s), 663 (m) cm^{-1}. The mass spectrum obtained by GC/MS (injector temperature = 150 °C) showed weak molecular ions at *m/e* 172, 174 (base peak 91).

In a 100-mL three-necked round-bottom flask fitted with an addition funnel, a magnetic stirrer, a reflux condenser, and an N_2 inlet (flame-dried under N_2) was placed cuprous chloride (1.2 g, 0.012 mol) and anhydrous ether (40 mL). A 1.55 M solution of methyllithium in ether (15.4 mL) was added to the stirred suspension by syringe. After stirring for 15 min at room temperature, the mixture was cooled in an ice bath, and a solution of the crude bromide from above in anhydrous ether (7 mL) was added dropwise over 15 min. After the mixture was stirred for 3 h at 0 °C, saturated aqueous ammonium chloride (25 mL) was added (vigorous reaction), the mixture was filtered into a separatory funnel, and the aqueous portion was discarded. The organic portion was washed with water (4 × 15 mL) and saturated brine (5 mL) and dried over anhydrous magnesium sulfate, and the solvent was evaporated to yield a light green oil, which was bulb-to-bulb distilled under a mild vacuum. GC/MS analysis of the distillate showed it to consist of a 60:40 mixture of (only) two components with *m/e* 108 molecular ions; these were identified as *exo*- and *endo*-**11** on the basis of comparisons of their ^{1}H NMR (see below and Figure 1, Table I), ^{13}C NMR (Table I), IR, and mass spectra with those of **17** (yield 0.40 g, 0.0037 mol, 57%).

The two isomers were separated by preparative VPC (column (a). The first to be eluted was *exo*-**11**: IR (CCl_4) 3035 (m), 2945 (br, s), 2860 (s), 1445 (m), 1365 (m), 1345 (m), 1070 (m), 915 (w), 625 (w) cm^{-1}; MS, *m/e* 80 (100), 39 (84), 27 (81), 79 (76), 77 (32), 41 (28), 51 (23), 93 (21), 91 (19), 108 (3); exact mass found 108.184 79 (calcd for C_8H_{12} 108.184 84). Next to be eluted was *endo*-**11**: IR (CCl_4) 3035 (m), 2945 (br, s), 2850 (s), 1450 (m), 1370 (w), 1350 (m), 1090 (w), 1070 (m), 915 (w), 670 (w), 630 (w) cm^{-1}; MS, *m/e* 80 (100), 79 (81), 39 (74), 27 (68), 77 (30), 41 (27), 51 (21), 91 (17), 93 (16), 108 (7); exact mass found 108.184 78 (calcd for C_8H_{12} 108.184 84).

^{1}H NMR Assignments for 17 and *exo*- and *endo*-11 (Figure 1, Table I). The 1 H multiplet at δ 3.20 present in all three ^{1}H NMR spectra is assigned to the allylic, bridgehead proton, H_1. Substitution at C_4 should have little effect on the chemical shift of the exo protons at C_6 and C_7, although they should appear downfield of the corresponding endo protons owing to eclipsing between the latter and the adjacent five-membered ring.[15] The multiplets appearing at $\delta \simeq 2.1$ and δ 2.2–2.3 in all three spectra are therefore assigned to these protons, although it is not possible to make a strong differentiation between the two. In the spectrum of **17**, the remaining bridgehead proton, H_5, is assigned to the multiplet at δ 2.87 and the endo protons at C_6,C_7 are assigned to the multiplet at δ 1.68. By comparison to the ^{1}H NMR spectrum of 17-*4,4-d*$_2$,[3] the exo and endo protons H_4 are assigned to the multiplets at δ 2.51 and 2.15, respectively; endo H_4 is expected to be shifted upfield relative to exo H_4 as a result of eclipsing interactions with the adjacent four-membered ring.[15]

The two-proton multiplets at δ 2.43 and 2.91 in Figures 1b and 1c are assigned to the H_4, H_5 protons in *exo*- and *endo*-**11**, respectively. The fact that this requires accidental equivalence of H_5 with H_{4N} in *exo*-**11** and H_{4X} in *endo*-**11** is decidedly unusual; the assignments, however, can be easily rationalized. Since the attachment of a methyl group at C_4 would not be expected to result in any increase in long-range steric interactions between H_4 and other protons, the only effect on the chemical shift will be a downfield shift of 0.3–0.5 ppm owing to the electronic effect of the methyl substituent,[15] shifting H_{4N} to *exo*-**11** to 2.43 ppm from 2.15 in **17** and H_{4X} in *endo*-**11** to 2.92 ppm from 2.51 in **17**. The effect of a methyl group at C_4 on the chemical shift of H_5, on the other hand, will be largely steric and should result in a significant upfield shift in *exo*-**11** (to δ 2.43) and very little shift in *endo*-**11** (δ 2.91) relative to its position in **17** (δ 2.87).[15]

5-Bromo-1,3-cycloheptadiene was prepared by refluxing 1,3-cycloheptadiene (4.8 g, 0.05 mol), *N*-bromosuccinimide (8.9 g, 0.05 mol), and azobis(isobutyronitrile) (0.2 g) in carbon tetrachloride (50 mL) for 3 h. The resulting mixture was cooled and filtered, and the solvent was evaporated to yield a yellow liquid. Distillation under reduced pressure afforded a colorless liquid (bp 31–32 °C (0.1 mm), 1.0 g, 0.005 mol, 10%) that was identified as 5-bromo-1,3-cycloheptadiene on the basis of the following data: ^{1}H NMR ($CDCl_3$) δ 5.76 (br m, 4 H), 4.98 (m, 1 H), 2.49 (m, 2 H), 2.15 (m, 2 H); IR (CCl_4) 3040 (s), 2950 (s), 2910 (m), 2840 (m), 1430 (m), 1335 (w), 1195 (s), 1141 (s), 689 (br s). The GC/MS showed two peaks, the first of which was identified as 1,3,5-cycloheptatriene on the basis of its mass spectrum and retention time and which decreased in proportion as the GC injector temperature was decreased. The mass spectrum of the second component showed weak molecular ions at *m/e* 172, 174.

5-Methyl-1,3-cycloheptadiene (12) was prepared by methylation of the bromide with lithium dimethylcuprate following the procedure outlined for *exo*- and *endo*-**11**. Bulb-to-bulb distillation of the crude product under a mild vacuum afforded a colorless liquid (22% yield) that was shown to consist of two components with *m/e* 108 parent ions by GC/MS. The two isomers were separated by preparative VPC (column (b). The minor component eluted first and was identified as 6-methyl-1,3-cycloheptadiene on the basis of its IR and ^{1}H NMR spectra: IR (CCl_4) 3020 (s), 2970 (s), 2940 (s), 2915 (s), 2860 (m), 2840 (m), 1455 (br m), 1430 (m), 1375 (w), 670 (m), 650 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.56 (m, 4 H), 2.28 (m, 4 H), 1.14 (d, 3 H). The second (major) component was identified as **12** on the basis of its IR, ^{1}H NMR, and off-resonance decoupled ^{13}CMR spectra: IR (CCl_4) 3010 (s), 2960 (s), 2920 (s), 2870 (s), 2850 (m), 1455 (m), 1430 (m), 1370 (w), 688 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.79 (m, 4 H), 2.67 (br m, 1 H), 2.40 (m, 2 H), 1.96 (m, 2 H), 1.16 (d, 3 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 28.7, 32.9, 36.1, 123.4, 125.1, 133.7, 139.1.

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Toluene (reagent grade) and pentane (Photrex grade) were used as received from J. T. Baker Co.

Photolysis Procedure. A. Direct Photolysis. All photolyses were conducted on a semipreparative scale on 0.015 M solutions of **2** and **3** in pentane (Baker-Photrex) in the apparatus described previously.[3] The lamp, a 100-W Philips 93106E zinc resonance lamp (214 nm), was given a warmup time of 10 min and was cooled with a stream of nitrogen during the photolyses. In preparative runs, 100 mL of solution was placed in the reaction vessel (120-mL volume), purged with a stream of nitrogen for 30 min, and irradiated with the Zn resonance lamp with vigorous stirring and under a slow stream of nitrogen for ca. 3 h (ca. 30% conversion). Two or three such runs were combined, the pentane was distilled off, and the products were separated by gas chromatography (column a). The products, identified by comparison of their spectral data with literature data and/or authentic samples, and starting materials are described below in order of their elution from column a. Representative VPC traces are available as supplementary material.

***cis*-5-Methyl-1,3,6-heptatriene** (*cis*-**9**) was identified on the basis of its spectral properties, and their comparison to those of *cis*-1,3,6-heptatriene[3] and *trans*-**9**: IR 3075 (m), 2960 (s), 2910 (m), 2865 (m), 1630 (m), 1450 (m), 1430 (m), 1419 (w), 1370 (w), 980 (m), 900 (s); ^{1}H NMR δ 1.10 (d, 3 H), 3.32 (m, 1 H), 4.80–6.70 (complex m, 8 H); MS, *m/e* 27 (100), 39 (87), 77 (59), 91 (49), 41 (49), 91 (49), 93 (40), 53 (29), 51 (26), 108 (7).

***trans*-5-Methyl-1,3,6-heptatriene (*trans*-9)** was identified by comparison of its spectral data and GC retention times with those of an authentic sample (Aldrich ABC).

***syn*-7-Methylnorbornene** (*syn*-**10**) was identified on the basis of comparison of its spectral data and VPC retention times with those of the authentic sample. Its absence in the photolysis of **3** was demonstrated by GC spiking experiments.

***anti*-7-Methylnorbornene** (*anti*-**11**) and ***exo*-4-methylbicyclo[3.2.0]hept-2-ene** (*exo*-**12**) eluted together on column a but could be separated on column c. This fraction isolated from the photolysate from **2** consisted of only *exo*-**12**. That from **3**, however, consisted of *anti*-**11** in addition to another, unidentified product. *exo*-**12** was shown by GC spiking experiments with column c not to be present in the photolysate from **3**.

***endo*-4-Methylbicyclohept-2-ene** (*endo*-**11**), **4-vinylcyclohexene (15)**, and **2-vinylbicyclo[3.1.0]hexene (16)** eluted together on column a but could be adequately resolved on column b. None of these products was present in significant quantity in the photolysate from **2**. *endo*-**11** and **15** were identified by comparison to authentic samples, while **16** was identified by comparison of its spectral data with that previously published.[29] The resolution achieved in the ^{1}H NMR spectrum of this compound was inadequate to firmly establish the stereochemistry with respect to the vinyl group.

***exo*-7-Methyl-2-norcarene (2)** and **1-ethyl-1,3-cyclohexadiene (14)** eluted together on column a but could be separated on column b. Thus, subsequent analysis of recovered **2** from its photolysate on column b enabled isolation and yield determination for **14**. This product was not present in the quantity of **2** isolated from the photolysis of **3**. The identification of **14** rests upon comparison of its spectral properties with those published:[30] IR (CCl_4) 3040 (m), 2960 (s), 2930 (s), 2860 (s), 2825 (s), 1455 (m), 1425 (br m), 860 (w), 680 (s); ^{1}H NMR ($CDCl_3$) δ 1.05 (t, 3 H), 1.82 (m, 2 H), 2.08 (m, 4 H), 5.50 (m, 3 H); UV λ_{max} 261 nm; MS, *m/e* 79 (100), 77 (60), 39 (53), 27 (54), 91 (37), 93 (30), 51 (27), 108 (24).

5-Methyl-1,3-cycloheptadiene (12) was identified by comparison of its spectral data with those of the authentic sample.

4-Ethylidenecyclohexene (13) was identified on the basis of its spectral data and their comparison to those published:[30] IR (CCl_4) 3005 (s), 2900 (br s), 2835 (s), 1435 (br m), 1380 (w), 1370 (w), 1160 (w), 1030 (m), 925 (s), 655 (s); ^{1}H NMR ($CDCl_3$) δ 1.57 (d, 3 H), 2.15 (br s, 4 H), 2.70 (br s, 2 H), 5.15 (m, 1 H), 5.60 (br s, 2 H); MS, *m/e* 79 (100), 39 (81), 27 (70), 77 (54), 108 (47), 91 (44), 93 (41), 41 (29), 51 (28). This compound was not present in the photolysate from **3**.

***endo*-7-Methyl-2-norcarene (3)** was eluted last from column a. No other product besides **3** was detected in the sample isolated from either photolysate.

In analytical runs, 50 mL of solution containing methylcyclohexane (3 μL) as internal standard was placed in the reaction vessel (50-mL volume) and purged with nitrogen with stirring for 30 min. The solution was irradiated with the Zn resonance lamp with vigorous stirring and under a slow stream of nitrogen. Aliquots were removed after appropriate irradiation periods for VPC analysis (column a, 85 °C). Irradiation was usually carried out to ca. 10% conversion (ca. 60 min). Product and starting material concentrations were evaluated from the measured ($H \times W_{1/2}$) peak areas (relative to internal standard) in the VPC traces. Plots of concentration vs. time were linear for all products and starting materials up to at least 10% conversion. Product yields, summarized in eq 2 and 3 for the direct photolyses, were obtained from the ratio of the slopes of the $[P_i]$ vs. t and $[\sum P_i]$ vs. t plots. For those products that eluted as mixtures on column a, the yield of the mixtures were determined as described above, and then the relative proportions of the components were evaluated with use of column b or c and the mixtures isolated from the preparative runs. Material balances were obtained from the ratio of the slopes of the $[\sum P_i]$ vs. t and [SM] vs. t plots, and were at least 80%. Representative VPC traces and $[P_i]$, $[\sum P_i]$, and [SM] vs. time plots are available as supplementary material.

Total product quantum yields for **2** and **3** relative to 2-norcarene (**1**) were estimated by photolyzing 0.015 M solutions of **2**, **1**, and **3** in a 1 cm × 3.6 cm round cell in the apparatus described previously,[1d] which had been adapted to accommodate the Zn resonance lamp. Standard volumes (9 mL) of the solutions, containing methylcyclohexane as internal standard, were purged with nitrogen at 0 °C for 30 min, analyzed by GC in duplicate, photolyzed for 60 min, and then analyzed in triplicate. Product and starting material concentrations were determined from the measured areas of the corresponding peaks in the GC traces.

B. Toluene-Sensitized Photolysis of 2 and 3. Solutions (10 mL) containing **2** or **3** (0.032 M), toluene (0.004 M), and internal standard were placed in 8-mm quartz tubes and purged with a stream of nitrogen for 30 min. The tubes were sealed with rubber septa and irradiated in a Rayonet reactor (2537-Å lamps) through a Vycor filter. Aliquots were removed during the first 5 min for VPC analysis (columns a and b), and then the photolyses were allowed to continue for 24 h in order to establish the photostationary state for **2** and **3**. *cis*- and *trans*-**9** were evident as minor products (in roughly equal yields) in both photolyses after 1-min irradiation, although their yields could not be determined. These products are apparently destroyed by secondary, degenerative reaction, as has been observed previously.[3] The only other products formed in significant yields were *endo*-**11**, **2**, and **3**, which were collected from the photolysates by preparative VPC and compared to authentic samples. Product and starting material concentrations were determined from the measured areas of their VPC peaks (relative to internal standard). The rates of product formation summarized in Scheme II were determined from the slopes of $[P]$ vs. time plots; since identical solutions were employed in the photolyses, these rates are proportional to the product quantum yields. The photolysates had not, in fact, come to complete photoequilibrium after 24-h, photolysis; the estimated photostationary state ratio ($\mathbf{2}/\mathbf{3} = 2.55 \pm 0.15$) is the average of the ratios from **2** ($\mathbf{2}/\mathbf{3} = 2.70$) and **3** ($\mathbf{2}/\mathbf{3} = 2.39$).

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Registry No. **2**, 36601-90-8; **3**, 36601-91-9; **6a**, 55984-24-2; *cis*-**9**, 86970-66-3; *anti*-**10**, 31002-67-2; *syn*-**10**, 31002-66-1; *endo*-**11**, 86970-67-4; *exo*-**11**, 87037-50-1; **12**, 38511-90-9; **13**, 16631-66-6; **14**, 19381-80-7; **16**, 86970-68-5; **17**, 7095-65-0; 7-chloro-7-methylbicyclo[4.1.0]hept-2-ene, 86970-69-6; 1,3-cyclohexadiene, 592-57-4; 1,1-dichloroethane, 75-34-3; 7-bromo-7-methylnorbornene,

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86970-70-9; 4-bromobicyclo[3.2.0]hept-2-ene, 38352-98-6; cuprous chloride, 7758-89-6; methyllithium, 917-54-4; 5-bromo-1,3-cycloheptadiene, 64392-84-3; 1,3-cycloheptadiene, 4054-38-0; lithium dimethylcuprate, 15681-48-8; toluene, 108-88-3.

Supplementary Material Available: Figures 1–4, showing representative VPC traces and $[P_i]$, $[\sum P_i]$, and [SM] vs. time plots (4 pages). Ordering information is given on any current masthead page.

Ring-Closure Reactions. 21.[1] Intramolecular β-Elimination Competing with Ring Formation from o-(ω-Bromoalkoxy)phenoxides over a Wide Range of Ring Sizes

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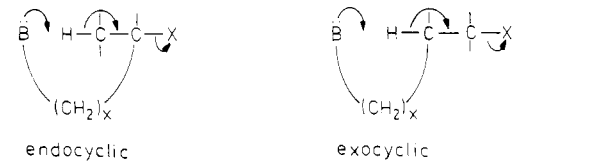
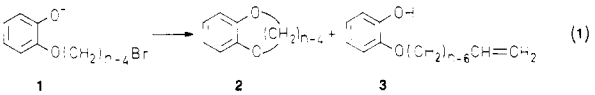
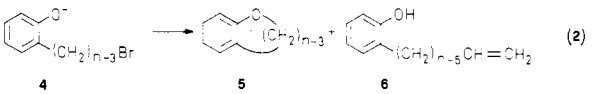
Unimolecular β-elimination of HBr from the CH_2CH_2Br end of o-$^-OC_6H_4O(CH_2)_{n-4}Br$ has been interpreted as an E2-type reaction promoted by the distal phenoxide group acting as a base. Combination of careful product analyses with kinetic data has provided rate constants and effective molarities for intramolecularly assisted elimination reactions occurring through 7-, 8-, 9-, 10-, and 14-membered ring transition states. A comparison is carried out with the competing intramolecular substitution reactions leading to ring formation. Attention is called to the specific entropic and geometrical requirements of intramolecular elimination in which the donor–proton-acceptor arrangement is a part of a cyclic structure. The importance of the present results in the general field of intramolecular acid or base catalysis phenomena is discussed.

In spite of the frequent occurrence of β-elimination besides substitution in reactions of basic nucleophiles at saturated carbon, evidence for such a competition in intramolecular reactions is scanty. In a few examples reported by Grob et al.,[2] an internal base such as N, O^-, or S^- was effective in promoting elimination via a six-membered transition state in which the incipient double bond is endocyclic. A different kind of intramolecular β-elimination reaction, namely, the one in which the incipient double bond is exocyclic, has been reported[3] in connection with our studies on the cyclization of **1** and **4** (eq 1 and 2), for which significant amounts of the olefins **3** and **6** were found to accompany the formation of the eight and nine-membered cyclic ethers **2** and **5**.







In order to provide a proper insight into the factors affecting reactivity in intramolecular proton-transfer reactions, we now report rate data for the intramolecular elimination of HBr from the o-(ω-bromoalkoxy)phenoxides (**1**) in 99% aqueous Me_2SO (v/v) in the range of n = 7–10 and 14, as well as an analogous study of the intermolecular reaction of the guaiacolate ion with decyl bromide. An attempt at determining the amount of olefin accompanying the cyclization of **4** (n = 6) is also described.

Results

The reactions were carried out in 99% Me_2SO at 25.0 °C. In all cases the initial concentration of **1** was 0.5 mM, i.e., low enough to ensure the intramolecular course of the reaction. Two sets of experiments were carried out. In one set, the anion was generated by the addition of a stoichiometric amount of KOH to the parent phenol, so that the reaction was run in the virtual absence of OH^-. In the other, a 2-fold quantity of base was added. GLC analysis of the reaction mixture showed only two peaks, namely, those of the expected **2** and **3** (comparison with authentic samples). The **3**:**2** ratio was in all cases independent of the presence of excess KOH (Table I) but was on the other hand markedly influenced by the chain length, which confirms the intramolecular nature of the elimination reactions and rules out any appreciable intermolecular contribution in all cases.

The rate constants for intramolecular elimination (k^E_{intra}) were calculated as

$$k^E_{intra} = k^S_{intra}\mathbf{3:2} \qquad (3)$$

where k^S_{intra} is the known rate constant for ring closure.[3d]

A similar procedure was applied to the model intermolecular reaction between guaiacolate ion and decyl bromide. Two independent experiments were carried out. In one experiment the concentrations of guaiacol, decyl bromide, and KOH were 1.6, 80, and 1 mM, respectively, and in the other 0.5, 10, and 0.5 mM. In both cases the yield of 1-decene relative to that of o-(decyloxy)anisole was the same within experimental errors, namely, $7.4 \pm 0.1 \times 10^{-3}$. The rate constant for the intermolecular elimination (k^E_{inter}) reported in Table I was calculated by combining

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