514 *J. Am. Chem. Soc.* **1983**, *105*, 514–519

Organic Photochemistry with 6.7-eV Photons: The Photochemistry of Bicyclo[4.1.0]hept-2-ene (2-Norcarene)

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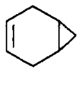
Abstract: The photochemistry of bicyclo[4.1.0]hept-2-ene (2-norcarene) upon direct and triplet-sensitized photolysis has been investigated. The results differ significantly from those of previous studies on related systems. Direct photolysis with monochromatic radiation in the region 185–230 nm leads to a variety of products, of which *cis*-1,3,6-heptatriene, the major product, is shown by deuterium labeling studies to result from formal electrocyclic ring opening in a manner analogous to the 1,3-cyclohexadiene/1,3,5-hexatriene interconversion. The evidence suggests that this process may occur via a concerted mechanism in the singlet state. The other products arise from activation of the two cyclopropane bonds that are in conjugation with the olefinic group. The product distribution is independent of both solvent and excitation wavelength and is unchanged by the addition of naphthalene. Toluene-sensitized photolysis results in the formation of *cis*-1,3,6-heptatriene and bicyclo[3.2.0]hept-2-ene, which can be rationalized as resulting from decay of a common biradical intermediate.

Systematic studies from this laboratory of the solution-phase photochemistry of aliphatic cyclopropanes with 185-nm light have included saturated mono-[1] and polycyclic[2] derivatives as well as rigid[3] and semirigid[4] nonconjugated bichromophoric systems in which some interaction between the cyclopropane moiety and an isolated carbon–carbon double bond is possible. In the semirigid system **1**, the wavelength-dependent product distribution suggests that the two chromophores behave as separate entities, the only interaction between the two being one which enables intramolecular energy transfer from the double bond to the cyclopropane ring to occur when high excitation energies are employed; with low-energy excitation, photoreactions of the isolated double bond prevail.[4] On the other hand, the lowest excited state of rigid systems such as **2** is postulated to consist of contributions from both chromophores, with the result that the photoreactivity of **2** differs considerably from that of **1**. In this report, we extend our study of the bicyclo[4.1.0]heptene system to the (conjugated) vinylcyclopropane derivative **3**.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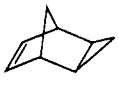
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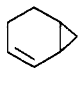
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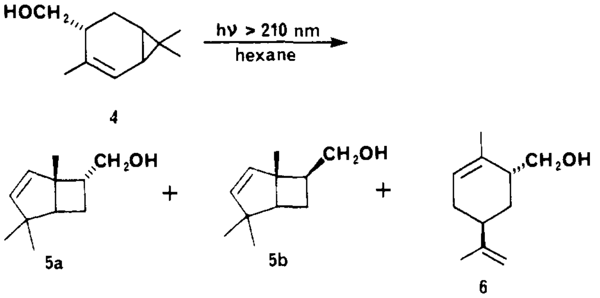
While the photochemistry of vinylcyclopropane derivatives has been widely studied,[5] a number of considerations suggested that this might be a fruitful area in which to apply solution-phase far-ultraviolet techniques. The majority of the systems which have been investigated bear substituents to extend the electronic absorption spectrum into what is generally viewed as an experimentally accessible range (i.e., >254 nm). The lowest excited singlet states in such systems are then 1–2 eV lower in energy, and the excitation is delocalized over a much larger portion of the molecule. This not only allows for facile excited-state relaxation via nonproductive pathways but may also have a profound effect on the photochemistry of the molecule. In the limited number of systems studied in which the vinylcyclopropane unit is the primary absorbing moiety, investigations appear to have been limited mostly to the triplet state. Triplet-sensitized photolysis of bicyclic vinylcyclopropanes leads generally to cyclopentene formation (the ubiquitous photochemical vinylcyclopropane rearrangement[5-9]) and cyclopropane ring isomerization.[10] It has been shown that isomerization proceeds via both internal and external bond cleavage, though the latter usually predominates.[10]

Direct photolysis has been investigated in only a couple of instances.[7-9] Most pertinent to the present study is Kropp's early investigation of the photochemistry of (+)-2-carene-4α-methanol (**4**).[7] It was demonstrated that while irradiation in the long-wavelength absorption tail produced isomeric bicyclo[3.2.0]-hept-2-enes (**5**) (eq 1), irradiation at shorter wavelengths produced complicated mixtures containing several other products in addition to those found at longer wavelengths. Given the variety of reaction pathways that have been observed (in addition to the vinylcyclopropane rearrangement) in related bicyclo[4.1.0]hept-2-ene[8,11] and vinylcyclopropane systems in general,[5] such as norbornene formation,[11] carbene extrusion,[12] bicyclopentane formation,[12b,13] and 1,3 hydrogen migration,[6,14] we were encouraged to investigate this apparent wavelength dependence in more detail, using the



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(1) Srinivasan, R.; Ors, J. A. *J. Org. Chem.* **1979**, *44*, 3246.

(2) (a) Srinivasan, R.; Ors, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 7089. (b) Srinivasan, R.; Ors, J. A.; Baum, T. *J. Org. Chem.* **1981**, *46*, 1950. (c) Srinivasan, R.; Baum, T.; Ors, J. A. *Tetrahedron Lett.* **1981**, *22*, 4795.

(3) Srinivasan, R.; Ors, J. A.; Brown, K. H.; Baum, T.; White, L. S.; Rossi, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 5297.

(4) (a) Srinivasan, R.; Ors, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 3412. (b) Srinivasan, R.; Baum, T.; Brown, K.; Ors, J.; White, L. S.; Rossi, A. R.; Epling, G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 973.

(5) Hixson, S. S. *Org. Photochem.* **1979**, *4*, 218.

(6) Cooke, R. S. *J. Chem. Soc., Chem. Commun.* **1970**, 454.

(7) Kropp, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 1126. See also ref 8.

(8) While this work was in progress, a product analogous to 7 was reportedly formed in low yield upon direct and triplet-sensitized photolysis of an extensively conjugated bicyclo[4.1.0]hept-2-ene derivative. However, the stereochemistry with respect to the C_3–C_4 double bond was not determined. See: Frei, B.; Wolf, H. R.; Jeger, O. *Helv. Chim. Acta* **1981**, *64*, 1235.

(9) Paquette, L. A.; Meehan, G. V.; Henzel, R. P.; Eizenber, R. F. *J. Org. Chem.* **1973**, *38*, 3250.

(10) (a) Garin, D. L.; Henderson, K. O. *Tetrahedron Lett.* **1970**, 2009. (b) Garin, D. L.; Cooke, D. J. *J. Chem. Soc., Chem. Commun.* **1972**, 33. (c) Kaplan, L.; Rausch, D. J.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1972**, *94*, 8638.

(11) Hart, H.; Takino, T. *J. Am. Chem. Soc.* **1971**, *93*, 720.

(12) (a) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537. (b) Jorgenson, M. J. *J. Am. Chem. Soc.* **1969**, *91*, 6432. (c) Weiss, R. G.; Hammond, G. S. *Ibid.* **1978**, *100*, 1172. (d) Pallmer, M.; Morrison, H. *J. Chem. Soc., Chem. Commun.* **1978**, 559.

(13) Kristinsson, H.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 5970.

(14) Sasaki, T.; Eguchi, S.; Ohno, M. *J. Org. Chem.* **1970**, *37*, 790.

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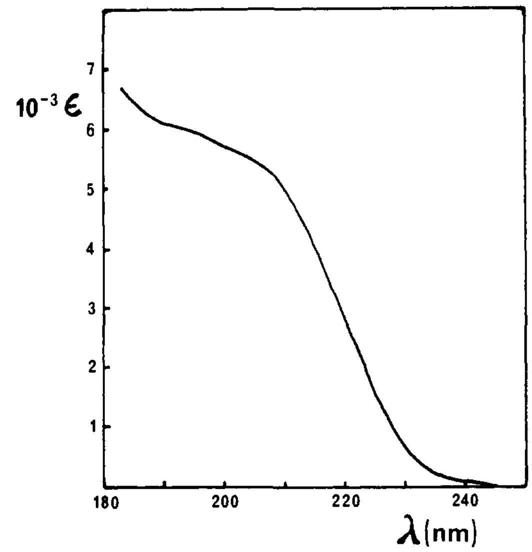


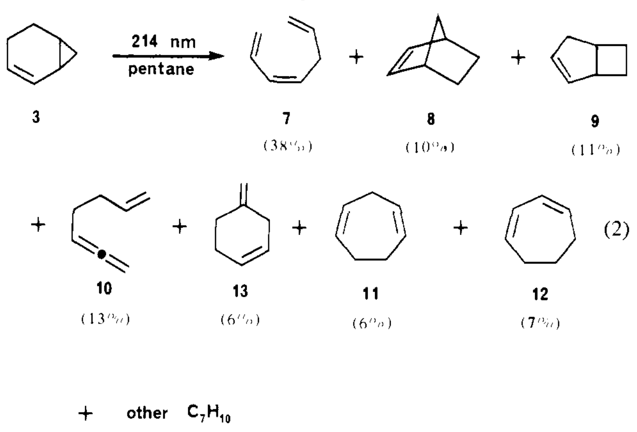
Figure 1. Ultraviolet absorption spectrum of **3** (pentane solution).

unsubstituted parent system, bicyclo[4.1.0]hept-2-ene (**3**). In addition to a complete study of the wavelength dependence of the photochemistry of this compound in the region 185–254 nm, its reactivity upon triplet sensitization was also studied, and partial mechanistic detail was obtained through deuterium labeling studies.

Results

The ultraviolet absorption spectrum of **3** in pentane solution is shown in Figure 1. Spectra of solutions of varying concentrations of **3** demonstrated adherence to Beer's law at wavelengths >196 nm.

Irradiation of a stirred 0.015 M solution of **3** in deoxygenated pentane solution with a zinc resonance lamp (λ 214 nm) produced the product mixture shown in eq 2, along with three other products (each in <4% yield) for which adequate quantities to enable positive identification could not be obtained. The products were isolated by preparative GLC from runs carried to ca. 25% 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 Experimental Section). Progress of the reaction was followed by gas chromatography, and product yields were calculated from the slopes of concentration vs. time plots, which were linear for all products and starting material up to ca. 10% conversion. The product mixtures invariably contained *trans*-**7** as well, but plots of [*trans*-**7**]/*t* vs. *t* at low (<10%) conversion demonstrated that this isomer was formed in <2% yield at zero conversion. The material balance (total products vs. consumed starting material) was at least 75%.

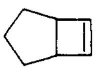


Irradiation of stirred 0.015 M solutions of **3** in deoxygenated pentane with light of wavelengths 185 + 254, 185, 193, and 228 nm produced product mixtures which were similar to that obtained in the 214-nm photolysis. Only one additional product was formed in the 185 and 185 + 254 nm photolyses, bicyclo[3.2.0]hept-6-ene (**14**). The product distributions obtained in these experiments are collected in Table I. The quantum yield for total product formation (ϕ = 0.26 ± 0.02) was determined for the 185-nm photolysis by cyclooctene actinometry.[15] Irradiation of **3** with a 450-W medium-pressure mercury lamp in conjunction with a Vycor filter for extended periods of time (20 h, 10% conversion) gave **9** (ca. 80%) along with a complex mixture of minor products. Examination of the photolysis mixture at very low conversion (ca. 2%), however, showed it to be roughly the same as that obtained in the 228-nm run.

Table I. Product Yields from the Direct and Triplet-Sensitized Photolyses of 2-Norcarene (**3**)[a,b]

	wavelength, nm						
product	185	185 (+254)	193	214	214[c]	228	sens[d]
cis-7	38	38	38	38	18	38	45
trans-7	<2	<2	<2	<2	25	<4	<1
8	7	7	8	10	11	12	
9	8	9	5	11	10	10	55
11	7	6	9	6	4	5	
12	1–2	4–5	9	7	2	4	
14	12	12	<1	0	4	<1	
10	9	8	14	13	13	13	
13	3	4	3	6	6	5	
	Material Balance,[e] %						
	62	50	76	73	67	96	~100

[a] Yields represent relative efficiencies of product formation (normalized). Error = ca. 10%. [b] All photolyses were carried out on degassed, 0.015 M pentane solutions, unless noted otherwise. See Experimental Section for a description of the light sources used. [c] Containing 0.003 M naphthalene. [d] Toluene; identical results were obtained with 0.015 M **3**/0.2 M sens and 0.05 M **3**/0.002 M sens solutions. [e] Ratio of slopes from $\Sigma(P_i)$ vs. *t* and [**3**] vs. *t* plots.



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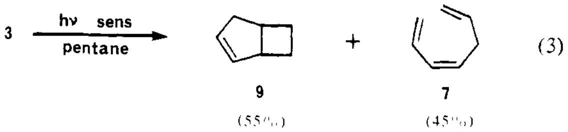
Irradiation of **3** (0.015 M) in deoxygenated methanol solution at 214 nm yielded a product mixture which was identical in all respects with that obtained upon irradiation in pentane under the same conditions. Similarly, 214-nm irradiation of **3** (0.015 M) in pentane containing 0.003 M naphthalene yielded a product mixture which differed only in the presence of **14** (4%) and both *cis*- and *trans*-**7**. The *c*/*t* ratio was invariant as a function of photolysis time.[16]

Toluene-sensitized photolysis of **3** in deoxygenated pentane solution produced **9** and *cis*- and *trans*-**7** in yields which varied with the extent of photolysis. At high (~50%) conversions, **9** predominated with *cis*- and *trans*-**7** being present as minor products (*c*/*t* = 1) along with a complicated mixture of high-boiling products. At very low (<2%) conversion however, extrapolation of concentration vs. time plots (Figure 2) gave the product mixture shown in eq 3. The product mixture was invariant as a function of sens/**3** concentrations at <2% conversion. Toluene-sensitized photolysis of *trans*-**7** resulted in cis–trans isomerization; no other products could be detected by GC, although the material balance was poor (<50%).



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(15) Schuchmann, H.-P.; von Sonntag, C.; Srinivasan, R. *J. Photochem.* **1981**, *15*, 159.

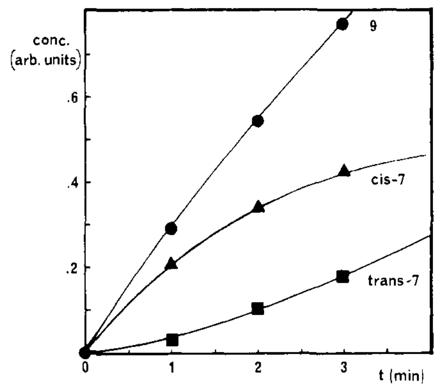
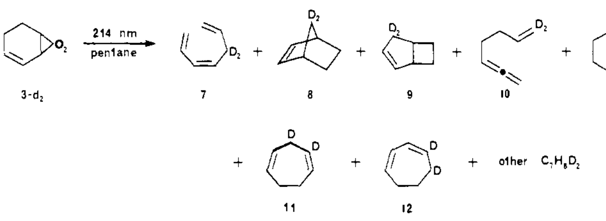


Figure 2. Concentration vs. time plot for the 0.2 M toluene-sensitized photolysis of **3** (0.015 M) in pentane solution (<5% conversion).

Photolysis of 2-norcarene-7,7-d_2 (**3**-d_2, 0.015 M) in deoxygenated pentane solution at 214 nm gave a product mixture which was identical in all respects with that obtained from **3** under the same conditions. Isolation of the products and unreacted starting material by preparative GLC, followed by proton and deuterium NMR analysis, allowed assignment of the positions of deuterium atoms in the products (eq 4). Scrambling of deuterium was not evident in the recovered starting material.



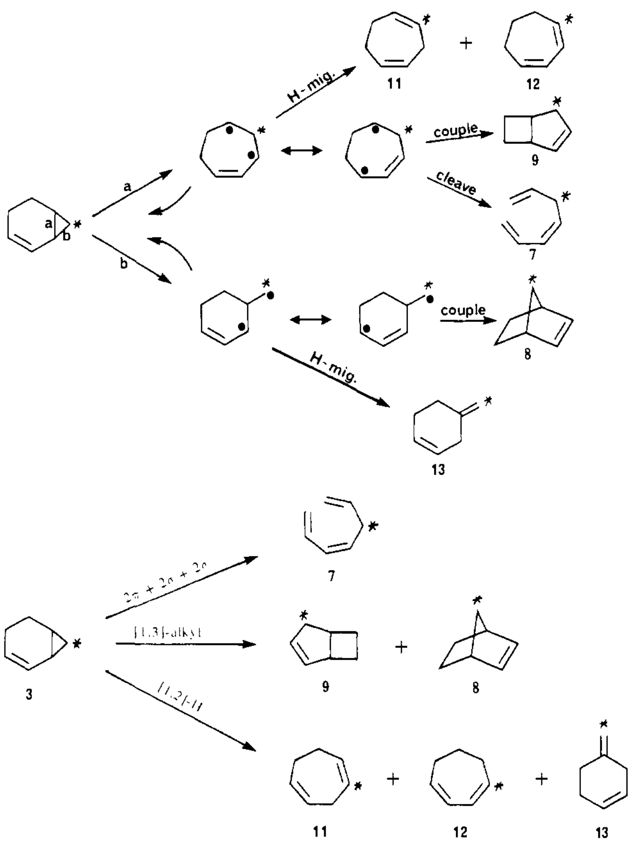
(4)

Discussion

Analysis of concentration vs. time data at low conversions (<10%) ensures that eq 1 represents the primary product mixture resulting from photolysis of **3** in the region of its lowest energy absorption band (185–230 nm). Given the low material balances (isolable volatile products vs. consumed **3**) and the plethora of products observed, the photolysis of **3** is of little synthetic utility, although the major products (viz., **7**–**10**) can be easily isolated in milligram quantities.

Since the product mixture was unchanged by the addition of naphthalene,[16] it is, presumably, entirely singlet derived, although it should be noted that **7** and **9** are formed in the toluene-sensitized photolysis as well. The result that the formation of **9** could not be quenched by naphthalene contrasts with the results of Kropp's study of the photochemistry of (+)-2-carene-4α-methanol (**4**) (eq 1). He reported that the two bicyclo[3.2.0]hept-2-ene products (**5a** and **5b**) were formed in the same ratio upon direct and triplet-sensitized photolysis, and furthermore, their formation in the direct photolysis could be quenched by the addition of naphthalene. In the present instance, direct photolysis of **3** with a medium-pressure mercury arc (Vycor filter) for extended periods of time (21 h, ~10% conversion) produced **9** as the only product present in significant amounts. Examination of the photolysate at very low (ca. 1%) conversion, however, revealed it to be qualitatively similar to that obtained with the cleaner zinc resonance lamp. This clearly shows that the broad emission of the medium-pressure Hg lamp tends to destroy all of the primary products other than the bicyclo[3.2.0]hept-2-ene(s). The discrepancy in the naphthalene quenching experiments is difficult to explain.[17] However, comparing the ratio of **7**:**9** formed in the direct photolysis (4:1) with that formed upon toluene sensitization (~1:1), it can be concluded that, at the very least, ca. 75% of the **7** formed in the direct photolysis must be singlet derived.

Scheme I. Biradical vs. Concerted Mechanisms for Decomposition of 3



Any mechanistic scheme to rationalize the products observed upon direct photolysis of **3** faces the usual problem of distinguishing between concerted and nonconcerted pathways. Ignoring, for the moment, the formation of 1,2,6-heptatriene (**10**), the two mechanistic extremes can be outlined as in Scheme I. The NMR spectral analyses of the products formed upon photolysis of **3**-d_2 demonstrate the formal course of product formation in each case. With the exception of **10**, none of the products formed upon photolysis of **3** are without precedent in cyclopropane photochemistry.[5-12] Thus, products analogous to 1,3,6-heptatriene (**7**),[8] bicyclo[3.2.0]hept-2-ene (**9**),[7,8,11] and norbornene (**8**)[11] have been observed previously upon direct photolysis of related bicyclo[4.1.0]hept-2-ene systems, while 1,3- and 1,4-cycloheptadiene and 4-methylenecyclohexene (**13**) are the products of cyclopropane ring opening/hydrogen migration.[5] Of particular interest, however, is the fact that *all* possible reaction pathways occur, and to comparable extents, upon excitation of the unsubstituted parent molecule **3** to its lowest excited singlet state.

The absence of stereochemical labels in **3** makes it impossible to distinguish between the two mechanistic extremes outlined in Scheme I, but several points are worth noting with respect to the mechanism for formation of the major product, *cis*-**7**. The stereospecific formation of the cis isomer is consistent with both concerted and biradical pathways, since the 1,4 biradical structure

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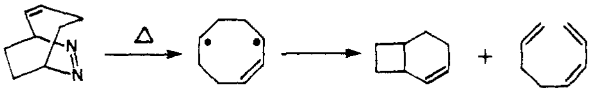
(16) The presence of *trans*-**7** (25%) and **14** (4%) is most likely the result of naphthalene-sensitized isomerization of *cis*-**7** and **12**, respectively. It was impossible to avoid irradition of the naphthalene to some extent in this experiment.

(17) A referee has suggested that the triplet of **3** might be too short-lived to be quenchable by 0.003 M naphthalene. This may certainly be the case; however, we note that our experimental conditions were nearly identical with those reported for **4**,[7] in which the formation of **5a,b** were apparently quenched. It does not seem likely that the triplet lifetimes of **3** and **4** should be too different. While it is alternatively possible that **5a,b** could have been removed from the photolysate by photocycloaddition to naphthalene[18] in the case of **4**, this does not account for all of the **5a,b** that should have been formed, according to the experimental details reported.[7]

(18) Bryce-Smith, D.; Gilbert, A.; Orger, B. H. *J. Chem. Soc., Chem. Commun.* **1966**, 512.

necessary for cleavage of the second bond (Scheme I) constrains the internal double bond in the product to have cis stereochemistry. With respect to the biradical mechanism, it is noteworthy that except for special cases (such as 1,2-dicarbinylcyclopropyl or -cyclobutyl systems),[19] there appear to be no example of cyclic, singlet 1,4 biradicals from which the ratio of cleavage/coupling (open-chain/bicyclic products) is greater than 1:3.[20] This is presumably because the geometry necessary for efficient cleavage[21] is precisely the same as that for bonding (if not even more rigorously required) and the two pathways are expected to proceed with similar (low) activation energies. Of special pertinence to the present study is the thermal decomposition of the azo compound **16** (eq 5), which proceeds to yield cleavage/coupling products in the ratio 1:3.[20b] While the ratio of **7**/**9** = 4:1 in the photolysis of **3** may seem to argue against the biradical pathway in this case, it may be unrealistic to compare the behavior of the ground-state biradical **17** (if it is indeed the only intermediate which leads to the observed products[22]) with a species that may well be reacting from an excited state.



(5)

16 **17** 75% 25%

Nevertheless, a concerted mechanism for the formation of *cis*-**7** is an attractive possibility, and orbital symmetry and least motion considerations predict the conrotatory (C_4–C_5)/disrotatory (C_1–C_6) pathway shown in eq 6 to be the most reasonable route.

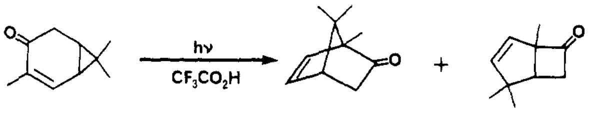
(6)

3 **cis-7**

Examination of molecular models reveals that the three other con/dis combinations, two of which lead to *trans*-**7**, are unlikely owing to geometric constraints and the large molecular motion that is necessary in order to proceed to products. This photorearrangement can be viewed as the homologue of the 1,3-cyclohexadiene/1,3,5-hexatriene interconversion and was predicted (but not observed) to be a reasonable reaction pathway upon photolysis of **4**.[7] Ultimate proof for these speculations awaits an investigation of a stereochemistry labeled (at C_4,C_5) system. It is interesting to note that thermolysis of **3** gives only a mixture of methylcyclohexadienes.[23]

The 1:1 ratio of **7**:**9** formed upon triplet-sensitized photolysis of **3** is, on the other hand, clearly consistent with a biradical mechanism. A concerted triplet pathway (leading to triplet products) is unlikely since only *cis*-**7** is formed at zero conversion. A possible explanation for the contrasting behavior of **3** and **4** with respect to 1,3,6-heptatriene formation can be offered within the framework of the concerted, electrocyclic pathway. Recent calculations of the potential energy curves for cyclopropane ring opening in both the ground and excited singlet states of variously substituted methylcyclopropanes[24] suggests that it is more difficult to break the C_2–C_3 bond in 1,1-dimethylcyclopropane than in cyclopropane itself, in both the ground and excited states. Thus, the absence of a 1,3,6-heptatriene product upon photolysis of **4** may be the result of the C_1–C_6 bond being somewhat stronger than it is in **3**. Alternatively, it may be noted that this product is particularly susceptible to secondary, degenerative reaction in both the direct (long wavelength) and triplet-sensitized photolyses of **3**.

The formation of norbornene (**8**) in the direct photolysis of **3** is noteworthy in that the reverse process (i.e., **8** → **3**) is known to occur upon mercury-sensitized photolysis of **8** in the gas phase.[25] However, **8** is not formed in the toluene-sensitized photolysis of **3** nor is it quenched by the addition of naphthalene. It therefore appears to be a singlet product in solution. A norbornene derivative has similarly been found in the direct irradiation of **18** in polar solvents[11] (eq 7), and its formation could not be quenched by the addition of trienes.

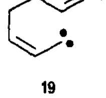


(7)

18

The formation of 1,2,6-heptatriene (**10**) is puzzling. The ^2H NMR spectrum of the **10**-d_2 isolated from the photolysis of **3**-d_2 showed a broad singlet at δ 5.03, which, in addition to the two proton multiplet at δ 4.60 (terminal allenic protons[26]) in the ^1H NMR spectrum, is most consistent with deuterium being at C_7 in **10**-d_2.

The most logical mechanism for the formation of **10** may seem to be a two-bond cleavage of **3**, leading to the vinylcarbene intermediate **19** followed by hydrogen migration. While one cannot rigorously exclude the involvement of **19** to some minor degree, it is doubtful that this intermediate is *primarily* responsible for the formation of **10** as a major product from the photolysis of **3**, even though two-bond cleavage is a well-documented photoreaction of cyclopropanes[5,12] and 1,2 hydrogen migration to allenes from vinylcarbenes does occur in some cases.[12b,27] The cyclopropene **20** is expected to be the major product from **19** (vinylcarbenes are known to undergo ring closure to cyclopropenes 4–9 times faster than hydrogen migration to yield allenes and 1,3-dienes[28]), and it can be calculated that the maximum yield of **20** that may have been undetectable under our GC conditions would be ca. 10%.[29] Also, vinylcarbenes such as **19** can be trapped by nucleophiles,[28] and no new products were evident in the photolysis of **3** in methanol solution. Finally, **19** is expected to partition as well to **7** by 1,4 hydrogen migration:[28] this would be expected to result in the formation of both the cis and trans isomers, as well as yield **7**-d_2 with deuterium in the 7-position in the photolysis of **3**-d_2. *trans*-**7** was shown to be formed in <2% yield at zero conversion, and the ^2H NMR spectrum of *cis*-**7**-d_2 was devoid of absorption in the vinyl region, illustrating that the **7**-d_2 formed



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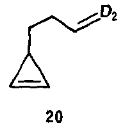

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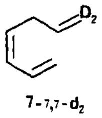

7-7,7-d₂

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[19] (a) Tanida, H.; Teratake, S.; Hata, Y.; Watanabe, M. *Tetrahedron Lett.* **1969**, 5341, 5345. (b) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

[20] See, for example: (a) Watson, C. R.; Pagni, R. M.; Dodd, J. R.; Bloor, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 2551. (b) Olsen, H.; Snyder, J. P. *Ibid.* **1978**, *100*, 285.

[21] (a) Bartlett, P. D.; Porter, N. A. *J. Am. Chem. Soc.* **1968**, *90*, 5317. (b) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *Ibid.* **1972**, *94*, 7506.

[22] (a) A bulk of evidence suggests that **16** may decompose via a stepwise process involving an allyl diazenyl diradical intermediate as a precursor to **17**.[19b] Molecular models indicate that this diradical may be flexible enough to allow N_2 displacement (via an intramolecular S_H2 process[22b]) to compete with the N_2 extrusion process that leads to **17**. Competition from this additional pathway would weigh the observed product mixture in favor of the coupling product. (b) Crawford, R. J.; Chang, M. H. *Tetrahedron* **1982**, *38*, 837.

[23] Mironov, V. A.; Fedorovich, A. D.; Mil'vitskaya, E. M.; Korner, O. Y.; Akhrem, A. A. *Dokl. Akad. Nauk SSR* (*Engl. Trans.*) **1972**, *203*, 347.

[24] Rossi, A. R. *J. Phys. Chem.* **1979**, *83*, 2554.

[25] Arnold, D. R.; Abraitys, V. Y. *Mol. Photochem.* **1970**, *2*, 27.

[26] Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: London, 1969; pp 190.

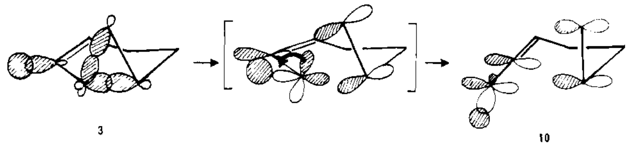
[27] Steinmetz, M. G.; Mayes, R. T.; Yang, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3518.

[28] For a general discussion of the behavior of vinyl carbenes as pertaining to cyclopropene formation and leading references, see: Padwa, A. *Org. Photochem.* **1979**, *4* (Chapter 4).

[29] This value was calculated assuming that the retention time of **20** under our GC conditions is the same as that for **3** and that we could have detected at least 3% of such an impurity in the ^1H NMR spectrum of recovered **3**. Neither the ^1H NMR nor IR spectra of **3** recovered after 214-nm photolysis showed any absorption attributable to a cyclopropene derivative.

in the photolysis of **3**-d_2 is at least 97% deuterated in the 5-position.[30] It is concluded, therefore, that two-bond cleavage leading to **19** as a discrete intermediate does not occur to any significant extent upon excitation of **3** to its lowest singlet state.

Similarly, the deuterium labeling experiment demonstrates that **10** is not formed as a secondary photolysis product arising from 1,3 hydrogen migration in **7**.[12b] Besides, concentration vs. time analysis at low conversion indicates that **10** is a *primary* product of **3**, and irradiation of **7** in pentane solution (214 nm) does not produce **10** in any detectable yield. It is tentatively suggested that **10** may be formed from **3** via a suprafacial 1,2 migration of the vinyl hydrogen to the backside of C_1, in concert with cyclopropane ring opening, in a manner which is formally illustrated in eq 8.[31a]



(8)

While this rearrangement is, as far as we know, unprecedented, we note that the transition state shown in eq 8 is a uninodal, six-electron array, leading to the prediction that such a process should be photochemically allowed.[31b] The reaction can be alternatively viewed as proceeding via initial development of carben*oid* character at C_1 with subsequent 1,2 H migration, although we stress that our results do not allow a mechanism involving a *discrete* vinylcarbene intermediate.

As the data in Table I reveal, there is essentially no wavelength dependence of the product mixture formed upon direct irradiation of **3** in the region 185–230 nm. Although the ratio of *trans*-/*cis*-**7** at a given degree of conversion varies as a function of excitation wavelength, this is presumably a secondary photolysis effect, since analysis of concentration vs. time data at low conversions demonstrates that *cis*-**7** is formed stereospecifically in each case. Similarly, the bicyclo[3.2.0]hept-6-ene (**14**) that is present in the 185-nm (Acton filter) and 185 + 254-nm runs is presumably a secondary photolysis product of 1,3-cycloheptadiene (**12**).[32] Although we had hoped that the use of the band-pass filter would suppress the formation of **14** entirely, we note that the transmittance of this filter is ca. 4.5% at 254 nm. Furthermore, the absence of **14** in the photolysis of **3** with the monochromatic argon fluoride laser (193 nm) provides additional evidence that this product most likely arises from photolysis of **12** at 254 nm, and not as a result of **12** being formed in a vibrationally excited ground state or electronically excited state.[4a]

The lack of wavelength dependence in the photochemistry of **3** is not surprising for a couple of reasons. First, although both the appearance of the absorption spectrum of **3** (Figure 1) and PMO calculations for vinylcyclopropane itself[33] indicate that S_1 and S_2 may be very similar in energy, the two states are likely to be very strongly coupled. This contrasts with the situation in weakly interacting bichromophoric systems (e.g., **1**) in which the two chromophores are essentially isolated. Although S_1 and S_2 may again be similar in energy, they are only weakly coupled.[3,4a] Secondly, the rigidity of a system such as **3** further simplifies the excited-state manifold in that only two conformations (with respect to the relative orientations of the π bond and the cyclopropane ring) are possible; furthermore, one of these is clearly less favorable owing to nonbonded H–H interactions.

The quantum yield for product formation of only 0.26 for the 185-nm photolysis of **3** suggests that cyclopropane cis–trans isomerization may be an important pathway for excited-state decay in this system, although we obviously have no way of detecting it in **3**. Further study in this area will focus on this aspect and probe the stereospecificity in the various photoreactions in this system.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded in carbon tetrachloride solution on a Beckman Acculab 6 spectrometer and are reported in wavenumbers. ^1H and ^2H NMR spectra were recorded in carbon tetrachloride solution on an IBM Instruments NR80 spectrometer, with benzene-d_6 as both internal lock and reference, and are reported in parts per million downfield from Me_4Si. The ultraviolet absorption spectrum of **3** was recorded in degassed pentane (Baker-Photrex grade) solution on a Cary 17D spectrometer and is reported in nanometers. Mass spectra were recorded on a Hewlett-Packard 5995 gas chromatograph/mass spectrometer equipped with a 3% OV-101 (12 × 0.25 in.) glass column.

Analytical and preparative gas chromatographic separations were carried out on a Hewlett Packard 5750B gas chromatograph equipped with flame ionization and thermal conductivity detectors and the following columns: (a) 20% DOPN on 80/100 Chromosorb PNAW, 24 ft × 0.25 in.; (b) 10% OV-101 on 80/100 Supelcoport, 14 ft × 0.25 in.; (c) 20% Apiezon L on 60/80 Chromosorb, 14 ft × 0.25 in. Column a was used in conjunction with the FID for quantitative runs. GC response factors were assumed to be identical for all products and starting material.

Bicyclo[4.1.0]hept-2-ene (3) was synthesized by the method of Winstein and Sonnenberg[34] from 1,3-cyclohexadiene and bromoform, followed by reduction of the dibromide with sodium and wet methanol. Distillation of the crude material after workup yielded **3** as a colorless liquid (bp 61–62 °C (200 mm)), which was purified 3 times by preparative GC (column (a), 80 °C). Its ^1H NMR, IR, and mass spectra were similar to those published.[35]

Bicyclo[4.1.0]hept-2-ene-7,7-d_2 (3-d_2) was synthesized in the same manner as was **3**, except methanol-o*d*/D_2O was used in the reduction of the dibromide. Workup, distillation (bp 62–64 °C (200 mm)), and three purifications by preparative GC (column (a), 80 °C) afforded material whose IR, ^1H NMR, and mass spectra coincided with those published.[35] The ^2H NMR (δ 0.65, br s) and ^1H NMR spectra demonstrated that the sample was >98% deuterated in only the 7-position.

Toluene (reagent grade) and **naphthalene** (reagent grade) were used as obtained from J. T. Baker Co. and Aldrich Chemical Co., respectively.

Apparatus. All photolyses (except the 193-nm, 185-nm (band-pass filter), and toluene-sensitized runs) were conducted on a semipreparative scale in pentane (Baker-Photrex) or methanol (Mallinckrodt Transistor) solutions in a water-jacketed, Pyrex reaction vessel bearing a gas inlet and sidearm, and fitted with a Suprasil or Vycor immersion well, reflux condenser, and magnetic stirrer. The light sources were a 10-W Osram HNS 10-W/U OZ low-pressure mercury resonance lamp (185 + 254 nm), a 100-W Philips 93106E zinc resonance lamp (214 nm), a 100-W Philips 93107E cadmium resonance lamp (228 nm), a Lambda-Physik EMG500 argon fluoride laser (193 nm, 25 mJ/pulse, 1 pulse/s), a Hanovia 0.5-W Ottawa-type cold cathode low-pressure mercury resonance lamp in conjunction with an Acton 185-nm band-pass filter (185 nm), a Hanovia 450-W medium-pressure mercury vapor lamp with Vycor filter (>220 nm), and a Rayonet reactor equipped with 2537-Å lamps. The lamps were given a warmup time of 10–30 min and were cooled with a stream of nitrogen during the photolyses.

Procedure. Direct Photolysis. Direct photolysis was carried out on 0.015 M solutions in every case. In preparative runs, 100 mL of a pentane solution of **3** 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 3 h (ca. 25% conversion). Two such runs were combined, the pentane was distilled off, and the products were separated by gas chromatography (column a). The products, described below in order of their elution from the column, were identified by comparison of their spectral data with literature data and/or authentic samples. **3** elutes between **13** and **11**.

Norbornene (8) was identified by comparison of its IR, ^1H NMR, and mass spectra and GC retention times with those of an authentic sample (Aldrich).

Bicyclo[3.2.0]hept-2-ene (9) was identified by comparison of its spectral data and GC retention times with those of an authentic sample, prepared by reductive dechlorination of 7,7-dichloro-bicyclo[3.2.0]-hept-2-en-6-one (Alfa) with zinc and acetic acid,[36] conversion of the resulting ketone to its semicarbazone (mp 217–219 °C dec), and reduction of the semicarbazone by the method of Herzog and Buchanan:[37]

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[30] Assuming a value of 3% for a realistic limit to detection by ^2H NMR.

[31] (a) For the sake of simplicity, we have used σ orbitals for the cyclopropane ring to illustrate this process. (b) Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272.

[32] Chapman, O. L.; Pasto, D. J.; Borden, G. W.; Griswold, A. A. *J. Am. Chem. Soc.* **1962**, *84*, 1220.

[33] Shanshal, M. *Z. Naturforsch. A* **1976**, *31A*, 488.

[34] Winstein, S.; Sonnenberg, J. *J. Am. Chem. Soc.* **1961**, *83*, 3235.

[35] Schneider, M.; Erben, A.; Merz, I. *Chem. Ber.* **1975**, *108*, 1271.

[36] Zimmerman, H. E.; Ago, *J. Am. Chem. Soc.* **1959**, *81*, 3644.

IR 3040 (m), 2960 (s), 2920 (s), 2898 (s), 2835 (m), 1438 (m), 1350 (m), 1050 (m), 922 (m), 680 (w); ^{1}H NMR 1.65 (d of d, 2 h), 2.00–2.57 (m, 4 H), 2.70–3.30 (cplx m, 2 H), 5.72 (s, 2 H); mass spectrum, *M/e* 94.

1,2,6-Heptatriene (10) was identified by comparison of its IR and ^{1}H NMR spectra with published data:[38] IR 3070 (m), 2988 (m), 2905 (m), 2840 (m), 1950 (s), 1638 (m), 1435 (m), 910 (s); ^{1}H NMR 2.07 (br s, 4 H), 4.62–5.03 (m, 4 H), 5.69 (m, 2 H); mass spectrum, *m/e* 94.

***trans*-1,3,6-Heptatriene (*t*-7)** was identified by comparison of its IR, ^{1}H NMR, and mass spectra and GC retention times with those of an authentic sample (Aldrich ABC).

***cis*-1,3,6-Heptatriene (*c*-7)** was identified by comparison of its spectra and GC retention times with those of an authentic sample, prepared by irradiation of a GC-purified sample of *t*-**7** in pentane solution at 228 nm for 5 h, and isolated by GC (column a).

4-Methylenecyclohexene (13) was identified by comparison of its spectral data with those published:[39] IR 3060 (w), 3010 (w), 2895 (m, br), 2815 (w), 1642 (m), 1430 (w, br), 1160 (w), 880 (s), 645 (w); ^{1}H NMR 2.17 (br s, 4 H), 2.68 (s, 2 H), 4.67 (s, 2 H), 5.59 (s, 2 H); mass spectrum, *m/e* 94.

1,4-Cycloheptadiene (11) was identified by comparison of its spectral data and GC retention times with those of an authentic sample:[40] IR 3005 (s), 2900 (s, br), 2830 (m), 1645 (m, br), 1430 (m, br), 680 (m), 610 (m); ^{1}H NMR 2.26 (m, 4 H), 2.84 (m, 2 H), 5.65 (n2, 4 H); mass spectrum, *m/e* 94.

1,3-Cycloheptadiene (12) was identified by comparison of its spectral data and GC retention times with those of an authentic sample (Wiley Organics).

Bicyclo[3.2.0]hept-6-ene (14) was isolated by GC from a 185 + 254-nm run (column a, elutes before norbornene) and was identified on the basis of a comparison of its spectral data with those of an authentic sample:[32] IR 3100 (w), 3021 (s), 2929 (s), 2842 (m), 1432 (m), 1315 (m), 1290 (m), 1045 (w), 930 (w), 886 (w); ^{1}H NMR 1.0–1.7 (cplx m, 6 H), 3.12 (d, 2 H), 5.80 (s, 2 H); mass spectrum, *m/e* 94.

Preparative-scale photolysis of **3**-d_2 and isolation of products was carried out as described above for **3**. Product identification was carried out by comparison of their GC retention times (columns a and b) with the corresponding products from **3**, and by ^{1}H and ^{2}H NMR spectra. The ^{1}H and ^{2}H NMR spectra of **3**-d_2 recovered after photolysis were identical with those obtained before photolysis.

8-d_2: ^{2}H NMR 1.07 (s, 1 D), 1.31 (s, 1 D); ^{1}H NMR 0.89 (d, 2 H), 1.53 (d, 2 H), 2.76 (s, 2 H), 5.87 (s, 2 H).

9-d_2: ^{2}H NMR 2.13 (s, 1 D), 2.52 (s, 1 D).

10-d_2: ^{2}H NMR 5.03 (s); ^{1}H NMR 2.04 (br s, 4 H), 4.59 (br s, 2 H), 4.99 (m, 1 H), 5.69 (m, 1 H).

cis-**7**-d_2: ^{2}H NMR 2.92 (s); the ^{1}H NMR spectrum was similar to that of *cis*-**7** except for the absence of the 2 H triplet at 2.92 ppm.

13-d_2: ^{2}H NMR 4.67 (br s); ^{1}H NMR 2.15 (m, 4 H), 2.66 (s, 2 H), 5.54 (s, 2 H).

11-d_2: ^{2}H NMR 2.80 (s, 1 D), 5.62 (s, 1 D); ^{1}H NMR 2.17 (br s, 4 H), 2.76 (m, 1 H), 5.57 (br s, 3 H).

12-d_2: ^{2}H NMR 2.24 (s, 1 D), 5.75 (s, 1 D); ^{1}H NMR 1.75 (m, 2 H), 2.20 (m, 3 H), 5.64 (s, 3 H).

In analytical runs (185 + 254, 214, 228 nm), 50 mL of solution containing methylcyclohexane (3 μL) as internal standard were placed in the reaction vessel (50-mL volume) and purged with nitrogen with stirring for 30 min. The solution was irradiated with the appropriate lamp with vigorous stirring and under a slow stream of nitrogen. Aliquots were removed every 3 min for GC analysis (column a, 70 °C). Irradiation was usually carried 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 the internal standard) in the GC traces. Plots of concentration vs. time were linear for all products and starting material up to at least 10% conversion. Product yields, collected in Table I, were obtained from the ratio of the slopes of the (P_i) vs. t and ($\sum P_i$) vs. t plots. Material balances were obtained from the ratio of the slopes of the ($\sum P_i$) vs. t and [**3**] vs. t plots.

In the 193-nm run, the unfocussed beam of the argon fluoride laser was trained on the face of a Suprasil cuvette (1 × 1 × 4 cm) which contained the degassed (30 min) solution of **3** (+internal standard). The fluence at the face of the cuvette was determined to be ca. 13 mJ/cm^2. The solution was irradiated with stirring, and aliquots were removed every 25 pulses for GC analysis as above. Product yields and material balances were determined as described above, and are collected in Table I.

In the 185-nm (band-pass filter) run, 10.0 mL of a degassed (30 min), 0.015 M solution of **3** (+internal standard) was irradiated in the apparatus described previously.[2c] Standard volume (100 μL) aliquots were removed every 30 min for GC analysis (as above). Irradiation for 6 h took the reaction to ca. 5% conversion. Concentration vs. time plots were linear for all products, and product yields, determined as described above, are collected in Table I. The quantum yield for total product formation was determined by cyclooctene actinometry,[15] which was conducted immediately after the run.

The photolysis of **3** in methanol was carried out in exactly the same manner as those in pentane. Progress of the reaction was followed by GC (column c); the appearance of the chromatogram was identical with that of a pentane photolysate run under the same conditions. After photolysis (1.5 h), water (150 mL) was added, and the solution was extracted with pentane (3 × 15 mL). The extract was dried over anhydrous sodium sulfate and filtered. The gas chromatogram of the mixture (column a) was identical with that of a pentane run under the same conditions.

In the naphthalene quenching experiment, a 0.015 M solution of **3** containing 0.003 M naphthalene and internal standard was degassed and irradiated as described above. Product yields were determined as described above and are collected in Table I.

Triplet-Sensitized Photolysis of 3 and 3-d_2. A solution containing **3**, toluene, and internal standard in pentane was placed in a 8-mm quartz tube and degassed for 30 min. The solution was irradiated in a Rayonet reactor (2537-Å lamps) through a Vycor filter. Aliquots were removed during the first 10 min for GC analysis, and then the photolysis was allowed to continue for several hours in order to examine the photolysate at high conversions. Plots of product concentration vs. time are shown in Figure 2 for a (0.015 M **3**/0.21 M sens) run; identical results were obtained in a (0.05 M **3**/0.003 M sens) run. At <3% conversion, no other products besides *cis*- and *trans*-**7** and **9** were evident in the photolysate, and the material balance was good. As the photolysis proceeded to higher conversion, **7** was consumed, and high-boiling products (a mixture of several, by GC/MS) began to appear. These were not isolated. **7** and **9** were isolated by GC from a preparative-scale run and were identified on the basis of spectral data and their GC retention times. The ^{2}H NMR spectra of **7**-d_2 and **9**-d_2 isolated from a preparative-scale photolysis of **3**-d_2 were identical with those obtained in the direct photolysis of **3**-d_2.

Acknowledgment. We thank T. H. Baum for authentic samples of **11** and **14** and Professor D. R. Arnold, Dalhousie University, for helpful discussion. This work was supported by a grant from the National Science Foundation to Dr. Gary Epling, University of Connecticut, under the University-Industry Cooperative Program.

Registry No. 3, 2566-57-6; **9**, 7095-65-0; toluene, 108-88-3; naphthalene, 91-20-3; 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one, 5307-99-3; bicyclo[3.2.0]hept-2-en-6-one, 13173-09-6; bicyclo[3.2.0]hept-2-en-6-one semicarbazone, 83968-13-2.

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(37) Herzog, H. L.; Buchanan, E. R. *J. Org. Chem.* **1951**, *16*, 99.

(38) Skattebol, L. *J. Org. Chem.* **1966**, *31*, 2789.

(39) Babad, H.; Felmon, W.; Wood, J. B. *J. Org. Chem.* **1967**, *32*, 2871.

(40) Doering, W. von E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715.