

1:96:3; 15-18, hexane, 298 mg of **9** and **10**, ratio 7:3; 19-24, hexane, 129 mg of **9** and **10**, ratio 4:6; 25-26, hexane, 23 mg of **9** and **10**, ratio 1:4; 27-30, 12 mg of **10**; 31-38, 1% ether-hexane, nil; 39-42, 1% ether-hexane, 210 mg of oligomeric material; 43-44, 5.0% ether-hexane, nil; 45-52, 5% ether-hexane, 17 mg of oligomeric material; 53-60, 10% ether-hexane, 45 mg of hexatriene dimers; 61-62, 10% ether-hexane, nil; 63-69, 10% ether-hexane, 62 mg of **40**.

Direct Irradiation of 3-Deuteriotriphenylallene (2d). Allene **2d** (100 mg) in pentane (200 mL) was cooled to -10°C , irradiated with 254-nm lamps for 1.0 h, and then was concentrated in vacuo. ^1H NMR analysis showed singlets at δ 4.70 (allylic proton of **9**) and broad singlets at 4.25, 3.90, and 4.97 (corresponding to **13**, **14**, and **12**, respectively). No signals at δ 5.21 (propyne) or 6.67 (vinyl proton of **9**) were observed.

Measurement of Deuterium Isotope Effect. Quartz tubes containing identical pentane solutions of **2** and **2d** (10.0 mg each) were purged with N_2 , cooled to -20°C , and irradiated in a Rayonett merry-go-round apparatus for 1-2 min. Internal standard was added, and the mixture was analyzed by HPLC. Three separate runs at 0.5-1% conversion yielded (HPLC analysis) the following results for $k_{\text{H}}/k_{\text{D}}$ (standard deviations shown): 1,3-diphenylindene (**9**), 1.13 ± 0.21 ; 1,3,3-triphenylcyclopropene (**10**), 1.39 ± 0.01 ; 1,3,3-triphenylpropyne (**11**), 3.72 ± 0.26 .

Quantum Yield Determination for Triphenylallene (2). A 1.54×10^{-3} M isooctane solution of **2** (50 mL) in a quartz cell was irradiated on the optical bench²¹ for periods of 40 min to 3 h. Internal standard was added, and the mixture was analyzed by HPLC. Four separate runs at 0.1%-1.0% conversion yielded the following quantum yields for product formation: cyclopropene (**10**), 0.004 ± 0.0006 ; 1,3-diphenylindene (**9**), 0.019 ± 0.004 ; 1,3,3-triphenylpropyne (**11**), 0.002 ± 0.0005 .

Quantum Yield Determination for 1,3,3-Triphenylcyclopropene (10). A quartz cell containing **10** (30 mg) and isooctane (50 mL) was irradiated on the optical bench for 7.5-14 h. Internal standard was added, and the solution was concentrated in vacuo. The product was analyzed by 300-MHz NMR integration. Five separate runs at 1-10% conversion yielded the following quantum efficiencies for products: triphenylallene

(**2**), 0.012 ± 0.003 ; 2,3-diphenylindene (**13**), 0.061 ± 0.01 ; 1,3-diphenylindene (**9**), 0.034 ± 0.006 .

Quantum Yield Determination for 1,3-Diphenylindene (9). A quartz cell containing **9** (25 mg) and isooctane (50 mL) was irradiated on the optical bench for 2-9 h. Internal standard was added, and the solution was concentrated in vacuo. Products were analyzed by 300-MHz NMR integration. Five separate runs at 0.5-20% conversion yielded the following quantum efficiencies for product formation: 2,3-diphenylindene (**13**), 0.12 ± 0.01 ; 1,2-diphenylindene (**12**), 0.031 ± 0.004 .

Thermolysis of 1,3,3-Triphenylcyclopropene (10). Samples of cyclopropene **10** (16 mg) in toluene (10 mL) were degassed with three freeze-pump-thaw cycles, sealed, and then thermolyzed at constant temperature. Internal standard was added, and solution was concentrated in vacuo. Products were analyzed by 300-MHz NMR integration. Three separate runs yielded the following results:

temp, $^{\circ}\text{C}$	time, h	% 9	% 13	conversion
196	1	78	22	100%
132	0.5	78	22	100%
85	0.5	75	25	6%

Acknowledgment. This work was generously supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. **1**, 1674-18-6; **2**, 966-87-0; **2-d**, 13210-94-1; **6**, 38274-35-0; **6a**, 4614-01-1; **7**, 19692-28-5; **8**, 67961-32-4; **9**, 4467-88-3; **10**, 87443-01-4; **11**, 5467-43-6; **12**, 18636-54-9; **13**, 5324-00-5; **14**, 201-65-0; **15**, 16510-49-9; **16**, 24435-50-5; **20**, 96348-43-5; **21**, 96348-44-6; **22**, 96348-45-7; **35**, 25683-83-4; **36**, 4023-77-2; **37**, 849-01-4; **38**, 87443-02-5; **39**, 25229-60-1; **40**, 25229-62-3; 2,3,3-triphenylpropenol, 25683-83-4; deuterium, 7782-39-0; 2,3-diphenylpropenoic acid, 3368-16-9; phenyllithium, 591-51-5; *p*-toluenesulfonylhydrazide, 1576-35-8.

Cumulene Photochemistry: Singlet and Triplet Photorearrangements of 1,2-Cyclononadiene

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Received August 20, 1984

Abstract: Direct solution-phase irradiation of 1,2-cyclononadiene (**1**) yields bicyclo[6.1.0]non-1(9)-ene (**6**), tricyclo[4.3.0.0^{2,9}]nonane (**3**), and cyclononyne (**7**) as primary photoproducts in a 94:3:3 ratio. Monodeuterated **1** shows a kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} = 1.30 \pm 0.06$ for the formation of **6**, which implies that hydrogen, rather than carbon, is migrating. Optically active **1** is rapidly photoracemized; the relative rate of racemization to isomerization to **6** is determined to be 70. Irradiation of **1** in methanol yields **6**, **7**, **3**, and *cis*-3-methoxycyclononene in a 90:2:3:3 ratio. Independent generation of vinylcarbenes potentially related to **1** and **6** was carried out through photolysis of tosylhydrazones sodium salts. These experiments provide argument that vinylcarbenes are not involved in solution-phase photoreactions of **1**, and a concerted rearrangement mechanism is proposed. Vapor-phase irradiation of **1** at 185 nm yields complex product mixtures. Among the major products is 1,3,8-nonatriene, the apparent product of β -homolytic cleavage. Benzene-sensitized vapor-phase irradiation of **1** yields the previously reported tricyclo[4.3.0.0^{2,9}]nonane (**3**, 89%), in addition to three bicyclics: *cis*-bicyclo[4.3.0]non-2-ene (**9**, 2%), bicyclo[4.3.0]non-1(2)-ene (**32**, 5%), and bicyclo[4.3.0]non-1(9)-ene (**33**, 4%). Ab initio calculations reported here show that cyclopropylidene should have a singlet ground state. Estimates of the energy of triplet cyclopropylidene (3.3-3.4 eV above allene) and planar triplet allene (2.2 eV) show that either species can result from nonvertical energy transfer from triplet benzene (3.66 eV). Competitive diradical and cyclopropylidene triplet mechanisms are proposed.

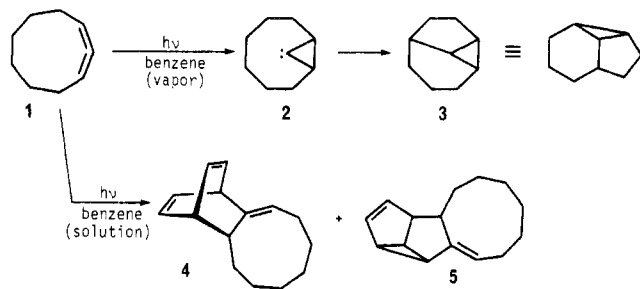
1,2-Cyclononadiene (**1**), with its allenic chromophore bent ca. 10° from linearity, is the smallest unsubstituted cyclic allene which is kinetically stable at ambient temperature.¹ The photochemistry of this archetypal cyclic allene was first described in a classic paper by Ward and Karafiath.² Benzene-sensitized irradiation yielded tricyclo[4.3.0.0^{2,9}]nonane (**3**, $\Phi = 0.17$ in the vapor phase), while

direct irradiation afforded four C₉ isomers, one of which was believed to be **3**. The remaining products were not identified. In what appeared to be a general reaction of both linear and cyclic allenes, a cyclopropylidene intermediate (**2**) was proposed. Subsequently, Gilbert reported formation of cycloadducts **4** and **5** from irradiation of **1** in benzene solution.^{3a}

(1) Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.*, **1985**, *107*, 532 and references therein.

(2) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 7475.

(3) (a) Berridge, J. C.; Forrester, J.; Foulger, B. E.; Gilbert, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2425. (b) The 4:5 ratio was determined by GLC analysis, and it is possible that isomer **5** is selectively destroyed under these conditions.

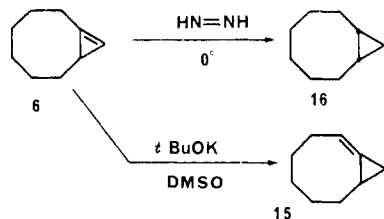


Our investigations of acyclic phenylallene photoreactions,^{4,5} parallel studies by Steinmetz,⁶ and an earlier report by Chapman,⁷ had suggested that 1,2-hydrogen migration might be an important singlet photoreaction of allenes. Because of their structural simplicity and ready synthetic accessibility, cyclic allenes seemed excellent substrates for exploratory and mechanistic studies, and we have sought to securely characterize their photoreactions. We report here details of our studies on 1,2-cyclononadiene.^{8a} Parallel studies on homologous allene 1,2-cyclodecadiene are reported separately.^{8b}

Exploratory Singlet Photochemistry. 1,2-Cyclononadiene (**1**) was prepared from cyclooctene according to the classic Doering–Moore–Skattebøl route.⁹ Allene **1** was >99.8% pure by capillary GLC and 300-MHz NMR but was further purified by preparative GLC for analytical studies.

Irradiation of dilute (10^{-3} M), argon-degassed pentane solutions of **1** with wavelengths > 220 nm (Vycor filter) yielded cyclopropene **6**, cycloalkyne **7**, and tricyclic **3** (ratio 94:3:3) as primary photoproducts (Scheme I). These were isolated by preparative GLC on glass columns and unambiguously characterized by spectral data and independent synthesis (vide infra). At low conversion of **1** (<2%), **6**, **7**, and **3** constituted >95% of the photoproducts, as judged by GLC and NMR analyses. Higher conversions led to significant secondary reactions of **6**, which are described below. UV spectra for **1** and **6** show maxima below 200 nm; however, both absorb weakly up to ca. 240 nm. Characterization of **6**, **7**, and **3** as primary photoproducts is based on capillary GLC analysis at very low conversions (0.2–2%). Isomers **7** and **3** were undetectable as primary products in our earlier study, due to less sensitive analytical conditions. The possibility of solution-phase wavelength effects was explored through irradiation of pentane solutions of **1** with 185 (+254 nm) light in a Rayonet photoreactor. No difference was observed in the low-conversion photoproducts.

Spectral data for **6** included a singlet in the ¹H NMR at δ 6.47 and a strong infrared absorption at 1780 cm^{-1} , both indicative of a cyclopropene moiety. Diimide reduction of **6** gave **16**, while brief base treatment yielded the known methylenecyclopropane **15**.¹⁰



(4) Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, 25, 2523.

(5) Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) Steinmetz, M. G.; Mayes, R. T.; Yang, J.-C. *J. Am. Chem. Soc.* **1982**, 104, 3518. Steinmetz, M. G.; Mayes, R. T. *J. Am. Chem. Soc.* **1985**, 107, 2111.

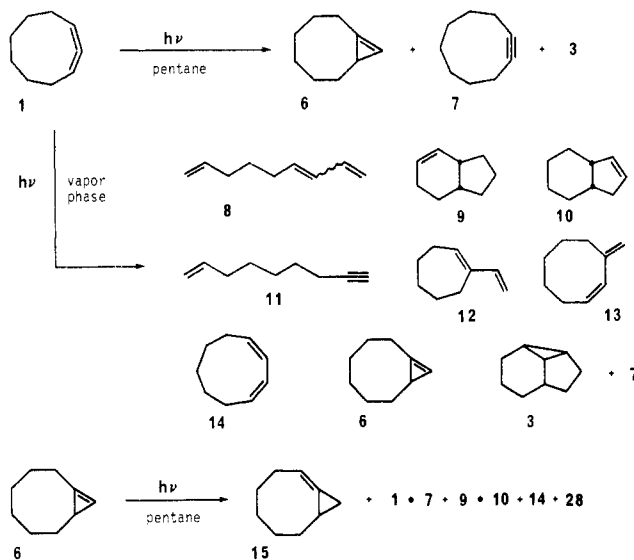
(7) Chapman, O. L. *Pure Appl. Chem.* **1974**, 40, 511.

(8) (a) Preliminary communication: Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, 105, 2492. (b) Price, J. D.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, 107, 2187.

(9) (a) Review: Hopf, H. In "The Chemistry of Ketenes, Allenes and Related Compounds" Patai, S., Ed.; Wiley: New York, 1980; Part 2, Chapter 20, p 779. (b) Skattebøl, L.; Solomon, S. *Org. Synth.* **1969**, 49, 35.

(10) Osborn, C. L.; Shields, T. C.; Shoulders, B. A.; Krause, J. F.; Cortez, H. V.; Gardner, P. D. *J. Am. Chem. Soc.* **1965**, 87, 3158.

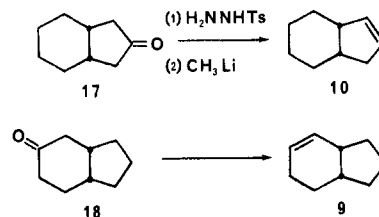
Scheme I. Singlet Photoreactions



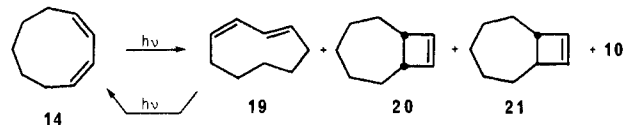
There are two previous reports of derivatives of **6**.¹¹ This strained bicyclic cyclopropene is of fundamental interest as an anti-Bredt olefin¹² and our photochemical route is its first synthesis.

Vapor-phase direct irradiation of allene **1** was next explored; this proved to be quite complex. Experiments were conducted with 5–10-mg samples of **1**, contained in an evacuated quartz vessel. Typical product distributions are summarized in Table I. Conversions were kept low (10–20%) to minimize secondary photoreactions; however, product ratios still proved quite variable. From irradiation at 185 (+254) nm, enediene **8** was reproducibly the major product (ca. 40%; trans/cis ratio 3:1). This structure and all others shown in Scheme I were proven through independent synthesis, comparison of 300-MHz ¹H NMR spectra, and capillary GLC retention times.

Cis bicyclics **9** and **10** were independently synthesized from the known ketones, as shown below. A previous assignment for **10** as a product of the thermolysis of **1** is incorrect.¹³ The thermal product is isomeric bicyclic **9**.¹³



Cyclopropene Singlet Photochemistry. Direct irradiation of pure cyclopropene **6** to low conversion in pentane at $\lambda > 220$ nm yielded isomers **1**, **7**, **9**, **10**, **14**, **15**, and **28** (Scheme I), in addition to one minor unidentified product. Ratios are given in Table I. Secondary reactions of 1,3-cyclononadiene (**14**) were observed at moderate conversions. Fonken has reported¹⁴ that irradiation



(11) Suda, M. *Tetrahedron Lett.* **1980**, 21, 4355. Baird, M. S.; Nethercott, W. *Tetrahedron Lett.* **1983**, 24, 605.

(12) (a) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; (b) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, 12, 464.

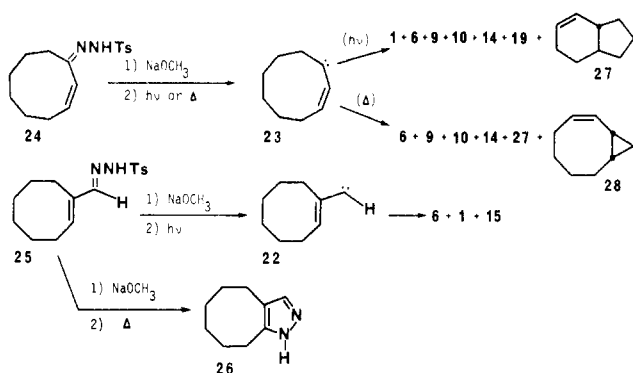
(13) (a) Crandall, J. K.; Watkins, R. J. *Tetrahedron Lett.* **1970**, 1251. Assignment of the structure of **10** was based on degradation to a dicarboxylic acid, which was identified by its melting point. (b) More recent studies have shown that pure *trans*-enediene **8** is a primary thermal product of **1** and that bicyclics **9** and **27** result from secondary Diels–Alder cyclizations: Price, J. D.; Johnson, R. P. *Tetrahedron Lett.*, in press.

Table I. Hydrocarbon Product Distributions

	observed products (% total)																
	1	3	6	7	8	9	10	11	12	13	14	15	19	27	28	32	33
soln irradiat of 1		3	94	3													
vapor-phase irradiat of 1 (185 nm)		9	15	4	~40	3	3	~7	5	4	7						
soln irradiat of 6	22			7		15	18				15	11	1		2		
vapor irradiat of 1 with benzene		89					2									5	4
soln irradiat of 1 with benzene ^a		1.0	2.0 ^b														
from tosylhydrazone 24 : photolysis	0.3		40			27	6				23		3	0.7			
from tosylhydrazone 24 : thermolysis			3			58	10				15			0.5	14		
from tosylhydrazone 25 : photolysis	10		78										12				

^aMajor products are cycloadducts **4** and **5**. ^bIdentified only by retention time.

Scheme II. Independent Vinylcarbene Generation



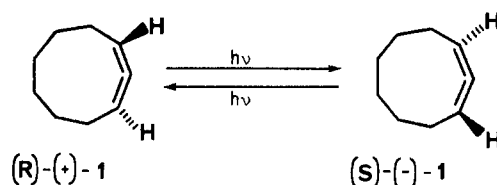
of **14** yields as major products cis-trans isomer **19**, bicyclic **10**, and cis and trans bicyclics **20** and **21**.

Especially noteworthy in photochemical reactions of **6** is the formation of allene **1** (22%), effectively reversing the $1 \rightarrow 6$ transformation. Additionally, cyclononyne is a primary photoproduct. Although thermal cyclopropene-propyne conversions are well-known,¹⁵ we believe this to have been the first reported example⁸ of an analogous photochemical reaction.¹⁶ Steinmetz has provided another recent photochemical cyclopropene \rightarrow alkyne conversion.¹⁷ The remaining products in reactions of **6** are characteristic of vinylcarbene intermediates (vide infra).

Mechanistic Studies: Singlet Reactions of Optically Active 1. Both allene **1** and cyclopropene **6** are inherently chiral; thus, optical activity offered the potential for probing reaction mechanisms. In principle, a concerted reaction might transform optically active **1** into active **6**. Racemization of **1** through π -bond rotation was expected to be a competitive reaction.^{18,19} Allene **1** ($[\alpha]_D^{24} = -24^\circ$; ca. 15% optical purity²⁰) was prepared by partial hydroboration with a chiral reagent, following the procedure of Byrd and Caserio.²¹ Irradiation of optically active **1** to low conversion (1–3%) to **6** was followed by preparative GLC isolation of **1** and **6**. As expected, recovered allene was substantially racemized; at 1.5% and 3.0% conversion to **6**, $[\alpha]_D$ for recovered **1** was -11.9° and -5.5° , respectively, corresponding to ca. 50% and 75% racemization. However, isolated cyclopropene **6** was found to be inactive, within detection limits at the sodium D line or by measurement of the optical rotatory dispersion (ORD) spectrum. In other experiments, the loss of solution optical activity and disappearance of allene were plotted according to eq 1. Here, $\log(\alpha_i/\alpha) = (1 + k_{\text{racemization}}/k_{\text{isomerization}}) \log([1]_i/[1])$ (1)

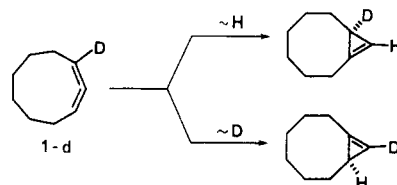
α and $[1]$ represent solution optical rotation and allene concentration, respectively, at initial (i) and subsequent values. This

basic kinetic scheme was derived by Wagner for a similar photoracemization.²² The resultant plot was linear (correlation coefficient 0.99) and gave $k_{\text{racemization}}/k_{\text{rearrangement}} = 70$. Thus, as expected, racemization is far more efficient than rearrangement to **6**. It is presumed that this is strictly a singlet process since intersystem crossing in **1** is not expected to be efficient. Given this rapid competitive reaction, and the minute amounts of cyclopropene which are isolable at such low conversion, a definitive result seems unobtainable. In experiments to date, either **6** is formed racemic or its optical activity is below our detection limit, due to an inherently low rotation.



This experiment provides the first direct comparison of the efficiency of allene π -bond rotation to other types of photoisomerization. Morrison has reported one example of triplet photoracemization.²³ Several earlier studies of allene racemizations yielded variable results.^{24,25} It is clear, however, that simple π -bond rotation is the most facile singlet photochemical reaction of allenes.

Deuterium Kinetic Isotope Effects on Singlet Photorearrangement. Kinetic isotope effects are commonly measured for ground-state reactions but have been used only infrequently in the study of photorearrangements.²⁶ Because of its C_2 symmetry, 1,2-cyclononadiene is an excellent candidate for such studies. Monodeuterated **1** (**1-d**, > 98% d_1) was prepared in straightforward fashion²⁷ and subjected to low-conversion direct irradiations. The isotope effect was measured directly by ^2H NMR,



through integration of appropriate resonances in **6**. As expected, preference for hydrogen migration was observed, with $k_{\text{H}}/k_{\text{D}} =$

(14) Shumate, K. M.; Fonken, G. J. *J. Am. Chem. Soc.* **1966**, *88*, 1073.
(15) Steinmetz, M. G.; Srinivasan, R.; Leigh, W. J. *Rev. Chem. Intermed.* **1984**, *5*, 57 and references therein.

(16) For a review of cyclopropene photoreactions, see: Padwa, A. *Org. Photochem.* **1979**, *4*, 261.

(17) Steinmetz, M. G.; Yen, Y.-P.; Poch, G. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1504.

(18) Borden, W. T. *J. Chem. Phys.* **1966**, *45*, 2512.

(19) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479.

(20) Pirkle, W. H.; Boeder, C. W. *J. Org. Chem.* **1977**, *42*, 3697 and references therein.

(21) Byrd, L. R.; Caserio, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 5758.

(22) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1971**, *94*, 7480.

(23) Rodriguez, O.; Morrison, H. *J. Chem. Soc., Chem. Commun.* **1971**, 679.

(24) Hornback, J. M. Reports of Research Sponsored by the Petroleum Research Fund, 1972.

(25) Borden, W. T. Ph.D. Dissertation, Harvard University, 1968. We thank Prof. Borden for discussions of this work.

(26) Recent examples: (a) Kropp, P. J.; Fravel, H. G., Jr.; Fields, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 840. (b) Paquette, L. A.; Bay, E. *J. Org. Chem.* **1982**, *47*, 4599. (c) Hemetsberger, H.; Neustern, F.-U. *Tetrahedron* **1982**, *38*, 1175. (d) Padwa, A.; Chou, C. S.; Rosenthal, R. J.; Rubin, B. *J. Am. Chem. Soc.* **1974**, *96*, 6773 and references therein.

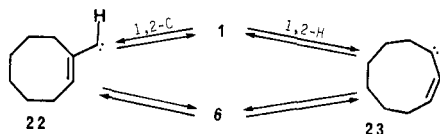
(27) 1-Bromocyclooctene was treated with 2 equiv of *t*-BuLi at -78°C in THF and then quenched with excess D_2O . The resultant 1-deuteriocyclooctene was converted to **1-d**.

1.30 ± 0.06. We have observed a very similar value (1.39 ± 0.01) for formation of triphenylcyclopropene from triphenylallene.⁵

These experiments also demonstrate that both cyclopropene hydrogens arise uniquely from the allenic hydrogens, thus eliminating the possibility of more complicated transpositions.

Independent Generation of Potential Vinylcarbene Intermediates. Vinylcarbenes are readily generated through cyclopropene photolysis and thermolysis.^{15,16} ESR experiments provide strong evidence for syn and anti isomers of a triplet ground state but suggest thermal conversion to a close-lying reactive singlet state.^{28,29} Recent theoretical studies by Yoshimine support the triplet ground state and show the lowest singlet to be slightly nonplanar, with low barriers for closure to cyclopropene or rearrangement to allene or propyne.^{30a}

Potential interconversions in reactions of **1** and **6** are shown below. For allene **1**, 1,2-hydrogen or 1,2-carbon shifts might afford **23** or **22**, respectively, while cyclopropene **6** can open to the same intermediates. To assess their potential intermediacy in photo-



reactions of **1** and **6**, independent generation of **22** and **23** was carried out through photolysis and thermolysis of tosylhydrazones lithium or sodium salts.³¹ Ideally, one might expect product "fingerprints" to be similar for the various means of vinylcarbene generation.³²

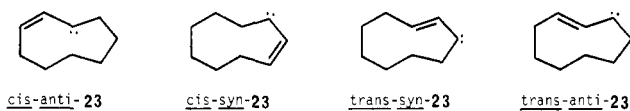
Tosylhydrazones **24** and **25** (Scheme II) were prepared by standard methods; both are known³³ but were not used for carbene generation in previous studies. Treatment with NaOCH₃ or *n*-BuLi was followed immediately by thermolysis (120 °C, diglyme) or by irradiation ($\lambda > 300$ nm). During the photochemical reactions, a transient pink color was observed; this is attributed to the vinylidiazole intermediate.³¹ Product distributions from thermal and photochemical experiments are summarized in Table I.

Both thermal and photochemical generation of carbene **23** afforded relatively similar products; however 1,2-cyclononadiene (**1**) and *cis,trans*-1,3-cyclononadiene (**19**) were absent in thermal runs, and the percentage of cyclopropene **6** was reduced. This may be due to their thermal sensitivity. Identification of *cis,trans*-1,3-cyclononadiene (**19**)¹⁴ and bicyclics **27** and **28** was based on comparison to authentic samples.

Photolytic generation of **22** yielded primarily **6** (78% of products; ca. 20% isolated yield after preparative GLC), and we believe this to be the best source of this interesting and previously unknown hydrocarbon. Thermolysis of the sodium salt of **25** yielded only pyrazole **26**, as previously reported.^{33b} This may arise from cyclization of the diazo intermediate and subsequent 1,5-hydrogen shift.

Cyclononyne was not detected as a product in any of these reactions.

Cyclononylidene (**23**) can exist as four discrete isomers, as shown below. Theoretical studies suggest a low barrier to syn-anti interconversion, or to π -bond rotation.³⁰ Thus, a significant degree



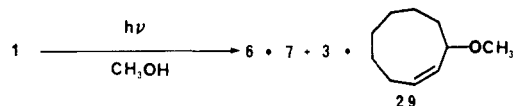
of interconversion seems likely, although we have no means of quantitatively assessing this.

From consideration of models, transannular insertion in *cis*-anti **23** seems the most likely route to bicyclics **9**, **10**, and **27**. The more favored insertion geometry would yield **9**, a result which is consistent with experiment. Importantly, the nearly exclusive *cis* stereoselectivity, seen by the dominance of **9** and **10**, accords with reaction from a singlet vinylcarbene. A stepwise triplet process presumably would yield more *trans* product. Similar results were obtained for the ten-membered ring.^{6b} Assignment of other specific isomers of **23** as precursors to specific products is problematic. Cyclopropene formation requires π -bond rotation, and we believe that any isomer might yield **6**.

It seems generally believed that vinylcarbenes do not rearrange to allenes; however, both **22** and **23** afford small amounts (10% and 0.3%, respectively) of allene **1**. This is consistent with Yoshimine's prediction that the barrier to vinylcarbene-allene rearrangement is low but larger than that for closure to cyclopropene.^{30a}

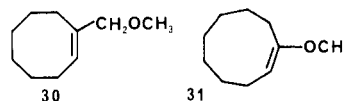
Irradiation of 1,2-Cyclononadiene in Methanol. We have previously observed that phenylallenes yield primarily allylic ethers upon direct irradiation in methanol.³⁴ Yates has reported similar results.^{35a} This photoaddition does not appear to result from trapping of a vinylcarbene but rather from central carbon protonation of singlet excited allene. In the case of 1,2-cyclononadiene (**1**), it was of interest to explore the generality of photoprotonation.

Irradiation of 1,2-cyclononadiene to low conversion (<2%) in neutral methanol had remarkably little effect on the hydrocarbon product distribution. This yielded as primary photoproducts cyclopropene **6**, cycloalkyne **7**, tricyclic **3**, and *cis*-allylic ether **29**, in the ratio 90:2:3:3. Cyclopropyl ethers expected from insertion



of singlet **2** into methanol were shown (capillary GLC) to be absent, by comparison to authentic samples. Ether **29** was identified by comparison of its capillary GLC retention time and 300-MHz NMR spectrum with those of authentic material. Continued irradiation led to characteristic reactions of **6**.

Careful analyses of low-conversion product mixtures gave no evidence for the presence of isomer **30** and established an upper limit of 0.4% for isomer **31** or the *trans* isomer of **29**. In principle,



ether **30** might arise if vinylcarbene **22** was an intermediate.

In one previous study, Fujita and co-workers reported that irradiation of **1** in acetic acid yielded a *cis*-allylic acetate.^{35b} A triplet mechanism was proposed.

Triplet Reactions of 1,2-Cyclononadiene. Ward and Karafiah first reported the benzene-sensitized vapor-phase isomerization of **1** to **3**.² Benzene intersystem crosses with moderate efficiency, thus, this is presumed to be a triplet process. In a later study, Gilbert isolated cycloadducts **4** and **5** (reported ratio 6:1) from solution-phase irradiation.³ Because neither previous study established whether significant quantities of tricyclic **3** are formed in solution, this was carefully examined. Irradiation of 10⁻³ M **1** in benzene, using an internal standard, gave only a 1% yield of **3**. Additionally, a minor component (2%) corresponding to the retention time of cyclopropene **6** was observed; however, the identity could not be verified by NMR. The major products of

(28) Hutton, R. S.; Manion, M. L.; Roth, H. D.; Wasserman, E. *J. Am. Chem. Soc.* **1974**, *96*, 4680.

(29) Palmer, G. E.; Bolton, J. R.; Arnold, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 3708.

(30) (a) Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.* **1984**, *106*, 5361. We are grateful to Dr. Yoshimine for communicating his results to us prior to publication. Previous ab initio studies^{30b} considered only planar vinylcarbene geometries. (b) Davis, J. H.; Goddard, W. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2427.

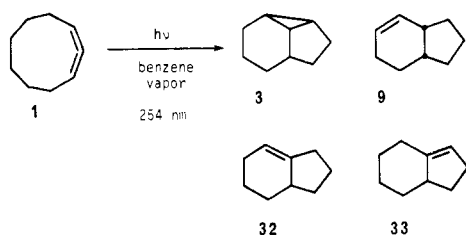
(31) (a) Dürr, H. *Chem. Ber.* **1970**, *103*, 369. (b) Nickon, A.; St. John-Zurer, P. *J. Org. Chem.* **1981**, *46*, 4685.

(32) Zimmerman has made similar arguments in cyclopropene photochemistry: Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331. See also: Pincock, J. A.; Mathur, N. C. *J. Org. Chem.* **1982**, *47*, 3699.

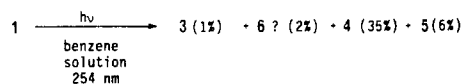
(33) (a) Grandi, R.; Pagnoni, U. M.; Travej, R. *J. Chem. Res. Synop.* **1979**, 246. (b) Bellella, F.; Grandi, R.; Pagnoni, U. M. *J. Chem. Res. Synop.* **1981**, 114.

(34) Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, 1.

Scheme III. Vapor-Phase Triplet Photochemistry of 1,2-Cyclononadiene



benzene-sensitized solution irradiation were cycloadducts **4** and **5** as previously reported.³ Our **4**:**5** ratio, which was reproducibly

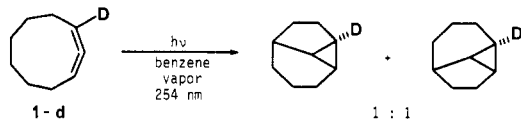


determined by high-field NMR analysis of the crude product, is exactly opposite to that previously reported.³

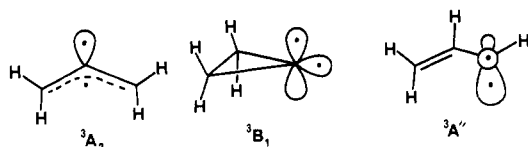
Benzene-sensitized solution-phase irradiation of optically active allene **1** led to facile racemization. A plot of solution optical activity vs. loss of starting allene (relative to internal standard) according to eq 1 was linear (correlation coefficient 0.99) and yielded $k_{\text{racemization}}/k_{\text{reaction}} = 60$. Thus, as in direct irradiation (presumably singlet), π -bond rotation is the most facile triplet process.

Irradiation at 254 nm of **1** and benzene in the vapor phase (10^{-1} torr) yielded predominantly (89%) **3**, as previously reported.² More careful scrutiny, however, reproducibly showed three minor isomeric (GLC-MS) products (Scheme III); these were isolated by preparative GLC and characterized as **9** (2%), **32** (5%), and **33** (4%). The ratio of these to tricyclic **3** proved invariant from 3% to >90% conversion of **1**. Isomers **32** and **33** were identified by comparison of their ¹³C and ¹H NMR spectra with those reported previously.³⁶

No deuterium isotope effect was observed in the benzene-sensitized vapor-phase irradiation of **1-d**. The ²H NMR spectrum of isolated tricyclic **3-d** displayed two cyclopropyl resonances of equal intensity, within experimental error.



Theoretical Studies of Triplet C₃H₄ Intermediates. Configuration interaction (CI) calculations show allene triplet states to be predominantly biconfigurational.³⁷ If the two π bonds may be considered to be canonically localized (i.e., π_x and π_y), then T₁ and T₂ (³A₁ and ³B₂) are comprised of localized excitations: $[(\pi_x \rightarrow \pi_x^*) \pm (\pi_y \rightarrow \pi_y^*)]$. These vertical triplets cannot be responsible for observed reactions of **1**, since a linear geometry does not permit transannular hydrogen abstraction. Thus, the location and character of bent triplet minima is of primary importance. Triplet cyclopropylidene (³B₁) and planar allene (³A₂) can result from simple C₂ torsional motions and, as originally observed by Ward and Karafiath,² either might play a key role in the chemistry of **1**. A third triplet minimum corresponds to



the vinylcarbene (³A''),³⁰ but such species do not appear to be involved in triplet reactions of **1**. This is consistent with the general

(35) (a) Rafizadeh, K.; Yates, K. *J. Org. Chem.* **1984**, *49*, 1500. (b) Fujita, K.; Matsui, K.; Shono, T. *J. Am. Chem. Soc.* **1975**, *97*, 6256.

(36) Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 68.

(37) Schaad, L. J.; Burnelle, L. A.; Dressler, K. P. *Theor. Chim. Acta* **1969**, *15*, 91.

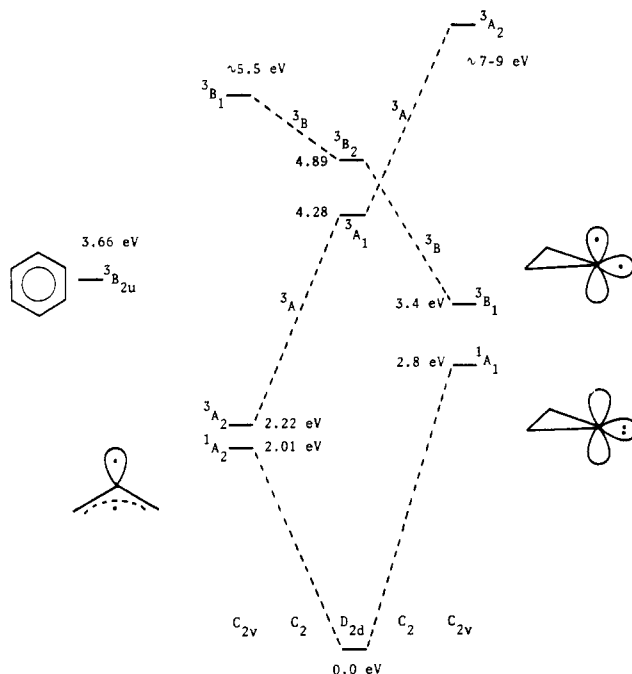


Figure 1. State correlations for allene and cyclopropylidene.

observation that 1,2-hydrogen migration does not occur in triplet states.

In the interpretation of experimental results, it was desirable to know the ground-state multiplicity for cyclopropylidene and for planar allene. For cyclopropylidene, this is not known experimentally, and previous theoretical studies have led to distinctly contradictory conclusions. An early MNDO/2 study³⁸ and more recent ab initio SCF calculations by Pasto, Haley, and Chipman³⁹ predicted a triplet ground state. By contrast, Dillon and Underwood⁴⁰ and Baird and Taylor⁴¹ predicted the singlet to be lower by 22 and 6.2 kcal/mol, respectively. Unfortunately, all these previous calculations are unreliable, either because of the limited basis set or the computational methodology, primarily lack of differential electron correlation in the singlet.

Geometries and energetics for the cyclopropylidene singlet and triplet states were calculated with a TCSCF (two-configuration SCF) wave function for the singlet (¹A₁) and ROHF (spin-restricted open-shell Hartree-Fock) wave function for the triplet.⁴² A split-valence 3-21G basis was augmented with a full set of polarization functions (d orbitals) at C₁. This general approach has proved satisfactory for most carbenes.⁴³ When this basis set and level of calculation are used, total energies (hartrees) and relative energies (kilocalories/mole) for the singlet and triplet of cyclopropylidene are as follows: ¹A₁ -115.176 06 (0.0); ³B₁ -115.152 50 (14.8). While the precise magnitude of this gap may change with higher level calculations, we believe the state ordering to be quite secure. Thus, in keeping with general ideas of energy vs. bending angle in carbenes,⁴¹ we predict cyclopropylidene to have a singlet ground state, ca. 0.6 eV below the triplet.

As a result of MCSCF calculations, we have recently concluded that the singlet also should be the ground state of planar C_{2v} allene (¹A₂ < ³A₂).¹ This is a consequence of better electron correlation for the singlet; at the SCF level, the triplet is slightly favored.¹ Thus, for both bent planar allene and for cyclopropylidene, our

(38) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095.

(39) Pasto, D. J.; Haley, M.; Chipman, D. M. *J. Am. Chem. Soc.* **1978**, *100*, 5272.

(40) Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 2435.

(41) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333.

(42) Calculations utilized the program GAMESS: Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Software Catalog 1, Program No. QG01 (GAMESS), Lawrence Berkeley Laboratory, University of California, Berkeley, CA, 1980.

(43) For an excellent review of theoretical methods in carbene chemistry, see: Davidson, E. R. "Diradicals"; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; Chapter 2, p 73.

calculations predict singlet ground states. Both results are opposite to previous predictions from lower-level calculations.

Figure 1 summarizes relative energies and state correlations along C_2 bending and twisting coordinates in allene. Relative energies (electronvolt) are from ab initio studies or from experiment. For allene T_1 and T_2 , energies of 4.28 and 4.89 eV were determined by electron-impact studies.⁴⁴ Ab initio studies yielded comparable values: 4.89 and 5.08 eV.³⁷ For planar singlet and triplet allene, our own MCSCF values are given.¹ The singlet energy corresponds to the allene ground-state rotational barrier and is in good agreement with experiment (ca. 2.1 eV).⁴⁵

Energies for cyclopropylidene relative to allene are not available from experiment. For the singlet, very high level ab initio calculations predict 2.7³⁰ or 2.8⁴⁶ eV, values significantly lower than previous predictions.³⁸ The triplet energy may be estimated from these energies and a singlet-triplet gap of 0.6 eV. Finally, energies for upper triplets of planar allene and cyclopropylidene were roughly estimated from 3-21G triplet CI calculations.⁴² Both lie above allene vertical triplet energies.

Ring opening of triplet cyclopropylidene probably is quite exothermic; however, Pasto, Haley, and Chapman predicted a 19 kcal/mol barrier, through a predominantly disrotatory pathway.³⁸ Chiu has argued for the possibility of direct triplet cyclopropylidene to singlet allene (D_{2d}) rearrangement,⁴⁷ although this seems to have assumed a triplet ground state for cyclopropylidene, which probably is incorrect.

We consider first simple state correlations. Along C_2 pathways, T_1 of allene correlates with the planar C_{2v} minimum, while T_2 correlates with triplet cyclopropylidene.⁴⁸ However, allene triplets usually are generated from energy transfer, and we conclude that, a priori, reaction might proceed to either triplet minimum if sufficient energy is available. From the relative energetics, it is apparent that $^3B_{2u}$ benzene (3.66 eV) cannot produce vertical triplet allene, a problem originally noted by Ward and Karafiath.² Nevertheless, two previous photophysical studies show allenes to efficiently quench benzene triplets.^{23,49} A short-lived triplet exciplex provides a reasonable mechanism for this distinctly nonvertical energy transfer. Although tricyclic **3** is not formed efficiently in benzene solution, energy transfer must occur, since **1** is easily photoracemized.

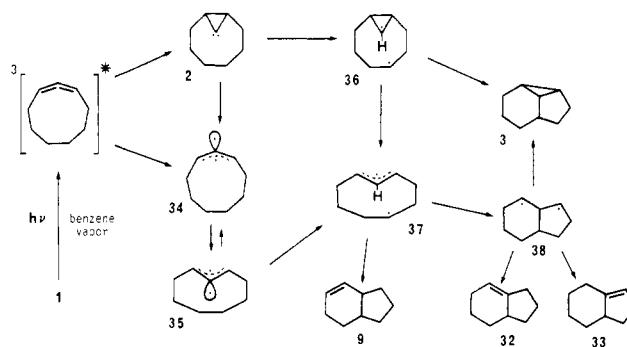
More importantly for potential mechanisms, we observe that energy transfer from triplet benzene (3.66 eV) can lead either to a planar allene triplet (2.22 eV) or to the higher energy triplet cyclopropylidene (3.3–3.4 eV). In solution, we expect the more exothermic process to dominate, with the result that rotation to a planar allene is preferred. However, in the vapor phase, closure to the cyclopropylidene may have a greater probability, since this requires dissipation of less energy. This may explain the phase dependence observed in formation of tricyclic **3**.

Discussion

Triplet Reaction Mechanisms. Allene **1** displays three general types of reaction upon benzene sensitization: (a) photoracemization; (b) cycloadduct formation in solution; (c) isomerization to **3**, **9**, **32**, and **33** in the vapor phase and small amounts of **3** (ca. 1%) in solution. Racemization is well precedented²⁹ and presumably proceeds through simple π -bond rotation and subsequent intersystem crossing. This is the most efficient reaction. Borden predicted in 1966 that π -bond rotation should be facile in triplet excited allene.¹⁸ Cycloaddition probably involves exciplex formation between ground-state **1** and singlet excited benzene. This yields predominantly the meta cycloadduct **5**.

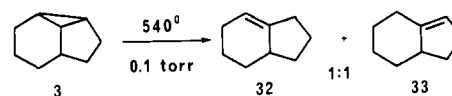
Suggested mechanisms for triplet isomerization are shown in Scheme IV. The lack of deuterium isotope effects implies a symmetrical intermediate, and the major unresolved question

Scheme IV. Potential Triplet Reaction Mechanisms



seems to be the timing of three-membered ring formation. Along one pathway, sequential triplet energy transfer, π -bond rotation, and in-plane bending afford syn triplet allene **35**, which abstracts the most proximate hydrogen. The resultant diradical **37** can close directly to **9**, following intersystem crossing, or to 1,3-diradical **38**. From examination of models, preference for the latter process seems dictated by proximity. At this point, three-ring closure or 1,2-hydrogen migration provides straightforward and well-precedented routes to **3** or **32** + **33**, respectively.⁵⁰ The cyclopropylidene mechanism ($2 \rightarrow 36 \rightarrow 3$) can also explain the observed minor products. This requires ring opening of **2** or **36** in formation of alkenes **9**, **32**, and **33**. Ring opening would be exothermic in both cases, since this relieves cyclopropyl ring strain. The predicted triplet-singlet gap in cyclopropylidene is large enough that the intersystem crossing may be slow relative to hydrogen abstraction.^{8b}

Flow vacuum thermolysis of tricyclic **3** offered a straightforward thermal route to 1,3-diradical **38**. Passage of **3** through a quartz tube in standard fashion led cleanly to a 1:1 mixture of **32** and **33**, the result of homolysis of the most strained σ bond. Thus,



the behavior of thermally generated **38**, especially the near-statistical product selectivity, corresponds to that postulated in Scheme IV. At higher temperatures, **32** and **33** underwent secondary conversion to 1-vinylcyclopentene (loss of ethylene) and bicyclo[4.3.0]nona-1(6),7-diene (loss of H_2), respectively. Both reactions are well precedented.

In summary, the triplet products from 1,2-cyclononadiene can be accommodated through initial formation (Scheme IV) of planar triplet allene (**35**) or cyclopropylidene (**2**) intermediates. Minor alkene products **9**, **32**, and **33** provide argument that biradicals **37** and **38** must be involved but do not discriminate between two possible origins. Experiments with 1,2-cyclodecadiene^{8b} provide strong arguments for triplet cyclopropylidenes as progenitors to tricyclic products. The most straightforward interpretation is that a duality of mechanisms exists.

Singlet Reaction Mechanisms. Upon direct excitation of 1,2-cyclononadiene (**1**), we observe the following dominant reactions: (a) photoracemization of optically active samples; (b) 1,2-hydrogen migration to cyclopropene **6** and, potentially, cyclononylidene (**23**); (c) effective 1,3-hydrogen migration to cyclononyne (**7**); (d) cleavage of the σ bond β to the allene chromophore, and subsequent closure or disproportionation; (e) formation of tricyclic **3**.

Among these processes, the 70:1 ratio of racemization to isomerization which we observe for **1** in pentane clearly shows π -bond rotation to be most efficient. This supports the general belief that allenes should be excellent "free rotors". Of course, in the absence of optically active substrate, this process will be undetectable since it simply interconverts enantiomers.

(50) For discussions of 1,3-diradical chemistry, see: Dervan, P. B.; Dougherty, D. A. In "Diradicals"; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; Chapter 3, p 107.

(44) Mosher, O. A.; Flicker, W. M.; Kuppermann, A. *J. Chem. Phys.* **1975**, *62*, 2600.

(45) Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974**, *107*, 48.

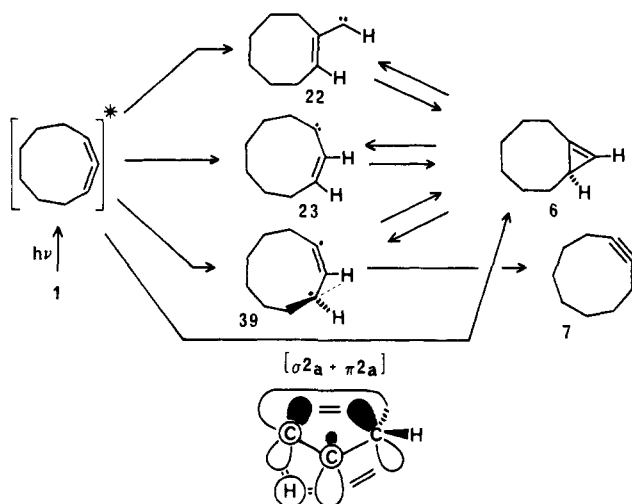
(46) Ruedenberg, K. R.; Valtazanos, P., unpublished results. We are grateful to Prof. Ruedenberg for communicating his results to us.

(47) Chiu, Y. N. *J. Am. Chem. Soc.* **1982**, *104*, 6937.

(48) Borden, W. T. *Tetrahedron Lett.* **1967**, *5*, 447.

(49) Schmidt, M. W.; Lee, E. K. C. *J. Am. Chem. Soc.* **1970**, *92*, 3579.

Scheme V. Singlet Reaction Mechanisms



Scheme V outlines proposed mechanisms for reactions b and c, which involve hydrogen migrations. At the two extremes, cyclopropene **6** may arise from a discrete vinylcarbene intermediate (**22** or **23**) or through a concerted process.⁸ The observed deuterium kinetic isotope effect for formation of **6**, $k_H/k_D = 1.3$, provides argument that hydrogen rather than carbon is migrating. We have also observed similar products and isotope effects in linear phenylallenes, where carbon migration is not possible.⁵ Additionally, the carbene products which are observed in vapor-phase irradiations of **1** (Scheme I) are characteristic of **23**, rather than **22**. Thus, we feel it reasonable to rule out vinylcarbene **22** as an intermediate in reactions of **1**.

Cyclononylidene (**23**) seems unlikely as a discrete solution-phase intermediate but probably is involved in vapor-phase reactions of **1**. Its independent generation (Table I) yields, in addition to **6**, substantial fractions of 1,3-cyclononadiene (**14**) and transannular insertion products **9** and **10**. These are not observed as significant primary products in solution-phase photoreactions of **1**. In the vapor, transannular products and diene **14** are observed as primary products.

One attractive possibility for the **1** → **6** conversion is a concerted $[\sigma_{2a} + \pi_{2a}]$ mechanism, with a Hückel transition state.^{8,51} This requires 1,2-hydrogen migration and simultaneous 1,3-bonding. Ab initio CI calculations for such a process⁵ show the expected pericyclic minimum, which exists due to approach of ground and excited states.^{51,52} Constraints imposed by the carbocyclic ring may be crucial in preventing rotation to vinylcarbenes. The concerted and vinylcarbene pathways undoubtedly are closely connected, and, in the vapor phase, incomplete thermal equilibration might permit both to be operative.

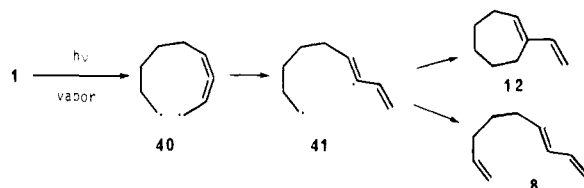
It may be argued that the various modes of carbene generation lead to different populations of the four possible isomers of **23** (vide supra) or to different electronic states of the vinylcarbene.^{15,17} We cannot rule these out; however, one might expect a high degree of equilibration among these species.³⁰

Failure to efficiently trap an intermediate through irradiation of **1** in methanol does not resolve the vinylcarbene vs. concerted mechanistic question, since the efficacy of carbene trapping is unknown. Indeed, we note that secondary reactions of **6**, which almost certainly involve vinylcarbenes, did not change dramatically in methanol.

Cyclononyne (**7**) is observed as a minor singlet photoproduct of both **1** and **6**; this implies mechanistic commonality. A vinylcarbene precursor to **7** is ruled out from independent generation

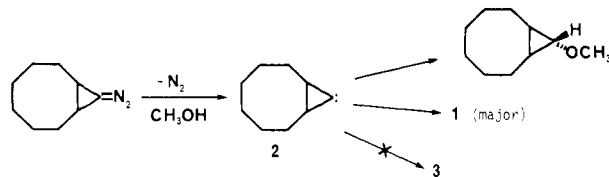
experiments. We believe a more likely possibility is internal conversion to the ground-state surface at a geometry close to the ground transition state which leads to alkyne^{30a}. This is approximated by structure **39** in Scheme V. Ab initio CI calculations along a C_2 reaction coordinate show that both allene and cyclopropene excited states can arrive at this point through in-plane 1,2-hydrogen migration or in-plane ring opening, respectively.⁵ Thus, mechanistic commonality may be due to access to the same point on excited-state potential surfaces from irradiation of allene or cyclopropene.

A simple β homolysis provides the most mechanistically economical route to enediyne **8** and vinylcycloheptene (**12**). The resultant diradical can either close to **12** or undergo disproportionation to **8**. These products are not observed in solution and



are minimized by irradiation at longer wavelengths in the vapor. Both observations argue that this cleavage is characteristic of an upper excited state of **1**. Doepker and co-workers have previously reported complex fragmentations and wavelength effects in vapor-phase reactions of 1,2-butadiene.⁵³ Enediyne **8** also is formed in the vapor-phase thermolysis of **1**,^{13b} which suggests an origin from a "hot ground state", as we propose below for enyne **11**. Further experiments with careful control of pressure and wavelength would be necessary to resolve these questions.

The remaining singlet photoproducts of **1** are **11**, **13**, and tricyclic **3**. Enyne **11** is a major product from vapor-phase thermolysis of **1**¹³ and may simply result from a "hot ground state", as mentioned above. The mechanism for formation of diene **13** is not clear; this may be a secondary photoproduct. Tricyclic **3** is formed in solution or vapor-phase direct irradiation of **1**, including experiments performed with solvent methanol. Intersystem crossing generally is not observed for simple alkenes and seems an unlikely source of **3** in these experiments. Kirmse has previously observed that generation of cyclopropylidene **2** (presumably singlet) in methanol yields predominantly allene **1** but no detectable tricyclic **3**.⁵⁴ This would appear to mitigate against singlet **2** as



a source of tricyclic **3** in our experiments. As an alternative, we suggest a singlet mechanism akin to that in Scheme IV; i.e., $^1\mathbf{1}^* \rightarrow ^1\mathbf{35} \rightarrow ^1\mathbf{37} \rightarrow ^1\mathbf{38} \rightarrow \mathbf{3}$.

Conclusion

1,2-Cyclononadiene (**1**) undergoes a rich variety of fundamental photoreactions. As expected, simple π -bond rotation occurs from both singlet and triplet excited states and is the most efficient reaction. Observation of this process requires experiments with optically active allene. More readily observed triplet reactions result from intramolecular hydrogen abstraction. Ward and Karafiath previously argued for intermediate cyclopropylidene **2**; however, our experiments implicate a competitive biradical pathway.

In the singlet manifold, 1,2-hydrogen migration and β homolysis account for most of the observed products. Photoprotonation in methanol does not compete significantly with rearrangements. β Homolysis appears to be an upper excited-state reaction. Cy-

(51) Zimmerman, H. E. "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Chapter 2, p 53.

(52) (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1566. (b) van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042. (c) Michl, J. *Mol. Photochem.* **1972**, *4*, 243, 287. (d) Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486. (e) Michl, J. *Top. Curr. Chem.* **1974**, *46*, 1. (f) Zimmerman, H. E. *Acc. Chem. Res.* **1982**, *15*, 312

(53) Doepker, R. D.; Hill, K. L. *J. Phys. Chem.* **1969**, *73*, 1313. Doepker, R. D.; Diaz, Z. *J. Phys. Chem.* **1977**, *81*, 1442.

(54) Kirmse, W.; Hellwig, G. *Chem. Ber.* **1982**, *115*, 2744.

clopropene **6** is the major solution-phase photoproduct, and we note that the photoisomerization of allene to cyclopropene and propyne may be the most general photoreaction of allenes, after π -bond rotation. In allene **1**, ring constraints may favor an effectively concerted reaction in solution, in contrast to linear phenylallene photoreactions, where vinylcarbene intermediates seem mandated.⁴⁻⁶ Present evidence argues against closure of **1** to a singlet cyclopropylidene.

We are continuing to explore many aspects of cumulene chemistry, including the effects of ring size and other structural features in cyclic allenes.

Experimental Section

General. Except as indicated, all ¹H NMR spectra were measured at 300 MHz with CDCl₃ as solvent. A 25-m Carbowax capillary column at 60 °C was used for all gas chromatographic analyses. Except as noted, a glass Carbowax column (15% on Chromosorb W; 10 ft × 0.25 in., 100 °C) was used for preparative separations. Melting points are uncorrected.

In all solution-phase photochemical experiments, spectroquality solvents were used. Argon was bubbled through solution prior to and during irradiations. The light source was either a Rayonett RPR-100 reactor, fitted with 185-(+254) or 300-nm lamps, or a 450-W Canrad-Hanovia mercury lamp, and standard immersion-well apparatus.

Direct Irradiation of 1,2-Cyclononadiene (1) in Pentane. A solution of 251 mg of **1** in 300 mL of pentane was irradiated for 9 h through a Vycor filter. The solution was concentrated under reduced pressure at 0 °C to give 240 mg of a clear oil. Capillary GLC and 300-MHz ¹H NMR analysis indicated 42% conversion to 11 products. These were isolated on a preparative scale and characterized by the identity of their capillary GLC retention times and ¹H NMR (300 MHz) spectra with those of authentic samples. GC-MS showed all components to be isomeric with starting material. Isolated products were as follows. *cis*-Bicyclo[5.2.0]non-8-ene (**20**; 2%, retention time 3.07 min): ¹H NMR δ 6.08 (s, 2 H), 2.95–2.85 (m, 2 H), 1.8–1.1 (m, 10 H). *cis*-Bicyclo[4.3.0]non-7-ene (**10**; 18%, 3.07 min). *trans*-Bicyclo[5.2.0]non-8-ene (**21**; 4%, 3.17 min): ¹H NMR δ 6.17 (s, 2 H), 2.6–2.5 (m, 2 H), 1.8–1.1 (m, 10 H). *cis*-Bicyclo[4.3.0]non-2-ene (**9**; 14%, 3.70 min). *cis*-Bicyclo[6.1.0]non-2-ene (**28**; 2%, 4.00 min): ¹H NMR δ 5.7–5.6 (m, 1 H), 5.41 (d, $J = 10.8$ Hz, 1 H), 2.5–0.8 (m, 10 H), 0.69 (td, $J = 8.4$, 4.2 Hz, 1 H), –0.18 (td, $J = 4.8$, 4.2 Hz, 1 H). *cis-cis*-1,3-Cyclononadiene (**14**; 2%, 4.07 min): ¹H NMR δ 5.90 (d, $J = 9.7$ Hz, 2 H), 5.71 (quartet, $J = 9.7$ Hz, 2 H), 2.2–2.1 (m, 4 H), 1.7–1.6 (m, 2 H), 1.54–1.46 (m, 4 H). Bicyclo[6.1.0]non-1(9)-ene (**6**; 36%, 4.45 min): ¹H NMR δ 6.47 (br s, 1 H), 2.71 (ddd, $J = 14.5$, 5.8, 3.8 Hz, 1 H), 2.32 (dddd, $J = 14.5$, 10.8, 4.9, 1.9 Hz, 1 H), 1.94–1.82 (m, 1 H), 1.74–1.18 (m, 10 H); ¹³C NMR δ 126.6, 102.1, 33.2, 29.7, 26.7, 25.6, 25.5, 20.7, 16.7; IR (neat) 2920, 2850, 1780, 1460 cm⁻¹; UV (pentane) $\lambda_{max} < 185$ nm; MS, m/e 121, 107, 93, 79, 67; high-resolution MS ($M^+ - H$) 121.1012 (calcd 121.1017). Tricyclo[4.3.0.0^{2,9}]nonane (**3**; 3%, 4.60 min): ¹H NMR δ 2.5–2.4 (m, 1 H), 2.3–2.15 (m, 1 H), 1.95–1.8 (m, 3 H), 1.75–1.6 (m, 1 H), 1.55–1.4 (m, 2 H), 1.4–1.2 (m, 5 H), 0.85–0.75 (m, 1 H). Bicyclo[6.1.0]non-1(2)-ene (**15**; 8%, 4.74 min): ¹H NMR δ 5.87 (br s, 1 H), 2.40–2.24 (m, 2 H), 2.09–1.84 (m, 3 H), 1.71–1.13 (m, 5 H), 0.88–0.78 (m, 1 H), 0.62–0.49 (m, 2 H). Unidentified (4%, 4.87 min). Cyclononyne (**7**; 7%, 8.68 min): ¹H NMR δ 2.2–2.1 (m, 4 H), 1.73–1.54 (m, 10 H).

In other experiments, the reaction was monitored at low conversion (0.25–2%). Isomers **6**, **7**, and **3** (ratio 94:3:3) were found to comprise >95% of the primary products.

Irradiation of pentane solutions at 185 (+254) nm in the Rayonet apparatus did not alter the low-conversion ratio.

Vapor-Phase Direct Irradiation of 1,2-Cyclononadiene (1). 1,2-Cyclononadiene (**1**, 5 μ L) was placed into a 230-mL quartz tube, the tube was cooled to –78 °C, and the system was degassed by evacuating to ca. 0.15 mmHg and backflushing with nitrogen several times. After evacuation to 0.15 mmHg, the tube was sealed, allowed to warm to room temperature, and irradiated in a Rayonet photoreactor fitted with 1849/2537-Å lamps for 30–60 min (10–20% conversion). The reaction vessel was then cooled to –78 °C and vented to nitrogen, and the product was collected with pentane. The pentane solution was filtered through neutral alumina and concentrated under reduced pressure at 0 °C to ca. 0.25 mL. Capillary GLC analysis revealed a very complex mixture of over 12 components. Product ratios proved quite variable from run to run; typical values for the major components of the mixture are reported. All identifications are based upon both capillary GLC retention times and 300-MHz ¹H NMR analysis of the crude mixture, with comparisons to authentic samples in hand. *cis*-Bicyclo[4.3.0]non-7-ene (**10**, 3%, retention time 3.04 min). 1,3,8-Nonatriene (**8**; 30–40%, 3.09 min): mixture of *cis* and *trans* isomers (ca. 1:3). *trans*: ¹H NMR δ 6.32 (dt, $J = 16.8$, 10.1

Hz, 1 H), 6.06 (dd, $J = 14.9$, 10.1 Hz, 1 H), 5.87–5.73 (m, 1 H), 5.68 (dt, $J = 14.9$, 7.2 Hz, 1 H), 5.08 (d, $J = 16.8$ Hz, 1 H), 5.05–4.93 (m, 3 H), 2.2–2.0 (m, 4 H), 1.6–1.4 (m, 2 H). *cis*: ¹H NMR δ 6.63 (dt, $J = 16.8$, 11.0 Hz, 1 H), 5.45 (dt, $J = 10.6$, 7.7 Hz, 1 H), 5.18 (d, $J = 16.8$ Hz, 1 H) *cis*-Bicyclo[4.3.0]non-2-ene (**9**; 3%, 3.67 min). *cis,cis*-1,3-Cyclononadiene (**14**; 7%, 4.08 min). Non-1-en-8-yne (**11**; 0–35%, typically 7%, 4.22 min): ¹H NMR δ 5.81 (ddt, $J = 17.0$, 10.3, 6.7 Hz, 1 H), 5.00 (d quartet, $J = 17.0$, 1.7 Hz, 1 H), 4.94 (dd, $J = 10.3$, 0.8 Hz, 1 H), 2.19 (td, $J = 6.9$, 2.6 Hz, 2 H), 2.1–2.0 (m, 2 H), 1.94 (t, $J = 2.6$ Hz, 1 H), 1.6–1.4 (m, 6 H). Bicyclo[6.1.0]non-1(9)-ene (**6**; 15%, 4.37 min). Tricyclo[4.3.0.0^{2,9}]nonane (**3**; 9%, 4.58 min). 1-Vinylcycloheptene (**12**; 5%, 4.68 min): ¹H NMR δ 6.32 (dd, $J = 17.4$, 10.7 Hz, 1 H), 5.89 (t, $J = 6.7$ Hz, 1 H), 5.09 (d, $J = 17.4$ Hz, 1 H), 4.90 (d, $J = 10.7$ Hz, 1 H), 2.33–2.29 (m, 2 H), 2.21 (dd, $J = 11.2$, 6.7 Hz, 2 H), 1.79–1.73 (m, 2 H), 1.55–1.49 (m, 4 H). 3-Methylenecyclooctene (**13**; 4%, 4.81 min): ¹H NMR δ 6.24 (d, $J = 11.7$ Hz, 1 H), 5.49 (dt, $J = 11.7$, 8.6 Hz, 1 H), 4.92 (d, $J = 2.3$ Hz, 1 H), 4.81 (s, 1 H), 2.58 (t, $J = 6.8$ Hz, 2 H), 2.5–2.4 (m, 2 H), 1.7–1.5 (m, 6 H). Cyclononyne (**7**; 4%, 8.58 min).

Diimide Reaction of Bicyclo[6.1.0]non-1(9)-ene (6). Acetic acid (10 mL) was added very slowly to a stirring mixture of dipotassium azodicarboxylate (1.1 g) and 64 mg of hydrocarbon mixture from vinylcarbene **22** (containing **6**, **15**, and **1** in the ratio 7:1:1) in 15 mL of methanol at room temperature under nitrogen. Stirring was continued overnight. The mixture was poured into 50 mL of water and extracted with pentane (3 × 25 mL). The pentane extracts were combined, washed with saturated NaHCO₃ (50 mL) and with water (3 × 50 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0 °C to give 46 mg of a slightly yellow oil. GLC analysis and 60-MHz ¹H NMR analysis indicated one major component (ca. 80%) identified as *cis*-bicyclo[6.1.0]nonane (**16**) by comparison with an authentic sample.

Base-Catalyzed Isomerization of Bicyclo[6.1.0]non-1(9)-ene (6). A solution of 30 mg of hydrocarbon mixture from vinylcarbene **22** (containing **6**, **15**, and **1** in the ratio 6:1:1) in 5 mL of dry Me₂SO was added to a stirring solution of 300 mg of potassium *tert*-butoxide in 5 mL of dry Me₂SO at room temperature under nitrogen. The mixture was stirred for 30 min, poured into 30 mL of water, and extracted with pentane (3 × 20 mL). The pentane extracts were combined, washed with water (3 × 20 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0 °C to yield 17 mg of a clear oil. GLC and 60-MHz ¹H NMR analyses indicated two components in a ratio of 5:1, identified as bicyclo[6.1.0]non-1(2)-ene (**15**) and 1,2-cyclononadiene (**1**), respectively.

Direct Irradiation of 1-Deuterio-1,2-cyclononadiene (1-d) in Pentane. A solution of 201 mg of 1-deuterio-1,2-cyclononadiene (**1-d**) in 250 mL of pentane was irradiated for 120 min through a Vycor filter. The solution was concentrated under reduced pressure at 0 °C to give 208 mg of a clear oil. GLC analysis indicated 3.3% conversion to the cyclopropene **6** with very little secondary chemistry observable (<0.5%). ²H NMR analysis of the crude product mixture indicated a ratio of 1.26:1 for the allylic cyclopropenyl signal to the vinylic signal. The experiment was repeated an additional 4 times at slightly different conversions to give a mean value of 1.30 ± 0.06.

Direct Irradiation of Bicyclo[6.1.0]non-1(9)-ene (6) in Pentane. A solution of 65 mg of **6** in 300 mL of pentane was irradiated for 60 min through a Vycor filter. The solution was concentrated under reduced pressure at 0 °C to give 75 mg of a clear oil. Capillary GLC and 300-MHz ¹H NMR analysis indicated 35% conversion to 11 products. All identifications are based upon both capillary GLC retention times and 300-MHz ¹H NMR analysis of the crude mixture, with comparisons to authentic samples in hand. GC-MS showed all components to be isomeric with starting material. Products were as follows. *cis*-Bicyclo[5.2.0]non-8-ene (**20**; 2%, retention time 3.07 min). *cis*-Bicyclo[4.3.0]non-7-ene (**10**; 18%, 3.07 min). *trans*-Bicyclo[5.2.0]non-8-ene (**21**; 4%, 3.18 min). *cis*-Bicyclo[4.3.0]non-2-ene (**9**; 15%, 3.70 min). *cis*-Bicyclo[6.1.0]non-2-ene (**28**; 2%, 4.00 min). *cis,cis*-1,3-Cyclononadiene (**14**; 9%, 4.08 min). Bicyclo[6.1.0]non-1(2)-ene (**15**; 11%, 4.75 min). Unidentified (8%, 4.87 min). *cis,trans*-1,3-Cyclononadiene (**19**; 1%, 4.98 min): ¹H NMR δ 6.14 (d, $J = 10.5$ Hz, 1 H), 5.78 (dd, $J = 10.5$, 5.6 Hz, 1 H), 5.70 (d, $J = 18.1$ Hz, 1 H), 5.65–5.55 (m, 1 H), 2.4–2.2 (m, 2 H), 2.2–2.0 (m, 2 H), 1.7–1.4 (m, 6 H). 1,2-Cyclononadiene (**1**; 22%, 6.38 min): ¹H NMR δ 5.25 (quintet, $J = 4.4$ Hz, 2 H), 2.29–2.17 (m, 4 H), 1.85–1.34 (m, 8 H). Cyclononyne (**7**; 7%, 8.66 min).

Capillary GLC analysis of the product mixture at low conversion (2%) indicated **20** and **21** to be secondary and derived from **14**. The amounts of **20**, **21**, and **14** observed at this conversion are 0%, 0%, and 15%, with the amounts of all other products remaining constant.

Direct Irradiation of 1,2-Cyclononadiene (1) in Methanol. A solution of **1** (300 mg) in 300 mL of methanol was irradiated for 40 min through a Vycor filter. The methanol solution was diluted with pentane (300

mL), washed with water (3 × 400 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0 °C to give 230 mg of a clear oil. Three 10-mL aliquots were taken at various times during the irradiation and worked up as described above. Capillary GLC analysis of these aliquots and the crude reaction product along with 300-MHz ¹H NMR analysis of the crude product mixture indicated conversion (1.4% at 40 min) to the four photoproducts described below (accounting for >95% of the product mixture). Products were as follows. **Bicyclo[6.1.0]non-1(9)-ene (6)**; 90%, 4.37 min). **Tricyclo[4.3.0.0^{2,9}]nonane (3)**; 3%, 4.58 min). **Cyclononyne (7)**; 2%, 8.44 min). **cis-3-Methoxycyclononyne (29)**; 3%, 11.13 min): ¹H NMR δ 5.70 (quartet, *J* = 9 Hz, 1 H), 5.35 (dd, *J* = 11, 9 Hz, 1 H), 4.2–4.1 (m, 1 H), 3.29 (s, 3 H), 2.2–2.05 (m, 2 H), 1.85–1.2 (m, 10 H).

A capillary GLC peak at room temperature 11.57 min (0.4%) represents the maximum amount of *cis*-1-methoxycyclononyne (**31**) which may be present, as determined by comparison with an authentic sample. This product, however, could not be detected in the crude 300-MHz ¹H NMR spectrum. Samples of *exo*- and *endo*-9-methoxybicyclo[6.1.0]nonanes were prepared by addition of methoxycarbene to cyclooctene. The *exo* isomer was shown not to be present by capillary GLC.

Benzene-Sensitized Solution-Phase Irradiation of 1,2-Cyclononyne (1). A solution containing 177 mg of **1** and 157 mg of tetradecane (internal standard) in 300 mL of benzene was irradiated for 48 h through a Corex filter. GLC analysis indicated 42% conversion of the allene at this time. GLC analysis at various points throughout the irradiation indicated the following isomeric products to be primary: bicyclo[6.1.0]non-1(9)-ene (**6**), 2%; and tricyclo[4.3.0.0^{2,9}]nonane (**3**), 1%. A 20-mL aliquot of the crude reaction solution was concentrated under reduced pressure at ca. 5 °C, and the residue was analyzed by 300-MHz ¹H NMR. The following cycloadducts were observed: meta cycloadduct **5**, 35%; para cycloadduct **4**, 6%. Spectral data (¹H NMR) were in agreement with those reported by Gilbert.^{3a}

Vapor-Phase Benzene-Sensitized Irradiation of 1,2-Cyclononyne (1). 1,2-Cyclononyne (**1**, 180 mg) and benzene (260 mg) were placed into a 3.7-L Vycor tube, the bottom portion of the tube was cooled to –78 °C, and the system was degassed by evacuating to ca. 0.15 mmHg and backflushing with nitrogen several times. After evacuation to 0.15 mmHg, the tube was allowed to warm to room temperature and was irradiated for 4.5 days in a Rayonet photoreactor fitted with 2537-Å lamps. The reaction vessel was then cooled to –78 °C and vented to nitrogen, and the product was collected with pentane. The pentane solution was filtered through neutral alumina and was concentrated under reduced pressure at 0 °C to give 165 mg of a clear oil. Capillary GLC analysis indicated 97% conversion to four major products. These were isolated on a preparative scale and identified as follows. **Bicyclo[4.3.0]non-1(9)-ene (33)**; 4%, retention time 3.41 min): ¹H NMR δ 5.23 (t, *J* = 2.0 Hz, 1 H), 2.5–2.4 (m, 1 H), 2.4–2.3 (m, 1 H), 2.3–2.2 (m, 2 H), 2.15–2.0 (m, 1 H), 2.0–1.85 (m, 2 H), 1.8–1.7 (m, 2 H), 1.4–1.1 (m, 3 H), 0.94 (quartet d, *J* = 3.0, 9.0 Hz, 1 H); ¹³C NMR δ 146.4, 120.1, 45.6, 35.9, 31.1, 30.8, 30.0, 27.4, 26.2. **cis-Bicyclo[4.3.0]non-2-ene (9)**; 2%, 3.67 min). **Bicyclo[4.3.0]non-1(2)-ene (32)**; 5%, 3.90 min): ¹H NMR δ 5.38 (br s, 1 H), 2.4–1.4 (m, 11 H), 1.1–0.9 (m, 2 H); ¹³C NMR δ 145.0, 116.9, 41.0, 33.6, 30.2, 29.2, 25.4, 23.3, 22.7. **Tricyclo[4.3.0.0^{2,9}]nonane (3)**; 89%, 4.67 min).

In other experiments conducted at lower conversion (4%–36%), the ratio of photoproducts remained unchanged.

Thermolysis of Tricyclo[4.3.0.0^{2,9}]nonane (3). Tricyclo[4.3.0.0^{2,9}]nonane (**3**, 120 mg) was passed slowly (45 min) through a horizontal quartz tube, packed with quartz chips, maintained at 660 °C and at a pressure of 0.15 mmHg. The product was collected in a cooled trap, rinsed out with pentane, and concentrated under reduced pressure at 0 °C to give 130 mg of a yellow oil. Capillary GLC analysis indicated 66% conversion to four major products. These were isolated on a preparative scale and identified as follows. **1-Vinylcyclopropane (40)**; 23%, retention time 2.13 min): ¹H NMR δ 6.58 (dd, *J* = 17.1, 10.8 Hz, 1 H), 5.72 (s, 1 H), 5.05 (d, *J* = 17.1 Hz, 1 H), 5.04 (d, *J* = 10.8 Hz, 1 H), 2.42 (t, *J* = 7.4 Hz, 4 H), 1.92 (quintet, *J* = 7.4 Hz, 2 H). **Bicyclo[4.3.0]non-1(9)-ene (33)**; 44%, 3.41 min). **Bicyclo[4.3.0]non-1(2)-ene (32)**; 23%, 3.90 min). **Bicyclo[4.3.0]nona-1(6),7-diene (41)**; 10%, 5.96 min): ¹H NMR δ 6.32 (dt, *J* = 5.3, 1.3 Hz, 1 H), 6.22 (d, *J* = 5.3 Hz, 1 H), 2.9–2.8 (m, 2 H), 2.35–2.25 (m, 4 H), 1.75–1.65 (m, 4 H).

In experiments conducted at lower temperatures (540 and 600 °C), the proportions of **40** and **41** were significantly decreased. At 540 °C (0.15 mmHg), capillary GLC analysis indicated 4% conversion to **32** and **33** in a ratio of 1:1.

Irradiation of Optically Active 1,2-Cyclononyne (1). A solution of 307 mg of **1**, [α]_D –24.0° (*c* 1.35, CHCl₃), in 300 mL of pentane was irradiated for 45 min through a Vycor filter. The solution was concentrated under reduced pressure at 0 °C to give 320 mg of a slightly yellow oil. GLC analysis indicated 4% conversion to cyclopropene **6**. The

cyclopropene and unreacted starting material were isolated on a preparative scale, and their rotations were measured. Recovered 1,2-cyclononyne had a specific rotation, [α]_D, of –3.2° (*c* 2.06, CHCl₃). No activity could be detected in the cyclopropene (ca. 10 mg/2 mL) down to 250 nm.

Several other experiments at different conversions of allene (1%–3%) gave similar results.

Singlet Racemization of Optically Active 1,2-Cyclononyne (1). A solution of 22 mg of **1**, [α]_D +29° (*c* 0.43, pentane), purified by preparative scale GLC, in 5 mL of pentane was irradiated for 40 min through a Vycor filter. The rotation of the solution at 300 nm was monitored at 10-min intervals. The appearance of product (i.e., cyclopropene **6**) was also monitored at these intervals, and the amount of **1** remaining was calculated. Data were plotted according to eq 1 in the text. A value of 70/1 (correlation coefficient = 0.99) was found for $k_{\text{racemization}}/k_{\text{isomerization}}$.

Triplet Racemization of Optically Active 1,2-Cyclononyne (1). A solution containing 23 mg of tetradecane (internal standard) and 22 mg of **1**, [α]_D +29° (*c* 0.43, pentane), purified by preparative scale GLC, in 5 mL of benzene was irradiated for 60 min through a Corex filter. The rotation of the solution at 450 nm was monitored at 10-min intervals. The disappearance of **1** was also monitored by GLC at these intervals. The data were plotted as before for the singlet. A value of 60/1 (correlation coefficient = 0.99) was found for k_{rac}/k_p . [This is the ratio of loss of rotation to reaction of starting allene.]

Cyclononyne Tosylhydrazone (24). Cyclononyne (4.0 g, 29 mmol) was added to a solution of tosylhydrazone (5.2 g, 28 mmol) and pyridine (ca. 40 drops) in 60 mL of methanol at 0 °C. Stirring was continued for 60 min at 0 °C, and water (ca. 25 mL) was added to induce crystallization. The crystals were collected, washed with cold 75% aqueous methanol, and dried to yield **24** (1.6 g, 18%) as off-white crystals melting at 111–114 °C [lit.^{33a} mp 115–117 °C]: ¹H NMR (60 MHz, CDCl₃) δ 7.9–7.1 (m, 4 H), 6.2–5.6 (m, 2 H), 2.38 (s, 3 H), 2.6–2.1 (m, 4 H), 1.6–1.1 (m, 8 H).

Cyclooctene-1-carboxaldehyde Tosylhydrazone (25). Cyclooctene-1-carboxaldehyde (2.0 g, 14.5 mmol) was added to a stirring suspension of tosylhydrazone (2.6 g, 14.0 mmol) in 20 mL of benzene. The mixture was stirred at room temperature for 60 min and cooled to 0 °C, and pentane (ca. 20 mL) was added to induce crystallization. The crystals were collected, washed with pentane, and dried to give **25** (4.4 g, 99%) as white crystals melting at 118.5–120 °C [lit.^{33b} mp 117–119 °C]: ¹H NMR (60 MHz, CDCl₃) δ 7.9–7.2 (m, 5 H), 5.92 (t, *J* = 8 Hz, 1 H), 2.40 (s, 3 H), 2.6–2.0 (m, 4 H), 1.7–1.2 (m, 8 H).

Vinylcarbene Generation from Tosylhydrazone Sodium Salts by Photolysis. General Procedure. The tosylhydrazone was dissolved in dry THF (200–400 mL/g of tosylhydrazone), the solution was degassed with nitrogen for 30 min, and sodium methoxide (4 equiv) was added. Irradiation through Pyrex quickly resulted in a red coloration (diazo intermediate), and the irradiation was continued until the color had completely faded (ca. 60 min). The mixture was poured into pentane, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0 °C. The residue was taken up in pentane, filtered through neutral alumina, and concentrated as above to afford the hydrocarbon products as a clear oil.

Photochemical Generation of Vinylcarbene 22. Reaction of cyclooctene-1-carboxaldehyde tosylhydrazone (**25**; 1.5 g, 4.9 mmol) at 0 °C and as described above gave 0.26 g (44%) of hydrocarbon product as a clear oil. Capillary GLC analysis indicated three components. These were isolated on a preparative scale and were characterized as follows. **Bicyclo[6.1.0]non-1(9)-ene (6)**; 78%, retention time 4.38 min). **Bicyclo[6.1.0]non-1(2)-ene (15)**; 12%, 4.70 min). **1,2-Cyclononyne (1)**; 10%, 6.32 min).

Photochemical Generation of Vinylcarbene 23. Reaction of cyclononyne tosylhydrazone (**24**; 500 mg, 1.6 mmol) as described above gave 140 mg (70%) of hydrocarbon product as a clear oil. Capillary GLC analysis indicated seven components. The five major components (**10**, **9**, **14**, **6**, and **19**) were isolated on a preparative scale and were characterized by the identity of their capillary GLC retention time and 300-MHz ¹H NMR spectra with those of authentic samples. The two minor components (**27** and **1**) were assigned based upon comparison of their capillary retention times with those of authentic samples.

cis-Bicyclo[4.3.0]non-7-ene (10); 6%, retention time 3.04 min). **trans-Bicyclo[4.3.0]non-2-ene (27)**; 0.7%, 3.37 min). **cis-Bicyclo[4.3.0]non-2-ene (9)**; 27%, 3.67 min). **cis,cis-1,3-Cyclononyne (14)**; 23%, 4.04 min). **Bicyclo[6.1.0]non-1(9)-ene (6)**; 40%, 4.38 min). **cis,trans-1,3-Cyclononyne (19)**; 3%, 4.94 min). **1,2-Cyclononyne (1)**; 0.3%, 6.32 min).

Vinylcarbene Generation from Tosylhydrazone Sodium Salts by Thermolysis. General Procedure. The tosylhydrazone was dissolved in dry diglyme (10–20 mL/g of tosylhydrazone), sodium methoxide (4 equiv) was added, and the mixture was stirred under nitrogen while

heating slowly. After the reaction was completed, the mixture was cooled, water was added, and the product was extracted into ether. The ether extracts were combined, washed with water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0 °C. The residue was taken up in pentane, filtered through neutral alumina, and concentrated as above to give the hydrocarbon product.

Thermal Generation of Vinylcarbene 22. Reaction of cyclooctene-1-carboxaldehyde tosylhydrazone (**25**; 1.0 g, 3.3 mmol) for 2 h at reflux and as described above, but without filtering through neutral alumina, gave 0.61 g of crude product as a yellow oil. Capillary GLC analysis and 300-MHz ¹H NMR analysis indicated that no C₉H₁₄ products were present. The crude product was bulb-to-bulb distilled at a bath temperature of 170 °C (0.15 mmHg) to give a clear oil which solidified upon standing and melted at 44–54 °C. This was identified as 3,4-hexamethylenepyrzole, **26** [lit. mp 45–46 °C].^{33b} ¹H NMR (300 MHz, CDCl₃) δ 9.4 (br s, 1 H), 7.27 (s, 1 H), 2.78 (t, *J* = 6.3 Hz, 2 H), 2.59 (t, *J* = 6.3 Hz, 2 H), 1.8–1.3 (m, 8 H).

Thermal Generation of Vinylcarbene 23. Reaction of cyclononene tosylhydrazone (**24**; 496 mg, 1.62 mmol) as described above gave 65 mg (33%) of product as a clear oil. During reaction, a red coloration developed at ca. 80 °C and had completely faded by the time the mixture reached 120 °C. The reaction was stopped at this point. Capillary GLC analysis indicated six isomeric C₉H₁₄ products, identified by their capillary GLC retention times and by 300-MHz ¹H NMR analysis of the crude reaction mixture (with the exception of **27**, identified only by capillary GLC retention time). *trans*-Bicyclo[4.3.0]non-2-ene (**27**; 0.5%, retention time 3.38 min). Bicyclo[4.3.0]non-7-ene (**10**; 10%, 3.04 min). Bicyclo[4.3.0]non-2-ene (**9**; 58%, 3.67 min). *cis*-Bicyclo[6.1.0]non-2-ene (**28**; 14%, 3.97 min). *cis,cis*-1,3-Cyclononadiene (**14**; 15%, 4.04 min). Bicyclo[6.1.0]non-1(9)-ene (**6**; 3%, 4.38 min).

Similar reaction using 1 equiv of *n*-butyllithium instead of the sodium methoxide gave 140 mg (70%) of product as a clear oil, with no change in the product ratios.

cis-Bicyclo[4.3.0]non-2-ene (**9**). *cis*-Bicyclo[4.3.0]nonan-3-one (**18**, 0.50 g, 3.6 mmol) was added to a stirring suspension of tosylhydrazide (0.67 g, 3.6 mmol) in 4 mL of methanol. The tosylhydrazide was quickly taken up, and precipitation of the tosylhydrazone followed. The mixture was stirred for 60 min at room temperature. After cooling, the crystals were collected, washed with cold methanol, and dried to give the desired tosylhydrazone (0.86 g, 78%) as white crystals melting at 161–162 °C; ¹H NMR (60 MHz, CDCl₃) δ 7.8–7.0 (m, 4 H), 2.40 (s, 3 H), 2.3–0.9 (m, 14 H); IR (KBr) 3220, 2920, 2850, 1640, 1595, 1390, 1330, 1160, 1025 cm⁻¹. Anal. Calcd for C₁₆H₂₂N₂O₂S: C, 62.72; H, 7.24; N, 9.14. Found: C, 62.80; H, 7.15; N, 9.16.

Sodium methoxide (350 mg, 6.5 mmol) was added to a solution of *cis*-bicyclo[4.3.0]nonan-3-one tosylhydrazone (500 mg, 1.63 mmol) in 20 mL of dry diglyme, and the mixture was heated while slowly stirring under nitrogen. The mixture was heated to 165 °C and stirred for 2 h. After the solution cooled, 40 mL of water was added, and the product was extracted into pentane (2 × 25 mL). The pentane extracts were combined, washed with water (5 × 50 mL), dried over magnesium sul-

fate, filtered through neutral alumina, and concentrated under reduced pressure at 0 °C to give a clear oil (177 mg, 89%). Capillary GLC analysis indicated two components in the ratio 76:24. These were isolated on a preparative scale and identified as follows. *cis*-Bicyclo[4.3.0]non-2-ene (**9**; 76%, retention time 3.67 min): ¹H NMR δ 5.66 (d, *J* = 1.5 Hz, 2 H), 2.4–2.3 (m, 1 H), 2.1–2.0 (m, 1 H), 2.0–1.9 (m, 2 H), 1.9–1.25 (m, 8 H); ¹³C NMR δ 131.1, 126.2, 39.4, 36.7, 32.4, 30.8, 25.9, 24.1, 23.3; IR (neat) 3020, 2940, 2870, 1650, 1450 cm⁻¹. *cis*-Bicyclo[4.3.0]non-3-ene (**42**; 24%, 3.85 min): ¹H NMR δ 5.64 (t, *J* = 1.4 Hz, 2 H), 2.2–2.05 (m, 2 H), 2.05–1.9 (m, 2 H), 1.9–1.75 (m, 2 H), 1.75–1.50 (m, 4 H), 1.45–1.32 (m, 2 H).

cis-Bicyclo[4.3.0]non-7-ene (**10**). *cis*-Bicyclo[4.3.0]nonan-8-one (**17**, 0.50 g, 3.6 mmol) and tosylhydrazide (0.67 g, 3.6 mmol) were reacted as above to give the desired tosylhydrazone (0.79 g, 72%) as white crystals melting at 198–199 °C: ¹H NMR (60 MHz, CDCl₃) δ 8.0–7.2 (m, 4 H), 2.43 (s, 3 H), 2.4–2.0 (m, 6 H), 1.6–1.2 (m, 8 H); IR (KBr) 3220, 2920, 2850, 1650, 1590, 1395, 1330, 1160 cm⁻¹. Anal. Calcd for C₁₆H₂₂N₂O₂S: C, 62.72; H, 7.24; N, 9.14. Found: C, 62.72; H, 7.11; N, 9.02.

Methylolithium (3.3 mL, 1.5 M, 4.95 mmol) was added dropwise to a stirring suspension of *cis*-bicyclo[4.3.0]nonan-8-one tosylhydrazone (503 mg, 1.64 mmol) in 20 mL of dry ether under nitrogen at room temperature. The mixture was stirred for 2 h and cooled to 0 °C, and 20 mL water was added carefully. The layers were separated, and the organic layer was washed with water (3 × 25 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure at 0 °C. The residue was taken up in pentane, filtered through neutral alumina, and concentrated under reduced pressure at 0 °C to give **10** (125 mg, 62%) as a clear oil: ¹H NMR (300 MHz, CDCl₃) δ 5.70 (s, 2 H), 2.58–2.48 (m, 1 H), 2.27 (ddd, *J* = 14.9, 6.9, 1.7 Hz, 1 H), 2.16 (sextet, *J* = 6.1 Hz, 2 H), 2.01 (dd, *J* = 14.9, 5.1 Hz, 1 H), 1.70–1.25 (m, 8 H); IR (neat) 3060, 2920, 2840, 1600, 1450 cm⁻¹.

Acknowledgment. This work was supported by the National Science Foundation, by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by Ames Laboratory, U.S. Department of Energy.

Registry No. (±)-**1**, 24373-47-5; (S)-(-)-**1**, 18526-52-8; (R)-(+)-**1**, 26114-92-1; (±)-*1-d*, 96308-34-8; (±)-**3**, 96308-35-9; (±)-**4**, 96308-36-0; **5**, 38385-27-2; **6**, 54031-22-0; **7**, 6573-52-0; *cis*-**8**, 96308-37-1; *trans*-**8**, 96308-44-0; (±)-**9**, 96308-38-2; (±)-**10**, 96308-39-3; **11**, 66031-49-0; **12**, 65811-18-9; **13**, 96308-40-6; **14**, 3726-88-3; (±)-**15**, 96308-41-7; **16**, 13757-43-2; **17**, 5689-04-3; **17** tosylhydrazone, 96308-50-8; (±)-**18**, 96308-51-9; (±)-**18** tosylhydrazone, 96308-49-5; **19**, 3776-88-3; (±)-**20**, 96308-42-8; (±)-**21**, 96308-43-9; **24**, 72357-98-3; **25**, 96308-45-1; **26**, 15984-10-8; **27**, 53225-39-1; (±)-**28**, 96391-89-8; **29**, 32393-43-4; **31**, 96308-46-2; **32**, 96308-52-0; **33**, 96308-47-3; **40**, 28638-58-6; **41**, 24279-06-9; **42**, 16613-73-3; *p*-MeC₆H₄SO₂NHNH₂, 1576-35-8; D₂, 7782-39-0; (Z)-cyclonon-2-en-1-one, 42052-30-2; (E)-cyclooctene-1-carboxaldehyde, 96308-48-4.