Materials. Hexafluoro-2-butyne (PCR Research Chemicals) was purified by repeated distillation at −107 °C. Nitrous oxide (Linde Gas) was purified by distillation at −130 °C. Both were thoroughly degassed prior to introduction into the photolysis cell.

Typical Photolysis Procedures. Nitrous oxide and hexafluoro-2-butyne were placed in the photolysis cell with a drop of mercury and photolyzed under the conditions listed in Table I. The yield of nitrogen was used to monitor the extent of the photolysis. After each run, the −195 °C noncondensible gases were measured in a gas buret and analyzed by gas-liquid chromatography on a molecular sieve column (6 mm × 2 m, 25 °C). The reaction mixture was then distilled through two −107 °C traps to separate the products from nitrous oxide and hexafluoro-2-butyne. The condensate, which contained the products, was then analyzed by GC/MS, using the same tricresyl phosphate column.

Products were identified by comparison with authentic samples. Complete spectral data for 4 have been reported.[6]

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Photocyclization of Cyclononene and Cycloundecene[1]

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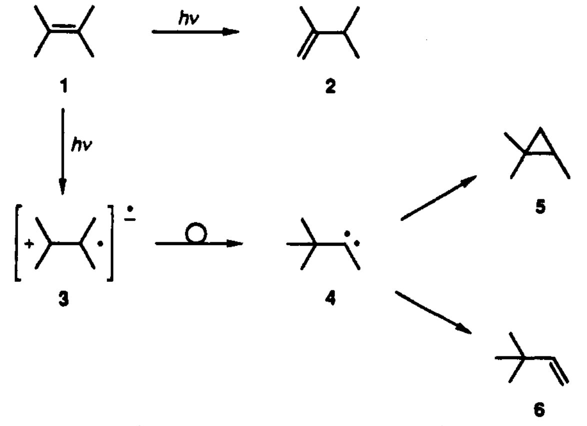
Irradiation of cyclononene (**7b**) and cycloundecene (**7d**) in pentane afforded *cis*-bicyclo[4.3.0]nonane (**10b**) and *cis*-bicyclo[6.3.0]undecane (**10d**), respectively. Small amounts of the fragmentation products 1-undecene (**14d**) and 1-undecyne (**15d**) were also obtained from cycloundecene (**7d**). The photobehavior of the series of medium- and large-ring alkenes **7a–e** is compared. Aside from $E \rightleftharpoons Z$ isomerization, the principal pathway in each case involves rearrangement of the π,R(3s) excited state to the cycloalkylidene intermediate **8**, which undergoes predominant, if not exclusive, 1,5-transannular insertion to afford the corresponding *cis*-bicyclo[*n*.3.0]alkane (**10**). The cycloalkylidenes **8** formed in this way exhibit behavior somewhat different from those generated by other methods. The possible contributory role of carbene intermediates derived from π,R(3s) excited states in $E \rightleftharpoons Z$ photoisomerization of acyclic alkenes is also discussed.

The deceptively simple chromophore of the isolated carbon–carbon double bond displays a surprisingly rich array of photobehavior.[2] Most well-known is $E \rightleftharpoons Z$ photoisomerization, involving the π,π^* excited state. However, alkenes also undergo competing 1,3-sigmatropic hydrogen migration and rearrangement via carbene intermediates on irradiation in nonnucleophilic media. Thus, for example, irradiation of 2,3-dimethyl-2-butene (1) in pentane affords a mixture of the double-bond migration product 2, formed via a 1,3-sigmatropic hydrogen shift,[3] and the cyclopropane 5 and rearranged alkene 6, formed via the carbene intermediate 4.[4] Carbene formation apparently involves rearrangement of the π,R(3s) Rydberg excited state 3, which has radical-cation character due to promotion of one of the π electrons to a large molecular orbital having approximately the same size and shape as the 3s atomic orbital of carbon.[4,5]



These two types of photobehavior are also exhibited by cyclic analogues.[2] However, the photobehavior of unsubstituted cycloalkenes is somewhat simplified by the fact that double-bond migration is an identity process—affording a product indistinguishable from the starting material and, in a sense, isolating the Rydberg-type photobehavior.

The π,R(3s) excited state of a cycloalkene such as cyclooctene (**7a**) can in principle undergo rearrangement to either a cycloalkylidene **8a** or a ring-contracted cycloalkylmethylene intermediate **9a**, depending on whether a hydrogen atom or alkyl group migrates. Thus, a mixture of products **10a–12**, arising from the two carbene intermediates **8a** and **9a**, was formed on irradiation of **7a** in pentane.[1b] By contrast, however, the higher homologues cyclodecene (**7c**) and cyclododecene (**7e**) afforded only

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[1] (a) Transannular Reactions of Cycloalkenes, Cycloalkadienes and Cycloalkatrienes. 16. Part 15: Haufe, G.; Alvernhe, G.; Laurent, A. *J. Fluorine Chem.* **1990**, *46*, 83–95. (b) Photochemistry of Alkenes. 10. Part 9: Kropp, P. J.; Mason, J. D.; Smith, G. F. H. *Can. J. Chem.* **1985**, *63*, 1845–1849.

[2] For reviews of the photobehavior of alkenes in solution, see: (a) Kropp, P. J. *Org. Photochem.* **1979**, *4*, 1–142. (b) Adam, W.; Oppenländer, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 661–766. (c) Steinmetz, M. G. *Org. Photochem.* **1987**, *8*, 67–158. (d) Collin, G. J. *J. Photochem.* **1987**, *38*, 205–215.

[3] Kropp, P. J.; Fravel, H. G., Jr.; Fields, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 840–841.

[4] Fields, T. R.; Kropp, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7559–7560.

[5] For support of our assignment of the π,R(3s) excited state as the origin of the carbene intermediate 4, see: (a) Hirayama, F.; Lipsky, S. *J. Chem. Phys.* **1975**, *62*, 576–583. (b) Inoue, Y.; Mukai, T.; Hakushi, T. *Chem. Lett.* **1983**, 1665–1668. (c) Inoue, Y.; Daino, Y.; Tai, A.; Hakushi, T.; Okada, T. *J. Am. Chem. Soc.* **1989**, *111*, 5584–5586.

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products derived from the cycloalkylidene intermediates **8c** and **8e**.[1b] Small amounts of the fragmentation products **14e** and **15e** were also formed in the latter case.

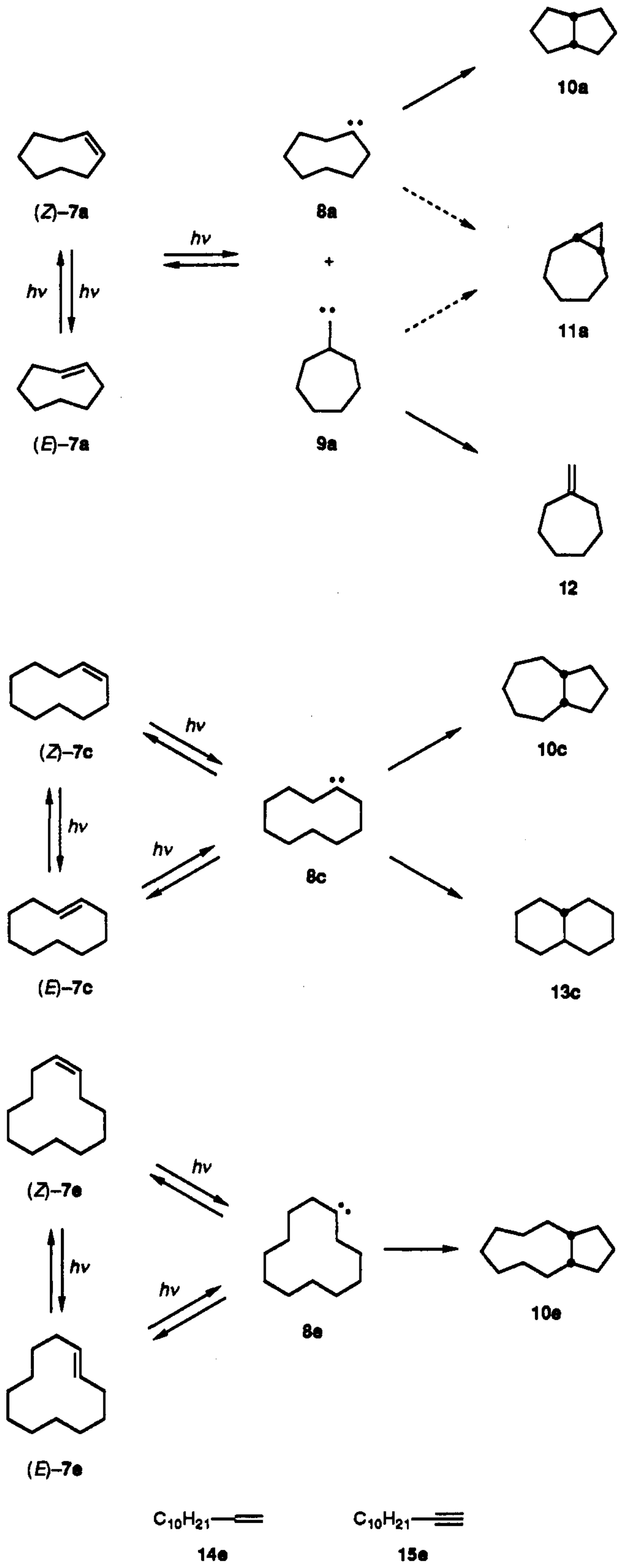


Table I. Irradiation of Cycloalkenes 7b and 7d[a]

cycloalkene	time, h	yield,[b] % (Z)-7	(E)-7	10	14	15
7b[c]	24	90[d]		7		
	48	78[d]		12		
	72	66[d]		18		
	96	48[d]		20	*e*	*e*
7d[f]	24	16	76	4	*e*	5
	48	16	42	11	1	6
	96	7	28	23	2	5
	120	6	21	24	3	4

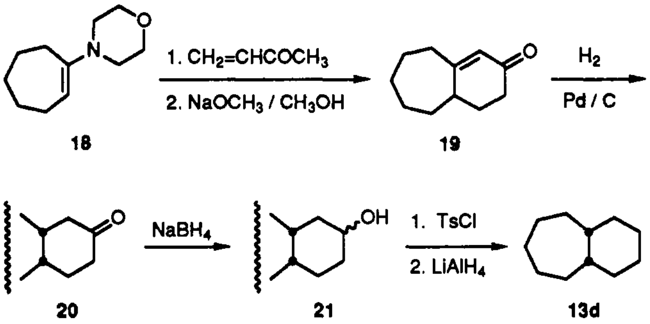
[a] Conducted as described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] 100% (Z)-**7b**. [d] (Z)- and (E)-**7b** could not be separated. [e] Trace. [f] A mixture of 25% (Z)-**7d** and 75% (E)-**7d**.

Table II. ^{13}C NMR Chemical Shifts of Bridgehead Atoms in Bicyclo[*n*.3.0]alkanes[a]

n	δ cis	trans
3 (**10a**)	43.3	
4 (**10b**)	39.6	47.0
5 (**10c**)	43.6	46.5
6 (**10d**)	42.1[b]	
7 (**10e**)	43.2[c]	

[a] Reference 10. [b] From this work. [c] Reference 1b.

Scheme I



Most cycloalkylidenes undergo principally 1,2-insertion to form the corresponding cycloalkene. However, medium- and large-ring cycloalkylidenes having close transannular interactions undergo competing transannular insertion. Indeed, irradiation of such cycloalkenes is not only a convenient method of generating cycloalkylidenes but also of isolating, in a sense, their transannular insertion reactions since any competing 1,2-insertion simply generates the starting alkene, which is recycled on continued irradiation, whereas bicyclic products from transannular insertion are photostable and accumulate in the reaction mixture. A case in point is cyclododecylidene (**8e**), which, when generated by the traditional base-initiated decomposition of the corresponding tosylhydrazone, afforded principally a mixture of (*E*)- and (*Z*)-cyclododecene (**7e**) from 1,2-insertion.[6] A bicyclic product, presumably **10e**, was also obtained, but in insufficient amount for structural characterization. By contrast, this product could be obtained in significantly higher yield by irradiation of (*E*)- and (*Z*)-cyclododecene (**7e**).[1b]

In view of the interesting aspects of the photobehavior of medium- and large-ring cycloalkenes and the various differences previously observed between alkenes **7a**, **7c**, and **7e**,[1b] we have now studied the photobehavior of the odd-membered homologues **7b** and **7d**, thereby completing the series. The solution-phase behavior of (*Z*)-cyclononene ((*Z*)-**7b**) is also of interest since in the gas phase it exhibits quite different photobehavior, giving principally 1,8-nonadiene (**16**) accompanied by vinylcycloheptane (**17**).[7]

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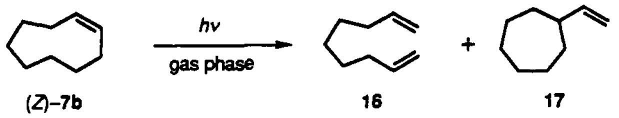
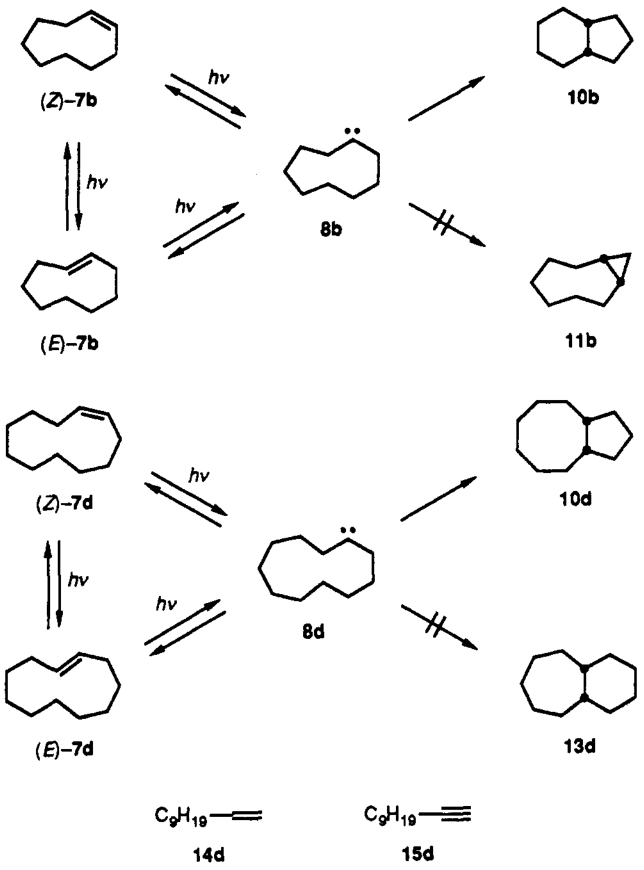
(6) Casanova, J.; Waegell, B. *Bull. Soc. Chim. Fr.* **1971**, 1289; **1975**, 598–606.

(7) Inoue, Y.; Takamuku, S.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1147–1148.



Results

(*Z*)-Cyclononene (**7b**) and a mixture of (*Z*)- and (*E*)-cycloundecene (**7d**) were prepared as previously described.[8] Irradiation of (*Z*)-**7b** in pentane afforded *cis*-bicyclo[4.3.0]nonane (**10b**) as the only significant product (Table I). Comparison of the irradiation mixture with an independently prepared specimen of the 1,3-insertion product **11b** indicated that there had been no detectable formation of this product. There was also formation of no more than a trace of 1,8-nonadiene (**16**), the principal product from vapor-phase photolysis of (*Z*)-**7b**.[7,9]



Similar irradiation of a 1:3 mixture of (*Z*)- and (*E*)-cycloundecene (**7d**) afforded a single major product, accompanied by small amounts of the fragmentation products 1-undecene (**14d**) and 1-undecyne (**15d**) (Table I). The principal product was shown not to be the 1,6-insertion product **13d** by comparison with a specimen prepared as outlined in Scheme I. Likewise, the product did not have spectral properties typical of a bicyclo[*n*.1.0]alkane **11**. Since cycloalkylidenes have never been observed to afford a bicyclo[*n*.2.0]alkane, the bicyclo[6.3.0]undecane structure **10d**, suggested previously as the structure of one of the two products obtained on base-initiated decomposition of the corresponding tosylhydrazone,[6] is assigned. In support of this assignment, the ^{13}C chemical shift of the bridgehead atoms is consistent with those of other *cis*-bicyclo[*n*.3.0]alkanes (Table II).[10,11]

Discussion

With the completion of the series **7a–e**, several trends in the Rydberg photobehavior of medium- and large-ring cycloalkenes are now clear. Only the largest members of the series, **7d** and **7e**, gave significant amounts of the fragmentation products **14** and **15**, and only the smallest member, **7a**, afforded material arising from the ring-contracted cycloalkylmethylene intermediate **9**. In all cases the major, if not exclusive, product was a *cis*-bicyclo[*n*.3.0]alkane **10** resulting from preferential or exclusive, 1,5-transannular insertion by the cycloalkylidene intermediate **8**.

This selectivity for 1,5-transannular insertion is surprisingly different from that previously observed on generation of the same intermediates by other means. Thus, generation of cyclononylidene (**8b**) by either base- or light-initiated decomposition of the corresponding tosylhydrazone, as well as by radiolysis of cyclononane, afforded 4–7:1 mixtures of the 1,5- and 1,3-transannular insertion products **10b** and **11b**, respectively.[6,12,13] Similarly, generation of cycloundecylidene (**8d**) by base-initiated decomposition of the corresponding tosylhydrazone gave an inseparable mixture of the 1,5- and 1,6-transannular insertion products **10d** and **13d**.[6] It is not clear why intermediates **8b** and **8d** display greater selectivity when derived from the corresponding π,R(3s) excited states. One possibility is that, arising via a rearrangement, they are formed with less excess vibrational energy than when generated by degradative means.[14]

It is interesting, too, that cycloundecene (**7d**) and -dodecene (**7e**) afforded transannular insertion products. Large-ring cycloalkylidenes have been found to undergo less transannular insertion, relative to 1,2-insertion, in hydrocarbon media than in the ether solvents commonly used for their generation. Thus, when generated by various methods in hydrocarbon media, cycloundecylidene (**8d**) and -dodecylidene (**8e**) afforded the corresponding cycloalkenes **7d,e** as the only detectable products.[13] As noted previously, any competing transannular insertion is magnified in the present study since 1,2-insertion simply regenerates the cycloalkenes **7**, which are recycled, whereas the bicyclic products **10** are photostable and accumulate in the irradiation mixture.

Since 1,2-insertion of the cycloalkylidene intermediate **8** can give either the *E* or *Z* stereoisomer of the starting cycloalkene **7**, a sequence of 1,2-hydrogen migration in the π,R(3s) excited state followed by 1,2-insertion of the resulting carbene intermediate to generate the cycloalkene is a second, previously unrecognized, pathway for $E \rightleftharpoons Z$ photoisomerization of alkenes, in addition to that involving the π,π^* excited state. It is clear that the π,(R3s) excited state plays a major role in the photochemistry of alkenes. Studies continue on unraveling the diverse photobehavior

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[8] (a) Gardner, P. D.; Narayana, M. *J. Org. Chem.* **1961**, *26*, 3518–3519. (b) Fawcett, R. W.; Harris, J. O. *J. Chem. Soc.* **1954**, 2673–2678. (c) Ziegler, K.; Sauer, H.; Bruns, L.; Froitzheim-Kühlhorn, H.; Schneider, J. *Liebigs Ann. Chem.* **1954**, *589*, 122–156.

[9] Although the 1,3-insertion product **11b** is photolabile under the irradiation conditions, its principal photoproduct is 1,8-nonadiene (**16**): Srinivasan, R.; Ors, J. A.; Baum, T. *J. Org. Chem.* **1981**, *46*, 1950–1951. Since no more than trace amounts of **16** were observed, the absence of **11b** appears not to be due to secondary photoconversion.

[10] Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 68–80.

[11] This comparison also permits assignment of cis stereochemistry to the bicyclo[7.3.0]dodecane product (**10e**) from irradiation of (*E*)- and (*Z*)-dodecane (**7e**), which had previously been unassigned.[1b]

[12] Friedman, L.; Schechter, H. *J. Am. Chem. Soc.* **1961**, *83*, 3159–3160.

[13] Wojnárovits, L. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1449–1451.

[14] In a previous study with acyclic alkenes, carbene intermediates derived from π,R(3s) excited states afforded the same 1,3-insertion products, although in different ratios, as when generated by base-initiated decomposition of the corresponding tosylhydrazones.[4]

of the carbon–carbon double bond.

Experimental Section

General Procedures. Infrared spectra were obtained on neat samples with a Nicolet 20 DX FTIR spectrophotometer and are reported to the nearest 2 cm^{-1}. ^{1}H NMR spectra were determined in CDCl$_3$ solution on a Bruker AC 200 spectrometer and ^{13}C spectra in CCl$_4$ solution on a Varian XL-400 spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 instrument equipped with a 12 ft × 0.125 in. stainless steel column containing either 20% SF-96 or 20% β,β-oxydiproprionitrile on 60–80 mesh Chromosorb W. Preparative gas chromatography was performed on a Varian Aerograph 90-P instrument equipped with 10 ft × 0.25 in. stainless steel columns packed as described previously.

Irradiations. Irradiations were conducted at 10 °C in a water-cooled quartz immersion well positioned 6 cm from a 450-W Hanovia medium-pressure mercury arc lamp and reflector. The quartz tubes were made of 1-mm wall thickness General Electric type 204 clear fused quartz tubing and were fused at the top to a standard taper 14/35 Vycor joint. Pentane was purchased from Burdick and Jackson and used as received. In a typical irradiation, 5 mL of a 0.05 M solution of the substrate in pentane and 30 μL of either tetradecane or nonane (internal standard) were added to an oven-dried quartz tube. The tube was then fitted with a rubber stopper pierced with two hypodermic needles, one of which was attached to a section of polyethylene capillary tubing for the introduction of N$_2$ into the solution and for the withdrawal of aliquots. The solution was deaerated by bubbling for several minutes, an aliquot was removed for gas chromatographic analysis, and irradiation was commenced. Aliquots were removed periodically during the course of the irradiation and analyzed by gas chromatography.

Preparative-scale irradiations were conducted with 0.05 M solutions containing 0.5 g of substrate. After irradiation, the solvent was removed by rotary evaporation, and the products were isolated by preparative gas chromatography.

Characterization of Photoproducts. From preparative-scale irradiations the following products were isolated. ***cis*-Octahydro-1*H*-indene (10b)** and **1-undecene (14d)** were obtained as colorless liquids that were identified by comparison of their gas chromatographic retention times and IR and NMR spectra with those of commercial samples.

***cis*-Bicyclo[6.3.0]undecane (10d)** was isolated as a colorless oil: IR 2980, 2929, 2857, 1457, 1449, 1119 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.1–1.0 (br m); ^{13}C NMR δ 42.1, 36.4, 33.9, 30.3, 29.4, 25.8 (lit.[15] no spectral data for pure cis isomer).

1-Undecyne (15d) was isolated as a colorless oil: IR 3316, 2959, 2929, 2858, 2121, 1466, 1457, 1261, 1097, 1019, 805 cm^{-1}; ^{1}H NMR δ 2.16 (d of t, 2 H, J = 6.9 and 2.6, CH$_2$-1), 1.92 (t, 1 H, J = 2.6, CH-2), 0.86 (br t, 3 H, J = 6.2, CH$_3$-1) (lit.[16] no spectral data).

Comparison with a sample of **11b**, prepared as described in the following text, and a commerical specimen of 1,8-nonadiene (**16**) showed that there was no detectable formation of these products.

Preparation of *cis*-Bicyclo[6.1.0]nonane (11b). In a modification of the general procedure of Kropp,[17] a solution of 1.10 g (10.0 mmol) of (*Z*)-cyclooctene and 8.04 g (30.0 mmol) of diiodomethane in 10 mL of 1,2-dichloroethane was placed in a 100-mL round-bottomed flask. Thirty milliliters of a mixture containing 15 mL of 10% Na$_2$SO$_4$ solution and 15 mL of 10% NaHCO$_3$ solution was added. The flask was fitted with a reflux condenser and placed 6 cm from a 450-W medium-pressure mercury lamp for 18 h while the heterogeneous mixture was stirred. Fifty milliliters of 2-methylbutane was added and the organic phase separated and washed with 100 mL of saturated NaCl solution. Removal of the solvent by distillation and isolation by preparative gas chromatography (20% SF-96) afforded **11b** as a colorless liquid: IR 2922, 2849, 1458 cm^{-1}; ^{1}H NMR δ 0.6 (m, 3, CH-1, -8, -9x), −0.28 (q, 1, J = 4.8 Hz, CH-9n) (lit.[18] ^{1}H NMR (300 MHz) δ 0.48–0.77 (m, 3), −0.305 (m, 1); ^{13}C NMR δ 29.7, 27.1, 26.5, 15.3, 9.6 (lit.[18] ^{13}C NMR δ 29.99, 27.35, 26.81, 15.59, 9.86).

Acknowledgment. Generous financial support by the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of North Carolina Research Council is gratefully acknowledged.

Supplementary Material Available: Experimental details for the synthesis of the 1,6-insertion product **13d** (Scheme I) and spectroscopic data for the product of each step (3 pages). Ordering information is given on any current masthead page.

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(15) (a) Ferber, P. H.; Gream, G. E.; Wagner, R. D. *Aust. J. Chem.* **1980**, *33*, 1569–1588. (b) Jendralla, H. *Synthesis* **1983**, 111–113.

(16) Villieras, J.; Perriot, P.; Normant, J. F. *Synthesis* **1975**, 458–461.

(17) Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* **1981**, *37*, 3229–3236.

(18) O'Connor, E. J.; Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1987**, *109*, 3739–3747.