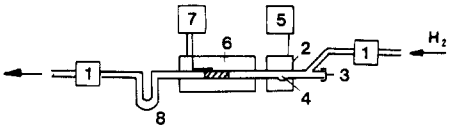

1, flow controller; 2, preheater; 3, injector port; 4, substrate chamber; 5, temperature controller for preheater; 6, reactor oven; 7, temperature controller (omega, Model 49); 8, cooled U tube for product collection

General Procedure. *n*-Hexylamine (154 mg, 2 mmol) was placed in the reaction tube by injection. The sample temperature was set to 50 °C with the preheater and the reaction temperature was set to 150 °C with the temperature controller. The substrate was passed through the reactor containing all the reduced catalyst by a slow stream of hydrogen (40 mL/min). The product was collected in a U tube cooled by dry ice. The product (144 mg, 100% yield) was identified by NMR and GC to be pure *n*-hexane.

Acknowledgment. We thank the Department of Chemistry at Berkeley which has provided the entire support for this and all our related investigations.

Registry No. N_2, 7727-37-9; Pt, 7440-06-4; H_2PtCl_6, 16941-12-1; hexylamine, 111-26-2; cyclohexylamine, 108-91-8; 1-adamantaneamine, 768-94-5; 1-(aminomethyl)adamantane, 17768-41-1; piperidine, 110-89-4; quinuclidine, 100-76-5; aniline, 62-53-3; diphenylamine, 122-39-4; decanenitrile, 1975-78-6; cyclohexanecarbonitrile, 766-05-2; 1-cyanoadamantane, 23074-42-2; 1-adamantaneacetonitrile, 16269-13-9; benzonitrile, 100-47-0; pyridine, 110-86-1; quinoline, 91-22-5; 1,2,3,4-tetrahydroquinoline, 635-46-1; indole, 120-72-9; indoline, 496-15-1; nitrohexane, 25495-95-8; nitrobenzene, 98-95-3; heptanamide, 628-62-6; 2-azacyclooctanone, 673-66-5; benzamide, 55-21-0; phthalamide, 88-96-0; phthalimide, 85-41-6; phenylhydrazine, 100-63-0; DL-α-phenylglycine, 2835-06-5; hexane, 110-54-3; cyclohexane, 110-82-7; 1-methyladamantane, 768-91-2; pentane, 109-66-0; 3-ethylpentane, 617-78-7; ethylcyclopentane, 1640-89-7; decane, 124-18-5; octane, 111-65-9; methylcyclohexane, 108-87-2; 1-ethyladamantane, 770-69-4; toluene, 108-88-3; benzene, 71-43-2; phenylamine, 110-58-7; propylcyclohexane, 1678-92-8; propylbenzene, 103-65-1; *o*-propylaniline, 1821-39-2; ethylcyclohexane, 1678-91-7; ethylbenzene, 100-41-4; *o*-ethylaniline, 578-54-1; azacyclooctane, 1121-92-2; *o*-xylene, 95-47-6; 1-adamantylethylamine, 26482-53-1; 3-pentanone, 96-22-0; cyclopentanone, 120-92-3.

Small-Ring Cyclic Cumulenes: The Structure and Energetics of Cyclic Butatrienes and the Synthesis of 1,2,3-Cyclononatriene

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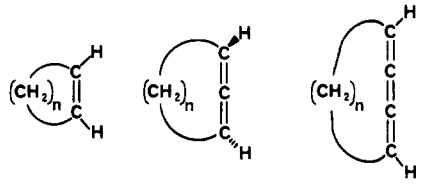
The possibility of incorporating a 1,2,3-butatriene moiety in various sized carbocyclic rings is explored through semiempirical (MNDO) and ab initio model calculations and through complete geometry optimization (MNDO) for five- through nine-membered rings. Strain in the butatriene is estimated to double with each decreasing carbon in the ring. 1,2,3-Cyclononatriene is synthesized for the first time. This is likely to be the smallest isolable cyclic butatriene.

Introduction

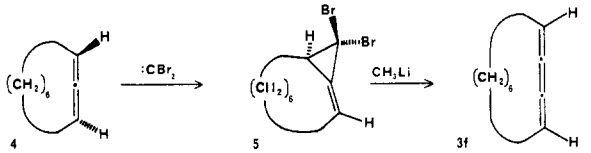
Experimentalists and theoreticians alike long have been fascinated by the incorporation of double and triple bonds in small carbocyclic rings.[1] Cyclic structures which contain noncumulated double bonds (**1**) are stable in any ring size.



1, $n \geq 1$ **2**, **2a**, $n = 3$ **3a**, $n = 1$; **3b**, $n = 2$; **3c**, $n = 3$; **3d**, $n = 4$; **3e**, $n = 5$; **3f**, $n = 6$

For allenes (**2**), small rings engender considerable deformation from a linear geometry in which π orthogonality is maintained. This results in increased kinetic reactivity with the result that the smallest kinetically stable cyclic allene is 1,2-cyclononadiene.[2] Ultimately, allene π bonding must yield to ring constraints. Through some very elegant experiments, Jones has trapped optically active 1,2-cyclohexadiene (**2a**)[3] and we have used ab initio MCSCF methods to calculate a barrier to racemization of 13 kcal/mol.[4] More recently, Wentrup has successfully trapped **2a** in a low temperature matrix.[5]

In contrast to the allenes, very little is known about the structure and chemistry of cyclic butatrienes (**3**).[1] The only stable example of simple cyclic butatrienes reported to date is 1,2,3-cyclodecatriene (**3f**), which was prepared (eq 1) by Moore and Ozretich in 1965.[6] This compound, generally



(1)

considered as the smallest stable cyclic butatriene,[1] was

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

(2) Hopf, H. "The Chemistry of Ketenes, Allenes and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; Part 2, Chapter 20, p 779.

(3) Balci, M., Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 7608.

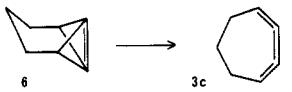
(4) Schmidt, M. W.; Angus, R. O., Jr.; Johnson, R. P *J. Am. Chem. Soc.* **1982**, *104*, 6838.

(5) Wentrup, C.; Gross, G.; Maquestiau, A.; Flammang, R. *Angew. Chem. Int. Ed. Engl.* **1983**, *27*, 542.

(6) Moore, W. R.; Ozretich, T. M. *Tetrahedron Lett.* **1967**, 3205.

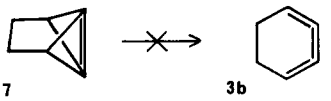
0022-3263/84/1949-2880$01.50/0

described as an air-sensitive oil which, like many acyclic butatrienes, easily polymerizes when not in solution. More recently, Szeimies has reported the successful generation and trapping of 1,2,3-cycloheptatriene (**3c**) from rearrangement of a bridged bicyclo[1.1.0]butene (eq 2).[7]



(2)

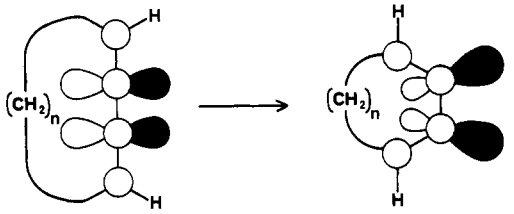
Analogous attempts to generate 1,2,3-cyclohexatriene (**3b**) were unsuccessful since **7** did not rearrange (eq 3) and was itself trapped by diphenylisobenzofuran.[8]



(3)

We report here the first synthesis of 1,2,3-cyclononatriene and results of semiempirical and ab initio molecular orbital calculations on cyclic butatrienes with ring sizes from five to nine carbons. Our intention is to explore the influence of ring constraint and strain on the butatriene moiety, with the goal of directing future expermental and theoretical efforts in this area.

Incorporation of a butatriene into a small ring will cause deformation of the normally linear geometry, with concomitant rehybridization at C_2 and C_3.[1] Bending should



not substantially affect the out-of-plane butadiene π system but should introduce considerable strain in the in-plane ethylene system due to weakening of the C_2C_3 in-plane π bond as hybridization changes from sp to sp^2. For smaller rings, the situation is quite similar to that of *o*-benzyne.[9]

Computational Methods. Geometries for cyclic butatrienes with 5–9 carbons (**3a–e**) were fully optimized using the MNDO method of Dewar and Thiel, with standard parameters.[10] This method was used both because of its computational economy (ca. 15 min of IBM-370 time for 1,2,3-cyclononatriene) and because it generally outperforms both STO-3G and 4-31G basis sets in reproducing butatriene experimental geometries.[10,11] Appropriate (C_2 or C_s) symmetry constraints were maintained during optimization. However, to ensure that this did not produce a false minimum, a final calculation was always performed in which *all* symetry constraints were removed. In every case, the symmetry restricted optimized geometry remained unchanged. Thus, at least within the MNDO approximations,[10] all the geometries represent stationary points. Realistically, we expect the accuracy of these MNDO single determinant geometries and heats of formations to diminish with smaller ring size.

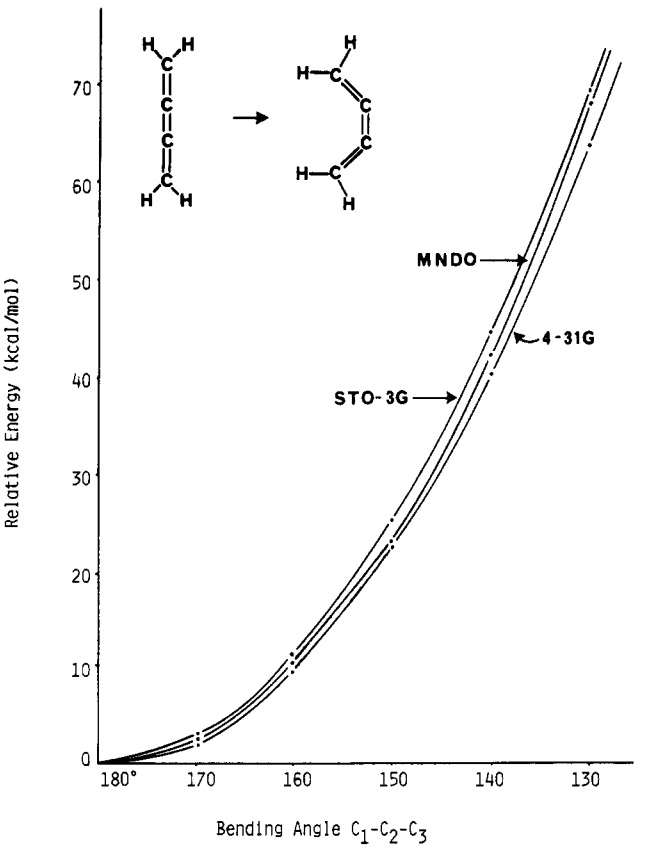


Figure 1. Planar bending potential for 1,2,3-butatriene. All calculations at MNDO optimized geometries.

Geometries chosen for optimization were estimated from molecular models. For five- to eight-membered rings, models indicated only one feasible symmetrical conformation due to restricted rotation of the butatriene moiety. In 1,2,3-cyclononatriene, conformations with C_2 and C_s symmetry seemed likely, thus geometries for both were optimized. Other, less symmetrical conformations are possible, but probably will be of higher energy. The structure for the known 1,2,3-cyclodecatriene[6] was not optimized since molecular models showed sufficient flexibility to contain a linear butatriene.

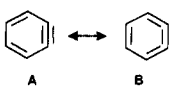
Single point STO-3G calculations were performed at all optimized geometries by using Gaussian 70.[12]

Model Calculations: Bending in Butatriene. In order to estimate the energetic consequences of bending the butatriene moiety, a series of model calculations were performed on 1,2,3-butatriene. For fixed bending angles, the remaining geometric parameters were optimized with MNDO. Single point ab initio calculations were then performed at each of these geometries by using STO-3G and split valence 4-31G basis sets.[12] Relative energies, summarized in Figure 1, show remarkably good agreement among the three levels of calculation. Especially noteworthy is the prediction that a 20° bending introduces only

(7) Zoch, H.-G.; Szeimies, G.; Romer, R.; Schmitt, R. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 877.

(8) Schluter, A.-D.; Belzner, J.; Heywang, V.; Szeimies, G. *Tetrahedron Lett.* **1980**, *24*, 891.

(9) (a) Formally, benzyne may be considered as an alkyne (structure A) or a butatriene (B). Based on its infrared spectrum,[9b] Chapman has argued for A. (b) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134.



(10) Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(11) Both STO-3G and 4-31G calculations predict bond lengths which are too short: Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941. Radom, L. *Aust. J. Chem.* **1978**, *31*, 12. Experimental geometry: Almenningen, A.; Batiansen, O.; Traetteberg, M. *Acta Chem. Scand.* **1961**, *15*, 1557.

(12) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. GAUSSIAN 70, *Quantum Chem. Program Exch.* No. 236.

Table I. Energies for Cyclic Butatrienes

compd	sym	ΔH_f (MNDO), kcal/mol	STO-3G total energy,[a] hartrees	est strain,[b] kcal/mol
1,2,3-cyclopentatriene (3a)	C_{2v}	186.28	−189.0279	~130
1,2,3-cyclohexatriene (3b)	C_2	129.46	−227.6845	60.5
1,2,3-cycloheptatriene (3c)	C_s	98.00	−266.3058	31.5
1,2,3-cyclooctatriene (3d)	C_2	74.94	−307.9137	14.0
1,2,3-cyclononatriene (3e)	C_2	64.80	−343.4971	8.0
	C_s	60.54	−343.5026	5.5
1,2,3-butatriene	D_{2h}	70.95		

[a] At MNDO geometry. [b] From plotting optimized bending angle (Table II) vs. Figure 1.

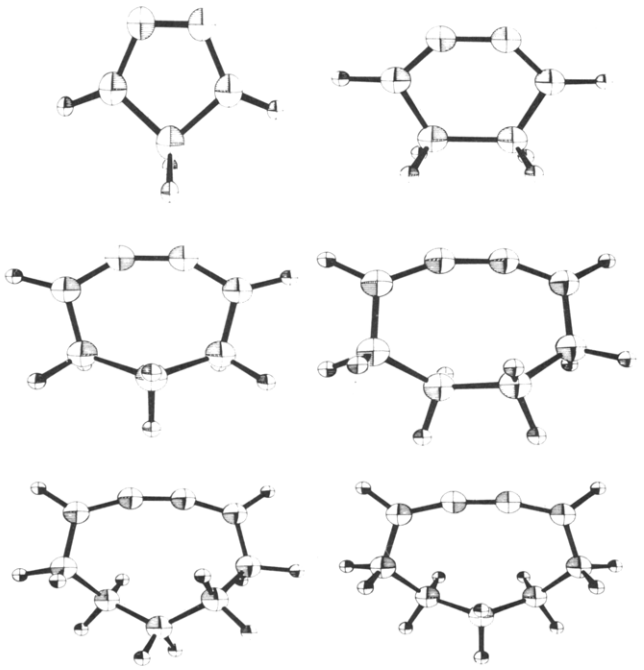


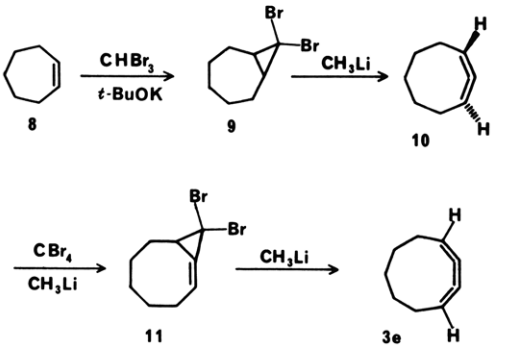
Figure 2. ORTEP structures for cyclic butatrienes.

ca. 10 kcal/mol of molecular strain.

Results of Calculations. For the cyclic butatriene series (**3a–e**), MNDO heats of formation and STO-3G total energies are summarized in Table I, while salient geometrical parameters are collected in Table II. Figure 2 shows a selection of ORTEP[13] representations for the optimized geometries.

In all structures, geometry optimization left the butatriene moiety essentially planar. Even 1,2,3-cyclohexatriene, which could have twisted to relieve methylene eclipsing torsional strain, remained planar. As the ring size is decreased, the C_1–C_2–C_3 angle decreases in a predictable fashion from 180° in butatriene to 116° in cyclopentatriene. The C_1–C_2 bond distance changes only ca. 1.5% over the **3a–e** series, while the C_2–C_3 distance increases from 1.270 to 1.312 Å, consistent with a decrease in bonding and changes in hybridization at C_2 and C_3 (sp toward sp^2). Similar trends were observed in model calculations. The allylic bond in cyclopentatriene is quite long (1.576 Å); this is a compromise between single bond stretching and butatriene bending strains.

Scheme I. Synthesis of 1,2,3-Cyclononatriene



For 1,2,3-cyclononatriene, MNDO and STO-3G (at the MNDO geometry) predict a conformational preference of C_s over C_2 by 4.3 or 3.5 kcal/mol, respectively. From strain estimates (Table I), this is primarily a consequence of greater butatriene bending in the C_2 structure.

Correlation energy corrections were not included in these calculations, however, this should provide somewhat greater relative stabilization for the smaller homologues.

Synthesis of 1,2,3-Cyclononatriene. With these predictions in hand, the synthesis of 1,2,3-cyclononatriene (**3e**) was undertaken. The optimal precursor of **3e** should be (Scheme I) methylenecyclopropane **11**, the expected product of dibromocarbene addition to 1,2-cyclooctadiene (**10**). Since this strained allene readily dimerizes at ambient temperature,[14] it was prepared at −78 to 0 °C and then immediately reacted at −78 °C with :CBr_2, generated from CBr_4 and CH_3Li. Adduct **11** proved isolable in 40–60% yield, after purification by chromatography and rapid distillation.

Treatment of **11** with CH_3Li at −78 to 0 °C yielded a colorless substance, which was securely characterized as 1,2,3-cyclononatriene (**3e**) by spectral and chemical data. The 300-MHz ^1H NMR spectrum of **3e** displayed a vinylic triplet (J = 3.1 Hz) at δ 5.58, essentially identical with that for an authentic sample of 1,2,3-cyclodecatriene.[6] The UV spectrum was slightly red shifted from that of 1,2,3-cyclodecatriene. The ^{13}C NMR showed resonances at 107.0 and 167.5 ppm. Hydrogenation over Pd/C yielded cyclononane. Samples of **3e** were moderately stable to silica gel chromatography and to storage in solution, but polymerized quickly upon concentration or exposure to air. Such behavior is common for butatrienes.

1,2,3-cyclononatriene is thus readily prepared and is stable under ordinary laboratory conditions; further exploration of its chemistry is in progress.

Discussion

Our calculations suggest that the 1,2,3-butatriene moiety is readily bent and may remain intact in essentially any ring size. It is remarkable that even 1,2,3-cyclopentatriene is predicted to be an energy minimum, although one must be quite suspicious of this particular result.

As one approximate estimate of butatriene strain, calculated bending angles for cyclic molecules **3a–e** can be plotted (with some extrapolation for **3a**) against the relative energies shown in Figure 1. These estimates, summarized in Table I, indicate that *strain in the butatriene moiety roughly doubles with each decreasing carbon.*

The strain in cyclopentatriene is sufficiently high that rearrangement to cyclopentadienylidene via 1,3-H shift or ring opening to a vinylcarbene would seem facile. 1,2,3-

(13) Johnson, Carroll, K. Oak Ridge National Laboratory, Oak Ridge, TN, Orn-3794 (Revised), FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustration.

(14) Marquis, E. T.; Gardner, P. *Tetrahedron Lett.* **1966**, 2793.

Table II. Selected MNDO Geometrical Parameters for Cyclic Butatrienes

		bond angles			bond lengths		
	n	C_1–C_2–C_3	C_5–C_4–C_3	C_2–C_1–H_6	C_2–C_3	C_1–C_2	C_4–C_5
3a	1	116.37	101.20	134.56	1.312	1.335	1.576
3b	2	132.23	109.06	131.11	1.292	1.317	1.547
3c	3	145.04	111.88	128.43	1.278	1.316	1.529
3d	4	156.29	115.98	126.08	1.271	1.315	1.519
3e	5 (C_2)	161.94	118.28	124.38	1.269	1.315	1.517
	5 (C_s)	165.14	120.05	123.35	1.268	1.315	1.513
butatriene		180.0	122.75	122.75	1.270	1.310	

Cyclohexatriene is also highly strained; this may undergo an allowed disrotatory ring opening to 1,5-hexadien-3-yne. Szeimies has ascribed his inability to generate **3b** from **7** (eq 3) to decreased exothermicity relative to the **6** → **3c** reaction.[8] This is quite consistent with our estimate that **3b** has double the strain of **3c**.

For the higher homologues, Szeimies has successfully trapped 1,2,3-cycloheptatriene (**3c**),[7] while the decatriene homologue (**3f**) is known to be stable at ambient temperature.[6] On the basis of its geometry and relative butatriene strain (vide supra), our best estimate was that 1,2,3-cyclononatriene would prove isolable, a prediction which was readily verified. In all probability, the strongly bent octatriene will be too kinetically reactive for isolation under ordinary conditions. By comparison, 1,2-cyclononadiene is predicted to be bent ca. 10° and is the smallest kinetically stable allene.[1]

Cyclic butatrienes comprise a fascinating and fundamental collection of molecules, for which very little data presently are available. On the basis of calculations, we suggest that cyclononatriene may be the smallest isolable homologue. As already shown by the work of Szeimies,[7,8] the remaining members of this series will be highly reactive compounds whose chemistry is well worth exploring.

Experimental Section

9,9-Dibromobicyclo[6.1.0]non-1-ene (11). A solution of dibromide **9** (9.71 g, 36.2 mmol) in dry ether (90 mL) was stirred at −78 °C during dropwise addition over 15 min of CH_3Li (36.2 mmol) while under an N_2 atmosphere. The mixture was warmed to 0 °C for 20 min to allow formation of allene **10**.[14] After cooling to −78 °C, CBr_4 (4.81 g, 14.5 mmol) was added, followed by CH_3Li (14.5 mmol). After 0.5 h, the mixture was warmed to 0 °C and quenched. The etheral solution, maintained at 0 °C, was washed with brine (3 × 50 mL) and then H_2O (50 mL), dried ($MgSO_4$), and concentrated at reduced pressure to yield 7.03 g of yellow oil. Chromatography over alumina (hexane elution at −25 °C), followed by Kugelrohr distillation (85–90 °C (0.15 torr)), yielded 2 g (ca. 50% based on CBr_4) of colorless oil. This was estimated to be 85–90% pure. Spectral data: 300-MHz ^1H NMR ($CDCl_3$) δ 6.58 (dd, J = 6.3, 3.1 Hz, 1 H), 2.53–0.96 (multiplet, 11 H); ^{13}C NMR δ 128.9, 126.6, 36.1, 31.4, 31.2, 28.9 (double intensity), 26.6, 23.8; IR (CCl_4) 1759 cm^{-1} (strong, C=C). The mass spectrum showed peaks at m/e 278, 280, and 282, in intensities consistent with a dibromide. Base peak: m/e 91.

1,2,3-Cyclononatriene (3e). Freshly prepared dibromide **11** (1.02 g, ca. 31 mmol) in ether (20 mL) was treated at −78 °C with CH_3Li (36 mmol). While being maintained under N_2, the mixture was allowed to warm to 0 °C, was stirred 0.5 h more, then was quenched, washed with 15-mL portions of brine (3×) and water, and finally was dried ($MgSO_4$). Chromatography of the partially concentrated solution over Florisil (pentane elution) yielded material estimated to be ca. 80% pure. Hydrogenation of an aliquot over Pd/C at 0 °C and 1 atm H_2 yielded cyclononane (ca. 40% from **11**), identical with an authentic sample. Concentration of solutions or prolonged exposure to oxygen yielded insoluble material. The spectral data for **3e**: 300-MHz ^1H NMR ($CDCl_3$) δ 5.58 (t, J = 3.1 Hz), 2.31 (complex m, allylic H), 1.73 (complex pentet, $J \sim 6$ Hz), 1.56 (complex pentet, $J \sim 6$ Hz); ^{13}C NMR ($CDCl_3$) δ 167.4 (sp), 107.0 (sp^2), 30.8, 28.9, 25.0; IR (CCl_4) 3021 (sh) 2930, 2870, 2835, 1463, 1454, 1442, 1427, 1323, 1245, 854, 667 cm^{-1}; UV (pentane) λ_{max} 232, 257, 292 nm.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research.

Registry No. **3a** (n = 1), 90866-89-0; **3b** (n = 2), 90866-90-3; **3c** (n = 3), 79005-31-5; **3d** (n = 4), 90866-91-4; **3e** (n = 5), 90885-93-1; **9**, 7124-41-6; **10**, 7124-40-5; **11**, 90866-92-5; CH_2=C=C=CH_2, 2873-50-9.