

afforded a pale yellow solid (108 mg). Purification by GLC gave **19** as a white solid: mp 288–293 °C; $^1\text{H NMR } \delta$ (CDCl_3) 4.11 (apparent t, $J = 3.7$ Hz, 1 H, CHOH), 3.41–1.37 (complex m, 15 H); IR ν (CCl_4) 3625, 3435, 2915, 2855, 1697, 1450, 1050, 930, 915 cm^{-1} .

Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.94. Found: C, 73.26; H, 8.86.

2,5-Homoadamantanedione (20). Chromium trioxide (336 mg, 3.36 mmol) was added in small portions to a mixture of pyridine (530 mg, 6.72 mmol) in methylene chloride (9 mL). To this complex was added a solution of **19** (50 mg, 0.28 mmol) in methylene chloride (0.5 mL). The reaction mixture was stirred at room temperature for 15 min, and the resulting inorganic precipitates were removed by filtration. The filtrate was washed successively with 5% aqueous sodium hydroxide, 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and brine and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave crude **20** which was purified by GLC (10 ft \times 0.25 in. SE-30 column, 225 °C). The IR spectrum of this material was identical with that of **20** prepared by an alternative procedure.^{2c}

3-Oxa-endo-tricyclo[6.3.1.0^{2,6}]dodecan-4-one (25). A solution of 20 mg of **19** in 2 mL of nitrogen-purged diethyl ether was irradiated through a Vycor filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (10 ft \times 0.25 in. SE-30 column, 235 °C) indicated a gradual disappearance of **19** with the concomitant formation of a photoproduct. After irradiation for 2 h, ca. 85% of **19** had reacted. Evaporation of the solvent at reduced pressure provided an oil

which by $^1\text{H NMR}$ analysis contained an ca. 25% yield of the photoproduct. Purification by GLC (above conditions) gave **25** as a colorless oil: $^1\text{H NMR } \delta$ (CCl_4) 4.97–4.59 (br m, 1 H, $-\text{CHO}-$), 2.76–0.96 (complex m, 15 H); IR ν (CCl_4) 2930, 2880, 1783, 1465, 1180, 1160, 1010, 975, 920 cm^{-1} .

Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.94. Found: C, 73.44; H, 8.68.

2,11-diendo-Dibromo-5-homoadamantanone (26). Bromine (8 μL , 0.15 mmol) was added to a stirred solution of **9** (25 mg, 0.15 mmol) in carbon tetrachloride (2 mL) at room temperature. The reaction mixture was stirred for 0.5 h and then diluted with ether (25 mL). The resulting solution was washed with 10% aqueous sodium bisulfite (2 \times 10 mL) and brine (10 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an orange oil which was shown by $^{13}\text{C NMR}$ to contain >90% of a single product: δ (CDCl_3) 207.6, 57.4, 46.8, 42.3, 41.3, 36.5, 34.8, 26.3 in the ratio of 1:2:1:1:1:2:2, respectively. Sublimation provided **26** as a white waxy semisolid: $^1\text{H NMR } \delta$ (CDCl_3) 4.69 (apparent t, $J = 4.7$ Hz, 2 H, CHBr), 3.16 (d, $J = 4.0$ Hz, 2 H, $-\text{CH}_2\text{CO}-$), 2.82–1.50 (complex m, 10 H); IR ν (CHCl_3) 3010, 2920, 2860, 1700, 1465, 1445, 1400, 1360, 1300, 1280, 1240, 1150, 1050 cm^{-1} ; m/e 322/324 = 2.13. Exact mass calcd for $\text{C}_{11}\text{H}_{14}\text{Br}_2\text{O}$: 319.941. Found: 319.942.

Registry No. 6, 71129-58-3; 7, 10497-56-0; 9, 71129-59-4; 12, 71129-60-7; 13, 71129-61-8; 14, 71129-62-9; 15, 59159-18-1; 16, 71183-74-9; 17, 55638-06-7; 19, 71183-75-0; 20, 55638-09-0; 25, 71129-63-0; 26, 71129-64-1; 30, 71129-65-2; *p*-toluenesulfonylhydrazine, 1576-35-8.

Synthesis of Substituted Cyclooctatetraenide Dianions

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Received February 12, 1979

Dilithioalkyl and -aryl monosubstituted cyclooctatetraenide dianions ($\text{Li}_2\text{C}_8\text{H}_7\text{R}$; R = methyl, *n*-butyl, *sec*-butyl, *tert*-butyl, phenyl, and benzyl) were synthesized by reaction of the appropriate organolithium reagent with cyclooctatetraene in diethyl ether or tetrahydrofuran. The reaction occurred cleanly and with a good yield of the dilithio monosubstituted cyclooctatetraenide dianion at ambient or lower temperature for all alkyl or aryl organolithium reagents studied except *tert*-butyllithium. (TMEDA is needed as an activator for CH_3Li .) A two-step mechanism for the reaction is proposed that involves addition of the organolithium reagent to cyclooctatetraene followed by proton removal to yield the appropriate dianion.

Organolithium reagents are known to readily add to conjugated olefins and styrenes.¹ Reaction of cycloheptatriene with organolithium reagents yields lithium 6-substituted cycloheptadienide.² In a similar way, reaction of organolithium reagents with cyclooctatetraene (**1a**) might be expected to yield lithium 8-substituted cyclooctatrienide. Hydrolysis of this anion would yield the monosubstituted cyclooctatriene. Cope et al.^{3a} in an early study of **1a** with *sec*-butyllithium observed monosubstituted cyclooctatrienes on hydrolysis. However, on reaction of **1a** with *n*-butyl- and phenyllithium,³ monosubstituted cyclooctatetraenes as well as monosubstituted cyclooctatrienes were observed on hydrolysis. In fact, this method has been used to prepare the monosubstituted cyclooctatetraenes, but the yields are low and the cyclo-

Table I. Reaction Data for Monosubstituted Cyclooctatetraenide Dianions

compd	temp, °C	solvent	reacn time ^c	% yield ^a
methylcyclooctatetraene ^b (2a)	25	Et_2O	18 h	60
<i>n</i> -butylcyclooctatetraene (3a)	25	Et_2O	45 min	70
<i>sec</i> -butylcyclooctatetraene (4a)	0	Et_2O	30 min	51
<i>tert</i> -butylcyclooctatetraene (5a)	-78	$\text{Et}_2\text{O}/$ pentane	5 min	45
phenylcyclooctatetraene (6a)	25	Et_2O	36 h	76
benzylcyclooctatetraene (7a)	0	THF	5 min	60

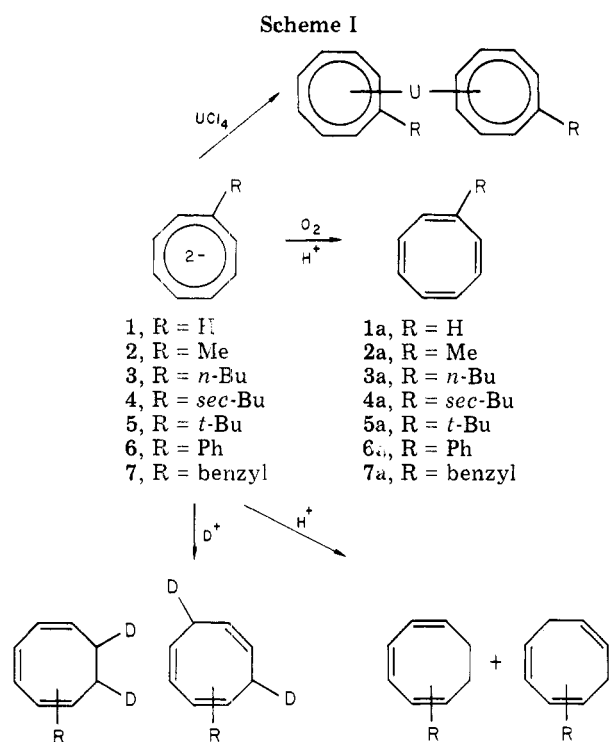
^a Based on O_2 oxidation to the monosubstituted cyclooctatetraene followed by hydrolysis. All yields are based on VPC data. ^b 1.2 TMEDA/ CH_3Li molar ratio. ^c Time for complete reaction.

octatetraenes and cyclooctatrienes must be separated by a time-consuming AgNO_3 extraction.^{4,5} Here we show

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(2) K. Haffner and W. Rellensmann, *Chem. Ber.*, **95**, 2567 (1962); R. B. Bates, S. Brenner, and B. I. Mayall, *J. Am. Chem. Soc.*, **94**, 4765 (1972).

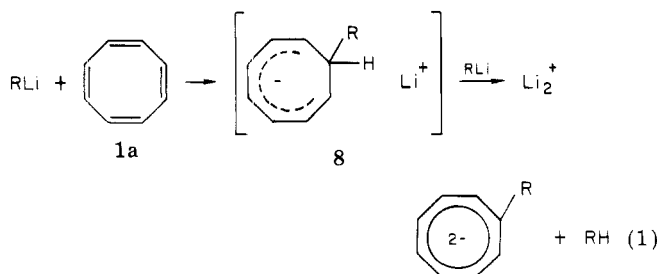
(3) (a) A. C. Cope and H. O. Van Orden, *J. Am. Chem. Soc.*, **74**, 175 (1952); (b) A. C. Cope and M. R. Kinter, *ibid.*, **73**, 3424 (1951); (c) A. C. Cope and W. R. Moore, *ibid.*, **77**, 4939 (1955).



that, when O_2 is rigorously excluded, the reaction between **1a** and alkyl- or aryllithium reagents yields the substituted cyclooctatetraene dianions, **2-7**.⁶ This was established by the reactions shown in Scheme I.

Addition of 2 equiv of *n*-butyllithium to **1a** in diethyl ether (Et_2O) produced a deep red to violet solution (solution A). Oxidation, using O_2 or air, of solution A yielded an orange solid which on subsequent hydrolysis with 1 M hydrochloric acid (HCl) gave *n*-butylcyclooctatetraene (**3a**). No trace of *n*-butylcyclooctatrienes was observed by VPC. Yields and reaction conditions for the substituted cyclooctatetraenes are shown in Table I. On the other hand, hydrolysis of solution A with 1 M HCl yielded *n*-butylcyclooctatrienes exclusively. No *n*-butylcyclooctatetraene was observed by VPC. Further confirmation of the dianion was observed by deuteriolysis of solution A, which yielded the dideuterio-*n*-butylcyclooctatrienes. Similar results were observed for all other dianions. Finally, treatment of solution A with UCl_4 dissolved in tetrahydrofuran (THF) yielded 1,1'-di-*n*-butyluranocene, confirmed by an identical match of its infrared, visible, 1H NMR, and mass spectra with the literature.^{7,8}

A possible mechanism for the formation of the mono-substituted cyclooctatetraene dianion is shown in eq 1.



The first step proceeds as a nucleophilic attack of the organolithium reagent on a carbon-carbon double bond

with the formation of a delocalized monoanion intermediate (**8**). The second step involves abstraction of a proton from **8** to yield the aromatic ten- π -electron dianion. The overall stoichiometry of eq 1 requires 2 equiv of *n*-butyllithium per equivalent **1a**. Experimentally, 1.7 equiv of *n*-butyllithium to 1 equiv of **1a** was needed. This ratio is consistent with an 85% yield of **3** as determined by hydrolysis to the *n*-butylcyclooctatrienes. Butane evolution, during formation of **3**, was observed and gives additional evidence for eq 1. Butane was identified by GC/mass spectrometry from the vapors above solution A. Attempted isolation of **8**, by addition of 0.5 equiv of *n*-butyllithium to 1 equiv of **1a**, resulted only in observation of **3**, butane, and residual **1a**. Deuteriolysis of this system, followed by GC/mass spectrometry, produced a parent ion peak at 164 only for the dideuterio-*n*-butylcyclooctatrienes. No 163 peak was observed. This suggests that proton abstraction from **8** is rapid and quantitative once **8** has formed. Proton abstraction from other similar anions has been observed, for example, in the formation of the cycloheptatrienyl trianion from 1,4-cycloheptadiene⁹ and in the formation of **1** from 1,5-cyclooctadiene or 1,3,6-cyclooctatriene.¹⁰ In both these cases, the base was *n*-butyllithium activated by *N,N,N',N'*-tetramethylethylenediamine (TMEDA).

Cope and Van Orden^{3a} report no reaction between methylithium and **1a**, and we confirm that observation. However, a reaction does occur with addition of TMEDA, as shown in Table I. The relative rates of addition of the organolithium reagents to **1a** were in the order *tert*-butyl > benzyl > *sec*-butyl > *n*-butyl > phenyl > methyl. No reaction occurred with lithium phenylacetylide, lithium cyclopentadienide, or vinylithium. This order of reactivity is very similar to that for the initiation of styrene polymerization with organolithium reagents.¹¹ We also found no reaction to occur between ethylmagnesium bromide, diisobutylaluminum hydride, or lithium ethoxide and **1a**.

Once the dianion is formed, no further substitution occurs. For *n*-butyl-, *sec*-butyl-, phenyl-, and benzyl lithium the only other observed product was 1-2% of **1**. The reaction gives a high yield of the monosubstituted dianion, but losses occur on oxidation to the substituted cyclooctatetraene. Hydrolysis results have generally given yields of substituted cyclooctatrienes 10% higher than the substituted cyclooctatetraene. In the case of *tert*-butyllithium, the most reactive lithium reagent studied here, **1** and **5** were observed together with some heavier non-lithium-containing compounds currently being studied. For CH_3Li , 30% of **1** was observed in addition to a 60% yield of **2**.

Cope and Moore^{3c} showed that disubstituted cyclooctatetraenes can be prepared by reacting the organolithium reagent with monosubstituted cyclooctatetraene. They prepared four isomers of diphenylcyclooctatetraene using this method. We prepared the disubstituted *n*-butylcyclooctatetraene by this method, but unfortunately, as Cope observed, the reaction is not regioselective and a number of isomers are formed.

The results presented here differ from the early work of Cope in two basic ways: (1) Cope³ et al. did not recognize the presence of the dianion; and (2) the present technique allows rigorous exclusion of oxygen and water, yielding only the substituted dianion. Cope's early work,

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(5) G. R. Stevenson and L. Echegoyen, *J. Phys. Chem.*, **79**, 929 (1975).

(6) For a review of cyclooctatetraene dianion chemistry, see L. A. Paquette, *Tetrahedron*, **31**, 2855 (1975).

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(9) J. J. Bahl, R. B. Bates, W. A. Beavers and C. R. Launer, *J. Am. Chem. Soc.*, **99**, 6126 (1977).

(10) W. Gausing and G. Wilke, *Angew. Chem. Int. Ed. Engl.*, **17**, 371 (1978).

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however, occurred before the discovery of the cyclooctatetraene dianion. It is clear from the present results that his system contained the dianion. Only inadvertent oxidation during reflux followed by hydrolysis allowed the isolation of the substituted cyclooctatetraenes. To check this point we did in fact follow his procedure exactly with careful exclusion of oxygen and water and did observe only the substituted dianion as confirmed by subsequent oxidation and hydrolysis results.

Experimental Section

Proton magnetic resonance spectra were recorded on a Varian HA-100 spectrometer with Me_4Si as a reference. GC-mass spectral data were obtained using a Varian MAT GmbH CH7 Massenspektrometer at an ionization potential of 70 eV interfaced with a Varian 1200 gas chromatograph. Reactions were carried out using a Schlenk line in an atmosphere of commercially prepurified nitrogen. All reactions were performed in Schlenk flasks capped with rubber septums and reactants were introduced from syringes. Yield data were obtained and preparative work was done on HP 5720A and Varian 920 gas chromatographs, respectively.

Commercial alkyl- or aryllithium reagents were purchased from Alfa Products, Danvers, Mass. 01923. Benzylolithium,¹² vinylolithium,¹³ and lithium phenylacetylide¹⁴ were prepared by published procedures. Diethyl ether and tetrahydrofuran were dried over sodium-benzophenone and distilled under nitrogen prior to use. Cyclooctatetraene (**1a**) was distilled onto Linde 4A molecular sieves and stored under nitrogen. *N,N,N',N'*-tetramethylethylenediamine, obtained from Aldrich Chemical Co., Milwaukee, Wis. 53233, was dried over Linde 4A molecular sieves and used without further purification.

Synthetic Procedures. The general procedure was the same for dianions 2-7. Dianion 2, in addition, requires TMEDA to activate the methylolithium. The procedure for dianion 3 is given below. Scale-up procedures present no additional problems. Products may be isolated using standard vacuum distillation techniques.

Preparation of *n*-Butylcyclooctatetraenide Dianion (3). In an atmosphere of prepurified nitrogen, 0.50 mL (4.4 mmol) of **1a** was added to 25 mL of Et_2O . A solution of 4.4 mL (2.0 M, 8.8 mmol) of *n*-butyllithium was added to this solution with rapid stirring which was continued for 1 h. Aliquots of the resulting red solution were taken for oxidation, hydrolysis, deuteriolysis, and yield data.

***n*-Butylcyclooctatetraene (3a).** At ambient temperature air or O_2 was bubbled through the solution, yielding an orange solid that was treated with 1 M HCl. Extraction with hexane (3 × 2 mL) and drying with MgSO_4 , followed by evaporation of the hexane, yielded a bright yellow liquid, which was isolated by preparative VPC and identified as **3a** by ^1H NMR and mass spectrometry. Spectral data are given below. The yield of **3a** by VPC (18 in. × 0.125 in 10% UCW 982 on AW-DMCS Chromosorb W, 120 °C) was 505 mg (70%) using an external standard.

***n*-Butylcyclooctatrienes and Dideuterio-*n*-butylcyclooctatrienes.** To the above solution of **3** at ambient temperature was added 1 M HCl or D_2O . Workup as above gave a pale yellow liquid consisting of a mixture of isomers of *n*-butylcyclooctatrienes and dideuterio-*n*-butylcyclooctatrienes, respectively. This mixture was isolated by preparative VPC (8 ft × 0.25 in. 10% Carbowax 4000, AW Chromosorb P, 120 °C). GC-mass spectral results for one of the observed four isomers is given below. The mass spectra of the individual isomers differed slightly from one another in intensity only. For all dianions, deuteriolysis gave dideuterio-*n*-butylcyclooctatrienes in excess of 98% by mass spectrometry. No evidence of monodeuteration was observed. The yield of *n*-butylcyclooctatrienes was 605 mg (85%) by VPC using an external standard.

Stoichiometry. The general procedure is the same as that described above using freshly distilled **1a** and titrated *n*-bu-

tyllithium (1.64 M). The amount of **1a** was fixed at 0.50 mL (4.4 mmol). Initially, 4.00 mL (5.5 mmol) of *n*-butyllithium was added and allowed to react for 12 h. An aliquot of the reaction solution was hydrolyzed with 1 M HCl and residual **1a** was determined by VPC (8 ft. × 0.125 in., 10% Carbowax 20 M on Chromosorb P, 140 °C). At this time, additional *n*-butyllithium (0.30 mL, 0.50 mmol) was introduced, and after 2.5 h a second aliquot of the reaction mixture was removed and residual **1a** was determined as before. Additions of 0.10 mL (0.16 mmol) of *n*-butyllithium were continued at 2.5-h intervals until no **1a** remained. At this point, 4.6 mL (7.5 mmol) of *n*-butyllithium had been added. Reaction stoichiometry, based on consumption of **1a**, is determined to be 1.7 equiv of *n*-butyllithium to 1.0 equiv of **1a**.

^1H NMR and Mass Spectrometric Data. Benzylcyclooctatetraene (**7a**): ^1H NMR (CCl_4) δ 3.31 (s, 2 H, $>\text{CH}_2$), 5.69 (m, 7 H, $-\text{C}_8\text{H}_7$ with a small shoulder at δ 5.53), 7.15 (s, 5 H, $-\text{C}_6\text{H}_5$); mass spectrum (70 eV) m/e 194 (M^+), 103 ($\text{M} - \text{C}_6\text{H}_5\text{CH}_2$), 91 ($\text{M} - \text{C}_8\text{H}_7\text{CH}_2$).

Benzylcyclooctatrienes: mass spectrum (70 eV) m/e ($\text{C}_{15}\text{H}_{14}$) 196 (M^+), 168 ($\text{M} - \text{C}_2\text{H}_4$), 105 ($\text{M} - \text{C}_7\text{H}_7$); ($\text{C}_{15}\text{H}_{12}\text{D}_2$) 198 (M^+), 169 ($\text{M} - \text{C}_2\text{H}_3\text{D}$), 168 ($\text{M} - \text{C}_2\text{H}_2\text{D}_2$), 107 ($\text{M} - \text{C}_7\text{H}_7$).

Methylcyclooctatetraene (**2a**):¹⁵ ^1H NMR (CCl_4) δ 1.72 (s, 3 H, $-\text{CH}_3$), 5.68 (s, 7 H, $-\text{C}_8\text{H}_7$ with a small shoulder at δ 5.50); mass spectrum (70 eV) m/e 118 (M^+), 117 ($\text{M} - \text{H}$), 103 ($\text{M} - \text{CH}_3$).

Methylcyclooctatrienes: mass spectrum (70 eV) m/e (C_9H_{12}) 120 (M^+), 119 ($\text{M} - \text{H}$), 105 ($\text{M} - \text{CH}_3$); ($\text{C}_9\text{H}_{10}\text{D}_2$) 122 (M^+), 121 ($\text{M} - \text{H}$), 107 ($\text{M} - \text{CH}_3$).

n-Butylcyclooctatetraene (**3a**): ^1H NMR (CCl_4) δ 0.87-0.98 (m, 3 H, $-\text{CH}_3$), 1.32-1.45 (m, 4 H, $-\text{CH}_2\text{CH}_2-$), 2.02 (t, 2 H, $>\text{CH}_2$), 5.71 (s, 7 H, $-\text{C}_8\text{H}_7$ with a small shoulder at δ 5.50); mass spectrum (70 eV) m/e 160 (M^+), 145 ($\text{M} - \text{CH}_3$), 131 ($\text{M} - \text{CH}_3\text{CH}_2$), 117 ($\text{M} - \text{CH}_2\text{CH}_2\text{CH}_2$).

n-Butylcyclooctatrienes: mass spectrum (70 eV) m/e ($\text{C}_{12}\text{H}_{18}$) 162 (M^+), 134 ($\text{M} - \text{C}_2\text{H}_4$), 119 ($\text{M} - \text{C}_3\text{H}_7$), 105 ($\text{M} - \text{C}_4\text{H}_9$); ($\text{C}_{12}\text{H}_{16}\text{D}_2$) 164 (M^+), 135 ($\text{M} - \text{C}_2\text{H}_3\text{D}$), 134 ($\text{M} - \text{C}_2\text{H}_2\text{D}_2$), 121 ($\text{M} - \text{C}_3\text{H}_7$), 107 ($\text{M} - \text{C}_4\text{H}_9$).

sec-Butylcyclooctatetraene (**4a**): ^1H NMR (CCl_4) δ 0.73-1.08 (m, 6 H, $-\text{CH}_3$), 1.14-1.50 (m, 2 H, $>\text{CH}_2$), 1.96-2.20 (quartet, 1 H, CH), 5.72 (s, 7 H, with a small shoulder at δ 5.48); mass spectrum (70 eV) m/e 160 (M^+), 145 ($\text{M} - \text{CH}_3$), 132 ($\text{M} - \text{C}_2\text{H}_4$), 131 ($\text{M} - \text{C}_2\text{H}_5$), 117 ($\text{M} - \text{C}_3\text{H}_7$), 105 ($\text{M} - \text{C}_4\text{H}_9$).

sec-Butylcyclooctatrienes: mass spectrum (70 eV) m/e ($\text{C}_{12}\text{H}_{18}$) 162 (M^+), 134 ($\text{M} - \text{C}_2\text{H}_4$), 133 ($\text{M} - \text{C}_2\text{H}_5$), 105 ($\text{M} - \text{C}_4\text{H}_9$); ($\text{C}_{12}\text{H}_{16}\text{D}_2$) 164 (M^+), 135 ($\text{M} - \text{C}_2\text{H}_5$), 107 ($\text{M} - \text{C}_4\text{H}_9$), 106 ($\text{M} - \text{C}_4\text{H}_9 - \text{H}$).

tert-Butylcyclooctatetraene (**5a**): ^1H NMR (CCl_4) δ 1.07 (s, 9 H, *t*-Bu), 5.53-6.02 m, 7 H, $-\text{C}_8\text{H}_7$); mass spectrum (70 eV) m/e 160 (M^+), 145 ($\text{M} - \text{CH}_3$), 130 ($\text{M} - 2\text{CH}_3$), 115 ($\text{M} - 3\text{CH}_3$).

tert-Butylcyclooctatrienes: mass spectrum (70 eV) m/e ($\text{C}_{12}\text{H}_{18}$) 162 (M^+), 147 ($\text{M} - \text{CH}_3$), 145 ($\text{M} - \text{CH}_3 - 2\text{H}$), 134 ($\text{M} - \text{C}_2\text{H}_4$), 119 ($\text{M} - \text{C}_2\text{H}_4 - \text{CH}_3$), 105 ($\text{M} - \text{C}_4\text{H}_9$); ($\text{C}_{12}\text{H}_{16}\text{D}_2$) 164 (M^+), 149 ($\text{M} - \text{CH}_3$), 135 ($\text{M} - \text{C}_2\text{H}_3\text{D}$), 134 ($\text{M} - \text{C}_2\text{H}_2\text{D}_2$), 120 ($\text{M} - \text{CH}_3 - \text{C}_2\text{H}_3\text{D}$), 119 ($\text{M} - \text{CH}_3 - \text{C}_2\text{H}_2\text{D}_2$), 107 ($\text{M} - \text{C}_4\text{H}_9$).

Phenylcyclooctatetraene (**6a**): ^1H NMR (CCl_4) δ 5.82-6.11 (m, 7 H, $-\text{C}_8\text{H}_7$), 7.13-7.29 (m, 5 H, $-\text{C}_6\text{H}_5$); mass spectrum (70 eV) m/e 180 (M^+), 179 ($\text{M} - \text{H}$), 178 ($\text{M} - 2\text{H}$), 102 ($\text{M} - \text{C}_6\text{H}_6$).

Phenylcyclooctatrienes: mass spectrum (70 eV) m/e ($\text{C}_{14}\text{H}_{12}$) 182 (M^+), 154 ($\text{M} - \text{C}_2\text{H}_4$); ($\text{C}_{14}\text{H}_{10}\text{D}_2$) 184 (M^+), 155 ($\text{M} - \text{C}_2\text{H}_3\text{D}$), 154 ($\text{M} - \text{C}_2\text{H}_2\text{D}_2$).

Acknowledgment. This research was supported by the National Science Foundation and the Oregon State Research Council. We thank especially Professor E. N. Marvell for a generous donation of cyclooctatetraene and Dr. Stanley Wilson for many stimulating discussions.

Registry No. **1a**, 629-20-9; **2**, 71204-95-0; **2a**, 2570-12-9; **3**, 71204-97-2; **3a**, 13402-37-4; **4**, 71204-99-4; **4a**, 629-20-9; **5**, 71205-01-1; **5a**, 61593-18-8; **6**, 71205-03-3; **6a**, 4603-00-3; **7**, 71205-05-5; **7a**, 56660-67-4; methylolithium, 917-54-4; butyllithium, 109-72-8; *sec*-butyllithium, 598-30-1; *tert*-butyllithium, 594-19-4; phenyllithium, 591-51-5; benzylolithium, 766-04-1.

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