(Cyclobutadiene)tricarbonyliron Complexes: Formation of 1,3- and 1,2,3-Substituted Derivatives[1]

Christopher M. Adams,* Scott A. Joslin,[2] Ellen S. Crawford, and John E. Schemenaur

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078-0447

Received July 15, 1992

Current methods available to modify or append alkyl groups to (cyclobutadiene)tricarbonyliron limit its use and study. Using selective alkylations and rearrangements on diisopropyl squarate, we have developed simple and efficient routes to specific 1,3-disubstituted (**2**) and 1,2,3-trisubstituted (**3**) (cyclobutadiene)tricarbonyliron complexes. These methods represent the first direct syntheses of these complexes and provide new entries into potentially novel cyclobutadiene-derived synthons and complexes.

Introduction

The paucity of methods to synthesize specific 1,2-, 1,3-, and 1,2,3-substituted cyclobutadiene complexes **1**, **2**, and **3**, respectively, limit their study and potential application as synthons in organic chemistry (Chart I). The syntheses of the few known 1,3-disubstituted (cyclobutadiene)-tricarbonyliron complexes involve many steps from the parent cyclobutadiene complex **4**. Examples of these complexes include ([2.2]-1,3-cyclobutadienophane)bis-(tricarbonyliron) (**5**),[3] [(1,8,9,10-η)bicyclo[6.1.1]-deca-1(10),8-dien-2-one]tricarbonyliron (**6**),[4] (1,3-di-*tert*-butylcyclobutadiene)tricarbonyliron (**7**),[5] and (1-acetyl-3-ethylcyclobutadiene)tricarbonyliron (**8**).[6] Free cyclobutadiene can be generated from the parent (cyclobutadiene)tricarbonyliron by oxidation.[7] The extremely reactive cyclobutadiene participates as a Diels-Alder partner[7] and in this manner has been used in the construction of strained caged compounds, for example, cubane[8] and caged keto-sulfides.[9] Early methods to synthesize disubstituted cyclobutadiene complexes have involved thermal and photochemical reactions to product suitably substituted, 4-membered ring precursors. Notable examples of these reactions are the [2 + 2] thermal cycloadditions of perhaloethylenes with alkylacetylenes[10] and dibromomaleic anhydride,[11] and [2 + 2] photochemical cycloaddition of vinylene carbonate with alkylacetylenes.[12] The regioselectivity of these reactions generally leads to 1,2-disubstituted products as components of complex mixtures. Such reactions are often plagued with undesired dimerizations, low yields, and difficulties with product isolation.[7] We recently reported new syntheses of 1,2-disubstituted (cyclobutadiene)tricarbonyliron complexes;[13] however, the 1,3-regioisomers do not lend themselves to facile synthesis through established thermal or photochemical reactions.

Results and Discussion

Our synthetic requirements for new, more desirable, and rare 1,3-disubstituted cyclobutadiene complexes **2** led us to investigate modifications of our reported 1,2-disubstituted cyclobutadiene complex syntheses based on diisopropyl squarate (**9**).[13] A retrosynthetic analysis for the preparation of 1,3-disubstituted cyclobutadiene metal complexes is shown in Scheme I. Selective Grignard additions, selective hydrolyses, and selective carbonyl reductions are used to furnish the 1,3-substitution pattern in the sequence.

A number of groups have reviewed the history and syntheses of substituted cyclobutenediones from squaric esters.[14-19] We sought to utilize and extend our facile preparative methodology for 1,2-disubstituted (cyclo-

(1) Preliminary work was presented in part at the 203rd ACS National Meeting, San Francisco, CA, April 5-10, 1992, Division of Organic Chemistry, Abstract No. 305.

(2) Summer 1990 recipient of Project SEED Fellowship, Petroleum Research Fund, American Chemical Society.

(3) Adams, C. M.; Holt, E. M. *Organometallics* **1990**, *9*, 980-986.

(4) Adams, C. M.; Crawford, E. S.; Salim, E. *Tetrahedron Lett.* **1992**, *33*, 3963-3966.

(5) Reeves, P.; Henery, J.; Pettit, R. *J. Am. Chem. Soc.* **1969**, *91*, 5888-5890.

(6) Marcinal, P.; Hannoir-Guisez, N.; Cuingnet, E. *Trav. Soc. Pharm. Mont.* **1973**, *33*, 281-288.

(7) (a) Efraty, A. *Chem. Rev.* **1977**, *77*, 691-743 and references cited therein. (b) Watts, L., Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253-3254. (c) Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131-133.

(8) Barborak, J. C.; Watts, J. C.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 1328-1329.

(9) Paquette, L. A.; Wise, L. D. *J. Am. Chem. Soc.* **1967**, *89*, 6659-6666.

(10) (a) Smutny, E. J.; Caserio, M. C.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 1793-1801. (b) Brune, H. A.; Hanebeck, H.; Hüther, H. *Tetrahedron* **1970**, *26*, 3099-3112. (c) Bloomquist, A. T.; LaLancette, E. A. *J. Org. Chem.* **1964**, *29*, 2331-2334.

(11) (a) Berens, G.; Kaplan, F.; Rimerman, R.; Roberts, B. W.; Wissner, A. *J. Am. Chem. Soc.* **1975**, *97*, 7076-7085. (b) Roberts, B. W.; Wissner, A.; Rimerman, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 6208-6209.

(12) (a) Grubbs, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6693. (b) Grubbs, R. H.; Pancoast, T. A.; Grey, R. A. *Tetrahedron Lett.* **1974**, 2425-2426. (c) Grubbs, R. H.; Grey, R. A. *J. Chem. Soc., Chem. Commun.* **1973**, 76-77.

(13) Adams, C. M.; Schemenaur, J. E.; Crawford, E. S.; Joslin, S. A. *Synth. Commun.* **1992**, *22* (10), 1385-1396.

(14) (a) Liebeskind, L. S.; Fengel, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482-2488. (b) Liebeskind, L. S.; Baysdon, S. L. *Tetrahedron Lett.* **1984**, *25*, 1747-1750.

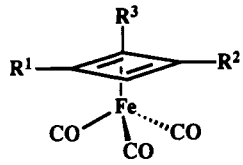
(15) Reed, M. W.; Pollart, D. J.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477-2482.

(16) For general reviews on the properties and the preparation of cyclobutanediones and squaric esters see: (a) Cava, M. P., Mitchel, M. J., Eds. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967; Vol. 10 and references cited therein. (b) Schmidt, A. H.; Ried, W. *Synthesis*, **1978**, 1-22. (c) Knorr, H.; Ried, W. *Synthesis* **1978**, 649-666. (d) Schmidt, A. H.; Ried, W. *Synthesis* **1978**, 869-880. (e) Martin, H.-D.; Oftring, A.; Iden, R. *Tetrahedron Lett.* **1982**, *23*, 841-844. (f) Dehmlow, E. V.; Schell, H. G. *Chem. Ber.* **1980**, *113*, 1-8. (g) Kraus, J. L. *Tetrahedron Lett.* **1985**, *26*, 1867-1870. (h) Paine, A. J. *Tetrahedron Lett.* **1984**, *25*, 135-138. (i) Chickos, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 5749-5750. (j) See ref 14.

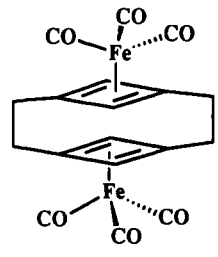
(17) Krysan, D. J.; Gurski, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1992**, *114*, 1412-1418.

0276-7333/93/2312-0656$04.00/0

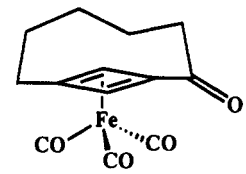
Chart I



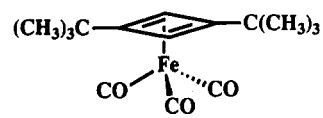
1: R^1,R^3 = alkyl; R^2 = H
2: R^1,R^2 = alkyl; R^3 = H
3: R^1,R^2,R^3 = alkyl
4: R^1,R^2,R^3 = H



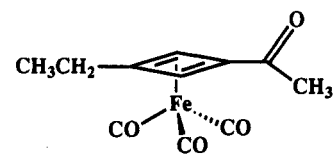
5



6

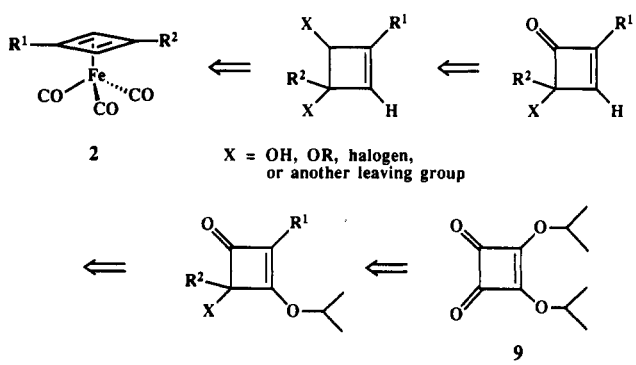


7



8

Scheme I



2

9

butadiene)tricarbonyliron compounds to form cyclobutadiene complexes from keto-esters **10**.[13] One requirement for the generation of the final 1,3-disubstituted complexes is retention of the cyclobutene unit. Selective addition of an organolithium reagent to the carbonyl group of the α,β-unsaturated ketone versus that of the α,β-unsaturated ester in **10** establishes the desired 1,3-disubstitution pattern (Scheme II).[16-18] Our initial investigations revealed alcohol **11** (R^1,R^2 = *n*-butyl) to be labile to reduction with lithium aluminum hydride. Alcohol **11** could be reduced and rearranged to **12** when protected with *tert*-butyldimethylsilyl chloride (TBDMSCl). Alternatively, methylation of **11** with sodium hydride and methyl iodide to produce **13** (R^1,R^2 = *n*-butyl) eliminated the expense of using TBDMSCl as well as the decomposition of **11**. Reduction of **13** with lithium aluminum hydride or Vitride, and subsequent rearrangement with HCl in one pot, gave keto-alcohol **12**. Reduction of **12** with $LiAlH_4$ led to intractable mixtures. Reduction of **13** proceeded smoothly to intermediate **14** in high yield (Scheme III). The crucial step to retain protection of the alcohol in **14** and yet rearrange the reduced ester was achieved by the selective rearrangement of allylic alcohol **14** with a mixture of trifluoroacetic anhydride and pyridine.[15] The mechanism for conversion of **14** to ketone **15** presumably involves the rearrangement of **14** to a hemiketal and hydrolysis, a mechanism previously suggested for substituted cyclobutenediones.[14] Cerium(III)-mediated reductions of ketones **15** with sodium borohydride or lithium aluminum hydride gave hydroxy–methoxy derivatives **16** in high yields.[13,19]

Bromination of **16** with phosphorus tribromide gave **17**, the desired precursor required to generate the final metal complex. Some reports indicate that a mixture of triphenylphosphine and carbon tetrachloride can effect chlorination of allylic alcohols.[17] However, we found phosphorus tribromide more convenient owing to the ease of workup and subsequent complex formation. Dibromides **17** were labile to chromatographic conditions and were sufficiently pure to allow their direct conversion to the corresponding iron complexes. Reductive elimination and complexation of **17** with $Fe_2(CO)_9$ gave the corresponding 1,3-disubstituted (cyclobutadiene)tricarbonyliron complexes **2** (Table I).[13]

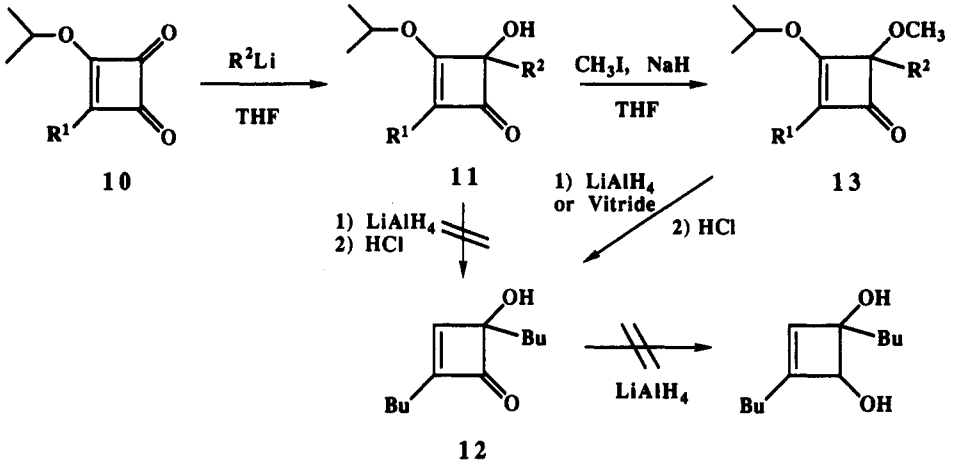
The reaction scheme was easily modified to allow formation of a 1,2,3-trisubstituted (cyclobutadiene)tricarbonyliron complex (Scheme IV). The most appropriate extension for this sequence was the addition of butyllithium to ester **13c** to give **18**. Alcohol **18** rearranged slowly when chromatographed on silica gel and could be more conveniently rearranged with acetic acid to **19** prior to workup. Reduction of **19** gave **20**, which was slowly brominated with PBr_3 to give **21**. Reductive elimination and complexation of **21** with $Fe_2(CO)_9$ gave 1,2,3-trisubstituted (cyclobutadiene)tricarbonyliron complex **22**.

In our scheme, it was imperative to retain functionality which could easily be transformed to a reducible group for the final step in complex formation. Reaction of ester **13c** with lithium aluminum hydride in THF reduced the double bond while leaving the ring carbonyl group intact and gave **23**, while reduction in ether gave the 1,2-reduced product **14c** (Scheme V). The preparative nature of our desired procedure using the formation of methyl ethers also avoided the use of expensive reagents such as TBDMSCl. As expected, the rate of formation of dibromides **17** or **21** was slowed by large alkyl groups adjacent to the methoxy group, and selective alkylation of the vinylogous ketone over the vinylogous ester in **10** was decreased when *tert*-butyl groups were appended. Unfortunately, phenyl groups significantly hindered carbonyl reductions, in

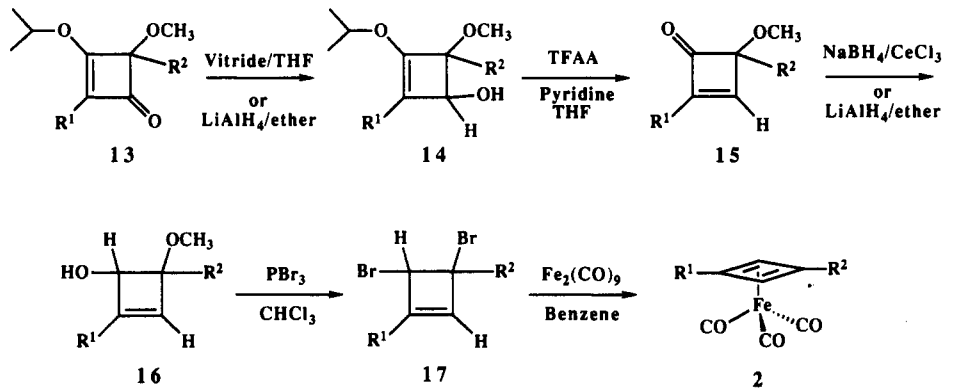
(18) (a) Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 4048–4050. (b) Xu, S. L.; Tiang, M.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 6104–6109. (c) Xu, S. L.; Xia, H.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 6094–6013.

(19) (a) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226–2227. (b) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 1607–1617.

Scheme II



Scheme III



Scheme IV

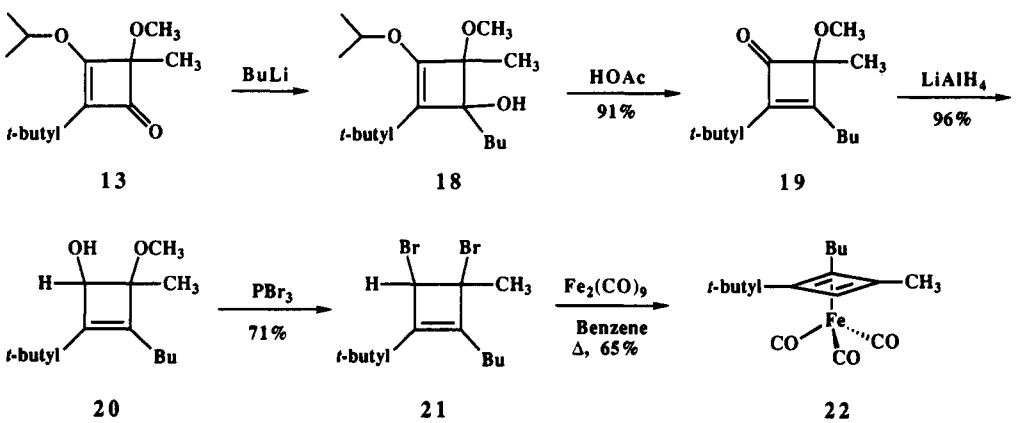


Table I. Preparation of 1,3-Dialkyl-Substituted Intermediates and Iron Complexes

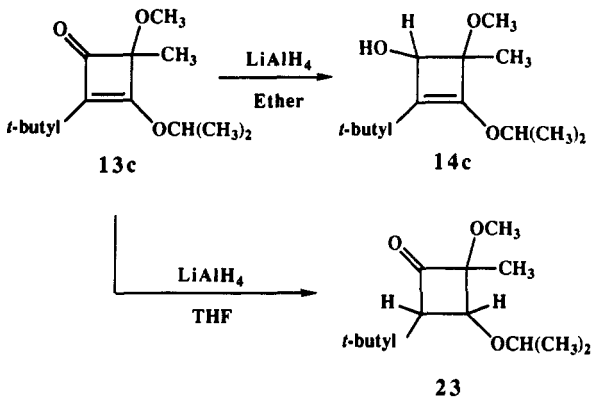
				yield (%)[a]						
compd	R^1	R^2	reduction method[b]	11	13	14	15	16	17[c]	2
a	*n*-butyl	CH_3	1	99	71	76	40	85	52	84
b	*n*-butyl	*n*-butyl	2	68	99	82	76	99	42	50
c	*tert*-butyl	CH_3	2	70	92	95	55	78	40	47

[a] Yields refer to isolated, purified products. [b] Method 1 = Vitride/THF; method 2 = $LiAlH_4$/ether. [c] Yields refer to crude products.

agreement with earlier reports.[10] We are continuing to investigate methods which would allow incorporation of these groups.

All compounds gave satisfactory proton, carbon, IR, and exact mass analyses characteristic of (cyclobutadiene)-tricarbonyliron complexes.[3,4,13] NMR signals for ring protons in cyclobutadiene are discernable near 4 ppm. Carbon signals are observed near 214 ppm (CO), 85 ppm (for the substituted ring carbon), and 60 ppm (for the protonated ring carbon). The complexes and fragment ions could be readily identified in the mass spectrum by their characteristic sequential loss of three carbonyl groups (M − 28, CO) and iron (M − 56). The susceptibility of the complexes to air oxidation limits their exhaustive purification; such oxidation results in broadening of signals in their NMR spectra. To obtain consistent NMR spectra,

Scheme V



the samples were routinely filtered through adsorption alumina immediately prior to analysis.

Conclusions

New approaches to the synthesis of pendant chain 1,3-disubstituted(cyclobutadiene)tricarbonyliron complexes allow choice in the placement of each chain and a greater latitude in the syntheses of (cyclobutadiene)tricarbonyliron complexes. The complexes were derived from readily available diisopropyl squarate by using selective alkylations and rearrangements which yield specific 1,3-disubstituted (2) and 1,2,3-trisubstituted (3) (cyclobutadiene)-tricarbonyliron complexes. Our procedures allow synthetic chemists to study and utilize cyclobutadiene complexes as viable and novel synthetic precursors. We are continuing to explore the potential of the cyclobutadiene complexes made possible by the methods described herein.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry nitrogen or argon. Air- and/or moisture-sensitive reagents were handled by using standard syringe transfer techniques and flasks capped with rubber septa. Tetrahydrofuran (THF), ether, and benzene were freshly distilled from potassium benzophenone ketyl just prior to use. Chloroform was washed twice with H_2O, dried with $MgSO_4$, and then distilled from phosphorus pentoxide. Trifluoroacetic anhydride was also distilled from phosphorus pentoxide. Anhydrous cerium(III) chloride was prepared according to Imamoto immediately prior to use.[20] Organolithium reagents were obtained from Aldrich or prepared from their corresponding bromides[21] and titrated according to Watson.[22] All other solvents and reagents were reagent grade and used without further purification. Reactions were monitored by means of thin-layer chromatography on silica gel plates (E. Merck Kieselgel 60 F254) and alumina (Aluminiumoxid 150 F254 neutral type T) with detection by UV or phosphomolybdic acid. Preparative column or filtration chromatography used silica gel (J.T. Baker, 80–200 mesh) and alumina (E.M. Science, 80–200 mesh). Substituted diones **10** were prepared from diisopropyl squarate according to published procedures as noted.[14-16]

High-field NMR spectra were recorded on a Varian XL-300 or a XL-400 superconducting FT spectrometer. ^{13}C NMR and ^1H NMR spectra were recorded at 75.43 and 299.94 MHz or 100.6 and 399.9 MHz, respectively. Chemical shifts are reported in δ units, parts per million downfield, $CDCl_3$ or TMS being used as the reference signal. Infrared spectra were obtained with a Perkin-Elmer 681 IR spectrometer and run as neat liquids on NaCl plates. Owing to their sensitivity to oxidation and decomposition, all iron complexes were further characterized by their corresponding mass spectra data. EI mass spectra were recorded on a VG TS-250 mass spectrometer operating at 70 eV, while FAB and exact mass determinations were recorded on a VG ZAB-2SE HR-HM spectrometer. Melting points were obtained on a Fisher-Johns melting point apparatus and are reported uncorrected.

Preparation of 2-*n*-Butyl-4-hydroxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-one (11a). To a solution of 3.693 g (18.8 mmol) of 4-*n*-butyl-3-(1-methylethoxy)cyclobut-3-en-1,2-dione (**10**)[14,15] in 75 mL of dry THF at −100 °C under nitrogen atmosphere was added 17.0 mL (18.7 mmol) of 1.1 M methyllithium dropwise over 1 h. The solution was kept at −100 °C and monitored by TLC for the disappearance of starting material. The reaction was quenched with 2 mL of saturated aqueous NH_4Cl, transferred to a separatory funnel, and diluted with 100 mL of diethyl ether. The organic layer was extracted with 2 × 50 mL of saturated aqueous NaCl, dried with $MgSO_4$, and concentrated under reduced pressure to give **11a** as a pale yellow oil: 3.940 g (18.6 mmol, 99% yield); R_f = 0.20 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 4.92 (septet, 1 H), 2.03 (t, 2 H), 1.56 (s, 3 H), 1.44 (d, 3 H), 1.42 (d, 3 H), 1.30 (m, 2 H), 0.89 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 195.32, 184.23, 124.55, 87.82, 29.10, 22.67, 22.52, 22.37, 21.65, 19.79, 13.57; IR (neat, cm^{-1}) 3600–3100 s br, 2980 s, 2934 s, 2869 m, 1753 s, 1607 s, 1458 m, 1387 m, 1336 m, 1314 m, 1218 m, 1186 m, 1142 m, 1101 m, 946 m, 919 m, 850 m, 788 m, 763 m; MS *m/z* calcd for $C_{12}H_{20}O_3$ 212.1412, obs 212.1404, 170, 169, 161, 151, 142, 133, 126, 113, 109, 100, 99, 95, 87 (100%), 81, 72, 71, 55.

The following compounds were prepared according to the procedure for **11a**.

2,4-Di-*n*-butyl-4-hydroxy-3-(1-methylethoxy)cyclobut-2-en-1-one (11b): 68%; R_f = 0.34 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 4.85 (septet, 1 H), 4.00 (s br, 1 H), 2.06 (m, 2 H), 1.90 (m, 1 H), 1.78 (m, 1 H), 1.49 (m, 2 H), 1.43 (d, 3 H), 1.41 (d, 3 H), 1.31 (m, 6 H), 0.90 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 194.32, 182.44, 126.14, 91.43, 76.53, 32.57, 29.54, 27.25, 22.74, 22.67, 22.53, 22.01, 13.83, 13.66; IR (neat, cm^{-1}) 3600–3100 s br, 2962 s, 2933 s, 2867 s, 1747 s, 1611 s, 1463 s, 1381 s, 1338 s, 1315 s, 1262 m, 1224 m, 1182 m, 1142 m, 1099 s, 1014 m, 974 m, 922 m, 804 m, 784 m, 761 m, 727 m; MS *m/z* calcd for $C_{15}H_{26}O_3$ 254.1882, obs 254.1881, 212, 211, 195, 184, 169, 155, 142, 141, 127, 99, 85 (100%), 57.

2-*tert*-Butyl-4-hydroxy-4-methyl-3-(1-methylethoxy)-cyclobut-2-en-1-one (11c). The crude orange crystalline product was recrystallized with boiling hexane. The crystals were isolated by vacuum filtration and washed with cold hexane. The white crystals were placed under vacuum (25 °C/6 mmHg) for 12 h to remove remaining solvent. **11c**: 70%; mp 125–126 °C; R_f = 0.21 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 5.01 (septet, 1 H), 4.80 (s br, 1 H), 1.62 (s, 3 H), 1.42 (d, 3 H), 1.40 (d, 3 H), 1.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 193.94, 183.25, 133.04, 88.13, 77.09, 30.74, 28.07, 23.20, 22.84, 20.74; IR (KBr, cm^{-1}) 3400–3100 m br, 2950 m, 2920 m, 2850 m, 1730 s, 1595 s, 1470 m, 1450 m, 1400 m, 1365 m, 1325 m, 1240 m, 1180 m, 1135 m, 1090 m, 920 m, 870 m; MS *m/z* calcd for $C_8H_{12}O_3$ (M − C_4H_8) 156.0786, obs 156.0789, 142, 127, 114 (100%), 86, 71, 57; MS *m/z* calcd for $C_{12}H_{16}O_3$ 208, obs (FAB+, thioglycerol) 213 (100%).

Preparation of 2-*n*-Butyl-4-methoxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-one (13a). A mixture of 1.5 g (40.0 mmol) of 60% NaH in oil was placed under nitrogen and washed twice with 10 mL of dry THF. Then 100 mL of dry THF, 3.986 g (18.8 mmol) of alcohol **11a**, and 10–20 mg of imidazole were added to the flask. The system was allowed to stir for 30 min at room temperature, and then 3.6 mL of methyl iodide (38.9 mmol) was added. The mixture was stirred an additional

(20) (a) Imamoto, T. *Pure Appl. Chem.* **1990**, *62*, 747–752. (b) Imamoto, T.; Kusumoto, T.; Yokoyama, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1042–1044. (c) Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Mita, T.; Hatanaka, Y.; Yokoyama, M. *J. Org. Chem.* **1984**, *49*, 3904–3912.

(21) Wakefield, B. J., Ed. *Organolithium Methods*, Academic Press: New York, 1990; pp 21–26.

(22) Watson, S. C.; Eastman, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–168.

15 min. The system was quenched with 1 mL of H_2O and diluted with 100 mL of diethyl ether. The mixture was extracted with 2 × 25 mL of saturated aqueous NaCl and the organic portion dried with $MgSO_4$ and concentrated under reduced pressure. Chromatography of the oil on silica with 15% ethyl acetate–hexane and concentration under reduced pressure gave **13a** as a pale yellow oil: 3.017 g (13.3 mmol, 71% yield); R_f = 0.66 (30% ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$) δ 4.82 (septet, 1 H), 3.30 (s, 3 H), 2.10 (t, 2 H), 1.48 (s, 3 H), 1.46 (d, 3 H), 1.44 (d, 3 H), 1.34 (m, 2 H), 0.91 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 192.93, 182.49, 126.19, 93.25, 76.12, 52.06, 29.12, 22.54, 22.28, 22.19, 21.60, 18.47, 13.33; IR (neat, cm^{-1}) 2966 s, 2932 s, 2875 m, 2864 m, 2830 m, 1757 s, 1718 m, 1618 s, 1458 m, 1442 m, 1386 m, 1342 m, 1317 m, 1272 m, 1179 m, 1149 m, 1002 m, 1067 m, 940 m, 919 m, 860 m, 842 m; MS *m/z* calcd for $C_{12}H_{22}O_3$ 226.1569, obs 226.1568, 212, 197, 184, 183, 169 (100%), 155, 139, 127, 113, 99, 95, 81, 67, 55.

The following compounds were prepared according to the procedure for **13a**.

2,4-Di-*n*-butyl-4-methoxy-3-(1-methylethoxy)cyclobut-2-en-1-one (13b): 99% R_f = 0.50 (30% ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$) δ 4.78 (septet, 1 H), 3.32 (s, 3 H), 2.13 (m, 3 H), 1.90 (m, 1 H), 1.74 (m, 1 H), 1.56 (m, 2 H), 1.42 (d, 6 H), 1.31 (m, 6 H), 0.92 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 193.11, 181.58, 127.63, 97.15, 76.27, 52.18, 31.99, 29.66, 29.58, 26.89, 22.80, 22.65, 22.54, 21.99, 13.76, 13.61; IR (neat, cm^{-1}) 2950 s, 2863 s, 2832 s, 1758 s, 1718 m, 1616 s, 1458 m, 1382 s, 1336 m, 1316 m, 1273 m, 1248 m, 1221 m, 1178 m, 1142 m, 1104 s, 1030 m, 975 m, 920 m, 851 m, 803 m, 750 m; MS *m/z* calcd for $C_{16}H_{28}O_3$ 268.2038, obs 268.2035, 226, 225, 211, 197, 183, 161, 125, 95, 85, 84, 69 (100%), 57.

2-*tert*-Butyl-4-methyl-3-(1-methylethoxy)-4-methoxycyclobut-2-en-1-one (13c): 92%; R_f = 0.55 (30% ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$) δ 4.81 (septet, 1 H), 3.33 (s, 3 H), 1.54 (s, 3 H), 1.34 (d, 6 H), 1.19 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 191.31, 181.60, 135.40, 93.95, 76.55, 52.21, 30.92, 27.99, 23.29, 22.84, 19.79; IR (neat, cm^{-1}) 2960 s, 2874 s, 2828 m, 1751 s, 1608 s, 1452 s, 1364 s, 1280 s, 1223 s, 1176 s, 1176 s, 1098 s, 1065 s, 953 m, 925 m, 855 m, 811 m, 776 m, 763 m, 747 m; MS *m/z* calcd for $C_{13}H_{22}O_3$ 226.1569, obs 226.1567 (100%), 184, 169, 155, 141, 127, 113, 99, 95, 83, 67, 57.

Preparation of 2,4-Di-*n*-butyl-4-hydroxycyclobut-2-en-1-one (12). Method 1. A solution of 0.342 g (1.3 mmol) of **14b** in 30 mL of CH_2Cl_2 and 10 mL of 6 N HCl was stirred for 10 h. The mixture was diluted with 100 mL of CH_2Cl_2, and the aqueous layer was removed. The organic phase was vacuum filtered through a pad of Na_2SO_4. The yellow solution was concentrated under reduced pressure. Chromatography of the oil on silica with 15% ethyl acetate–hexane and concentration under reduced pressure gave **12** as a golden yellow oil: 0.187 g (1.0 mmol, 73% yield).

Method 2. A solution of 0.519 g (1.4 mmol) of 1,3-di-*n*-butyl-4-(*tert*-butyldimethylsiloxy)-2-(1-methylethoxy)cyclobut-2-en-1-ol in 30 mL of CH_2Cl_2 was stirred with 10 mL of 1 N HCl for 9 h. The mixture was diluted with 100 mL of CH_2Cl_2, the mixture shaken, and the aqueous layer removed. The organic phase was vacuum filtered through a pad of Na_2SO_4. The yellow solution was concentrated under reduced pressure. Chromatography of the oil on silica with 15% ethyl acetate–hexane and concentration under reduced pressure gave **12** as a golden yellow oil: 0.192 g (1.0 mmol, 70% yield); R_f = 0.55 (30% ethyl acetete–hexane); ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 1 H), 3.50 (s, br, 1 H), 2.17 (t, 2 H), 1.79 (t, 2 H), 1.51 (s, 2 H), 1.33 (m, 6 H), 0.91 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 198.11, 164.57, 159.10, 93.65, 33.78, 28.35, 26.95, 24.06, 22.78, 22.24, 13.79, 13.58; IR (neat, cm^{-1}) 3600–3100 s br, 3067 m, 2962 s, 2934 s, 2867 s, 1754 s, 1603 m, 1469 m, 1382 m, 1329 m, 1259 m, 1235 m, 1182 m, 1143 m, 1103 m, 1058 m, 994 m, 922 m, 880 m, 837 m, 786 m, 762 m, 732 m; MS *m/z* calcd for $C_{12}H_{20}O_2$ 196.1463, obs 196.1466, 179, 168, 162, 153, 139, 111 (100%), 97, 83, 69, 57, 55.

Preparation of 2-*n*-Butyl-4-methoxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-ol (14a). To a solution of 0.764 g (3.4 mmol) of **13a** in 30 mL of THF at 0 °C was added a solution of 0.5 mL (1.3 mmol) of Vitride (70% in toluene) in 2 mL of dry THF over 18 h. The reaction mixture was quenched with 1 mL of saturated NH_4Cl and diluted with 150 mL of diethyl ether. The mixture was extracted with 50 mL of saturated NaCl, and the organic phase was dried with $MgSO_4$ and concentrated under reduced pressure to give a yellow oil. Chromatography of the oil on silica with 5% ethyl acetate–hexane and concentration under reduced pressure gave **14a** as a colorless oil: 0.575 g (2.5 mmol, 76% yield); R_f = 0.29 (15% ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$) δ 4.38 (septet, 1 H), 4.01 (s, 1 H), 3.41 (s, 3 H), 2.26 (d, 1 H), 2.10 (m, 2 H), 1.51 (m, 2 H), 1.36 (s, 3 H), 1.29 (d, 3 H), 1.23 (d, 3 H), 0.91 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 151.10, 117.57, 81.23, 73.37, 70.95, 52.80, 29.84, 25.13, 22.70, 22.41, 22.07, 17.12, 13.77; IR (neat, cm^{-1}) 3600–3200 s br, 2973 s, 2933 s, 2865 s, 2840 m, 1675 s, 1466 m, 1454 m, 1369 m, 1329 m, 1308 m, 1255 m, 1220 m, 1188 m, 1139 m, 1115 m, 1058 m, 960 m, 937 m, 847 m, 788 m, 762 m; MS *m/z* calcd for $C_{12}H_{24}O_3$ 228.1725, obs 228.1724 (100%), 211, 197, 186, 171, 169, 168, 153, 137, 127, 111, 97, 88, 85, 83, 67, 59, 57, 55.

The following compounds were prepared according to the procedure for **14a**.

2,4-Di-*n*-butyl-4-methoxy-3-(1-methylethoxy)cyclobut-2-en-1-ol (14b): 82% R_f 0.50 (30% ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$) δ 4.38 (septet, 1 H), 4.06 (s br, 1 H), 3.44 (s, 3 H), 2.40 (s, br, 1 H), 2.07 (m, 2 H), 1.83 (m, 1 H), 1.49 (m, 3 H), 1.35 (m, 6 H), 1.29 (d, 3 H), 1.23 (d, 3 H), 0.94 (t, 3 H), 0.93 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 150.48, 118.10, 83.63, 71.02, 70.98, 53.06, 30.40, 29.99, 26.15, 25.37, 23.01, 22.81, 22.47, 22.21, 13.97, 13.85; IR (neat, cm^{-1}) 3600–3200 m br, 2900 s, 2850 s, 1660 m, 1440 m, 1360 m, 1275 m, 1245 m, 1210 m, 1170 m, 1060 s, 990 m, 920 m, 840 m; MS *m/z* calcd for $C_{16}H_{30}O_3$ 270.2195, obs 270.2199 (100%), 228, 227, 210, 195, 185, 167, 153, 139, 127, 125, 111, 101, 85, 69, 57, 55.

2-*tert*-Butyl-4-methoxy-4-methyl-3-(1-methylethoxy)-cyclobut-2-en-1-ol (14c): 95%; R_f = 0.48 (30% ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$ δ 4.37 (septet, 1 H), 4.10 (s br, 1 H), 3.37 (s, 3 H), 1.80 (s, 1 H), 1.46 (s, 3 H), 1.24 (d, 3 H), 1.23 (d, 3 H), 1.11 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 150.54, 131.81, 84.18, 73.61, 71.60, 52.02, 28.94, 23.06, 22.61, 17.92; IR (neat, cm^{-1}) 3600–3200 m br, 2950 s, 2860 s, 2825 m, 1760 s, 1640 m, 1595 m, 1460 s, 1360 s, 1285 s, 1140 s br, 1060 s, 930 m, 880 m, 780 m, 740 m; MS *m/z* calcd for MS of $C_{13}H_{24}O_3$ spontaneously rearranged to intermediate $C_{10}H_{16}O_2$ 168.1150, obs 168.1148, 153, 125 (100%), 112, 93, 83, 77, 67, 57.

Preparation of 2-*n*-Butyl-4-methoxy-4-methylcyclobut-2-en-1-one (15a). To a solution of 0.563 g (2.5 mmol) of **14a** and 0.3 mL of pyridine (3.5 mmol) in 20 mL of dry THF at 0 °C was added 0.5 mL of trifluoroacetic anhydride. The mixture was stirred for 30 min, quenched with 1 mL of H_2O, and then diluted with 100 mL of diethyl ether. The organic layer was extracted with 20 mL of saturated aqueous $NaHCO_3$ and 20 mL of saturated aqueous NaCl. The organic solution was dried with $MgSO_4$ and concentrated under reduced pressure. Chromatography of the oil on silica with 5% ethyl acetate–hexane and concentration under reduced pressure gave **15a** as a pale yellow oil: 0.165 g (1.0 mmol, 40% yield); R_f = 0.58 (15% ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$) δ 8.16 (t, 1 H), 3.27 (s, 3 H), 2.19 (td, 2 H), 1.54 (s, 2 H), 1.45 (s, 3 H), 1.34 (septet, 2 H), 0.92 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.61, 165.95, 158.71, 95.80, 52.62, 28.33, 23.98, 22.19, 19.52, 13.51; IR (neat, cm^{-1}) 3073 w, 2958 s, 2932 s, 2873 s, 2833 m, 1763 s, 1666 m, 1602 m, 1460 m, 1442 m, 1372 m, 1289 m, 1263 m, 1178 m, 1154 m, 1129 m, 1067 m, 937 m, 899 m, 879 m, 834 m, 811 m, 759 m; MS *m/z* calcd for $C_{10}H_{16}O_2$ 168.1150, obs 168.1141, 153, 141, 137, 126, 125, 111, 109, 98, 97, 93, 88, 85, 83 (100%), 81, 79, 72, 67, 57, 55.

The following compounds were prepared according to the procedure for **15a**.

2,4-Di-*n*-butyl-4-methoxycyclobut-2-en-1-one (15b): 76%; R_f = 0.59 (15% ethyl acetate–hexane); ^{1}H NMR ($CDCl_3$) δ 8.15 (d, 1 H), 3.26 (s, 3 H), 2.20 (m, 2 H), 1.77 (m, 2 H), 1.54 (m, 2 H), 1.32 (m, 6 H), 0.92 (t, 3 H), 0.89 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.76, 165.01, 159.44, 99.35, 52.59, 33.24, 28.51, 26.90, 24.04,

22.87, 22.30, 13.81, 13.60; IR (neat, cm^{-1}) 3069 m, 2963 s, 2933 s, 2875 s, 2833 m, 1761 s, 1602 m, 1461 m, 1379 m, 1310 m, 1156 m, 1131 m, 1075 m, 975 m, 918 m, 876 m; MS *m/z* calcd for $C_{13}H_{22}O_2$ 210.1620, obs 210.1621, 195, 168, 167, 153, 125 (100%), 113, 97, 86, 84, 79, 67, 57.

2-*tert*-Butyl-4-methoxy-4-methylcyclobut-2-en-1-one (15c): 55%; R_f = 0.46 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 8.03 (s, 1 H), 3.26 (s, 3 H), 1.44 (s, 3 H), 1.18 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 196.58, 167.24, 161.82, 95.06, 52.58, 31.52, 27.46, 19.54; IR (neat, cm^{-1}) 3060 w, 2980 s, 2880 s, 2840 m, 1760 s, 1600 m, 1470 m, 1370 m, 1290 m, 1210 m, 1150 m br, 1070 m, 930 m, 880 m, 850 m, 780 m, 650 m; MS *m/z* calcd for $C_{10}H_{16}O_2$ 168.1141, obs 168.1150, 153, 151, 125 (100%), 109, 93, 83, 77, 67, 57, 55.

Preparation of 2-*n*-Butyl-4-methoxy-4-methylcyclobut-2-en-1-ol (16a). To a solution of 0.178 g (1.1 mmol) of **15a** in 5 mL of absolute ethanol was added a solution of 0.8 g (2.1 mmol) of $CeCl_3 \cdot 7H_2O$ in 10 mL of ethanol. This mixture was stirred for 15 min and then cooled to 0 °C; 0.25 g (6.6 mmol) of $NaBH_4$ was added portionwise. The reaction was followed by TLC until complete and then quenched with 2.0 mL of saturated aqueous NH_4Cl. The mixture was extracted with 100 mL of diethyl ether and the aqueous layer removed. The organic layer was extracted with 50 mL of saturated aqueous NaCl, dried with $MgSO_4$, and concentrated under reduced pressure to give **16a** as a pure colorless oil: 0.154 g (0.9 mmol, 85% yield); R_f = 0.59 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 6.07 (s, 1 H), 4.18 (s, 1 H), 3.36 (s, 3 H), 2.75 (s br, 1 H), 2.08 (m, 2 H), 1.47 (m, 2 H), 1.35 (s, 3 H), 1.26 (m, 2 H), 0.91 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.13, 132.92, 80.75, 77.47, 51.49, 28.18, 27.35, 22.36, 19.27, 13.71; IR (neat, cm^{-1}) 3600–3100 m br, 3039 m, 2965 s, 2920 s, 2869 s, 2834 m, 1768 m, 1733 m, 1698 m, 1668 m, 1635 m, 1461 m, 1383 m, 1327 m, 1280 m, 1210 m, 1182 m, 1142 m, 1087 s br, 939 m, 899 m, 866 m, 841 m, 766 m, 731 m; MS *m/z* calcd for $C_{10}H_{18}O_2$ 170.1307, obs 170.1304, 155, 141, 139, 128, 127, 123, 109, 99, 95, 88, 85, 81, 72, 67 (100%), 57, 55.

Preparation of 2,4-Di-*n*-butyl-4-methoxycyclobut-2-en-1-ol (16b). To a solution of 0.108 g (0.51 mmol) of **15b** in diethyl ether at 0 °C was added 0.05 g (1.3 mmol) of $LiAlH_4$ portionwise. The mixture was stirred for 30 min, quenched with 1 mL of saturated NaCl, and then shaken with 100 mL of diethyl ether. The organic phase was extracted with 25 mL of saturated aqueous NaCl, dried with $MgSO_4$, and concentrated under reduced pressure to give **16b** as a pure colorless oil: 0.108 g (0.51 mmol, 99% yield); R_f = 0.39 (15% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 6.09 (t, 1 H), 4.21 (s, 1 H), 3.33 (s, 3 H), 2.80 (s br, 1 H), 2.11 (m, 2 H), 1.70 (m, 1 H), 1.46 (m, 4 H), 1.33 (m, 6 H), 0.91 (t, 6 H); ^{13}C NMR ($CDCl_3$) δ 159.02, 132.00, 83.31, 75.75, 51.58, 32.62, 28.27, 27.49, 26.71, 22.94, 22.44, 13.98, 13.78. IR (neat, cm^{-1}) 3600–3100 m br, 3041 m, 2963 s, 2937 s, 2866 s, 2830 m, 1776 m, 1728 m, 1700 m, 1633 m, 1466 m, 1434 m, 1382 m, 1387 m, 1301 m, 1274 m, 1199 m, 1178 m, 1096 m, 1071 m, 1031 m, 999 m, 915 m, 840 m, 765 m, 732 m; MS *m/z* calcd for $C_{13}H_{24}O_2$ 212.1776, obs 212.1777, 185, 181, 169, 156, 155, 127, 125, 109, 108, 101, 95, 85, 81, 69, 59, 58 (100%).

Alcohol **16c** was prepared according to the procedure for **16b**.

2-*tert*-Butyl-4-methoxy-4-methylcyclobut-2-en-1-ol (16c): 78%, R_f = 0.41 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 6.01 (s, 1 H), 4.31 (s, 1 H), 3.36 (s, 3 H), 2.60 (s, br 1 H), 1.33 (s, 1 H), 1.09 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 166.13, 129.95, 79.51, 76.31, 51.54, 32.47, 27.75, 19.26; IR (neat, cm^{-1}) 3600–3100 s br, 2990 s, 2880 s, 2830 m, 1755 m, 1720 m, 1690 m, 1620 m, 1460 m, 1360 m, 1290 m, 1100 m br; MS *m/z* calcd for $C_9H_{15}O_2$ 155.1072 (M – CH_3), obs 155.1072 (100%), 123, 95, 88, 85, 73, 57.

Preparation of 1,3-Dialkyl-3,4-dibromocyclobut-1-enes 17. To a solution of 0.147 g (0.86 mmol) of **16a** in 15 mL of chloroform at –60 °C was added dropwise 0.1 mL (0.55 mmol) of phosphorus tribromide. The solution was stirred for 1 h and then refluxed for 12 h. After cooling to room temperature, the solution was quenched with 30 mL of ice cold saturated aqueous $NaHCO_3$. The mixture was extracted with 3 × 75 mL of CH_2Cl_2, and the combined organic layers were washed with 50 mL of saturated aqueous NaCl, dried with $MgSO_4$, and then concentrated under reduced pressure to give **17a** as a crude dark oil: 0.127 g (0.45 mmol, 52% yield). Attempts to chromatograph the crude dibromides were unsuccessful because of decomposition on SiO_2 and Al_2O_3. The dibromides were sufficiently pure for the iron complex formation.

Preparation of (Cyclobutadiene)tricarbonyliron Complexes: Tricarbonyl[(1,2,3,4-η)-1-*n*-butyl-3-methyl-1,3-cyclobutadiene]iron (2a). To a 50-mL 3-neck round-bottom flask, with attached condenser and nitrogen inlet, was added 0.125 g (0.4 mmol) of dibromide **17a**, 40 mL of dry benzene, and 0.5 g (1.4 mmol) of $Fe_2(CO)_9$. The system was warmed to 65 °C. After 1 h, 0.5 g (1.4 mmol) of $Fe_2(CO)_9$ was added, and the mixture was stirred an additional 2 h. The dark solution was allowed to cool to room temperature and then filtered through a pad of silica, followed by a diethyl ether wash. Concentration of the filtrate under reduced pressure gave a dark green oil. Chromatography of the oil on alumina with ether and concentration under reduced pressure gave **2a** as a yellow oil: 0.098 g (0.37 mmol, 84% yield); R_f = 0.64 (5% chloroform-hexane); ^1H NMR ($CDCl_3$) δ 4.05 (s, 1 H), 1.98 (t, 2 H), 1.75 (s, 3 H), 1.35 (m, 2 H), 1.26 (m, 2 H), 0.90 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 215.55, 84.02, 80.72, 65.68, 29.70, 26.74, 22.44, 13.78, 13.03; IR (neat, cm^{-1}) 2965 s, 2929 s, 2860 s, 2072 m, 2037 s, 1956 s, 1863 m, 1765 m, 1735 m, 1670 m, 1455 m, 1380 m, 1312 m, 1277 m, 1190 m, 1105 m, 1047 m, 1028 m, 825 m; MS *m/z* calcd for $C_{12}H_{14}O_3Fe$ 262.0292, obs 262.0293, 234, 206, 178 (100%), 176, 175, 148, 136, 134, 125, 110, 96, 56.

The following compounds were prepared according to the procedure for **2a**.

Tricarbonyl[(1,2,3,4-η)-1,3-di-*n*-butyl-1,3-cyclobutadiene]iron (2b): 50%; R_f = 0.63 (15% chloroform-hexane); ^1H NMR ($CDCl_3$) δ 4.03 (s, 2 H), 2.00 (t, 4 H), 1.36 (m, 8 H), 0.90 (t, 6 H). ^{13}C NMR ($CDCl_3$) δ 215.65, 85.27, 64.55, 31.77, 26.71, 22.44, 13.79; IR (neat, cm^{-1}) 2950 s, 2925 s, 2850 s, 2025 s, 1960 s br, 1460 m, 1420 m, 1370 m, 625 s; MS *m/z* calcd for $C_{15}H_{20}Fe$ 304.0762, obs 304.0765, 276, 248, 220 (100%), 178, 162, 148, 136, 134, 121, 110, 96, 79, 55.

Tricarbonyl[(1,2,3,4-η)-1-*tert*-butyl-3-methyl-1,3-cyclobutadiene]iron (2c): 47% R_f = 0.68 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 4.00 (s, 2 H), 1.82 (s, 3 H), 1.02 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 215.77, 83.85, 62.95, 31.13, 30.26, 12.87; IR (CCl_4) 2980 s, 2940 s, 2865 s, 2040 s, 1965 s br, 910 m, 625 s; MS *m/z* calcd for $C_{12}H_{14}O_3Fe$ 262.0292, obs 262.0292, 234, 206, 178, 162, 147, 138, 123, 95, 84 (100%), 57.

Preparation of 2-*n*-Butyl-3-*tert*-butyl-4-methoxy-4-methylcyclobut-2-en-1-one (19). A solution of 1.079 g (4.8 mmol) of **13c** in 30 mL of dry THF at –78 °C was treated with 5.0 mL (6.5 mmol) of 1.3 M *n*-butyllithium dropwise over 15 min. The reaction was quenched with 1 mL of saturated aqueous NH_4Cl and diluted with 50 mL of diethyl ether. The organic layer was extracted with 25 mL of saturated aqueous NaCl, dried with $MgSO_4$, and concentrated under reduced pressure to give **18** as a crude pale yellow oil. Chromatography of **18** on silica with 5% ethyl acetate–hexane and concentration under reduced pressure resulted in partial rearrangement of **18** to **19**. The oil was diluted with a mixture of 20 mL of CH_2Cl_2 and 5 mL of glacial acetic acid. The solution was stirred for 2 h, and the aqueous phase was removed. The organic phase was washed with 2 × 25 mL of saturated aqueous $NaHCO_3$ and 25 mL of saturated aqueous NaCl, dried with $MgSO_4$, and then concentrated under reduced pressure to give **19** as a colorless oil: 0.971 g (4.3 mmol, 91% yield); R_f = 0.62 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 3.24 (s, 1 H), 2.01 (m, 2 H), 1.62 (q, 2 H), 1.43 (m, 2 H), 1.40 (s, 3 H), 1.23 (s, 9 H), 0.97 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 196.16, 178.84, 158.37, 95.54, 52.04, 32.45, 29.51, 28.10, 27.44, 23.33, 18.98, 13.62; IR (neat, cm^{-1}) 2950 s, 2820 s, 2810 m, 1740 s, 1610 m, 1450 m, 1360 m, 1290 m, 1265 m, 1195 m, 1125 s, 1055 m, 910 m, 845 m, 770 m, 750 m, 725 m; MS *m/z* calcd for $C_{14}H_{24}O_2$ 224.1776, obs 224.1776 (100%), 209, 181, 168, 167, 153, 139, 125, 109, 95, 83, 69, 57.

Preparation of 3-*n*-Butyl-2-*tert*-butyl-4-methoxy-4-methylcyclobut-2-en-1-ol (20). To a solution of 0.970 g (4.3

mmoles) of **19** in 20 mL of ether was added portionwise 0.025 g (0.66 mmol) of $LiAlH_4$, and the mixture was stirred for 15 min. The reaction was quenched with 1 mL of saturated aqueous NH_4Cl and diluted with 50 mL of ether. The mixture was extracted with 20 mL of saturated aqueous NaCl, dried with $MgSO_4$, and concentrated under reduced pressure to give **20** as a colorless oil: 0.913 g (4.0 mmol, 93% yield); R_f = 0.47 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 4.20 (s br, 1 H), 3.37 (s, 3 H), 2.20 (d, 1 H), 2.12 (m, 2 H), 1.45 (m, 2 H), 1.34 (s, 3 H), 1.13 (s, 9 H), 0.91 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.35, 145.63, 81.02, 76.45, 52.10, 33.19, 30.99, 29.02, 26.42, 23.24, 18.09, 13.83; IR (neat, cm^{-1}) 3600–3200 m br, 2920 s, 2850 s, 1450 m, 1355 m, 1260 m, 1185 m, 1100 s, 1030 s, 935 m, 895 m, 860 m, 820 m, 725 m; MS *m/z* calcd for $C_{14}H_{26}O_2$ 226.1933, obs 226.1932, 211, 195, 179, 169, 168, 151, 141, 137, 123, 114, 109 (100%), 95, 85, 84, 83, 81, 67, 57.

Preparation of 3,4-Dibromo-2-*n*-butyl-1-*tert*-butyl-3-methylcyclobut-1-ene (21). To a solution of 0.183 g (0.81 mmol) of **20** in 20 mL of carbon tetrachloride at −20 °C was added dropwise 0.1 mL (0.55 mmol) of phosphorus tribromide. The solution was stirred for 3 h and then was allowed to warm to 25 °C. The solution was quenched with 10 mL of saturated aqueous $NaHCO_3$ and extracted with 3 × 50 mL of CCl_4. The combined organic layers were washed with 2 × 25 mL of saturated aqueous $NaHCO_3$ and 25 mL of saturated aqueous NaCl, dried with $MgSO_4$, and concentrated under reduced pressure to give **21** as a crude dark oil: 0.195 g (0.58 mmol, 71% yield). The dibromide was sufficiently pure for the iron complex formation.

Preparation of Tricarbonyl[(1,2,3,4-η)-2-*n*-butyl-1-*tert*-butyl-3-methyl-1,3-cyclobutadiene]iron (22). In a 100-mL 3-neck, round-bottom flask, with attached condenser and nitrogen inlet, was placed 0.195 g (0.58 mmol) of **21**, 20 mL of dry benzene, and 1.0 g (2.8 mmol) of $Fe_2(CO)_9$. The system was slowly warmed to 65 °C and stirred for 1 h. To the mixture was added 0.5 g (1.4 mmol) of $Fe_2(CO)_9$, and the system was stirred for an additional 2 h. The solution was cooled and concentrated under reduced pressure. Chromatography of the oil on alumina with ether and concentration under reduced pressure gave a crude dark yellow oil. Chromatography of the oil on silica with 5% chloroform–pentane and concentration under reduced pressure gave **22** as a yellow oil: 0.120 g (0.38 mmol, 65% yield); R_f = 0.44 (15% chloroform–hexane); ^1H NMR ($CDCl_3$) δ 3.97 (s, 1 H), 2.20 (m 1 H), 2.00 (m, 1 H), 1.82 (s, 3 H), 1.43 (m, 2 H), 1.23 (m, 2 H), 1.07 (s, 9 H), 0.94 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 216.33, 93.49, 87.28, 84.99, 60.63, 32.39, 31.06, 30.55, 26.99, 22.92, 13.87, 11.68; IR (neat, cm^{-1}) 2930 s, 2850 s, 2005 s, 1940 s br, 1450 m, 1355 m, 1200 m, 610 s; MS *m/z* calcd for $C_{16}H_{22}O_3Fe$ 318.0918, obs 318.0887, 290, 262, 234 (100%), 218, 192, 190, 176, 162, 151, 148, 136, 134, 122, 110, 96, 83, 69, 57.

Preparation of 4-*tert*-Butyl-2-methoxy-2-methyl-3-(1-methylethoxy)cyclobutanone (23). To a solution of 1.499 g (6.6 mmol) of **13c** in 50 mL of anhydrous THF cooled to −40°C was added over 1 h 0.27 mL (7.1 mmol) of $LiAlH_4$ suspended in 20 mL of dry THF. The reaction mixture was quenched with 2 mL of saturated 10% HCl, diluted with 150 mL of diethyl ether, and allowed to warm to 25 °C. The mixture was extracted with 2 × 50 mL of saturated aqueous NaCl, dried with $MgSO_4$, and concentrated under reduced pressure to give a yellow oil. Chromatography of the oil on silica with 15% ethyl acetate–hexane and concentration under reduced pressure gave **23** as a colorless oil: 1.398 g (6.1 mmol, 93% yield); R_f = 0.54 (30% ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 3.85 (d, 1 H, J = 7.76), 3.75 (septet, 1 H), 3.47 (s, 3 H), 3.20 (d, 1 H, J = 7.76), 1.27 (s, 3 H), 1.24 (d, 3 H), 1.22 (d, 3 H), 0.99 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 211.29, 90.22, 75.67, 75.37, 72.22, 54.42, 31.50, 27.62, 23.03, 21.51, 16.82; IR (neat, cm^{-1}) 2950 s, 2880 s, 2840 m, 1775 s, 1470 m, 1370 m, 1330 m, 1290 m, 1260 m, 1220 m, 1190 m, 1120 (s, br), 1050 s, 980 m, 940 m, 790 m, 750 m; MS *m/z* calcd for $C_{13}H_{24}O_3$ 228.1725, obs 228.1717, 213, 186, 172, 141, 130 (100%), 115, 101, 97, 88, 85, 57.

Acknowledgment. Support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, AFOSR through the Research and Development Laboratories, and the Halliburton Foundation Inc. is gratefully acknowledged.

OM920427H