112713-89-0; 3-((*E*)-1-phenylpropen-1-yl)cyclohexanone, 112713-90-3; ((*E*)-1-phenylpropen-1-yl)tributylstannane, 112713-91-4; methyl 7-formylheptanoate, 3884-92-2; methyl 7-formyl-4-(*Z*)-heptenoate, 82302-70-3; 5-fluoro-1-(tributylstannyl)-4-(triethylsilyloxy)-4-methyl-1-octene, 112713-95-8; 1-propyl-1-[5-(tributylstannyl)-2-(triethylsilyloxy)-(*E*)-4-penten-2-yl]cyclobutane, 112713-96-9.

Supplementary Material Available: Experimental and spectral data for entries 2–7 in Table I, the product with 73% yield in Scheme I, and compounds **5–9** in Scheme II (5 pages). Ordering information is given on any current masthead page.

Semibullvalenes IV: 2,6- and 2,8-Trapping of the Bicyclo[3.3.0]octadienyl Diradical with Oxygen[†]

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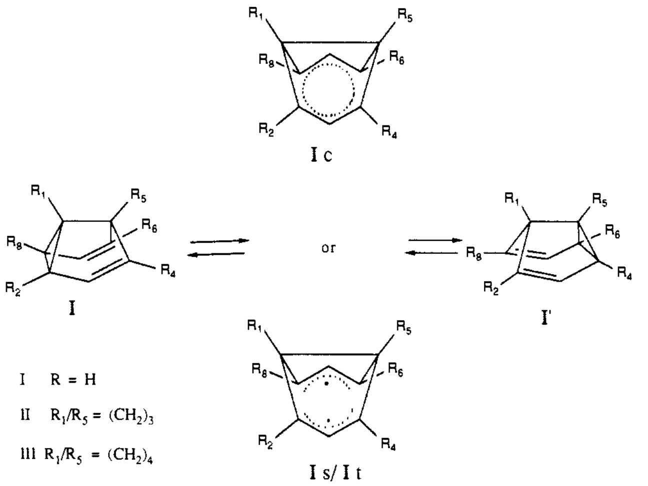
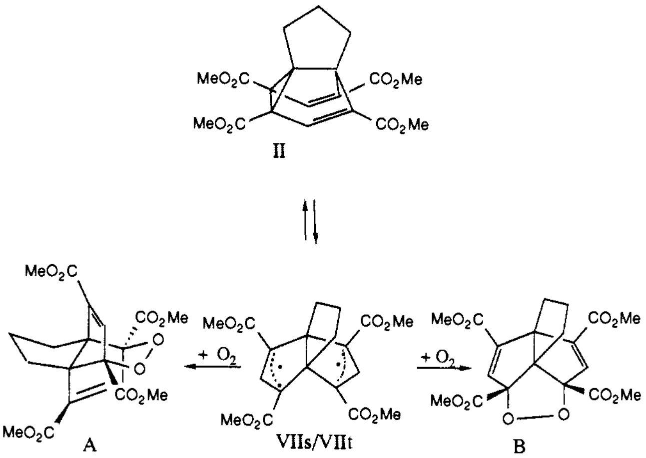
Semibullvalenes undergo a facile degenerate Cope rearrangement I to I′ whose activation energy barrier is the lowest known to date.[1,2] They are also, together with cyclooctatetraenes, members of the C_8H_8 hydrocarbon family interrelated through a multitude of thermal and photochemical rearrangements.[3,4] Among the transition states considered for the Cope rearrangement, Is (singlet) and It (triplet), the two states of the bicyclooctadienyl diradical involving bond breaking before significant bond forming, and Ic (concerted), the bishomoaromatic state with synchronous bond breaking and bond forming, have been the focus of many investigations.[5] In our continuing study of substituted semibullvalenes aimed toward crossing the bridge between valence tautomerism and resonance, we investigated the 1,5-annulated 2,4,6,8-tetrcarbomethoxysemibullvalenes II through V[6,7] (see Scheme I).

Scheme I. The Cope Rearrangement in Semibullvalenes

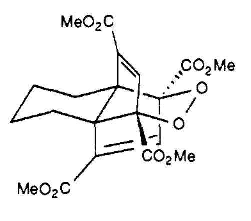


I R = H
II R_1/R_5 = $(CH_2)_3$
III R_1/R_5 = $(CH_2)_4$
IV R_1/R_5 = $(CH_2)_5$
V R_1/R_5 = $(CH_2)_6$
($R_{2,4,6,8}$ = COOMe)

Scheme II



The behavior of these closely related molecules showed some rather striking differences among each other and in comparison to 1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene.[6] 1,5-Cyclohexano-2,4,6,8-tetracarbomethoxysemibullvalene (III), a yellow crystalline compound mp 128–129 °C, converted readily in the dark, in solution, and as a solid into a colorless compound VI mp 151.5–153 °C.[7] The mass spectrum and the microanalysis indicated the presence of two oxygen atoms in the molecule.[8] The X-ray determination[9] proved the structure of VI to be an adduct of one oxygen molecule to positions 2 and 6 of semibullvalene III yielding a doubly bridged *trans*-dioxadecalin structure VI.



1,5-Cyclopentano-2,4,6,8-tetracarbomethoxysemibullvalene (II)

[†] A preliminary account of these results has been reported at the 192nd National Meeting of the American Chemical Society, Anaheim, CA; 1986; Paper no. 255, Organic Section and at the 193rd National Meeting of the American Chemical Society, Denver, CO; 1987; Organic Poster Session, Poster No. 2.

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was highly air sensitive. Oxygen absorption of II in CCl_4 under identical conditions as for III gave a rate of endoperoxide formation of $k = 4.8 \times 10^{-4}$ s^{-1}, with $t_{1/2} = 0.4$ h, approximately 30 times faster than III. But most interesting was the observation that II did not form a single endoperoxide but two isomers A and B (see Scheme II) in a ratio of 2:1. They were separated by chromatography on silica gel. Both formed colorless crystals analyzing correctly for the oxygen addition products.[8] The spectral data suggest that A in analogy to endoperoxide VI obtained from semibullvalene III has the *trans*-dioxaperhydroindane structure, while B has the unique dioxatriquinacene structure, based upon the lack of symmetry in the carbon NMR spectrum with three different signals for the quarternary carbons and three different carbon resonances for the cyclopentane section of the molecule. A on the other hand has a center of symmetry as documented in the carbon NMR spectrum. The X-ray analysis of both isomers confirms these assignments.[9]

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene[6] does not react with oxygen, neither at room temperature nor at 78 °C. Instead, it isomerizes thermally to 1,5-dimethyl-2,4,6,8-tetracarbomethoxycyclooctatetraene.[7,8,10] The oxygenation data suggest that semibullvalenes II and III reversibly open to the respective singlet bicyclo[3.3.0]octadienyl diradicals, e.g., VIIs, ring opening of which to a highly strained cyclooctatetraene is energetically disfavored.[14] Singlet VIIs can undergo spin inversion to triplet VIIt which adds triplet oxygen to positions 2 and 6 or 2 and 8 giving endoperoxides A and B.[12] A similar behavior was observed by W. R. Roth et al.[11] for the two states of the 2,3-dimethylene-1,4-cyclohexadiyl diradical. However, a direct attack of oxygen on semibullvalene II or III cannot be ruled out especially since III is characterized by an extremely long (weak) C_2–C_8 bond (1.828 Å).[7,15] Oxygenation of semibullvalene III occurred only across positions 2 and 6 to endoperoxide VI with a more stable, less strained *trans*-4,5-dioxadecalin structure. In no case did we observe the formation of 3,7-endoperoxides, trapping products of the theoretically possible 1,4-cyclohexadiyl diradical.[5] It should be noted that octamethylsemibullvalene has been reported by Criegee and Askani in 1968 to react with oxygen forming a peroxide for which the dioxatriquinacene structure was assigned based on its proton NMR spectrum.[13a,b] The results obtained for the dimethyl compound suggest that the singlet bicyclooctadienyl diradical rearranges much faster into the corresponding cyclooctatetraene than undergoing spin inversion into the triplet.

Neither cycloheptano- nor cyclooctano-2,4,6,8-tetracarbomethoxysemibullvalene (IV) and (V) reacted with oxygen. The structural and spectroscopic studies of the 1,5-annulated-2,4,6,8-tetracarbomethoxysemibullvalenes will be reported in a subsequent paper.[15] Further experiments are under way in order to unravel the surprising behavior of these amazing molecules.

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Registry No. II, 113451-36-8; III, 113451-35-7; VI, 113430-99-2; A, 113431-00-8; B, 113431-01-9.

Supplementary Material Available: NMR and mass spectral data, ORTEP drawings, and tables of crystal data, final atomic parameters, temperature factors, and bond lengths and bond angles for endoperoxide VI, EP-5A, and EP-5B (18 pages); table of observed and calculated structure factors for endoperoxide VI (6 pages). Ordering information is given on any current masthead page.

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(9) Details of the X-ray structure analyses of the endoperoxides will be reported in the full paper. Relevant structural data are included as Supplementary Material.

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(12) Cycloadducts of azodicarboxylic esters and *N*-phenyltriazolinedione to semibullvalenes possessing the diazadecalin and the diazatriquinacene structure have been reported. See, for example: Borden, W. T.; Toong, Y. C.; Gold, A. *Tetrahedron Lett.* **1975**, 1549. See also ref 13a.

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(14) After completion of this study the successful synthesis of 1,5-bridged cyclooctatetraenes through thermal opening of 1,5-annulated semibullvalenes above 500 °C has been reported; Paquette, L. A.; Trova, M. P. *Tetrahedron Lett.* **1987**, 2795.

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Electrophilic Activation of Benzene in $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$

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It is well established that arenes are activated toward nucleophiles by coordination to the $[Cr(CO)_3]$ moiety.[3] The cyclohexadienyl products[4] may eliminate substituent anions to give nucleophilic arene substitution[3b,5] or may be oxidized or protonated to release a substituted arene or cyclohexadiene, respectively.[3,4] In the case of $[Cr(\eta\text{-}C_6H_6)(CO)_3]$, the parent benzene complex, the range of addends is, however, restricted to stabilized carbanions which are more nucleophilic than ester enolates but which do not metalate the arene[3a] (MeLi and BuLi metalate, for example). We now wish to report that cyclohexadienyl complexes can be prepared in a complementary manner by *electrophilic* addition to the activated η^4-arene in the dianionic reduction product of $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ (Scheme I).

We have previously reported that $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$ can be prepared by naphthalenide reduction of $[Cr(\eta\text{-}C_6H_6)(CO)_2\text{(pyridine)}]$,[6] and the possibility of more convenient access to the dianion led us to examine naphthalenide reduction of the readily available[7] precursor $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ (**1**). Dropwise addition

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