evaporation of the effluent, and steam distillation of the acidified residue. The acetic acid samples were subjected to chirality analysis by the method of Cornforth *et al.*[27] and Arigoni and co-workers,[28] using the procedure described by Floss and Tsai.[29]

The samples of chiral methyl methyltetrahydrofolate had been degraded in earlier work[26] and found to contain 44% ee (*R*)-methyl groups and 37% ee (*S*)-methyl groups, respectively. The acetic acid obtained from the (*R*)-methyltetrahydrofolate gave an *F* value[17] of 59.5, corresponding to 33% ee *R* configuration of the methyl group. Analysis of a sample from a second incubation with the same substrate gave *F* equals 58.3% or 29% ee *R* configuration. The acetic acid generated from (*S*)-methyltetrahydrofolate in two independent analyses gave *F* values of 37.2 and 37.2, corresponding to 44% ee *S* configuration of the methyl group.[30] It follows that the methyl group of methyltetrahydrofolate is converted by *C. thermoaceticum* into the methyl group of acetic acid with overall retention of configuration. This result argues against acetyl group formation directly from the B_{12} enzyme but is consistent with the mechanism proposed by Wood and collaborators[5,15] involving transfer of the methyl group from methyltetrahydrofolate to B_{12} and then to CO dehydrogenase followed by carbonylation on the latter (Scheme I).

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(30) *F* values in our assay are accurate to ±2; the *F* values of precursor and product are the same within the limits of accuracy of the assay.

Synthesis of [4.4.4]Propellahexaene

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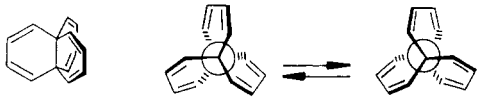
Two limitations have severely restricted synthetic access to [4.4.4]propellahexaene (**1**) and its derivatives. Due to proximity

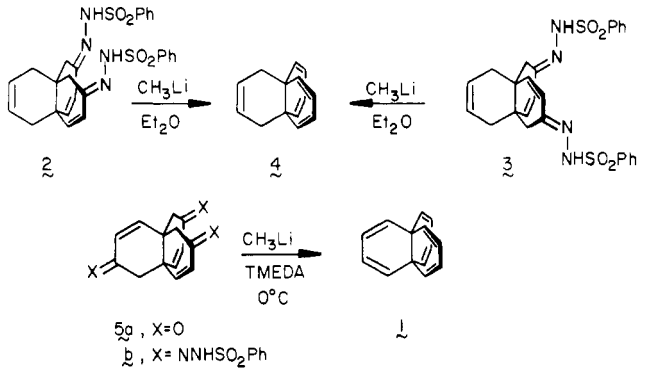


1 **1′** **1″**

factors, intraring reactions are not easily inhibited.[1] Neither are cationic rearrangements capable of profoundly reorganizing the carbocyclic framework readily circumvented.[2] One fundamental property of the maximally unsaturated D_3-symmetric hydrocarbon **1** and its derivatives relates to the unusual arrangement of the constituent six-membered rings, which radiate as blades from a common axis (see **1′** ⇄ **1″**). Extensive theoretical[3] and experimental[4] discussion attests to the general interest attached to this dynamical conformation question.

The present purpose is to detail the first synthesis of **1** and to call attention to unprecedented reactions that can materialize upon the attempted preparation of **1** substituted with methoxyl groups. To construct **1**, the pitfalls alluded to above had to be consciously avoided and reactions promising little or no risk of intramolecularity implemented.

In order to evaluate the possible merits of the Shapiro reaction,[5] a mixture of the bis(phenylsulfonyl)hydrazones **2** and **3** was prepared and treated with methyllithium in ether (0 °C → room temperature). Following the identification of **4** as product, the previously described [4.4.4]propellatrienetrione **5a**[4a] was similarly transformed almost quantitatively into **5b** (mp 195 °C). Base-induced elimination of benzenesulfinic acid and nitrogen from **5b** (CH_3Li, TMEDA, 0 °C) expediently gave the desired **1** (colorless needles, mp 48 °C, 15% isolated). To our knowledge, this reaction sequence represents only the second time a triple-Shapiro degradation has been deployed in a synthetic strategem.[6]



The NMR spectra of **1** reflect its D_3 symmetry. In $CDCl_3$ at 500 MHz, the vinyl protons appear as an AA′XX′ pattern with A centered at δ 5.91 and X at δ 5.27. Its three carbon types resonate in $CDCl_3$ at 129.44, 122.65, and 34.35 ppm. The electronic spectrum (in isooctane) is characterized by several maxima: 234 (ε 25730), 242 (24100), 251 (27780), 271 (9560), 279 (7615), and 291 nm (6975).

The hexaene is remarkably stable in air. After heating bromobenzene-d_5 solutions of **1** at 105 °C for 4.5 h, the ^1H NMR spectrum remained unaltered. An increase in temperature to 150 °C caused gradual decomposition to unidentified *nonaromatic* products ($t_{1/2} \approx 5$ h). We cannot exclude the possibility that this destruction was catalyzed by traces of acid.

In an attempt to produce **9**, triketone **6**[4a] was treated sequentially with excess potassium *tert*-butoxide in dry DMF and dimethyl sulfate,[7] all at 0 °C. Chromatography of the resulting mixture on basic alumina afforded the dimethoxy pentaenone **7** (31%),[8] 2,7-dimethoxynaphthalene (**8**, 3.4%), and trace quantities of **9**, which were visible only in the ^1H NMR spectrum of the unpurified product. Complex mixtures were obtained when **7** was resubmitted to the original reaction conditions or to the action of $KN(SiMe_3)_2$/THF–Me_2SO_4 at low temperatures. In contrast, the combination of KH in anhydrous DMF (0 °C) and Me_2SO_4 gave rise to **8** and **9** in a 17:1 ratio (^1H NMR analysis).[9] Since

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(8) ^1H NMR (300 MHz, $CDCl_3$) δ 6.27 (d, *J* = 10 Hz, 1 H), 6.02 (d, *J* = 10 Hz, 1 H), 5.92 (dd, *J* = 9.7, 2.1 Hz, 2 H), 5.51 (d, *J* = 9.7 Hz, 2 H), 4.29 (d, *J* = 2.1 Hz, 2 H), 3.51 (s, 6 H), 2.48 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 199.23, 152.33, 144.32, 128.85, 127.64, 124.50, 99.45, 54.38, 46.87, 42.13, 41.08; MS, *m/z* (M^+) calcd 256.1099, obsd 256.1109.
(9) (a) The IR and ^1H NMR spectra of **8** (mp 137–139 °C) were identical with those of a commercial sample (Aldrich). (b) For **9**: ^1H NMR (300 MHz, C_6D_6) δ 5.99 (dd, *J* = 9.8, 2.1 Hz, 3 H), 5.19 (d, *J* = 9.8 Hz, 3 H), 4.35 (d, *J* = 2.1 Hz, 3 H), 3.23 (s, 9 H); MS, *m/z* (M^+) calcd 270.1256, obsd 270.1235.

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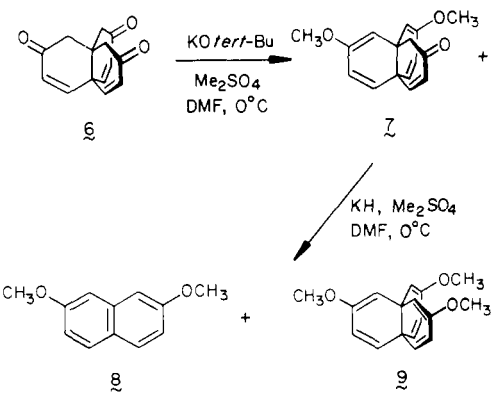
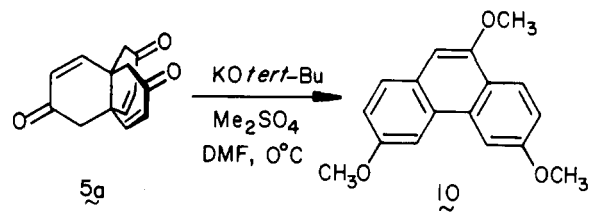


6 7 8 9

9 proved to be a stable substance at room temperature and above (80 °C, 4 h with no decomposition), it is apparent that fragmentation of the tricyclic framework with liberation of **8** materializes once **7** reacts with the strong base. Although the mechanism of this process is not known, the strikingly different chemical response of the regioisomeric series is especially noteworthy.

Under essentially identical conditions, trienetrione **5a** underwent conversion predominantly to trimethoxyphenanthrene **10** (17% isolated). The structure of **10** was deduced by using a combination of 1-D (difference NOE) and 2-D (COSY, COLOC) NMR techniques. No evidence was obtained for the formation of **8**.[10]

(10) A second trimethoxyphenanthrene isomer, present in considerably smaller amounts (2–4%), could be observed spectroscopically but was neither isolated nor characterized further.



5a 10

That two sequential [1,5]-sigmatropic carbon shifts are possible in this series is not surprising (a subsequent dehydrogenative oxidation is necessary to deliver **10**), but it is not a reaction pathway readily adopted by either **1** or **9**. Consequently, consistency is best served at present if the bond relocations associated with the **5a** → **10** process are viewed as occurring within one or more anionic intermediates.

Our results display an interesting divergence in reactivity patterns that are embodied in compounds at the [4.4.4]propellahexaene oxidation level. Although the neutral polyolefins such as **1** and **9** are shelf-stable within reasonable time limits and this property is shared by dimethoxypentaenone **7**, the carbanions derived by deprotonation of **5a**, **6**, and **7** exhibit a tendency for fragmentation or skeletal rearrangement, with the particular pathway being strongly dependent on the relative positioning of the oxygenated carbon centers.

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