agent, a strikingly different result is obtained. The iodolactones (Figure 3, R = CN) derived from the products of oxidation of **3** in the presence of the dienophile still show a "triplet" resonance for H_b. However, when the cyclobutadiene-*1,2-d*$_2$ is generated from **4**, the corresponding iodolactones show only *a singlet resonance for* H_b.[10a]

Three important conclusions follow.[10b] (1) Singlet cyclobutadiene cannot have a D_{4h} equilibrium geometry in solution. If it did, the two sources of cyclobutadiene-*1,2-d*$_2$ would have given identical label distributions in the adducts with methyl (*Z*)-3-cyanoacrylate. (2) The $\Delta G^{\ddagger}$ for interconversion of isomeric (presumably rectangular) cyclobutadienes is comparable with that for trapping. With 3.6 M methyl acrylate as trap, geometrical isomerism is faster than adduct formation, whereas with 2.8 M methyl (*Z*)-3-cyanoacrylate trapping appears to be the faster process. (3) The formation of cyclobutadiene-*1,2-d*$_2$ from **4** and the subsequent trapping with methyl (*Z*)-3-cyanoacrylate must both be concerted pericyclic processes since involvement of a biradical intermediate in either step would have resulted in formation of **5a** and **5c** in equal amounts.[11]

The mechanism in Figure 2 requires that the ratio of **5a:5c** vary with the concentration of trapping reagent (T) according to the equation[11,12]

$$[\mathbf{5a}]/[\mathbf{5c}] = 1 + (k_2/k_1)[\mathrm{T}]$$

Measurement of the **5a:5c** ratio as a function of [T] should, therefore, provide a quantitative determination of k_2/k_1. Independent measurement of k_2 for a variety of dienophiles would then yield several estimates of k_1, the rate constant for geometrical isomerism of cyclobutadiene-*1,2-d*$_2$. This in turn could lead to evaluation of the activation parameters for the process, by studies at several different temperatures. Experiments of this kind are in progress.

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(2) If geometrical isomerism were faster than *all* other processes, then cyclobutadiene would exhibit *effective* D_{4h} symmetry even though D_{4h} may not represent a local minimum in the potential energy surface. By "chemically significant" we mean that the reactive intermediate can undergo chemical reactions with rates comparable with or greater than the rate of its isomerism.

(3) Recent experiments[1y,z] show that, when CO_2 is produced as a byproduct in the formation of cyclobutadiene in an argon matrix, its infrared spectrum shows abnormal symmetry, apparently because of complex formation between the CO_2 and cyclobutadiene. The spectrum of the cyclobutadiene does not appear to be seriously perturbed by this interaction, however.

(4) For an alternative preparation of the unlabeled azo compound see: Masamune, S.; Nakamura, N.; Spadaro, J. *J. Am. Chem. Soc.* **1975**, *97*, 918.

(5) The synthesis of the 5,6-dicarbomethoxy-5,6-diazabicyclo[2.2.0]hex-2-ene-*1,4-d*$_2$ is based on Altman, L. J.; Semmelhack, M. F.; Hornby, R. B.; Vederas, J. C. *Chem. Commun.* **1968**, 686.

(6) The synthesis of cyclobutadiene *1,2-d*$_2$ iron tricarbonyl is based on Grubbs, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6693.

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(8) The experimental results presented in this communication do not distinguish between $_{\sigma}2_s + {}_{\sigma}2_s$ and $_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s$ mechanisms for the deazetation and trapping. Figure 2 arbitrarily depicts the latter mechanism.

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(10) (a) The signal to noise ratio in the NMR spectrum is such that up to 5% of the doublet component would have been undetectable. (b) We cannot absolutely rule out the possibility of adduct formation by direct attack of the dienophile on azo compound **4**. However, in all trapping reactions studied thus far, the total amount of deuterium at the bridgehead sites in the primary products is equal[11] to the total amount of deuterium at the vinyl sites. We have been unable to find a mechanism for direct reaction between **4** and a dienophile which would lead to this result without coincidental equality of rate for two different processes. Note also that the equal amounts of **5a** and **5c** obtained with methyl acrylate as trap would require coincidental equality of rate for three different processes.

(11) We have found no evidence for a significant isotope effect on the product distribution. The most easily measured case comes from trapping cyclobutadiene-*1,2-d*$_2$ with diethyl azodicarboxylate. The resulting adduct shows two singlets for the bridgehead and vinyl protons ($J \simeq 0$ Hz between vicinal bridgehead and vinyl protons). The integral ratio of these two singlets is 1.00 ± 0.05. It seems reasonable to expect that cyclobutadiene cycloadditions would have early transition states with relatively little rehybridization and consequent small secondary isotope effects.

(12) This equation is derived on the assumption that the initially formed cyclobutadiene-*1,2-d*$_2$ from **4** consists of only a single isomer.

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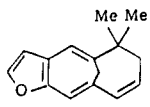
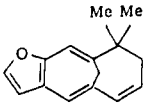
Total Synthesis of (±)-Dihydrospiniferin-1: A Furanosesquiterpene with a 1,6-Methano[10]annulene Carbon Skeleton

Sir:

Spiniferin-1, an unstable furanosesquiterpene from the Mediterranean sponge *Pleraplysilla spinifera*, was recently reformulated as I or, less likely, II through careful NMR spectral analysis.[1,2] Accordingly, spiniferin-1 would appear to be the first known natural product incorporating the novel 1,6-methano[10]annulene carbon framework.[3]



I



II

Its unique carbon skeleton, its chemical instability, and the unresolved ambiguity between structures I and II[2] stimulated our interest in developing a structurally definitive synthesis of spinferin-1. In this report we offer support for structure I through a rational total synthesis of the known[2] dihydro derivative **11** (Scheme I).

Dienone **2**[4] was prepared by an improved sequence through addition of methyllithium to 6-methoxy-1-tetralone (**1**), Birch reduction,[5] and acid-catalyzed hydrolysis-elimination. Conjugate addition of lithium dimethylcuprate afforded the unsaturated ketone **3**. Attempted Simmons-Smith cyclopropanation[6] of enone **3** caused conjugation of the double bond. As expected,[6] the related alcohol yielded to cyclopropanation, but even here the reaction proved capricious and numerous trials were needed to optimize conditions.[7] Jones oxidation[8] of the derived tricyclic alcohol led to the corresponding ketone **4**: ν_{max} 1710, 1465 cm^{-1}; δ 2.5 (s, H-1), 2.1 (m, H-3), 1.1, 1.0 (s, CH_3's), 0.4 ppm (s, H-11).

Formylation[9a] of ketone **4** occurred as planned at the less hindered (C-3) α position[9b] to give the hydroxymethylene

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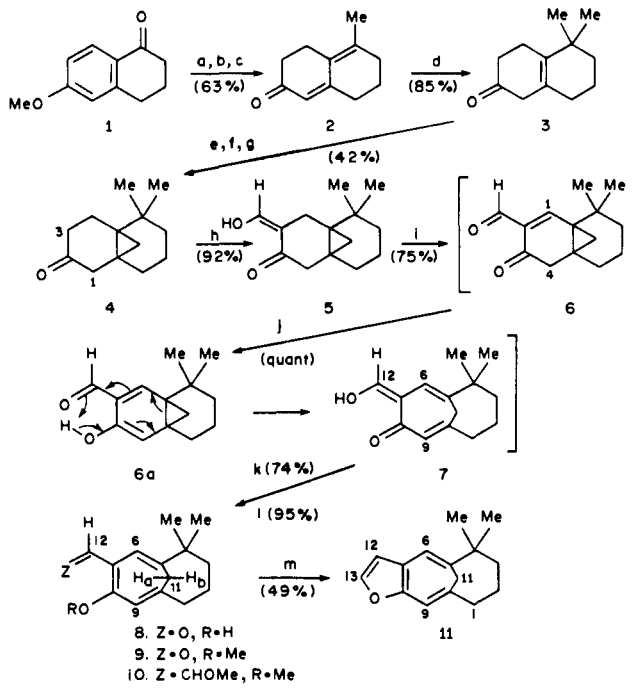
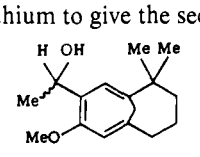
Scheme I[a]

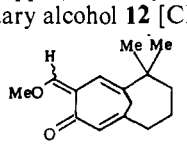


[a] (a) MeLi, Et_2O, THF; (b) Na, NH_3, EtOH; (c) HCl, H_2O, Et_2O; (d) Me_2CuLi, Et_2O; (e) $NaBH_4$, EtOH; (f) Zn(Cu), CH_2I_2, Et_2O; (g) H_2CrO_4, H_2SO_4, Me_2CO; (h) HCO_2Et, NaOMe, C_6H_6; (i) DDQ, C_6H_6; (j) HCl, H_2O, EtOAc; (k) MeI, K_2CO_3, DMF; (l) $Ph_3P^+CH_2OMe$, Cl^-, KO-*t*-Am, $CH_3C_6H_5$; (m) HCl, H_2O, Et_2O.

ketone **5**. Other, less sterically demanding enol and enolate reactions (various bases plus Me_3SiCl;[10] various bases plus PhSeCl[11]) led to mixtures of C-1–C-3 regioisomeric products. Ketone **5** was smoothly dehydrogenated at room temperature with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[12] in benzene to give the acid labile enone **6**: ν_{max} 1695, 1680, 1600 cm^{-1}; δ 9.8 (s, CHO), 8.2 (s, H-1), 2.7 (AB, H-4, J_{AB} = 18 Hz, $\Delta\nu$ = 13), 1.15 (s, CH_3's), 0.5 ppm (d, H-11, J = 4 Hz). Enone **6** rearranged with startling ease to enol **8** [ν_{max} 1630, 1600, 1515, 1365, 1280, 1195 cm^{-1}; δ 9.4 (s, H-12), 6.0, 5.8 (s, H-6, H-9), 3.05 (d, H-11b, J = 10 Hz), 1.25, 1.1 ppm (s, CH_3's)] upon treatment with a trace of acid or elution though silica gel. This remarkably facile ring expansion[13] was attended by dramatic changes in the NMR spectrum highlighted by the appearance of a distinctive doublet at 3.05 ppm attributable to the deshielded methano bridge endo proton (**8**, H-11b, J = 10 Hz)[2] and the concomitant disappearance of the shielded cyclopropane protons of enone **6** (δ 0.5 ppm).[14]

Alkylation of the hydroxy aldehyde **8** with methyl iodide-potassium carbonate in dimethylformamide yielded the enol ether **9**: mp 127–129 °C; ν_{max} 1650, 1615, 1390, 1275, 1145 cm^{-1}; δ 10.3 (s, H-12), 6.3, 5.8 (s, H-6, H-9), 3.8 (s, CH_3O), 3.1 (d, H-11b, J = 10 Hz), 1.25, 1.0 ppm (CH_3's)]. This structure was confirmed both by the ^{13}C NMR spectrum (aldehyde CO doublet at 191 ppm) and by addition of methyllithium to give the secondary alcohol **12** [CH_3 doublet


12


13

at 1.3 ppm (J = 6 Hz), broad carbinyl H quartet at 5.0 ppm]. The isomeric enol ether **13** was evidently not present to an appreciable extent.

Aldehyde **9** condensed readily with methoxymethylenetriphenylphosphorane in toluene[15] to give the bis enol ether **10**. Treatment with aqueous HCl in ethyl ether slowly gave rise to the furan **11**: δ 7.2, 6.45 (d, H-12, H-13, J = 2 Hz), 6.2 (s, H-6, H-9), 3.1 (d, H-11b, J = 10 Hz), 2.3 (m, H-1), 1.3, 1.0 ppm (s, CH_3's). The ^1H and ^{13}C NMR spectra of **11** were in complete agreement with those of dihydrospiniferin-1.[2]

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(13) The ring cleavage is a thermally allowed disrotatory electrocyclic reaction. It may also be viewed as a retro-Michael reaction in which case the proton transfer depicted in **6a** may play an important role. We have not yet examined the influence of base on enone **6**. Analogy with sigmatropic rearrangements would suggest that the enolate rearrangement would likewise be facile. (Steigerwald, M. L.; Goddard, W. A., III; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994–97. Ireland, R. E.; Mueller, R. H.; Willard, A. K. *Ibid.* **1976**, *98*, 2868–2877.) The oxalo derivative of enone **6** ($COCO_2Et$ instead of CHO) undergoes comparable ring expansion upon base treatment.
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(16) National Science Foundation Predoctoral Fellow, 1979–1982.

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Electron-Transfer Photooxygenation. 4. Photooxygenation of *trans*-Stilbene Sensitized by Methylene Blue[1]

Sir:

Methylene Blue (MB) and other dyes are widely used as sensitizers of photooxygenations.[2] Usually, excited singlet oxygen ($^1O_2$) is produced by energy transfer from triplet dye to oxygen and reacts with acceptor (A) to give the product (AO_2).

In 1969, Rio and Berthelot[3] reported a very slow photooxygenation of *trans*-stilbene (TS) sensitized by MB to give 2 mol of benzaldehyde. These authors assumed that the reaction involved $^1O_2$. Other $^1O_2$ sensitizers, however, including Rose Bengal (RB), failed to sensitize the reaction.[3] The alcohol used to dissolve the RB was thought to cause this inefficiency.[3] However, it is difficult to understand this explanation because the lifetime of $^1O_2$ is not shortened sufficiently in methanol to account for these results.[4]

We have previously shown that the cyanoaromatic-sensitized photooxidation of TS to benzaldehyde in MeCN occurs

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