would be a plausible oxygen transfer reagent in the present system.

Low-oxidation-state dioxygen complexes react with electron-deficient, but not electron-rich, olefins to give stable complexes. A nucleophilic zwitterion intermediate (**13**) analogous to the Criegee intermediate has been suggested.[17e] The oxidation of cyclohexene catalyzed by these metal complexes has been shown to give radical autoxidation products.[17b] The results presented here clearly indicate that the reactivity of our intermediate toward olefins is quite different from these complexes.

In summary, we have found a new oxygen-transfer agent which involves an intermediate metal oxygen-carbene complex and which epoxidizes olefins. Investigation of the mechanism and scope of the reaction is currently underway.

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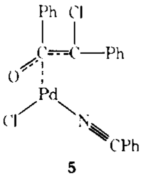

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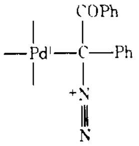
(19) The reaction was checked by GC and LC at −30, −10, 0, 10, and 20 °C after removal of O_2 by flushing with N_2. Below 10°, no epoxidation was observed.

(20) An alternative path in which N_2 evolution and O_2 attack occur simultaneously in intermediate **7** might be considered. However, **6** is a preferable formulation because the formation of benzophenone as an oxidation product would require the formation of a free ketocarbene which could be formed by a nucleophilic attack of acetonitrile on **6**, but not on **7**. This formulation is consistent with the effects of base on the reaction of $Cu(acac)_2$ with diazoacetophenone[22] and the instability of carbene complexes to nucleophiles.[23]



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Synthesis and Absolute Configuration of 4,5-Diazatwist-4-ene

Sir:

Relative to the work which has been expended on its isoelectronic counterparts (olefins and ketones), the azo group has been neglected. To the spectroscopist, the underlying reason probably resides in the fact that diimide, the parent azo compound, has only a transient existence,[1] unlike ethylene and formaldehyde. Nevertheless, the optical activities of a few trans azo alkanes[2] and several chiral pyrazolines[3,4] have been measured. In fact, the rotational strengths of the circular dichroic (CD) spectra of these compounds suggest the possible utilitarian role of the azo group as a probe of asymmetric environment within molecules. In view of these earlier findings and the considerable interest which twistene has commanded,[5] we have been prompted to prepare 4,5-diazatwist-4-ene (**1**) in optically active form with full knowledge of the absolute configuration. The molecular rigidity present in **1** presumably[6] fixes the -N═N- unit into an essentially planar cisoid geometry.

The pivotal substrate in this study is (−)-*endo*-bornyl-1,2,4-triazolinedione (**3***) which is readily synthesized in optically pure form from *d*-camphor.[7] The absolute configuration of this dienophile is, therefore, as drawn.[8] Addition of **3*** to cyclooctatetraene dibromide (**2**) afforded an adduct, which when directly debrominated[9] delivered **4***, mp 193–194 °C, $[\alpha]_D$ −6.6° (*c* 12.8, C_2H_5OH), in 92% overall yield.[10] The subsequent irradiation of **4*** in benzene-acetone solution (1:1) with a 450-W Hanovia lamp through a Vycor filter resulted in cyclization (84%) to **5***, mp 192.5–193 °C, $[\alpha]_D$ −4.34° (*c* 8.3, C_2H_5OH). By means of regiocontrolled hydrogenolysis,[11] this basketane derivative was quantitatively converted into a mixture of the diheterotwistane diastereomers **6*** and **7***, $[\alpha]_D$ −6.0° (*c* 7.5, C_2H_5OH). Repeated recrystallization of this product from an ethyl acetate-pentane solvent system afforded colorless crystals, mp 213–213.5 °C, whose rotation, $[\alpha]_D$ −53.9° (*c* 5.9, C_2H_5OH), did not change upon further processing. Hydrolysis-oxidation of this material by suitable modification of the conditions of Askani and Schwertfeger[12]

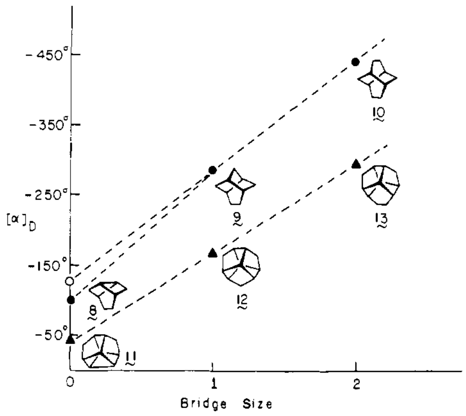


Figure 1. Correlation of bridge span with optical rotation in two series of gyrochiral cage-shaped molecules.

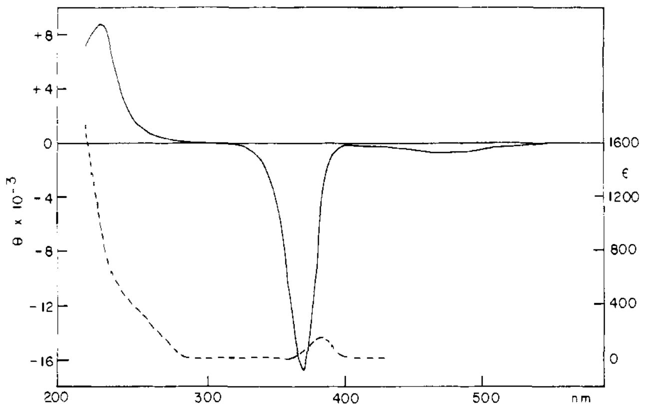
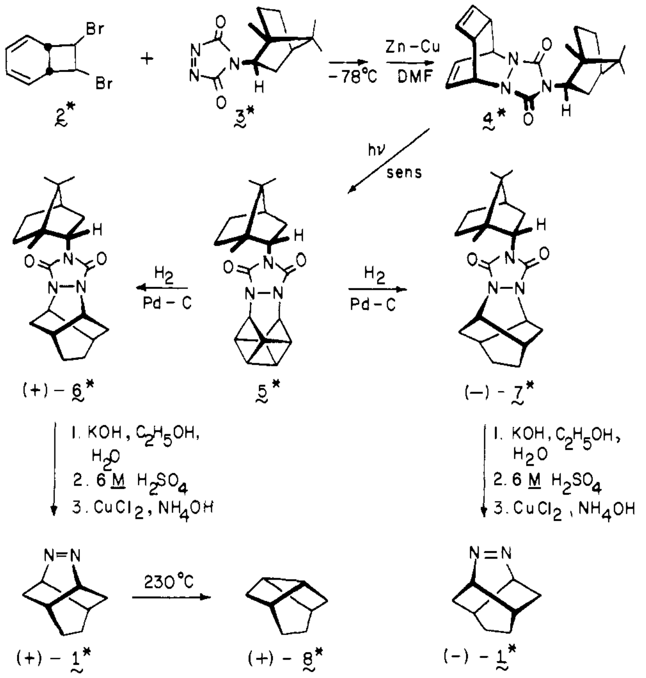


Figure 2. UV (- - -) and CD(—) spectra of (−)-4,5-diazatwist-4-ene (**1***) as determined in hexane solution.

led to the isolation of **1***, $[\alpha]_D$ −925° (*c* 7.5, C_2H_5OH). Samples of the dextrorotatory diazatwistene were prepared in similar fashion.

For the purpose of establishing the absolute configuration of these enantiomers, (+)-**1***, $[\alpha]_D$ +201° (*c* 9.0, C_2H_5OH), was heated at 230 °C for 15 min in a sealed tube. Preparative vapor phase chromatography gave (+)-9-nortwistbrendane (**8***) in 16.5% yield as a colorless oil, $[\alpha]_D$ +21.5° (*c* 10.6, hexane). On the assumption that diastereomeric purity had earlier been realized, the corrected rotation of (+)-**8*** is $[\alpha]_D$ +99°. It becomes important to note that hydrocarbon **8** represents the smallest gyrochiral cage-shaped molecule presently known. Higher homologues such as twistbrendane (**9**), twistane (**10**), C_2-bishomocubane (**11**), D_3-trishomocubane (**12**), and C_2-bismethanotwistane (**13**) have been prepared in optically active form. Their absolute configurations, established chiefly by Nakazaki and co-workers,[13] reveal that all levorotatory enantiomers possess a bicyclo[2.2.2]octane core fixed in an M helical conformation. It follows that (+)-**8*** is also constructed with a P helicity about its C_2 axis and that its precursor (+)-**1*** has the 1(*R*),3(*R*),6(*R*),8(*R*) configuration as shown.



As in the case for **11**, the presence of a zero bridge in 9-nortwistbrendane is reflected in a markedly decreased optical rotation relative to **9** and **10** (Figure 1). For the series **11–13**, a remarkably linear correlation between $[\alpha]_D$ and bridge size is observed. Should this relationship also hold for **8–10**, the implication would be that **8*** had actually not been obtained in maximum enantiomeric purity (extrapolated rotation of 125°). If adjustment is made along these lines, it becomes possible that the absolute rotation of **1*** could be as high as $[\alpha]_D$ 1165°. In either event, the rotatory power of 4,5-diazatwist-4-ene is significantly higher than that of twistene, $[\alpha]_D$ −423°,[14] whose optical rotation closely approximates that exhibited by twistane, $[\alpha]_D$ −440°.[13d]

The interesting CD spectrum of (−)-**1*** is characterized by a rather intense band at 370 nm showing a negative Cotton effect and a second weaker absorption of opposite sign centered near 222 nm (Figure 2). The essentially Gaussian low-energy band can, on the basis of earlier considerations,[15] be confidently assigned to an $n_+ \rightarrow \pi^*$ electronic transition while the second band which appears in the 222–230-nm region is comparable in direction and magnitude with that exhibited by (+)-twistene (200 nm, $\Delta\epsilon$ +11.6)[16] and may arise from a low-lying $n_- \rightarrow \pi^*$ transition.[17] As expected, (+)-9-nortwistbrendane (**8***) does not give rise to a magnetic dipole-allowed, but electric dipolar-forbidden transition.[18] Only end absorption is seen in the UV spectrum and its CD spectrum exhibits no observable Cotton effect.[19]

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Ficisterol (23-Ethyl-24-methyl-27-norcholesta-5,25-dien-3β-ol). A Biosynthetically Unprecedented Sterol from the Marine Sponge *Petrosia ficiformis*[1]

Sir:

Petrosterol (**1**, 26,27-cycloaplysterol), a novel cyclopropane-containing sterol, has recently been identified in a Pacific sponge, *Halichondria* sp.[2] and as the major sterol from *Petrosia ficiformis* collected in the Bay of Naples.[3,4] In view of our interest in the biosynthetic origin of the cyclopropane function in the sterol side chain, we have carefully analyzed the minor and trace components of *P. ficiformis* with the hope of identifying possible related biosynthetic intermediates. We now report the presence of a new C_{29} sterol with an unprecedented side chain, shown to be 23-ethyl-24-methyl-27-norcholesta-5,25-dien-3β-ol (**2**), which we have named ficisterol.

Argentic TLC separation of *P. ficiformis* sterol acetates[3] using 5:2[6] (v/v) hexane-benzene or hexane-toluene gave several bands, the most polar of which contained four major components. Repeated TLC with hexane-toluene (1:1) and reversed-phase HPLC on C_{18} μBondapak[7] gave **2** (0.6% of total sterol fraction), M^+ 412.3701 ($C_{29}H_{48}O$), whose GC (OV-17 column) retention time (cholesterol, 1.00) was 1.58, acetate mp 99–100 °C. Since the presence of the usual Δ^5-3β-hydroxy sterol nucleus was demonstrated[8] by the peaks at *m/z* 271, 255, 231, and 213, the sterol must possess one degree of unsaturation in the side chain. The 360-MHz ^{1}H NMR spectrum in C_6D_6 (δ, parts per million) of the acetate of **2** shows six methyl group signals (see Table I), with one of the signals clearly a triplet, suggesting the presence of a $-CH_2-CH_3$ entity on the side chain. Significantly, doublets due to a terminal isopropyl group are absent. A multiplet at 5.85 is assigned to the vinylic proton at C-25, while other easily recognizable signals are 5.38 (C-6 H) and 4.85 (m) (3α-H acetate). A pair of doublets (2 H) at 5.03 and 5.06 is typical for a terminal methylene group,[9] and double resonance experiments showed that these protons at C-26 are coupled with the C-25 vinylic hydrogen at 5.85.

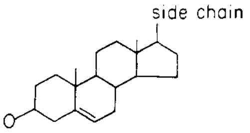
Irradiation of the allylic C-24 proton at 2.27 collapsed the 28-methyl doublet at 0.95 to a singlet, and at the same time simplified the complex vinylic proton region at 5.85. Irradiation of the C-26 geminal protons also simplified the vinylic C-25 hydrogen and the resonance due to the C-24 allylic proton. Irradiation of the vinylic C-25 hydrogen collapses the geminal C-26 protons and simplified the allylic C-24 hydrogen. The presence of part of the side chain as a 3-substituted but-1-ene is thus established, which with the addition of the requisite ethyl group leads to structure **2** or **4**, both of them being unprecedented in terms of a 22- or 23-ethyl substituent.

Triple irradiation experiments performed by simultaneously irradiating the 28-methyl group *and* C-25 vinylic hydrogen clearly produced a *doublet* ($J \sim 5$ Hz) for the allylic hydrogen at C-24, thus demonstrating that position 23 is monosubstituted (i.e., **2**). The lower homologue **3** ($C_{28}H_{46}O$, M^+ 398) has also been isolated as a 1:1 acetate mixture with 24-methylenecholesterol (**5**), but the difference in the chemical shift of the C-21 and C-28 methyl protons (Table I) of the acetate suggest differences in stereochemistry.

Table I. ^{1}H Chemical Shifts of the Acetates of Ficisterol (**2**) and 23,24-Dimethyl-27-norcholesta-5,25-dien-3β-ol (**3**) (360 MHz, C_6D_6)

carbon	**2**	**3**
18-CH_3	0.686 (s)	0.684 (s)
19-CH_3	0.918 (s)	0.925 (s)
21-CH_3	0.984 (d, J = 6.5)[a]	1.017 (d, J = 6.9)
30-CH_3	0.887 (t, J = 7.3)	
29-CH_3		0.867 (d, J = 6.7)
28-CH_3	0.955 (d, J = 6.9)	0.972 (d, J = 6.4)
C-25 H	5.85 (m)	5.78 (m)
C-26 (2 H)	5.03, 5.06 (d)	5.03, 5.06 (d)
C-6 H	5.35 (m)	5.38 (m)
C-3 ($COCH_3$)	1.75 (s)	1.75 (s)
3-α-H of acetate	4.85 (m)	4.86 (m)

[a] Coupling constants J are in hertz.



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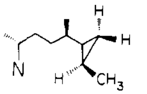

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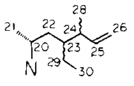

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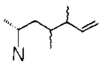

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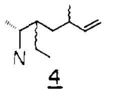

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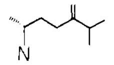

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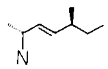

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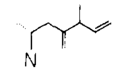

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Ficisterol (**2**) is biosynthetically intriguing since it lacks the normal terminal isopropyl functionality and therefore resembles occelasterol (**6**), isolated from a marine annelid.[10] Even more unusual is the presence of the C-23 ethyl substituent; although several marine sterols (e.g., gorgosterol,[11] 23,24-dimethylcholesta-5,22-dien-3β-ol,[12] and dinosterol[13]) have been shown to be methylated at C-23 and C-24, ficisterol (**2**) is the first example of C-23 ethylation in a naturally occurring sterol. This suggests that methylation of a hitherto undetected 23-methylene sterol (e.g., **7**) is a new mode of sterol-side-chain bioalkylation and we are actively engaged in searching in marine organisms for further examples.

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