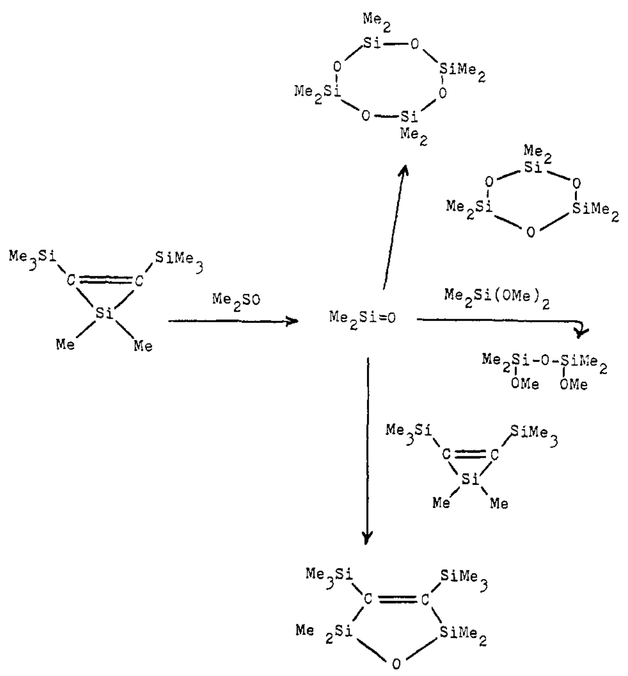
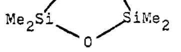
Scheme II



δ 0.04 (s, 12 H) and 3.40 ppm (s, 6 H). In a similar Me_2SO/I reaction carried out in the presence of an excess of hexamethylcyclotrisiloxane (D_3) in benzene at 0 °C, dimethyl sulfide (93%) and bis(trimethylsilyl)acetylene again were formed as well as the $Me_2Si{=}O$ trapping product, octamethylcyclotetrasiloxane (D_4) (66% yield, based on I), and IV (32%). Thus $Me_2Si{=}O$ is an intermediate in these reactions which can be trapped (Scheme II). The insertion of $Me_2Si{=}O$ into the Si—O bonds of D_3[5,6] and of dimethyldimethoxysilane[7] are known processes, but its insertion into a strained three-membered ring had not been reported to date.

Similar chemistry was observed with hexamethylsilirane, although it appeared to be less reactive toward Me_2SO than the silirene. Thus a reaction of 1.65 mmol of II with 0.75 mmol of Me_2SO under argon resulted in an only mildly exothermic reaction which produced cyclic siloxane V ($n^{25}{}_D$ 1.4524 (lit.[1b]


V

$n^{25}{}_D$ 1.4531)) in 53% yield, based on Me_2SO, tetramethylethylene (97%, based on Me_2SO), as well as dimethyl sulfide. The dimethylsilanone generated in the Me_2SO-II interaction also could be intercepted when this reaction was carried out in the presence of an excess of dimethyldimethoxysilane. *sym*-Tetramethyldimethoxydisiloxane was formed in 69% yield. When a mixture of ~1 molar equiv each of silirene I and silirane II was treated with 1 molar equiv of Me_2SO at 0 °C, followed by 1-h reaction time at room temperature, the yield of bis(trimethylsilyl)acetylene was 36%, of dimethyl sulfide, 66%, of IV, 17%, and of V, 29%, a finding in line with the already observed greater reactivity of I as compared with that of II.

Pyridine *N*-oxide and trimethylamine *N*-oxide also reacted with silirene I to give dimethylsilanone. Such reactions, carried out in dimethyldimethoxysilane at room temperature, were mildly exothermic and gave *sym*-tetramethyldimethoxydisiloxane in 59% yield in the case of pyridine *N*-oxide and in 32% yield in the case of the reaction with anhydrous trimethylamine *N*-oxide. The lower yield in the latter case may be due to the fact that trimethylamine *N*-oxide is only poorly soluble in the dimethyldimethoxysilane medium.

The insertion of dimethylsilanone into the Si—C bonds of silirane II and silirene I bears a formal similarity to the insertion of aldehydes and ketones into these ring systems.[1a,c] However, in terms of mechanism, the $RCH{=}O$ and $R_2C{=}O$ insertion reactions, believed to be radical processes on the basis of limited evidence,[1a] may be quite different from the $Me_2Si{=}O$ insertion reactions. The evidence which has accumulated thus far suggests that the species containing silicon-heteroatom double bonds are quite polar,[5,6] $R_2Si^{\delta+}{=}Y^{\delta-}$, and so the $Me_2Si{=}O$ insertion may well be a polar, not a radical, process.

We have pictured the formation of $Me_2Si{=}O$ in the Me_2SO-I reaction as shown in Scheme I. We note, however, that Weber and his coworkers have reported that dimethylsilylene deoxygenates Me_2SO, giving $Me_2Si{=}O$, which they intercepted with D_3.[6b] This possibility, Me_2Si extrusion prior to reaction with Me_2SO, is unlikely in the case of silirene I. This compound is thermally very stable and resistant to extrusion of dimethylsilylene. Only upon photolysis or transition metal catalysis does this process occur,[1a,c,9] conditions which are absent in the present reactions.

The reactions of silirene I and silirane II with other 1,2-dipolar reagents are under active investigation.

Acknowledgment. The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this research under Grant AF-AFOSR-76-2917 and to Union Carbide Corporation for gifts of chemicals.

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(1) For recent papers describing our results in this area see (a) D. Seyferth, S. C. Vick, M. L. Shannon, T. F. O. Lim, and D. P. Duncan, *J. Organomet. Chem.*, **135,** C37 (1977); (b) D. Seyferth and S. C. Vick, *ibid.*, **125,** C11 (1977); (c) D. Seyferth, D. P. Duncan, and S. C. Vick, *ibid.*, **125,** C5 (1977).
(2) A reaction carried out at room temperature was exothermic and product yields were lower.
(3) The melting point of IV in ref 1b was erroneously reported as 62–64 °C. It should read 72–74 °C.
(4) The generation and the chemistry of $Me_2Si{=}O$ has been the subject of several reports by Sommer,[5] Weber,[6] and Ando.[7]
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Dietmar Seyferth,* Thomas F. O. Lim, Don P. Duncan
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
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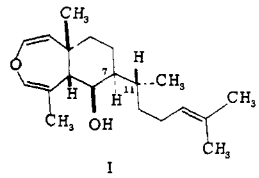
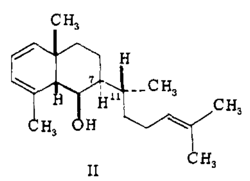
Stereorational Total Synthesis of the Marine Diterpene Dictyolene and Its C-11 Epimer

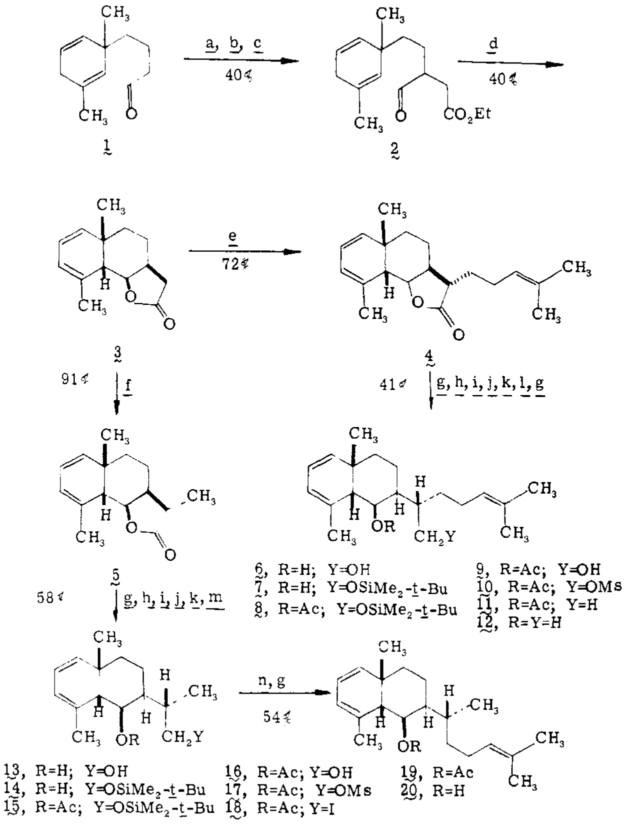
Sir:

Recently Erickson et al. reported the isolation of two novel diterpenoids, dictyoxepin (I) and dictyolene (II), from antibiotic extracts of the marine alga *Dictyota acutiloba.*[1]


I


II

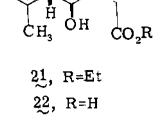
Scheme I[a]



[a] a, *i*-Pr_2NH; b, $BrCH_2CO_2Et$; c, H_2O; d, $HClO_4$, EtOAc; e, LiN(*i*-Pr)$_2$, $I(CH_2)_2CH{=}C(CH_3)_2$; f, LiN(*i*-Pr)$_2$, CH_3I; g, $LiAlH_4$, Et_2O; h, *t*-$BuMe_2SiCl$; i, Ac_2O, *p*-$Me_2NC_5H_4N$, py; j, H_2O, HCl, THF; k, MsCl, Et_3N, CH_2Cl_2; l, $NaB(CN)H_3$, NaI, HMPA; m, NaI, acetone; n, $([CH_3)_2C{=}CH{=}CH_2]NiBr)_2$, DMF.

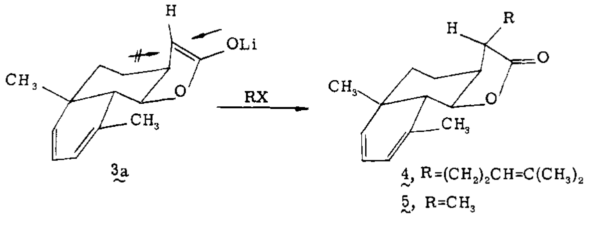
Whereas the dictyoxepin structure has been confirmed by the x-ray crystallographic work of Clardy,[1] that of dictyolene rests solely upon spectral data and biogenetic analogy to dictyoxepin, especially with regard to the stereochemistry at C-7 and C-11. In this report, we describe definitive stereorational total syntheses of dictyolene (**20**) and its C-11 epimer **12** which fully support the assigned structure II.

Dienal **1**, readily prepared from *m*-toluic acid in 71% overall yield,[2] upon alkylation with ethyl bromoacetate via the diisopropyl enamine and subsequent hydrolysis, afforded the ester aldehyde **2** in 40% yield[3] (Scheme I). Cyclization of this aldehyde with perchloric acid in ethyl acetate led to the cis,anti,-cis tricyclic lactone **3**, mp 69–71 °C, along with the isomeric cis,anti,trans hydroxy ester **21**. These two products, formed as a roughly 1:1 mixture in 90% yield, could be separated by saponification and careful acificiation, whereupon a mixture of lactone **3** and hydroxy acid **22** was produced. Acid **22** could then be removed through base extraction. The assignment of structure for lactone **3** follows from (1) the established course of such cyclizations,[2] (2) its ready formation upon acidification of the hydroxy acid salt mixture,[4] and (3) comparison with an independently synthesized sample.[5]



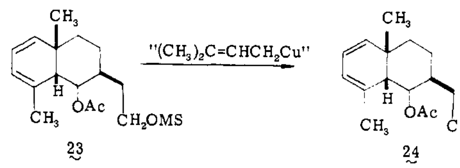
21, R=Et
22, R=H

Alkylation of lactone **3** with 2-methyl-5-iodo-2-pentene[6] yielded lactone **4** while the use of methyl iodide gave rise to the crystalline lactone **5**, mp 96–97 °C (91% yield). In each case, the stereochemical outcome conforms to approach from the least hindered face of the lactone enolate **3a** by the alkylating agent (kinetic alkylation). Furthermore, since treatment with lithium diisopropylamide failed to epimerize lactones **4** and **5**, we surmise that they represent the more stable alkyl epimers, as well. Inspection of molecular models (see conformational drawings) allows a clear choice of stereochemistry for these key lactone intermediates.



According to the assignment suggested by Erickson, Clardy, et al.,[1] conversion of the lactone carbonyl of **4** to a methyl grouping should lead to the C-11 epimer of dictyolene, **12.** Indeed, this was found to be the case. Reduction of lactone **4** with lithium aluminum hydride gave diol **6** which could be selectively protected with *tert*-butyldimethylsilyl chloride to give ether **7.**[7] Acetylation of this intermediate followed by cleavage of the silyl ether **8** with aqueous hydrochloric acid and mesylation of the resulting alcohol **9** afforded acetoxy mesylate **10.** This mesylate was reduced with sodium cyanoborohydride and sodium iodide in HMPA[8] to acetate **11** which, upon treatment with lithium aluminum hydride, yielded alcohol **12.** The infrared and NMR spectra of this alcohol closely resembled those of dictyolene (II) but clear differences could be readily discerned, particularly in the chemical shift of the C-11 methyl group.[9]

In our initial planning, we had hoped to convert mesylate **17,** prepared from lactone **5** using the sequence employed in the conversion of lactone **4** to mesylate **10,** to dictyolene through coupling with a 3,3-dimethylallylcopper reagent.[10] However, preliminary experiments with either catalyzed or stoichiometric reagents on the mesylate **23** were totally unpromising; only the reduction product **24** was formed.[11] Accordingly, we turned to the use of 3,3-dimethylallylnickel bromide, a reagent employed by Corey and Semmelhack in their synthesis of α-santalene.[12,13] Reaction in dimethylformamide with the iodo acetate **18,** derived from mesylate **17** using sodium iodide in acetone,[6] afforded the prenylated homologue **19.** Cleavage with lithium aluminum hydride gave racemic dictyolene (**20**) whose spectral properties were identical with those of authentic material.[9]



Acknowledgments. We are indebted to the National Institutes of Health for support of this work through Research Grant CA 11089 awarded by the National Cancer Institute.

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James A. Marshall,* Peter G. M. Wuts
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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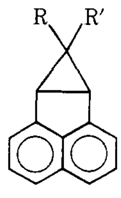
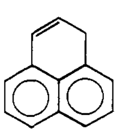
π,π-Biradicaloid Hydrocarbons: Spectral Characterization of Singlet and Triplet 1,3-Perinaphthadiyl and Observation of Thermal and Photochemical 2,3-Hydrogen Shifts[1]

Sir:

Although biradicaloid geometries[2] are likely to play a fundamental role in molecular photochemical processes,[3,4] very little is known from direct observations about molecules at such geometries and, in particular, about the reactivity and physical properties of their excited states. We now wish to report the preparation and spectral characterization of the lowest singlet and triplet states of a trimethylene biradical constrained to a π,π geometry by interaction with the peri positions of naphthalene, as well as the kinetics of a thermal 2,3-hydrogen shift and the observation of a photochemical 2,3-hydrogen shift in the biradical.

When I[5] is irradiated at 77 K in a rigid glass ($\lambda \approx 260$ nm, $\sim 10^{-3}$ M solution in degassed 3-methylpentane, 2-methyltetrahydrofuran, 1-pentanol, or EPA), its UV absorption, emission, and excitation spectra are gradually replaced by those of a new species stable for many hours (Figure 1). Simultaneously, the characteristic lines of a triplet appear in the ESR spectrum ($D/\hbar c = 0.026 \pm 0.001$ cm^{-1}, $E/\hbar c < 0.002$ cm^{-1}). Each member of the two $\Delta m = 1$ pairs of observed lines of the species produced from Ia, as well as the $\Delta m = 2$ line, is split into a triplet. The coupling constant is approximately the same for both pairs, $a_H = 26 \pm 2$ G. The lines of the species produced from Ib are similarly split into very poorly resolved doublets. Temperature variation of the ESR intensity (93–123 K, 1-pentanol) is strong, and standard analysis shows that the triplet state lies 640 ± 40 cal above the ground state. The UV-vis absorption spectrum shows only a very slight decrease in intensity when temperature is raised from 77 to 110 K, while the shapes of the fluorescence and fluorescence excitation spectra show no significant change. All of the bands in the optical spectra appear to belong to only one species (fluorescence excitation follows absorption). Thus, they are either all due to light absorption by the singlet ground state, whose fraction in the S_0–T_1 mixture should only vary between 95 and 86% over this temperature range, or else are all due to a completely unrelated species. The latter alternative is made extremely unlikely by the observation that at higher temperatures both the ESR and the UV signals exhibit a first-order decay in time and that all of the rate constants fall on the same straight line in an Arrhenius plot (119–133K, annealed 1-pentanol, $\Delta E_{act} = 4.5 \pm 0.6$ kcal/mol, $A = 10^{4.5\pm1}$ s^{-1}). Our failure to observe the UV-vis absorption of the T_1 state is understandable, since it comprises only a minor fraction of the mixture and its calculated (PPP[6]) transition energies and intensities lead us to suspect strong overlap with the UV–vis absorption of the S_0 state.


Ia, R = R′ = H
b, R = H; R′ = D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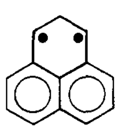
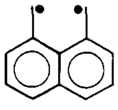
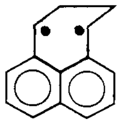

III


IV


V


VI

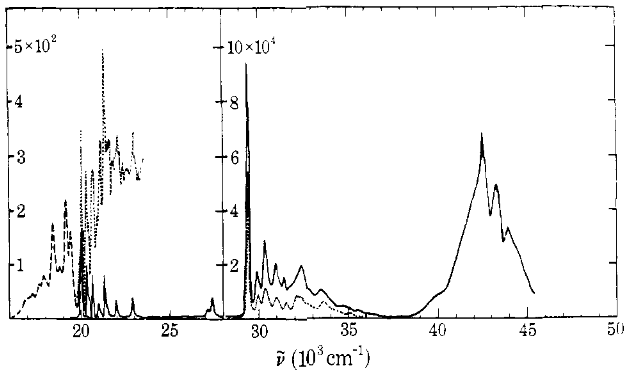


Figure 1. Absorption (—), fluorescence (- - -), and fluorescence excitation (· · ·) spectra of II (3-MP, 77 K). The excitation spectrum is on two unrelated scales.

The product of the thermal transformation of the new species is II, easily identified by its UV absorption, emission, and excitation spectra. Measurement of its rate of formation by UV absorption yields the same rate constants as above. Also, UV or visible irradiation of the new species produces II (77 K). Comparison of quantitative absorption spectra of I, of the new species, and of II showed that both photochemical steps are quantitative and this permitted us to estimate the extinction coefficients of the new species given in Figure 1 (uncorrected for the fraction present in T_1). Similarly, the thermal reaction is found to be quantitative in the thermal range given. At higher temperatures in 1-pentanol, and already at lower temperatures in less viscous glasses, thermal disappearance of the new species is more complex. The phenalenyl radical is observed in ESR and naphthalene-like absorption in UV spectra. Bimolecular reactions are presumably facile at these lower viscosities, and some return to I may be occurring as well.

On basis of the combined evidence, we postulate the planar structure III for the new species and presume that S_0–T_1 equilibration is rapid (cf. the related 1,8-naphthoquinodimethanes IV[7] ($D/\hbar c = 0.0218$ cm^{-1}, $E/\hbar c = 0.0021$ cm^{-1}, T_1 45 cal/mol above S_0, stable at 77 but not at 87 K) and V[8] ($D/\hbar c = 0.018$ cm^{-1}, $E/\hbar c < 0.003$ cm^{-1}, T_1 200 cal/mol above S_0), as well as the related localized 1,3 biradical, VI[9] ($D/\hbar c = 0.084$ cm^{-1}, $E/\hbar c = 0.0020$ cm^{-1}), with poorly resolved hyperfine structure). The larger S_0–T_1 splitting in III is readily assigned to the effect of cyclic hyperconjugation with the methylene group, which raises the energy of the symmetrical nonbonding orbital and leaves that of the antisymmetric nonbonding orbital essentially intact. Such splitting of the two orbitals should be even larger in VI (by about a factor of 1.5

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