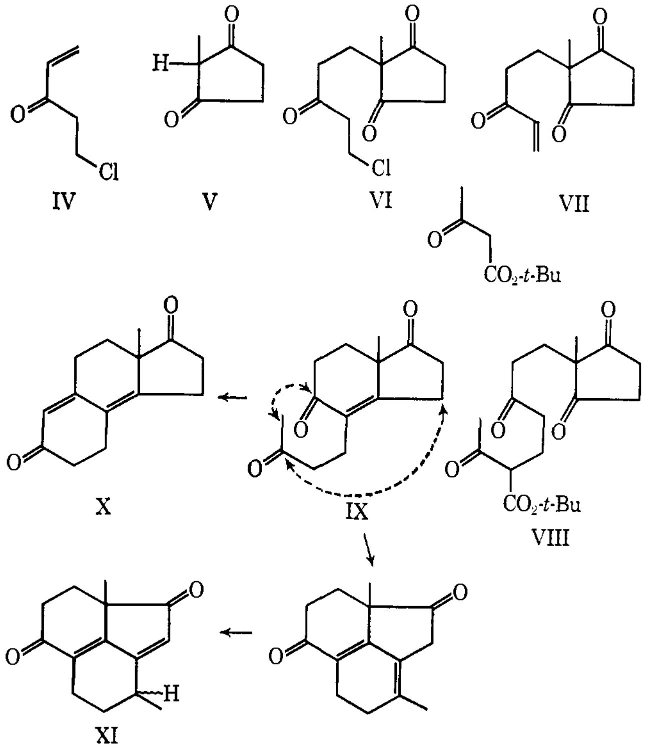
52 ± 2% yield (from VII) of the tricyclic ketone, X,[3,9,10] mp 56–58°; λ_{max}^{EtOH} 296 mμ (ε 17,500); $\lambda_{max}^{CHCl_3}$ 5.75, 6.01, 6.10, 6.30 μ; τ (CDCl$_3$) 4.22 (1 H), s; 8.80 (3 H), s. The genesis of X clearly entails the formation of the desired 2,6,10-triketo system, VIII, which undergoes some, as yet undefined, sequence of twofold cyclodehydration, *t*-butyl ester cleavage, and β-keto acid decarboxylation.



Two minor products each isolated in 3% yield bear on the sequence in the transformation of VIII → X. One of these is assigned as compound IX[3] by the correspondence of its melting point (95–96°) and spectral properties with those previously reported.[10] The other is assigned as a diastereomeric mixture corresponding to gross structure XI.[3] Its broad melting range (76–96°) and nmr (CDCl$_3$) spectrum [τ 8.67 and 8.72 (sum = 3 H), two doublets, J = 7Hz for each] attest to its being a mixture of two components, each bearing a secondary methyl group. Its infrared [$\lambda_{max}^{CHCl_3}$ 5.88 (conjugated cyclopentenone), 6.01, and 6.08 μ], nmr [τ 3.98 (1 H), s (vinylic hydrogen); 8.72 (3 H), s (angular methyl)], and mass [*m/e* 216 (P), 182 (base peak)] spectra support the assigned gross structure. A sequence which embodies these results is VIII → IX → X + XI.[11]

The CVK method has been applied to other cases and has led to the total synthesis of steroids. The results of these studies will be reported soon.

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[9] This compound was previously reported[10] as an oil. We obtained it in crystalline form by chromatography on silicic acid and crystallization from ether–hexane. The yield was obtained through gas chromatographic analysis and was reproducible in three runs under varying work-up conditions.

[10] O. I. Fedorova, G. S. Grinenko, and V. I. Maksimov, *Zh. Org. Khim.*, **4**, 611 (1968); *Chem. Abstr.*, **69**, 3061 (1968).

[11] While this sequence seems to be occurring, it is probably not the sole source of compound X. Thus, when a pure sample of compound IX was subjected to the simulated reaction conditions of TsOH–HOAc, the ratio of X:XI produced was 7:1. Since the reaction by way of VII produces these products in a ratio of *ca.* 17:1, a concurrent route to X which does not involve IX is suggested.

Acknowledgment. We are grateful to Dr. E. P. Oliveto and Hoffmann-LaRoche Inc., Nutley, N. J., for a generous gift of 2-methyl-1,3-cyclopentanedione. We thank the National Institutes of Health for its support of this research (Grants AM-08696-04 and 05) and for providing the LKB-9000 combined gas chromatograph–mass spectrometer used in these studies. We also thank Mr. John Naworal for recording the mass spectra.

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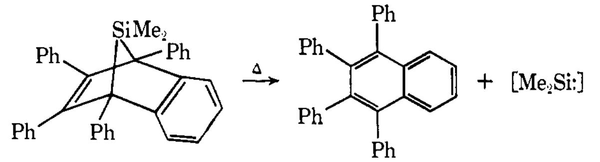
Received January 31, 1969

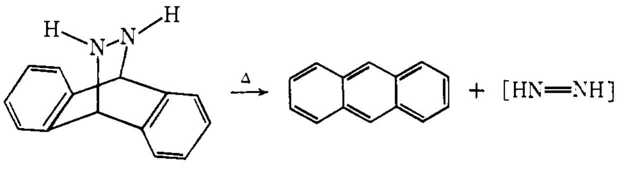
7,8-Disilabicyclo[2.2.2]-2,5-octadienes. An Approach to Tetramethyldisilene

Sir:

The thermal dissociation of bicyclo[2.2.1]heptadienes and of bicyclo[2.2.2]octadienes has been used to prepare a variety of unstable intermediates. Thus Gilman, Cottis, and Atwell[1] prepared dimethylsilene by the pyrolysis of **1** and Corey and Mock prepared diimide by the pyrolysis of **2**.[2] We wish to report the results of a systematic attempt to prepare tetramethyldisilene *via* the retrodiene reaction[3] of a 7,8-disilabicyclo[2.2.2]-octadiene.



1



2

The addition of a dilute solution of 1,2-dichlorotetramethyldisilane (0.4 mol) in THF (375 ml) to the dianion of anthracene (0.4 mol) in THF (450 ml) gave a mixture of products from which **3**, mp 162–164°[4] (2%), was isolated by recrystallization from ethanol. Similarly, the dianion of naphthalene gave **4**, mp 64–66°.[5]

At temperatures below 450°, **3** was stable. However, when heated for 12 hr at 500° it dissociated to give anthracene and a mixture of high molecular weight silicon compounds. By analogy with the proposals

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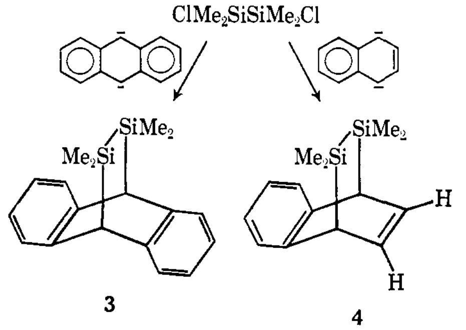
[1] H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 1596 (1964).

[2] E. J. Corey and W. L. Mock, *ibid.*, **84**, 685 (1962).

[3] H. Kwart and K. King., *Chem. Rev.*, **68**, 415 (1968).

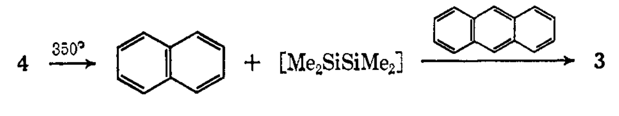
[4] The nmr spectrum (CCl$_4$) of 3 had singlets at τ 3.01, 6.29, and 10.13 with relative areas of 4:1:6, respectively. Satisfactory carbon–hydrogen analyses were obtained for all compounds reported.

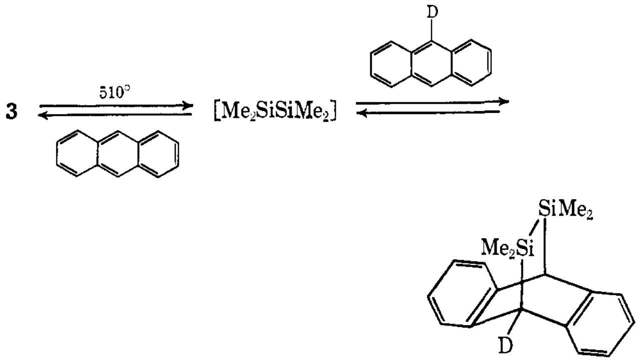
[5] The nmr spectrum of 4 had singlets at τ 2.95, 9.81, and 10.18 and multiplets at τ 3.97 and 6.61, with relative areas of 2:3:3:1:1, respectively.



for the reaction of $(SiF_2)_n$, $n = 1, 2, 3\ldots$,[6] the tetramethyldisilene formed by the retrodiene reaction of 3 would be expected to polymerize to give a mixture of organosilicon compounds. Similar polymers have been observed from the polymerization of other reactive organosilicon intermediates.[7,8]

Since tetramethyldisilene may be formed *via* a retrodiene reaction it seemed reasonable to attempt to trap it *via* a Diels–Alder reaction. When 4 was pyrolyzed for 12 hr at 350° in the presence of 2 equiv of anthracene quantitative transfer of the tetramethyldisilene bridge occurred to give 3 and naphthalene. Similarly when 3 was pyrolyzed at 510° for 2 hr in the presence of 10 equiv of 9-deuterioanthracene, exchange of the tetramethyldisilene bridge occurred to give a statistical mixture of 1-deuterated and undeuterated 3.





There is currently an increasing interest in the analogy between pyrolysis and electronolysis reactions.[9] One of the most extensively investigated systems is the analogous thermal and electron impact induced retrodiene reactions.[10,11] The mass spectra of 3 and 4 provided evidence that the most favored electronolysis reaction is dissociation to give the radical cation of tetramethyldisilene. Under electron impact using 10-V electrons 3 showed only two fragments $3\cdot^+$ (87%) and $Me_4Si_2\cdot^+$ (13%). At 15 eV three fragments were observed, $3\cdot^+$ (38%), $C_{14}H_{10}\cdot^+$ (3%), and $Me_4Si_2\cdot^+$ (59%). At 10 eV 4 gave only radical cations for $4\cdot^+$ (37%) and $Me_4Si_2\cdot^+$ (63%), and at 15 eV $4\cdot^+$ (20%) and $Me_4Si_2\cdot^+$ (80%).

All the fragments observed in the low-energy electronolysis of 3 and 4 arise *via* a retrodiene reaction. Further, the electron impact induced retrodiene reactions of 4 appear to be more facile than those of 3.

Thus the products from electronolysis of 3 and 4, the relative stabilities of 3 and 4 to electronolysis and pyrolysis, the thermally induced transfer of the bridge in 3 and 4 to another diene, and finally the analogy with previously studied decompositions in bicyclic dienes[1-3] all suggest the formation of tetramethyldisilene by the retrodiene reaction of 3 and 4.

Acknowledgment. This work was supported by the National Research Council of Canada.

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(6) R. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brinckman, T. C. Farrar, and T. D. Coyle, *J. Amer. Chem. Soc.*, **87**, 3818 (1965); P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *ibid.*, **88**, 940 (1966); H. P. Hopkins, J. C. Thompson, and J. L. Margrave, *ibid.*, **90**, 901 (1968); J. M. Bassler, P. L. Timms, and J. L. Margrave, *Inorg. Chem.*, **5**, 729 (1966); J. C. Thompson, J. L. Margrave, and P. L. Timms, *Chem. Commun.*, 566 (1966).

(7) O. N. Nefedov and M. N. Manakov, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1021 (1966).

(8) M. C. Flowers and L. E. Guselnikov, *J. Chem. Soc., B*, 419 (1968), and references therein.

(9) A. Maccoll in "Modern Aspects of Mass Spectrometry," R. I. Reed, Ed., Plenum Press, New York, N. Y., 1968, pp 143–168.

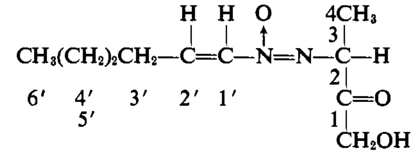
(10) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

(11) R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 5780 (1968).

A Novel α,β-Unsaturated Azoxy-Containing Antibiotic

Sir:

We wish to report the isolation and characterization of a potent, new antifungal agent, LL-BH872α, from *Streptomyces hinnulinus* n.s.[1] [Lederle Culture No. BH872]. Spectral and chemical evidence is presented to show that LL-BH872α has structure I.



$$\begin{array}{lcccccl}
 & \mathrm{H} & \mathrm{H} & \mathrm{O} & & & \mathrm{4CH_3} \\
 & | & | & \uparrow & & & 3| \\
\mathrm{CH_3(CH_2)_2CH_2}- & \mathrm{C}= & \mathrm{C}- & \mathrm{N}= & \mathrm{N}- & & \mathrm{C}-\mathrm{H} \\
6'\quad 4'\quad 3' & 2' & 1' & & & & 2| \\
\quad\; 5' & & & & & & \mathrm{C}{=}\mathrm{O} \\
 & & & & & & 1| \\
 & & & & & & \mathrm{CH_2OH}
\end{array}$$

I

The material is a light yellow oil which undergoes decomposition even when stored in the dark under nitrogen at −15°. It was obtained from the fermentation beer by solvent extraction followed by partition chromatography over acid-washed diatomaceous earth using a hexane–ethyl acetate–methanol–water system. The optically active oil ($[\alpha]^{25}\mathrm{D}$ $+157 \pm 1.7°$ (c 1.7, methanol)) has the formula $C_{10}H_{18}N_2O_3$ as indicated by a tiny molecular ion peak at m/e 214 in the mass spectrum. There is, however, a large peak at m/e 198 indicating the facile loss of an oxygen atom. Compound I forms a reasonably stable acetate. The mass spectrum of the acetate has a molecular ion peak of medium abundance at m/e 256 while the peak at m/e 240 indicates oxygen loss to be quite small.

The uv maximum of I at 238 mμ (ϵ 9000) is virtually identical with that of elaiomycin, a stable, tuberculostatic oil characterized by Stevens and others[2] which they showed to contain the then unique α,β-unsaturated azoxy chromophore.

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(1) We wish to thank Dr. H. Tresner of Lederle Laboratories for culture identification.

(2) C. L. Stevens, B. T. Gillis, J. C. French, and T. H. Haskell, *J. Am. Chem. Soc.*, **78**, 3229 (1956).