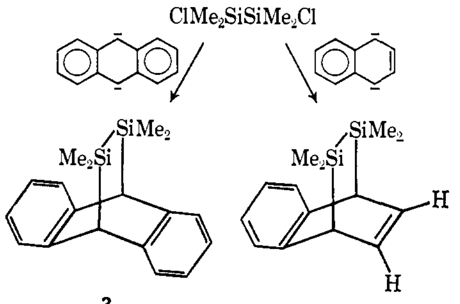
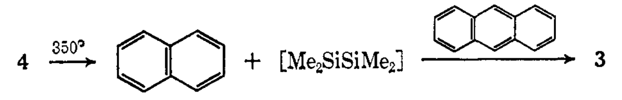
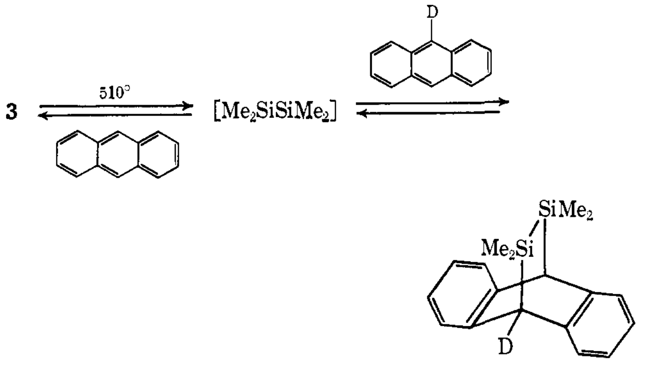


3 4

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 $\mathbf{3}^{\cdot +}$ (87%) and $Me_4Si_2^{\cdot +}$ (13%). At 15 eV three fragments were observed, $\mathbf{3}^{\cdot +}$ (38%), $C_{14}H_{10}^{\cdot +}$ (3%), and $Me_4Si_2^{\cdot +}$ (59%). At 10 eV **4** gave only radical cations for $\mathbf{4}^{\cdot +}$ (37%) and $Me_4Si_2^{\cdot +}$ (63%), and at 15 eV $\mathbf{4}^{\cdot +}$ (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**.

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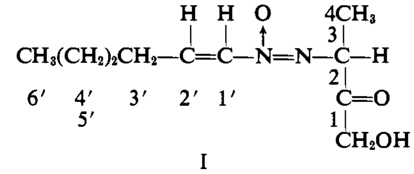
A Novel α,β-Unsaturated Azoxy-Containing Antibiotic

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.



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

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 ($[\alpha]^{25}D$ +157 ± 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.

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

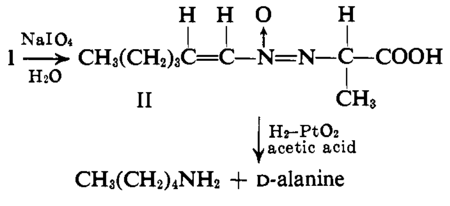
(2) C. L. Stevens, B. T. Gillis, J. C. French, and T. H. Haskell, *J. Am. Chem. Soc.*, 78, 3229 (1956).

The nmr spectrum of a freshly isolated sample of LL-BH872α is most revealing. A typical terminal methyl signal is observed at δ 0.90. A broad multiplet at δ 1.40 integrating for four protons represents the $C_{4'}$ and $C_{5'}$ methylene protons. Impressed on this multiplet is a ringing doublet ($J \sim$ 6–7 Hz) at δ 1.43 which is assigned to the C_4 methyl group. A multiplet consistent with the allylic $C_{3'}$ methylene group is centered at δ 2.62 and a fairly broad exchangeable signal at δ 3.25 is assigned to the hydroxyl hydrogen. A sharp doublet ($J \sim$ 2–3 Hz) integrating for two protons and located at δ 4.38 becomes a singlet in the acetate spectrum and shifts to δ 4.87 and hence is logically associated with the C_1 methylene protons. The single C_3 hydrogen appears as a quartet ($J \sim$ 6–7 Hz) at δ 4.65. The $C_{2'}$ vinyl proton appears to a first approximation as a quartet ($J \sim$ 9 Hz) centered at δ 5.83 indicating approximately equivalent coupling with the $C_{1'}$ vinyl proton and the $C_{3'}$ allylic protons. A doublet of triplets located around δ 6.83 accounts for the $C_{1'}$ vinyl proton. The doublet feature (J = 9 Hz) is due to *cis* coupling with the $C_{2'}$ vinyl proton while the triplet splitting ($J \sim$ 1.5 Hz) occurs because of allylic coupling with the $C_{3'}$ protons. Elaiomycin[3] exhibits an identical doublet of triplets at δ 6.83.

The acetate of I when reduced catalytically over 5% rhodium on alumina takes up 1 mol of hydrogen to give a colorless oil. The uv characteristics of this material with peak absorption at 223 mμ (ε 4600) and a broad shoulder at 275 mμ (ε 258) fit exactly those of the aliphatic azoxy compounds described by Langley and others[4] in their work on macrozamin.

In addition the ir spectrum of the reduced material exhibits the characteristic asymmetric stretching mode of the azoxy group at 1498 cm^{-1}. The nmr spectrum of the reduced compound is similar to that of the acetate of I except that the multiplet at δ 1.38 now integrates for the six protons associated with the $C_{5'}$, $C_{4'}$, and $C_{3'}$ carbons, the $C_{2'}$ methylene protons appear as a broad signal at δ 2.06, the $C_{1'}$ protons being adjacent to the electronegative azoxy group appear as a triplet (J = 7 Hz) at δ 4.25, and of course the vinyl proton area is blank.

Periodate oxidation[5] of I gives the acid II, an unstable oil which upon treatment with diazomethane gives the more stable methyl ester. Stevens, *et al.*,[6] cleaved the azoxy linkage of elaiomycin by hydrogenation over platinum dioxide in acetic acid to get D-threonine. Under similar conditions freshly prepared II was cleaved to get D-alanine which was isolated as the benzyloxycarbonyl derivative. Hence, LL-BH872α may be described as D-1-hydroxy-3-(1′-*cis*-hexenylazoxy)-2-butanone.



$$\mathrm{I} \xrightarrow[\mathrm{H_2O}]{\mathrm{NaIO_4}} CH_3(CH_2)_3\overset{H}{C}=\overset{H}{C}-\overset{\overset{O}{\uparrow}}{N}=N-\underset{CH_3}{\overset{H}{C}}-COOH$$

II

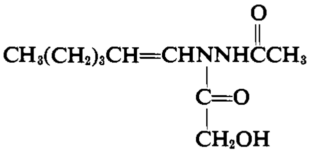
$$\big\downarrow{\scriptstyle H_2\text{–}PtO_2,\ \text{acetic acid}}$$

$$CH_3(CH_2)_4NH_2 + \text{D-alanine}$$

At room temperature I is converted in a few days in 50% yield to an optically inactive crystalline compound having the same formula, $C_{10}H_{18}N_2O_3$. Refluxing of I in methanol in the presence of sodium bicarbonate gives the crystalline compound in up to 90% yield in a few minutes.

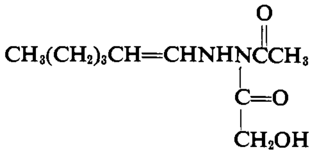
The crystalline conversion product yields valeraldehyde upon ozonolysis. When the same material is subjected to mild aqueous alkaline hydrolysis caproaldehyde is liberated, while refluxing with methanolic sodium hydroxide gives glycolic acid and a compound, mp 59–60°, with the formula $C_8H_{16}N_2O$ which is readily identified on the basis of its spectral properties as the acetylhydrazone of caproaldehyde. All physical data on this latter compound are identical with those on a synthetic material obtained by condensing acetylhydrazine with caproaldehyde.

Careful acidic hydrolysis of the crystalline conversion product yields caproaldehyde, glycolic acid, and the hydrochloride of acetylhydrazine. Based on the data cited, two possible structures, III and IV, may be written for the compound in question.



$$CH_3(CH_2)_3CH=CH\underset{\substack{|\\ C=O\\ |\\ CH_2OH}}{N}NH\overset{\overset{O}{\|}}{C}CH_3$$

III



$$CH_3(CH_2)_3CH=CHNH\underset{\substack{|\\ C=O\\ |\\ CH_2OH}}{N}\overset{\overset{O}{\|}}{C}CH_3$$

IV

Two further pieces of evidence confirm III as being the correct structure. The ir spectrum of the material shows strong carbonyl absorption at 1680 cm^{-1} and a weaker band at 1535 cm^{-1} which constitutes a classic example of the amide I and amide II bands of a secondary amide. It has been demonstrated that secondary amide vibrations are little affected by the presence of an additional nitrogen.[7] Structure IV does not contain a secondary amide.

Reduction of the double bond of this compound gives a crystalline material, mp 77–78°, $C_{10}H_{20}N_2O_3$, which is perfectly stable to methanolic alkaline conditions. Since reduction of the double bond in IV should not affect the elimination of the glycoloyl substituent the evidence again points to structure III. In addition the nmr spectrum of the material has a doublet signal ($J \sim$ 10 Hz, indicating *cis* vinyl coupling) located at δ 6.30 which is unchanged upon exchanging the N–H proton with deuterium, again pointing to structure III. Hence, the structure of the conversion product from LL-BH872α is 2-acetyl-1-glycoloyl-1-(1′-*cis*-hexenyl)-hydrazine.

In conclusion it is of interest to consider the mechanism of conversion I → III. Although few experimental data have been obtained to date which bear directly on the mechanism, a consideration of the conditions under which the conversion takes place along with theoretical aspects[8] indicates it is likely to occur *via* a 1,3 shift of the N-oxide oxygen to C_3 (probably as a hydroxyl), followed by intramolecular cyclization

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(3) Dr. T. H. Haskell of the Parke Davis Company graciously supplied us with a sample of elaiomycin.

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(8) We wish to thank Dr. A. S. Kende of the University of Rochester and Dr. H. E. Zimmerman of the University of Wisconsin for advice on mechanistic possibilities.

involving the nitrogen of the former N-oxide with C_1, and finally cleavage of the bond between C_2 and C_3 by a retrograde aldol-type condensation, all with appropriate isomerizations of the various enolic systems.

Acknowledgments. We wish to express our appreciation to our colleagues, Dr. P. Shu and staff for fermentations and large-scale concentration, Mr. L. Brancone and staff for microanalyses, Mr. W. Fulmor and staff for spectra and optical rotations, and Dr. J. Karliner for mass spectra.

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Proton Affinities of the Alkali Hydroxides

Sir:

Recent experiments in our laboratory have allowed measurements of the gas-phase equilibria of the reactions

$$M^+(OH_2)_{n-1} + H_2O = M^+(OH_2)_n \qquad (n-1, n)$$

where M^+ is the alkali ion. These measurements allow the determination of $\Delta H_{n-1,n}$ and $\Delta S°_{n-1,n}$ which are of interest in a number of fields including that of ionic solvation. These data will be published in a separate paper.[1] The enthalpy changes $\Delta H_{0,1}$ relating to the reaction

$$M^+ + H_2O = (MOH_2)^+ \qquad (0,1)$$

when combined with available thermochemical data allow the determination of the proton affinities of the (gaseous) alkali hydroxides. These proton affinities which are of considerable chemical interest especially when compared to those of other related compounds are the subject of the present communication.

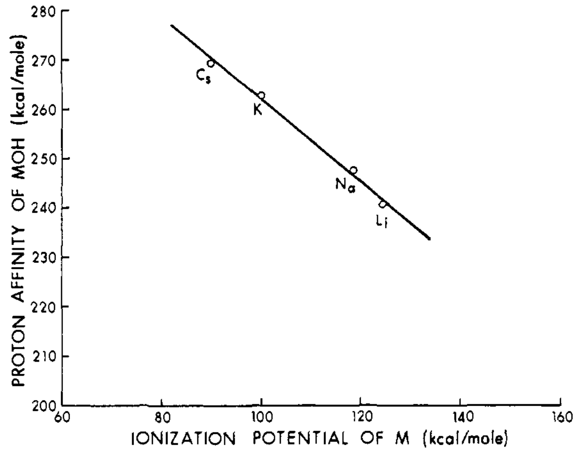

Figure 1.

The proton affinity (PA) of the hydroxides, corresponding to the exothermicity of the gas-phase reaction (eq 1), can be evaluated from the enthalpy of formation

$$MOH + H^+ = (MOH_2)^+ \quad PA(MOH) = -\Delta H_1 \qquad (1)$$

of the reactants. The enthalpies of formation of MOH and H^+ are available. The enthalpy of formation of $(MOH_2)^+$ can be evaluated from reaction 0,1 since $\Delta H_{0,1}$ was determined and $\Delta H_f(M^+)$ and $\Delta H_f(H_2O)$ are available. Thus the proton affinity is given by eq

$$PA(MOH) = \Delta H_f(MOH) - \Delta H_{0,1} - \Delta H_f(M^+) + \Delta H_f(H^+) - \Delta H_f(H_2O) \qquad (2)$$

2. The results and the data used for their calculation are given in Table I. The values $\Delta H_f(H^+) = 367$ and $\Delta H_f(H_2O) = -57.8$ kcal/mole were also used.

The proton affinities of the hydroxides which are in the range 240–270 kcal/mole are considerably larger than those of water, methanol, and ammonia which are approximately 170, 185, and 216 kcal/mole, respectively.[2] It has been pointed out[3,4] that in the series R–OH the proton affinity should increase with the electron-donating ability of the substituent R. The very high proton affinity of the alkali hydroxides can be thus understood in terms of the very high electron-donating ability of the substituent M. This ability is so extreme that in the protonated species essentially all the charge resides in M; *i.e.*, the resulting structure is that of the hydrated alkali ion as indicated by the conventional formula $M^+ \cdot OH_2$.

The variation of the proton affinity in the MOH series with the electron-releasing ability of M is illustrated in Figure 1, where the proton affinities are plotted as a function of the ionization potential of the alkali atoms, the rationale of the plot being that the electron-releasing ability decreases with the ionization potential of the alkali atom. It can be seen that an almost linear relationship is obtained. Considering the proton affinity as a measure of the base strength of a (gas phase) Brønsted base, we find that the base strength of the hydroxides increases from Li- o CsOH. This order of

Table I. Proton Affinities of Alkali Hydroxides MOH and Thermochemical Data Used for Their Evaluation[a]

	$\Delta H_f(M)$	$I_p(M)$[b]	$\Delta H_f(M^+)$	$-\Delta H_{0,1}$[c]	$\Delta H_f(M^+H_2O)$	$-\Delta H_f(MOH)$	PA(MOH)
Li	38.0	124.3	162.3	34	71.3	55	240.7
Na	25.9	118.5	144.4	24.0	63.4	56	247.6
K	21.6	100.1	121.7	17.9	46.8	57.6	262.6
Cs	18.7	89.8	108.5	13.7	37.8	60.0[d]	269.2

[a] All values in kcal/mole refer to gas-phase species at 300°K. All data except $\Delta H_{0,1}$ taken from Vedeneyev, *et al.*[2] [b] $I_p(M)$ = ionization potential of M. [c] From ref 1. [d] Estimated from heat of formation of other alkali hydroxides.

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