dibenzo crown ether is probably caused by a more effective shielding of the cation by the nonplanar dicyclohexyl crown ether.[9]

That the decrease in rate on addition of crown ether is due to a 1:1 complex with carbanion salt is demonstrated when larger than equimolar quantities were added. No further change in rate was observed. Particularly effective (150 times) in reducing the cleavage rate was the diazahexaoxobicyclic polyether, $N[CH_2CH_2(OCH_2CH_2)_2]_3N$ (Table I).[10] This is not unreasonable since in this case the metal ion is effectively shielded by the bicyclic cavity.

The cleavage reaction is most likely due to nucleophilic attack of carbanion or carbanion alkali pair on cation complexed ethylene oxide. Both ions, however, may exist in a variety of ionic forms such as ion pairs, triple ions, free ions, etc. Consequently, the reaction may proceed corresponding to a variety of kinetic orders having first- or second-order kinetics or a mixture thereof.[11] Not unexpectedly, therefore, the reaction in some cases was found to be between first and second order in carbanion concentration. A comparison between the pseudo-first-order rate constants of Table I is consequently not strictly correct, and the data have, therefore, only qualitative or semiquantitative significance. In the presence of sodium tetraphenylborate, however, FD^-Na^+ reacts according to first-order kinetics through 90% conversion, indicating a reaction between FD^-Na^+ and $Na^+BPh_4^-$ complexed EO. This is also suggested by the kinetic order of two observed in the absence of $BPh_4^-Na^+$. At higher FD^-Na^+ concentration the order decreases somewhat, possibly because of the formation of triple ions.[11]

It is anticipated that cation participation in these cleavage reactions is quite general. We observed similar phenomena in the cleavage of propylene oxide by alkali carbanions. Other obvious indications of cation participation in small ring cyclic ether cleavage reactions are the trimethylene oxide cleavage by fluorenyl salts. In this case the Li salt cleaves the ether rapidly and the Ba salt less so, while salts containing lower electrostatic field strength cations such as Na and K are essentially stable in this solvent.[12]

In conclusion it was shown that the differences in epoxide cleavage rate initiated by fluoradenyl alkali salts are due to specific cation effects[13] and not as was shown in other reactions[14] to the presence or absence of certain ion pair types or free ions.

Acknowledgment. This work was supported in part by the National Science Foundation, Grant GH-34512, and by the University of Florida through a stipend to one of us (C. J. C.).

(9) H. K. Frensdorff, *J. Amer. Chem. Soc.*, **93**, 600 (1971).

(10) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885 (1969). We thank Dr. Lehn for a sample of the ether.

(11) Kinetic orders expected in the cases below, for example, are: $FD^- + [M(EO)]^+ \rightarrow FDCH_2CH_2O^-M^+$, order 1; $M^+FD^- + M^+EOFD^- \rightarrow FDCH_2CH_2O^-M^+ + FD^-M^+$, order 2; $M^+FD^- + [M(EO)]^- \leftrightarrows [(M^+)_2EOFD^-]^+ \rightarrow FDCH_2CH_2O^-M^+ - M^+$, order 1.5, assuming that ion pair dissociation and triple ion formation constants are $\ll 1$. Kinetic orders between 1 and 2 are also expected if the proportion of the unreactive free anions is substantial.

(12) J. Smid and T. Hogen-Esch, unpublished results.

(13) Specific cation effects have recently been reported for alkyl–acyl migratory insertions: J. P. Collman, J. N. Cawse, and J. I. Braumann, *J. Amer. Chem. Soc.*, **94**, 5905 (1972); for proton transfer reactions: S. Bank and B. Bockrath, *ibid.*, **94**, 6076 (1972); T. E. Hogen-Esch and J. Smid, *ibid.*, **89**, 2764 (1967).

(14) See, for example, M. Shinohara, J. Smid, and M. Szwarc, *ibid.*, **90**, 2175 (1968).

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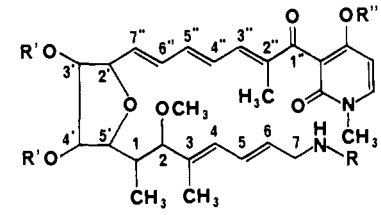
Antibiotic X-5108. IV. Structure of Goldinamine[1]

Sir:

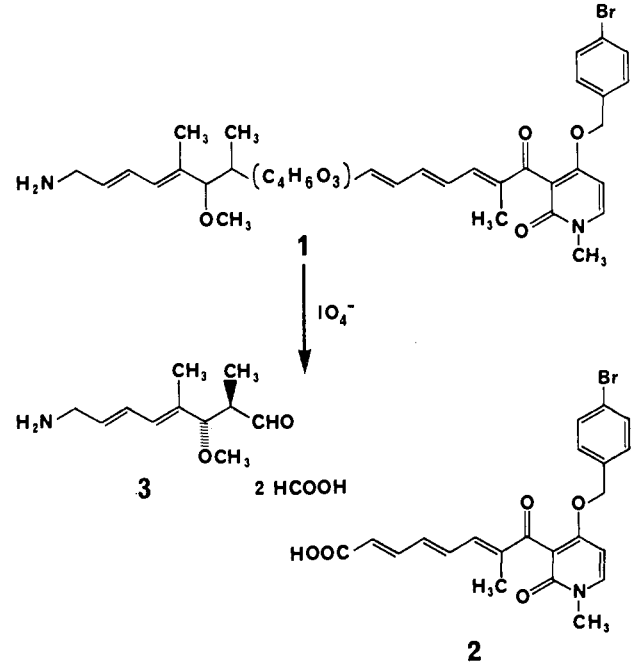
Goldinamine 4-bromobenzyl ether (**1**) is a degradation product of antibiotic X-5108 4-bromobenzyl ether[1] with an empirical formula of $C_{35}H_{43}BrN_2O_7$ derived from elemental analyses of **1** and derivatives thereof. The composition of goldinamine (**1e**), $C_{28}H_{38}N_2O_7$, was further confirmed by low- and high-resolution mass spectra of derivatives of **1d**.



1, R = R′ = H; R″ = 4-BrBzl (goldinamine 4-bromobenzyl ether)
1a, R = 2,4-DNP; R′ = H; R″ = 4-BrBzl
b, R = 2,4-DNP; 2R′ = $(CH_3)_2C$; R″ = 4-BrBzl
c, R = 2,4-DNP; R′ = CH_3CO; R″ = 4-BrBzl
d, R = R′ = H; R″ = (goldinamine methyl ether)
e, R = R′ = R″ = H (goldinamine)

Periodate oxidation of **1** (Scheme I) afforded **2**[1] and

Scheme I



an unstable aldehyde, **3**, or its enantiomer, which was characterized as the *N*-2,4-dinitrophenyl derivative and converted to methyl acetal **4**: mp 124°; $[\alpha]_D$ +34.7° (*c* 0.5, dioxane); $C_{19}H_{27}N_3O_7$, calcd mol wt 409, found *m/e* (%) 409 (<0.1), 377 (0.3), [M − MeOH], 75 (100).

(1) Paper III in this series: H. Maehr, J. F. Blount, M. Leach, A. Stempel, and G. Büchi, *Helv. Chim. Acta*, **55**, 3054 (1972).

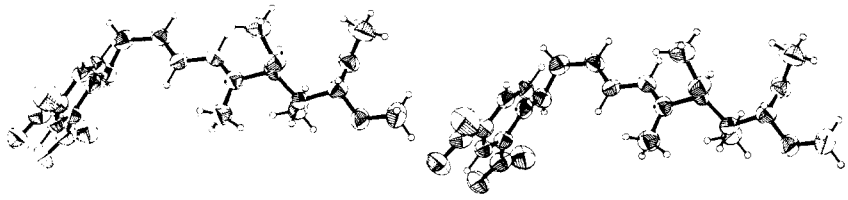
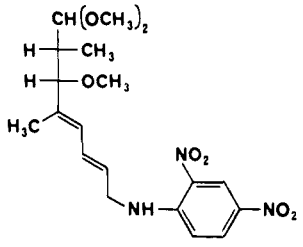


Figure 1. Stereodrawing of conformation of **4** in the crystal.



4

Crystals of **4** are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 7.945$ (5), $b = 9.026$ (8), $c = 29.22$ (2) Å, and $d_{calcd} = 1.297$ g cm^{-3} for $Z = 4$. The structure was elucidated by a multiple solution procedure.[2] Hydrogen atoms were located from a difference Fourier calculated after preliminary refinement of the structure. The final refinement was carried out by full-matrix least squares with anisotropic thermal parameters for all atoms except hydrogen atoms; the hydrogen atoms were held fixed at their calculated positions. The final discrepancy index, R, was 5.9%. A stereodrawing of the conformation of **4** in the crystal is shown in Figure 1.

Although the absolute stereochemistry of **4** could not be deduced from Roentgen data, gross structure, threo configuration and all-trans isomerism, was established.

The partial structure of **1** derived by degradation reactions is shown in Scheme I. In addition to fragments **2** and **3**, periodate oxidation of **1** liberated 2 mol of formic acid from the central $C_4H_6O_3$ moiety identified as a 2,5-disubstituted 3,4-dihyroxyfuran ring based on the following evidence.

N-Protected derivatives of **1** and **1d** readily formed di-*O*-acetyl and *O*-isopropylidene compounds and benzeneboronic acid esters; two of the unassigned oxygen atoms in **1** (Scheme I) are thus most likely vicinal, nontertiary hydroxyl groups. The 100-MHz nmr spectra of **1b** show, in addition to peaks due to the isopropylidene group and peaks indicative of the **2** and **3** moieties, signals for four hydrogen atoms bonded to carbon as follows: $\delta_{TMS}^{CDCl_3}$ 3.56 (m, H-5′, partly hidden by NCH_3), 3.98 (dd, H-2′, $J = 7$ and 4 Hz), 4.68 (m, H-3′ and H-4′). The corresponding signals were also found in spectra of **1a**: $\delta_{TMS}^{CDCl_3}$ 3.53 (dd, H-5′, $J_{1,5'} = 7$ and $J_{4',5'} = 4$ Hz), 4.17 (H-2′, masked by NCH_2), and 4.36 (m, H-3′ and H-4′). These spectral assignments were based on comparisons with those of the di-*O*-acetyl compound **1c**: $\delta_{TMS}^{CDCl_3}$ 2.19 (ddq, H-1, $J_{1,2} = 10$ and $J_{1,5'} = J_{1,Me} = 7$ Hz; irradiation at this field collapsed the H-2 doublet at δ 3.21 to a singlet, and the H-5′ dd at δ 3.92 to a doublet with $J_{4,'5'} = 4$ Hz), 4.59 (t, H-2′, $J_{2',3'} = J_{2'7''} = 7$ Hz; irradiation at this field collapsed the H-3′ dd at δ 5.42 to a doublet with $J_{3',4'} = 5$ Hz and the H-7′′ dd at δ 5.85 to a doublet with $J_{6'',7''} = 15$ Hz), 5.52 (dd, H-4′, $J_{3',4'} = 5$ and $J_{4'5'} = 4$ Hz).

The periodate oxidation products of **1** (Scheme I) are explained by inferring glycol cleavage of the 2,5-disubstituted 3,4-dihydroxytetrahydrofuran ring to afford a dialdehyde with subsequent enolization and oxidative cleavage of the 2′,3′ bond analogous to the periodate oxidation of 3-hydroxy-2-methoxy-2-cyclopentenone.[3] This would produce formic acid and an ester which, upon hydrolysis, yields the corresponding trienoic acid **2** and an α-hydroxyaldehyde, further degradable to formic acid and octadienal **3**. In analogy to 2,3-dihydroxy-2-cyclopentenone and related compounds,[3] oxidation of **1** proceeded with the transient appearance of free iodine.

Therefore, goldinamine (**1e**) is identified as 4-hydroxy-3-{2-methyl-1-oxo-7-[3,4-dihydroxy-5-(*threo*-7-amino-2-methoxy-1,3-dimethyl-3(*trans*),5(*trans*)-heptadienyl)-tetrahydro-2-furyl]-2(*trans*),4(*trans*),6(*trans*)-heptatrienyl}-1-methyl-2(1*H*)-pyridone.

Acknowledgment. We are grateful to Professor G. Büchi for helpful discussions.

(2) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).

(3) G. Hesse and K. Mix, *Chem. Ber.*, **92**, 2427 (1959).

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Antibiotic X-5108. V. Structures of Antibiotic X-5108 and Mocimycin[1,2]

Sir:

In previous communications[1,3] we reported the degradation of **2b** yielding goldinono-1,4-lactone-3,7-hemiketal and goldinamine 4-bromobenzyl ether. These degradation products account for all atoms of the antibiotic molecule. The structure of antibiotic X-5108 is represented by **2**; the primary amino group of goldinamine and the carboxyl group of goldinonic acid 3,7-hemiketal[3] form an amide bond linking the two moieties. This assignment is based on the absence of amino, carboxyl, and γ-lactone groups in the intact antibiotic and the formation of two fragments with amine[1] and γ-lactone[3] functions upon mild acid treatment of **2a** and **2b**.

(1) Paper IV in this series: H. Maehr, M. Leach, T. H. Williams, W. Benz, J. F. Blount, and A. Stempel, *J. Amer. Chem. Soc.*, **95**, 8448 (1973).

(2) The structure determination of antibiotic X-5108 was presented at the Gordon Research Conference on Natural Products, New Hampton, N. H., July 30–Aug 3, 1973.

(3) H. Maehr, J. F. Blount, R. H. Evans, Jr., M. Leach, J. W. Westley, T. H. Williams, A. Stempel, and G. Büchi, *Helv. Chim. Acta*, **55**, 3051 (1972).