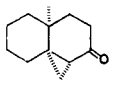
Table I. Production of Optically Active Cyclopropyl Ketones

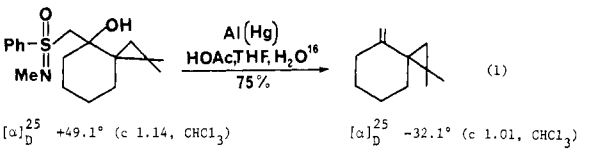
entry	method[a]	cyclopropyl ketone	$[\alpha]_D^{25}$ ($CHCl_3$), deg
1	A		+160.6 (*c* 2.17) −164.9 (*c* 2.33)
2	B		+15.3 (*c* 2.04) −15.5 (*c* 1.28)
3	A		+47.3 (*c* 0.51) −50.8 (*c* 1.31)
4	A		+162.3 (*c* 0.63) −171.9 (*c* 1.11)
5	A		+97.7 (*c* 1.76) −95.3 (*c* 1.47)
6	B		+215.3 (*c* 1.08) −214.5 (*c* 1.02)
7	A		+101.4 (*c* 2.09)

[a] Method A sequence: (1) addition of 1 to enone (yields ~95%); (2) separation of diastereomeric enone adducts by medium-pressure liquid chromatography on silica gel with EtOAc/hexanes (combined recovery 85–96%); (3) cyclopropanation (yields 77–96%); (4) thermal release of cyclopropyl ketone (yields 73–98%). Method B sequence: (1) addition of 1 to enone (yields ~95%); (2) cyclopropanation (yields 91–98%); (3) chromatographic separation (as above) of cyclopropanated adducts (combined recovery 65–98%); (4) thermal release of cyclopropyl ketones (yields 60–75%).

identical conditions gave, after chromatography, an 86% yield of the unnatural enantiomeric (+)-thujopsene (**9**) as a colorless oil, $[\alpha]^{25}_D$ +107.6° (*c* 2.04, $CHCl_3$) (98% optically pure). Alternatively the β-hydroxysulfoximines **5** and **6** were desulfurized with Raney nickel[13] and dehydrated to obtain the same products (**9** and **10**), but in reduced yield (~56%).

This new methodology for the optical activation of cyclopropyl ketones represents a viable alternative to other resolution[14] or asymmetric induction[15] techniques. Additional examples are shown in Table I. Generally both enantiomers are obtained in high optical purity, and the resolving reagent **1** can be readily recovered. In some instances, e.g., Table I, entries 2 and 6, it was found to be more expedient to separate the diastereomers after cyclopropanation. As anticipated, the method when applied to enones in which the carbonyl is acyclic presents special problems. The addition of **1** to 1-(1-cyclohexenyl)ethone (Table I, entry 7) provided readily separable diastereomeric adducts. Each of these pure diastereomers with nonrigid carbinol sites underwent the Simmons–Smith reaction to give two cyclopropyl diastereomers. From the enone adduct of lower R_f one of the cyclopropyl diastereomers was obtained pure by chromatography and thermolyzed to the ketone noted in Table I.

The resolved cyclopropanated adducts and ketones are amenable to further elaboration, e.g., **8** → **10** and eq 1, allowing for extensions of the utility of the method. Work is continuing on the exploration of the β-hydroxysulfoximine moiety as a chiral directing group in other additions to neighboring alkenes.



(1)

$[\alpha]^{25}_D$ +49.1° (c 1.14, $CHCl_3$) $[\alpha]^{25}_D$ −32.1° (c 1.01, $CHCl_3$)

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Registry No. 1, 33993-53-2; **2**, 17299-44-4; **3**, 82198-83-2; **4**, 82198-84-3; **5**, 82198-85-4; **6**, 82262-78-0; **7**, 82262-79-1; **8**, 7129-16-0; **9**, 82262-80-4; **10**, 470-40-6; (+)-4,4,6-trimethylbicyclo[4.1.0]heptan-2-one, 82198-86-5; (−)-4,4,6-trimethylbicyclo[4.1.0]heptan-2-one, 82198-87-6; (+)-bicyclo[4.1.0]heptan-2-one, 82334-95-0; (−)-bicyclo[4.1.0]heptan-2-one, 58072-38-1; (+)-1,1-dimethylspiro[2.5]octan-4-one, 82198-88-7; (−)-1,1-dimethylspiro[2.5]octan-4-one, 82198-89-8; (+)-1,1-dimethylspiro[2.4]heptan-4-one, 82198-90-1; (−)-1,1-dimethylspiro[2.4]heptan-4-one, 82198-91-2; (+)-4a-methylperhydrocyclopropa[*d*]naphthalen-2-one, 82262-81-5; (−)-4a-methylperhydrocyclopropa[*d*]naphthalen-2-one, 82262-82-6; (+)-4,4-dimethylbicyclo[4.1.0]heptan-2-one, 82198-92-3; (−)-4,4-dimethylbicyclo[4.1.0]heptan-2-one, 82198-93-4; (+)-1-acetylbicyclo[4.1.0]heptane, 82198-94-5; 4,4a,5,6,7,8-hexahydro-4a-methyl-2(3*H*)-naphthalenone, 826-56-2; methyl bromide, 74-83-9.

(13) Johnson, C. R.; Stark, C. J. *J. Org. Chem.* **1982**, 47, 1193.

(14) For example, partially resolved 2-cycloalken-1-ols have been cyclopropanated by the Simmons–Smith method followed by oxidation to optically active cyclopropyl ketones: Hill, R. K.; Morgan, J. W. *J. Org. Chem.* **1968**, *33*, 927. Lightner, D. A.; Jackman, D. E. *Tetrahedron Lett.* **1975**, 3051. A cyclopropyl ketone has been converted to an amine which was resolved with (−)-malic acid followed by regeneration of the ketone in optically active form: Zimmerman, H. E.; Hancock, K. G.; Licke, G. C. *J. Am. Chem. Soc.* **1968**, *90*, 1892.

(15) Enones have been transformed to optically active cyclopropyl ketones by using optically active oxosulfonium ylides: Johnson, C. R.; Schroeck, C. W. *J. Am. Chem. Soc.* **1968**, *90*, 6852. A cyclopropyl ketone of low ee has been obtained in a Simmons–Smith reaction of an enone in the presence of (−)-menthol: Sawada, S.; Oda, J.; Inouye, Y. *J. Org. Chem.* **1968**, *33*, 2141.

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Metathesis of Tungsten–Tungsten Triple Bonds with Acetylenes and Nitriles To Give Alkylidyne and Nitrido Complexes[1]

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We recently reported that $W(CCMe_3)(OCMe_3)_3$ will rapidly and catalytically convert an unsymmetric alkyne into a mixture containing the unsymmetric alkyne and the two possible symmetric alkynes (alkyne metathesis).[2] Although the catalyst is long-lived in the absence of air and water, we thought it possible that it is eventually deactivated by bimolecular decomposition of intermediate $W(CR)(OCMe_3)_3$ species to give $W_2(OCMe_3)_6$[3] or by some as yet undefined reaction involving β protons in the alkylidyne ligand. The fact that we found no evidence for bimolecular decomposition suggested to us that that $W_2(OCMe_3)_6$ would react with alkynes to give the alkylidyne complexes $W(CR)(OCMe_3)_3$. We report here that first, this is indeed the case, second, that alkylidyne complexes that contain β protons in the alkylidyne ligand can be isolated, and third, that nitriles also react with $W_2(OCMe_3)_6$ to give a mixture of $W(N)(OCMe_3)_3$ and $W(CR)(OCMe_3)_3$. This metathesis-like reaction of a W≡W bond is not only an excellent route to tungsten alkylidyne complexes but is a unique example of rapid cleavage of a W≡W bond at 25 °C by mild reagents.[4]

(1) Multiple Metal–Carbon Bonds. 27.

(2) (a) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932. (b) Sancho, J.; Schrock, R. R. *J. Mol. Catal.* **1982**, *15*, 75.

(3) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

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An approximately 0.1 M solution of $W_2(OCMe_3)_6$[5] in benzene reacts completely with 1 equiv of 4-octyne at ~25 °C in less than 1 h to give $W(CPr)(OCMe_3)_3$ quantitatively (eq 1). If a large

$$(Me_3CO)_3W{\equiv}W(OCMe_3)_3 + RC{\equiv}CR \rightarrow 2(Me_3CO)_3W{\equiv}CR^7 \quad (1)$$
$$(R = Me, Et, Pr)$$

excess of 4-octyne is added the reaction is over in minutes. A sample of $W(CPr)(OCMe_3)_3$ prepared in this manner is identical in all respects with one prepared by reacting $W(CCMe_3)(OCMe_3)_3$ with excess 4-octyne.[8,9] The reaction between $W_2(OCMe_3)_6$ and 3-hexyne is even faster, and between $W_2(OCMe_3)_6$ and 2-butyne the fastest, to yield $W(CEt)(OCMe_3)_3$ and $W(CMe)(OCMe_3)_3$, respectively. All three compounds (especially the last) sublime readily at room temperature. In pure form they are all colorless.

$W_2(OCMe_3)_6$ does not react with diphenylacetylene to give known, thermally stable $W(CPh)(OCMe_3)_3$[2a] before it decomposes extensively (refluxing benzene). However, EtC≡CPh does react to give a mixture of $W(CEt)(OCMe_3)_3$ and $W(CPh)(OCMe_3)_3$. Since the benzylidyne complex appears to be more favored thermodynamically[2b] it is convenient to add 2 equiv of EtC≡CPh to $W_2(OCMe_3)_6$ in order to form $W(CPh)(OCMe_3)_3$ exclusively (eq 2). Similarly, while $Me_3SiC{\equiv}CSiMe_3$ will not react readily

$$(Me_3CO)_3W{\equiv}W(OCMe_3)_3 + 2EtC{\equiv}CR \rightarrow 2(Me_3CO)_3W{\equiv}CR + EtC{\equiv}CEt \quad (2)$$
$$(R = Ph, SiMe_3, -CH{=}CH_2)$$

with $W_2(OCMe_3)_6$, $EtC{\equiv}CSiMe_3$ does (eq 2). Two equivalents of 1-hexen-3-yne react readily with $W_2(OCMe_3)_6$ to give $W(CCH{=}CH_2)(OCMe_3)_3$. All the reactions in eq 2 are quantitative.

$W_2(OCMe_3)_6$ reacts rapidly with 1 equiv of acetonitrile or benzonitrile to give the alkylidyne complexes quantitatively and sparingly soluble, but sublimable, white fluffy needles of $W(N)(OCMe_3)_3$ (eq 3).[10] The fact that benzonitrile reacts with

$$(Me_3CO)_3W{\equiv}W(OCMe_3)_3 + RC{\equiv}N \rightarrow (Me_3CO)_3W{\equiv}CR + (Me_3CO)_3W{\equiv}N \quad (3)$$

$W_2(OCMe_3)_6$ almost as readily as acetonitrile does suggests that the nitrile reaction may allow us to prepare some alkylidyne complexes that we cannot prepare from $W_2(OCMe_3)_6$ and an alkyne.

In contrast to the reactions of $W_2(OCMe_3)_6$, neither $W_2(NMe_2)_6$[12] nor $W_2(CH_2SiMe_3)_6$[13] reacts with 4-octyne. Both $W(CPr)(NMe_2)_3$ and $W(CPr)(CH_2SiMe_3)_3$ are expected to be stable since white, sublimable $W(CCMe_3)(NMe_2)_3$[14] and yellow $W(CSiMe_3)(CH_2SiMe_3)_3$[16,17] are both known. Reactions involving $W_2Cl_6(THF)_4$[6] or $W_2Cl_2(NMe_2)_4$[18] and acetylenes also do not appear to be analogous to those involving $W_2(OCMe_3)_6$.

It is interesting to note that alkyne adducts (ethyne, propyne, 2-butyne) of $M_2(OCHMe_2)_6$ (M = Mo or W) of the type $M_2(OR)_6(py)_2(C_2H_2)$ have been structurally characterized (py = pyridine). In $Mo_2(OCHMe_2)_6(py)_2(C_2H_2)$[19] the ethyne is bound to both metals perpendicular to the Mo≡Mo bond in a manner well-known for $M_2(\mu$-alkyne) complexes in which M is in a lower oxidation state (e.g., in $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}C_2H_2)$[20]), two of the isopropoxide ligands are bridging, and the C–C distance (1.368 Å) is longer than that in ethylene. In $W_2(OCHMe_2)_6(py)_2(C_2H_2)$, which is isostructural with $Mo_2(OCHMe_2)_6(py)_2(C_2H_2)$, the C–C distance is 1.413 (19) Å.[21] It is logical to assume that a molecule containing the cagelike $M_2(OR)_2(C_2R_2)$ unit is the immediate precursor to a monomeric alkylidyne complex, but we cannot exclude the possibility that a molecule containing a square-planar M_2C_2 core, with or without additional bridging ligands, is actually the immediate, and perhaps required, precursor. In either case an important question is whether $Mo_2(OCMe_3)_6$,[22] a compound that presumably is isostructural with $Mo_2(OCH_2CMe_3)_6$[22] and $W_2(OCMe_3)_6$,[23] will also react with alkynes and nitriles to give known $Mo(CCMe_3)(OCMe_3)_3$[24] and $Mo(N)(OCMe_3)_3$. Surprisingly, $Mo_2(OCMe_3)_6$ does *not* react with excess 4-octyne or propionitrile, even after several hours at 80 °C.[25]

To our knowledge the results reported here are the first examples of a metathesis-like reaction involving a metal–metal multiple bond. In addition to a few other possible reactions of X≡X or X≡Y molecules with M≡M bonds, it is now perhaps also worthwhile to at least consider the possibility that certain X=X or X=Y molecules (O_2, ketones, olefins, etc.) might react cleanly with the unfortunately rather rare[4b,c] M=M double bond to give monomers containing M=X or M=Y bonds.

Acknowledgment. R.R.S. thanks the National Science Foundation for generous support of this research (Grant CHE 82-21282). M.L.L. thanks the National Science Foundation for a predoctoral fellowship. L.G.S. acknowledges a postgraduate scholarship from the Natural Sciences and Engineering Research Council of Canada.

Registry No. $W_2(OCMe_3)_6$, 57125-20-9; $W(CPh)(OCMe_3)_3$, 82228-87-3; $W(CMe)(OCMe_3)_3$, 82209-23-2; $W(N)(OCMe_3)_3$, 82209-24-3; $W(CPr)(OCMe_3)_3$, 82209-25-4; $W(CEt)(OCMe_3)_3$, 82228-88-4; EtC≡CPh, 622-76-4; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $EtC{\equiv}CSiMe_3$, 62108-37-6; $W(CCH{=}CH_2)(OCMe_3)_3$, 82209-26-5; $W_2(NMe_2)_6$, 54935-70-5;

(4) (a) Metal–metal triple bonds (M = Mo or W)[4b,c] have been cleaved by NO,[4d,e] aryl azides,[4f] molecular oxygen,[4f] carbon monoxide,[4g] and bipyridyl.[4h] (b) Chisholm, M. H., Ed. "Reactivity of Metal–Metal Bonds"; American Chemical Society, Washington, D.C. 1981; ACS Symp. Ser. No. 155. (c) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982. (d) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 3354. (e) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116. (f) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C.; Ratermann, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 1305. (g) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *Ibid.* **1979**, *101*, 7615. (h) Chisholm, M. H.; Huffmann, J. C.; Rothwell, I. P. *Ibid.* **1981**, *103*, 4945.

(5) We prepared $W_2(OCMe_3)_6$ by the unexceptional, high-yield reaction of $LiOCMe_3$ with $W_2Cl_6(THF)_4$.[6] The yield of $W_2(OCMe_3)_6$ from the reaction between $W_2(NMe_2)_6$ and *tert*-butyl alcohol[3] was not reported, but in our hands this route overall gives $W_2(OCMe_3)_6$ in much lower yield than the above route. Details of this and related reactions of $W_2Cl_6(THF)_4$ will be reported separately.

(6) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.

(7) δC_α = 254 (R = Me), 263 (R = Et), 262 (R = Pr) in C_6D_6.

(8) Pedersen, S. F., unpublished results.

(9) This reaction is driven to give $W(CPr)(OCMe_3)_3$ by removing lower boiling $Me_3CC{\equiv}CPr$ in vacuo. If the initial metathesis product is not the most volatile, the end result upon removing all volatiles is largely $W(CCMe_3)(OCMe_3)_3$.

(10) Anal. Calcd for $WC_{12}H_{27}O_3N$: N, 3.36. Found: N, 3.56. ν_{WN} = 1010 cm^{-1} (Nujol). $W(N)(OCMe_3)_3$ has also been prepared by reacting $[W(N)Cl_3]_x$ with $LiOCMe_3$.[8] It may be a tetramer in the solid state with a square array of W≡N→W bonds analogous to the structure of $[Mo(N)Cl_3]_4$.[11]

(11) (a) Dehnicke, K.; Strähle, J. *Angew Chem., Int. Ed. Eng.* **1981**, *20*, 413. (b) Strähle, J. *Z. Anorg. Allg. Chem.* **1971**, *96*, 380.

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(14) This species was prepared by adding $LiNMe_2$ to $[NEt_4][W(CCMe_3)Cl_4]$[2a] in THF.[15] Anal. Calcd for $WC_{11}H_{27}N_3$: C, 34.30; H, 7.07. Found: C, 34.08; H, 6.88.

(15) Sancho, J. Ph.D. thesis, Massachusetts Institute of Technology, 1982.

(16) Rocklage, S. M.; Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1981.

(17) Andersen, R. A.; Chisholm, M. H.; Gibson, J. F.; Reichert, W. W.; Rothwell, I. P.; Wilkinson, G. *Inorg. Chem.* **1981**, *20*, 3934.

(18) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407.

(19) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1981**, *103*, 4245.

(20) Bailey, W. I. Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

(21) Chisholm, M. H.; Huffman, J. C.; Leonelli, J., In "Proceedings of Inorganic Chemistry Towards the 21st Century"; Indiana University, May 16–19, 1982, M. H. Chisholm, Symposium Chairman; *ACS Symp. Ser.*

(22) Chisholm, M. H.; Reichert, W. W.; Cotton, F. A.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 1801.

(23) The structure of neither $Mo_2(OCMe_3)_6$ nor $W_2(OCMe_3)_6$ has been determined. There is no compelling reason to suspect that they are not isostructural nor significantly different from the known structure of $Mo_2(OCH_2CMe_3)_6$.[22]

(24) The route to prepare $Mo(CCMe_3)(OCMe_3)_3$[25] is analogous to that used to prepare $W(CCMe_3)(OCMe_3)_3$.[2]

(25) McCullough, L. G., unpublished results.

$W_2(CH_2SiMe_3)_6$, 36643-37-5; $W(CPr)(NMe_2)_3$, 82209-27-6; $W(CPr)(CH_2SiMe_3)_3$, 82209-28-7; $W(CCMe_3)(NMe_2)_3$, 82209-29-8; $W(CSiMe_3)(CH_2SiMe_3)_3$, 78638-62-7; $W_2Cl_6(THF)_4$, 77479-88-0; $W_2Cl_2(NMe_2)_4$, 63301-81-5; $Mo_2(OCHMe_2)_6(py)_2(C_2H_2)$, 78736-93-3; $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}C_2H_2)$, 64973-91-7; $W_2(OCHMe_2)_6(py)_2(C_2H_2)$, 82281-73-0; $Mo_2(OCMe_3)_6$, 60764-63-8; $Mo_2(OCH_2CMe_3)_6$, 62521-24-8; $Mo(CCMe_3)(OCMe_3)_3$, 82209-30-1; $Mo(N)(OCMe_3)_3$, 82209-31-2; 4-octyne, 1942-45-6; 3-hexyne, 928-49-4; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; 1-hexen-3-yne, 13721-54-5; acetonitrile, 75-05-8; benzonitrile, 100-47-0; ethyne, 74-86-2; propyne, 74-99-7; propionitrile, 107-12-0.

Structure of the Glycopeptide Antibiotic Vancomycin. Evidence for an Asparagine Residue in the Peptide

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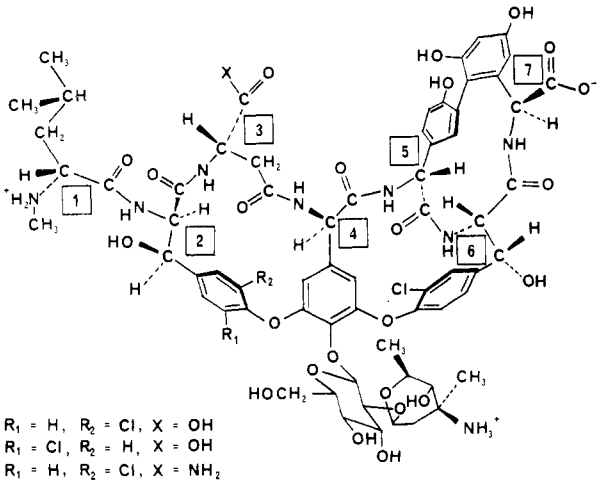
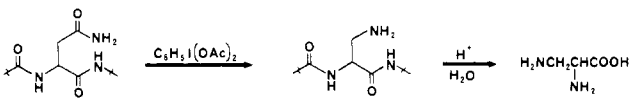
Vancomycin and related antibiotics have recently been the subject of intense investigation with respect to their structures and mechanism of action.[1] None of the antibiotics have yielded crystals of sufficient size and quality to permit structural solution by X-ray crystallography, but vancomycin undergoes a slow transformation on heating at pH 4–5 to a crystalline degradation product (CDP-I)[2] for which structure **1a** was obtained by Sheldrick et al.[3] Williams,[4,5b] Feeney,[5] and their co-workers have made extensive chemical and spectroscopic studies of vancomycin and have concluded that the only major structural difference between vancomycin and CDP-I is the presence of an isoasparaginyl residue in the antibiotic and an isoaspartyl residue in the degradation product. Although unusual structural features are common in peptide antibiotics, the vancomycin structure (**2**) attracted our attention because of the possibility that the unique isoasparagine residue might actually be the more common asparagine, with rearrangement to isoaspartate occurring during hydrolysis to form CDP-I. Examples of aspartyl → isoaspartyl rearrangements have been documented during acid and base treatment of peptides containing aspartate esters and asparagine.[6]



1a, R_1 = H, R_2 = Cl, X = OH
b, R_1 = Cl, R_2 = H, X = OH
2a, R_1 = H, R_2 = Cl, X = NH_2
b, R_1 = Cl, R_2 = H, X = NH_2

Scheme I



Two approaches were taken to search for the presence of a normal asparagine in vancomycin. In the first of these, vancomycin aglycone,[2b] treated with CH_2N_2 to protect the phenolic hydroxyl groups, was reduced with diborane in THF[7] and hydrolyzed.[8] Ion-exchange chromatography[8] of the hydrolysate gave a minor component having the same retention time, ninhydrin color, and TLC behavior as 2,4-diaminobutyric acid, which is the product that would result from reduction of the β-carboxamido group of asparagine. Acylation of the amino acid with benzoyl chloride followed by esterification (CH_2N_2) gave the *N,N*-dibenzoyl methyl ester, which was identical by TLC, MS, and ^1H NMR with authentic material. No 3,4-diaminobutyric acid (which would be the product from reduction of isoasparagine) was detected; neither was any 2,4-diaminobutyric acid detected in hydrolysates of unreduced material. The yield of 2,4-diaminobutyric acid was very low because diborane reduces secondary peptide linkages more rapidly than it reduces the primary amide of the asparaginyl group.

The second approach for establishing the presence of the asparaginyl residue involved a Hofmann-type oxidative degradation of the primary carboxamide (Scheme I).[9] Treatment of O-methylated aglycovancomycin with 5 equiv of (diacetoxyiodo)benzene (18 h, 20 °C, 1:1 CH_3CN/H_2O) followed by peptide hydrolysis and ion-exchange chromatography[8] gave the asparagine degradation product 2,3-diaminopropionic acid, identical in all respects (TLC, ninhydrin color, ^1H NMR) with authentic material. Quantitative amino acid analysis was complicated by the fact that a significant portion of O-methylated aglycovancomycin is resistant to acid hydrolysis under the conditions that were employed; hydrolysis of unoxidized O-methylated aglycovancomycin gave only 51% of the theoretical yield of aspartic acid. Analysis of the products of oxidative degradation indicated an 18% yield of 2,3-diaminopropionic acid and 13% yield of unaltered aspartic acid. It was not feasible to force the oxidative degradation to completion by the use of a larger excess of oxidant or more vigorous conditions because the free amino group of the diaminopropionyl residue is also susceptible to oxidation. The oxidative degradation was repeated with vancomycin itself to avoid the risk that an isoasparagine → asparagine rearrangement occurs during formation of the protected aglycone.[10] The oxidation again gave 2,3-diaminopropionic acid although the yield was lower on account of depletion of the oxidant by reaction with the phenolic groups and/or condensation of the new amino group with quinoidal products resulting from phenolic oxidations. Isoasparagine, had

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(10) Such a rearrangement appears unlikely since the aglycone retains much of the antibiotic activity of the parent antibiotic.[2b]

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