ried out to eliminate the possibility that radioactivity found in echinulin was due to degradation of the ^{3}H-MICAT to small tritiated compounds which would serve as precursors of echinulin. Table I compares the incorporation of ^{14}C and ^{3}H from the doubly labeled MICAT into samples of echinulin isolated in experiment 3. The results indicate the same ratio of ^{14}C to ^{3}H in MICAT as observed in echinulin, indicating that echinulin biosynthesis from metabolic breakdown products of MICAT is highly improbable.

Table I. Incorporation of ^{3}H,^{14}C-MICAT into Echinulin

	Radioactivity			Moles isoprene^a/mole cyclic dipeptide
	^{14}C μCi $\times 10^{+5}$	^{3}H μCi $\times 10^{+3}$	(μCi ^{14}C/ μCi ^{3}H) $\times 10^{-2}$	
^{3}H,^{14}C-MICAT	5.80	1.53	3.79	1.16
Echinulin fraction from silica gel chromatography	2.59	0.68	3.81	1.17
Recrystallized echinulin	2.91	0.76	3.83	1.17

^{a} Specific activities were determined as previously described.[3] Ratios are accurate to ±10%.

It is apparent from these experiments that monoisoprenylated *cyclo*-L-alanyl-L-tryptophanyl is a good biosynthetic precursor of echinulin and is a likely intermediate on the natural metabolic pathway.

Acknowledgments. I wish to thank Mr. Joseph Nolan for his technical assistance. This work was also supported in part by the Florida Foundation for Future Scientists.

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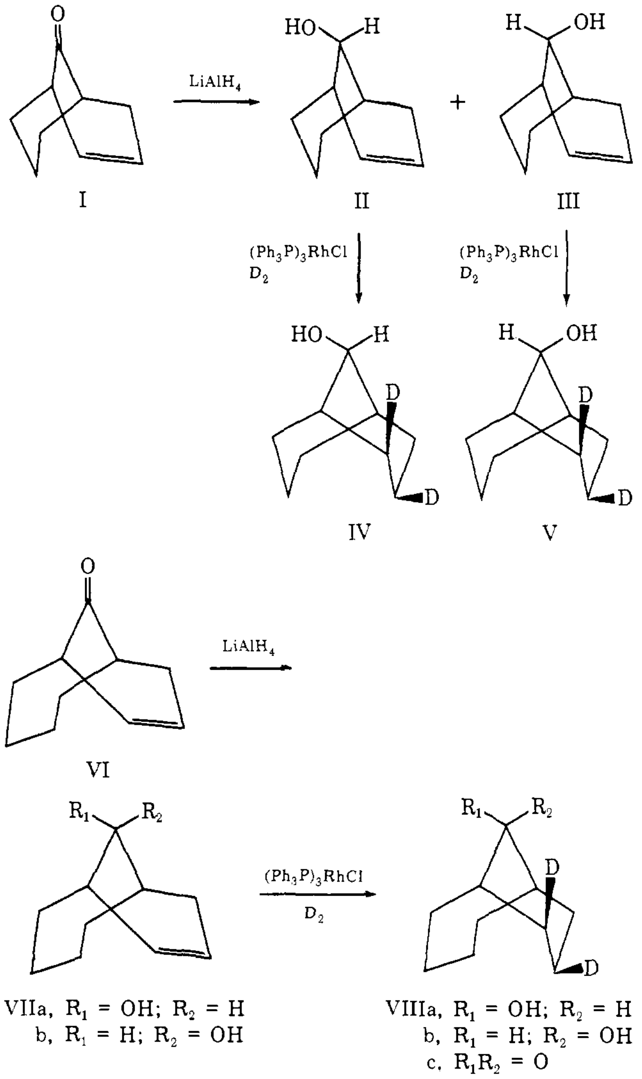
An Unequivocal Stereochemical Assignment by Mass Spectrometry

Sir:

There have been many attempts to utilize mass spectrometry for stereochemical assignments in cyclic systems,[1] and considerable effort also has been devoted to analyzing those factors which determine the specificity of mass spectrometric loss of water from cyclic alcohols.[2] Although it seems reasonably well accepted that such specificity as exists in this elimination process in six-membered rings (1:4 cis > 1:3 loss) is determined by the spatial relationships of the hydroxyl group with neighboring hydrogen atoms in the molecular ion (proximity effects), attempts to use this acquired knowledge for stereochemical assignments have not proved to be particularly convincing.[1] Green[2b] has predicted that "deuterium labeling studies of electron impact induced elimination reactions are the likely road to gain the so far unrealized but expected potential for mass spectrometry in stereochemical studies." We wish to report the use of precisely this approach to determine the configuration of the hydroxyl substituent on the bridging carbon atom in 2-bicyclo[4.3.1]decen-10-ol.



While undertaking a general study into the specificity of mass spectrometric water loss in isomeric bicyclo[3.3.1]nonanols,[3] we had occasion to prepare two cis deuterated 9-ols IV and V. These were readily available *via* lithium aluminum hydride reduction of 2-bicyclo[3.3.1]nonen-9-one (I) followed by homogeneous catalytic reduction of the double bond using tris(triphenylphosphine)rhodium chloride and deuterium gas in dry benzene solution. The anti (II) and syn (III) compounds were separated by preparative gas chromatography. In order to substantiate that specific cis deuteration had occurred at the exo face in II and III, the pmr spectra of IV and V were analyzed using the Eu(FOD)$_3$ shift reagent to separate the proton signals.[4] From the relative magnitudes of the proton shifts, the reduction in peak integration values, the splitting patterns, and the effect of the deuterium substitution on the signal shapes of adjacent protons, it was confirmed that these assignments were correct. Be-

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(1) For a general review, see S. Meyerson and A. W. Weitkamp, *Org. Mass Spectrom.*, 1, 659 (1968).

(2) (a) M. M. Green, R. J. Cook, J. M. Schwab, and R. B. Roy, *J. Amer. Chem. Soc.*, 92, 3076 (1970), and references therein; R. S. Ward and D. H. Williams, *J. Org. Chem.*, 34, 3373 (1969); (b) M. M. Green and R. B. Roy, *J. Amer. Chem. Soc.*, 92, 6368 (1970).

(3) J. K. MacLeod, M. R. Vegar, and R. J. Wells, *Recent Develop. Mass Spectrosc., Proc. Int. Conf. Mass Spectrosc.*, 1197 (1970).

(4) A similar study on *exo*-3-bicyclo[3.3.1]nonanol has been reported: M. R. Vegar and R. J. Wells, *Tetrahedron Lett.*, 2847 (1971).

cause the relative intensity of the molecular ion in 9-bicyclo[3.3.1]nonanol is low (*ca.* 2%), the deuterium content in IV and V was calculated from the molecular ion in the low voltage mass spectra of the corresponding ketone[5] to which the two alcohols were converted by Jones' oxidation.[6]

Under low voltage (nominal 12 eV) electron impact conditions the molecular ions of the deuterated 9-bicyclo[3.3.1]nonanols IV and V lost H_2O and HDO in the ratio of 100:0 and 10:90, respectively.[7] This is in accord with the results obtained from previous studies of deuterated cyclohexanols,[2] that 1:4 cis and to a lesser extent 1:3 loss are the predominant modes of water elimination from six-membered rings in mass spectrometry. That the hydroxyl substituent retained its stereochemical identity in the mas sspectral (M^+ − water) decomposition of the two isomers rules out any appreciable α cleavage which is thought to precede 1:3 water elimination, and therefore we conclude that 1:4 cis loss is the major contributor (>80%).[8] Use of this result to confirm the original anti and syn assignments to II and III, respectively, lead us to believe that this technique could be applied to deduce stereochemistry in similar bicyclic systems.

2-Bicyclo[4.3.1]decen-10-one (VI) is the product of the resin-catalyzed condensation and subsequent dehydration of 3-(2′-oxocycloheptyl)propanal, the method[9] being a general one for the synthesis of bicyclo[*n*.3.1]alk-2-enones ($n > 2$). Reduction of the ketone using a variety of reagents gave a single alcohol as product (VIIa or b), the stereochemistry of which could not be definitely ascertained from its ir and pmr spectra, *in the absence of the other stereoisomer.* After carrying out the homogeneous catalytic deuteration of VII the mass spectrum of the product, 10-bicyclo[4.3.1]-decanol-2,3-d_2 (VIIIa or b; 5% d_1, 88% d_2, 7% d_3) was recorded. This showed that the molecular ion predominantly lost H_2O (>96%) thereby ruling out structure VIIIb, a result that could only be interpreted[10] as establishing an anti configuration VIIa for the parent 2-bicyclo[4.3.1]decen-10-ol. Oxidation of VIIIa by Jones' reagent[6] to the saturated ketone VIIIc followed by lithium aluminum hydride reduction gave a product whose mass spectrum exhibited losses of H_2O (>96%) and HDO identical with those in the original alcohol, indicating that those factors responsible for a selective hydride attack on the ketone in VI were also acting in the reduction of VIIIc.

In a similar case, Marshall and Partridge[11] reported some difficulty in confirming the assignment of the stereochemistry at C-10 in a methyl substituted 2-bicyclo[4.3.1]decen-10-ol. Again, a single isomer was formed stereoselectively from reduction of the corresponding unsaturated ketone. The authors proposed that it was probably the anti isomer since trigonal hybridization at C-10 should favor the boat-cycloheptane ring conformation for the ketone and inhibit hydride attack from the 4-carbon tetramethylene face. This assignment was subsequently confirmed by chemical means. It appears obvious therefore that mass spectrometry coupled with deuterium labeling offers a simple and unequivocal alternative method of verifying such assignments in this bicyclic system.

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(5) From a typical preparation the isotopic composition of IV was calculated to be 2% d_1, 78% d_2, 20% d_3; that of V, 5% d_1, 54% d_2, 41% d_3. Although reductions were carried out under conditions known to exclude or minimize scrambling in simple systems (R. L. Augustine and J. F. Van Peppen, *Chem. Commun.*, 495 (1970)) different preparations of the catalyst all produced similar deuteration results. Exchange has previously been observed in the reduction of some substituted cyclohexenes (A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, **91**, 672 (1969)) and larger ring cycloalkenes (J. G. Atkinson and M. O. Luke, *Can. J. Chem.*, **48**, 3580 (1970)). From the pmr spectral study of V it was evident that the d_3 species was deuterated in the 2-, 3-, and 4-exo positions.

(6) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 142.

(7) From the mass spectra of different preparations of IV and V the reproducibility of results was ±2% for IV and ±5% for V. If the loss from V is calculated from the d_3 value, it is 5:95 ± 2%; based on the d_2 isotopic species it is 12:88 ± 2%.

(8) This is supported by the observed 86% HOD loss from *exo*-3-bicyclo[3.3.1]nonanol-*9,9*-d_2.[3]

(9) R. D. Allan and R. J. Wells, *Aust. J. Chem.*, 23, 1625 (1970); R. D. Allan, B. G. Cordiner, and R. J. Wells, *Tetrahedron Lett.*, 6055 (1968).

(10) The possibility of a completely specific endo approach by the reducing agent to compound VII in the boat-cycloheptane ring conformation was considered to be untenable since models suggest that the cycloheptane chair conformation will be preferred when the carbon at C-10 is tetrahedral (see ref 11).

(11) J. A. Marshall and J. J. Partridge, *Tetrahedron*, **25**, 2159 (1969).

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Received November 27, 1972

Structure of the $[HFe(CO)_4]^-$ Anion

Sir:

The geometry of $HCo(CO)_4$ has been the subject of one of the classic controversies in inorganic chemistry.[1] The issues in question were (i) whether the hydrogen atom occupied a "sterically active" position in the molecule (*i.e.*, whether the coordination about the metal was tetrahedral or trigonal bipyramidal) and (ii) whether the metal–hydrogen distance was "short" (1.2–1.4 Å) or "long" (~1.6 Å).

The structure of $HCo(CO)_4$ itself has never been solved by diffraction methods; this is probably due to the fact that the compound is quite unstable (it decomposes above −20°). We have, however, been able to isolate suitable single crystals of the isoelectronic anion $[HFe(CO)_4]^-$, whose geometry is generally regarded to be closely related to that of $HCo(CO)_4$. In this communication we describe the structure determination of the $[HFe(CO)_4]^-$ ion.

$[HFe(CO)_4]^-$ was prepared by a standard method[2] and precipitated as its $[(Ph_3P)_2N]^+$ salt by addition of a methanolic solution of $[(Ph_3P)_2N]^+Cl^-$.[3] Recrystallization from a hot 1:1 ethanol–ethyl acetate mixture produced very pale yellow plate-like crystals of $[(Ph_3P)_2N]^+[HFe(CO)_4]^-$. *Crystal data:* space group $P2_1/c$ (monoclinic); $a = 17.701$ (9), $b = 9.136$ (4), and $c = 22.251$ (12) Å; $\beta = 95.87$ (4)°; $V = 3579$ Å³, $Z = 4$; $d_{\text{measd}} = 1.29$, $d_{\text{calcd}} = 1.31$. Two quadrants of data were collected on a fully automated Nonius CAD-3

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(1) Accounts of this controversy have been given on several occasions: (a) J. A. Ibers, *Annu. Rev. Phys. Chem.*, **16**, 375 (1965); (b) A. P. Ginsberg, *Transition Metal Chem.*, **1**, 112 (1965); (c) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, p 33.

(2) R. B. King, "Organometallic Syntheses," Vol. I, Academic Press New York, N. Y., 1965, p 96.

(3) J. K. Ruff and W. J. Schlientz, *Inorg. Syn.*, in press.