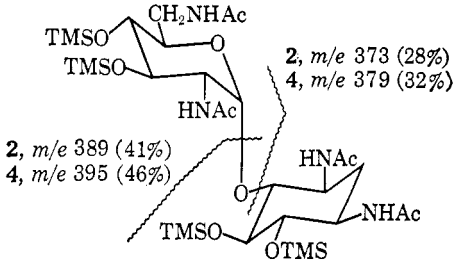
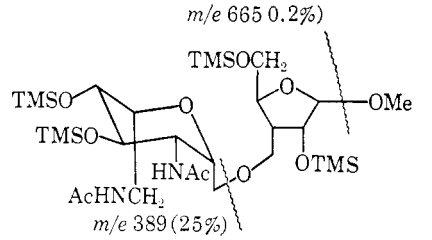
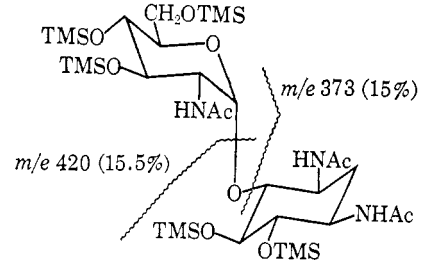
Prominent peaks at *m/e* 389 are also present in the mass spectra of model compounds **2** and **3** and shift to *m/e* 395 in the spectrum of the d_6 analog **4**. The mass spectra of compounds **5** and **6** have peaks at *m/e* 420, as does the spectrum of **1**. A few other important peaks are indicated in **2**–**6**. All peak intensities are relative to *m/e* 73, $(CH_3)_3Si^+$.



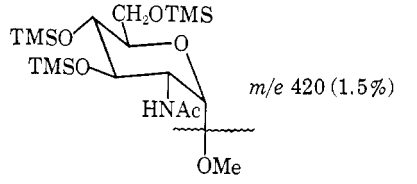
2, Ac = CH_3CO (M − CH_3, *m/e* 763, 8%)
4, Ac = CD_3CO (M − CH_3, *m/e* 775, 11%)



3 (M − CH_3, *m/e* 681, 4%)



5 (M − CH_3, *m/e* 794, 4%)



6 (M − CH_3, *m/e* 436, 13%)

From these data, it is possible to recognize the sequential arrangement and gross structures of the units of which the saccharides are comprised. Differences in stereochemistry and ring size most likely will not affect the indicated fragmentation paths. Compound **1** shows a preferential cleavage of glycosidic bonds, placing the charge on the carbon next to a ring oxygen where it can be stabilized by the nonbonding electrons on oxygen. Although all of the mass spectra in this study exhibited only minute molecular ion peaks (0.2–1% relative intensity), molecular weights can be readily determined from the more intense peaks 15 mass units lower.

Whereas the characterization of various amino and deoxy sugars derived from antibiotic substances has been successfully accomplished by mass spectrometric techniques,[4,9,10] the detailed analysis of intact antibiotics containing sugars is still relatively unexplored.[4] The few recorded examples belong to the class of macrolide (chalcomycin,[10] pimaricin,[11] and aldgamycin[12]) and nucleoside (cordycepin,[13] puromycin[14]) antibiotics. The present investigation represents the first reported example of the application of mass spectrometry to the study of the gross structure of *intact* aminocyclitol antibiotics. It demonstrates the potential usefulness of this technique in providing crucial information concerning the structure of related compounds, from submilligram quantities of the appropriate derivatives and from minutes of instrument time. Experiments on the electron-impact-induced fragmentation of related aminocyclitol antibiotics are in progress.

(9) D. C. DeJongh and S. Hanessian, *J. Am. Chem. Soc.*, **87**, 3744 (1965); **88**, 3114 (1966).
(10) K. L. Rinehart, Jr., R. F. Schimbor, and T. H. Kinstle, *Antimicrobial Agents Chemotherapy*, 119 (1965).
(11) O. Ceder, *Acta Chem. Scand.*, **18**, 126 (1964); B. T. Golding, R. W. Rickards, W. E. Meyer, J. B. Patrick, and M. Barber, *Tetrahedron Letters*, 3551 (1966).
(12) M. P. Kunstmann, L. A. Mitscher, and N. Bohonos, *ibid.*, 389 (1966).
(13) S. Hanessian, D. C. DeJongh, and J. A. McCloskey, *Biochim. Biophys. Acta*, **117**, 480 (1966).
(14) S. H. Eggers, S. I. Biedron, and A. O. Hawtrey, *Tetrahedron Letters*, 3271 (1966).
(15) The support of the Public Health Service of the Department of Health, Education, and Welfare, through Grant AI 07570, is gratefully acknowledged.

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Received April 1, 1967

Metal–Ammonia Reduction of Nonconjugated Dienes and Enones[1]

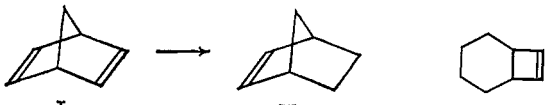
Sir:

A consequence of a structurally imposed close proximity of two nonconjugated double bonds is that the energy of the lowest antibonding orbital of one is raised while that of the other is lowered. One of the several consequences of this which might be anticipated is the increased ability of the molecule to accept an electron in the relatively low energy antibonding orbital. It might be expected that the activation energy will be lowered and the equilibrium constant raised for the reversible process $M + e^- \rightleftarrows M\cdot^-$. An example of this structural feature is norbornadiene (I). It appears to have no resonance energy in the ground state, and thus can in no sense be considered aromatic, but it has a significant 2–6 bonding contribution in the excited state.[2] A spectroscopic manifestation of this is its relatively long wavelength untraviolet absorption (λ_{max} 211 mμ). We wish now to describe a chemical consequence of this perturbation, the reduction of such nonconjugated dienes and enones by metal–ammonia systems.

The reduction of I with sodium or lithium in carefully dried ammonia (−33°) afforded norbornene (II) in 98% yield.[3] No evidence for even traces of

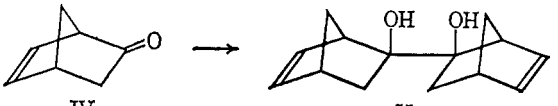
(1) The authors are indebted to the National Science Foundation, Grant GP 6757, and to the University of Utah Research Fund for the support of this study.
(2) C. F. Wilcox, S. Winstein, and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

norbornane or nortricyclene in the product could be found.[4] To rule out the possibility that the difference in ease of reduction of I and II might be due to their difference in strain energy rather than to a double bond perturbation in I, a cyclobutene (III) was examined and found to be inert.



I II III

Norbornenone (IV, λ_{max} 301 mμ (ε 292)) was found to be reduced under these conditions to a mixture of diastereomeric pinacols (V).[7] Similar treatment of norbornanone (λ_{max} 287 mμ (ε 29)) gave only recovered starting material.

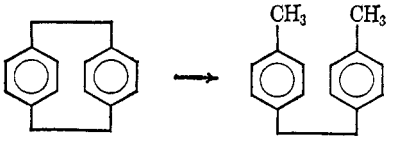


IV V

It is thus clear that the light absorption properties of a molecule, which reflect the difference between its ground- and excited-state energies, may be used qualitatively to predict the ease with which it can accept an electron in its lowest lying antibonding orbital. The energy of the excited molecule will obviously be different from that of the radical ion which is intermediate to the reduction product because the latter possesses one more electron.

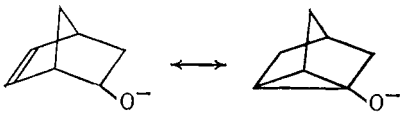
This correlation predicts that a number of other types of compound might also be reducible by metal–ammonia systems. 1-*t*-Butyl-3,3-dimethylcyclopropene (VI,[8] λ_{max} 195 mμ (ε 4400)) was examined and found to be reduced extremely rapidly to the corresponding cyclopropane[8] (VII, 85%). Similarly, [2.2]paracyclophane (VIII)[9] underwent reduction to di-*p*-tolylethane (IX, 100%) under conditions employed with other substrates.

VI VII



VIII IX

An intriguing question posed in the facile reductions of I and IV is whether or not nonclassical radical ions are involved. Particularly in the reduction of IV there can be little doubt that the intermediate X is extremely long-lived relative to typical nonconjugated radical ions. Repeated attempts[10] to obtain evidence for nonclassical behavior in the norbornenyl radical have failed, and it appears there is none. The radical ion in question here is electronically quite different, however, and its pronounced stability (long life) is suggestive of a nonclassical structure. An alternate



X

rationale based on steady-state concentration differences of radical ions cannot be dismissed (M + $e^- \rightleftarrows M\cdot^-$, k_1 being very different but k_{-1} being similar for norbornanone and norbornenone), but it is considered unlikely.

(3) "Isolated" double bonds are not reduced without an added proton source and even then only terminal double bonds are affected: H. Greenfield, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, 76, 1258 (1954).

(4) The reduction of I to norbornane and nortricyclene with lithium in ethylamine (Benkeser conditions[5]) has been reported.[6] It should be noted that this technique is effective in reducing virtually all isolated double bonds.

(5) R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, *J. Org. Chem.*, 28, 1094 (1963), and many references cited therein.

(6) J. G. Trayhnam, *ibid.*, 25, 833 (1960).

(7) The mixture (60%, mp 80–83°) was not separated but gave satisfactory nmr, infrared, and mass spectral data and analyzed correctly for $C_{14}H_{18}O_2$. Periodic acid cleaved it to norbornenone (83%).

(8) T. C. Shield and P. D. Gardner, manuscript in preparation.

(9) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, 76, 6132 (1954), describe the spectral properties of [2.2]paracyclophane. We are indebted to Professor Cram for a generous sample of this material.

(10) *Cf.* C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, 31, 3381 (1966), and references cited therein.

(11) National Science Foundation Predoctoral Fellow, 1962–1963.

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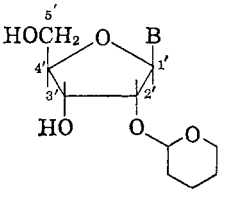
A Symmetrical Alternative to the Tetrahydropyranyl Protecting Group

Sir:

An obvious inherent disadvantage in the use of the tetrahydropyranyl group for the protection of optically active alcohols is that it leads to the introduction of an additional asymmetric carbon center (or centers), and thereby to mixtures of diastereoisomers being obtained.[1]



I

In connection with our work on oligoribonucleotide synthesis,[2] we undertook the preparation of a series of 2′-O-tetrahydropyranyl ribonucleosides (I) and obtained mixtures of diastereoisomers.[3] Although the latter could be separated and obtained crystalline,[4] the yield of pure isomer did not normally exceed 50%. However, after an unsuccessful attempt to isolate a pure crystalline 2′,5′-bis(tetrahydropyranyl) ribonucleoside derivative, the search for an alternative, symmetrical acid-labile protecting group become more urgent. Unlike other workers engaged in oligoribonucleotide synthesis,[5] we have concluded[3] that the tetrahydropy-

(1) C. W. Greenhalgh, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 1190 (1951); A. N. de Belder, P. J. Garegg, B. Lindberg, G. Petropavlovskii, and O. Theander, *Acta Chem. Scand.*, 16, 623 (1962).

(2) B. E. Griffin and C. B. Reese, *Tetrahedron Letters*, 2925 (1964).

(3) B. E. Griffin, M. Jarman, and C. B. Reese, *Tetrahedron*, in press.

(4) As it is intended that the synthetic oligomers should contain only 3′→5′ internucleotidic linkages, it is a reasonable precaution to use only pure crystalline 2′-protected ribonucleoside derivatives (*e.g.*, I) as intermediates.

(5) D. H. Rammler and H. G. Khorana, *J. Am. Chem. Soc.*, 84, 3112 (1962); J. Smrt and S. Chládek, *Collection Czech. Chem. Commun.*,