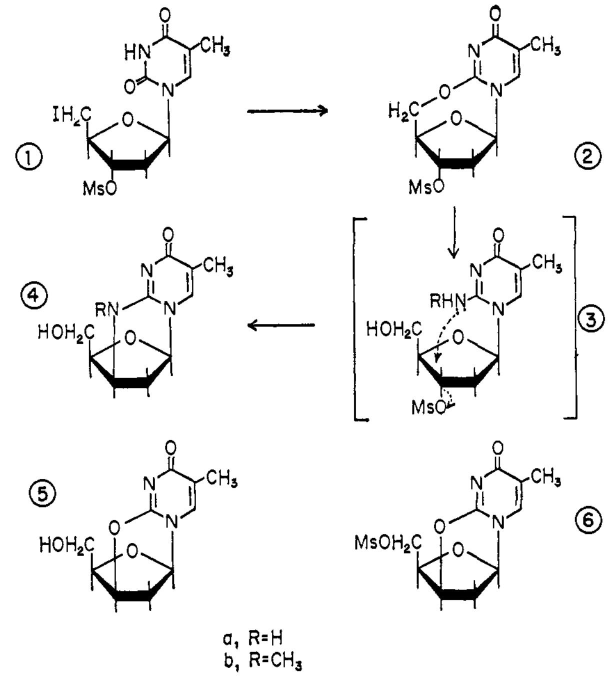
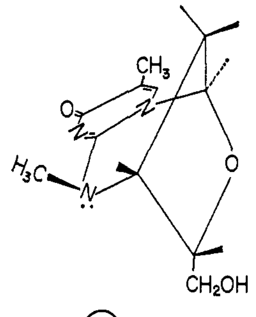
Chart I



Treatment of **2** with liquid ammonia for 5 days at room temperature yielded a crystalline product, **4a** (from ethanol), in 85% yield, mp 258–261° dec, $[\alpha]^{26}\text{D}$ +23° (*c* 0.7, 0.1 *N* HCl), $\lambda_{\max}^{N\,\text{HCl}}$ 240 (ϵ 7440) and 266 mμ (ϵ 8100); $\lambda_{\min}$ 218 (ϵ 4850) and 250 mμ (ϵ 7050). *Anal.* Found for $C_{10}H_{13}N_3O_3$: C, 53.54; H, 5.87; N, 19.05. Proof of structure of **4a** rests on the following. The ultraviolet absorption spectrum of **4a** in 1 *N* HCl resembles that for 1-β-D-arabinofuranosyl-5-methylisocytosine[2] (maxima at 225 and 260 mμ). Compound **4a** was sulfur free (ammonium mesylate was present in the reaction mixture). The nmr spectrum of **4a** in DMSO-d_6 shows a broad singlet (1 H) at δ 9.65 (>NH) and a broad triplet (1 H) at δ 5.16 (–OH), both of which were exchanged by the addition of D_2O. As expected, the $H_{3'}$ signal (broad multiplet) in **4a** centered at δ 3.52 is shifted considerably upfield when compared with the $H_{3'}$ signal (δ 5.31) of 2,3′-anhydro-1-(2-deoxy-β-D-*threo*-pentofuranosyl)thymine (**5**),[7] which further supports the 2,3′-imino bridge structure for **4a**.

Final confirmation of the structure of **4a** was obtained by the synthesis of **4b** (72% yield) by treatment of **2** with methylamine for 5 days at room temperature. Crystalline **4b** (from water) exhibited the following properties: mp 343–345° dec, $[\alpha]^{26}\text{D}$ ~0° (*c* 0.7, 0.1 *N* HCl), $\lambda_{\max}^{N\,\text{HCl}}$ 244 and 270 mμ ($\epsilon_{\max}$ 9450 and 8030, respectively), $\lambda_{\min}$ 220 and 260 mμ ($\epsilon_{\min}$ 6150 and 7760, respectively). *Anal.* Found for $C_{11}H_{15}N_3O_3$: C, 55.60; H, 6.32; N, 17.82. The ultraviolet absorption spectrum of **4b** in acid is similar to that for **4a**. The nmr spectrum in DMSO-d_6 of **4b** exhibits (in addition to the C_5 methyl doublet at δ 1.76) a sharp singlet for N–CH_3 at δ 3.14. The fact that the N–CH_3 signal was not split provides further confirmation of the 2,3′-imino bridge in **4b** and thereby in **4a**. It is clear that the isocytidine derivatives (**3**) are intermediates which formed *in situ* during the over-all conversion of **2** and **4**.

Compounds **4** may be viewed as derivatives of 2,4-diaza-6-oxabicyclo[3.2.1]octane which, to our knowledge, is a new ring system. From an examination of a



④c

molecular model, the methyl group on nitrogen probably exists as the *exo* conformer as shown in **4c**. The alternate *endo* conformer would not be favored due to steric hindrance imposed by the bulky 4′-hydroxymethyl group of the sugar moiety.[8]

The synthesis of nitrogen bridge analogs of other anhydronucleosides is currently under investigation in these laboratories along with a study of their chemical properties.

Acknowledgment. The authors are indebted to Dr. Robert J. Cushley for assistance in the interpretation of the nmr spectra.

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[7] The authors are indebted to Mrs. N. C. Miller for a sample of **5**.

[8] An nmr study of the conformation of the N–CH_3 group is contemplated.

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The Stereochemistry of Deamination of *cis*- and *trans*-2,3-Butenimines with Difluoramine

Sir:

The deamination of aziridines by means of difluoramine was reported previously to give nitrogen and olefin.[1]

In view of the recent development of the Woodward–Hoffmann theory, which has so successfully predicted the stereochemical course of many organic reactions,[2] it seemed of interest to determine the course of the deamination reaction of an aziridine which could yield products of different stereochemistry. This experiment seemed especially timely because Hoffmann has predicted that, according to the orbital symmetry theory, the elimination of nitrogen from a three-membered ring should be nonstereospecific.[3] The correlation diagram, kindly prepared by Dr. D. M.

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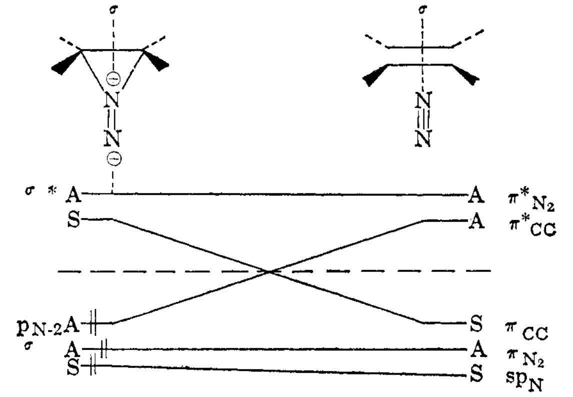
[1] C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Am. Chem. Soc.*, **85**, 98 (1963).

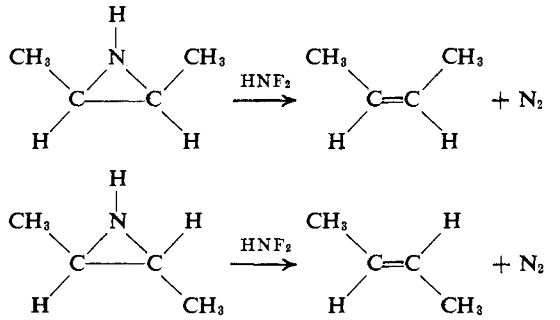
[2] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 396 (1965).

[3] R. Hoffmann and R. B. Woodward, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 85.

Lemal, Dartmouth College, is

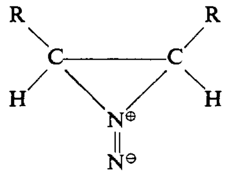


Treatment of *cis*- and *trans*-2,3-butenimines[4] with difluoramine at 0° has been found to give olefin of the same configuration as the aziridine. The product composition was determined by means of infrared and vapor phase chromatographic analysis. In both cases stereochemistry was retained to the extent of 96% or more.



The known[5] stereospecific elimination of nitrous oxide from N-nitrosoaziridines has been cited as an example of the application of the orbital symmetry theory,[3] and it has also been suggested that the stability of N-nitroso-3-pyrroline[6] confirms the theory's predictive power. However, in order to construct the orbital correlation diagrams for these nitroso compounds, the plane of the $N{=}O$ π bond must be rotated so that it is orthogonal to the orbital of the unshared electrons on the amino nitrogen. A number of studies[7] have shown that there must be considerable $N{=}N$ double bond character in the ground state of nitrosamines, indicating considerable overlap of these orbitals. The transition state leading to elimination may not resemble the ground state, however, but there are no data available to bear on this point. It would appear that more rehybridization would be required from the orthogonal transition state, suggesting that it would be of higher energy.

If the postulated intermediate, **1**, is the species involved in the elimination under study,[8] then its decomposition and the stereospecific decomposition of episulfones[9] constitute exceptions to the applicability of the Hoffmann–Woodward theory. At this point it seems reasonable to adopt the view that the theory as presently constituted is not in fact applicable to three-membered rings and that the apparent correspondence with it of the nitrous oxide elimination is a red herring.[10] In any case the exceptions now outnumber the applications.[11]



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Acknowledgment. This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021 AMC-11536 (Z).

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[4] We are grateful to Professor G. K. Helmkamp, University of California, Riverside, Calif., for generous samples of both isomers of the aziridine.

[5] R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

[6] S. D. McGregor and D. M. Lemal, *J. Am. Chem. Soc.*, **88**, 2858 (1966).

[7] For a summary of leading references, see G. J. Karabatsos and R. A. Teller, *ibid.*, **86**, 4373 (1964).

[8] In order to establish this point securely, Dr. D. M. Lemal is attempting to prepare the corresponding N-(toluenesulfonylamino) derivative in order to subject it to base-catalyzed decomposition.

[9] N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963); N. P. Neureiter, *ibid.*, **88**, 558 (1966); N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966).

[10] Alternatively the reaction could be nonconcerted as predicted by theory, but two-step processes could produce a stereochemical result identical with that of a concerted reaction.

[11] Recently it has been reported [G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, 32, 459 (1967)] that the elimination of SO from the 2-butene episulfoxides is nonstereospecific. Such a result is predicted by the Woodward–Hoffmann theory.

[12] Alfred P. Sloan Fellow, 1966–present.

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The Geometric Stability of 1,3-Diphenylallyllithium

Sir:

It has been established that allylic anions,[1] cations,[2] and radicals,[3] when generated as transient intermediates, resist rotation about their partial double bonds long enough to maintain the geometry imposed by their progenitors. It is of obvious interest to learn if this result is applicable to long-lived allylic species, and we now report results on anions generated from *cis*- and *trans*-1,3-diphenylpropene (*cis*- and *trans*-I).[4]

Addition of 1.1 equiv of butyllithium in hexane to either *cis*- or *trans*-I in THF and subsequent quenching of the resulting magenta solution with D_2O affords a 97:3 mixture of *trans*-:*cis*-I-3*d*. To study the geometrical lability of the anionoid intermediate, we have examined the nmr spectrum of purified 1,3-diphenylallyllithium from *cis*- and *trans*-I and have concluded that we are dealing with a largely delocalized, anionoid species which requires an extraordinarily low $\Delta G^{\ddagger}$ for rotation about bonds which simple Hückel theory predicts to have considerable double bond character.

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[1] D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.*, **86**, 5478 (1964).

[2] W. G. Young, S. H. Sharman, and S. Winstein, *ibid.*, **82**, 1376 (1960).

[3] C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

[4] *cis*- and *trans*-I were prepared by a modified Wittig reaction and were separated by gas phase partition chromatography. Each isomer was >95% pure and their spectral properties agreed with those of authentic samples kindly supplied by G. W. Griffin and R. C. Petterson (*cf.* G. W. Griffin, *et al.*, *ibid.*, **87**, 1410 (1965).