COMMUNICATIONS TO THE EDITOR

THE NITROGEN INVERSION FREQUENCY IN CYCLIC IMINES

Sir:

Considerable effort has been expended in attempts to prepare substances with optical forms due to asymmetry of trivalent nitrogen.[1] Suitably substituted ethylenimines are thought to be particularly favorably constituted for existence of stable, optically active antipodes.[1,2] Successful resolution of such imines has not yet been achieved.

The nuclear magnetic resonance spectra of N-ethylethylenimine (I) and N-ethylallenimine[3] (II) has now been studied as a function of temperature (Fig. 1).

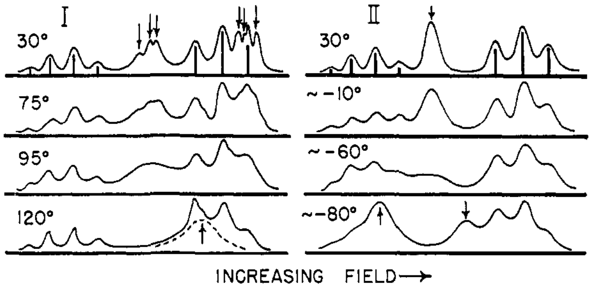
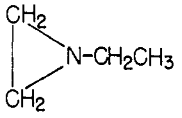
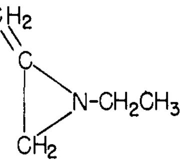


Fig. 1.—Nuclear magnetic resonance spectra of protons of N-ethylethylenimine (I) and N-ethylallenimine (II) as a function of temperature. Samples in 0.5 mm. tubes and Varian Associates High Resolution Spectrometer (V-4300) at 40 mc. with vacuum-jacketed probe insert and 12-in. magnet equipped with Super Stabilizer. Heavy vertical lines mark characteristic bands of ethyl group while vertical arrows indicate absorption of ring hydrogens. The temperature-invariant absorption of the double-bond methylene protons of II is off scale on the left.

At room temperature, I shows the characteristic bands of the ethyl group and two slightly split triplet band systems separated by 27 c.p.s. at 40 mc. These latter band systems are best interpreted as being due to the two groups of ring hydrogens which are either *cis* or *trans* to the N-ethyl group. In such event, the mean lifetime of a given imine molecule before the nitrogen inverts must be much greater than 0.04 sec.[4] On heating to 120–130°, the ring hydrogens appear to completely lose their identity with respect to the position of the ethyl group and the mean lifetime before nitrogen inversion must be substantially less than 0.04 sec. The intermediate temperature with a mean lifetime of 0.04 sec. is estimated to be about 110°. The rate of nitrogen inversion of I would thus seem to preclude successful resolution of substituted ethylenimines except at rather low temperatures.


I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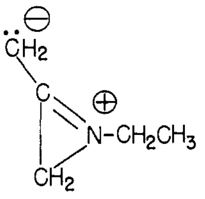
III

N-Ethylallenimine (II) shows only one band for the ring methylene group at room temperature. However, at and below −80°, this band is sharply split into two components separated by about 30 c.p.s. The intermediate temperature is estimated to be between −60 and −70°, at which point the mean lifetime before inversion of the nitrogen is about 0.03 sec.

The tremendously faster inversion rate of II compared to I is expected on the basis of contribution of electron delocalization involving the nitrogen and double bond as indicated by structure III. Such delocalization would markedly aid the attainment of a planar inversion transition state.

So far, no similar temperature behavior has been noted in the n–m–r spectra N-methylpyrrolidine or N-methylpiperidine and related compounds. These studies are being continued.

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[1] *Cf.*, R. L. Shriner, R. Adams and C. S. Marvel in H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1943, Vol. I, pp. 402–413; V. Prelog and P. Wieland, *Helv. Chim. Acta*, **27**, 1127 (1944).

[2] R. Adams and T. L. Cairns, This Journal, **61**, 2464 (1939); J. F. Kincaid and F. C. Henriques, Jr., *ibid.*, **62**, 1474 (1940); T. L. Cairns, *ibid.*, **63**, 871 (1941); H. M. Kissman, D. S. Tarbell and J. Williams, *ibid.*, **75**, 2959 (1933), and earlier references there cited to papers by Tarbell and co-workers and others.

[3] (a) M. G. Ettlinger and F. Kennedy, *Chem. and Ind.*, 166 (1956); (b) A. T. Bottini and J. D. Roberts, This Journal, **79**, 0000 (1957).

[4] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

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ENZYMATIC FORMATION OF OXALATE AND ACETATE FROM OXALOACETATE

Sir:

Oxalic acid is one of the major products of carbohydrate metabolism in molds and higher plants but the precise metabolic pathway by which it is produced has not been elucidated to date. In this communication we are reporting the formation of oxalate and acetate from oxaloacetate by a soluble enzyme preparation obtained from *Aspergillus niger* (ATCC 10582).

The organism was grown at 25° with shaking on a medium containing 10% dextrose, 0.3% $(NH_4)_2SO_4$, 0.1% K_2HPO_4, 0.1% KH_2PO_4, 0.05% $MgSO_4 \cdot 7H_2O$, 1% Difco malt extract at *p*H 6.0. After 72 hours the *p*H of the medium was adjusted between 7.5 and 8.5 with sterile 2 *M* Na_2CO_3 solution and the mycelia were harvested 12 hours later. The enzyme was prepared by grinding the well-washed and frozen mycelia and extracting with three volumes of tris-hydroxymethylaminomethane buffer