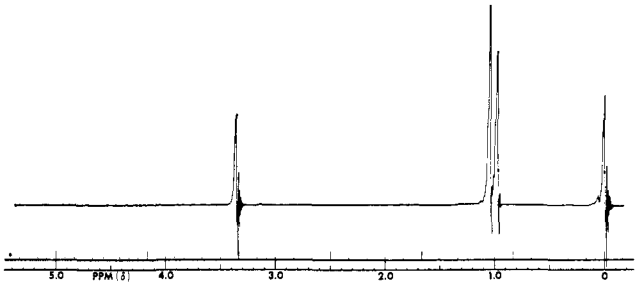
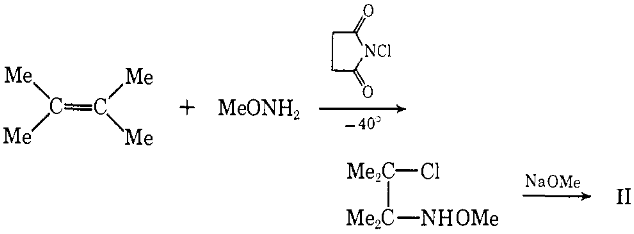


Figure 1. Proton spectrum of 1-methoxy-2,2,3,3-tetramethylaziridine (II) as a 20% solution in benzene-d_6.

of neat II was unusually simple and showed two very prominent peaks at 9.47 and 12.62 μ. Significantly, its proton spectrum in benzene (Figure 1) exhibited a singlet (MeO) at δ 3.36 and a *doublet* (Me_2C) at δ 1.04 and 0.97 in the expected intensity ratio.

Clinching evidence for the 1-alkoxyaziridine structure II stems from its synthesis *via* an alternate route recently uncovered in our laboratory.[5] In accord with Scheme I, the addition of N-chlorosuccinimide to equivalent amounts of 2,3-dimethyl-2-butene and methoxyamine in methylene chloride at −40° affords the distillable hydroxylamine analog III[6] in good yield. The cyclization of III with sodium methoxide in methanol gave a volatile liquid which was spectroscopically identical with II.

Scheme I



At present we speculate that the O-nitrene intermediate (IV) is generated *via* lead tetraacetate oxidation of methoxyamine and trapped in the singlet state. The alleged singlet nitrene (IV) can be effectively stabilized by delocalization and is most likely in the ground state. It is reasonable to expect, by analogy with certain N-nitrenes,[4e] that IV should possess nucleophilic character and should add to olefins in a stereospecific manner. We are presently investigating these possibilities.

$$\mathrm{MeO}\ddot{\mathrm{N}}: \longleftrightarrow \mathrm{MeO}\overset{+}{=}\mathrm{N}^-$$

IV

It is noteworthy that the N-nitrene, V, which is presumably formed *via* lead tetraacetate oxidation of 1,1-dimethylhydrazine under identical reaction conditions, did not

$$\mathrm{Me_2N}\ddot{\mathrm{N}}: \longleftrightarrow \mathrm{Me_2N^+{=}N^-}$$

V

react with tetramethylethylene to afford an aziridine but rather dimerized to give predominantly (~75% yield) tetramethyltetrazene.[4a] Apparently, the proclivity of nitrenes,[4] notably such stabilized species as IV and V, to react with alkenes to form aziridines is sensitively governed by subtle steric and/or electronic factors.

An especially significant feature of the proton spectrum of II (Figure 1) at ambient temperature is the conspicuous nonequivalence of the geminal methyl protons. Clearly, the pyramidal inversion process in 1-alkyoxyaziridines is slow on the nmr time scale at room temperature. Furthermore, nmr studies at elevated temperatures revealed that coalescence of the *gem*-methyl resonance signals in the proton spectrum of II in xylene did not occur *even at 130°*.

In accord with expectation,[1] 1-alkoxyaziridines do indeed exhibit an appreciable energy barrier ($\Delta F^* > 22$ kcal/mol) to nitrogen inversion, and by analogy with N-haloaziridines,[7] N-aminoaziridines,[8] and oxaziridines[1] exist as stable pyramids at room temperature. Apparently, a favorable combination of inductive and electrostatic factors[1,9] effectively stabilizes the pyramidal configuration of those aziridines in which the ring nitrogen is attached to a halogen, nitrogen, or oxygen atom.

Complete details of the synthetic, spectroscopic, and mechanistic aspects of the present study will be reported in due course.[10]

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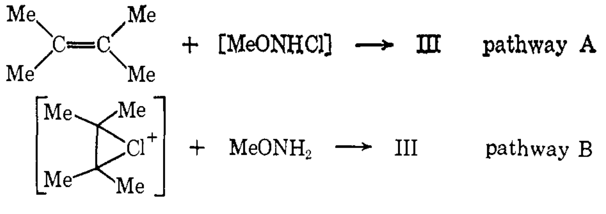
[5] S. J. Brois, unpublished results.

[6] Two plausible reaction pathways to III can be envisaged. Pathway A involves the addition of the intermediary N-chloromethoxyamine to the olefin. The alternate mechanism (pathway B) invokes the intermediacy of a halonium ion which undergoes subsequent reaction with methoxyamine. Studies designed to clarify the mechanism of formation of III *via* Scheme I are in progress. Satisfactory elemental analyses and consistent spectral data were obtained for III.



[7] S. J. Brois, *J. Amer. Chem. Soc.*, **90**, 506, 508, 1680 (1968); J. M. Lehn and J. Wagner, *Chem. Commun.*, 148 (1968); D. Felix and A. Eschenmoser, *Angew. Chem. Intern. Ed. Engl.*, **1**, 224 (1968); R. G. Kostyanovskii, I. I. Chervin, and O. A. Panshin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1423 (1968).

[8] S. J. Brois, *Tetrahedron Lett.*, 5997 (1968); R. S. Atkinson, *Chem. Commun.*, 676 (1968).

[9] F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 357 (1967).

[10] We acknowledge support of this work by the U. S. Army Medical and Research Development Command.

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Nuclear Magnetic Resonance. Intermolecular Exchange of Methyl Groups in Methylcadmium Compounds[1]

Sir:

We wish to report nmr measurements of intermolecular exchange rates of methyl groups in dimethylcadmium. Our interest in this kind of problem has continued for some years,[2] and it seems important to clarify the matter of exchange[3,4] or nonexchange[5] as the

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[1] Supported by the National Science Foundation.

[2] (a) F. J. Weigert, M. Winokur, and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 1566 (1968); (b) M. Winokur, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1968.

[3] N. S. Ham, E. A. Jeffery, T. Mole, J. K. Saunders, and S. N. Stuart, *J. Organometal. Chem.*, **8**, P7 (1967).

[4] E. A. Jeffery and T. Mole, *Aust. J. Chem.*, **21**, 1187 (1968).

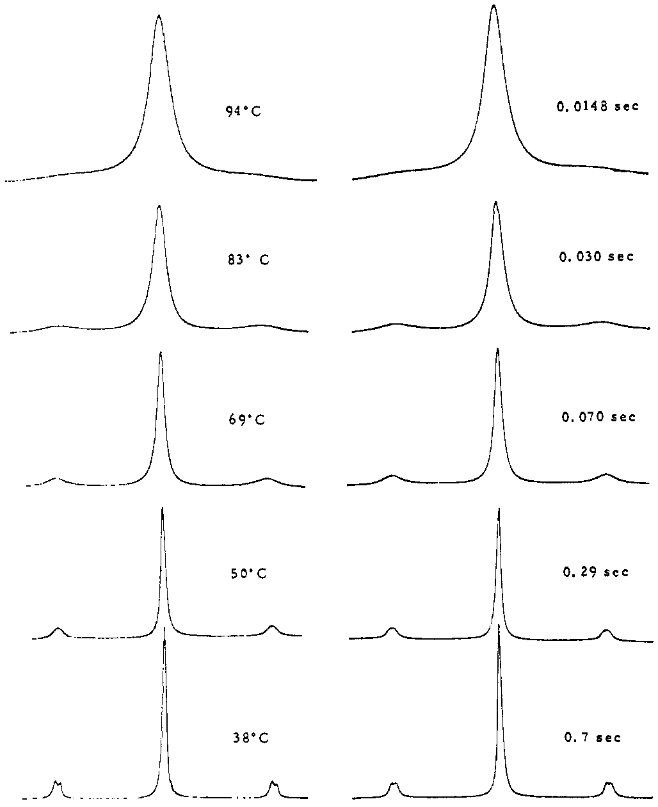

Figure 1. Experimental and calculated proton nmr spectra for a neat sample of dimethylcadmium. The experimental spectra were taken on a Varian A56/60 spectrometer with the temperatures calibrated by the temperature dependence of the chemical shift of the ethylene glycol hydroxyl proton. The spectra on the right were drawn by a Calcomp plotter connected to an IBM 360/75 computer using the program GMW.[6] The spectrum may be calibrated by knowing that the distance between the outer satellites corresponds to 103.6 Hz.

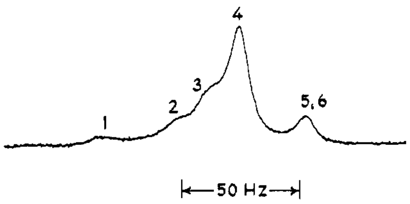

Figure 2. Proton nmr spectrum of a 1.4 *M* solution of dimethylcadmium in tetrahydrofuran saturated with cadmium bromide at −110°. The highest peak marked 4 is at about 52 ± 2 cps upfield from tetramethylsilane.

case may be. Actually, detection of intermolecular exchange of methyl groups in dimethylcadmium is relatively easy because of the spectral changes which occur as the result of such exchange on the ^{111}Cd–C–H and ^{113}Cd–C–H spin–spin couplings. The isotopes ^{111}Cd (12.9%) and ^{113}Cd (12.3%) each have spin $^1/_2$ while the other abundant cadmium isotopes, mainly ^{112}Cd, have zero spin. The proton spectra in the absence of exchange therefore display five lines, the center line of which represents the molecules with cadmium having zero spin. Exchange of methyls proceeds between cadmium atoms in five nuclear states, $+^1/_2$ and $-^1/_2$ for ^{111}Cd and ^{113}Cd, and zero for the other isotopes, thereby providing a five-site random intermolecular exchange problem, the line shapes for which can be simulated by the procedure of Sack.[6]

A substantial sensitivity of the exchange to catalytic amounts of methylcadmium methoxide has been reported earlier[3,4] and was confirmed in this work. With considerable care in handling the sample by vacuum-line techniques, we achieved exchange rates comparable to those of Ham and coworkers[3] but not zero as has been suggested recently.[5] Experimental proton spectra of neat dimethylcadmium as a function of temperature and theoretical spectra as a function of the lifetime τ are shown in Figure 1. The coalescence temperature corresponding to these spectra is about 100°, the activation energy E_a 15.7 ± 0.1 kcal/mol, and $\Delta S^{\ddagger}$ −9.8 ± 0.2 eu.[7] Both the activation energy and entropy are similar to the values reported for methyl exchange between dimethylcadmium and dimethylzinc[5] and suggest a similar mechanism for exchange.

The rate of exchange is very much increased in tetrahydrofuran, the coalescence temperature in 10% solution being −10° with an E_a of 6.8 ± 0.1 kcal/mol and $\Delta S^{\ddagger}$ of −28.3 ± 0.4 eu. Cadmium bromide further increases the rate of exchange and it is probably significant in this connection that cadmium bromide is not very soluble in tetrahydrofuran unless dimethylcadmium is present. At −110°, solutions of dimethylcadmium in tetrahydrofuran saturated with cadmium bromide show proton resonances which correspond to methylcadmium bromide (Figure 2). The peaks 2, 4, and 5 in Figure 2 are assigned to dimethylcadmium and its Cd–C–H satellites with *J* of 52 Hz while 1, 3, and 6 are assigned to methylcadmium bromide and its Cd–C–H satellites with *J* of about 80 Hz. The large change in *J* in going from $(CH_3)_2Cd$ to CH_3CdBr has a parallel in similar mercury derivatives.[8] This spectrum provides the first clear evidence for a Schlenk-type equilibrium involving alkylcadmium compounds.

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[5] K. Henold, J. Soulati, and J. P. Oliver, *J. Amer. Chem. Soc.*, **91**, 3171 (1969).

[6] R. A. Sack, *Mol. Phys.*, **1**, 163 (1958). We use the computer program GMW developed by G. M. Whitesides and J. M. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967), and adapted for use with our computers with the help of Dr. F. J. Weigert.

[7] For comparison with results reported by Ham and coworkers,[3] we assume toluene to be an inert solvent and the exchange rate $v = 1/\tau = k_1[Cd(CH_3)_2]$. From this equation and Ham's data we estimate a mean lifetime of 0.007 ± 0.002 sec for neat dimethylcadmium at 120°. Extrapolation of our rate to 120° gives 0.004 sec which is in reasonable agreement considering the difference in the experimental conditions.

[8] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Long Island City, N. Y., 1966, pp 689–690.

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The Te_n^{n+} Cation

Sir:

In a recent communication[1] we showed that tellurium can be oxidized in strongly acidic media, *e.g.*, HSO_3F or oleum to the red cation Te_4^{2+} and that this cation could be further oxidized to a yellow species which was not at that time identified. We have now found that in solution in fluorosulfuric acid at room temperature,

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[1] R. J. Gillespie, J. Barr, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, **90**, 6855 (1968).