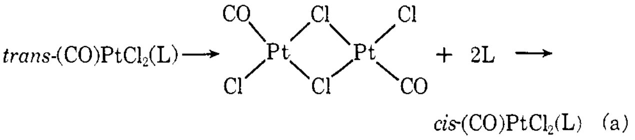
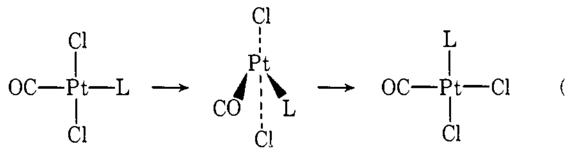
loss in the first step (~200°) corresponds very closely to the loss of both organic ligands. It is not known at this time whether the CO comes off as such, or is combined with the amine, *e.g.*, as the amide. The second stage loss corresponds to the decomposition of $PtCl_2$ to metal.

In another experiment, the heating was interrupted at about 120°, the material dissolved in acetone, and the solution examined in the infrared. The carbonyl stretching band appeared at 2109 cm^{-1}, identical in shape and position with that of authentic *cis* isomer. The original *trans* complex in acetone had $\nu_{C\equiv O}$ of 2126 cm^{-1}. Infrared examination of samples heated to 70° showed only *trans* present, while between 95 and 110° both isomers are present and at 120° only the *cis* isomer is present.

Because of the implications for catalytic reactions, the *trans* → *cis* rearrangement is of intrinsic interest. At least two possible routes (a and b) to such a rearrangement need be considered. Mechanism a or any related mechanism involving free L appears unlikely since we have been able to also achieve the rearrangement of *trans*-**1** (L = $NH_2CH_2CH_2CH_3$) to the *cis* isomer at 115°, a temperature appreciably higher than the boiling point (49°) of *n*-propylamine. Route b involves the intermediacy of a tetrahedral configuration. Even though such complexes of Pt(II) have been proposed,[3] they have never, to our knowledge, been shown to exist. Such an intermediate would provide a low-energy path to the isomerization. Studies designed to demonstrate a tetrahedral intermediate are under investigation.





The DTA/TGA curves were obtained using a Mettler thermoanalyzer-2. The sample chamber was swept with air and heated at a rate of 15°/min. The complexes *cis*- (melting with decomposition from 180 to 200°) and *trans*-$(CO)PtCl_2[(+)\text{-}NH_2CH(CH_3)C_6H_5]$ (mp 71–73°) and the *trans*-$(CO)PtCl_2(NH_2CH_2CH_2CH_3)$ (mp 48–49°) are new complexes prepared using known procedures.[4–6] All complexes gave satisfactory analyses. The infrared spectrum of the *trans*-*n*-propylamine complex had $\nu_{C\equiv O}$ of 2125 cm^{-1} and after heating at 115°, $\nu_{C\equiv O}$ shifted to 2109 cm^{-1}. The carbonyl bands are essentially identical with those in the spectra of the *cis*- and *trans*-$(CO)PtCl_2[(+)\text{-}NH_2CH(CH_3)C_6H_5]$.

Acknowledgment. We are grateful to Mettler Instrument Company for determining the DTA/TGA curves and to Englehard Industries, Inc., for a generous supply of platinum. We also wish to thank the donors to the Petroleum Research Foundation of the American Chemical Society for partial support of this research. The possibility of tetrahedral intermediacy was brought out in a discussion with Dr. I. Mador. One of us (R. E.) thanks the Procter and Gamble Co. for a fellowship.

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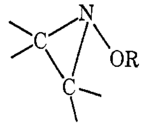
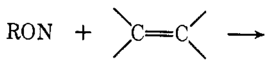
Stable Nitrogen Pyramids. IV. 1-Alkoxyaziridines. A New Aziridine Synthesis *via* O-Nitrenes

Sir:

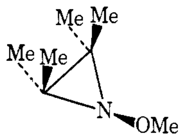
The hypothesis[1] that 1-alkoxyaziridines should exhibit high pyramidal stability at room temperature prompted the synthesis of I for nmr spectroscopic study. Since the known synthetic routes[2] to the few reported 1-alkoxyaziridines appeared unadaptable to the preparation of our model aziridines, we investigated the intriguing possibility of adding the hitherto unknown[3] O-nitrenes to alkenes, by analogy with the addition of C- and N-nitrenes to olefins.[4] In this communication, we wish to present persuasive evidence for the existence of O-nitrenes and more importantly, describe the facile addition of alkoxynitrenes to alkenes as a new route to pyramidally stable aziridines.



I



Accordingly, the oxidation of methoxyamine with lead tetraacetate in the presence of excess tetramethylethylene at −50° afforded 1-methoxy-2,2,3,3-tetramethylaziridine (II) in *ca.* 30% yield. Analytically pure product was obtained by preparative gas chromatography.



II

The 1-alkoxyaziridine (II) featured a mass spectrum which contained the molecular ion peak at *m/e* 129 and a base peak at *m/e* 98. The appearance of the latter peak indicates that the dominant mode of fragmentation of II upon electron impact involves scission of the labile nitrogen–oxygen bond. The infrared spectrum

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(1) S. J. Brois, *Trans. N. Y. Acad. Sci.*, **31**, 931 (1969).

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(4) (a) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964); (b) J. S. McConaghy and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 3457, 4450 (1967); (c) R. S. Atkinson and C. W. Rees, *Chem. Commun.*, 1230 (1967); (d) W. Nagata, S. Hirai, K. Kawata, and T. Aoki, *J. Amer. Chem. Soc.*, **89**, 5045 (1967); (e) D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Commun.*, 146 (1969).

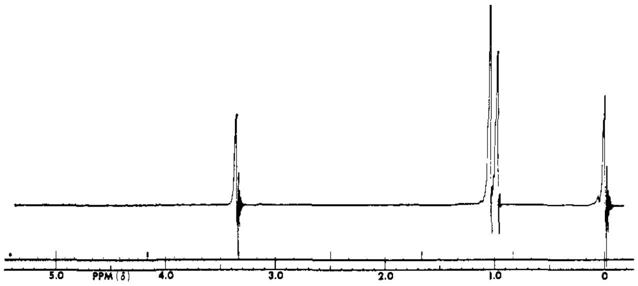
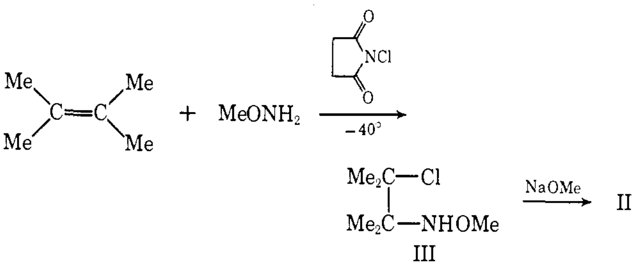


Figure 1. Proton spectrum of 1-methoxy-2,2,3,3-tetramethylaziridine (II) as a 20% solution in benzene-d_6.

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.

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

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

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

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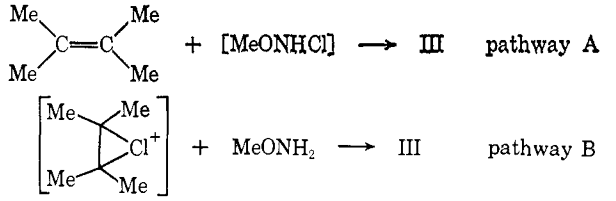
[5] S. J. Brois, unpublished results.

[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.



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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.

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