parable results were obtained using the methanesulfonyl derivative.[4]

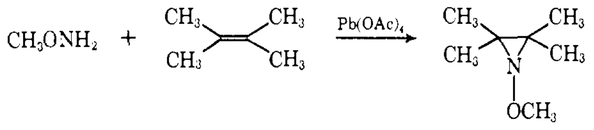
To ensure that proton abstraction from nitrogen and not from carbon was responsible for the rearrangement, $Ph_2CHON(CH_3)Ts^4$, mp 104–105°, was prepared from the sodium salt of **4** and methyl iodide in tetrahydrofuran (98%) and heated with 2 equiv of sodium hydride (200°, 19 hr). The products isolated by preparative tlc were benzhydrol (71%), benzophenone (8%), and *N*-methyl-*p*-toluenesulfonamide (47%). When the experiment was repeated using $Ph_2CDON(CH_3)Ts$ and sodium hydride, the benzhydrol isolated in 65% yield was found to contain no deuterium at the benzylic position, thereby indicating that the carbanion, once formed, cleaves to benzophenone and *N*-methyl-*p*-toluenesulfonamide ion. Reduction of benzophenone to benzhydrol by sodium hydride completes the process.[5]

O to N migration also occurs when *N*-*p*-toluenesulfonyl-*O*-benzylhydroxylamine[6] (**6**) is allowed to react under these conditions. The rearranged product obtained in this case was benzonitrile in 34% yield.[7]

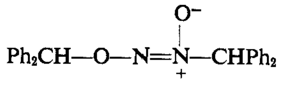
$$PhCH_2ONHTs \xrightarrow[\text{2. triglyme, 165°}]{\text{1. NaH}} PhC{\equiv}N$$

6

Brois[8] has recently reported that lead tetraacetate oxidation of *O*-methylhydroxylamine in the presence of tetramethylethylene gave *N*-methoxyaziridine and proposed methoxynitrene as an intermediate.[9]



We have also examined lead tetraacetate oxidations as a route to **2** but have been concerned primarily with intramolecular rearrangements rather than intermolecular trapping. In most of the cases we have studied, cleavage of the weak O–N bond occurs; for example, *p*-nitrobenzyl alcohol was isolated in 68% yield when *O*-*p*-nitrobenzylhydroxylamine[10] reacted with lead tetraacetate in methylene chloride for 10 min at 25°. With **3**, however, again an interesting rearrangement of diphenylmethyl occurs in that the major product after 10 min at 0° with lead tetraacetate in methylene chloride is a white solid (**7**), mp 147–148°, isolated in 32% yield. Elemental analysis and a molecular weight determination (Rast, 375; calcd, 394.5) established **7** as $C_{26}H_{22}N_2O_2$, and the spectral data permit identification of **7** as *N*-diphenylmethoxy-*N*′-diphenylmethyldiazine *N*′-oxide.[11]



$$Ph_2CH{-}O{-}N{=}\overset{O^-}{\underset{+}{N}}{-}CHPh_2$$

7

The isolation of **7** is interesting in that not only has O to N rearrangement taken place, but also there exists an analogy in the observation that azoxybenzene is formed during deoxygenation of nitrosobenzene by triphenylphosphine, which has been interpreted as arising from reaction of phenyl nitrene with nitrosobenzene.[12]

While these experiments were designed to yield **2** by using the techniques employed for **1**, and the observation of O to N migration is consistent with the expected behavior of **2**, further experiments are planned to test the reasonableness of other reaction mechanisms and to ascertain whether rearrangement is concerted or involves fragmentation–recombination.

(5) F. W. Swamer and C. R. Hauser, *J. Amer. Chem. Soc.*, **68**, 2647 (1946).

(6) J. H. Cooley, B. N. Misra, J. R. Throckmorton, and W. D. Bills, *J. Med. Chem.*, **11**, 196 (1968).

(7) Benzamide has been isolated in *ca.* 20% yield from the reaction of *N*-chloro-*O*-benzylhydroxylamine with sodium ethoxide followed by thermal rearrangement: L. A. Paquette, *Tetrahedron Lett.*, 485 (1962).

(8) S. J. Brois, *J. Amer. Chem. Soc.*, **92**, 1079 (1970).

(9) For other attempts to generate *O*-nitrenes, see J. H. Boyer and J. D. Woodyard, *J. Org. Chem.*, **33**, 3329 (1968); A. Hassner, R. Wiederkehr, and A. J. Kascheres, *ibid.*, **35**, 1962 (1970).

(10) O. L. Brady and L. Klein, *J. Chem. Soc.*, 874 (1927).

(11) Spectral data have been reported for compounds of this type: ir, M. V. George, R. W. Kierstead, and G. F. Wright, *Can. J. Chem.*, **37**, 679 (1959); nmr, J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).

(12) P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 42 (1963).

* Author to whom inquiries should be addressed.

Francis A. Carey,* Larry J. Hayes
Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

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Structure of the Trimethylamine Adduct of Diboron Tetrachloride

Sir:

Diboron tetrachloride reacts readily with 2 mol of trimethylamine to form a white crystalline solid.[1] The material has been reported to be tetrameric in the vapor phase and in benzene solution, and considerable speculation has appeared concerning the structure of this molecule.[2] The problem presented warranted direct structural determination by X-ray diffraction.

Initial photographs were indexed in the space group $P2_1/n$. Lattice parameters $a = 7.557 \pm 0.004$, $b = 9.592 \pm 0.006$, $c = 9.308 \pm 0.005$, and $\beta = 92.13°$ were determined by least-squares fit of observations made with an automated Picker diffractometer. The high solubility of the compound in common solvents precluded experimental density measurements, but the calculated density for two molecules of monomer per unit cell is 1.4 g/cm³. It seems quite apparent that no more than two monomeric molecules can be present in the unit cell, and this observation alone precludes the tetrameric molecular formula. It appears highly unlikely that a more polymerized form will exist in solution or in gas phase. Furthermore, a mass spectrum of the material obtained with an MS-9 mass spectrometer shows no ions of mass greater than the parent monomeric molecule. Three-dimensional intensity data were collected using Cu Kα radiation with a Picker automated diffractometer. Only 294 of 779 independent reflections exceeded 2.3σ and were used in subsequent analysis. The structure was solved using direct methods and the sequence of programs previously described by one of us.[3] Using these programs,

(1) G. Urry, T. Wartik, R. E. Moore, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **76**, 5293 (1954).

(2) See, for example, G. Urry in "The Chemistry of Boron and its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 352.

it was necessary to reindex data in the $P2_1/c$ system with corresponding lattice constants of $a = 9.310$, $b = 9.592$, $c = 11.750$, and $\beta = 140.09°$. All subsequent work was carried out in the new system.

The initial R value was 0.30 for the structure selected from the three-dimensional plot of the E map. Refinement using isotropic temperature factors led to a final value of 0.16. Introduction of anisotropic temperature factors on the chlorine atoms alone reduced the R factor to 0.10. The quality of data obtained with this crystal did not warrent further refinement.

Several new crystals were examined in an effort to obtain better data. Both crystals mounted directly in air and those mounted in sealed glass capillaries changed during the data collection process. In the case of one crystal mounted in a capillary, we were able to collect the complete set of redundant data on indices $\pm h, k$, and $\pm l$ using Mo radiation to a 2θ value of 30°. Three standard reflections were monitored once every 30 observations. All three standards decayed uniformly with time and at the end of data collection intensities of the standards had been reduced by 25%. At this time it was deemed that further data collection with this crystal was undesirable and no additional suitable crystals were available for study. All 981 observed reflections were used to calculate F^2 values. Data on the standard reflections were fitted to a linear decay curve by a least-squares procedure and the F^2 value of each reflection was corrected for the decay in crystal quality. Average values for a set of nonredundant data were calculated and in no case did independent observations differ by more than 2σ. The order of data collection was such that symmetry-equivalent reflections were symmetrically placed about the median data point and thus the excellent average values obtained suggested that the data were adequate for further refinement. The new set of 210 observations was used for isotropic refinement using the parameters determined for the previous data set, leading to a value of $R = 0.13$ when isotropic temperature factors were used for all atoms. Introduction of nonisotropic temperature factors for the chlorines alone led to an R value of 0.074 in the first cycle and ultimately to 0.071. Parameters for each atom at this stage of refinement are listed in Table I. Temperature factors are normal although slightly high for carbons (up to 8.2), as expected in slight compensation for missing hydrogen atoms Bond distances derived from these parameters are: BB, 1.72; BN, 1.75; BCl-1, 1.86; BCl-2, 1.89; NC-1, 1.57; NC-2, 1.54; NC-3, 1.53 Å. All angles are satisfactory at this stage of refinement.

Table I. Atomic Parameters Based in $P2_1/c$ Cell

Atom	X	Y	Z
Cl-1	0.7411	0.0010	0.4878
Cl-2	0.7152	0.8701	0.7607
N	0.6514	0.2834	0.0926
C-1	0.8753	0.1723	0.7882
C-2	0.2933	0.6791	0.4691
C-3	0.5138	0.7925	0.9304
B	0.5367	0.4394	0.9720

At this moment we have no explanation for the molecular weight measurements made 20 years ago. We suggest that they were in error and point out that the chemically reactive nature of the molecule may have made valid measurements difficult. In light of both the present structural analysis and the new data on the mass spectrum of the total sample, we believe that the problem is completely resolved.[4,5]

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(3) Q. Johnson, G. S. Smith, and E. Kahara, *Science*, **164**, 1163 1969).

(4) The authors regret the length of this communication produced by inclusion of details of experimental procedure and results that we do not believe to be of general interest. They are included only at the insistence of the referees and the editor. The reader is warned that the values listed in Table I may be slightly incorrect owing to both the incomplete data set used and the failure to find the nine hydrogens in the asymmetric unit. The basic structural conclusion is in no way affected by these technical limitations.

(5) This work was supported in part by the Atomic Energy Commission and in part by the National Science Foundation.

* Address correspondence to this author.

Quintin Johnson
Lawrence Radiation Laboratory, University of California
Livermore, California 94550

James Kane, Riley Schaeffer*
Contribution No. 1886, Department of Chemistry
Indiana University, Bloomington, Indiana 47401

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Synthesis of Slaframine

Sir:

Slaframine, a metabolite isolated from the fungus *Rhizoctonia leguminicola*,[1] is responsible for producing salivation in cattle.[2] Studies on slaframine have indicated that it has potential value—both as a research tool, for the isolation of the acetylcholine receptor site, and as a medicinal agent for the treatment of the cystic fibrosis syndrome, since it stimulates pancreatic secretion.[3,4] However, slaframine has thus far only been produced in low yield, by surface cultures of *R. leguminicola*;[5] thus, difficulty in obtaining the metabolite from its natural source has limited its study and made its chemical synthesis an attractive prospect.

Structure **1** has been assigned to slaframine.[6] We should like to report here the preparation of racemic *cis,cis*-1-acetoxy-6-acetamidoindolizidine (**2**) and its identity with *N*-acetylslaframine, prepared earlier[1,6] from the natural compound. We also report the conversion of *N*-acetylslaframine to slaframine. Thus, the present report describes the total synthesis of slaframine.

The route chosen for the synthesis proceeded from 2-bromo-5 nitropyridine (**3**) (prepared from 2-hydroxy-5-nitropyridine by the method of Binz and Schickh,)[7] which was converted to 5-acetamido-2-carbethoxypyridine (**4**) by a modification of the route of Schmidt-Thomé and Goebel.[8] Fusion of **3** with cuprous cyanide and acidic hydrolysis of the resulting nitrile gave the carboxylic acid **5**,[9] mp 211–212° (lit.[8] 211–212°), which

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(1) S. D. Aust, H. P. Broquist, and K. L. Rinehart, Jr., *J. Amer. Chem. Soc.*, **88**, 2879 (1966).

(2) J. H. Byers and H. P. Broquist, *J. Dairy Sci.*, **43**, 873 (1960); **44**, 1179 (1961).

(3) S. D. Aust, *Biochem. Pharmacol.*, **18**, 929 (1969).

(4) T. E. Spike, M.S. Thesis, Michigan State University, 1969.

(5) S. D. Aust, Ph.D. Thesis, University of Illinois, 1965.

(6) R. A. Gardiner, K. L. Rinehart, Jr., J. J. Snyder, and H. P. Broquist, *J. Amer. Chem. Soc.*, **90**, 5639 (1968).

(7) A. Binz and O. von Schickh, *Chem. Ber.*, **68**, 315 (1935).

(8) J. Schmidt-Thomé and H. Goebel, *Z. Physiol. Chem.*, **288**, 237 (1951).