cipally by hydrogenolysis of the strained C(1)–C(8) bond in **7** is shown by the fact that the even more strained **3a** was hydrogenated to yield *ca.* 90% *trans*-bicyclo[6.1.0]-nonane[12] under identical conditions.

From the area ratio (1.31 ± 0.03) of the vinyl and nonvinyl multiplets at −76 and 2.5°, an equilibrium constant (K_{eq}) of 1.48 ± 0.2 can be calculated for $\mathbf{6} \rightleftharpoons \mathbf{7}$. In addition, it can be calculated from the chemical shift of the coalesced peak (τ 6.18), and of those for H-1 and H-8 in **6** (4.83) and **7** (7.16), that $K_{eq} = 1.38 \pm 0.2$ at 76°.[9] It can be seen from the near constancy (*ca.* −0.2 kcal/mol) of the corresponding values of the Gibbs energy of isomerization (ΔG_{isom}) that ΔS_{isom} for this process is essentially zero, thereby indicating that tetraene **6** has a rigidity comparable to that of its bicyclic isomer (**7**). The nonequivalency of the two protons at C-9 (or C-10) in **6** (see nmr data) lends support to this conclusion.

One can also calculate (from T_c and the chemical shifts of H-1 and H-8 in **6** and **7** at −76°) that $\Delta G^{\ddagger}$ for either the forward or reverse reaction is *ca.* 15 kcal/mol at 48°.[9,13] This value agrees closely with $\Delta H^{\ddagger}$ for the cyclization of *trans,cis,cis,trans*-2,4,6,8-decatetraene to *trans*-7,8-dimethyl-1,3,5-cyclooctatriene, for which $\Delta S^{\ddagger} = -19$ eu,[14] and suggests that $\Delta S^{\ddagger}_{6\rightarrow 7} \approx 0$; *i.e.*, the restriction of internal rotation in the ground and transition states is comparable. This is consistent with the conclusion that ΔS_{isom} is also *ca.* 0.

Although the ambient temperature nmr spectrum of $\mathbf{6} \rightleftharpoons \mathbf{7}$ can be reproduced after heating the sample to 76°, these isomers are transformed into *trans*-1,2-divinyl-1,3-cyclohexadiene (**9**)[15] on heating at 98° (0.15% (v/v) in refluxing heptane). This conversion, which has an approximate half-life of 1 hr, can be formulated as an "allowed" [3,3] sigmatropic (Cope) rearrangement of **6**.[16] Additional products, which apparently arise from **9**, are formed at higher temperatures or over longer periods of time.

Finally, it is of interest to note that a related compound, **5**, exists essentially completely in the bicyclic form.[7] Thus the effect of substituents appears to parallel that found for the 1,3,5-cyclooctatriene–bicyclo-[4.2.0]octa-2,4-diene equilibrium;[17] the same effects are presumably responsible for the similar behavior of these two systems.[18]

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* Address correspondence to this author.

Stuart W. Staley,* Timothy J. Henry
Department of Chemistry, University of Maryland
College Park, Maryland 20742

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[12] E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968).

[13] Strictly, this calculation requires that $K_{eq} = 1$; however, the deviation from 1 is small in the present case.

[14] R. Huisgen, A. Dahmen, and H. Huber, *Tetrahedron Lett.*, 1461 (1969).

[15] This structure assignment, which is consistent with ir and nmr spectral data and an elemental analysis, was confirmed by catalytic hydrogenation (4 mol equiv) to *trans*-1,2-diethylcyclohexane.[16a] We thank Professor C. A. Grob for a copy of the ir spectrum of the latter compound.

[16] For related rearrangements of *trans,trans*-1,5-cyclodecadiene and derivatives see (a) C. A. Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, **46**, 483 (1963); (b) T. G. Halsall and D. W. Theobald, *Quart. Rev., Chem. Soc.*, **16**, 101 (1962); (c) P. S. Wharton and R. A. Kretchmer, *J. Org. Chem.*, **33**, 4258 (1968); (d) E. N. Marvell and W. Whalley, *Tetrahedron Lett.*, 509 (1970); (e) A. J. Weinheimer, W. W. Youngblood, P. H. Washecheck, T. K. B. Karns, and L. S. Ciereszko, *ibid.*, 497 (1970), and references cited; (f) T. C. Jain, C. M. Banks, and J. E. McCloskey, *ibid.*, 841 (1970); (g) K. Takeda, I. Horibe, and H. Minato, *J. Chem. Soc. C*, 1142 (1970), and references cited.

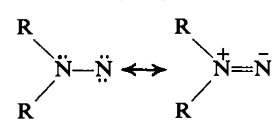
[17] R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *ibid.*, 5215 (1968).

[18] The complexity of this problem is illustrated by a recent study in which five different effects were used to rationalize the positions of seven related tautomeric equilibria: L. A. Paquette, T. Kakihana, J. F. Kelly, and J. R. Malpass, *ibid.*, 1455 (1969).

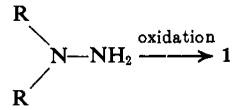
O to N Migration in Reactions of O-Substituted Hydroxylamines[1]

Sir:

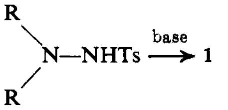
Nitrene intermediates stabilized by electron donation from adjacent atoms have been studied in detail only for the case of adjacent nitrogen.[2] These *N*-nitrenes (**1**, diazenes, azanitrenes) have been generated by a number of techniques including oxidation of 1,1-disubstituted hydrazines (eq 1) and base-catalyzed α elimination from *p*-toluenesulfonyl hydrazines (eq 2).



1



(1)



(2)

We have applied these methods to the generation of *O*-nitrenes (**2**, oxyazenes, oxynitrenes) and have observed several instances in which migration of the substituent from oxygen to nitrogen occurs.

$$\underset{\mathbf{2}}{\mathrm{R{-}O{-}\ddot{N}}} \longleftrightarrow \mathrm{R{-}\overset{+}{O}{=}\overset{-}{N}}$$

O-Diphenylmethylhydroxylamine (**3**)[3] was converted to the corresponding *N*-*p*-toluenesulfonyl derivative **4**,[4] mp 182°, then to the lithium salt of **4** with 1.1 equiv of butyllithium and heated at 165° in triglyme for 18 hr to afford, after work-up, quantitative yields of benzophenone oxime (**5**) and *p*-toluenesulfinic acid.

$$\underset{\mathbf{4}}{\mathrm{Ph_2CHONHTs}} \xrightarrow{\mathrm{BuLi}} \mathrm{Ph_2CHO\overset{-}{N}Ts} \xrightarrow{165^\circ} \underset{\mathbf{5}}{\mathrm{Ph_2C{=}NOH}} + \mathrm{Ts^-}$$

Similarly, the sodium salt of **4** was prepared with sodium hydride in tetrahydrofuran, isolated, and pyrolyzed in triglyme to again yield **5** (57%). Com-

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[1] Research supported by a grant from the National Science Foundation (No. GP-9550).

[2] (a) C. G. Overberger, M. Valentine, and J.-P. Anselme, *J. Amer. Chem. Soc.*, **91**, 687 (1969), and references cited therein; (b) D. M. Lemal, F. Menger, and E. Coats, *ibid.*, **86**, 2395 (1964); (c) D. M. Lemal, T. W. Rave, and S. D. McGregor, *ibid.*, **85**, 1944 (1963).

[3] E. L. Schumann, R. V. Heinzelman, M. E. Greig, and W. Veldkamp, *J. Med. Chem.*, **7**, 329 (1964).

[4] Satisfactory analyses (C, H, N, and S) and consonant ir and nmr spectra were obtained for all new compounds.

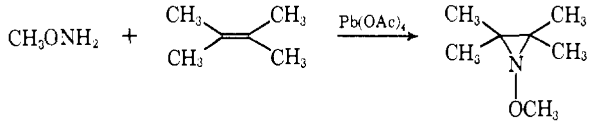
parable results were obtained using the methanesulfonyl derivative.[4]

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]

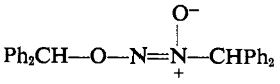
O to N migration also occurs when *N*-*p*-toluenesulfonyl-*O*-benzylhydroxylamine[6] (**6**) is allowed to react under these conditions. The rearranged product obtained in this case was benzonitrile in 34% yield.[7]

$$\underset{\mathbf{6}}{PhCH_2ONHTs} \xrightarrow[\text{2. triglyme, 165°}]{\text{1. NaH}} PhC{\equiv}N$$

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.

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[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/cm^3. 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,

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[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.