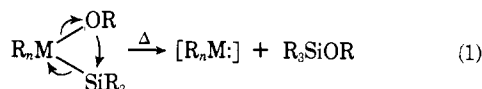


α -Deoxysilylation of Hydroxylamine Derivatives. A New Method for Nitrene Generation

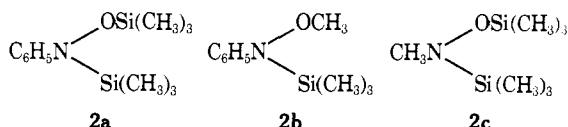
Sir:

Elimination of alkoxy silanes according to eq 1, which may be described as an α -deoxysilylation process,



1, M = C, Si; $n = 2$

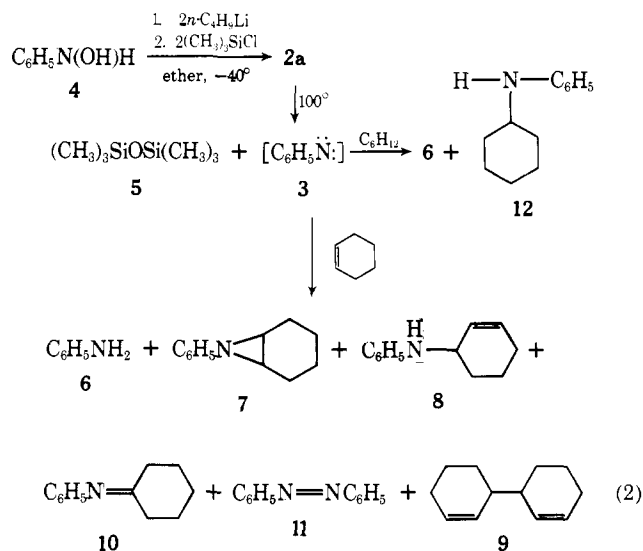
2, M = N; $n = 1$



has been heretofore restricted to pyrolyses of systems (1) wherein the central atom (M) is a member of the group IV elements, *viz.*, carbon¹ and silicon.^{2,3} We now report preliminary product and kinetic studies which indicate that the scope of eq 1 may be usefully extended to nitrene ($\text{R}\ddot{\text{N}}\cdot$) generation *via* pyrolysis of molecules in which the elimination center is nitrogen (2), the first representative of group V elements.

For comparative purposes, our initial investigations focused on hydroxylamine derivatives that would in principle generate phenyl nitrene (3), since a considerable body of data^{4a} is available on this reactive intermediate. Thus, *N,O*-bis(trimethylsilyl)phenylhydroxylamine⁵ (2a) was prepared (20%, nonoptimized) from *N*-phenylhydroxylamine (4) according to the reaction sequence in eq 2. The propensity of 2a toward fragmentation according to eq 1 was first evidenced by its mass spectrum (70 eV), which featured a relatively weak parent ion and a base peak at m/e 91, presumably due to $[\text{C}_6\text{H}_5\ddot{\text{N}}\cdot]^+$. This tentative conclusion was substantiated by the observation that 2a undergoes essentially complete reaction at 100° (16 hr) in cyclohexene (0.1 *M*) to yield hexamethyldisiloxane (5, *ca.* 100%, vpc), and at least eight additional products (vpc). Preparative vpc of this mixture led to isolation and identification (ir, nmr) of aniline (6, 20%), 7-phenyl-7-azabicyclo[4.1.0]heptane⁶ (7, 2%), secondary amine 8 (4%), and bicyclohexyldiene⁷ 9. Trace amounts (<1%) of imine 10⁸ and azobenzene (11) also eluted shortly before two final and as yet unidentified minor (<1%)

components. The yield of aniline is not appreciably altered by heating 2a in either toluene or cyclohexane, although the latter solvent does yield a small amount of *N*-cyclohexylaniline (12, 5%, vpc), as expected^{4a} for 3. Formation of products 6 and 8–10 from 2a in cyclohexene is neatly accommodated by application and simple extension of known^{4a,8} intermolecular reaction modes for ground state (triplet) 3, and it should be emphasized that isolation of 7 is particularly significant, since there is currently little evidence that *aryl* nitrenes (whether singlet or triplet) form aziridines by reaction with any olefin.^{4a} Kinetic studies which address this important point and are designed to exclude conceivable non-nitrene pathways to 7 are in progress.



To quantify the rate for α -deoxysilylation of 2a and provide information regarding the transition state for this novel reaction, kinetic measurements were carried out using 0.10 *M* solutions in toluene (sealed ampoules, *o*-dibromobenzene vpc internal reference). Linear least-squares analysis of first-order plots for the disappearance of 2a with time at temperatures of 90, 100, and 110° were clearly linear (two–three half-lives, $\pm 10\%$ slope error), as was a least-squares fit ($\pm 5\%$ slope error) of $\log(k/T)$ vs. $1/T$ which led to values of $\Delta H^\ddagger = 27.7$ kcal/mol and $\Delta S^\ddagger = -3.8$ eu ($\Delta G^\ddagger_{100^\circ} = 29.1$ kcal/mol). The unimolecular nature of the fragmentation was confirmed by appropriate kinetic experiments with various concentrations of 2a. Comparison of these rate data with those reported⁹ for phenylazide (13) in decalin reveals that elimination in 2a is almost 300 times faster than N_2 evolution from 13 and suggests that the present method may compete favorably with azide pyrolysis as a technique for nitrene generation under nonionic thermal conditions, especially in view of new and improved methods¹⁰ for synthesis of aryl- and alkylhydroxylamine derivatives.

If one assumes, as has been suggested^{1b,2a} for α -deoxysilylation of 1, that a "concerted" elimination (*cf.* 14) is operative for 2a, then requisite decrease in

(1) (a) W. H. Atwell, D. R. Weyenberg, and J. G. Uhlmann, *J. Amer. Chem. Soc.*, **91**, 2025 (1969); (b) A. G. Brook and P. J. Dillon, *Can. J. Chem.*, **47**, 4347 (1969); (c) A. G. Brook and J. M. Duff, *ibid.*, **51**, 352 (1973); (d) for analogous transformations with silanecarboxylate esters and acylsilanes see, respectively, A. G. Brook, *J. Amer. Chem. Soc.*, **77**, 4827 (1955), and A. G. Brook and J. M. Duff, *ibid.*, **89**, 454 (1967).

(2) (a) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968); (b) *J. Organometal. Chem.*, **5**, 594 (1966).

(3) The α -deoxygermylation of alkoxy polygermanes to yield germynes ($\text{R}_2\text{Ge}\cdot$) has recently been reported: P. Riviere, J. Satge, and D. Soula, *J. Organometal. Chem.*, **72**, 329 (1974).

(4) (a) P. A. S. Smith in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, Chapter 4; (b) F. D. Lewis and W. H. Saunders, Jr., *ibid.*, Chapter 3.

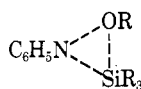
(5) Unless stated otherwise, all new compounds exhibited spectral (ir, nmr) properties wholly consistent with their assigned structures and gave acceptable ($\pm 0.3\%$) combustion analyses.

(6) R. A. Clark, Ph.D. Thesis, University of Maryland (1966); K. R. Henery-Logan and R. A. Clark, *Tetrahedron Lett.*, 801 (1968).

(7) M. Tada, T. Kosubo, and T. Sato, *Bull. Chem. Soc. Jap.*, **43**, 2162 (1970).

(8) J. H. Hall, J. W. Hill, and J. M. Fargher, *J. Amer. Chem. Soc.*, **90**, 5313 (1968).

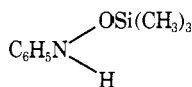
(9) K. E. Russell, *J. Amer. Chem. Soc.*, **77**, 3487 (1955).



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rotational/vibrational degrees of freedom is consistent with the negative (albeit small) ΔS^\ddagger value observed. The possible oversimplification of this interpretation is underscored, however, by noting that $\Delta S^\ddagger = -4.3$ eu for N_2 elimination from **13**. In connection with transition state considerations it is interesting that fragmentation of *O*-methyl-*N*-trimethylsilylphenylhydroxylamine^{5,11} (**2b**) in toluene at 170° to yield methoxytrimethylsilane and aniline (50% at low conversion) proceeds with a rate roughly 200 times *less* than that of **2a**. This reactivity order is opposite that predicted on purely steric grounds and is tentatively ascribed to the electropositive nature of the oxygen-bound silicon nucleus in **2a**, relative to its carbon counterpart in **2b**, which can lead to increased oxygen nucleophilicity and/or inductive stabilization of transition state **14**.

Like other reactions peculiar to organosilicon chemistry,¹³ the "driving force" for α -deoxysilylation of **2** may be reasonably associated (in part) with Si-O bond formation in **14**; especially in view of our finding that *O*-trimethylsilylphenylhydroxylamine⁵ (**15**) is essentially inert toward pyrolysis under those conditions (100°, 19 hr) which cause complete fragmentation of **2a**.



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An additional substituent effect in the pyrolysis of **2**, akin to those manifest with **1**,^{1b} was revealed by studies with *N,O*-bis(trimethylsilyl)methylhydroxylamine¹⁴ (**2c**) in cyclohexane (*ca.* 200°) since elimination of hexamethyldisiloxane from **2c** was found to be approximately 1000 times *slower* than elimination from **2a**. While this relative reactivity order parallels that for nitrene generation from ethylazide¹⁵ and **13**,⁹ evidence for methyl-nitrene (**16**) production from **2c** is presently tenuous for it rests on our isolation of only a trace amount (1.5%) of hexamethylenetetramine together with white crystalline polymer, which are considered to be characteristic^{4b} of **16** when thermally produced under a variety of conditions. No ammonia, methylamine, or *N*-methylcyclohexylamine were detectable (vpc).

Our study of photochemically induced α -deoxysilylation of **2** has, to date, been limited to **2a** ($\lambda_{\text{max}}^{\text{C}_6\text{H}_5\text{I}_2}$ 249 m μ , log ϵ 3.88) and **2b** ($\lambda_{\text{max}}^{\text{C}_6\text{H}_5\text{I}_2}$ 247 m μ , log ϵ 3.93). Both systems undergo complete reaction within 10 min at *ca.* 35° when irradiated at 2537 Å in cyclohexane (0.005 *M*), but at this wavelength product

(10) T. B. Patrick, J. A. Schield, and D. G. Kirchner, *J. Org. Chem.*, **39**, 1758 (1974); C. Bernhart and C.-G. Wermuth, *Tetrahedron Lett.*, 2493 (1974); Y. Isowa and H. Kurita, *Bull. Chem. Soc. Jap.*, **47**, 720 (1974).

(11) Prepared (43%) by analogy to **2a** starting with *O*-methylphenylhydroxylamine.¹²

(12) W. Walter and E. Schaumann, *Justus Liebig's Ann. Chem.*, **743**, 154 (1971).

(13) C. Eaborn, "Organosilicon Compounds," Butterworth, London, 1960; L. M. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

(14) O. Smrekar and U. Wannagat, *Monatsh. Chem.*, **100**, 760 (1969).

(15) G. Geiseler and W. König, *Z. Phys. Chem. (Leipzig)*, **227**, 81 (1964).

studies are complicated by extensive photodecomposition of the products, *viz.*, **6** and **12**. A comparison of thermal and photochemical reactions of **2**, together with an investigation dealing with the application of α -deoxysilylation to other group V elements will be reported in the future.

Acknowledgments. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for their partial support of this work. We also thank the Catholic University of America for a Biomedical Sciences Research Grant-in-Aid, and Professor Richard B. Timmons for assistance in mass spectroscopic measurements.

(16) PRF-ACS Undergraduate Research Participant, 1973-1974.

Fai P. Tsui,¹⁶ Theresa M. Vogel,¹⁶ Gerald Zon*
Maloney Chemical Laboratory,
The Catholic University of America
Washington, D.C. 20064
Received August 14, 1974

Mechanistic Studies of Oxidative Addition to Low-Valent Metal Complexes. III. Mechanism of Formation of Platinum to Carbon Bonds

Sir:

Although addition reactions of zerovalent d¹⁰ complexes have been extensively studied¹ and offer considerable practical utility,² few mechanistic studies are presently available.³ We present evidence that a major (but not sole) pathway for the addition of alkyl halides to the complexes M(PEt₃)₃ (**1**) (M = Pt, **1a**; M = Pd, **1b**)^{4,5} involves a radical chain process. Further observations on reactions of certain very reactive halides⁶ will be described in a following communication.

Despite earlier reports,⁷ addition reactions of alkyl halides with Pt⁰ complexes are often quite complex. For example, excess 1-bromobutane reacts with **1a** in degassed toluene at 25° for 2 hr to produce *trans*-Pt-RBr(PEt₃)₂ **2a** (R = Bu), *trans*-PtHBr(PEt₃)₂ **3a**, and *trans*-PtBr₂(PEt₃)₂ **4a** (approximate relative yields 95:4:1), as well as small quantities ($\approx 5\%$) of butane and but-1-ene.⁸ Further reaction causes the growth of **4a**, alkene, and alkane at the expense of **2a**, while

(1) See for example (a) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968); (b) A. J. Deeming, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Inorg. Chem., Series One*, **9**, 117 (1972).

(2) See M. F. Semmelhack, *Org. React.*, **19**, 115 (1972).

(3) The few mechanistic studies that have been performed generally utilize CH₃I or benzyl halides as addend, but these appear to be atypical alkyl halides. See (a) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968); (b) K. S. Y. Lau, R. W. Fries, and J. K. Stille, *ibid.*, **96**, 4983 (1974); (c) J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, **7**, 2672 (1968); (d) R. G. Pearson and J. Rajaram, *ibid.*, **13**, 246 (1974).

(4) (a) D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 3543 (1971); (b) A. Musco, W. Kuran, A. Silvani, and M. W. Anker, *J. Chem. Soc., Chem. Commun.*, 938 (1973).

(5) Although most of our studies involved the very reactive **1a**, we find reactions of Pt(PPh₃)₃ appear to follow similar, if considerably slower, paths.

(6) A. V. Kramer and J. A. Osborn, submitted for publication in *J. Amer. Chem. Soc.*

(7) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).