The study of the temperature-dependent pmr spectrum of *N*-fluoro-*N*-*tert*-butylbenzylamine (II_F)[13] leads to the determination of the inversion barrier of nitrogen ($\Delta G_c^{\ddagger}$) at the coalescence temperature T_c (Table II). In the case of $PhCH_2NF$-*t*-Bu (II_F) the spectrum due to the CH_2 group should be, at low temperature, decomposed into two AB subspectra because of the coupling $^3J_{AX}$ and $^3J_{BX}$ with fluorine X ($^3J_{HCNF} \sim 50$ Hz[10]). In fact, one of the AB subspectra is a real quadruplet and gives an A_2 spectrum by increasing the temperature;[14] the other AB subspectrum is a singlet the shape of which is not changing with temperature (Figure 2). The whole pmr spectrum of the CH_2 group leads to a calculation of $^3J_{AX}$ and $^3J_{BX}$, and thus allows the discovery of the X part of the spectrum (F nmr), which is in agreement with what is expected. The effect of fluorine is therefore to increase the barrier of inversion in amines by about 9 kcal/mol, if we compare it to the *N*-methyl homolog (II_F compared to II_{CH_3}), and we can conclude that *the effect of fluorine on the inversion barrier of amines (+9 kcal/mol) is of the same order of magnitude as its effect on the rotation barrier in amides (−10.5 kcal/mol) but, of course, in the opposite sense.*

Acknowledgment. We thank Professor J. J. Delpuech from Nancy who did computations and one of us (J. Leroy) thanks the French Commissariat on Atomic Energy (C.E.A.) for a doctoral fellowship.

(13) The compound II_F has been prepared by the reaction of $FClO_3$ with *N*-*tert*-butylbenzylamine according to a previously described procedure.[10] The elemental analysis, the mass spectrum, and the pmr spectrum are in agreement with the assigned structure: mass m^+/e, M = 181 (0.13); M − CH_3 = 166 (0.47); M − HF = 161 (0.18); M − NF = 148 (1). *Anal.* Calcd for $C_{11}H_{16}NF$: C, 72.89; H, 8.89; N, 7.73; F, 10.48. Found: C, 73.16; H, 9.05; N, 7.75; F, 9.60.

(14) This allows the calculation of $\Delta G_c^{\ddagger}$, according to the formula[7]

$$\Delta G_c^{\ddagger} = 4.57 T_c \left[9.97 + \log \frac{T_c}{(\Delta\nu^2 + 6J^2)^{1/2}} \right]$$

(15) Centre National de la Recherche Scientifique.

(16) C. E. A., Etablissement T.

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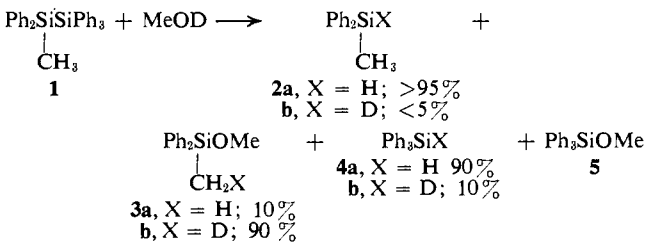
Photochemical Dehydrosilylation of Pentaphenylmethyldisilane. Generation and Trapping of an Unstable Intermediate Containing a Silicon–Carbon Double Bond or Its Equivalent

Sir:

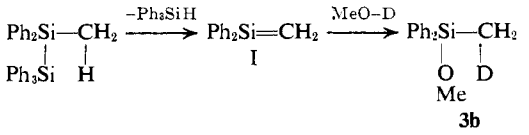
While there has been intense activity in the field of the photochemistry of carbon compounds, photochemical studies of organosilicon compounds have received comparatively little attention. We have initiated an investigation of the photochemistry of organodisilanes and we believe we have firmly established the formation of $Ph_2Si{=}CH_2$ or its close equivalent, the diradical $Ph_2\dot{S}i{-}\dot{C}H_2$.

Absorption of the Ph–Si–Si moiety in the accessible ultraviolet region[1] suggested that phenyl-substituted disilanes would be interesting subjects for photochemical investigations. We have found that when pentaphenylmethyldisilane[2] (**1**) is photolyzed at 2537 Å for 2 hr at 55° in methanol-d_1 and cyclohexane, $Ph_2(CH_2D)SiOMe$



(**3b**) and Ph_3SiH (**4a**) are obtained in approximately 60% yield.[3] **3b** was characterized using nmr and mass spectral techniques. The relative areas of the Si–C–H (m, τ 9.38) and O–C–H (s, τ 6.45) protons show that the isotopic purity is about 90%. An exact *m/e* measurement of the parent peak was carried out and a value of 229.1031 was obtained. This compares well with the calculated *m/e* of 229.1029. The structure and purity of **4a** were determined by comparison of its ir, nmr, and vpc spectra with those of a known sample.[4] It is important to note that the ir spectrum of this compound showed no band at 1550 cm^{-1} where the intense Si–D band is normally found.

These products are consistent with a dehydrosilylation mechanism[5] in which an intermediate like I must be important.[6,7] The overall yield is approximately 90% and the reaction is comparatively free of side reactions. The silanes **2a** and **5** occur in roughly equal amounts



and account for about 20% of the product mixture. These are probably formed from homolytic cleavage of the Si–Si bond in **1** followed by attack of the silyl radicals on the solvents. This process could also account for the presence of **3a** and some of **4a**. Nucleophilic attack on the Si–Si bond by methanol-d_1 is not occurring to a significant extent as shown by the small amounts of **2b** and **4b** in the products.

Further support for the intramolecular nature of this reaction comes from the photolysis of $Ph_2(CD_3)$-$SiSiPh_3$ (**6**) in methanol. The major products were $Ph_2(CD_2H)SiOMe$ (**7**) and Ph_3SiD (**4b**). An exact *m/e*

(1) H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organometal. Chem.*, 4, 176 (1964).

(2) H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. Ind. (London)*, 1479 (1958).

(3) Vpc analysis of the product mixture showed six peaks, two of which were less than 2% of the sum of the peak areas and could not be isolated. The remaining four peaks were collected by vpc preparative methods.

(4) Pure samples of **2a**, **3a**, **4a**, and **5** were obtained by independent syntheses and their spectra used for comparison with the spectra of the reaction products.

(5) Intramolecular hydrogen transfer has been observed in the pyrolysis of disilane: P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *Inorg. Chem.*, **9**, 1068 (1970).

(6) Photolysis of **1** (2537 Å) in cyclohexane gave an insoluble yellow polymer resulting from polymerization of I in the absence of a methanol trap. Formation of dimer or trimer was not observed. The other major product was Ph_3SiH.

(7) It has been observed that the thermolysis of 1,1-dimethyl-1-silacyclobutane yields $Me_2Si{=}CH_2$ which dimerizes in the vapor phase and polymerizes in the liquid phase: M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968). These authors have also reported vapor-phase addition of water to give Me_3SiOH.

measurement (calcd, 230.1096; found, 230.1086) and nmr spectroscopy were used to characterize **7** and to estimate its isotopic purity (90%). Nmr and ir spectroscopy showed that **4b** and **4a** were present in approximately a 9:1 ratio. The minor products were $Ph_2(CD_3)SiH$ (**8**) and **5**.

These reactions provide the first examples in which photolytically generated intermediates like I have been trapped and the products characterized.[8] Another unique feature of this reaction is that it is formally the reverse process of the well-known addition reaction of Si–H compounds to alkenes.[9]

Acknowledgment. We thank the National Science Foundation for vital support which made this work possible and Mr. Kei Miyano for vital mass spectral studies.

(8) The diradical $H_2\dot{C}$–$\dot{S}iH_2$ was postulated as an intermediate upon photolysis of CH_3SiH_3: K. Obi, A. Clement, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, **91**, 1622 (1969).

(9) C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960.

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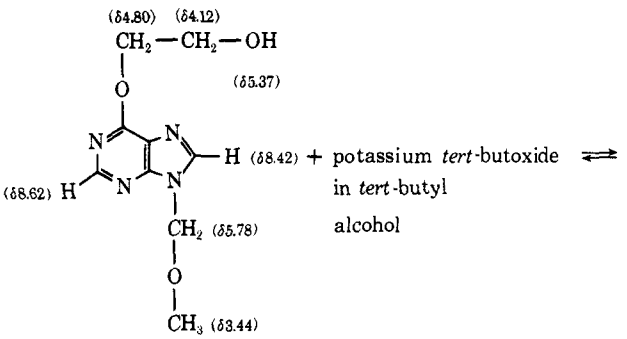
Direct Observation of Reversible Formation of Anionic σ Complexes[1] Related to Transition State Analogs for Adenosine Deaminase

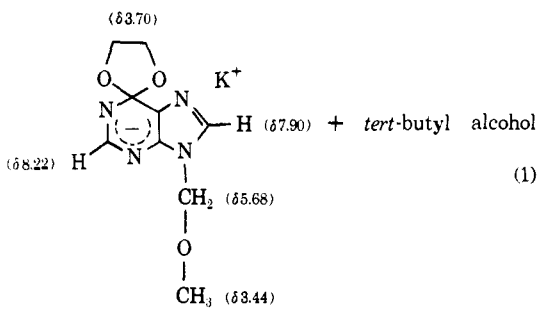
Sir:

Adenosine deaminase has been reported to catalyze the hydrolysis of nitrogen, halogen, oxygen, and sulfur leaving groups located at the 6 position of purine ribonucleosides.[2] Evidence has been presented which indicates that the mechanism involves nucleophilic substitution of water or enzyme-bound water on the purine nucleus proceeding *via* a tetrahedral intermediate.[3-7] Recently, Evans and Wolfenden[8,9] have prepared purine analogs with tetrahedral carbon at C-6 *via* photochemical addition of methyl alcohol to purine ribonucleoside and have shown that these act as powerful enzyme inhibitors. *We now report (1) the first direct observation of the reversible formation of purine analogs with tetahedral carbon at C-6 via a nucleophilic addition mechanism, and (2) the first observable σ anionic complexes not stabilized by nitro groups.*

The reaction of 6-(β-hydroxyethoxy)-9-methoxymethylpurine (I) (0.32 *M*) with potassium *tert*-butoxide (0.32 *M*) in *tert*-butyl alcohol to form anionic σ complex II was followed using nmr spectroscopy (eq 1). The cyclization was essentially complete within 90 min. The peak assignments are illustrated in eq 1. The negative charge introduced in the ring[10] and/or the diminished diamagnetic anisotropy resulting from decreased ring current[11] causes the absorptions of the protons attached to C-2 and C-8 to shift from δ 8.62 and 8.42 to 8.22 and 7.90, respectively. The methylene protons of the hydroxyethoxy group in I show two absorptions (δ 4.80 and 4.12) which become a broad absorption at 3.70 in II.[12,13] The methylene protons of the methoxymethyl group are shifted from δ 5.78 to 5.68 while the methoxy protons remain unchanged.



I



(1)

II

The reaction of 6-methoxy-9-methoxymethylpurine (III) (0.48 *M*) with potassium methoxide (0.48 *M*) in *tert*-butyl alcohol to form anionic σ complex IV was followed using nmr spectroscopy (eq 2). After 60 min the ratio of III/IV was 62:38.[14] The nmr assignments of III and IV are indicated in eq 2. These appear to be consistent with those of eq 1.

Wolfenden[9] has speculated that the protonated form of structure V is a reasonable representation of the intermediate formed in the adenosine deaminase catalyzed nucleophilic attack of water on 6-aminopurine ribonucleoside. The work presented in this communication indicates two important points related to structure V: (1) stable anionic σ complexes with two electronegative atoms attached to the tetrahedral carbon can form at the C-6 position of the purine ring system by an aromatic nucleophilic addition mechanism and (2) the presence of nitro groups on the aromatic ring is not a necessary condition for the formation of such complexes.

(1) For an excellent comprehensive review of anionic σ complexes through Jan 1970, see M. J. Strauss, *Chem. Rev.*, 667 (1970).
(2) R. Wolfenden, *J. Amer. Chem. Soc.*, **88**, 3157 (1966).
(3) R. Wolfenden, T. K. Sharpless, I. S. Ragade, and N. J. Leonard, *ibid.*, **88**, 185 (1966).
(4) R. Wolfenden and J. F. Kirsch, *ibid.*, **90**, 6849 (1968).
(5) B. T. Walsh and R. Wolfenden, *ibid.*, **89**, 6221 (1967).
(6) R. Wolfenden, *Biochemistry*, **8**, 2409 (1969).
(7) R. Wolfenden, J. Kaufman, and J. B. Macon, *ibid.*, **8**, 2412 (1969).
(8) B. Evans and R. Wolfenden, *J. Amer. Chem. Soc.*, **92**, 4751 (1970).
(9) R. Wolfenden, *Accounts Chem. Res.*, **5**, 10 (1972).
(10) M. R. Crampton and V. Gold, *J. Chem. Soc.*, 3293 (1964).
(11) P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zollinger, *Helv. Chim. Acta*, **50**, 848 (1967).
(12) It should be emphasized that the four methylene protons in II are not equivalent since two of the protons will be directed toward the imidazole ring and two away from it.
(13) The unsymmetrical spiro complex formed from the reaction of 2-(β-hydroxyethoxy)-3,5-dinitropyridine and sodium methoxide in DMSO also shows a singlet for the methylene protons; C. A. Fyfe, *Tetrahedron Lett.*, 659 (1968).
(14) This ratio does not represent the final equilibrium. It is merely an indication of the rate of formation of IV as compared to II.