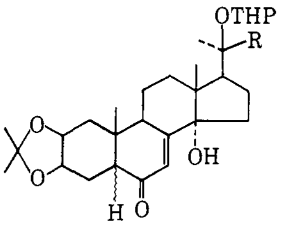

VI , 5α-H, R = (22*R*)-CH(OH)C≡CC(CH$_3$)$_2$OTHP
b, 5β-H, R = (22*R*)-CH(OH)C≡CC(CH$_3$)$_2$OTHP
c, 5β-H, R = (22*R*)-CH(OH)CH$_2$CH$_2$C(CH$_3$)$_2$OTHP

acid hydrolysis of the protecting groups of VIc and chromatographic purification of the product afforded crustecdysone (Ia) [mp 240–242° (from methanol–ethyl acetate); λ_{max}^{EtOH} 240 mμ (ϵ 12,670); ν_{max}^{KBr} 1656, 1615, 1387, 1229, 1053, 917, and 878 cm^{-1}; nmr (pyridine-d_5) 1.07 (19-H), 1.20 (18-H), 1.36 (26- and 27-H), 1.56 (21-H), and 6.17 (7-H)].

A mixture melting point with authentic crustecdysone[15] (mp 247–248°) showed no depression. The two samples were identical in spectroscopic[16] and chromatographic behavior and biological activity in *Samia cynthia* silkmoth assay for moulting hormone activity.

Further evidence for the stereochemical identity of the natural and synthetic crustecdysones is available from alkylation of the 20*S* isomer Vf and subsequent elaboration of the products by the above method. This led to two compounds (isomeric at C$_{22}$), one considerably more polar than authentic crustecdysone and the other closely similar in R_f to Ia. However, chemical shifts of the latter compound [nmr (pyridine-d_5) 1.38 (21-H) and 1.48 (26- and 27-H)] showed it to be a stereoisomer (probably 20*S*,22*R*) of the natural product.

(15) We are deeply indebted to Dr. D. H. S. Horn for this sample.

(16) Mass spectra of synthetic and natural crustecdysone determined on an Atlas CH-4 spectrometer showed a fragment m/e 462 (M − H$_2$O) followed by loss of three molecules of water. Fragments observed at m/e 363 and 117 are characteristic of C$_{20}$–C$_{22}$ cleavage of the trihydroxylated side chain.

(17) Syntex Postdoctoral Fellow, 1966–1967.

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The Electronic Absorption Spectra of Aminosilanes[1]

Sir:

The departure from tetrahedral geometry[2] and the anomalously weak donor properties[2,3] of various aminosilanes provide positive experimental evidence for the existence of (p → d)π Si–N bonding. On the basis of a Pariser–Parr–Pople SCF treatment, Perkins[4] has estimated that the energy of this bond in trisilylamine is ~16 kcal. However, this assessment must be contrasted with the agnostic attitude of Randall and Zuckerman,[5] who failed to observe any difference in J(^{15}N–H), and hence the nitrogen hybridization, on trimethylsilylation of [^{15}N]aniline. Similarly, nmr experiments[6] designed to evaluate the transmission of substituent effects through the N–Si–N system in silaimidazolidines did not reveal any differences from the analogous carbon system (N–C–N), and the force constant of the Si–N bond is more consistent with single than with double bond character.[7] We have now measured the electronic absorption spectra of selected aminosilanes and have found this to be a fruitful approach to the understanding of the nature of the (p → d)π Si–N bond.

In contrast to alkyl substitution,[8] stepwise silylation of ammonia results in a progressive hypsochromic shift of the absorption maxima (Table I). The transparency of the analogous carbon[9] and oxygen[10] derivatives (Me$_3$Si–X–SiMe$_3$, X = O, CH$_2$) in the ultraviolet, coupled with the weak hypsochromic shift on changing the solvent from isooctane to ethanol and the strong hypsochromic shift on N-acetylation, demonstrates that the nonbonding nitrogen electrons rather than σ electrons are involved in the transition. The excited state of the transition may be the Si–N σ^* orbital. In this case the transition corresponds to the long-wavelength absorption of alkylamines, and the hypsochromic shift produced on progressive substitution with the more electropositive trialkylsilyl group[11] is explained in terms of the delocalization (and hence stabilization) of the nitrogen lone pair into the silicon d orbitals and is in agreement with the reported[3] trend in the basicity of

Table I. Absorption Maxima and Basicities of Aminosilanes

Compd	λ_{max}, mμ[a]	ϵ	$\Delta\nu$,[b] cm^{-1}
Et$_3$SiNH$_2$	208.8	1780	38
(Et$_3$Si)$_2$NH	205.5	1810	*e*
(Me$_3$Si)$_2$NH	203.7 202.6[c]	2870	30[d]
(Me$_3$Si)$_3$N	200.4 200.1[c]	4850	*d*, *e*
Me$_3$SiNHCOMe	<195.0	2200 (200 mμ)	
(Me$_3$Si)$_2$NCOMe	<195.0	3700 (200 mμ)	
PhNH$_2$	233.7, 287.5	9130, 1860	
PhNHSiMe$_3$	239.8, 291.0	10700, 1860	
PhN(SiMe$_3$)$_2$	234.0, 265.0	3250, 445	
Me(Me$_2$SiNH)$_2$SiMe$_3$	200.0	4840	30
Me(Me$_2$SiNH)$_3$SiMe$_3$	201.8	6800	29
(Me$_2$SiNH)$_3$	201.8	6160	31[d]
(Me$_2$SiNH)$_4$	201.1	7730	
Me$_8$Si$_3$	216.5	7900	
n-Me$_7$Si$_3$NH$_2$	213.0[f]	6420	39
(*n*-Me$_7$Si$_3$)$_2$NH	217.5[f]	13200	*e*

[a] Determined in dry spectral grade isooctane using 1-mm cells and a Cary 14 spectrometer. [b] C–D stretching frequency shift of CDCl$_3$ (~1 mole) in amine (~10 mole) relative to corresponding mode of gaseous CDCl$_3$. [c] Determined in absolute ethanol; extinction coefficient uncertain because of ethanolysis. [d] Values from Abel, Armitage, and Willey.[3] [e] No trace of shifted C–D absorption. [f] Inflection point.

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(1) This work was supported in part by the Electronic Technology Division of the Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio, under Contract No. AF-33(615)-67-C-1175.

(2) For recent summaries, see R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961); U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964). For a discussion of the relationship between geometry and the magnitude of (p → d)π bonding, see E. A. V. Ebsworth, *Chem. Commun.*, 530 (1966).

(3) E. W. Abel, D. A. Armitage, and G. R. Willey, *Trans. Faraday Soc.*, **60**, 1257 (1964); E. W. Abel, D. A. Armitage, and D. B. Brady, *ibid.*, **62**, 3459 (1966).

(4) P. G. Perkins, *Chem. Commun.*, 268 (1967).

(5) E. W. Randall and J. J. Zuckerman, *ibid.*, 732 (1966).

(6) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **6**, 103 (1967).

(7) E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *Spectrochim. Acta*, **13**, 202 (1958).

(8) E. Tannenbaum, E. M. Coffin, and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).

(9) Unpublished results, C. G. Pitt.

(10) A. P. Kreshkov, Yu. Ya. Mikhailov, and I. P. Smirenkina, *Zh. Fiz. Khim.*, **32**, 834 (1958).

(11) D. R. M. Walton, *J. Organometal. Chem.* (Amsterdam), **3**, 438 (1965).

these compounds. The increase in the s character of the Si–N σ bonds on partial rehybridization of the nitrogen atom from sp^3 to sp^2 may also contribute to the hypsochromic shift by increasing the energy of the excited state.[12] Alternatively, the absorption can be attributed to the $\pi \rightarrow \pi^*$ transition of the $(p \rightarrow d)\pi$ Si–N bond, where the ground and excited states are largely n and 3d(Si) in character, respectively. For this situation, the excited state is slightly stabilized (because of an averaging of the perturbation) while the ground state becomes substantially stabilized by the progressive introduction of silicon atoms.

Mono-N-trimethylsilylation of an arylamine such as aniline produces a bathocromic shift of *both* the primary and secondary bands of the same order found for mono-N-alkylation of aniline.[13] This observation is consistent with ^{15}N nmr experiments[6] where the invariance of $J(^{15}N\text{–}H)$ on silylation has been attributed[4] to competition of both the silicon atom and the benzene ring for the nitrogen lone pair. In this circumstance the inductive electron supply[14] of the silicon atom becomes dominant. Bis(N-trimethylsilylation) of aniline must result in severe steric inhibition of resonance,[13] because the secondary band undergoes a large hypsochromic shift and the extinction coefficients of both transitions are greatly reduced.

The invariance of the absorption (200–202 mμ) of both the linear and cyclic polydimethylsilazanes and the proportionality of the extinction coefficient to the number of Si–N bonds in the molecule indicate there is essentially no delocalization or aromaticity associated with the total Si–N framework. This conclusion is supported by the similarity of the base strengths of the silazanes (Table I), as determined by the shift of the C–D stretching frequency ($\Delta\nu$) of $CDCl_3$–amine mixtures.[3] Delocalization in p_π–d_π systems has been discussed in molecular orbital terms by a number of groups. The identical electronic properties of the silazanes may be attributed to the symmetry of the 3d orbitals which, as in the case of the phosphonitrilics,[16] may lead to isolated allylic type (Si–N–Si) chromophores. Alternatively, the large difference in the Coulombic integrals of nitrogen and silicon, possibly coupled with a small resonance integral, will dictate an essentially localized $(p \rightarrow d)\pi$ bond.[17]

A second method of evaluating transmission through the Si–N bond is to examine the modification of the ultraviolet absorption of polysilanes on nitrogen substitution. For example, $n\text{-}Me_7Si_3NH_2$ exhibits a hypsochromic shift while $n\text{-}(Me_7Si_3)_2NH$[18] exhibits a bathochromic shift when compared with the unsubstituted trisilane, Me_8Si_3. Thus, although the nitrogen atom is interacting with the ground and/or excited states of the silicon chain there is very little interaction of the two Si_3 units across the nitrogen atom in the secondary amine. The basicity of $n\text{-}Me_7Si_3NH_2$ is not significantly different from that of triethylsilylamine (Table I), demonstrating the same order of $(p \rightarrow d)\pi$ delocalization in both compounds.

Electronic absorption spectroscopy promises to be a useful technique for the study of other group IV derivatives in which $(p \rightarrow d)\pi$ bonding is postulated.

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[12] An inherent shortcoming of electronic absorption spectroscopy is this inability to quantitatively assess the relative contributions of the ground and excited states to the shifts in the absorption maxima.

[13] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 410.

[14] Electron-withdrawing groups may also cause a bathochromic shift of the primary band, but their effect on the secondary band is much less significant. For example, N-acetylation of aniline results in a bathochromic shift of the primary band but a hypsochromic shift of the secondary band.[15]

[15] H. E. Ungnade, *J. Am. Chem. Soc.*, **75**, 432 (1953).

[16] M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

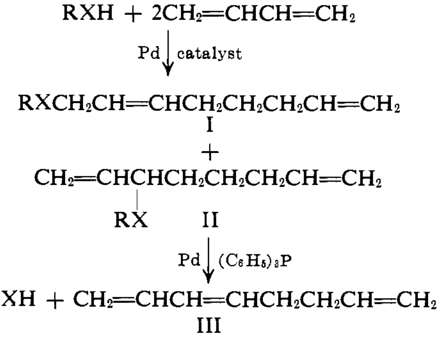
[17] D. P. Craig, *ibid.*, 997 (1959).

[18] Satisfactory elemental analyses and infrared spectra have been obtained for all new compounds described in this communication.

Oligomerization and Dimerization of Butadiene under Homogeneous Catalysis. Reaction with Nucleophiles and the Synthesis of 1,3,7-Octatriene

Sir:

Palladium salts participate in stoichiometric reactions with olefins to form π complexes,[1] with nonconjugated dienes to form σ complexes,[2] and with conjugated dienes to form π-allyl complexes.[3] In solution, palladium salts catalyze the dimerization of olefins.[4] The catalytic activity of supported noble metals, particularly nickel, palladium, and platinum, in hydrogenation and dehydrogenation reactions is equally well known. Previously unknown is a homogeneous reaction between dienes and nucleophiles catalyzed by soluble palladium complexes. We wish to report just such a reaction that involves, in effect, an anti-Markovnikov addition of nucleophiles to a linear butadiene dimer.[5]



$$\begin{array}{c} RXH + 2CH_2{=}CHCH{=}CH_2 \\ \Big\downarrow \scriptstyle{Pd\ catalyst} \\ \underset{\text{I}}{RXCH_2CH{=}CHCH_2CH_2CH_2CH{=}CH_2} \\ + \\ CH_2{=}CH\underset{\underset{RX}{|}}{C}HCH_2CH_2CH_2CH{=}CH_2 \quad \text{II} \\ \Big\downarrow \scriptstyle{Pd\ (C_6H_5)_3P} \\ RXH + \underset{\text{III}}{CH_2{=}CHCH{=}CHCH_2CH_2CH{=}CH_2} \end{array}$$

Condensation of phenol and butadiene at 60° for 24 hr in the presence of the butadiene–palladium chloride–π–allyl complex[3] leads to a mixture of *o*- and *p*-butenylphenols and phenoxybutene in low conversion (5–10%) and yield (30%). Most solvents are of little effect. However, with pyridine the reaction takes a completely different and unexpected course: 1-phenoxyoctadiene-

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[1] M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938); J. N. Dempsey and N. C. Baenziger, *ibid.*, **77**, 4984 (1955); J. R. Holden and N. C. Baenziger, *ibid.*, **77**, 4987 (1955).

[2] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957); J. K. Stille, R. A. Morgan, D. D. Whitehurst, and J. R. Doyle, *J. Am. Chem. Soc.*, **87**, 3282 (1965); J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966); W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966).

[3] B. L. Shaw, *Chem. Ind.* (London), 1190 (1962); S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963); S. D. Robinson and B. L. Shaw, *ibid.*, 5002 (1964); E. J. Smutny, unpublished results.

[4] J. T. van Gemert and P. R. Wilkinson, *J. Phys. Chem.*, **68**, 645 (1964); A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967); R. van Helden, C. F. Kohll, and G. Verberg, unpublished results.

[5] Netherlands Patent Application No. 6,606,567 (Nov 15, 1966); E. J. Smutny, U. S. Patent 3,267,169 (Aug 16, 1966).