15   16

Catalytic reduction of **9** with hydrogen in ethanol (Pd/C, 25°, 1 atm) gave **15**[6] as an oil, which appeared homogeneous on a variety of tlc plates. When mixed with dimethyl acetylenedicarboxylate, **9** gave a one-to-one complex, **17**[6a,c,12] (74%), mp 72–73°, which although sublimable from its melt separated into its components upon a gel permeation chromatographic column and in a mass spectrometer. When heated at 110° with excess dimethyl acetylenedicarboxylate, **9** gave **16**[6b,c] (~100%), mp 55–60°. The pmr spectrum of **16** is temperature dependent and consistent with a steric barrier at 25° for the carbon bridges of the bicyclic system passing through the center of the major ring. The complexing properties of these multiheteromacrocycles are reported elsewhere.[13] The reactions and properties of these and other furan-containing multiheteromacrocycles are under active investigation.

(12) The X-ray crystal structure will be reported by Drs. I. Goldberg and K. N. Trueblood.
(13) J. M. Timko, R. C. Helgeson, M. Newcomb, G. W. Gokel, and D. J. Cram, *J. Amer. Chem. Soc.*, **96**, 7097 (1974).

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Tin(II) Organosilylamines[1]

Sir:

Bis[N,N-bis(trimethylsilyl)amino]tin(II) (A), a novel, dimeric organosilylamino derivative in which tin is stabilized as Sn(II), has been prepared analytically pure in 50% yield by the lithioamination of tin(II) chloride by hexamethyldisilazane in a 1:2 ratio. A is isochrom-

$$2[(CH_3)_3Si]_2NLi + SnCl_2 \longrightarrow (\{[(CH_3)_3Si]_2N\}_2Sn)_2 \quad (1)$$
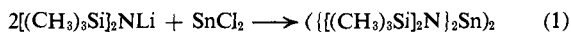
ous with Lappert's isoelectronic bis[bis(trimethylsilyl)-methyl]tin(II)[2] in being a chinese red (λ_{max} 3870 Å) distillable liquid (bp 109–110°, 0.75 Torr), which solidifies to an orange-yellow solid at room temperature, but not isostructural with it or the Zn,[3] Cd,[3] Hg,[3] or Be[4] analogs in being a dimer (mol wt 439.5, found 880 and 884 (osmometry in benzene); the highest observed ion at 70 eV in the mass spectrum is 2P+, with seven polyisotopic ditin fragments[5] appear-

(1) Preliminary reports of this work have been presented at the 1974 Organosilicon Award Symposium, St. Louis, Mo., March 1974 and at the 168th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1974.
(2) P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 317 (1973).
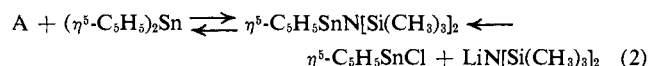(3) H. Bürger, W. Sowodny, and U. Wannagat, *J. Organometal. Chem.*, **3**, 113 (1965).
(4) A. H. Clark and H. Haaland, *Chem. Commun.*, 912 (1969).
(5) Intensity ratios clearly distinguish tin- and ditin-bearing fragments in mass spectra.

ing between P+ and 2P+ associated with loss of CH_3, $Si(CH_3)_3$, $N[Si(CH_3)_3]_2$, etc., in various combinations). The ^{119m}Sn Mössbauer isomer shift (IS) of 2.88 mm/sec[6] confirms tin as Sn(II),[7] but the quadrupole splitting (QS) of 3.52 mm/sec[8] is among the largest ever recorded for a tin(II) species.[9] We have recorded the nmr couplings shown in the scheme. The trimethylsilyl protons give a singlet resonance at δ 0.23 ± 0.01 ppm in benzene, $CDCl_3$, THF, or in the neat liquid, and to −150° at 251 MHz in dimethyl ether,[10] giving no indication of a monomer–dimer equilibrium.

A reacts with methanol to give dimethoxytin(II),[11] and with oxygen to give bis[bis(trimethylsilyl)amino]-tin(IV) oxide as a white, infusible solid (IS = 0.56, QS = 0.83 mm/sec), and exchanges with stannocene to give η^5-cyclopentadienyl[bis(trimethylsilyl)amino]-tin(II)[12] which is also formed by lithioamination of η^5-

$$A + (\eta^5\text{-}C_5H_5)_2Sn \rightleftharpoons \eta^5\text{-}C_5H_5SnN[Si(CH_3)_3]_2 \longleftarrow$$
$$\eta^5\text{-}C_5H_5SnCl + LiN[Si(CH_3)_3]_2 \quad (2)$$

cyclopentadienyltin(II) chloride,[13] but reverts to A and stannocene on attempted isolation.

Lithiobis(trimethylsilyl)amination of tin(II) chloride in a 1:1 ratio gives N,N-bis(trimethylsilyl)aminotin(II) chloride (B) as a white solid in 50% yield.
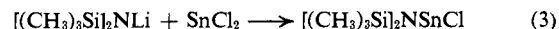
$|^3J(^{119}SnNSi^{13}C)| = 24.9$ Hz $|^4J(^{119}SnNSiC^1H)| = 2.5$ Hz

$|[(^1H_3^{13}C)_3{}^{29}Si]_2N^{119}SnN[^{29}Si(^{13}C^1H)_3]_2$
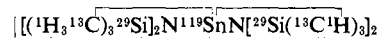
$|^2J(^{29}SiC^1H)| = 6.5$ Hz $|^2J(^{119}SnN^{29}Si)| = 16.2$ Hz

$|^1J(^{29}Si^{13}C)| = 55.3$ Hz

$|^1J(^{13}C^1H)| = 116.0$ Hz

$$[(CH_3)_3Si]_2NLi + SnCl_2 \longrightarrow [(CH_3)_3Si]_2NSnCl \quad (3)$$

The IS (3.18 mm/sec) confirms tin as Sn(II),[5] but the QS (2.64 mm/sec) is smaller by nearly 1 mm/sec than in the apparently symmetrical A.[14] The syntheses of other derivatives are underway using B as starting material.

The heterocyclic N,N'-bis(trimethylsilyl)tin(II) imidazolidine (mp 134–135°; IS = 2.66, QS = 2.50 mm/sec), perhydropyrimidine (mp 108–109°; IS = 2.71, QS = 2.34 mm/sec), and 1,3-perhydrodiazepin (mp 83.5–84.5°; IS = 2.67, QS = 2.24 mm/sec) form in ca. 50% yield from the lithioamination of tin(II)

(6) IS error limits ±0.06 mm/sec at 77°K *vs.* Ba^{119m}SnO$_3$ at room temperature.
(7) J. J. Zuckerman, *Advan. Organometal. Chem.*, **9**, 21 (1970).
(8) QS error limits ±0.12 mm/sec.
(9) Among tin(II) species, only 3-stanna-1,2-dicarba-*closo*-dodeca-carborane(II) (IS = 4.67 ± 0.04, QS = 3.84 ± 0.04 mm/sec) has a larger splitting (R. W. Rudolph and V. Chowdhry, *Inorg. Chem.*, **13**, 248 (1974). Dimethoxytin(II), for example, gives QS = 2.00 ± 0.12 mm/sec (W. D. Honnick and J. J. Zuckerman, unpublished results).
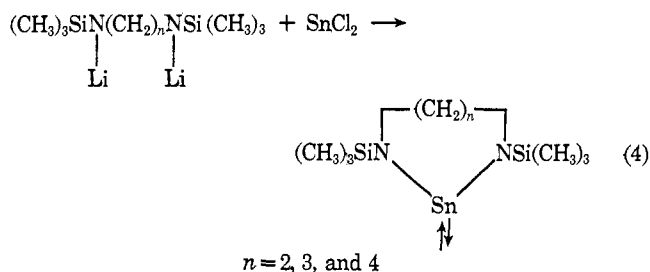(10) We are grateful to Professor F. A. L. Anet of UCLA for carrying out this experiment.
(11) J. S. Morrison and H. M. Haendler, *J. Inorg. Nucl. Chem.*, **29**, 393 (1967).
(12) The tin-119 coupling to the protons of the cyclopentadienyl group changes from 15.9 Hz in stannocene (L. D. Dave, D. F. Evans, and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959)) to 12.5 ± 0.3 Hz in the mixed derivative.
(13) K. D. Bos, E. J. Bulten, and J. G. Noltes, *J. Organometal. Chem.*, **39**, C52 (1972).
(14) The QS of stannocene (0.86 ± 0.12 mm/sec) (P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **92**, 2577 (1970)) and of tin(II) chloride (none) (J. J. Zuckerman, *J. Inorg. Nucl. Chem.*, **29**, 2191 (1967)) are both smaller than that of the chloride, C_5H_5SnCl (1.05 mm/sec).[13]

$$(CH_3)_3SiN(CH_2)_nNSi(CH_3)_3 + SnCl_2 \longrightarrow$$

with Li and Li substituents shown below the nitrogens.

$$(CH_3)_3SiN \overset{\overset{\displaystyle \lceil (CH_2)_n \rceil}{}}{} NSi(CH_3)_3 \quad (4)$$
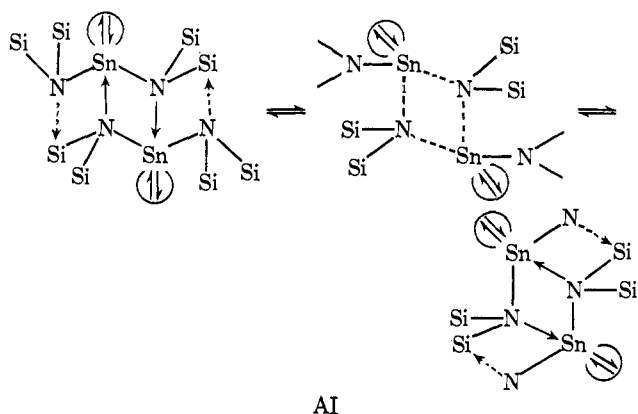
with Sn below.

$$n = 2, 3, \text{ and } 4$$

chloride by the corresponding diamine.[15] The aliphatic heterocycles have QS values smaller by >1 mm/sec than for A, but the analogous products from N,N'-bis(trimethylsilyl)-o-phenylenediamine[16] (mp 88° dec; IS = 2.67, QS = 2.85 mm/sec) and 1,8-diamino-naphthalene[17] (mp 82.5° dec; IS = 2.70, QS = 3.31 mm/sec) are yellow 1:1 adducts of the reaction solvent.

C   D
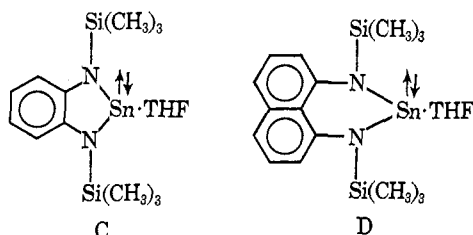
C darkens on removal of THF at room temperature *in vacuo* to give the free heterocycle (oil, IS = 2.57, QS = 2.41 mm/sec). The larger QS values of the adducts, as in A, arise from the higher coordination at the tin(II) atom.

Prominent absorptions in the far infrared, absent in the starting materials, can be assigned to $\nu_a(\text{Sn(II)}-\text{N})$ at 402 (m) in A, and at 372 (m), 398 (s), and 396 (s) in the $n = 2$, 3, and 4 aliphatic heterocycles, while adducts C and D show bands at 358 (s, br) and 365 (m) cm^{-1}, respectively. Unresolved, weak shoulder bands, probably associated with $\nu_s(\text{Sn(II)}-\text{N})$ are found 10–22 cm^{-1} to lower energy, consistent with the data for the Cd analog ($\nu_a(\text{Cd}-\text{N}) = 410$; $\nu_s(\text{Cd}-\text{N}) = 385$ cm^{-1}).[3]

A conventional, three-coordinated structure (AI)

AI

for dimeric A could be stabilized by additional N → Si interaction in a ladder configuration analogous to that shown in the tin(IV) siloxydistannoxanes,[18] but contains nonequivalent trimethylsilyl groups in the static structure. Mutual chelation by the nitrogens would raise the coordination number at tin to four (pseudo-square pyramidal, including the exo lone pair) and provide for equivalent trimethylsilyl groups in AII.

AII
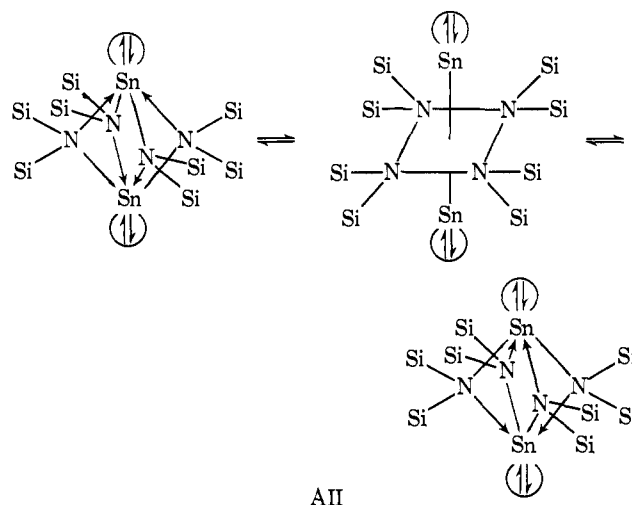
Combining chelation with donor–acceptor bonding by tin,[19] however, gives the bicyclobutanoid structure AIII containing three- and five-coordinated tin atoms

AIII
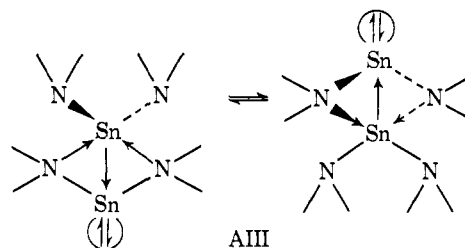
which could equilibrate the trimethylsilyl protons by a rapid, concerted, double inversion through the tin atoms, while dissociation of monomer would nevertheless preserve the integrity of the same monomer unit, consistent with the observation of the couplings in the scheme. The electric field gradient arising from the Sn → Sn ⇅ interaction rationalizes the unusually large QS.[20]

(15) Synthesized from the parent diamines and hexamethyldisilazane in the presence of trimethylchlorosilane as a catalyst: R. West, M. Ishikawa, and S. Murai, *J. Amer. Chem. Soc.*, **90**, 727 (1968).

(16) L. Birkofer, H. P. Kühlthal, and A. Ritter, *Chem. Ber.*, **93**, 2810 (1960).

(17) N,N'-Bis(trimethylsilyl)-1,8-diaminonaphthalene is a viscous liquid (bp 165–166° (0.6 Torr)), synthesized in 73% yield from the parent diamine and trimethylchlorosilane in the presence of triethylamine.

(18) Tetramethyl-1,3-bis(trimethylsiloxy)distannoxane dimerizes to form a Sn$_2$O$_2$ ring: R. Okawara, *Proc. Chem. Soc., London*, 383 (1961); R. Okawara and M. Wada, *Advan. Organometal. Chem.*, **5**, 137 (1967).

(19) The lone pair in subvalent tin is chemically active in (η-C$_5$H$_5$)$_2$-SnBF$_3$: P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **91**, 6885 (1969).

(20) We learned during the course of processing of this report that A has been independently obtained by Professor M. F. Lappert and coworkers at the University of Sussex, England. We thank Professor Lappert for sharing his results with us.

Professor G. Eadon of SUNY-Albany for the mass spectra, and Professor C. H. Yoder of Franklin and Marshall College for helpful discussions.

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Alkyl Substituent Effects on the Stability of Protonated Benzene

Sir:

The Baker–Nathan order of alkyl substituent effects (Me > Et > *i*-Pr > *t*-Bu) has engendered much experimental work and controversy.[1] Although the results of theoretical molecular orbital calculations on model systems[2] seem to support the contention that this reverse inductive ordering is due primarily to a differential inhibition of solvation by the alkyl substituents,[3] experimental tests in solution have not led to unambiguous conclusions.[1]

Recently Arnett and Larsen[4a] reported what must be the largest Baker–Nathan effect to date, noting that in superacid media the proton affinity of toluene is nearly 4 kcal/mol greater than that of *tert*-butylbenzene. It is on this observation that we focus our attention in the present communication. We have employed experimental pulsed ion cyclotron resonance techniques[5] as well as theoretical *ab initio* molecular orbital calculations[6] to investigate the effect of alkyl substituents on the stability of protonated benzene. As both of our tools provide information on the ions in their isolated—dilute gas—state, comparison of our data with that of Arnett and Larsen should afford a quantitative assessment of the importance of solvation.

Experimental values for the relative basicity of the alkyl benzenes in the gas phase were obtained by measuring equilibrium constants for reaction 1, where A

$$AH^+ + B = BH^+ + A \quad (1)$$

and B are alkyl benzenes. The pulsed ion cyclotron resonance techniques utilized in this study were identical with those described previously[7] with the exception that

(1) Reviews: (a) "Conference on Hyperconjugation," *Tetrahedron* 5, 105 (1959); (b) M. J. S. Dewar, "Hyperconjugation," Ronald Press New York, N. Y., 1962; (c) J. W. Baker, "Hyperconjugation," Oxford University Press, Oxford, 1952. For more recent papers on this subject, see (d) W. M. Schubert and D. F. Gurka, *J. Amer. Chem. Soc.,* **91**, 1443 (1969); (e) A. Himoe and L. M. Stock, *ibid.,* **91**, 1452 (1969); (f) E. M. Arnett and J. W. Larsen, *ibid.,* **91**, 1438 (1969); (g) F. R. Jensen and B. E. Smart, *ibid.,* **91**, 5686 (1969); (h) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.,* **93**, 5715 (1971); (i) J. M. Jerkunica and T. G. Traylor, *ibid.,* **93**, 6278 (1971); (j) J. W. Larsen, P. A. Bouis, M. W. Grant, and C. A. Lane, *ibid.,* **93**, 2067 (1971).

(2) (a) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.,* **94**, 5935 (1972); (b) L. Radom, *Aust. J. Chem.,* **27**, 231 (1974).

(3) W. M. Schubert and W. A. Sweeney, *J. Org. Chem.,* **21**, 119 (1956).

(4) (a) E. M. Arnett and J. W. Larsen, *J. Amer. Chem. Soc.,* **91**, 1438 (1969); see, however: (b) D. M. Brouwer and J. A. Van Doorn, *Recl. Trav. Chim. Pays-Bas,* **89**, 88 (1970).

(5) (a) R. T. McIver, Jr., *Rev. Sci. Instrum.,* **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.,* **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass. Spectrom. Ion Phys.,* **7**, 471 (1971).

(6) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.,* **51**, 2657 (1969).

(7) (a) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Amer. Chem. Soc.,* **93**, 4314 (1971); (b) R. T. McIver, Jr., and
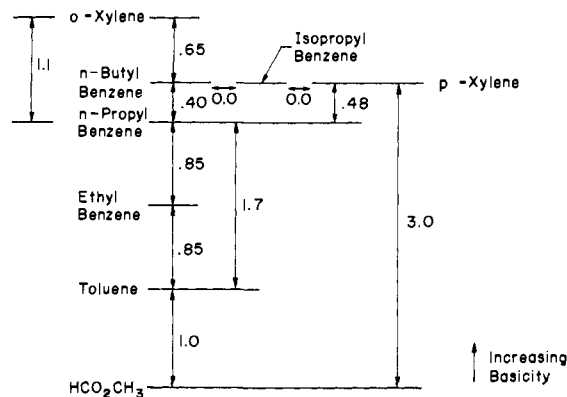
Figure 1. Pulsed ion cyclotron resonance measurements of ΔG°_{298} (kcal/mol) for the proton transfer reactions: $AH^+ + B \rightarrow BH^+ + A$.

a fivefold excess of phosphine was added to the system as a source of protons since alkyl benzenes self-protonate very slowly. Our experimental data are shown in Figure 1. The multiple overlap method was used to check the data for internal consistency and to confirm that equilibrium was attained. For example, direct measurements of the proton transfer equilibrium between toluene and *n*-propylbenzene gave $\Delta G^\circ = 1.7$ kcal/mol. Separate measurements between toluene and ethylbenzene and between ethylbenzene and *n*-propylbenzene gave $\Delta G^\circ = 0.85 + 0.85 = 1.7$ kcal/mol. Comparisons of this type establish an internal consistency of ± 0.1 kcal/mol. Assuming zero entropy change for the gas-phase reactions (1) our values of ΔG° may be used to calculate the relative proton affinities of the alkyl benzenes and the heats of formation of the protonated alkyl benzenes.

STO-3G energies for the *isodesmic*[8] processes (eq 2),
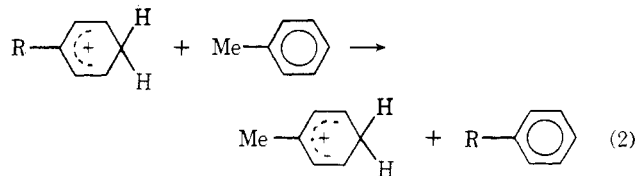
providing a measure of the basicity of an alkyl benzene relative to that of toluene, are presented along with the experimental icr data in Table I.[9] The agreement is remarkably good! Calculations on all positional isomers confirm experimental results in superacid

J. R. Eyler, *ibid.,* **93**, 6334 (1971); (c) R. T. McIver, Jr., and J. H. Silvers, *ibid.,* **95**, 8462 (1973); (d) R. T. McIver, Jr., and J. S. Miller, *ibid.,* **96**, 4323 (1974).

(8) W. J. Hehre, D. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.,* **92**, 4796 (1970).

(9) (a) Standard model geometries[10] used throughout. For protonated benzene: $r(C_1C_2) = 1.485$ Å, $r(C_2C_3) = r(C_3C_4) = 1.40$ Å, $r(C_1H)$
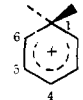
$= 1.09$ Å, $r(C_2H) = r(C_3H) = r(C_4H) = 1.08$ Å; $\angle(C_6C_1C_2) = 109.47°$, $\angle(C_1C_2C_3) = 125.66°$, $\angle(C_2C_3C_4) = \angle(C_3C_4C_5) = 120°$, $\angle(HC_1H) = 109.47°$, other hydrogens bisect ring CCC angles. Connecting (ring-substituent) bond lengths set at 1.52 Å. (b) For the STO-3G geometry optimized structure of protonated benzene, see W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.,* **94**, 6901 (1972).

(10) J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.,* **89**, 4253 (1967).