plus benzene), which explains why H-exchange does not occur. The interaction energy for the more stable π-complex structure is 56 kJ/mol.

The stability of π-complexes is a general phenomenon. In a further publication we will give other theoretical and experimental evidences which confirm their existence in related cases.

Crystal Structure and Reactivity of a Pentacoordinate 1,2-Oxastannetanide: An Intermediate of the Tin-Peterson Reaction

Takayuki Kawashima,* Naoshi Iwama, and Renji Okazaki*

Department of Chemistry, Faculty of Science
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

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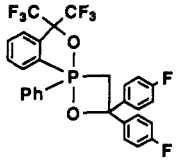
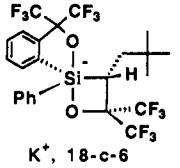
The Peterson reaction has been widely utilized for olefin synthesis as a silicon analog of the Wittig or Horner-Emmons reaction, providing the method for selective synthesis of (*E*)- or (*Z*)-isomer from a single diastereomer of (β-hydroxyalkyl)silanes.[1] The reactions using homologs such as β-hydroxy germanes, stannanes, and plumbanes are well-known to give the corresponding olefins under acidic and neutral (or basic) conditions.[1e,2] Very recently, we succeeded in the synthesis of pentacoordinate 1,2-oxaphosphetane **1**[3] and 1,2-oxasiletanide **2**[4] bearing the Martin ligand, intermediates of the Wittig and the Peterson reactions, respectively.



1



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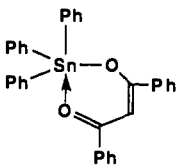


9

We now report the first synthesis, crystal structure, and reactivities of a 1,2-oxastannetanide, an intermediate of the tin-Peterson reaction.

Sequential treatment of [(phenylthio)methyl]triphenylstannane (**3**)[5] with 3 equiv of lithium diisopropylamide (LDA) (THF, −20 °C, 2 h), 5 equiv of HMPA, excess hexafluoroacetone (THF, −78 °C, 15 min), and aqueous NH_4Cl gave the corresponding β-hydroxy stannane **4a** (23%) with recovery of **3** (50%) (Scheme I).[6]

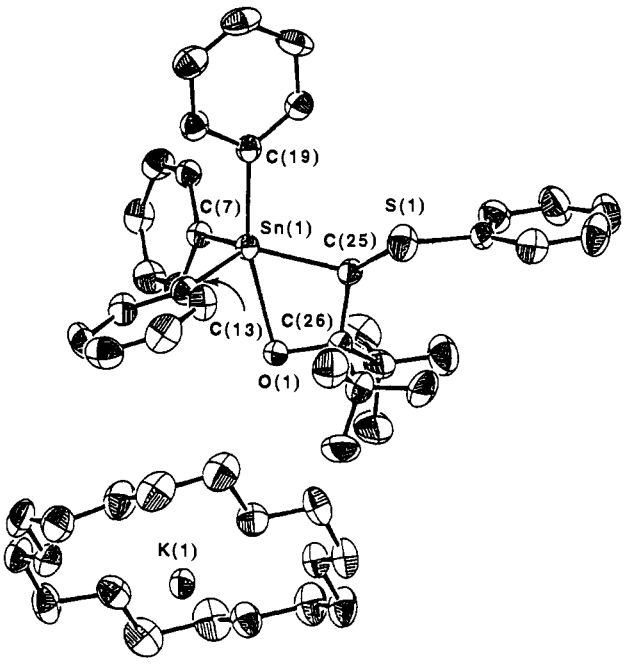
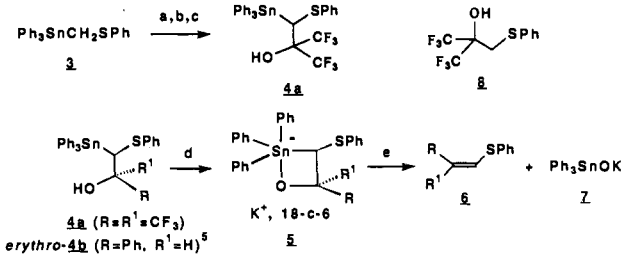


Figure 1. ORTEP drawing of **5a** (omitting CH_2Cl_2 and H_2O). Selected bond lengths (Å) and bond angles (deg): Sn(1)–O(1), 2.401(5); Sn(1)–C(7), 2.140(7); Sn(1)–C(13), 2.136(8); Sn(1)–C(19), 2.188(8); Sn(1)–C(25), 2.200(7); O(1)–C(26), 1.370(8); C(25)–C(26), 1.55(1); O(1)–Sn(1)–C(19), 165.1(2); C(7)–Sn(1)–C(13), 111.1(3); C(7)–Sn(1)–C(25), 113.5(3); C(13)–Sn(1)–C(25), 123.1(3); O(1)–Sn(1)–C(25), 61.3(2); O(1)–C(26)–C(25), 107.2(6); Sn(1)–O(1)–C(26), 93.2(4); Sn(1)–C(25)–C(26), 96.5(5).

Scheme I[a]



[a] (a) 3 equiv of LDA, THF, −20 °C, 2 h; (b) $(CF_3)_2C{=}O$, THF, −78 °C, 15 min; (c) aqueous NH_4Cl, −78 °C; (d) KH, 18-crown-6, THF, room temperature (**4a**) or −30 °C (**4b**); (e) 70 °C, CH_3CN, 36 h (**5a**) or 50 °C, THF, 5 h (**5b**).

Deprotonation of **4a** with KH in the presence of 18-crown-6 in THF was monitored by ^{19}F and ^{119}Sn NMR spectroscopy to show that 1,2-oxastannetanide **5a** was formed quantitatively as evidenced by the appearance of a double quartet with centers of δ_F −75.09 ($^4J_{FF}$ = 8.8 Hz) and −71.77 ($^4J_{FF}$ = 8.8 Hz) and a singlet (δ_{Sn} −229.65), respectively. The large upfield shift (105 ppm) in δ_{Sn} from **4a** (−125.09) to **5a** (−229.65) strongly supports the structure of a pentacoordinate tin ate complex.[7] The ^1H and ^{13}C NMR spectra showed only one set of signals for Sn–Ph, indicating the presence of very fast pseudorotation. It is surprising that a stable pentacoordinate 1,2-oxastannetanide can be obtained even without resort to the Martin ligand.

It was found by ^{19}F NMR spectroscopy that **5a** provided olefin **6a**[8] (95%) and probably potassium triphenylstannoxide (**7**) upon heating (70 °C, CH_3CN, 36 h), indicating that **5a** has a reactivity similar to that of silicon analog **2**.[4] In contrast to **2**, **5a** was

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(6) **4a**: colorless viscous oil; HRMS (70 eV) *m/z* calcd for $C_{28}H_{22}F_6OS^{120}Sn$ 640.0317, found 640.0312; ^1H NMR ($CDCl_3$) δ 3.75 (s, 1 H, $^2J_{HSn}$ = 67 Hz, C*H*SPh), 4.36 (s, 1 H, O*H*), 7.16–7.20 (m, 4 H), 7.33–7.41 (m, 10 H), 7.55–7.67 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 37.83 (s, $^1J_{CSn}$ = 290 Hz, Sn*C*H), 77.21 [sept, $^2J_{CF}$ = 30 Hz, *C*(CF_3)$_2$], 122.83 [q, $^1J_{CF}$ = 287 Hz, C(*C*F_3)(C′F_3)], 123.18 [q, $^1J_{CF}$ = 288 Hz, C(CF_3)(*C*′F_3)], 127.50, 128.60 ($^3J_{CSn}$ = 54 Hz, *m*-C of SnPh), 129.18, 129.39 ($^4J_{CSn}$ = 12 Hz, *p*-C of SnPh), 129.86, 136.71 ($^3J_{CSn}$ = 22 Hz, *ipso*-C of SPh), 137.17 ($^2J_{CSn}$ = 38 Hz, *o*-C of SnPh), 137.67 ($^1J_{CSn}$ = 556 Hz, *ipso*-C of SnPh); the coupling constants (J_{HSn} and J_{CSn}) for **4a** and **5b**[11] were obtained from the satellite peaks; ^{19}F NMR ($CDCl_3$) δ −74.84 (q, $^4J_{FF}$ = 9.0 Hz, 3 F), −73.78 (q, $^4J_{FF}$ = 9.0 Hz, 3 F); ^{119}Sn NMR (THF) δ −125.09 (m).

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decomposed to give 1,1,1,3,3,3-hexafluoro-2-[(phenylthio)-methyl]-2-propanol (**8**)[9] in almost quantitative yield upon prolonged exposure to air. On the other hand, similar treatment of the benzaldehyde adduct *erythro*-**4b**[5] with KH gave a signal at δ_{Sn} -239.52 at -30 °C, suggesting the formation of 1,2-oxastannetanide **5b**. When **5b** was heated without isolation (50 °C, THF, 5 h), (*Z*)-phenyl β-styryl sulfide (**6b**) was exclusively obtained in 82% yield, showing that the olefin formation proceeds in the same manner as that using *erythro*-**4b** itself although the reaction conditions are much milder.[10]

Product **5a** was recrystallized from dichloromethane–hexane to afford colorless needles, which melted at 125–130 °C with decomposition.[11] The X-ray crystallographic analysis of **5a** indicated that it has a very distorted TBP (trigonal bipyramid) structure (Figure 1).[12] This is the first example of an anionic pentacoordinate tin compound with a four-membered ring.[13] Oxygen and one phenyl group on the stannetanide occupy apical positions. The bond angle O(1)–Sn(1)–C(19) between two apical bonds deviates by 14.9(2)° from 180°. The bond length of Sn-(1)–O(1) [2.401(5) Å] is longer than that of Sn–O(ax) [2.276(7) Å] reported for compound **9**.[14] The axial bond Sn(1)–C(19) [2.188(8) Å] is longer than exocyclic equatorial bonds Sn(1)–C(7) [2.140(7) Å] and Sn(1)–C(13) [2.136(8) Å], but is slightly shorter than the endocyclic Sn(1)–C(25) bond [2.200(7) Å].

The most outstanding structural feature is that the Sn atom is not on the plane of three equatorial ligands [C(7), C(13), and C(25)], but is located 0.442 Å above it. On the other hand, the four-membered ring is approximately coplanar, being one of the common features for pentacoordinate compounds such as **1** and **2**. The strain of the four-membered ring seems to be reduced by elongating the apical Sn–O(1) bond and making the angle O-(1)–Sn–C(25) acute.

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Supplementary Material Available: X-ray crystallographic data with tables of thermal and positional parameters, bond lengths, and bond angles for **5a** (14 pages). Ordering information is given on any current masthead page.

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(10) Heating *erythro*-**4b** (110 °C, toluene, 45 min) afforded (*Z*)-**6b** in 89.7% yield (see ref 5).

(11) **5a**: colorless crystals; mp 125–130 °C (dec) (CH_2Cl_2–hexane); ^{1}H NMR (CD_3CN) δ 3.56 [s, 24 H, (OCH_2CH_2)$_6$], 5.05 (s, 1 H, $^2J_{HSn}$ = 98 Hz, C*H*S), 7.03–7.25 (m, 14 H, SC_6H_5 and *m*- and *p*-H of $SnPh_3$), 7.72 (dd, $^4J_{HH}$ = 2 Hz, $^3J_{HH}$ = 7 Hz, 6 H, *o*-H of $SnPh_3$); ^{13}C NMR (CD_3CN) δ 55.78 ($^1J_{CSn}$ = 462 Hz, Sn*C*H), 70.24 (OCH_2CH_2), 80.71 [sept, $^2J_{CF}$ = 25 Hz, $C(CF_3)_2$], 125.12, 126.49 [q, $^1J_{CF}$ = 292 Hz, $C(CF_3)(C'F_3)$], 127.38, 127.42, 127.57 ($^2J_{CSn}$ = 50 Hz, *o*-C of SnPh), 127.65 [q, $^1J_{CF}$ = 291 Hz, $C(CF_3)(C'F_3)$], 128.80 ($^3J_{CSn}$ = 70 Hz, *m*-C of SnPh), 137.87 ($^4J_{CSn}$ = 38 Hz, *p*-C of SnPh), 141.83 ($^3J_{CSn}$ = 55 Hz, *ipso*-C of SPh), 148.87 ($^1J_{CSn}$ = 525 Hz, *ipso*-C of SnPh); ^{19}F NMR ($CDCl_3$) δ -75.09 (q, $^4J_{FF}$ = 8.8 Hz, 3 F) and -71.77 (q, $^4J_{FF}$ = 8.8 Hz, 3 F); ^{119}Sn NMR (THF) δ -229.65. Anal. Calcd for $C_{40}H_{45}F_6KO_7SSn\cdot H_2O$: C, 50.06; H, 4.73. Found: C, 50.14; H, 4.70.

(12) $C_{40}H_{45}F_6KO_7SSn\cdot CH_2Cl_2\cdot H_2O$, FW = 1044.58, crystal dimensions (mm) 0.500 × 0.250 × 0.250, triclinic, space group $P\bar{1}$, a = 13.789(2) Å, b = 14.522(2) Å, c = 12.550(3) Å, α = 92.46(2)°, β = 95.25(2)°, γ = 69.93(1)°, V = 2350.5(7) Å^3, Z = 2, D_{calcd} = 1.476 g/cm^3, R = 0.054 (R_w = 0.053). Full details of the crystallographic structure analysis are described in the supplmentary material.

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Electron Transfer in DNA: Predictions of Exponential Growth and Decay of Coupling with Donor–Acceptor Distance

Steven M. Risser and David N. Beratan*

Department of Chemistry, University of Pittsburgh Pittsburgh, Pennsylvania 15260

Thomas J. Meade*

Beckman Institute, California Institute of Technology Pasadena, California 91125

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Experimental and theoretical work indicates the importance of protein structure in controlling electron-transfer (ET) reactions.[1] Recently, great interest has been shown in exploring electronic coupling interactions in DNA. We report here that the electronic coupling calculated for a recently synthesized class of DNA oligomers with rigidly attached donors and acceptors[3] displays a remarkable dependence on the nucleic acid structure. Indeed, a reversal in the *sign* of the exponential decay parameter is found in some cases if the donor–acceptor couplings are fit to a single exponential expression. The sign reversal reflects the inadequacy of single exponential models for describing bridge-mediated electron-transfer reaction rates. These effects in DNA oligomers arise from the three-dimensional structure of the double helix. The couplings do decay monotonically with the tunneling pathway length[4] between donor and acceptor, σl (estimated from tunneling pathway analysis), but not with the direct through-space donor–acceptor separation distance.

The rate of long-range electron transfer is proportional to the electron tunneling matrix element squared, $|T_{DA}|^2$. Within the Born–Oppenheimer and Franck–Condon approximations,[4,5] the matrix element can be written

$$T_{DA} = \sum_{ij} V_{Di} G_{ij} V_{jA}$$

where $V_{Di(jA)}$ is the coupling between the donor (acceptor) and bridge site i (j) and G_{ij} is the Green's function of the bridge. The matrix form of the Green's function at energy E is $(\mathbf{H} - E\mathbf{S})\mathbf{G} = \mathbf{S}$ where $\mathbf{H}$ is the bridge Hamiltonian and $\mathbf{S}$ is the overlap matrix.[4] We have used an extended-Hückel Hamiltonian (used successfully in prior studies of macromolecule ET[6]) to calculate the Green's function for double-stranded DNA oligomers up to eight units in length. From the elements of the Green's function, we calculate the component in the ribose 2′ carbon sp^3 orbital (C atom adjacent to the base pair connection), as this is the attachment site in specific redox-labeling studies.[3] This method of calculating T_{DA} has the advantage that it includes all multiple pathways and interference effects to all orders, so the accuracy of the coupling element is limited only by the choice of electronic Hamiltonian.

We have calculated the bridge contribution to $T_{DA}/(V_{D1}V_{NA}) = G_{1N}$ for a series of DNA oligomers of one to eight AT base pairs

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