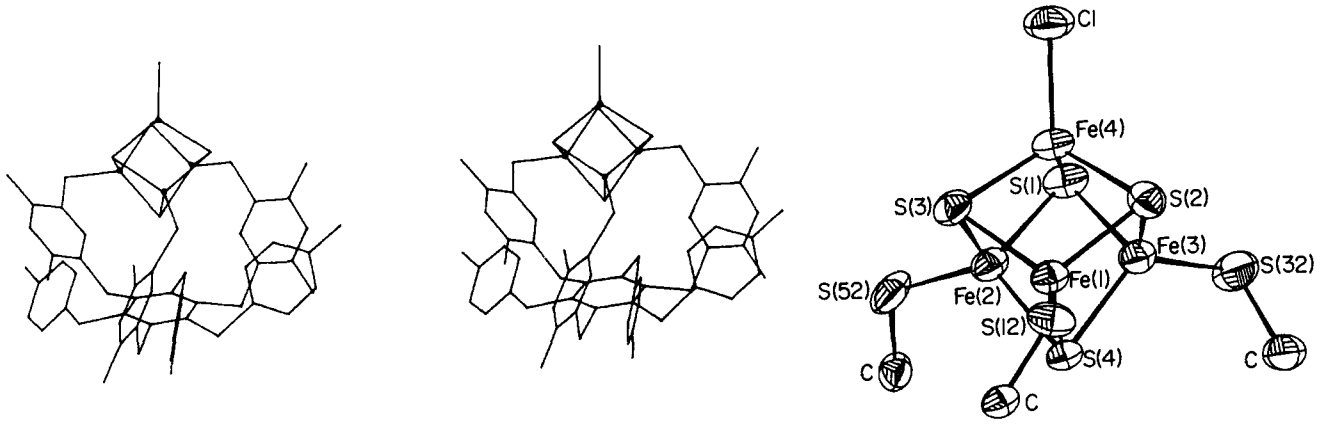

Figure 1. Left: Stereoview representation of the structure of **7**, showing binding of the cluster and the *aaaaab* conformation of legs (• = Fe). Right: Structure of the cluster portion of **7**. Mean values (Å, deg) of selected structural parameters: Fe–Cl, 2.226 (2); Fe ··· Fe, 2.766 (1); Fe–S, 2.287 (2); Fe-S(C), 2.261 (2); S–C, 1.772 (6); S–Fe–S, 103.64 (9); Fe–S–Fe, 74.41 (7).

is 3.74 Å from the centroid of the central ring, ~0.3 Å beyond van der Waals contact. Cluster dimensions are normal, and the only apparent ligand structural effect is suppression of the usual core tetragonal distortion of $[Fe_4S_4L_4]^{2-}$.[7] The ligand has the unprecedented *aaaaab* conformation.

In DMF solution cluster **7** exhibits λ_{max} (ϵ_M) = 480 (sh, 10000) and two one-electron reductions at −1.03 (reversible) and −1.80 V (irreversible) vs. SCE. A potential separation $\Delta E \approx 0.75$ V assures the presence of a Fe_4S_4 cluster.[17] Further, **7** shows *one* set of ^1H and ^{13}C NMR signals[18] indicative of a single species with effective trigonal symmetry. In contrast, $(Ph_4P)_2[Fe_4S_4(SPh)_2Cl_2]$[19] displays four meta H signals in CD_3CN (8.1–8.4 ppm),[12a] consistent with statistical disproportionation to $[Fe_4S_4(SPh)_{4-n}Cl_n]^{2-}$ (n = 0–3). Reactions 1–6 (R = 2,6-$C_6H_3Cl_2$) in situ, conducted stoichiometrically and monitored by ^1H NMR,[12a] have been shown to proceed with conversions of >90%. Thiolate groups are readily detected by their characteristic shifts: 13.2 ppm (SCH_2) in **6** and 8.34 ppm (meta H) in **8**. The spectra of **6** and **8** also consist of a single set of signals. Given the sensitivity of isotropically shifted cluster resonances to structural differences,[20] we conclude that in solution **6–8** possess trigonal symmetry. This requires a conformational change of two R_1 legs to generate *ababab*. Rotational barriers may be low inasmuch as C_6(S-2-$MeC_6H_4)_6$ (**9**, two conformers: *aabbab* + *aaabbb*) and **4** (*aabaab*), whose indicated conformations have been established by X-ray crystallography,[21] show ^1H and ^{13}C NMR spectra (CD_2Cl_2, 210–300 K) consistent with trigonal symmetry.

These results demonstrate that a Fe_4S_4 cluster can be mounted on the semirigid tridentate ligand **5** with cavity occupancy and that the differentiated subsite is susceptible to high-yield substitution reacitons. These are the first *subsite-specific* reactions of synthetic Fe_4S_4 clusters. Cluster **7** in particular appears to be a potentially suitable vehicle for expression of the protein structural and reactivity features noted at the outset. Ligand **5** should accommodate the Fe_3S_4 cubane fragment (conceivably obtainable by oxidative removal of the unique subsite) proposed for protein sites[22,23] and is designed so as not to stabilize the alternative linear $Fe_3(\mu_2\text{-}S)_4$ unit found in the synthetic clusters $[Fe_3S_4SR_4]^{3-}$[24] and the unfolded form of aconitase.[25] These matters will be the subjects of future reports.

Acknowledgment. This research was supported by National Institutes of Health Grant GM 28856. X-ray diffraction equipment was obtained by NSF Grant CHE 80-00670 and NIH Grant 1 S10 RR 02247 and NMR equipment by NSF Grant 84-10774.

Supplementary Material Available: Tables of atom coordinates and thermal parameters for $(Ph_4P)_2[Fe_4S_4(L\text{-}S_3)Cl]$ (8 pages). Ordering information is given on any current masthead page.

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Et_3B-Induced Radical Addition of R_3SnH to Acetylenes and Its Application to Cyclization Reaction

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Received January 12, 1987

The cyclization of vinyl acetylene to methylene-substituted five-membered rings has been described by Stork and Mook.[1] We have studied this reaction further and report that trialkylborane mediates a facile addition of R_3SnH to an acetylenic bond to give vinylstannane regioselectively, and this new method is applied to vinyl radical cyclization reactions[2,3] effectively.

The hydrostannation of acetylenes[4] takes place readily either in the absence of a catalyst or in the presence of a catalytic amount of free radical initiator such as azobisisobutyronitrile (AIBN),[5] but these reaction conditions (without solvent, heat to 80–100 °C)

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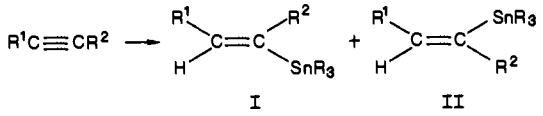
Table I. Triethylborane-Induced Hydrostannation of Acetylenes[a]



I II

entry	substrate R¹	substrate R²	reagent	reaction time, h	Y, %	product ratio I:II
1	n-$C_{10}H_{21}$	H	Ph_3SnH	0.3	80	79:21
2			n-Bu_3SnH	2.0	40	80:20
3	$PhCH_2OCH_2CH_2$	H	Ph_3SnH	0.3	79	69:31
4			n-Bu_3SnH	10	71	90:10
5	$THPOCH_2CH_2$	H	Ph_3SnH	0.3	81	80:20
6			n-Bu_3SnH	2.0	49	90:10
7	$HOCH_2CH_2$	H	Ph_3SnH	0.3	87	82:18
8			n-Bu_3SnH	2.0	40	69:31
9	Ph	H	Ph_3SnH	0.3	75	100:0
10	Me_3Si	H	Ph_3SnH	0.3	83[b]	100:0
11	n-C_5H_{11}	n-C_5H_{11}	Ph_3SnH	10	86[c]	0:100
12	Ph	Me	Ph_3SnH	1.0	74	25:75

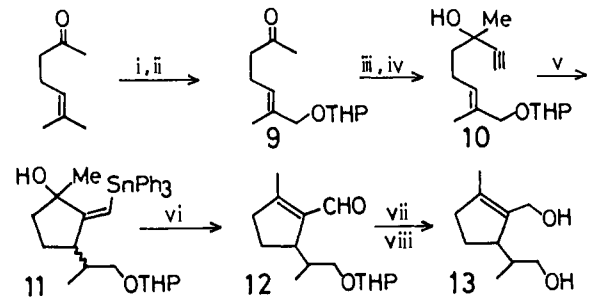
[a] Acetylene (1.0 mmol), R_3SnH (1.2 mmol) and Et_3B (0.1 mmol) were employed. [b] Excess of (trimethylsilyl)acetylene (5.0 mmol) and Ph_3SnH (1.0 mmol) was employed, and the yield was based on Ph_3SnH. [c] Excess of Ph_3SnH (5.0 mmol) was used.

may not always be suitable for an intramolecular radical cyclization reaction.[3f]

We have found that an addition of a catalytic amount of Et_3B to a solution of acetylenic compound and Ph_3SnH (or n-Bu_3SnH) in toluene promotes the formation of vinylstannanes effectively. A typical procedure is as follows. A hexane solution of Et_3B[6] (1.0 M, 0.1 mL, 0.1 mmol) was added to a solution of 1-dodecyne (0.17 g, 1.0 mmol) and triphenyltin hydride (0.42 g, 1.2 mmol) in toluene (8.0 mL) at 25 °C under an argon atmosphere. After stirring for 20 min at 25 °C, the reaction mixture was poured into water and extracted with ethyl acetate 3 times. Combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was submitted to preparative TLC on silica gel to give vinylstannane as a mixture of (*E*)- and (*Z*)-1-(triphenylstannyl)-1-dodecene (0.41 g, 80% yield, E/Z = 79/21). The representative results are summarized in Table I. Triphenylstannyl group adds to terminal acetylenic carbon regioselectively but nonstereoselectively to give a mixture of (*E*)- and (*Z*)-1-(triphenylstannyl)-1-alkenes. The E/Z ratios of double bonds were generally 8/2 to 7/3[7] and were not affected by solvents. The ratios of (*E*)-1-(triphenylstannyl)-1-dodecene and the *Z* isomer were 79/21, 80/20, 77/23, and 63/37 in toluene, benzene, Et_2O, and THF, respectively. Phenylacetylene and (trimethylsilyl)acetylene provided (*E*)-vinylstannanes exclusively. An addition of n-Bu_3SnH had longer reaction time and gave the corresponding vinylstannanes in poor yields.

The reaction was successfully applied to the radical cyclization reaction shown in eq 1–4.[8] The concentration of Ph_3SnH affected the yield and distribution of the products. Uncyclized product

Scheme I



i) SeO_2/EtOH-H_2O ii) Dihydropyran, TsOH iii) $Me_3SiC{\equiv}CLi$ iv) KF/DMSO v) Ph_3SnH, Et_3B vi) $CrO_3{\cdot}2Py$ vii) $^iBu_2AlH$ viii) TsOH/MeOH

was obtained in addition to the cyclized desired compound in a higher concentration. For instance, the compound **1a** gave cyclized product **2a** exclusively at 0.012 M concentration of Ph_3SnH, while, at 0.30 M concentration, **2a** and uncyclized product $Me_2C{=}CHCH_2CH_2C(OH)MeCH{=}CHSnPh_3$ were obtained in 60% and 15% yield, respectively.[9] It is worth noting that the serious limitation, nonstereoselectivity shown in Table I, was overcome in these cyclization reactions and the cyclized products consist of only *Z* isomer without contamination by the other stereoisomer.[10] The compound **4d**[11] derived from **4a** by de-

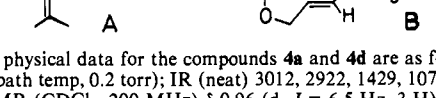
(6) i-Pr_3B and (n-C_8H_{17})$_3B$ were as effective as Et_3B. We thank Toyo Stauffer Chemical Company for a gift of a hexane solution of Et_3B (1.0 M).

(7) In the case of uncatalyzed hydrostannation, the E/Z ratios depend on the reaction temperature as described in ref 5. Heating a mixture of 1-dodecyne and Ph_3SnH at 80 °C for 1.5 h gave a mixture of (*E*)- and (*Z*)-1-(triphenylstannyl)-1-dodecene (E/Z = 22/78) in 53% combined yield. A mixture of *E* and *Z* isomer (E/Z = 75/25, 65% yield) was obtained after 5 h at 150 °C.

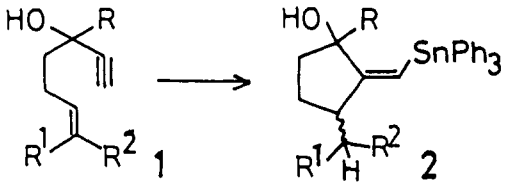
(8) Transformation of **1a** into **2a** is representative. A hexane solution of Et_3B (1.0 M, 0.2 mL, 0.2 mmol) was added to a solution of Ph_3SnH (0.42 g, 1.2 mmol) and the acetylene **1a** (0.15 g, 1.0 mmol) in toluene (100 mL) at 25 °C under an argon atmosphere. After stirring for 3 h at 25 °C, the reaction mixture was poured into water and extracted with ethyl acetate. Purification by preparative TLC on silica gel gave the cyclized product **2a** (0.37 g, 75% yield) as a stereoisomeric mixture (78/22): IR (neat) 3566, 3058, 2954, 1428, 1195, 1073, 727, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.84 (d, J = 6.5 Hz, 3 H), 0.96 (s, 3 H), 1.00 (d, J = 6.5 Hz, 3 H), 1.2–2.1 (m, 5 H), 2.64 (m, 1 H), 6.03 (d, J = 2.2 Hz, for minor compound), 6.10 (d, J = 2.2 Hz, for major compound, total 1 H), 7.25–7.80 (m, 15 H); ^{119}Sn NMR δ −147.8 (minor), −150.2 (major). Anal. Calcd for $C_{28}H_{32}OSn$: C, 66.83; H, 6.41. Found: C, 66.71; H, 6.34. In the case of **1b**, six-membered-ring product, 1-methyl-2-(triphenylstannyl)methylene-1-cyclohexanol, was also obtained (31% yield) in addition to **2b**.

(9) Heating a mixture of **1a** and Ph_3SnH without solvent at 80 °C for 15 h gave a complex mixture consisting of (*E*)- and (*Z*)-vinylstannanes ($Me_2C{=}CHCH_2CH_2C(OH)MeCH{=}CHSnPh_3$, 46%), regioisomer ($Me_2C{=}CHCH_2CH_2C(OH)MeC(SnPh_3){=}CH_2$, 9%), and the desired cyclized product **2a** (38% yield).

(10) The compounds **4a**, **4b**, **6**, and **8** showed one signal each for olefinic protons on ^1H NMR spectra and also on ^{119}Sn NMR. The formation of a single isomer may be explained by assuming the equilibrium between A and B. The intermediate A cyclized more readily than B.



(11) The physical data for the compounds **4a** and **4d** are as follows. **4a**: bp 165 °C (bath temp, 0.2 torr); IR (neat) 3012, 2922, 1429, 1074, 726, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.96 (d, J = 6.5 Hz, 3 H), 1.03 (d, J = 6.5 Hz, 3 H), 2.05 (m, 1 H), 2.73 (m, 1 H), 3.82 (dd, J = 5.5, 9.0 Hz, 1 H), 3.95 (dd, J = 7.5, 9.0 Hz, 1 H), 4.08 (brs, 2 H), 6.12 (m, 1 H), 7.3–7.8 (m, 15 H); ^{119}Sn NMR δ −142.9. Anal. Calcd for $C_{26}H_{28}OSn$: C, 65.72; H, 5.94. Found: C, 65.55; H, 5.82. **4d**: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.88 (d, J = 7.0 Hz, 3 H), 0.95 (d, J = 7.0 Hz, 3 H), 1.84 (m, 1 H), 2.53 (m, 1 H), 3.80 (dd, J = 5.0, 9.0 Hz, 1 H), 3.92 (dd, J = 7.0, 9.0 Hz, 1 H), 4.95 (m, 1 H), 5.00 (m, 1 H).



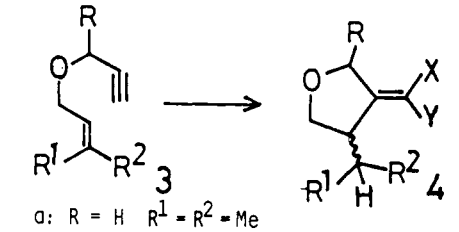
(1)

a: R = Me $R^1 = R^2$ = Me 75% (78/22)

b: R = Me $R^1 = R^2$ = H 50% (80/20)

c: R = Me R^1 = Me $R^2 = CH_2CH_2CH{=}CMe_2$ 78% (79/21)

d: R = $^nC_5H_{11}$ R^1 = H R^2 = Ph 87% (63/37)



(2)

a: R = H $R^1 = R^2$ = Me X = $SnPh_3$ Y = H (Y, 78%)

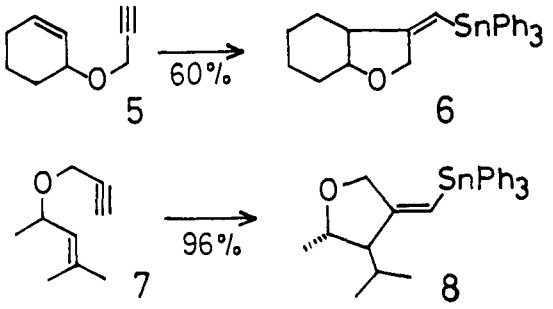
b: R = H R^1 = H $R^2 = {}^nC_3H_7$ X = $SnPh_3$ Y = H (Y, 85%)

c: R = ^nBu $R^1 = R^2$ = Me X = $SnPh_3$ Y = H (Y, 69%, 64/36)

d: R = H $R^1 = R^2$ = Me X = Ha Y = Hb

e: R = H $R^1 = R^2$ = Me X = $SnPh_3$ Y = D

f: R = H $R^1 = R^2$ = Me X = H Y = D



(3)

(4)

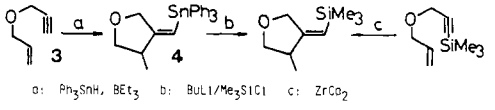
stannylation (*n*-BuLi/THF, H_2O)[12] showed ^1H NMR signals at δ 5.00 (m, Ha) and 4.95 (m, Hb). Treatment of the deuteriated acetylene **3a** ($DC{\equiv}CCH_2OCH_2CH{=}CMe_2$) with Ph_3SnH followed by destannylation provided **4f**, whose ^1H NMR spectrum showed only one signal in the olefinic region at δ 4.99. The complete disappearance of the higher field signal is consistent with a formation of single stereoisomer **4e**.[13] The compounds **1a-d** and **3c** provided cis-trans stereoisomeric mixtures concerning the substituents on a five-membered ring. In contrast, the compound **7** gave trans isomer **8**[14] as a single product.

Scheme I illustrates the synthesis of dehydroiridodiol and isodehydroiridodiol. The triethylborane-induced triphenyltin radical addition-cyclization process provided vinylstannane **11** (84%) starting from readily available propargylic alcohol **10**. Collins oxidation of **11** gave **12** (54%).[15] Diisobutylaluminum hydride reduction followed by treatment with *p*-TsOH provided a mixture of dehydroiridodiol (3*R**,8*S**) and isodehydroiridodiol (3*R**,8*R**) (26/74, 58% overall yield from **12**),[16] which was easily separated by preparative TLC on silica gel.

The reaction was not so effective for the formation of a six-membered ring. For instance, treatment of $HC{\equiv}CCH_2OCH_2CH_2CH{=}CMe_2$ gave the desired cyclized product in only 28% yield along with uncyclized vinylstannane (49%). An addition of galvinoxyl to a reaction mixture of 1-dodecyne, Ph_3SnH, and Et_3B resulted in a recovery of the acetylene (73%).[17,18]

(12) (Triphenylstannyl)alkenes were easily transformed into alkenyllithium as (trialkylstannyl)alkenes following the procedure described in ref 5.

(13) The structure of the cyclized product was also confirmed as follows. Treatment of **3** (R = R^1 = R^2 = H) with our new method provided **4** (32% yield) along with six-membered-ring product 3-(triphenylstannyl)methylene-tetrahydropyran (45%). The vinylstannane **4** was converted into vinylsilane by treatment with *n*-BuLi and Me_3SiCl, which was identical with the sample prepared from allyl (trimethylsilyl)propargyl ether following Negishi's procedure (Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2827. Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568).



a: Ph_3SnH, BEt_3 b: BuLi/Me_3SiCl c: $ZrCp_2$

(14) **8**: bp 170 °C (bath temp, 0.1 torr); IR (neat) 3062, 2958, 1619, 1429, 1075, 727, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.98 (d, *J* = 7.0 Hz, 3 H), 1.02 (d, *J* = 7.0 Hz, 3 H), 1.25 (d, *J* = 6.0 Hz, 3 H), 2.02 (m, 1 H), 2.30 (m, 1 H), 3.95-4.25 (m, 3 H), 6.08 (m, 1 H), 7.3-7.8 (m, 15 H); ^{119}Sn NMR δ -142.6. Anal. Calcd for $C_{27}H_{30}OSn$: C, 66.29; H, 6.18. Found: C, 66.43; H, 6.29.

(15) **12**: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.67 (d, *J* = 7.0 Hz), 0.72 (d, *J* = 7.0 Hz), 0.94 (d, *J* = 2.5 Hz), 0.97 (d, *J* = 2.5 Hz, total 3 H), 1.4-2.0 (m, 8 H), 2.14 (brs, 3 H), 2.2-2.7 (m, 3 H), 3.0-4.0 (m, 5 H), 4.5-4.7 (m, 1 H), 10.0 (s, 1 H).

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(18) After this work was completed we were informed by Professor G. Stork that he has reached a similar cyclization reaction. We thank Prof. G. Stork for giving us information prior to publication.

Synthesis and Characterization of Five-Coordinate High-Spin Iron(II) Porphyrin Complexes with Unusually Large Quadrupole Splittings. Models for the P460 Center of Hydroxylamine Oxidoreductase from *Nitrosomonas*

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Hydroxylamine oxidoreductase from *Nitrosomonas europeae* catalyses the oxidative conversion of NH_2OH to NO_2^-.[2] The enzyme, which has an $(\alpha,\beta)_3$ subunit containing seven-eight c-type hemes contains also an unusual prosthetic group, termed P460. This P460 center is also found in a $M_r \simeq 17000$ protein fragment. Mössbauer spectra of the reduced P460 groups in hydroxylamine oxidoreductase and the fragment exhibit nearly identical quad-

Table 1. Electronic Spectra of Complexes **1**, **2**, and **3** at 25 °C in Chlorobenzene

	λ_m (log ϵ), nm
$\|Fe(OCH_3)TP_{piv}P\|^-$ **1**	456 (4.83), 580 (3.86), 622 (3.71)
$\|Fe(O_2CCH_3)TP_{piv}P\|^-$ **2**	448 (5.32), 572 (4.22), 611 (3.81)
$\|Fe(OC_6H_5)TP_{piv}P\|^-$ **3**	450 (5.02), 576 (4.09), 616 (3.89)

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