Multiplicity information for 1a, shown in Table I, was obtained exclusively by the application of the SESFORD technique. Particularly illustrative of its capability is the SES-FORD trace (Figure 1) for the degenerate resonance at δ 20.1 for the C-2 methylene and the C-22 acetate methyl, which showed a symmetrically overlapped triplet and quartet pattern. Chemical shift assignments for 1a were made largely from nerolidol (2),¹⁸ which serves as an excellent model for the C-4 through C-12 portion of the carbocyclic nucleus. Signal assignments for the remainder of the molecule were based on empirical chemical shift relationships^{19,20} in conjunction with T_1 inversion-recovery relaxation measurements²¹⁻²³ for dis-crimination among methyl^{24,25} and carbonyl²⁶ resonances.

Complete correspondence between the observed SESFORD multiplicities and the multiplicities inferred from T_1 inversion recovery spin-lattice relaxation studies further served to establish that **1a** is subject to isotropic tumbling (see Table I).⁵ The multiplicities shown in Table I for 1b and 1c were consequently established from T_1 studies alone. Chemical shift assignment for the latter two compounds, also shown in Table I, are based on those established for 1a, with adjustments by standard empirical correlations as appropriate for their functional modification.

The successful application of SESFORD to the problem of crassin acetate multiplicities amply demonstrates the utility of the technique with complex molecules. It is evident that SESFORD should be useful for the unequivocal resolution and determination of the spin multiplicity of any resonance in even the most complex natural product.27

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References and Notes

- A. J. Weinheimer and J. A. Matson, *Lloydia*, **38**, 378 (1975).
 For a review, see A. J. Weinheimer, C. W. J. Chang, and J. A. Matson, *Fortschr. Chem. Org. Naturst.*, **36**, 285 (1978).
- (3) R. R. Ernst, J. Chem. Phys., 45, 3845 (1966).
- (4) F. J. Weigert, M. Jautelat, and J. D. Roberts, Proc. Natl. Acad. Sci. U.S.A., 60, 1152 (1968) (5) A. Allerhand, D. Doddrell, and R. Komorski, J. Chem. Phys., 55, 189
- (1971)(6) D. Doddrell and A. Allerhand, Proc. Natl. Acad. Sci. U.S.A., 68, 1083
- (1971)
- E. Wenkert et al., J. Am. Chem. Soc., 95, 4990 (1973).
 R. A. Newmark and J. R. Hill, J. Am. Chem. Soc., 95, 4135 (1973).
 G. Jikeli, W. Herrig and H. Gunther, J. Am. Chem. Soc., 96, 323 (1974).
- (10) H. Fritz and H. Sauter, J. Magn. Reson., 15, 177 (1975).
 (11) G. Bodenhausen, R. Freeman, and G. A. Morris, J. Magn. Reson., 23, 171 (1976).
- R. Freeman and H. D. W. Hill, J. Magn. Reson., 5, 278 (1971).
 G. E. Martin, J. Heterocycl. Chem., 15, 1539 (1978).

- (14) J. C. Turley and G. E. Martin, Spectrosc. Lett., 11, 681 (1978).
 (15) G. A. Morris and R. Freeman, J. Magn. Reson., 29, 433 (1978).
 (16) While in development in our laboratories, the concept of this technique While in development in our laboratories, the concept of this technique was suggested in the review of selective excitation in Fourier transform NMR by Morris and Freeman cited in ref 15.
 H. Y. Carr and E. M. Purcell, *Phys. Rev.*, 94, 630 (1954).
 E. Wenkert et al., *Top. Carbon-13 NMR*, 92 (1972).
 G. C. Levy and G. N. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972, p 47.
 F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heuden New York, 1975, p 47.

- Heyden, New York, 1976, p 47.

- R. L. Vold et al., J. Chem. Phys., 48, 3831 (1968).
 R. L. Vold et al., J. Chem. Phys., 48, 3831 (1968).
 R. Freeman and H. D. W. Hill, J. Chem. Phys., 51, 3140 (1969).
 D. Canet, G. C. Levy, and I. R. Peat, J. Magn. Reson., 18, 199 (1975).
 W. T. Huntress, Jr., Adv. Magn. Reson., 4, 1 (1970).
- (25) G. C. Levy, Acc. Chem. Res., 6, 161 (1973).
- (26) F. W. Wehrli, Adv. Mol. Relaxation Processes, 6, 161 (1973).

(27) Selective excitation of resonances separated by 1 Hz (at 25 MHz) can comfortably be achieved by this technique. With some effort, resonances separated by 0.2 Hz have been resolved.

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Reduction of

1.3-Dimethyl-5-(p-nitrophenylimino)barbituric Acid by Thiols. A High-Velocity Flavin Model Reaction with an Isolable Intermediate¹

Sir:

Strong kinetic evidence exists for a thiol addition intermediate, 1, involving the C(4a)—N(5) bond, in nonenzymatic reductions of flavins and analogues by thiols.²⁻⁵ We have re-



cently proposed the C=N bond of 5-aryliminobarbituric acids as a simple model for the C(4a)—N(5) bond of flavins.⁶ We report here our observation of an isolable covalent intermediate, 3b, in the reduction of the highly activated imine 2 by a thiol. This provides the first direct nonkinetic demonstration of such an intermediate in a flavin model reaction and confirms the structural assignment of flavin-thiol intermediates 1 previously proposed on the basis of kinetic evidence.



The reaction of 1,3-dimethyl-5-(p-nitrophenylimino)barbituric acid (2, prepared by a modification of the published procedure⁶ for the 5-p-tolylimino derivative) with excess methyl thioglycolate at 25 °C exhibits biphasic kinetics at 360 nm (Figure 1A) consistent with accumulation and decay of an intermediate (eq 1). Kinetics of the two phases could be studied



independently, by stopped-flow spectrophotometry, at 379 nm, the isosbestic point for intermediate and product (Figure 1B), and at 415 nm (Figure 1C). The reaction followed at 379 nm was pseudo first order as indicated by agreement of two successive half-times for the reaction, and k_1' was determined from $t_{1/2}$ or from linear plots of $(A_{\infty} - A_0)$ vs. time; similar plots at 415 nm were linear after an initial lag phase and were used for determination of k_2' . No evidence⁷ was obtained for significant reversal of the initial step. Both processes, k_1' and $k_{2'}$, are dependent on the first power of the thiol anion concentration, as shown from the dependence of the rate on total thiol concentration and on pH at pH 3.8-5.2. The corresponding rate laws are given by

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Figure 1. Time-dependent absorbance changes at 360 (curve A), 379 (curve B), and 415 nm (curve C) for the reaction of 4×10^{-3} M methyl thioglycolate with 5×10^{-5} M 2 in 0.54 M formic acid-potassium formate buffer, 60% anion, at 25 °C, measured by stopped-flow spectrophotometry. The position of absorbance 0 on the scale is arbitrary.

$$k_1' = k_{1RS} - [RS^-]$$
 (2a)

$$k_{2}' = k_{2RS} - [RS^{-}]$$
 (2b)

Formation of the intermediate from methyl thioglycolate, but not its further reaction, is general acid catalyzed by formic acid-potassium formate buffers according to

$$k_{1RS^{-}} = k_1^{0}_{RS^{-}} + k_1^{c}_{RS^{-}}[HA]$$
(3)

Values of $k_1^{c}_{RS}$ - for cyanoacetic, formic and acetic acids are 3.4 × 10⁷, 4.5 × 10⁷, and ~3 × 10⁷ M⁻² s⁻¹, respectively, corresponding to a Brønsted α value no larger than 0.05 for these acids. For these acids, this observation is consistent with rate-determining diffusion-controlled trapping of an anionic thiol adduct of **2** by HA, or with a preassociation mechanism involving rate-determining attack of RS⁻ on **2** in a termolecular complex containing a molecule of HA.⁸

The reduction product of **2** was isolated from the reaction of **2** (0.67 mmol) with methyl thioglycolate (1.13 mmol) in 20 mL of 50% aqueous acetonitrile containing 0.05 M acetic acid-potassium acetate buffer (50% base). Crude product was obtained in 97% yield (based on thiol) after acidification and concentration of the reaction mixture. A twice-recrystallized sample gave a correct analysis for dihydro compound 4: ¹H NMR (Me₂SO-d₆/CDCl₃, Me₄Si) δ 3.28 (s, -CH₃), 6.62 (d, aromatic), 7.96 (d, aromatic). In this solvent the O-H and N-H protons of **4** gave an extremely broad signal around 6.5-7.5 ppm that interfered with integration of this region of 28.4



^a Assignments are based on analogies with those in L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley, New York, 1972, Nos. 12 (mercaptoethanol), 135 (methionine), 170 (1,3-dimethyluracil), and 178 (monomethylol dimethylhydantoin); G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, 1972, Chapter 4 (aromatics) and p 126 (substituted uracils); K. Oyama and R. Stewart, *Can. J. Chem.*, **52**, 3879 (1974) (alloxanic acid methylamide).

 $h(h^{\dagger})$

59.5 33.6

29.5

ř

the spectrum; the ratio of peak areas at δ 3.28 and 6.4-8 is 1.0:1.1. The ¹³C NMR spectrum⁹ of 4 in Me₂SO-d₆ (Table 1) is consistent with the assigned structure. In particular the signal at 91.9 ppm is more consistent with the enolic structure shown than with alternative structures involving hydrogen addition to any of the alloxan ring carbons. The structure as written has ten nonequivalent carbons; observation of only eight peaks presumably results either from overlapping of peaks or from rapid equilibration of the two identical enolic forms of 4 leading to equivalence of carbons a and a' and of h and h'. Anal. Calcd for C₁₂H₁₂N₄O₅: C, 49.31; H, 4.03; N, 19.18. Found: C, 49.87; H, 4.15; N, 18.91.

An ether extract of an unbuffered reaction mixture containing 0.5 mmol of 2 and 1.0 mmol of methyl thioglycolate in 60% acetonitrile was shown to contain a compound whose gas chromatographic retention time was identical with that of authentic disulfide produced by alkaline iodine oxidation of methyl thioglycolate.

At weakly acidic pH values the overall reaction of mercaptoethanol, $pK_a = 9.61$, is much slower than that of the more acidic ($pK_a = 7.91$) methyl thioglycolate because of the smaller fraction of anion that is present. For this compound k_2' is sufficiently slow that the spectrum of the intermediate can be observed by conventional spectrophotometry. Figure 2 shows the time dependence of the spectrum of a buffered reaction mixture containing 5×10^{-5} M 2 and 10^{-3} M mercaptoethanol. For mercaptoethanol, rate constants, k_1' , were measured by stopped-flow spectrophotometry at 379 nm, and k_2' by conventional spectrophotometry at 405 nm. Values of rate constants, extrapolated to 0 buffer concentration, for the two phases of reaction of 2 with two thiols are given in Table II.

Our observation of a spectrophotometrically detectable intermediate in the reaction of 2 with mercaptoethanol led us to attempt the isolation of this intermediate. Mercaptoethanol (1 mmol) was added to 1 mmol of 2 in 2 mL of acetonitrile, and the product that precipitated upon cooling of the reaction mixture was isolated in ~55% yield: ¹H NMR (Me₂SO-*d*₆/ CDCl₃, Me₄Si) δ 2.95 (t, 2 H, -CH₂S-), 3.32 (s, 6 H, -CH₃),



Figure 2. Spectral changes during the reaction of 2×10^{-3} M mercaptoethanol with 5×10^{-5} M 2 in 0.02 M formic acid-potassium formate buffer, 60% anion: curve A, spectrum immediately after initiation of reaction; curve B, after ~ 5 min. Broken line is the spectrum of 5×10^{-5} M 2, in the absence of thiol, in 0.02 M acetic acid-potassium acetate buffer, 50% anion.

Table II. Rate Constants for Reaction of 2 with Thiol Anions at 25 °C, Ionic Strength 1.0 M (KCl)

| RSH | pK _a | $k_1^{0}_{RS^{-}}, M^{-1} s^{-1}$ | k_{2RS} -, M ⁻¹ s ⁻¹ |
|---|-----------------|-----------------------------------|--|
| CH ₃ OC(0)CH ₂ SH | 7.91 <i>ª</i> | 2.5×10^{7} | 8.5×10^{6} |
| HOCH ₂ CH ₂ SH | 9.61 <i>ª</i> | 3.8×10^{8} | 3.0×10^{6} |

^a W. P. Jencks and K. Salvesen, J. Am. Chem. Soc., 93, 4433 (1971).

3.65 (q, 2 H, -CH₂O-), 5.37 (t, 1 H, -OH), 6.49 (d, 2 H, aromatic), 7.90-7.99 (3 H, aromatic plus -NH-). Anal. Calcd for C₁₄H₁₆N₄O₆S: C, 45.65; H, 4.35; N, 15.22. Found: C, 45.76, H, 4.41; N, 15.35.

The ${}^{13}C$ NMR spectrum⁹ in Me₂SO- d_6 (Table I) indicates the presence of ten nonequivalent types of carbon nuclei, of which only six are sp^2 hybridized, consistent with structure **3b**. If RSH adds to nitrogen rather than to carbon the most probable structure for the adduct would be 5, by analogy with 4. That structure 5 is incorrect is shown by the absence in the



adduct of a peak near 90 ppm predicted (by analogy with 4) for carbon g of 5. An observed chemical shift of \sim 60 ppm for this carbon of the adduct is consistent with sp³ hybridization, leading to the assignment of structure 3b. The tautomeric structure of sulfenamide 5 derived from 1,2 addition of RSH across the -N=C < bond is inconsistent with the ¹H NMR peak at \sim 7.99 ppm which is more reasonably assigned to an N-H proton than to the C-H proton in such an adduct.¹⁰

That 3b is identical with the intermediate in the reaction of 2 with excess thiol was shown by the identity of rate constants measured at 405 nm for the reaction of 3b and of 5×10^{-5} M 2 with 0.002-0.006 M (total) mercaptoethanol in 0.05 M acetic acid-potassium acetate buffer, 10% anion.

The results obtained for reaction of 2 with thiols are in complete agreement with the mechanisms proposed by Yokoe and Bruice³ and by Loechler and Hollocher⁴ for analogous reactions of flavin derivatives.¹¹ In particular our results confirm the geminal amino thioether structures 1 proposed by these authors, and our observation of general acid catalysis of intermediate formation, but not of its further reaction with thiol, is consistent with the behavior of the flavin reactions. The argument that such catalysis can provide a driving force for reaction only in the step that involves protonation of N(5)provided the rationale for proposing an intermediate of structure 1 as opposed to the alternative intermediate from conjugate addition involving S-N bond formation. For 3b the same structural assignment is both consistent with our kinetic observations and confirmed by spectroscopic data.

The reaction of 2 with thiols is extraordinarily fast relative to that of flavins. For example, k_{1RS} - for mercaptoethanol is at least ten orders of magnitude faster than the corresponding rate constant for attack of dithiothreitol monoanion on 3carboxymethyllumiflavin.⁴ Both this large rate enhancement and the existence of an isolable intermediate that is formed in an essentially irreversible addition step must be consequences of the much greater electrophilicity of the C=N bond of 2 relative to C(4a)—N(5) of flavin derivatives. The strongly electron-withdrawing nitro group, as well as destabilization of the nonplanar alloxan imine molecule, is presumably the source of this remarkable enhancement of reactivity, which is analogous to the observed enhancement of the rate of alkaline hydrolysis of 1,3-dimethyl-5-(p-tolylimino)barbituric acid⁶ relative to 3-methyl-10-arylisoalloxazines.

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References and Notes

- (1) Supported in part by a Frederick Gardner Cottrell grant from the Research Corporation and by a grant (GM22938) from the National Institute of General Medical Sciences of the National Institutes of Health.
- I. M. Gascoigne and G. K. Radda, Biochim. Biophys. Acta, 131, 498 (2)(1967).
- I. Yokoe and T. C. Bruice, J. Am. Chem. Soc., 97, 450 (1975).
- (4) E. L. Loechler and T. C. Hollocher, J. Am. Chem. Soc., 97, 3235 (1975).
- (5)
- J. C. Bruice, Prog. Bioorg. Chem., 4, 1 (1976).
 J. M. Sayer and M. DePecol, J. Am. Chem. Soc., 99, 2665 (1977) (6)
- (7) A plot (A. R. Fersht and W. P. Jencks, *J. Am. Chem. Soc.*, **92**, 5432 (1970)) of (k₁' + k₂'), which is equivalent to (λ₁ + λ₂), against total [RSH] for the reaction of **2** with 2–4 × 10⁻³ M methyl thioglycolate in 0.1 M acetic acid-potassium acetate buffer, pH 3.85, gave a zero ordinate intercept indicating that k_{-1} in the scheme shown is negligible.

$$2 \xleftarrow{k_1[RSH]}{k_{-1}} 3a \xrightarrow{k_2[RSH]} 4$$

- (8) Analogous mechanisms have been described for additions of thiol anions to acetaldehyde: H. F. Gilbert and W. P. Jencks, J. Am. Chem. Soc. 99, 7931 (1977)
- Fourier transform ¹³C NMR spectra (at room temperature) were measured at 67.9 MHz. A solution of 3b in Me₂SO- d_6 was shown to be stable at 25 °C for the time (~1.5 h) required for NMR spectral measurement, by the observation of less than a 5% change during this time in its absorption at 372 nm.
- The chemical shift for this C–H proton is estimated to be ~5 ppm by the use of Shoolery's rules (L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Second (10)ed., Pergamon, Oxford, 1969, p 181); the analogous proton of a similar compound, diethyl acetamidomalonate, has a chemical shift of 5.45 ppm ("Nuclear Magnetic Resonance Spectra", Sadtler Research Laboratories, Philadelphia, 1967, No. 730). In contrast, the chemical shift for the N-H proton of the geminal amino thioether o-NO2C6H4NHCH(C6H5)SC6H4-p is 8.64 ppm (R. Marshall and D. M. Smith, J. Chem. Soc. C, 3510 (1971))
- NOTE ADDED IN PROOF. The observation of large rate accelerations for thiol oxidation by flavins in the presence of cationic polymer micelles has re-

cently been reported. An interpretation involving thiol activation in the attack on the flavin-thiol intermediate is consistent with the mechanisms discussed in this paper for the flavin-thiol reaction in the absence of micelles: S. Shinkai, R. Ando, and T. Kunitake, *J. Chem. Soc., Perkin Trans.* 2, 1271 (1978).

(12) National Science Foundation Undergraduate Research Participant.

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Desulfurizative Stannylation of Propargylic or Allylic Sulfides via an S_H' Process

Sir:

The reactions of organotin hydride with double or triple bond normally yield hydrostannylated species, which are useful as synthetic intermediates.¹

In connection with our work on the desulfurization with organotin compounds,² we found an unusual desulfurizative stannylation of propargyl or allyl sulfides with organotin hydride. We report here the first clear-cut example of an $S_{H'}$ process³ involving an organotin radical (attacking group) and an organosulfur-centered radical (eliminating group). Thus the tri-*n*-butyltin radical generated from azobisisobutyronitrile (AIBN) and tri-*n*-butyltin hydride⁴ (2 equiv) reacted with 2-(propargylthio)benzothiazole (1)⁵ to give tri-*n*-butyl-stannylallene (2) in 90–93% yield without contamination of propargyltri-*n*-butylstannane (3) as shown in the eq 1.⁶

$$\underset{1}{\overset{N}{\longrightarrow}} \overset{N}{\xrightarrow{}} \overset{Bu_{3}SnH}{\xrightarrow{}} \overset{Bu_{3}SnH}{\xrightarrow{}} \overset{Bu_{3}SnCH=C=CH_{2}}{\xrightarrow{}} \overset{R}{\xrightarrow{}} \overset{R}{$$

When an equimolar amount of tri-*n*-butyltin hydride was employed, 2-mercaptobenzothiazole (4) was isolated in 36% yield in addition to the desired stannylallene (2) in 65% yield. Instead of using the isolated tri-*n*-butyltin hydride, the present stannylation reaction was conveniently carried out by the in situ technique⁷ using bis(tri-*n*-butyltin) oxide (5) and poly-(methyl hydrogen siloxane) (6).

$$s \xrightarrow{N}_{s} \xrightarrow{O} + (Bu_{3}sn)_{2}O + (\frac{Me}{siO})_{n} \xrightarrow{AIBN} Bu_{3}snCH=C=CH_{2}$$

$$1 \qquad 5 \qquad 6 \qquad 2$$

A typical procedure⁸ is as follows. A mixture of bis(tri-*n*-butyltin) oxide (5, 2.5 mL, 4.9 mmol) and polysiloxane 6 (0.7 g, 11.6 mmol) was stirred at room temperature for 30 min under argon. Then propargyl sulfide 1 (1.0 g, 4.9 mmol) and catalytic amount of AIBN (10 mg) were added and the resulting mixture was heated at 80–100 °C until the disappearance of the absorptions of acetylene at 3250 and 2100 cm⁻¹ and tin hydride at 1800 cm⁻¹ (~4–5 h). Stannylallene 2 was isolated by direct distillation from the reaction mixture in 93% yield: bp 80–82 °C (0.15 mmHg); IR (film) 1920 cm⁻¹ ($\nu_{CH=C=CH_2}$); NMR (CDCl₃) δ 5.0 (t, J = 8 Hz, 1 H, CH=C), 4.16 (d, J = 8 Hz, 2 H, C=CH₂), 0.8–1.6 (m, 27 H, Bu₃); *m/e* 330 (M⁺), 291, 290, 234, 232, 179, 177, 120, 118, 39.

Similar result was obtained with the tri-*n*-butyltin radical generated photolytically. Thus **2** was isolated in 68% yield by irradiation of a degassed benzene (15 mL) solution of **1** (3.9 mmol) and tri-*n*-butyltin hydride (4.9 mmol) with a 100-W high-pressure mercury lamp for 5 h at room temperature in a Pyrex tube.⁹

In order to assess the effect of the organosulfur moiety, we further investigated the several propargyl sulfides $(7, {}^{10}8, 9)$ and sulfone 10.

Among these organosulfur compounds, 2-(propargylthio)-



1,3-thiazoline (7) and propargyl phenyl sulfide (8) gave the desired allene (2) as main product (>50% yield)¹¹, while propargyl dithiocarbamate (9) and sulfone 10 could not give any allenic products at all under similar conditions at 80-110 °C.¹²

It is quite interesting to note the completely different behavior of propargyl ether toward the tri-*n*-butyltin radical reported by Corey et al.¹³ They obtained the normal hydrostannylation product (**12**) in high yield.

The results obtained so far suggest a principal reaction scheme, as shown in Scheme I.

Scheme I



The most important key step is the elimination of the stable sulfur-centered radical such as the benzothiazolythio radical 14 (1,3-thiazolinylthio or phenylthio radical in the case of the compound 7 or 8, respectively) from the initial adduct such as 13 accompanied with the formation of 2 (step b). The relatively more stable benzothiazolythio radical 14^{14} in comparison with the other two sulfur radicals seems to give the highest yield of 2 from 1. On the other hand, in the case of propargyl ether (11), the cleavage to the highly unstable alkoxy radical is extremely unfavorable.

Steps c, d, and e are supported by the well-known reaction of the thiyl radical (RS-) with triorganotin hydride.¹⁵ Isolation of **4** in an equimolar reaction also indicates the relatively faster reaction of step c in comparison with step d or e.

Direct homolytic substitution (S_H process) at the sulfur atom is excluded, since such a process should afford a mixture of acetylene and isomeric allene as reported in the case of the reaction of propargyl chloride and tri-*n*-butyltin hydride.¹⁶



Furthermore, we have found that successful allylic stannylation also proceeds under similar conditions. Thus 2-(allylthio)-1,3-benzothiazole (16) reacted with twice the molar amount of tri-*n*-butyltin hydride in the presence of AIBN at 90 °C for 5 h to give tri-*n*-butylallyltin (17)¹⁷ in 88% yield: bp 80 °C (0.28 mmHg).

$$s \xrightarrow{N}_{s} \xrightarrow{0} \frac{Bu_{3}^{SnH}}{888} \xrightarrow{Bu_{3}^{Sn}} 17$$

This allyl transfer as well as allenyl transfer seems to be synthetically useful, since allyltin has potential reactivity toward various electrophiles involving $\sigma-\pi$ resonance stabilization similar to that of allylsilane.¹⁸

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