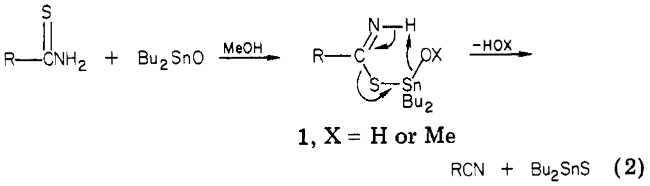
several aromatic (2–5) and aliphatic (6 and 7) thio amides into the corresponding nitriles. In all cases these conversions were completed within 30 min. Further studies indicated that bis(tri-*n*-butyltin) oxide, also a readily available organotin, is equally useful, if not superior. Thus, conversion of thio amides with 1.1 molar equiv of $(n\text{-}Bu_3Sn)_2O$ in boiling benzene under azeotropic conditions afforded the desired nitriles in very good to excellent yields in similarly short reaction times. These reactions appear to be specific for thio amides, since, under the same conditions, primary amides were unaffected by treatment with either butyltin oxide reagent.

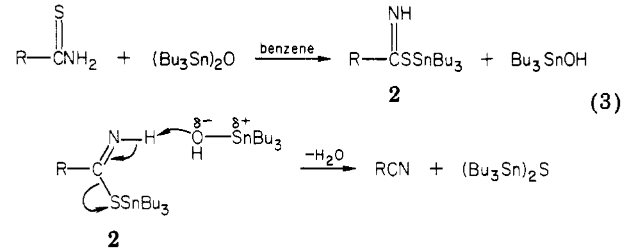
A plausible mechanism for the conversion of thio amides to nitriles with $n\text{-}Bu_2SnO$ in methanol is shown in eq 2 and



1, X = H or Me

(2)

involves nucleophilic attack by sulfur on the Sn=O function to give reactive intermediate 1, where X = H. It is known, however, that dibutyltin oxide and methanol rapidly forms dibutyldimethoxytin.[14] It is therefore probable that attack by sulfur at the tin atom also involves this dimethoxytin derivative to give intermediate 1, where X = Me. Either form of 1 can undergo a β elimination (presumably by the E_1 mechanism illustrated) to generate the nitrile with concomitant formation of dibutyltin sulfide. The possibility of an E_2 mechanism involving proton abstraction by methoxide ions formed by dissociation of dibutyldimethoxytin, however, cannot be precluded. The general mechanism offered is based on the isolation of dibutyltin sulfide as the only major byproduct of the reaction and on the reported ease with which thiols[14] and N-substituted thio amides[14c] undergo S-stannylation. An analogous mechanism for the dehydrosulfurization with bis(tri-*n*-butyltin) oxide is offered in eq 3 and involves



2

(3)

2

initial formation of sulfur–tin intermediate 2 and of tributyltin hydroxide. Subsequent β elimination would then afford the nitrile and bis(tri-*n*-butyltin) sulfide after water elimination.

Because of the usefulness of carbodiimides as versatile dehydrating reagents,[15] it was of interest to explore the possible application of the dehydrosulfurization reactions outlined above to the synthesis of carbodiimides from thioureas. Treatment of *N,N'*-diphenylthiourea with a slight excess of bis(tri-*n*-butyltin) oxide in benzene afforded instead the corresponding urea derivative (8, Table I) in good yields. The possibility that the diimide might have served as a transient intermediate in this conversion is under investigation.

The studies outlined above complement earlier reports on dehydrosulfurization of thio amide derivatives[5–13] and provide a simple and efficient procedure for the synthesis of nitriles from primary thio amides under mild, neutral conditions with readily available organotin reagents.

Experimental Section

The thio amides 1–3 were obtained from the corresponding nitriles[4,16] by treatment with hydrogen sulfide in pyridine and triethylamine.[17] The thio amides 4, 5, and 8 were commercially available. *p*-Nitrophenylthioacetamide (6) was obtained by treatment of *p*-nitrophenylacetonitrile with thioacetamide under acidic conditions.[18] Thiolauramide (7) was obtained from the reaction of lauramide with phosphorus pentasulfide in dioxane. Preparative TLC was performed on 500 μm silica gel GF plates (Analtech, Inc.).

General Procedure of Dehydrosulfurization (1–7). Method A. A mixture of the thio amide (1 mmol) and dibutyltin oxide (1.1 mmol) in methanol (8 mL) was heated to reflux for 30 min. For compound 7, the reaction was carried out on a 10-mmol scale. After evaporation of the solvent, the product was isolated by the method specified in Table I and identified by comparison (^{1}H NMR, IR, and/or mp) with an authentic sample.

Method B. A mixture of the thio amide (1 mmol for 1–4 and 6) and bis(tri-*n*-butyltin) oxide (1.1 mmol) in benzene (8 mL) was heated to reflux with azeotropic removal of water for 30 min. For compounds 5 and 7, the reaction was carried out on a 10-mmole scal. Except for 8 (see Table I), the workup was identical with that described in method A.

Acknowledgment. We thank Marvin Olsen for recording the ^{1}H NMR spectra.

Registry No. 1, 83060-69-9; 2, 83060-70-2; 3, 83060-71-3; 4, 4621-66-3; 5, 2227-79-4; 6, 76254-70-1; 7, 56352-45-5; 8, 102-08-9; 1 nitrile, 77691-00-0; 2 nitrile, 83060-72-4; 3 nitrile, 83060-73-5; 4 nitrile, 100-54-9; 5 nitrile, 100-47-0; 6 nitrile, 555-21-5; 7 nitrile, 2437-25-4; *N,N'*-diphenylurea, 102-07-8; dibutyltin oxide, 818-08-6; bis(tri-*n*-butyltin) oxide, 56-35-9.

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(14) See: (a) W. P. Neumann, "The Organic Chemistry of Tin", Interscience, New York, 1970; (b) R. C. Poller, "Chemistry of Organotin Compounds", Academic Press, New York, 1970; (c) A. K. Sawyer, "Organotin Compounds", Marcel Dekker, New York, 1971.

(15) (a) H. G. Khorana, *Chem. Rev.*, **53**, 145 (1953); (b) K. L. Agarwal, A. Yamazaki, and H. G. Khorana, *J. Am. Chem. Soc.*, **93**, 2754 (1971); (c) M. Mikolajczyk and P. Kielbasinski, *Tetrahedron* **37**, 233 (1981).

(16) The nitriles 2 and 3 were obtained by a general approach to 3-amino-2-cyanothiophenes recently developed in this laboratory. This method, which makes use of addition of an α-mercaptoacetonitrile derivative to 3-substituted cyanoacetylenes, followed by ring closure under basic conditions, will be reported elsewhere.

(17) A. Albert and C. J. Lin, *J. Chem. Soc., Perkin Trans. 1*, 210 (1977).

(18) E. C. Taylor and J. A. Zoltewicz, *J. Am. Chem. Soc.*, **82**, 2656 (1960).

(*E*)-3-(Trimethylsilyl)-2-propen-1-ol. An Improved Preparation

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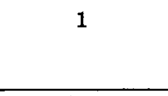
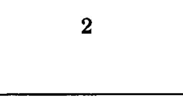
Received May 25, 1982

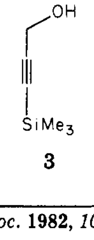
In connection with a research program on silicon-directed electrocyclic reactions[1] we required large quantities of (*E*)-3-(trimethylsilyl)propenal (1). This compound has



1



2



3

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(1) Denmark, S. E.; Jones, T. K. *J. Am. Chem. Soc.* **1982**, *104*, 2642.

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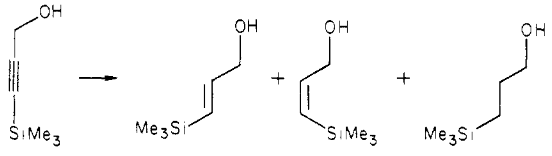
Table I[a]



3 2t 2c 4

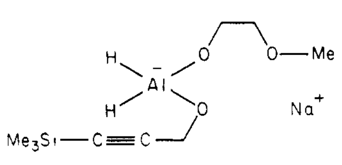
expt	reducing agent	solvent	no. of hydrides[b]	time, h	temp, °C	ratio of 2t/2c/4
1	$LiAlH_4$ (powder)	Et_2O	4	6	0 → 25	19:49:32
2	$LiAlH_4$ (powder)	Et_2O	4	24	0	21:73:6
3	$LiAlH_4$ (solution)[c]	Et_2O	4	24	0	23:66:11
4	$LiAlH_2(OCH_3)_2$[d]	Et_2O	2.1	24	0	26:63:11
5	$LiAlH_4$ (powder)	THF	4	24	0	95:3:2
6	$LiAlH_4/NaOCH_3$ (1/2)	THF	4	5	0 → 25	90:6:4
7	$LiAlH_4$ (powder)	DME	4	24	0	98:1.5:0.5
8	$NaAlH_2(OCH_2CH_2OCH_3)_2$[e]	Et_2O	3.2	1	0 → 25	100:0:0[f]

[a] All reactions were done with 100 mg of 3 unless otherwise specified. [b] Moles of H^- per mole of 3. [c] 4.6 M in Et_2O. [d] Prepared in situ from $LiAlH_4$ solution and 2 equiv of MeOH. [e] 3.67 M in toluene. [f] Preparative-scale reaction (see Experimental Section); 85% yield.

been prepared by a number of different methods including oxidation[2a,b] of (*E*)-3-(trimethylsilyl)-2-propen-1-ol (2), formylation of (*E*)-2-(trimethylsilyl)vinyllithium,[2c] and Friedel–Crafts formylation of (*E*)-1,2-bis(trimethylsilyl)ethene.[2d] From a practical standpoint, the first route appeared most attractive. Indeed, both Jung[2a] and Fleming[2b] have communicated improved procedures for this oxidation. Curiously, however, we were unable to find an adequate description[3] for the preparation of the precursor alcohol, 2. This note provides such an experimental procedure as well as an improved preparation of 3-(trimethylsilyl)-2-propyn-1-ol[4] (3).

According to three independent reports, the alcohol 2 is easily prepared by $LiAlH_4$[2b,3] or $LiAlH_2(OCH_3)_2$[2a,5] reduction of 3, itself obtained by silylation of propargyl alcohol dianion.[4] After several unsuccessful attempts to prepare 2 as described we decided to examine, in detail, the course of the reaction with a variety of reducing agents and solvents. These results are summarized in Table I. Gas chromatographic analysis[6] of the product mixtures obtained from reduction with $LiAlH_4$ or $LiAlH_2(OCH_3)_2$ in Et_2O (expts 1–4) indicated the presence of three compounds. Tentative assignment of the major product (73% in mixture, expt 2) as the cis isomer, **2c**, was based on a 13.5-Hz coupling constant for the olefinic protons in a ^1H NMR spectrum of that mixture.[7a] Another ABX_2 pattern was visible in the olefinic region with J_{AB} = 18 Hz which was assigned to **2t** and subsequently verified (vide infra). The resonances for the saturated alcohol 4 are sufficiently well isolated as to be diagnostic.[7b] Thus, while overreduction is not a problem at lower temperatures, **2t** is never the major product in Et_2O.[8]

Earlier studies by Borden[9] and Djerassi[10] show that the use of more strongly Lewis basic (cation coordinating) solvents increases the proportion of trans reduction. This proved to be the case with 3 as well. Experiments 5 and 7 show that with THF or DME a striking reversal in stereochemistry is observed. Interestingly, the addition of 2 molar equiv of sodium methoxide[11] (expt 6) has a less dramatic effect.[12] The most stereospecific, fastest, *and* highest yielding reduction was obtained with sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al or SMEAH).[13,14] GC analysis showed complete consumption of 3 within 1 h to give exclusively **2t** in 85% yield (after distillation) on a decagram scale. This is consistent with the observations that the rate and stereoselectivity of propargylic alcohol reduction are both increased by cation complexation,[10,1b] a situation which clearly obtains with SMEAH (e.g., it is soluble in hydrocarbons[14a]). Interestingly, we have observed that 1.1 equiv of SMEAH (based on aluminum, i.e., 2.2 equiv of hydride) is insufficient to effect reduction of 3, even in refluxing Et_2O. However, addition of another 0.5 equiv of SMEAH led to facile reduction at 0–25 °C. We interpret this stoichiometry to implicate the dihydrido species i as the active reducing agent.[15]



i

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(2) (a) Jung, M. E.; Gaede, B. *Tetrahedron* **1979**, *35*, 621. (b) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, *2415*. (c) Cunico, R. F.; Clayton, F. J. *J. Org. Chem.* **1976**, *41*, 1480. (d) Magnus, P. *Aldrichimica Acta* **1980**, *13*, 43.

(3) The original preparation of 2 was mentioned briefly within a larger context: Stork, G.; Jung, M. E.; Colvin, E.; Noel, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3684.

(4) Mironov, V. F.; Maksimova, N. G. *Bull. Acad. Sci. USSR, Div. Chem. Sic.* (*Engl. Transl.*) **1960**, 1911.

(5) After this study was in progress we learned from Professor Jung that the reagent he used, with success, was $LiAlH_4/NaOCH_3$; $LiAlH_2(OCH_3)_2$ in that paper is a misprint (private communication).

(6) Column: Carbowax 12M (6 ft × 1/8 in.) 5% on Chromosorb W. Temperature program: initial temperature 70 °C (2 min) and then 10 °C/min up to 150 °C. Retention times (min): **4**, 4.88; **2c**, 5.81; **2t**, 6.12; **3**, 8.04.

(7) ^1H NMR signals (a) for **2c**: δ 0.2 (s, 9 H), 1.76 (br s, 1 H), 4.73 (d, J = 6 Hz, 2 H), 5.73 (d, J = 13.5 Hz, 1 H), 6.47 (dt, J_d = 13.5 Hz, J_t = 6 Hz, 1 H). (b) For **4**: δ 0.1 (s, 9 H), 0.8 (t, J = 7 Hz, 2 H), 1.25 (m, 2 H), 1.76 (br s, 1 H), 3.35 (m, 2 H).

(8) The similarity of results from experiments 3 and 4 suggests that disproportionation of $LiAlH_2(OCH_3)_2$ is rapid and that $LiAlH_4$ is the actual reducing agent.

(9) Borden, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 4898.

(10) Grant, B.; Djerassi, C. *J. Org. Chem.* **1974**, *39*, 968.

(11) (a) Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. *J. Am. Chem. Soc.* **1968**, *96*, 4245. (b) Molloy, B. B.; Hauser, K. L. *J. Chem. Soc., Chem. Commun.* **1968**, 1017.

(12) Direct comparison is difficult because temperature effects are also apparently important; cf. experiments 1 and 2.

(13) (a) Chan, K.; Specian, A. C.; Saucy, G. *J. Org. Chem.* **1978**, *43*, 3435. (b) Chan, K.; Cohen, N.; DeNoble, J. P.; Specian, A. C.; Saucy, G. *Ibid.* **1976**, *41*, 3497.

(14) For recent summaries of the uses of SMEAH see: (a) Vit, J. *Eastman Org. Chem. Bull.* **1970**, *42*, No. 3; **1974**, *46*, No. 1. (b) Hajos, A. "Complex Hydrides"; Elsevier: New York, 1979; pp 159–167.

Finally, we have found that the preparation of **3**, sparsely outlined by Mironov[4,16] (44% yield), is extremely capricious and requires many more manipulations than are described. A detailed, improved procedure appears below which can reliably be done on a 4-mol scale in 66% yield.

Experimental Section

^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz) spectrometer. In all cases $CDCl_3$ was used as the solvent with $CHCl_3$ (δ 7.27) as an internal reference. GC analyses were performed on a Varian 3700 instrument with N_2 as the carrier gas at 30 mL/min. Retention times and integrals were recorded on a Hewlett-Packard 3390 recording integrator. All reactions were done in flame-dried glassware under a N_2 atmosphere. Anhydrous Et_2O, Mg turnings, and ethyl bromide were Mallinckrodt AR grade and used as received. Propargyl alcohol was distilled from K_2CO_3, and THF was distilled freshly from sodium benzophenone ketyl.

3-(Trimethylsilyl)-2-propyn-1-ol (3). In a three-necked, 2-L, round-bottomed flask fitted with mechanical stirrer, addition funnel, and condenser were placed 97.4 g (4 mol) of magnesium turnings and 700 mL of anhydrous Et_2O. To the stirred suspension was added 436 g (300 mL, 4 mol) of ethyl bromide at such a rate as to maintain gentle reflux. The mixture was refluxed 1 h further after complete addition. After the Grignard solution was cooled in an ice bath, 80 g (83 mL, 1.43 mol) of propargyl alcohol was slowly added with external cooling. Upon complete addition, the ice bath was removed, and the mixture was stirred overnight, during which time it slowly solidified. The mass was cooled in an ice bath and treated dropwise with 435 g (508 mL, 4 mol) of trimethylsilyl chloride. After approximately 100 mL of Me_3SiCl was added, the mass disintegrated into a slurry, at which point the ice bath was removed and the slurry allowed to warm to room temperature for the remainder of the addition. A Liebig condenser was then attached, and the Et_2O was distilled out (boiling range 38–40 °C). The resulting solid was heated on a steam bath for 3 h and cooled to room temperature. The mixture was suspended in 400 mL of Et_2O, treated dropwise with 200 mL of 1 N H_2SO_4, and stirred for 2 h. The Et_2O layer was separated and washed with water (2 × 300 mL) and brine (1 × 300 mL). The aqueous layer was diluted with 800 mL of 1 N H_2SO_4 and extracted with Et_2O (2 × 400 mL), and the Et_2O extracts were washed with water (2 × 300 mL) and brine (1 × 300 mL). All Et_2O extracts were combined, dried (Na_2SO_4), and concentrated in vacuo. The residue was distilled at reduced pressure (capillary) to yield 160 g of a 57:43 mixture of **3** and the trimethylsilyl ether of **3**; bp 76–80 °C (24–30 mm). This mixture was divided in half and hydrolyzed in portions as follows. A solution of 78.1 g of the mixture in 340 mL of THF was treated with 40 mL of 1 N H_2SO_4. After the mixture was stirred for 5 min, 250 mL of NaH_2PO_4 buffer solution (pH 7.04) was added followed by sufficient saturated $NaHCO_3$ solution to neutralize the acid. The solution was extracted with Et_2O (3 × 200 mL), and the Et_2O extracts were washed with water (2 × 250 mL) and brine (1 × 250 mL). The combined Et_2O layers were dried ($MgSO_4$) and concentrated in vacuo. The residual liquids thus obtained from two identical hydrolyses were combined and distilled to afford 120 g [66% yield (lit.[4] yield 44%)] of **3**: bp 56 °C (7 mm); ^{1}H NMR δ 0.27 (s, 9 H), 1.6 (t, J = 6 Hz, 1 H), 4.28 (d, 2 H, J = 6 Hz).

(*E*)-3-(Trimethylsilyl)-2-propen-1-ol (2). In a three-necked, 1-L, round-bottomed flask fitted with a thermometer, addition funnel, and N_2 inlet was placed 136 mL (0.50 mol) of a 3.67 M solution of sodium bis(methoxyethoxy)aluminum hydride in toluene followed by 200 mL of anhydrous Et_2O. The solution was cooled to 0 °C on ice and treated dropwise with a solution of 40 g (0.312 mol) of **3** in 200 mL of Et_2O. Ten minutes after complete addition the ice bath was removed, and the reaction was complete (GC[6] monitoring) within 1 h. The reaction was quenched by the dropwise addition of 400 mL of 2 N H_2SO_4. The organic layer was separated and washed with water (2 × 200 mL) and brine (1 × 200 mL). The aqueous layer was extracted with Et_2O (2 × 300 mL), and all the Et_2O phases were combined, dried ($MgSO_4$), and concentrated in vacuo. The residual liquid was distilled to yield 34.5 g (85%) of **2**: bp 80–81 °C (40 mm); ^{1}H NMR δ 0.23 (s, 9 H), 1.5 (t, J = 6 Hz, 1 H), 4.22 (dd, J = 6, 4 Hz, 2 H), 5.93 (d, J = 18 Hz, 1 H), 6.23 (dt, J_d = 19 Hz, J_t = 4 Hz, 1 H).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. **1**, 33755-86-1; **2t**, 59376-64-6; **2c**, 62861-80-7; **3**, 5272-36-6; 3-(Me_3Si)-**3**, 50965-66-7; **4**, 2917-47-7; sodium bis(2-methoxyethoxy)aluminum hydride, 22722-98-1.

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[15] Apparently a complex containing three oxygen ligands and only one hydride is insufficiently reactive to reduce the triple bond. This may not be unique to SMEAH since an excess of hydride is usually required with $LiAlH_4$ also.

[16] **Note Added in Proof**: A similar procedure for the preparation of **3** has recently appeared: Brandsma, L.; Verkruisse, H. O. "Synthesis of Acetylenes, Allenes and Cumulenes"; Elsevier: Amsterdam, 1981; p 58.

Communications

Regioselective Photoisomerizations of Bridgehead Substituted Dibenzobarrelenes and Benzonorbornadienes. The Implication of Excited-State Secondary Deuterium Isotope Effects of Benzo–Vinyl Bridging

Summary: Replacement of a bridgehead hydrogen by deuterium in the title compounds leads to k_H/k_D values of 1.11–1.27 (cyclopropyl substitution disfavored); these effects are opposite to those seen with other substitutents (except bromine) and demand that bridged radicals such as **2** be formed reversibly or not at all.

Sir: Di-π-methane photorearrangements have long been considered to proceed in stepwise fashion via a pair of biradical intermediates.[1] When benzo–vinyl bridging is involved, the conversion to product has been formulated as the result of initial bond making to generate a cyclopropane moiety followed by cleavage of an alternate three-membered ring bond. Direct proof of the existence of two discrete intermediates such as **2** and **3** has been exceedingly difficult to obtain, although Schaffner and co-workers have presented ESR and IR evidence for the intervention of two biradical intermediates during the low-temperature photoisomerization of **1** (R = COC_6H_5) to **4**. The other plausible alternative is, of course, a direct light-induced 1,2 aryl shift within such systems to generate rearranged biradicals directly (e.g., **1** → **3** → **4**). We now

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[1] (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Chapter 16.

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