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Supplementary Material Available: Experimental details for the reduction of decalones 8, 13, and 19 by method A and method B (3 pages). Ordering information is given on any current masthead page.

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- (4) When the reduction (lithium–ammonia) of 24-nor-5 β -cholan-12-one (i) was carried out in the presence of methanol, there was produced (79% yield) a 29:71 ratio of the 12 β -ol (ii) and the 12 α -ol (iii), respectively.³ However, if methanol was added to quench the metal–ammonia reduction of i, the ratio of ii/iii changed to 81:19. Similarly, 23,24-dinor-5 β -cholan-12-one (iv) upon reduction in the presence of methanol gave predominantly the C-12 axial alcohol.³ The ratio of 12 β -ol to 12 α -ol was 27:73. The reduction of iv in the absence of methanol was not performed.
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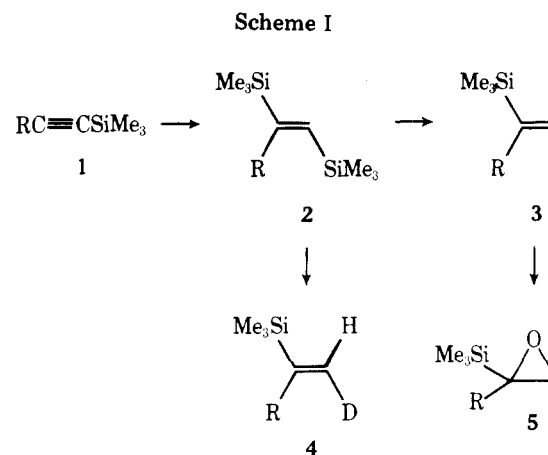
Regioselective Hydrosilylation–Desilylation: Convenient Preparation of a 2-(Trimethylsilyl)-1-alkene¹

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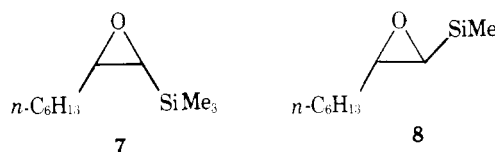
Vinylsilanes are compounds of increasing importance in organic synthesis,³ in part because they undergo electrophilic substitution reactions with a variety of reagents and thus serve as vinyl anion equivalents^{3,4} and in part because the derived α,β -epoxysilanes can serve as versatile vinyl cation equivalents.⁵ A number of methods for the synthesis of vinylsilanes have been reported,^{6,7} but few of these are suited for the preparation of 2-(trimethylsilyl)-1-alkenes.⁷



We wish to report a new method for the synthesis of vinylsilane **3** ($R = n\text{-C}_6\text{H}_{13}$), featuring a highly regioselective hydrosilylation and protodesilylation sequence, shown in Scheme I, which should be applicable to the synthesis of other 2-(trimethylsilyl)-1-alkenes.⁸ The protodesilylation reaction has a precedent in the work of Dunogues et al., who reported that 1-phenyl-1,2-bis(trimethylsilyl)ethene (**2**, $R = \text{Ph}$) was converted to 1-phenyl-1-(trimethylsilyl)ethene (**3**, $R = \text{Ph}$) by prolonged treatment with refluxing acetic acid.⁹

We have found that chloroplatinic acid catalyzed hydrosilylation of 1-(trimethylsilyl)-1-octyne (**1**, $R = n\text{-C}_6\text{H}_{13}$) occurs in a highly regioselective manner to give (after treatment with MeMgBr) (*E*)-1,2-bis(trimethylsilyl)-1-octene (**2**, $R = n\text{-C}_6\text{H}_{13}$) in 96% yield. Only traces (not more than 4%) of what may be the alternate regioisomer ($n\text{-C}_6\text{H}_{13}\text{CH}=\text{C}(\text{SiMe}_3)_2$, **6**) could be detected by VPC but were not visible in the NMR. The stereochemistry of **2** was assigned by analogy to other chloroplatinic acid catalyzed hydrosilylations of alkynes which are known to occur exclusively in a syn manner.¹⁰ The high regioselectivity observed here is noteworthy, since hydrosilylations of alkynes generally give mixtures of regioisomers, even with terminal alkynes.^{11,12} It should also be noted that hydroborations¹³ and hydroaluminations¹⁴ of alkynylsilanes proceed with opposite regiochemistry to put the boron or aluminum on the carbon bonded to silicon.

Treatment of **2** with proton acids resulted in selective removal of the terminal trimethylsilyl group to give **3** ($R = n\text{-C}_6\text{H}_{13}$) in 96% yield. The optimum results were obtained using acetic acid containing about 5% water. The regiochemical purity of **3** was best determined by conversion to the epoxide **5**. Analysis by VPC showed that less than 0.1% of the cis or trans epoxides **7^{5b}** or **8^{5b}** were present, indicating the extremely high regioselectivity of the reaction.



A similar reaction using deuterated acetic acid gave the deuterated vinylsilane **4**, in which the deuterium was largely or completely cis to the alkyl group, consistent with retention of configuration in the desilylation step.^{15,16}

Although the exact mechanism of the desilylation reaction is not known,¹⁷ the regiochemistry can be rationalized by assuming addition of acetic acid to the double bond with Markovnikoff orientation, followed by β -elimination of the resulting β -acetoxysilane. The fact that a simple alkyl group is sufficient to induce highly regioselective desilylation of a bis silylated alkene under conditions which maintain the stereoselectivity of the reaction suggests that the concept of regioselective desilylation of bis or higher silylated alkenes will

prove useful for the synthesis of vinylsilanes, especially as new methods, such as the one described in this work, for the synthesis of bis silylated alkenes become available.¹⁸

Experimental Section

All reactions were carried out in a nitrogen atmosphere. The use of the verb "concentrated" refers to evaporation of solvent under reduced pressure (water aspirator) using a rotary evaporator. Infrared (IR) spectra were obtained using Perkin-Elmer Models 137 or 727B or Beckman IR-33 spectrometers. Nuclear magnetic resonance (NMR) spectra were obtained using Varian T-60 or Varian A-60 spectrometers using chloroform (δ 7.27) as an internal reference. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-7E instrument or a Finnigan 3200 automated gas chromatograph-mass spectrometer. Vapor phase chromatographic (VPC) analyses were performed on a Varian Aerograph Model 90-P instrument using helium as the carrier gas.²⁰ Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

Commercially available compounds were used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from a deep purple solution from sodium and benzophenone. Methylchlorosilane was freshly distilled from calcium hydride. Chloroplatinic acid was dried under vacuum before use.

(E)-1,2-Bis(trimethylsilyl)-1-octene (2). A mixture of 2.60 mL (2.87 g, 25 mmol) of methylchlorosilane and a trace (3–5 mg) of chloroplatinic acid was stirred in an ice bath for 10 min. 1-(Trimethylsilyl)-1-octyne (1)^{6c} (2.95 g, 16.2 mmol) was added, and the mixture was stirred at ice temperature for 10 min and then allowed to warm to room temperature, whereupon a vigorous reaction occurred and the mixture assumed a dark brown color. After stirring at room temperature for 23 h and at 50 °C for 2 h, the mixture was cooled (ice bath) and diluted with 25 mL of ether and 40 mL (92 mmol) of methylmagnesium bromide (2.3 M in ether) was added. The resulting mixture was stirred for 5 h at room temperature and then added to aqueous NH₄Cl and extracted with petroleum ether. The extracts were washed with saturated NH₄Cl and saturated NaCl, dried (MgSO₄), concentrated, and distilled (bulb to bulb, oil pump vacuum, 140 °C), giving 3.98 g (96%) of 2 as a colorless liquid: IR (film) 3.4, 6.44, 6.85, 8.04, 11.9, 13.3, 14.6 μ m; NMR (CCl₄) δ 6.05 (s, 1.0 H), 2.6–2.1 (2.2 H), 1.7–1.17 (8.4 H), 1.17–0.8 (3.3 H), 0.17 and 0.12 (both singlets, 18.0 H); MS *m/e* (relative intensity) 256 (0.2, M⁺) 241 (2.4), 186 (21), 167 (15), 98 (30), 73 (100), 59 (9).

VPC analysis (SE-30,^{20a} 128 °C, tetradecane = 6.21 min) showed the major peak at 4.40 min (93% of peak area).

The product from a similar reaction was purified by preparative VPC^{20a} (128 °C) followed by bulb to bulb distillation. Anal. Calcd for C₁₄H₃₂Si₂: C, 65.54; H, 12.57. Found: C, 65.69; H, 12.82.

Products from several different runs were obtained in similar purities. The isomeric disilyl olefin 6 (see below) was not visible in the NMR spectra of the products; however, VPC analysis generally showed a small peak (3–4% of peak area) at longer retention time corresponding to compound 6.

A comparison sample of 1,1-bis(trimethylsilyl)-1-octene (6) was obtained from the reaction of tris(trimethylsilyl)methylolithium¹⁹ and heptanal (THF, –78 °C, warm to room temperature). Preparative VPC (Carbowax,^{20b} 110 °C, retention time = 6.17 min when C₁₃H₂₈ = 4.60 min) yielded a pure sample of compound 6; IR (film) 3.4, 6.41, 8.05, 11.9 μ m; NMR (CCl₄) δ 6.59, (1 H, t, *J* = 7 Hz), 2.5–2.0 (2 H), 1.6–1.1 and 1.1–0.7 (11.9 H), 0.15 and 0.07 (18 H, both singlets); MS *m/e* (relative intensity) 256 (0.5, M⁺), 241 (13), 186 (8), 167 (40), 98 (33), 73 (100), 59 (19).

2-(Trimethylsilyl)-1-octene (3). A stirred solution of 3.07 g (12.0 mmol) of (E)-1,2-bis(trimethylsilyl)-1-octene (2) in 31 mL of glacial acetic acid and 1.6 mL of water was heated at 110 °C for 29 h. The mixture was cooled (ice bath), 60 mL of 9 M NaOH was added, and the resulting mixture was extracted with 50 mL of ether. The ether extract was washed with saturated NaHCO₃ and saturated NaCl, dried (MgSO₄), concentrated, and distilled (bulb to bulb, oil pump vacuum, 106 °C), giving 2.13 g (96%) of 3²¹ as a colorless liquid: IR (film) 3.4, 8.02, 10.84, 11.9, 13.2, 14.5 μ m; NMR (CCl₄) δ 5.55 (m, 1.0 H), 5.32 (m, 1.0 H), 2.4–1.9 (2.3 H), 1.7–1.1 (8.3 H), 1.1–0.7 (3.0 H), 0.08 (s, 9.0 H); MS²² *m/e* (relative intensity) 184 (0.8, M⁺), 169 (10.5), 99 (17), 73 (100), 59 (24).

VPC analysis (Carbowax,^{20b} 158 °C, undecane = 1.53 min) showed peaks at 1.57 (3, 95.7%), 2.08 (0.4%), 2.28 (0.4%), and 3.64 min (2, 3.5% of peak area).

The product from a similar reaction was purified by preparative VPC followed by bulb to bulb distillation. Anal. Calcd for C₁₁H₂₄Si: C, 71.65; H, 13.12. Found: C, 71.59; H, 13.00.

In a similar experiment, compound 2 (688 mg) was treated with acetic-*d*²³ acid to yield 393 mg (79%) of (E)-1-deuterio-2-(trimethylsilyl)-1-octene (4). The IR spectrum was similar to that of 3 except for a band at 2220 cm⁻¹; the NMR spectrum corresponded exactly to that of 3, except that the peak at δ 5.55 was much smaller (integration 0.3 H).

2-(Trimethylsilyl)-1-octene Oxide 5. To a stirred suspension of 604 mg (3.0 mmol) of *m*-chloroperbenzoic acid (85%) and 568 mg (4.0 mmol) of Na₂HPO₄ in 4.0 mL of CH₂Cl₂ was added 476 mg (2.6 mmol) of 2-(trimethylsilyl)-1-octene (3) in 4.0 mL of CH₂Cl₂. The mixture was stirred at room temperature for 24 h, 15 mL of saturated NaHSO₃ was added, and the mixture was stirred for 2 h. Then 10 mL of 10% NaOH was added, and the mixture was stirred for 0.5 h. The mixture was extracted with ether; the ether phase was washed with saturated NaHSO₃, 10% NaOH, and saturated NaHCO₃, dried (MgSO₄), concentrated, and distilled (bulb to bulb, oil pump vacuum, 110 °C), giving 471 mg (90%) of 7 as a colorless liquid: IR (film) 3.4, 8.00, 11.9, 13.3 μ m; NMR (CCl₄) δ 2.44 (s, 2.0 H), 1.64–1.07 (9.7 H), 1.07–0.64 (3.2 H), 0.02 (s, 9.0 H); MS *m/e* (relative intensity) 200 (2.3, M⁺), 185 (7.6), 143 (26), 130 (13), 129 (32), 115 (39), 75 (64), 73 (100), 59 (12).

VPC analysis (SE-30,^{20a} 96 °C, docosane = 1.57 min) showed the major peak at 2.32 min (96% of peak area). Further VPC analysis (DC-550,^{20c} 115 °C, tridecane = 11.3 min) showed peaks at 10.82 (trans epoxide 8, 0.06%), 11.50 (epoxide 5, 99.86%), and 13.73 min (cis epoxide 7, 0.08%).

The product from a similar reaction²⁴ was purified by preparative VPC followed by bulb to bulb distillation. Anal. Calcd for C₁₁H₂₄O_{Si}: C, 65.93; H, 12.07. Found: C, 65.87; H, 12.26.

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Registry No.—1, 15719-55-8; 2, 68185-84-2; 3, 63883-63-6; 4, 68185-85-3; 5, 62427-10-5; 6, 68185-86-4; 7, 62427-11-6; 8, 62427-09-2; methylchlorosilane, 75-54-7; acetic-*d* acid, 758-12-3; methylmagnesium bromide, 75-16-1.

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- (21) Compound **3** ($\text{R} = \textit{n}\text{-C}_3\text{H}_7$) has been recently prepared by Chamberlin, Stemke, and Bond.^{7c}
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New Method for the Preparation of Bismuth(III) Triesters

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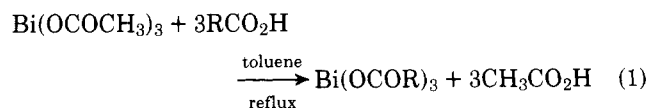
Bismuth(III) salts of organic acids have been shown to be useful in the catalysis of aromatic substitution,¹ in the catalysis of high temperature esterification of alcohols with organic acids or their derivatives,² and as mild oxidants for the conversion of acyloins to diketones.³ We have recently shown they can be used in the acylation of amines, alcohols, amides, and esters.⁴

In our continuing study of the reactions of these compounds, we found it necessary to synthesize a wide variety of them. Previously reported methods for the synthesis of bismuth(III) triesters⁵ were not widely applicable. We have therefore developed a new procedure which is useful for the preparation of bismuth(III) triesters that cannot be produced in high temperature reactions or which decompose easily in the presence of water.

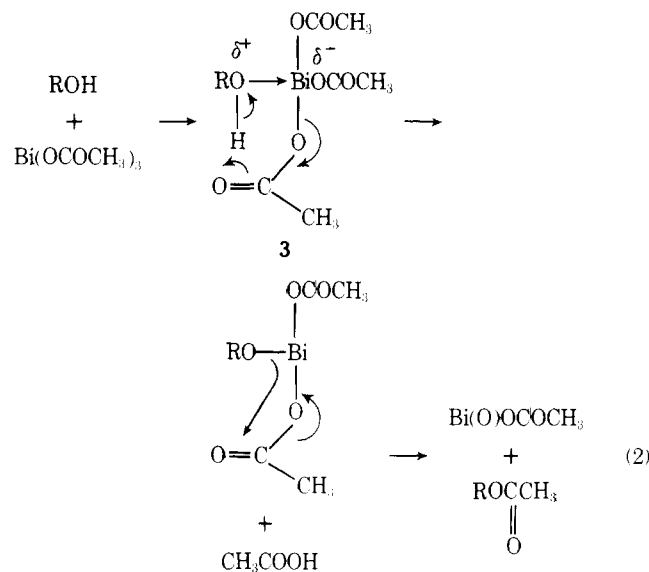
Three general procedures have been claimed to be useful for the preparation of bismuth(III) triesters. Early workers prepared bismuth(III) compounds by a "decomposition reaction" of bismuth(III) nitrate with an organic acid^{6–11} or with the salt of an organic acid.^{12–18} Reactions of triarylbismuth compounds with some organic acids to yield such compounds have been reported.^{19,20} The third procedure involves the

reaction of bismuth(III) oxide (**2**) with an organic acid, usually at temperatures of 150 °C or greater.²¹ None of these procedures are widely satisfactory for such syntheses. Analyses reported for the products indicate the presence of mixtures of various bismuth compounds. Thus, substantial confusion in the literature has resulted from a dearth of satisfactory widely applicable procedures for the preparation of bismuth(III) triesters and a lack of reliable information on methods for their characterization.

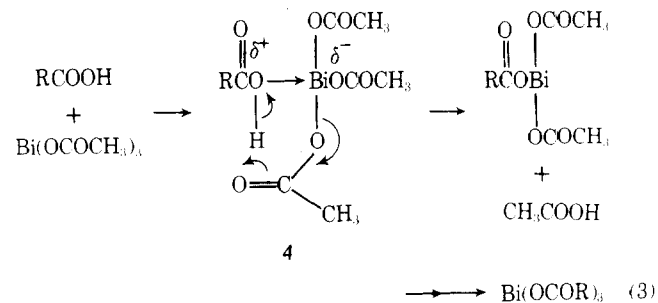
In an attempt to prepare such bismuth(III) triesters, it was discovered that reaction of bismuth(III) triacetate (**1**) with an organic acid yielded a mixture of acetic acid, the initial organic acid, and a new bismuth(III) triester. When the reaction was conducted in toluene, and acetic acid was removed by azeotropic distillation, **1** was smoothly converted into various bismuth(III) triesters in high yields (see eq 1). Table I summarizes the results obtained with a variety of carboxylic acids.



This transesterification reaction which compound **1** undergoes with organic acids appears to be very similar to the reaction of **1** with alcohols and amines.⁴ For example, the reaction of **1** with an alcohol is thought to proceed through **3**, which decomposes to form bismuthyl acetate and an ester (eq 2).



The ability of **1** to function as a Lewis acid is also essential in the proposed mechanism for the new reaction, shown in eq 3, which involves a similar attack on the electron-deficient



bismuth atom. The proposed intermediate **4** is similar to the BiCl_3 -dimethylformamide complex reported by Kuhn and