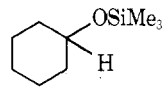
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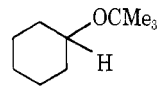
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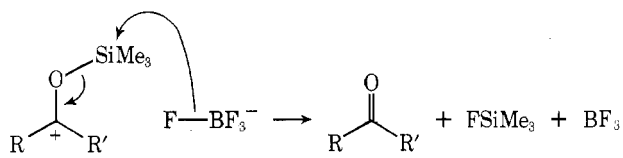
tert-butyl group is somewhat bulkier than the trimethylsilyl group.

The crude trimethylsilyl ether **2**, produced from the alcohol **1** by silylation in a few minutes at room temperature, is generally >95% pure and can be used directly in the oxidation step without further purification.

In all of the reported reactions trityl tetrafluoroborate (**3**) was employed as the hydride abstractor.[5] It is commercially available,[6] although it can be easily prepared in two steps from benzene and carbon tetrachloride by the method of Dauben.[7] The progress of the oxidation can be easily monitored by GC or NMR. Reaction times range from 1 min for the cinnamyl ether to 4 days for the 2-octyl ether. Thus far the reaction is not very useful for saturated aldehydes. The rate of oxidation is very slow and the aldehyde begins to decompose before the reaction is completed. All of these oxidations can be speeded up by using refluxing dichloroethane as solvent, but this causes some decomposition of the carbonyl products.[8]

Analysis of the crude reaction mixtures by NMR indicates the presence of the carbonyl compound before addition of water. This implies that the cation **4** probably decomposes by attack of a fluoride ion from BF_4^- to give the carbonyl compound and Me_3SiF directly. To support this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hypothesis, when the reaction mixture is heated, one can detect the evolution of an acidic gas, probably BF_3 or Me_3SiF. It is postulated that hydride abstraction is a discrete step that precedes fluoride transfer to silicon. The alternative of a concerted pathway involving concomitant hydride abstraction and fluoride transfer is unlikely for entropy reasons, since it would require the correct alignment of three distinct species in the transition state, namely, the trityl cation, the silyl ether, and the tetrafluoroborate anion.

Since the ethers of primary alcohols oxidize slower than those of secondary alcohols (stability of a secondary vs. a tertiary carbonium ion), we are now pursuing the use of this procedure in oxidizing a primary, secondary diol to the primary hydroxy ketone. In addition, the oxidations of silylated amines to carbonyl compounds[9] and of silyl enol ethers to enones,[10] as well as other oxidations, are currently being investigated.

Experimental Section

The following is a typical experimental procedure.

Cyclohexanone. Cyclohexanol was converted into its trimethylsilyl ether **9** by stirring for a few hours at room temperature with a silylating solution consisting of pyridine, hexamethyldisilazane, and trimethylchlorosilane in the ratio of 10:2:1. A solution of the crude ether **9** (1.72 g, 10 mmol) and Ph_3CBF_4 (**3**, 4.95 g, 15 mmol) in 200 ml of CH_2Cl_2 was allowed to stir at room temperature under nitrogen. After 9 h, GC analysis of an aliquot showed completion of reaction. Addition of water, extraction, and distillation afforded 901 mg of cyclohexanone (92% yield).

Acknowledgment. The author wishes to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No.—**2** (R = CH_3; R′ = C_6H_{13}), 18023-52-4; **2** (R = C_2H_5; R′ = C_4H_9), 18132-91-7; **2** (R = H; R′ = C_6H_5), 14642-79-6; **2** (R = H; R′ = PhCH=CH), 18042-41-8; **2** (R = H; R′ = C_6H_{13}), 18132-93-9; **3**, 341-02-6; **9**, 13871-89-1; Me_3SiCl, 75-77-4; $(Me_3Si)_2NH$, 999-97-3.

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(5) Trityl salts with different counterions, e.g., PF_6^-, SbF_6^-, were also employed, as well as other hydride abstracting reagents. A comparison of the reactivities will be described elsewhere.
(6) Commercial samples from both the Aldrich Chemical Co. and Cationics, Inc. were used successfully.
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(8) Solid Na_2CO_3 was added in an attempt to trap any acidic products which might be causing decomposition (e.g., BF_3), but without significant effects. Acetonitrile was also employed but the oxidation was very slow in this solvent.
(9) M. E. Jung and G. S. Tennyson, unpublished results.
(10) M. E. Jung and Y.-G. Pan, unpublished results.

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trans-β-Trimethylsilylvinyllithium

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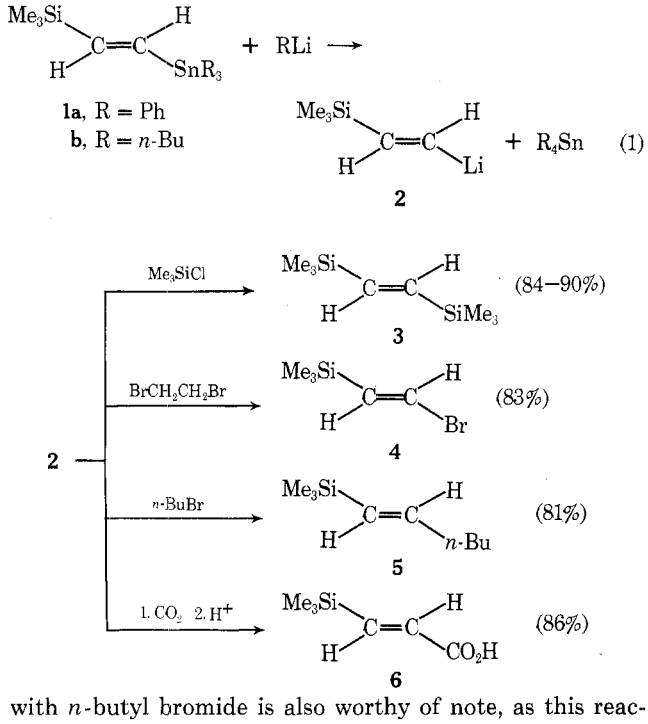
In connection with other investigations we required a synthetically useful preparation of *trans*-β-trimethylsilylvinyllithium (**2**). This reagent was unavailable at the time this work was begun, but has since been prepared by the reaction of *trans*-β-bromovinyltrimethylsilane with either lithium metal[1] or *tert*-butyllithium.[2] Synthetically useful yields of the reagent are realized by only the latter of these two methods. Our approach, different from either of these, but also affording excellent yields of **2**, is presented here.

The preparation of **2** involved the transmetalation reaction between organolithium reagents and vinyltin substrates developed by Seyferth and co-workers.[3] Thus, treatment of either *trans*-1-trimethylsilyl-2-triphenylstannylethylene (**1a**) or *trans*-1-trimethylsilyl-2-tri-*n*-butylstannylethylene (**1b**) with respectively phenyllithium or *n*-butyllithium led to high yields of **2**, as determined by subsequent derivatization (eq 1).

Although the transmetalation of **1a** with phenyllithium could be effected at 25 °C to afford, after trimethylchlorosilane derivatization, 84% of *trans*-1,2-bis(trimethylsilyl)ethylene (**3**), the reaction of **1b** with *n*-butyllithium gave better results at low temperature. Thus, **3** was obtained in only 53% yield from the transmetalation of **1b** at 25 °C, but 90% of **3** was afforded when transmetalation was effected at −70 °C.[4] The reaction of **2** with a variety of other electrophiles was examined in order to assess its utility in this regard. As shown in eq 1, *trans*-1-bromo-2-trimethylsilylethylene (**4**), *trans*-1-trimethylsilyl-1-hexene (**5**), and *trans*-3-trimethylsilylpropenoic acid (**6**) were all obtained in excellent yield. NMR and VPC analysis of these products indicated the absence of detectable amounts of corresponding cis isomers.

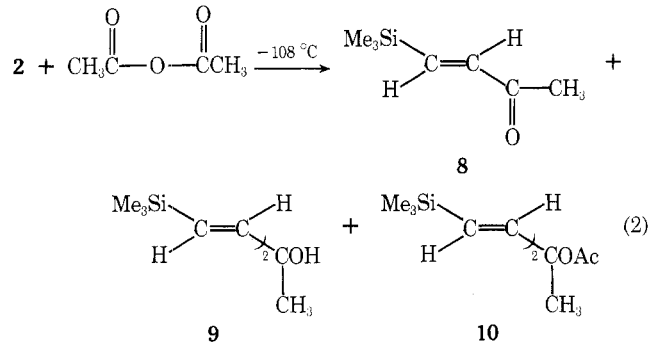
Of particular interest was the observation that the present procedure led to preparatively useful conversions

of **2** into **6**, as the approach to **6** via carbonation of *trans*-β-trimethylsilylvinylmagnesium bromide (**7**) affords only a moderate yield (46%) of acid.[5] The efficient coupling of **2**



with *n*-butyl bromide is also worthy of note, as this reaction is representative of a new mode of entry to the 1-trimethylsilyl-1-alkene series, compounds which have potential for considerable synthetic utility.[6,7]

In an attempt to improve the yield (66%) of *trans*-4-trimethylsilyl-3-buten-2-one (**8**) reported from the low-temperature reaction of **7** with acetic anhydride,[8] the parallel reaction of **2** was examined (eq 2). However, these conditions led to the formation of **8** in only 30% yield accompanied by significant amounts of *trans,trans*-1,5-bis(trimethylsilyl)-3-methyl-1,4-pentadien-3-ol (**9**) and *trans,trans*-1,5-bis(trimethysilyl)-3-methyl-3-acetoxy-1,4-pentadiene (**10**).



Experimental Section

The normalities of solutions of *n*-butyllithium in hexane and phenyllithium in ether were determined by the double titration method using 1,2-dibromoethane.[9] Ether and tetrahydrofuran used as solvents were distilled from $LiAlH_4$. All experiments were carried out under a nitrogen atmosphere. NMR spectra (solvent, internal standard) were obtained with either Varian A-60A or JEOL PFT-100 spectrometers (chemical shift values are assigned from the center of a multiplet); infrared spectra (neat) were obtained with a Beckman IR-8 spectrophotometer. Elemental analyses were performed by Mr. J. Darby, Faraday Microanalytical Laboratory, Northern Illinois University, or Spang Laboratories, Ann Arbor, Mich.

Transmetalation of *trans*-1-Trimethylsilyl-2-triphenylstannylethylene (1a). A solution of 4.16 g (9.26 mmol) of **1a**[10] and 0.368 g of *o*-xylene (internal standard) in 20 ml of ether was treated with 11.7 ml (9.36 mmol) of 0.80 N phenyllithium in ether. A precipitate of tetraphenyltin appeared immediately. After 40 min at 25 °C, a 1-ml aliquot was withdrawn by syringe and injected into 4 ml of 1,2-dibromoethane. Chlorotrimethylsilane (3.0 ml, 23 mmol) was added to the remaining mixture and work-up carried out after overnight stirring. VPC analysis of the aliquot portion showed it to contain 1.37 g (83%) of **4** and 0.14 g (94%) bromobenzene. No *cis*-1-bromo-2-trimethylsilylethylene was present as determined by retention time check with an authentic sample.[11] Following $NaHCO_3$ hydrolysis, the solid was removed from the Me_3Si-Cl-derivatized mixture by filtration and sublimed to give 3.72 g (94%) of tetraphenyltin, mp 223–225 °C (lit.[12] mp 224–225 °C). Examination of the filtrate by VPC indicated the presence of 1.34 g (84%) **3** and 0.17 g (13%) of phenyltrimethylsilane. No *cis*-1,2-bis(trimethylsilyl)ethylene was detectable upon retention time check with an authentic sample.[13]

***trans*-1-Trimethylsilyl-2-tri-*n*-butylstannylethylene (1b).** A mixture of 58.3 g (0.20 mol) of tri-*n*-butyltin hydride and 24.5 g (0.25 mol) of ethynyltrimethylsilane[10] was heated to 100 °C for 83 h, affording 76.5 g (98%) of **1b:** bp 96–102 °C (0.5 mm); ir 6.50 μ (C=C); NMR ($CDCl_3$, CH_2Cl_2) δ 0.12 (9 H, s), 0.95 (9 H, t, J = 7 Hz), 1.41 (18 H, m), 6.65 and 7.08 (2 H, AB pattern, J = 23 Hz).

Anal. Calcd for $C_{17}H_{38}SiSn$: C, 52.45; H, 9.84. Found: C, 52.24; H, 9.57.

Transmetalation of *trans*-1-Trimethylsilyl-2-tri-*n*-butylstannylethylene (1b). The general procedure involved the addition of 1.50 N *n*-butyllithium to a precooled (−70 to −75 °C) solution of **1b** in THF or 1:1 THF–ether. After 1 h at this temperature, the mixture was allowed to warm to −30 °C over 30–40 min and then recooled to −75 °C prior to derivatization.

A. Chlorotrimethylsilane Derivatization. A solution of **2** prepared from 5.99 g (0.0154 mol) of **1b** and 0.0154 mol of *n*-butyllithium in 50 ml of THF–ether was treated with 1.89 g (0.017 mol) of chlorotrimethylsilane to afford 2.39 g (90%) of **3** and 0.037 g (2%) of *n*-butyltrimethylsilane, as determined by VPC (nonane internal standard).

B. Ethylene Bromide Derivatization. A 7-ml aliquot was removed from the solution of **2** generated in part A at −75 °C and added to 4.5 g (0.024 mol) of ethylene bromide in 10 ml of ether at −75 °C. VPC analysis indicated an 83% yield of **4** and 1% of *n*-butyl bromide.

C. Carbon Dioxide Derivatization. To a cooled (−110 °C) solution of **2** prepared from 14.4 g (0.0370 mol) of **1b** in 100 ml of THF and 1.1 equiv of *n*-butyllithium was added ca. 150 ml of pulverized dry ice which had been precooled to −100 °C. The reaction mixture was mechanically stirred at −110 °C for 0.5 h and then allowed to warm to 25 °C overnight. After extraction with aqueous NaOH, the organic phase afforded 12.4 g (97%) of tetrabutyltin, bp 84–87 °C (0.2 mm) [lit.[14] bp 94–96 °C (0.28 mm)] containing less than 1% unreacted **1b**, as determined by VPC. After acidification, the NaOH extracts yielded 4.90 g of material, bp 68–74 °C (0.5 mm), which NMR indicated contained 7% of *n*-pentanoic acid [86% yield of **6**; ir 3.4 s, 5.88 s, 6.17 w, 6.25 w, 7.08 s, 7.69 s, 7.97 s, 8.35 m, 10.00 m, 10.63 m, 10.87 m, 11.63 s, 11.90 s, 12.82 w, 13.16 w, 13.70 w, 14.37 μ; NMR (CCl_4, CH_2Cl_2) δ 0.28 (9 H, s), 6.33 and 7.49 (2 H, AB pattern, J = 18.5 Hz), 12.51 (1 H, s)].

No *cis*-3-trimethylsilylpropenoic acid could be detected by NMR analysis of a concentrated sample.

D. *n*-Butyl Bromide Derivatization. Addition of *n*-butyl bromide to a solution of **2** in THF gave an 86% yield of **5**, determined by using *n*-decane as internal VPC standard. In a larger scale reaction, 6.6 g (0.048 mol) of *n*-butyl bromide precooled to −50 °C was added to a solution of **2** prepared from 13.2 g (0.034 mol) of **1b** in 90 ml of THF and 1.1 equiv of *n*-butyllithium. This afforded 4.20 g (81%) of **5**, bp 94–97 °C (110 mm).

E. Acetic Anhydride Derivatization. A precooled (−90 °C) solution of 3.24 g (0.032 mol) of acetic anhydride in 10 ml of ether was added at −108 °C to a solution of **2** prepared from 6.13 g (0.0158 mol) of **1b** in 60 ml of THF and 1.1 equiv of *n*-butyllithium. After standing at 25 °C overnight, work-up afforded 0.66 g (30%) of **8**, 0.42 g (23%) of *trans,trans*-1-5-bis(trimethylsilyl)-3-methyl-1,4-pentadien-3-ol (**9**), and 0.29 g (14%) of *trans,trans*-1,5-bis(trimethylsilyl)-3-acetoxy-3-methyl-1,4-pentadiene (**10**), as determined by a combination of distillation and VPC analysis. Alcohol **9**, mp 47–49 °C, showed (melt) principal ir bands at 2.92 m, 3.36 s, 6.24 m, 8.04 s, 10.12 s, 11.85 vs, 13.52 m, 13.76 m, and 14.52 m μ; NMR ($CDCl_3$, CH_2Cl_2) δ 0.13 (18 H, s), 1.39 (3 H, s), 1.68 (1 H, broad s), 5.86 and 6.16 (4 H, AB pattern, J = 19 Hz).

Anal. Calcd for $C_{12}H_{26}OSi_2$: C, 59.43; H, 10.81. Found: C, 59.69; H, 10.94.

Ester **10** showed principal ir bands at 3.36 s, 5.78 s, 6.23 w, 7.32 m, 8.06 s, 8.50 m, 9.44 m, 10.15 m, 11.56 s, 11.98 s, 13.56 m, 13.75 m, and 14.50 μ m; NMR ($CDCl_3$) δ 0.06 (18 H, s) 1.56 (3 H, s), 2.02 (3 H, s), 5.73 and 6.12 (4 H, AB pattern, J = 19 Hz).

Anal. Calcd for $C_{14}H_{28}O_2Si_2$: C, 59.10; H, 9.92. Found: C, 58.86; H, 9.81.

Registry No.—**1a,** 17146-54-2; **1b,** 58207-97-9; **2,** 55339-31-6; **3,** 18178-60-4; **4,** 41309-43-7; **5,** 54731-58-7; **6,** 58207-98-0; **8,** 49750-09-6; **9,** 58207-99-1; **10,** 58208-00-7; phenyllithium, 591-51-5; chlorotrimethylsilane, 75-77-4; bromobenzene, 108-86-1; tetraphenyltin, 595-90-4; phenyltrimethylsilane, 768-32-1; tri-*n*-butyltin hydride, 688-73-3; ethynyltrimethylsilane, 1066-54-2; *n*-butyllithium, 109-72-8; *n*-butyltrimethylsilane, 1000-49-3; ethylene bromide, 106-93-4; *n*-butyl bromide, 109-65-9; carbon dioxide, 124-38-9; tetrabutyltin, 1461-25-2; *n*-pentanoic acid, 109-52-4; acetic anhydride, 108-24-7.

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A Novel Synthesis of Pyrrolo[1,2-*c*]pyrimidine-3-carboxylic Acid Esters[1]

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Pyrrolo[1,2-*c*]pyrimidine compounds are pharmaceutically interesting compounds[2] and several synthetic methods of the compounds have been reported.[3]

In the course of our studies on the reaction of isocyano compounds with various electrophiles,[4] we wish now to report the reaction of methyl isocyanoacetate (**1**) with pyrrole-2-carboxaldehydes (**2**) to afford pyrrolo[1,2-*c*]pyrimidine-3-carboxylic acid esters (**4**) as shown in Scheme I.

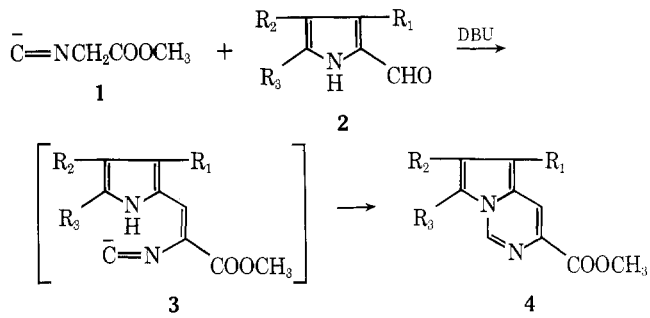
Condensation of the aldehydes (**2**) with isocyano compound **1** was carried out in THF solution, using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base (Table I). The structure of the resulting products (**4**) was confirmed by spectral and analytical data. The formation of compounds **4** probably proceeds via intramolecular cycloaddition of the intermediates **3**.

Table I. Preparation of Methyl Pyrrolo[1,2-*c*]pyrimidine-3-carboxylates (4)

Registry no.	R_1	R_2	R_3	Mp, °C[a,b]	Yield, %
58298-71-8	H	H	H	78–80	69
58298-72-9	COO-C_2H_5	CH_3	COO-C_2H_5	144–145	59
58298-73-0	CH_3	COO-CH_3	CH_3	215–219	55
58298-74-1	3,4-Methylenedioxy Ph	H	H	199–200	57
58298-75-2	3-Methoxy Ph	H	H	162–164	50

[a] Recrystallization from ethyl acetate or methanol. [b] Satisfactory analytical values (±0.3% for C, H, N) for all compounds were submitted. Ed.

Scheme I



Experimental Section

Typical Procedure. To a solution of DBU (19.8 g, 0.13 mol) in THF (200 ml) was added dropwise a mixture of pyrrole-2-carboxaldehyde (12.4 g, 0.13 mol) and methyl isocyanoacetate (12.9 g, 0.13 mol) dissolved in THF (90 ml) at 40–45 °C for a period of 30 min with stirring. After stirring for 2 h at the same temperature, 10% acetic acid (70 ml) was added to the mixture and then the solvent was removed under reduced pressure. The resulting residue was extracted with ethyl acetate and the extract was further extracted with 5% hydrochloric acid (300 ml). The acidic solution was neutralized with sodium bicarbonate and the resulting products were sufficiently extracted with ethyl acetate. The extract was washed with saturated sodium chloride solution, dried, and then evaporated in vacuo. Methyl pyrrolo[1,2-*c*]pyrimidine-3-carboxylate (15.7 g), recrystallized from ethyl acetate, showed mp 78–80 °C; ir (Nujol) 3100 (CH), 1710 cm^{-1} ($COOCH_3$); NMR (Me_2SO-d_6) δ 9.20 (s, 1, C-1 H), 8.25 (s, 1, C-4 H), 7.90 (d, 1, C-7 H), 7.05 (double d, 1, C-6 H), 6.87 (d, 1, C-5 H), 3.87 (s, 3, OCH_3).

Registry No.—**1,** 39687-95-1; **2** (R_1 = R_2 = R_3 = H), 1003-29-8; **2** (R_1 = R_3 = $COOC_2H_5$; R_2 = CH_3), 2199-60-2; **2** (R_1 = R_3 = Me; R_2 = $COOCH_3$), 58298-68-3; **2** (R_1 = 3,4-methylenedioxy Ph; R_2 = R_3 = H), 58298-69-4; **2** (R_1 = 3-methoxy Ph; R_2 = R_3 = H), 58298-70-7.

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