– HCN), 165 (33, fluorenyl cation), 163 (21), 149 (18); UV (95% EtOH) λ_{max} 207 nm (log ϵ 4.45), 239 (4.58), 255 (4.40), 376 (4.36). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.84; H, 5.43; N, 10.73.

Registry No. 2, 10183-82-1; 3, 5455-00-5; (*E*)-7, 83026-87-3; MeCN, 75-05-8; fluorenone, 486-25-9.

Silicon-Substituted Cyclopropylcarbinyl Cations

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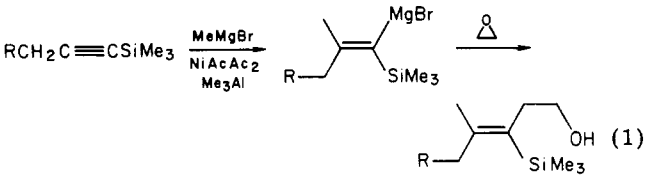
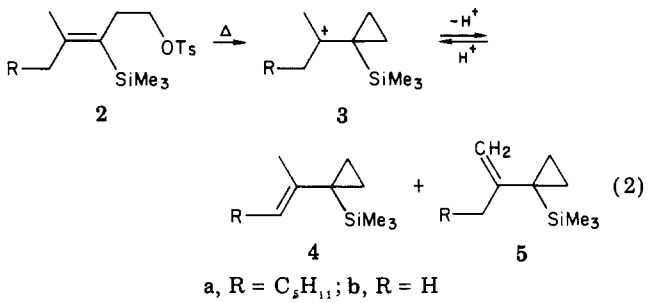
The electrophilic substitution of allyl- and vinylsilanes has proven to be a useful synthetic method.[2] We set out to explore the use of vinylsilanes as terminating groups for cation–olefin cyclizations.[3] The nickel-catalyzed addition of MeMgBr to alkynylsilanes which we have recently reported[4] leads directly to the fully substituted vinylsilane **1** (eq 1) with control of double bond stereochemistry.



(1)

1

Unfortunately, treatment of the sodium salt of Hagemann's ester with the tosylate **2a** gave none of the desired alkylation product, even though the procedure used[5] led to a high yield of product when similar homoallylic bromides, which lacked the trimethylsilyl group, were used as alkylating agents.[6,7] Analysis of the reaction mixture indicated that **2a** had reacted to give a mixture of **4a** and **5a** (eq 2).



(2)

2 **3** **4** **5**

a, R = C_5H_{11}; b, R = H

Solvolysis of the tosylate **2a** in refluxing *tert*-butyl alcohol for 12 h gives the cyclopropylsilane **4a** in ca. 70% yield.[8] If this solvolysis is carried out in the presence of an excess of sodium *tert*-butoxide, a 1.6:1 mixture of **4a** and **5a** is obtained in 57% yield.[8] Solvolysis of **2a** gives the cyclopropylcarbinyl cation[9] **3a** which loses a proton to give allylsilanes **4a** and **5a**. In the absence of a proton scavenger, equilibration of **4a** and **5a**, via **3a**, occurs to give a ca. 16:1 mixture of **4a** and **5a**. As expected, isomerization of a 1.6:1 mixture of **4a** and **5a** in refluxing benzene containing a trace of *p*-toluenesulfonic acid gives the same 16:1 mixture.[8]

The tosylate **2b** behaves similarly, giving the cyclopropylsilane **4b** on solvolysis in refluxing *tert*-butyl alcohol containing potassium carbonate as a proton scavenger.[8]

Two points of general interest emerge from these reactions. The allylic silanes **4** and **5**, unlike other allylic silanes,[2] do not undergo desilylation with double bond migration on treatment with acid. Although the double bond is readily protonated to give the cyclopropyl cation **3a**, as evinced by the conversion of **5a** to **4** in acid, desilylation would require rehydribidization of the cyclopropyl carbon with introduction of additional strain into the molecule. Cation **3** can react with nucleophiles to give homoallylic species analogous to **2** in which the vinylsilane can readily desilylate. Analogous results have been obtained by Paquette, Horn, and Wells.[10]

The presence of silicon on the double bond appears to accelerate the solvolysis of the tosylate **2a**, since the analogous compound 1-bromo-4-methyl-3-pentene alkylates Hagemann's ester under conditions which lead only to solvolysis of **2a**. More detailed studies will be required to establish this since these differences could also result from steric interactions.

Experimental Section

All GC analyses were performed on a 0.25 in. × 9 ft Carbowax 20M on Chromoasorb PNAW column. Benzene and THF were distilled from sodium/benzophenone ketyl. *tert*-Butyl alcohol was distilled from calcium hydride.

Preparation of 1a. Nickel acetylacetonate (128.5 mg, 0.5 mmol) was introduced into a flame-dried Schlenk flask. The flask was flame dried again and purged with nitrogen. THF (5 mL) was added, and the solution was stirred until all the solid had dissolved. Then, as rapidly as possible, the following were added: Me_3Al (0.91 M in hexane, 0.36 mL, 0.33 mmol; the solution turns brown in 15 s); 1-(trimethylsilyl)-1-octyne (0.91 g, 5.0 mmol); MeMgBr (2.03 M in THF/benzene, 9.85 mL, 20.0 mmol). The reaction mixture was stirred for 24 h at 25 °C, diluted with 15 mL of THF, and cooled to −78 °C. Ethylene oxide was bubbled through the solution for 5 min, and the mixture was allowed to warm to 25 °C. Quenching with water and sodium dihydrogen phosphate solution gave a thick precipitate. The entire mixture was filtered with suction. The residue was washed with 100 mL of pentane. The layers were separated, and the aqueous layer was washed with three portions of pentane. The combined organic layers were washed with water, dried (Na_2SO_4), and evaporated to give 1.16 g of crude product. Chromatography of 1.05 g of crude product on silica gel (3:1 pentane–ether) gave 0.58 g (53%) of **1a**

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(8) Several minor products, most of which no longer contained silicon, were present in these reactions. Reactions in acidic media gave a greater percentage of desilylated products, none of which, however, appears to arise from an alkylidenecyclopropane. Specifically, homoallylic tosylates resulting from disilylation of **2** were formed along with products derived from them such as the corresponding *tert*-butyl ether and cyclopropylcarbinyl *tert*-butyl ether.

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and 0.07 g (7%) of the *E* isomer of **1a**.

The spectral data for **1a** follow: NMR ($CDCl_3$) δ 3.49 (t, 2, *J* = 7.2 Hz), 2.40 (t, 2, *J* = 7.2 Hz), 1.96–2.26 (m, 2), 1.76 (s, 3), 1.53–1.12 (m, 9), 1.04–0.70 (m, 3), 0.12 (s, 9); IR (neat) 3320, 2958, 2928, 2875, 2860, 1608, 1250, 1040 cm^{-1}; MS, *m/e* (relative intensity) 243 (1), 242 (3, M^+), 229 (2), 228 (8), 227 (17), 209 (5), 172 (7), 157 (5), 151 (3), 143 (2), 141 (2), 139 (2), 137 (2), 125 (4), 124 (4), 116 (4), 103 (6), 95 (4), 82 (49), 75 (77), 73 (100); mol wt calcd for $C_{14}H_{30}OSi$ 242.2064, found 242.2065. Anal. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47. Found: C, 69.50; H, 12.47.

The spectral data for the *E* isomer of **1a** follow: NMR ($CDCl_3$) δ 3.49 (t, 2, *J* = 7.2 Hz) 2.42 (t, 2, *J* = 7 Hz), 1.97–2.28 (m, 2), 1.82 (s, 3), 1.13–1.64 (m, 9), 0.75–1.04 (m, 3), 0.13 (s, 9); IR (neat) 3310, 2960, 2932, 2872, 2860, 1608, 1251, 1042; MS, *m/e* (relative intensity) 227 (20, M^+ – Me) 209 (3, M^+ – (Me + H_2O), 172 (4), 156 (5), 103 (12), 95 (11), 75 (75), 73 (100).

Preparation of 1b. A similar procedure on 10 times the scale with 1-(trimethylsilyl)-1-propyne (5.2 g, 46 mmol) gave, after chromatography on silica gel (4:1 pentane–ether), 4.04 g (52%) of **1b**: NMR (CCl_4) δ 3.32 (t, 2, *J* = 7.8 Hz), 2.8 (br s, 1, OH), 2.29 (t, 2, *J* = 7.8 Hz), 1.77 (s, 3), 1.70 (s, 3), 0.06 (s, 9); IR (neat) 3330 (br), 3000, 2950, 2900, 2875, 1610, 1450, 1380, 1370, 1260, 1250, 1040, 1015, 1000, 865, 830, 755, 680 cm^{-1}. Anal. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.69; Si, 16.29. Found: C, 62.61; H, 11.89; Si, 16.07.

Preparation of 2a. *p*-Toluenesulfonyl chloride (0.4029 g, 2.1 mmol) was added to a soolution of **1a** (0.254 g, 1.05 mmol) in anhydrous pyridine. The solution was stirred 6 h at 25 °C and worked up to give 2.81 g (68%) of 95% pure **2a**: NMR (CCl_4) δ 7.74 (d, 2, *J* = 8 Hz), 7.33 (d, 2, *J* = 8 Hz), 3.81 (t, 2, *J* = 8 Hz), 2.47 (s, 3), 2.45 (t, 2, *J* = 8 Hz), 2.1 (br m, 2), 1.68 (s, 3), 1.3 (m, 8), 0.90 (br t, 3, *J* = 6 Hz), 0.07 (s, 9); IR (neat) 2960, 2935, 2860, 1600, 1460, 1375, 1250, 1188, 1176, 1097, 953, 833, 812, 755, 660 cm^{-1}.

Tosylate **2b** was prepared in a similar manner: NMR (CCl_4) δ 7.73 (d, 2, *J* = 8.0 Hz), 7.31 (d, 2, *J* = 8.0 Hz), 3.78 (t, 2, *J* = 8.0 Hz), 2.45 (s, 3), 2.43 (t, 2, *J* = 8.0 Hz), 1.80 (s, 3), 1.60 (s, 3), 0.07 (s, 9); IR (neat) 3070, 2957, 2930, 2895, 1607, 1600, 1450, 1375, 1360, 1250, 1187, 1175, 1095, 950, 855, 770 cm^{-1}.

Solvolysis of 2a. A solution of tosylate **2a** (220 mg, 0.55 mmol) in anhydrous *tert*-butyl alcohol (10 mL) was added to 22 mg of oil-free sodium hydride. The resulting solution was heated at reflux for 3 h and cooled to 25 °C. Water (20 mL) and hexane (30 mL) were added. The organic layer was washed four times with water and once with brine, dried ($MgSO_4$), and evaporated in vacuo to give 139 mg of product. Chromatography on silica gel (hexane) gave 69 mg (57%) of a 1.6:1 mixture of **4a** and **5a**. The NMR spectral data for **5a** were determined from this mixture: NMR (CCl_4) δ 4.75 (br s, 2), 2.0 (br m, 2), 1.3 (m, 8), 0.90 (t, 3, *J* = 6 Hz), 0.51 (s, 4), –0.08 (s, 9); ^{13}C NMR ($CDCl_3$) δ 154.0, 109.7, 36.3, 31.9, 29.4, 28.0, 22.7, 14.1, 10.5, 9.4, –2.6; GC/MS, *m/e* (relative intensity) 224 (0.3, M^+), 2.09 (0.1), 196 (0.1), 181 (0.2), 167 (0.1), 154 (1), 150 (1), 139 (1), 107 (2), 97 (1), 95 (1), 93 (1), 73 (100); GC t_R = 19.5 min (135 °C).

Isomerization of 5a to 4a. *p*-Toluenesulfonic acid (2 mg) was added to a solution of a 1.6:1 mixture of **4a** and **5a** (115 mg) in 5 mL of benzene. The resulting solution was refluxed for 24 h under nitrogen. Hexane and aqueous sodium bicarbonate were added. The organic layer was separated, washed with aqueous sodium bicarbonate, dried (Na_2SO_4) and evaporated to give 107 mg, which was purified by chromatography on silica gel (hexane) to give 45 mg (39%) of a 16:1 mixture of **4a** and **5a**. The spectral data of **4a** were determined from this mixture: NMR (CCl_4) δ 5.13 (br t, 1, *J* = 7 Hz), 1.95 (m, 2), 1.62 (br s, 3), 1.28 (m, 6), 0.89 (br t, 3, *J* = 6 Hz), 0.46 (s, 4), –0.09 (s, 9); in C_6D_6 the four-proton singlet at δ 0.46 was split into a multiplet at δ 0.38–0.56 typical of an AABB' system; ^{13}C NMR ($CDCl_3$) δ 138.4, 127.2, 31.5, 29.6, 28.0, 22.6, 17.5, 14.1, 10.6, 9.6, –2.7; IR (neat) 3075, 2935, 2860, 1460, 1378, 1260, 1250, 1190, 1180, 835, 748, 685 cm^{-1}; GC t_R = 17.4 min (135 °C); GC/MS, *m/e* (relative intensity) 224 (M^+, 0.5), 209 (0.2), 181 (0.2), 167 (0.1), 153(2), 109(1), 107(2), 97(2), 95 (2), 94 (3), 93 (5), 91 (1), 73(100). Anal. Calcd for $C_{14}H_{28}Si$: C, 74.91; H, 12.57. Found: C, 74.13; H, 11.89.

Solvolysis of 2b. Tosylate **2b** (0.653 g, 2.0 mmol) and anhydrous K_2CO_3 (0.57 g, 4.0 mmol) in anhydrous *tert*-butyl alcohol (40 mL) were heated at reflux under nitrogen for 14 h. A workup as above using pentane gave 0.287 g of product which was purified by evaporative distillation (25 °C, 0.5 torr) to give 86.3 mg of 90% pure **4b** (25%). The low yield is a result of the volatility of the desired product. A pure sample was obtained by preparative GC: NMR ($CDCl_3$) δ 4.76 (br, 1), 4.68 (br, 1), 1.74 (br s, 3), 0.54 (s, 4), –0.02 (s, 9); NMR (C_6D_6) δ 4.83 (br, 1), 4.80 (br, 1), 1.70 (br s, 3), 0.51–0.56 (m, 4), –0.04 (s, 9); ^{13}C NMR ($CDCl_3$) δ 149.9, 111.6, 23.3, 16.0, 9.7, –2.6; IR ($CDCl_3$) 3080, 3000, 2965, 2915, 2905, 1630, 1440, 1370, 1297, 1250, 1212, 1025, 835 cm^{-1}; GC t_R = 14.5 min (60 °C); MS, *m/e* (relative intensity) 154 (2, M^+), 139 (2), 112 (1), 111 (3), 99 (1), 97 (4), 86 (1), 85 (2), 83 (3), 81 (1), 79 (2), 77 (1), 73 (100).

Registry No. (*Z*)-**1a**, 83025-23-4; (*E*)-**1a**, 83025-24-5; **1b**, 83025-25-6; (*Z*)-**2a**, 83025-26-7; **2b**, 83043-20-3; (*E*)-**4a**, 83025-27-8; **4b**, 83025-28-9; **5a**, 83025-29-0; 1-(trimethylsilyl)-1-octyne, 15719-55-8; methyl bromide, 74-83-9; ethylene oxide, 75-21-8; 1-(trimethylsilyl)-1-propyne, 6224-91-5.

Circular Dichroic Method for Determining the Position of Glycosidic Linkages of Deoxy Sugar Moieties. Antitumor Antibiotic Chromomycin A_3

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We describe a three-step method for determining glycosidic linkages in complex natural products as exemplified by chromomycin A_3[2,3] (Chart I) which contains five 2,6-dideoxy sugars[4] attached to a tricyclic aglycon. The method can be carried out on a small scale and leads to determinations of intersugar linkages as well as configurational series, i.e., D or L series. We recently showed that an additivity relation exists in the amplitudes of exciton-split circular dichroism curves (CD) of pyranose benzoates,[5,6] and on this basis a submilligram method was developed to determine the position of glycosidic linkages at *branching points* in oligosaccharides without reference to authentic samples.[7] A variant of this method described below is applicable to various complex antibiotics, e.g., chromomycin A_3, which consists of sugar moieties linked to an aromatic aglycon; it is part of several micromethods[8] we are currently investigating to examine oligosaccharide structures.

The chromomycins,[2] olivomycins,[9] and mitramycins[10] belong to a group of structurally related antitumor anti-

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