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Compatibility Studies of Dimethyl(phenyl)silyl Group as a Masked Hydroxyl Group in Compounds Containing Cyclopropane Rings and in Compounds Containing the Enone Functionality

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COMPATIBILITY STUDIES OF DIMETHYL (PHENYL)SILYL GROUP AS A MASKED HYDROXYL GROUP IN COMPOUNDS CONTAINING CYCLOPROPANE RINGS AND IN COMPOUNDS CONTAINING THE ENONE FUNCTIONALITY.

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ABSTRACT

Compatibility of the phenyl(dimethyl)silyl group as a masked hydroxyl group in the presence of cyclopropane rings and the enone functionality was studied. The result showed that conditions for the silyl-to-hydroxyl group conversion is not compatible with cyclopropane rings. However, under a modified two-step transformation procedure, the silyl group is converted to a hydroxyl group in the presence of an enone group without disturbing the carbon-carbon double bond, to a certain extent.

The use of phenyl(dimethyl)silyl group as a masked hydroxyl group in syntheses has been well established.¹ An attractive feature of the silyl-to-hydroxyl group conversion is that the reaction proceeds with retention of configuration at the carbon to which the silyl group is attached.² The conversion methods of the phenyl(dimethyl)silyl group to a hydroxyl group

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Scheme 1

requires an electrophilic attack on the aryl group attached to the silicon in the first step.^{2,3} Hence, the phenyl(dimethyl)silyl group is not a suitable candidate as masked hydroxyl group in compounds containing functional groups that are susceptible to electrophilic attack. It has been shown, for example, that in phenylallylsilanes, the allylic carbon-carbon double bond in the molecule is activated and hence, more susceptible to electrophilic attack than the phenyl group in the conditions of this conversion procedure.⁴,⁵

Recently, it was discovered that the phenyl(dimethyl)silyl group is also incompatible as a masked hydroxyl group in compounds containing cyclopropane rings.⁶ Although cyclopropanes are generally less reactive than alkenes, their reactivity towards electrophiles mimics that of the π -bond of alkenes in many respects.^{7,8,9}

In the compatibility study of the phenyl(dimethyl)silyl group as a masked hydroxyl group with cyclopropane rings, it was found that no recognisable product was isolated when the cyclopropane (1) was subjected to the conditions of the one-pot silyl-to-hydroxyl group transformation (scheme 1) developed by Sanderson.² However, when it was treated with boron trifluoride-



acetic acid complex, the first of the two-step silyl-to-hydroxyl conversion method, ring opened products were isolated, as shown in scheme 2. These products indicated that electrophilic attack on the cyclopropane ring had taken place by a proton, forming the intermediate (7), and the plausible pathways from this intermediate (7) to each of the products are shown in scheme 3. It is probable that the silyl group speeded up the electrophilic attack, by analogy with the way arylsilanes are activated towards electrophilic attack. An isolated cyclopropane ring, however, may conceivably be compatible with the silyl-tohydroxyl conversion procedures.

Although it is known that the phenyl(dimethyl)silyl group is not compatible as a masked hydroxyl group in compounds containing carboncarbon double bond, particularly in allylsilanes, no direct work had been done to study the compatibility of the phenyl(dimethyl)silyl group as a masked hydroxyl group in compounds containing conjugated enone. The presence of the carbonyl



Scheme 3

group in the enone in the α position would destabilise the intermediate cation corresponding to 11 (scheme 4). It is hoped that when both a phenyl ring and an enone are attached to the silicon, the electron-withdrawing effect of the carbonyl system may allow preferential electrophilic attack on the phenyl ring. Thus, it might be possible to transform the phenyl(dimethyl)silyl group to transform the phenyl(dimethyl)silyl group to a hydroxyl group without disturbing the carbon-carbon double bond in compounds containing the enone functionality.







The aliphatic enone (12) chosen for this study was synthesized from mesityl oxide. Neither of the one-pot transformation processes^{3,4} on the enone (12) gave the desired alcohols (13a and b) (scheme 5). The ¹H n.m.r. spectra of the product from both these reactions showed the loss of the signal at δ 5.76, which was the signal for the olefinic proton on the enone (12). However, no corressponding signals in this region for the olefinic proton for the alcohol (13a and b) was observed. It is not known whether this loss of the carbon-carbon double bond is a result of electrophilic attack on the double bond by the bromine or mercuric acetate, or of an epoxidation reaction by the peracetic acid used in excess for these reactions.



Scheme 7

Hence, the enone (12) was treated with boron trifluoride-acetic acid complex, the first of the two-step silyl-to-hydroxyl group transformation procedures.³ The proton n.m.r. spectrum from this reaction showed that the carbon-carbon double bond of the enone (13) had remained intact, and that the silyl fluorides (14a and b) were the products (scheme 6). The product isolated from the oxidation of the silyl fluorides (14) under Tamao's neutral oxidation conditions were uninterpretable by the proton n.m.r. spectrum. However, when these silyl fluorides (14) were treated with 30% hydrogen peroxide under basic conditions¹⁰ a mixture of the desired alcohols (13) was obtained in 18% yield (scheme 7).

This result indicated that it is at least possible to convert the phenyl(dimethyl)silyl group to a hydroxyl group without disturbing the carboncarbon double bond of the enone that ia also an allylsilane. However, a modification of the conversion of the two-step procedure is required to make the transformation of the silyl-to-hydroxyl group more effective and generally applicable. The electrophilic removal of the phenyl group was high-yielding but the oxidation step was low-yielding in this case, as we have found before with a quarternary centre adjacent to the silyl group.³

Experimentals.

Trans-(1-Dimethyl(phenyl)silyl)-2-undecylcyclopropane (1).-Base on the method developed by Yamamoto, 10 trimethylaluminium (1.0 ml of a 2M solution in hexane) was added slowly at 0 °C to a solution of (E)-1dimethyl(phenyl)silyltridec-1-ene⁹ (0.427 g, 1.35 mmol) and diiodomethane (0.17 ml, 2.11 mmol) in dry carbon tetrachloride (6 ml) under argon and stirred for 3 h. Dichlorometane (20 ml), sodium fluoride (4 g), and water (1.3 ml) were added in succession. The reaction mixture was stirred for 10 min, filtered, dried (MgSO₄), and chromatographed on silica to give the silylcyclopropane (1) (0.50 g, 91%), Rf (CH2Cl2) 0.78, v(max.) (CH2Cl2) 3 110 (Ar-H), 3 015 (cyclopropane C-H), 2 995 (saturated C-H), 1 125 (SiMe), and 1 115 cm⁻¹ (SiPh), δ (CDCl₃) 7.7-7.34 (5 H, m, SiPh), 1.29 (20 H, m, C₁₀H₁₀), 0.91 (3 H, t, J 6 Hz, CH₂Me), 0.45 (1 H, dt, J 7 and 4 Hz, C₁₁H₂₃CHCHSi), 0.39 (2 H, dd, J 4 and 7 Hz, C11H23CHCH2CHSi), 0.22 (3 H, s, SiMe), 0.20 (3 H, s, SiMe), and -0.44 (1 H, dt, J 7 and 4 Hz, CH₂CHCHSi) (Found: M⁺, C22H38Si requires M, 330.2743),m/z 330 (25%, M+), 301 (80, 330.2736.

 $C_9H_{18}CHCH_2CHSiPhMe_2$), 161 (90, PhMe₂SiCHCH), and 135 (100, PhMe₂Si).

Reaction of the Cyclopropane (1) using Boron Trifluoride-Acetic Acid. --- Based on the reaction by Plaut ³ the cyclopropane (1) (0.055 g, 0.17 mmol) was dissolved in dry dichloromethane (1 ml) under argon. Boron trifluoride (0.024 ml of a 40% by weight in acetic acid, 0.20 mmol) was added dropwise and the reaction was stirred for 4 h. Work-up by washing with saturated sodium bicarbonate solution (2 ml) and brine (1 ml), drying (MgSO₄), and removal of solvent in vacuo gave the crude product as a yellow oil. This reaction was carried out at 0 °C and at room temperature (25 °C), with reaction times ranging from 15 min to 5 h. The products isolated were: (a) the alkenes (5) and (6) (0.013 g, 28%), Rf (CH2Cl2) 0.79, δ(CDCl3) [for the terminal alkene (4)] 5.9-5.7 (1 H, m, CH₂CH=CH₂), 4.88-5.05 (2 H, m, CH₂CH=CH₂), and 2.1-0.9 (25 H, m, C1₂H₂₅) (Found: <u>M</u>⁺, 196.2174. C₁₄H₂₈ requires <u>M</u>, 196.2190), m/z 196 (55%, M⁺), 125 (45, M-C₅H₁₁), 97 (70, C₇H₁₃), 83 (50, C₆H₉), 55 (100, C_4H_7); (b) 3-acetoxytetradecane (4) (0.013 g, 21%), <u>R</u>_f(CH₂Cl₂) 0.58, δ(CDCl₃) 4.87-4.72 (1 H, tt, J 6 and 6 Hz, RCH₂CH(OAc)CH₂), 2.03 (3 H, s, OCMe), 1.69-0.76 (28 H, m, C11H23 and C2H5) (Found: M+ - Et, 227.2031. C14H27O2 - Et requires 227.2010), m/z 227 (50%, M+), 196 (65, C11H23CHCHMe), 125 (40, C9H17), 111 (50, C8H15), 101 (100, EtCOAc), 97 (80, C₆H₁₁), 69 (80, C₅H₉), 57 (95, C₃H₅), 55 (90, C₃H₃O); and (c) 3acetoxy-1-dimethyl -(phenyl)silyltetradecane (3) (0.049 g, 51%), Rf(CH2Cl2) 0.69, δ(CDCl₃) 7.6-7.3 5 H, m, SiPh), 4.79 (1 H, m, CCHOAc), 2.02 (3 H, s, OCMe), 1.67-0.58 (27 H, m, C11H23 and C2H4Si), and 0.25 (6 H, s, SiMe2)

(Found: \underline{M}^+ - Me, 375.2713. C₂₄H₄₂SiO₂ - Me requires 375.2720), <u>m/z</u> 375 (30%, <u>M</u>-Me), 313 (60, <u>M</u>-Ph), 297 (55, C₁₁H₂₃CH(OAc)C₂H₄SiCH₂), 179 (80, OCH₂CH₂SiMe₂Ph), 135 (80, SiMe₂Ph), and 117 (100, Me₂SiCH₂CH₂CH₂OH).

(E)-3-(1-Dimethyl(phenyl)silyl-1-methylethyl)pent-3-ene-2-one (12) ---3-(1-Dimethyl(phenyl)silyl-1-methylethyl)-4-hydroxypentan-2-one 6 (1.698 ml, 16.9 mmol) was dissolved in dry dichloromethane (10 ml) and cooled to 0 °C under argon. Methanesulphonyl chloride (0.50 ml, 6.11 mmol) and triethylamine (1.70 ml, 12.20 mmol) were added in succession and stirred at 0 °C for 1 h. DBU (4.6 ml, 30.76 mmol) was added slowly and the mixture stirred at room temperature for another 17 h and then refluxed for 7 h. Saturated ammonium chloride solutrion (10 ml) was added and the reaction mixture was extracted with ether (2 x 10 ml). Standard work-up and silica gel chromatography gave a mixture of the enone (3) (0.867 g, 55%) as pale yellow oil, R_f(hexane-ethyl acetate 4:1 v/v) 0.57, vmax.(CCl₄) 3 100 (Ar-H), 2 900 (saturated C-H), 1 710 (C=O) and 1 690 cm⁻¹ (C=C-C=O), δ(CDCl₃) 7.6-7.1 (5 H, m, SiPh), 4.90 (1H, q, J 6 Hz, C=CHMe), 2.1 (3 H, s, CH₃CO), 1.45 (3 H, d, J 6 Hz, C=CHMe), 1.0 (6 H, s, Me₂CSi), and 0.28 (6 H, s, Me₂Si)(Found: M⁺, 260.1573. C₁₆H₂₄OSi requires M, 260.1550), m/z 260 (10%, M⁺), 245 (60, M-Me), 169 (45, (SiMe₂H)Me₂CCHMeCOMe), 135 PhSiMe₂), and 69 (80, MeCHCHCO). 3-(1,1-(100%)Methyl(dimethyl(phenyl)silyl)-ethyl)pent-4-one-2-yl-methanesulphonate (15) was isolated as the second product (0.948 g, 45%), Rf(hexane-ethyl acetate 4:1 v/v) 0.15, δ(CDCl₃) 7.6-7.1 (5 H, m, SiPh), 4.80 (1H, m, MeCHOMs), 2.8 (3 H,

s, C<u>H</u>₃CS), 2.5 (1 H, d, <u>J</u> 6 Hz, MsOCHC<u>H</u>CO), 1.90 (3 H, s, <u>Me</u>₂CO), 1.3 (3 H, d, <u>J</u> 6 Hz, <u>Me</u>CHOMs), 1.0 (6 H, s, Me₂CSi), and 0.20 (6 H, s, Me₂Si). Heating this mesylate (15) (0.95g, 2.8 mmol) in DBU (10.0 ml, 66.9 mmol) at 90 °C for 1 h and work-up as above gave the *enone* (12) (0.948 g, 100%).

3-(1-Dimethyl(fluoro)silyl-1-methylethyl)pent-3-ene-2-one (14) -Based on the reaction conditions developed by Plaut,³ the enone (12) (0.269 g, 1.04 mmol) was dissolved in dry dichloromethane (0.5 ml) under argon. Boron trifluoride-acetic acid (0.13 ml of a 40% (by weight) solution in acetic acid) was added dropwise with stirring and the reaction mixture was stirred for 3 h at room temperature. Saturated sodium bicarbonate solution (10 ml) was added. The reaction mixture was extracted with dichloromethane (2 x 5 ml). dried (MgSO₄), and the solvent was removed in vacuo to give a mixture of the silyl fluoride (14) (0.269 g, 100 %) as brown oil which was used without any purification in the next step. $\delta(CDCl_3)$ (one isomer) 5.5 (1 H, q, J 6 Hz, C=CHMe), 2.3 (3 H, s, MeCO), 1.8 (3 H, d, J 6 Hz, CH3CS), 1.1 (6 H, s, Me₂CSi), 0.2 (6 H, 2d, J 8 Hz, FSiMe₂), and (second isomer) 6.9 (1 H, q, J 6 Hz, C=CHMe), 2.3 (3 H, s, MeCO), 2.1 (3 H, d, J 6 Hz, C=CHMe), 1.3 (6 H, s, Me2CSi), and 0.30 (6 H, 2d, J 8 Hz, Me2SiF).

(E)-3-(1-Hydroxy-1-methylethyl)pent-3-ene-2-one (13) —-Hydrogen peroxide (10 ml of a 30% solution in water) was added with stirring to a mixture of the silyl fluoride (14) (0.2694 g) and potassium bicarbonate (0.708 g, 7.08 mmol) in methanol-tetrahydrofuran (1:1 v/v, 16 ml). The reaction mixture was refluxed under argon for 6 h, resulting in the formation of white insoluble

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solids. Dilute sodium bisulfite solution (5 ml) was added at 0 °C. Standard ethereal work-up and silica gel chromatography gave a mixture of the *enones* (13) as oil (0.0271 g, 18% based on the enones (3)), <u>R</u>_f(hexane-ethyl acetate 2:1 v/v) 0.21, v_{max.}(CCl₄) 3 500 (OH), 2 995 (saturated C-H), and 1 700 cm⁻¹ (C=O), δ (CDCl₃) 5.76 (1 H, q, J 6.5 Hz, <u>H</u>CMe), 2.35 (3 H, s, MeCO), 1.90 (1 H, s, OH), 1.70 (3 H, d, <u>J</u> 6.5 Hz, <u>Me</u>CH), and 1.35 (6 H, s, CMe₂)(Found: <u>M</u>⁺-Me, 127.0746. C₇H₁₁OSi requires <u>M</u>-Me127.0759), *m*/z 127 (30%, <u>M</u>-Me), 109 (20, MeCHCCOMeCMe), 83 (100, MeCHCCOMe), 69 (35, MeCOCHCH), 67 (33, MeCOC=C), and 59 (35%, Me₂COH).

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