

NSF synthetic inorganic organometallic chemistry program.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond distances and angles for [Ru₃(CO)₉(μ₃-CO)(μ₃-CC(O)CH₃)⁻ (1) and the mass spectral data for the acetone-d₁ produced from 4-d₁ (7 pages); a listing of F_o and F_c (9 pages). Ordering information is given on any current masthead page.

Weak Carbon-Carbon Bonds. Synthesis, Structure, and Reactions of 7-Methyl-1,3,5-triphenyl-2,4,9-trithia-1,3,5-tristannaadamantane

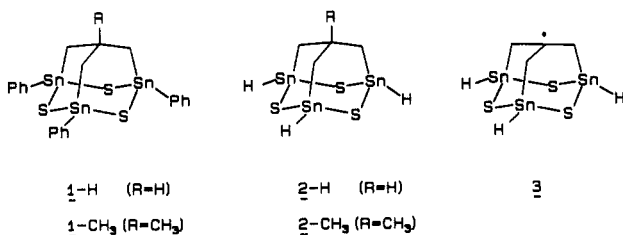
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7-Methyl-1,3,5-triphenyl-2,4,9-trithia-1,3,5-tristannaadamantane (1-CH₃) was synthesized to test the possibility that a carbon-methyl bond activated by three antiperiplanar carbon-tin bonds might be a reactive donor of methyl. MNDO calculations suggest that the strength of the carbon-methyl bond in compound 1-CH₃ should be about 40 kcal/mol. Nevertheless, the reactivity of this bond is not conspicuously high. This is presumably because the methyl group is neopentyl and sterically hindered and because other weak bonds in compound 1-CH₃ are even more reactive and obscure the intrinsic activation of the carbon-methyl bond by making reactions occur elsewhere.

Carbon-hydrogen bonds adjacent to properly oriented lone pairs or carbon-metal bonds are unusually weak and reactive, and compounds containing these activated carbon-hydrogen bonds are effective donors of hydrogen in redox reactions.²⁻⁴ For example, stannaadamantane 1-H



incorporates a carbon-hydrogen bond activated by three antiperiplanar carbon-tin bonds.³ Its strength, calculated to be 61 kcal/mol,^{5a} is much lower than that of the methine carbon-hydrogen bonds in isobutane (95 kcal/mol)⁶ or adamantane (99 kcal/mol)⁶ and appears to be even lower than that of a typical tin-hydrogen bond (72 kcal/mol in

Table I. Average Bond Lengths (Å) and Bond Angles (deg) Observed for Stannaadamantane 1-H^{3c} and Calculated for Stannaadamantanes 2-H and 2-CH₃ Using MNDO^{5c}

parameter	1-H	2-H	2-CH ₃
Sn-S	2.408	2.279	2.277
Sn-C	2.153	2.096	2.099
CH ₂ -C	1.529	1.546	1.558
CH ₃ -C			1.570
S-Sn-S	108.7	109.1	109.2
S-Sn-C	108.8	108.2	108.7
Sn-CH ₂ -C	119.3	118.2	120.4
CH ₂ -C-CH ₂	114.1	113.9	111.7
Sn-S-Sn	94.3	98.1	97.2

trimethylstannane).⁷ As a result, abstraction of hydrogen from stannaadamantane 1-H by alkyl radicals is generally quite exothermic, allowing compound 1-H to act like a tin hydride and reduce activated halides to the corresponding hydrocarbons.^{3a}

The use of properly oriented lone pairs or carbon-metal bonds to produce highly reactive carbon-hydrogen bonds is a general strategy that can be exploited to create other weak bonds as well. To test the possibility that a carbon-methyl bond activated by three antiperiplanar carbon-metal bonds might be a reactive donor of methyl, we decided to prepare methylstannaadamantane 1-CH₃ and study its structure and reactions.⁸

To help accommodate the characteristically long tin-sulfur bonds, the bridgehead carbon of stannaadamantane

(1) Fellow of the Natural Sciences and Engineering Research Council of Canada.

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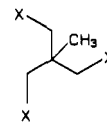
(8) For other recent studies of organometallic derivatives of adamantane, see: Haas, A.; Kutsch, H.-J.; Krüger, C. *Chem. Ber.* 1987, 120, 1045-1048. Ellermann, J.; Veit, A. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* 1985, 40B, 948-953. Boudjouk, P.; Kapfer, C. A.; Cunico, R. F. *Organometallics* 1983, 2, 336-343. Fritz, G.; Gompfer, K. Z. *Anorg. Allg. Chem.* 1981, 478, 94-96. Mironov, V. F.; Gar, T. K.; Fedotov, N. S.; Evert, G. E. *Usp. Khim.* 1981, 50, 485-521.

1-H is known to be dramatically flattened, and the C-H₂-CH-CH₂ angles open to an average value of 114.1°. Other measured bond lengths and angles are listed in Table I, along with values calculated by the MNDO procedure^{5,9} for the simplified derivative 2-H. We expected flattening of the bridgehead of methylstannaadamantane 1-CH₃ to be less impressive, since it is opposed by increased interactions of the methyl group with the three geminal methylenes. This was confirmed by using MNDO to calculate the optimized geometry of simplified methylstannaadamantane 2-CH₃. The parameters listed in Table I reveal that deformation of the bridgehead should be significantly smaller (widening of the CH₂-C-CH₂ angles to only 111.7°) at the expense of increased Sn-CH₂-C angles, decreased Sn-S-Sn angles, and somewhat longer carbon-carbon bonds.

Since the activated carbon-hydrogen bond in stannaadamantane 1-H is much weaker than normal carbon-hydrogen bonds and even weaker than typical tin-hydrogen bonds, we expected the activated carbon-methyl bond in methylstannaadamantane 1-CH₃ to be much weaker than the carbon-methyl bonds in neopentane (82 kcal/mol)¹¹ or 1-methyladamantane (90 kcal/mol)^{6,12} and even weaker than the tin-methyl bonds in tetramethylstannane (65 kcal/mol).⁷ The heats of formation of simplified methylstannaadamantane 2-CH₃ and radical 3, calculated by MNDO to be 41.9 and 46.8 kcal/mol, respectively, can be combined with the measured heat of formation of methyl (35.1 kcal/mol)¹³ to yield an estimate of 40 kcal/mol for the strength of the carbon-methyl bond in methylstannaadamantane 2-CH₃. This remarkably low value presumably reflects the great stability of radical 3 and the inescapably large strain energy of compound 2-CH₃. Methylstannaadamantane 1-CH₃ was therefore expected to show high homolytic reactivity. It is also thermodynamically well-designed to transfer methyl heterolytically, since loss of methyl anion would produce a bridgehead cation strongly stabilized by the inductive and hyperconjugative effects of the three adjacent carbon-tin bonds.

Despite its anticipated instability, methylstannaadamantane 1-CH₃ was relatively easy to synthesize and isolate. Reaction of the methanesulfonate 4 of 2-(hydroxymethyl)-2-methyl-1,3-propanediol with (triphenylstannyl)lithium produced [2-methyl-2-[(triphenylstannyl)methyl]-1,3-propanediyl]bis[triphenylstannane] (5) in 64% yield.¹⁴ Addition of 6 equiv of iodine to compound 5 cleanly yielded intermediate hexaiodide 6. Subsequent treatment of iodide 6 with 3 equiv of bis(triphenyltin) sulfide¹⁵ produced methylstannaadamantane 1-CH₃ in 85% overall yield from compound 5.

The final product had the simple ¹H and ¹³C NMR spectra expected for a compound of C_{3v} symmetry. The ¹H and ¹³C chemical shifts of the methyl group (δ 1.46 and 45.2, respectively) proved to be significantly downfield of those of 1,3,5,7-tetramethyladamantane (δ 0.81¹⁶ and 30.3,¹⁷



- 4 (X=OSO₂CH₃)
 5 (X=SnPh₃)
 6 (X=SnPhI₂)
 7 (X=SnPhBr₂)

respectively). This deshielding, which is also observed for the methine hydrogen of stannaadamantane 1-H, is presumably due to an anisotropic effect involving the atoms of tin and sulfur. The remarkably large coupling constant (average ³J(^{117,119}Sn,C) = 88.4 Hz) between tin and the carbon of the methyl group confirmed that all three carbon-tin bonds are antiperiplanar to the carbon-methyl bond.¹⁸

Surprisingly, the reactivity of the carbon-methyl bond in methylstannaadamantane 1-CH₃ is not conspicuously high under any conditions. For example, compound 1-CH₃ could be recovered in 98% yield after it had been heated in benzene at 120 °C for 72 h,¹⁹ and neither irradiation (360 nm)²⁰ nor ultrasonic irradiation (65 kHz, 100 W)²¹ of compound 1-CH₃ in toluene-*d*₈ yielded detectable amounts of methane-*d*.

Since the carbon-methyl bond in methylstannaadamantane 1-CH₃ was expected to be even more reactive than the tin-methyl bonds in tetramethylstannane, we treated compound 1-CH₃ with reagents known to react with tetramethylstannane. For example, homolytic or heterolytic iodinolysis of tetramethylstannane produces iodotrimethylstannane and iodomethane.²² In contrast, treatment of compound 1-CH₃ with 3 equiv of iodine in chloroform-*d*₁ yielded only hexaiodide 6 and elemental sulfur. No iodomethane or iodobenzene could be detected by ¹H NMR, indicating that electrophilic iodinolysis of the tin-sulfur bonds of compound 1-CH₃ is much faster than cleavage of the carbon-methyl or tin-carbon bonds. Attempts to promote homolytic iodinolysis of compound 1-CH₃ by adding iodine in carbon tetrachloride at low temperature (-10 °C)²² also failed to produce iodomethane and again yielded only hexaiodide 6. We demonstrated that tin-sulfur bonds are generally more reactive than tin-carbon bonds toward iodinolysis by observing that treatment of equimolar amounts of bis(triphenyltin) sulfide¹⁵ and tetramethylstannane with 1 equiv of iodine yielded iodotriphenylstannane (73%) and sulfur (66%) and left the tetramethylstannane unchanged. Failure of the carbon-methyl bond of methylstannaadamantane 1-CH₃ to react with iodine is therefore not surprising.

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(19) If E_a = 40 kcal/mol and A = 10¹⁴ s⁻¹ for homolysis of the activated carbon-methyl bond of methylstannaadamantane 1-CH₃, then t_{1/2} at 120 °C should be approximately 4 years; if A = 10¹⁵ s⁻¹, then t_{1/2} should be about 5 months. Nearly complete recovery of compound 1-CH₃ after 72 h is therefore reasonable.

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(9) The parameters reported in Table I for compound 2-H differ slightly from those published earlier^{5a} because an improved set of MNDO parameters for sulfur¹⁰ has been used.

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(14) An analogous reaction with 2-(bromomethyl)-2-methyl-1,3-dibromopropane was unsuccessful.

(15) Prepared from chlorotriphenylstannane and sodium sulfide by a procedure similar to one used to synthesize the corresponding selenide: Schmidt, M.; Ruf, H. *Chem. Ber.* 1963, 96, 784-785.

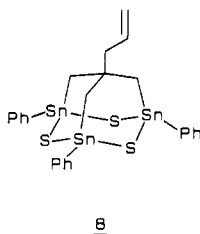
A similar cleavage of tin-sulfur bonds also occurred when compound 1-CH₃ was heated with excess carbon tetrabromide in benzene (120 °C, 120 h). This reaction cleanly produced hexabromide 7, which was identical by ¹H NMR to an authentic sample prepared by bromination of compound 5. Under similar conditions, the reaction of bis(triphenyltin) sulfide¹⁵ with carbon tetrabromide produced bromotriphenylstannane in 63% yield. Both reactions appear to involve a radical chain process in which a key step is selective attack by tribromomethyl radicals at sulfur.²³ Failure of the weak carbon-methyl bond of methylstannaadamantane 1-CH₃ to react with tribromomethyl radicals is therefore understandable.

Tetramethylstannane is known to react with tetracyanoethylene (TCNE) by an electron-transfer process that leads to insertion of TCNE into the tin-methyl bond.²⁴ In contrast, methylstannaadamantane 1-CH₃ could be recovered in 53% yield after long exposure to TCNE in hot benzene (100 °C, 48 h). Decomposition of compound 1-CH₃ in the presence of excess neat TCNE at higher temperatures (170 °C, 24 h) yielded only insoluble, uncharacterized solids.

In the presence of catalytic amounts of Pd(0), tetramethylstannane can convert acid chlorides to methyl ketones,²⁵ so we tried a similar reaction with methylstannaadamantane 1-CH₃. Unfortunately, treatment of 4-nitrobenzoyl chloride with an equimolar amount of compound 1-CH₃ and 1 mol % chloro(phenylmethyl)bis(triphenylphosphine)palladium did not produce detectable amounts of 4-nitroacetophenone, whereas a similar reaction with tetramethylstannane provided 4-nitroacetophenone in 81% yield.

All of these experiments demonstrate that the reactivity of the carbon-methyl bond of methylstannaadamantane 1-CH₃ is not conspicuously high, even though it must be exceptionally weak. This is partly because the methyl group is neopentyllic and sterically hindered. As a result, even significant weakening of the carbon-methyl bond is not enough to overcome the intrinsic reluctance of saturated carbon atoms to undergo homolytic substitution reactions. Other weak bonds in compound 1-CH₃ therefore show greater reactivity and obscure the intrinsic activation of the carbon-methyl bond by making reactions occur elsewhere.

To demonstrate experimentally that carbon-carbon bonds can be activated by properly oriented adjacent carbon-metal bonds, we need a compound similar to methylstannaadamantane 1-CH₃ but with an even more accessible and reactive carbon-carbon bond. Allylstannaadamantane 8 should satisfy these requirements,



since allylic resonance (11 kcal/mol)²⁶ will further reduce

the strength of the central carbon-carbon bond to approximately 30 kcal/mol, and initial attack by radicals or electrophiles can occur easily at the terminal carbon of the allyl group. The synthesis and isolation of allylstannaadamantane 8 will therefore present a rewarding and difficult challenge.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 spectrometer. Bruker WH-90 and WH-400 spectrometers were used to obtain ¹H and ¹³C nuclear magnetic resonance (NMR) spectra. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ). Low-resolution mass spectra were recorded on a V.G. Micromass 12-12 quadrupole spectrometer using chemical ionization (CI) mass spectrometry or on a Kratos MS-50 TA spectrometer using fast atom bombardment (FAB) mass spectrometry. Characteristic isotopic distributions were observed for all ions containing tin, but the only peaks reported are those that correspond to ions containing uniquely ¹²⁰Sn. Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Melting points were recorded on a Thomas-Hoover capillary apparatus and are not corrected. Pyridine and diisopropylamine were dried by distillation from calcium hydride, and tetrahydrofuran was dried by distillation from the sodium ketyl of benzophenone. Methanesulfonyl chloride and triphenylstannane were purified by distillation before use. All other common reagents were commercial products of the highest purity available.

2-Methyl-2-[(methylsulfonyl)oxy]methyl]-1,3-propanediol Dimethanesulfonate (4). Methanesulfonyl chloride (22.6 g, 197 mmol) was added dropwise at 0 °C under N₂ to a stirred solution of 2-(hydroxymethyl)-2-methyl-1,3-propanediol (7.81 g, 65.0 mmol) in pyridine (16 mL). The viscous mixture was kept at 0 °C for 15 h and then poured into ice water (250 mL). The crystalline precipitate was separated by filtration and washed thoroughly with water. Recrystallization from 95% ethanol yielded fine colorless needles of analytically pure 2-methyl-2-[(methylsulfonyl)oxy]methyl]-1,3-propanediol dimethanesulfonate (4; 11.6 g, 32.7 mmol, 50.3%): mp 79.5–80.5 °C; IR (KBr) 3030, 1350, 1175, 975, 850 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 1.18 (s, 3 H), 3.08 (s, 9 H), 4.16 (s, 6 H); mass spectrum (CI, isobutane), *m/e* 355, 259, 163. Anal. Calcd for C₈H₁₈O₉S₃: C, 27.11; H, 5.13. Found: C, 27.33; H, 5.18.

[2-Methyl-2-[(triphenylstannyl)methyl]-1,3-propanediol]bis[triphenylstannane] (5). Butyllithium (5.0 mL, 1.4 M in hexane, 7.0 mmol) was added dropwise at 0 °C under N₂ to a stirred solution of diisopropylamine (0.72 g, 7.1 mmol) in tetrahydrofuran (15 mL). After 15 min, triphenylstannane (2.5 g, 7.1 mmol) was added dropwise, and the resulting solution was stirred at 0 °C for 30 min. A solution of 2-methyl-2-[(methylsulfonyl)oxy]methyl]-1,3-propanediol dimethanesulfonate (4; 0.517 g, 1.46 mmol) in tetrahydrofuran (15 mL) was then added dropwise, and the mixture was kept at 0 °C for 2 h and at 25 °C for 18 h. Water (30 mL) was added, and the mixture was extracted with dichloromethane. The organic extracts were washed with brine and dried, and solvent was removed by evaporation under reduced pressure. Flash chromatography²⁷ of the residue (silica, hexane (80%)/dichloromethane (20%)) provided pure [2-methyl-2-[(triphenylstannyl)methyl]-1,3-propanediol]bis[triphenylstannane] (5; 1.04 g, 0.929 mmol, 63.6%). Recrystallization from hexane/ethyl acetate provided analytically pure, colorless plates: mp 168–169 °C; IR (KBr) 3070, 1465, 1425, 1070, 720, 695 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 1.20 (s, 3 H), 2.02 (s, 6 H), 7.3 (m, 45 H); mass spectrum (FAB, 18-crown-6), *m/e* 1045, 351. Anal. Calcd for C₆₉H₅₄Sn₃: C, 63.31; H, 4.87. Found: 63.33; H, 5.63.

[2-Methyl-2-[(diiodophenylstannyl)methyl]-1,3-propanediol]bis[diiodophenylstannane] (6). Iodine (118 mg, 0.465 mmol) was added to a solution of [2-methyl-2-[(triphenylstannyl)methyl]-1,3-propanediol]bis[triphenylstannane] (5; 80.3 mg, 0.0717 mmol) in dichloromethane (6 mL), and the mixture was stirred at 25 °C for 24 h. Volatiles were then removed

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by evaporation under reduced pressure, and the residue was dried in vacuo. This yielded a sample of [2-methyl-2-[(diiodophenylstannyl)methyl]-1,3-propanediyl]bis[diiodophenylstannane] (6) that was sufficiently pure for immediate use in the following reaction: ^1H NMR (90 MHz, CDCl_3) δ 1.47 (s, 3 H), 2.71 (s, 6 H), 7.4–7.7 (m, 15 H).

7-Methyl-1,3,5-triphenyl-1,3,5-tristanna-2,4,9-trithiatricyclo[3.3.1.1^{3,7}]decane (1-CH₃). A sample of [2-methyl-2-[(diiodophenylstannyl)methyl]-1,3-propanediyl]bis[diiodophenylstannane] (6) derived from [2-methyl-2-[(triphenylstannyl)methyl]-1,3-propanediyl]bis[triphenylstannane] (5; 80.3 mg, 0.0717 mmol) was treated with a solution of hexaphenyldistannathiane (317 mg, 0.433 mmol)¹⁵ in dichloromethane (10 mL), and the mixture was stirred at 25 °C for 2 h. Solvent was then removed by evaporation under reduced pressure. Flash chromatography²⁷ of the residue (silica, hexane (60%)/dichloromethane (40%)) provided an analytically pure sample of 7-methyl-1,3,5-triphenyl-1,3,5-tristanna-2,4,9-trithiatricyclo[3.3.1.1^{3,7}]decane (1-CH₃; 45.9 mg, 0.0610 mmol, 85.1%) as a white solid: mp 240–243 °C; IR (KBr) 1480, 1430, 1070, 725, 695 cm^{-1} ; ^1H NMR (400.13 MHz, CDCl_3) δ 1.46 (s, average $^4J(^{117,119}\text{Sn}, ^1\text{H}) = 26.1$ Hz, 3 H), 1.79 (s, average $^2J(^{117,119}\text{Sn}, ^1\text{H}) = 42.4$ Hz, 6 H), 7.5 (m, 9 H), 7.7 (m, 6 H); ^{13}C NMR (100.62 MHz, 5% CD_2Cl_2 in CH_2Cl_2 , gated proton decoupling) δ 34.5 (s, $^1J(^{117}\text{Sn}, ^{13}\text{C}) = 381$ Hz, $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 398$ Hz), 45.2 (s, average $^3J(^{117,119}\text{Sn}, ^{13}\text{C}) = 88.4$ Hz), 45.8 (s, average $^2J(^{117,119}\text{Sn}, ^{13}\text{C}) = 26.7$ Hz), 128.9 (s), 130.2 (s), 134.7 (s), 139.5 (s); mass spectrum (FAB, 18-crown-6), *m/e* 756, 679, 265. Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{Sn}_3$: C, 36.70; H, 3.22. Found: C, 36.85; H, 3.58.

Reaction of Hexaphenyldistannathiane and Tetramethylstannane with Iodine. A solution of hexaphenyldistannathiane (107 mg, 0.146 mmol)¹⁵ and tetramethylstannane (25.8 mg, 0.144 mmol) in chloroform (15 mL) was treated with a solution of iodine (37.2 mg, 0.147 mmol) in chloroform (10 mL), and the mixture was stirred at 25 °C in the dark for 13 h. Volatiles were then removed by evaporation under reduced pressure, and

the residue was extracted with acetonitrile. The insoluble fraction, a pale yellow solid, was further washed with ether, dried, and identified by its characteristic solubility and chromatographic properties as elemental sulfur (3.1 mg, 0.097 mmol, 66%). Concentration of the acetonitrile solution of the soluble fraction produced colorless crystals of iodotriphenylstannane (101 mg, 0.212 mmol, 72.6%): mp 119–120 °C (lit.²⁸ mp 121 °C).

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Registry No. 1-H, 87922-35-8; 1-CH₃, 111769-98-3; 2-H, 88212-59-3; 2-CH₃, 111769-99-4; 3, 96504-44-8; 4, 111770-00-4; 5, 111770-01-5; 6, 111770-02-6; 7, 111770-03-7; 12, 639-58-7; bis-(triphenyltin) sulfide, 77-80-5; tetramethylstannane, 594-27-4; iodotriphenylstannane, 894-09-7; bromotriphenylstannane, 962-89-0; 4-nitrobenzoyl chloride, 122-04-3; 4-nitroacetophenone, 100-19-6; 2-(hydroxymethyl)-2-methyl-1,3-propanediol, 77-85-0; triphenylstannane, 892-20-6.

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Synthesis and Reactions of (Trimethylgermyl)acetates

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Base-assisted trimethylgermylation of ethyl acetate gave high yields of ethyl (trimethylgermyl)acetate (2), bis(trimethylgermyl)acetate (5), and tris(trimethylgermyl)acetate (6). The Peterson reaction of (trimethylgermyl)(trimethylsilyl)acetate (4), prepared from ethyl (trimethylsilyl)acetate (1), with aldehydes selectively yielded α -(trimethylgermyl)- α,β -unsaturated alkenoates (15). The addition of fluoride anion to 4 successfully induced selective desilylation. Some chemical properties of 6 were also examined.

Although the synthetic utility of α -trimethylsilyl esters has been amply demonstrated,^{1,2} there is no direct method to prepare them from the corresponding esters. All reports to date on the direct trimethylsilylation of esters have shown that the predominant product is that due to O-silylation and not C-silylation.^{1,3} One exception to this

general observation is that of *tert*-butyl acetate, which can be attributed to a larger steric effect in the O-silylated material than in the C-silylated isomer.⁴ However, the trimethylsilylation of *tert*-butyl (trimethylsilyl)acetate gave a mixture of both the C-silylated and O-silylated products.⁵ Larson reported that methyl-diphenylsilylation of esters favors the formation of the C-silylation product.⁶ Previously we reported that the trimethylgermyl group tended to be introduced on the α -carbon rather than the carbonyl oxygen of ketones, whereas the trimethylsilyl group was usually introduced on the oxygen.⁷ This paper describes

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