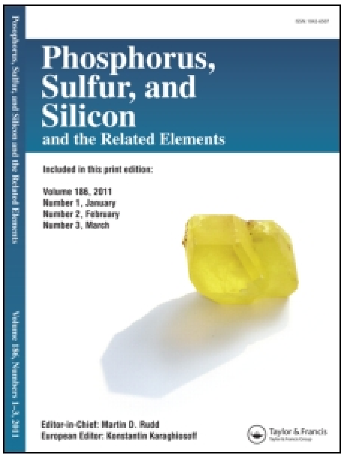

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Study of Fragmentation Reactions of Highly Sterically Hindered Organosilicon Compounds with Alcoholic Sodium Alkoxides

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The compounds $(Me_3Si)_3CSiXX'X''$ *[*$X = Me$, $X' = (C_6H_4Me\text{-p})$, $X'' = I$; $X = Et$, $X' = X'' = Cl$; $X = Bu$, $X' = X'' = Cl$*)] reacted with boiling RONa/ROH [R = Pr, iso-Pr, Bu, Et, Benzyl, iso-Amyl] to give the fragmentation products of the type* $(Me_3Si)_2CHSiXX'(OR)$ *and* $Me_3SiCH_2SiXX'(OR)$ *[*$X = Me$, $X' = (C_6H_4Me\text{-p})$*] or* $(Me_3Si)_2CHSiX(OR)_2$ *[X = Et or Bu]. Study of the products showed that alkoxides as nucleophile cannot attack the silicon center bearing the* $(Me_3Si)_3C$*- group because of steric hindrance. It is suggested that the reaction proceeds through an elimination, analogous to the E2 elimination of alkyl halides, involving the synchronous attack of* RO^- *at a* Me_3Si *group, the liberation of* X^-*, and the formation of* $(Me_3Si)_2C{=}SiXX'$*.*

Keywords Alkoxide; fragmentation; organosilicon; trisyl

INTRODUCTION

The tris(trimethylsilyl)methyl ligand, $(Me_3Si)_3C$, is a highly sterically hindered ligand in which three organosilyl substituents are attached to the central carbon atom. It is referred to as the "trisyl" ligand and commonly denoted by Tsi. A large number of metal compounds containing the bulky $(Me_3Si)_3C$- group have been synthesized and their reactions have been studied.[1–6] The presence of the trisyl ligand in organosilicon compounds of the type $(Me_3Si)_3CSiR_2X$ or $(Me_3Si)_3CSiRX_2$ [X = halogen] causes a very large steric hindrance toward the nucleophilic displacement of X.[7–9] Therefore, these compounds undergo the direct biomolecular nucleophilic displacement of X

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only with difficulty, and this permits observations of other reactions not normally encountered.[10,11] This is the case in the reactions with sodium alkoxides, which we describe below.

RESULTS AND DISCUSSION

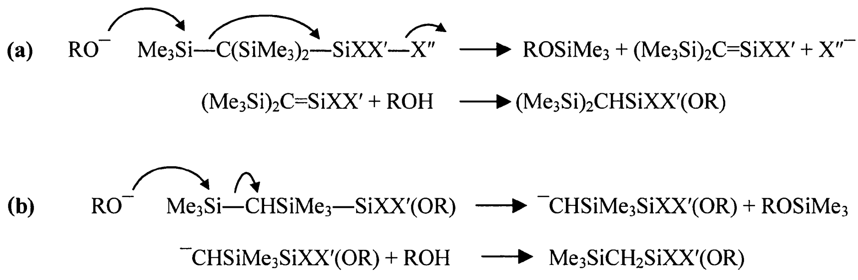
The study began with TsiSiMe(C_6H_4Me-*p*)I, which was made as described previously by the treatment of TsiSiMe(C_6H_4Me-*p*)H with one molar proportion of ICl in carbon tetrachloride at room temperature.[3] When the compound TsiSiXX′X″ (X = Me, X′ = C_6H_4Me-*p*, X″ = I) was treated for several hours with refluxing 2 M sodium alkoxide (NaOR) in alcohol (ROH), the product was of the type $(Me_3Si)_2CHSiXX'OR$ (Equation 1) or $Me_3SiCH_2SiXX'OR$ (Equation 2):

$$(Me_3Si)_3CSiXX'X'' + RONa + ROH \rightarrow (Me_3Si)_2CHSiXX'(OR) + Me_3SiOR + NaX'' \quad (1)$$

$$(Me_3Si)_2CHSiXX'(OR) + RONa + ROH \rightarrow Me_3SiCH_2SiXX'OR \quad (2)$$

The possible route for these products is shown in Scheme 1. The initial process is analogous to an E2 elimination from organic halides, but with an attack at the β-silicon rather than the β-hydrogen. Alkoxide as a nucleophile attacks at a Me_3Si bond rather than the electronically favored XX′SiX″ center, which can be attributed to the fact that attack at the former relieves steric strain. Therefore, the corresponding sila-olefin $(Me_3Si)_2C{=}SiXX'$ is obtained, which then rapidly adds alcohol to give the observed product $(Me_3Si)_2CHSiXX'(OR)$ with less steric hindrance. The absence of the halide group in the newly obtained organosilicon compound causes an alkoxide attack at a Me_3Si bond to give a carbanion. The addition of alcohol to the carbanion results in $Me_3SiCH_2SiXX'(OR)$ as a silyl ether compound.

Details of the reaction of TsiSiMe(C_6H_4Me-*p*)I in various alcoholic sodium alkoxides medium are given in Table I. With increasing



SCHEME 1

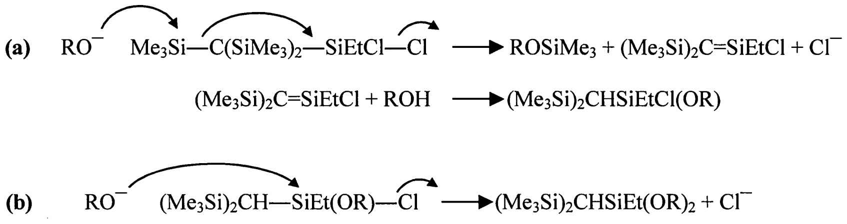
TABLE I Reaction of $TsiSiMe(C_6H_4Me\text{-}p)I$ With Alkoxides

Alkoxide solution	Time (day)	Product	Yield (%)
$^nPrONa/^nPrOH$ (2.5 M)	5	$(Me_3Si)_2CHSiMe(C_6H_4Me\text{-}p)(O^nPr)$	28
$^iPrONa/^iPrOH$ (2.5 M)	18	$(Me_3Si)_2CHSiMe(C_6H_4Me\text{-}p)(O^iPr)$	34
$^nBuONa/^nBuOH$ (2.5 M)	6	$(Me_3Si)_2CHSiMe(C_6H_4Me\text{-}p)(O^nBu)$	24
$PhCH_2ONa/PhCH_2OH$ (2.5 M)	20	$Me_3SiCH_2SiMe(C_6H_4Me\text{-}p)(OCH_2Ph)$	27
$^iAmONa/^iAmOH$ (2.5 M)	10	$Me_3SiCH_2SiMe(C_6H_4ME\text{-}p(O^iAm)$	32

bulkiness of the alkoxide groups, direct nucleophilic displacement was difficult and elimination–addition reactions were favored.

We next prepared $TsiSiEtCl_2$ by the reaction of TsiLi with $EtSiCl_3$ in THF. Then $TsiSiEtCl_2$ and $TsiSiBuCl_2$[11] were treated for several hours with 2 M or 1.5 M NaOR/ROH. The obtained products $(Me_3Si)_2CHSiEt(OR)_2$ and $(Me_3Si)_2CHSiBu(OR)_2$ showed that all the chlorine ligands have been displaced with alkoxide reagents. Table II shows details of the results.

The suggested mechanism for these reactions is shown in Scheme 2. These reactions confirmed the fragmentation mechanism that have been proposed by Eaborn,[8,9] and some new organosilicon compounds were prepared.



SCHEME 2

EXPERIMENTAL

Solvents and Reagents

The reactions involving organolithium reagents and alkoxides were carried out under dry argon to exclude oxygen and moisture from the reaction systems. Solvents were dried by standard methods.

Spectra

^{1}HNMR and ^{13}CNMR spectra were run on a Bruker 400 MHz spectrometer at room temperature using $CDCl_3$ as a solvent containing

TABLE II Reaction of TsiSiXCl_2 With Alkoxides

TsiSiXCl_2	Alkoxide solution	Time (h)	Product	Yield (%)
TsiSiEtCl_2	EtONa/EtOH (2.0M)	24	$(Me_3Si)_2$CHSiEt$(OEt)_2$	48
TsiSiEtCl_2	^{n}BuONa/^{n}BuOH (1.5M)	48	$(Me_3Si)_2$CHSiEt$(O^nBu)_2$	58
TsiSiEtCl_2	$PhCH_2ONa/PhCH_2OH$ (1.5 M)	72	$(Me_3Si_2$CHSiEt$(OCH_2Ph)_2$	47
TsiSiBuCl_2	^{n}PrONa/^{n}PrOH (2.0 M)	48	$(Me_3Si)_2$CHSiEt$(O^nPr)_2$	35
TsiSiBuCl_2	^{i}PrONa/^{i}PrOH (2.0 M)	48	$(Me_3Si)_2$CHSiBu$(O^iPr)_2$	45

tetramethyl silane as a reference. Mass spectra were obtained by the use of a Shimadzu QP-100X spectrometer at 70 eV. Elemental analyses were carried out with a Heareus CHN-ORAPID instrument. The melting point was determined on an electrothermal 9100-digital apparatus.

Reaction of TsiSi(C_6H_4Me-*p*)MeI With NaO^{n}Pr/^{n}PrOH

A solution of TsiSi(C_6H_4Me-*p*)Mel (0.2 g, 0.4 mmol) in 2.5 M NaO^{n}Pr/^{n}PrOH (50 mL) was refluxed for 5 days and then added to water. Extraction was carried out with n-hexane (50 mL) and the organic layer was washed several times with water. The organic layer was separated, dried (Na_2SO_4), filtered, and evaporated. The liquid residue was purified by TLC (silicagel, 4:1 dichloromethane:n-hexane as an eluent) to give $(Me_3Si)_2$CHSi(C_6H_4Me-*p*)Me(O^{n}Pr).

^{1}HNMR ($CDCl_3$), −0.28 (s, 1H, CH), 0.21 (s, 18H, Me_3Si), 0.42 (s, 3H, SiMe), 0.85 (t, 3H, CH_3), 1.5 (m, 2H, CH_2), 2.4 (s, 3H, Me-aryl), 3.5 (t, 3H, OCH_2), 7.2–7.5 ppm (m, 4H, aryl-H); ^{13}CNMR ($CDCl_3$): −2.3 (1C, CH), 0.11 (6C, $SiMe_3$), 1.8 (1C, SiMe), 20.5 (1C, Me-aryl), 24.7 (1C, CH_3), 49.9 (1C, CH_2), 63.7 (1C, OCH_2), 127.4–132.5 ppm (6C, aryl); m/z (EI): 352 (2%, $[M]^+$), 337 (30%, $[M\text{-}Me]^+$), 265(77%), 131 (100%), 73 (10%).

Reaction of TsiSi(C_6H_4Me-*p*)MeI With NaO^{i}Pr/^{i}PrOH

TsiSi(C_6H_4Me-*p*)MeI (0.2 g, 0.4 mmol) was refluxed in 2.5 M NaO^{i}Pr/^{i}PrOH (50 mL) for 18 days. n-Hexane (50 mL) was added and the organic layer washed several times with water. The organic layer was separated, dried (Na_2SO_4), filtered, and evaporated. The liquid residue was purified by TLC (silicagel, 4:1 dichloromethane:n-hexane as an eluent) to give $(Me_3Si)_2$CHSi(C_6H_4Me-*p*)Me(O^{i}Pr).

^{1}HNMR ($CDCl_3$), −0.23 (s, 1H, CH), 0.22 (s, 18H, Me_3Si), 0.42 (s, 3H, SiMe), 1.1 (d, 6H, CH_3), 2.4 (s, 3H, Me-aryl), 3.9 (m, 1H, OCH), 7.2–7.5 ppm (m, 4H, aryl-H); ^{13}CNMR ($CDCl_3$): −1.7 (1C, CH), 0.18

(6C, $SiMe_3$), 2.5 (1C, SiMe), 21.1 (1C, Me-aryl), 24.6 (2C, CH_3), 64.1 (1C, OCH), 127–138 ppm (6C, aryl); m/z (EI): 351 (3%, $[M-1]^+$), 337 (25%, $[M-Me]^+$), 265(79%), 223 (100%), 131 (80%).

Reaction of TsiSi(C_6H_4Me-*p*)MeI With $NaO^nBu/^nBuOH$

A solution of TsiSi(C_6H_4Me-*p*)MeI (0.2 g, 0.4 mmol) in 2.5 M $NaO^nBu/^nBuOH$ (50 mL) was refluxed for 6 days. Then n-hexane (50 mL) was added and the organic layer washed several times with water. The organic layer was separated, dried (Na_2SO_4), filtered, and evaporated. The liquid residue was purified by TLC (silicagel, 4:1 dichloromethane:n-hexane as an eluent) to give $(Me_3Si)_2CHSi(C_6H_4Me$-*p*)Me(O^nBu).

^{1}HNMR ($CDCl_3$), −0.38 (s, 1H, CH), 0.21 (s, 18H, Me_3Si), 0.42 (s, 3H, SiMe), 0.91 (t, 3H, CH_3), 1.3–1.5 (m, 4H, $CH_2—CH_2$), 2.4 (s, 3H, Me-aryl), 3.6 (t, 3H, OCH_2), 7.3–7.5 ppm (m, 4H, aryl-H); ^{13}CNMR ($CDCl_3$): −2.3 (1C, CH), 0.15 (6C, $SiMe_3$), 2.4 (1C, SiMe), 12.9 (1C, CH_3), 18.4 (1C, CH_2), 20.5 (1C, Me-aryl), 33.7 (1C, CH_2), 61.6 (1C, OCH_2), 127.5–138.5 ppm (6C, aryl); m/z (EI): 366 (10%, $[M]^+$), 351 (5%, $[M-Me]^+$), 293 (22%), 131 (100%), 73 (10%).

Reaction of TsiSi(C_6H_4Me-*p*)MeI With $NaOCH_2Ph/PhCH_2OH$

TsiSi(C_6H_4Me-*p*)MeI (0.2 g, 0.4 mmol) was refluxed in 2.5 M $NaOCH_2Ph/PhCH_2OH$ (50 mL) for 20 days. The mixture then was worked up, extracted with n-hexane (50 mL), and washed several times with water. The organic layer was separated, dried (Na_2SO_4), filtered, and evaporated. The liquid residue was purified by TLC (silicagel, 4:1 dichloromethane:n-hexane as an eluent) to give $Me_3SiCH_2Si(C_6H_4Me$-*p*)Me(OCH_2Ph).

^{1}HNMR ($CDCl_3$), −0.12 (s, 2H, $SiCH_2$), 0.022 (s, 9H, Me_3Si), 0.41 (s, 3H, SiMe), 2.4 (s, 3H, Me-aryl), 4.6 (s, 2H, OCH_2), 7.2–7.5 ppm (m, 9H, aryl-H); m/z (EI): 328 (2%, $[M]^+$), 313 (10%, $[M—Me]^+$), 241(12%), 131 (100%), 91 (62%).

Reaction of TsiSi(C_6H_4Me-*p*)MeI With $NaO^iAm/^iAmOH$

A solution of TsiSi(C_6H_4Me-*p*)MeI (0.2 g, 0.4 mmol) in 2.5 M $NaO^iAm/^iAmOH$ (50 mL) was refluxed for 10 days. Then n-hexane (50 mL) was added and the organic layer washed several times with water. The organic layer was separated, dried (Na_2SO_4), filtered, and evaporated. The liquid residue was purified by TLC (silicagel, 5:1

dichloromethane:n-hexane as an eluent) to give $Me_3SiCH_2Si(C_6H_4Me\text{-}p)Me(O^iAm)$.

^{1}HNMR ($CDCl_3$), −0.49 (s, 2H, $SiCH_2$), 0.07 (s, 9H, Me_3Si), 0.41 (s, 3H, SiMe), 0.89 (d, 6H, CH_3), 1.3 (m, 2H, CH_2), 1.6 (m, 1H, CH), 2.4 (s, 3H, Me-aryl), 3.6 (t, 2H, OCH_2), 7.3–7.5 ppm (m, 4H, aryl-H); ^{13}CNMR ($CDCl_3$): −2.34 (1C, $SiCH_2$), 0.12 (3C, $SiMe_3$), 2.4 (1C, SiMe), 18.9 (2C, CH_3), 21.1 (1C, CH), 22.5 (1C, Me-aryl), 40.6 (1C, CH_2), 60.1 (1C, OCH_2), 127.5–138.2 ppm (6C, aryl); m/z (EI): 294 (50%, $[M\text{-}Me]^+$), 223 (68%, $[M\text{-}O^iAm]^+$), 131 (100%), 105 (58%), 73 (72%).

Preparation of $TsiSiEtCl_2$

$EtSiCl_3$ (8.17 g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (50 mL) that had been made by the reaction of TsiH (11.5 g, 50 mmol) with MeLi (0.84 g, 120 mmol). The mixture was refluxed for 30 min, aqueous NH_4Cl was added, and the organic layer was extracted with Et_2O. The extract was dried (Na_2SO_4), filtered, and evaporated. The solid residue was recrystallized from EtOH to give $TsiSiEtCl_2$ (62%), m.p. 308°C.

^{1}HNMR ($CDCI_3$) 0.34 (s, 27H, Me_3Si), 1–1.25 ppm (m, 5H, CH_2CH_3); ^{13}CNMR ($CDCl_3$) 1.7 (1C, C—$SiMe_3$), 3.8 (9C, Me_3Si), 6.0 (1C, CH_3), 16.2 ppm (1C, CH_2); m/z (EI): 344 (100%, $[M\text{-}Me]^+$), 330 (5%, $[M\text{-}Et]^+$), 140 (5%), 128 (20%), 73 (20%). (Found: C, 39.8; H, 8.8. $C_{12}H_{32}Cl_2Si_4$Calc.: C,40.1; H, 8.9%).

Reaction of $TsiSiEtCl_2$ With NaOEt/EtOH

$TsiSiEtCl_2$ (1 g, 2.78 mmol) was refluxed in 2 M NaOEt/EtOH (50 mL) for 24 h and added to n-hexane (50 mL). The organic layer was washed several times with water and separated. Then the organic layer was dried (Na_2SO_4), filtered, and evaporated. The liquid residue was purified by TLC (silicagel, 9:1 n-hexane:dichloromethane as eluent) to give $(Me_3Si)_2CHSiEt(OEt)_2$.

^{1}HNMR ($CDCl_3$), −0.62 (s, 1H, SiCH), 0.12 (s, 18H, Me_3Si), 0.51–1.5 (m, 5H, Et), 1–1.5 (m, 6H, Me-C), 3.6 ppm (q, 4H, OCH_2); ^{13}CNMR ($CDCl_3$): 0.12 (1C, SiCH), 1.9 (6C, $SiMe_3$), 5.8, 10.3 (2C, Et), 31.3 (2C, Me), 59.2 ppm (2C, OCH_2); m/z (EI): 306 (45%, $[M]^+$), 305 (83%, $[M\text{-}1]^+$), 291 (100%, $[M\text{-}Me]^+$), 277 (40%), 217 (32%), 159 (49%), 144 (55%), 73 (22%). (Found: C, 50.5; H, 10.4. $C_{13}H_{34}Si_3$ Calc.: C, 51.0; H, 11.1%).

Reaction of $TsiSiEtCl_2$ With $NaO^nBu/^nBuOH$

A solution of $TsiSiEtCl_2$ (1 g, 2.78 mmol) in 1.5 M $NaO^nBu/^nBuOH$ (50 ML) was refluxed for 48 h. n-Hexane (50 mL) was added and the organic layer washed several times with water. The n-hexane solution was separated, dried (Na_2SO_4), filtered, and evaporated. The liquid residue was purified by TLC (silicagel, 2:3 n-hexane:dichloromethane as an eluent) to give $(Me_3Si)_2CHSiEt(O^nBu)_2$.

^{1}HNMR ($CDCl_3$), −0.45 (s, 1H, SiCH), 0.11 (s, 18H, Me_3Si), 0.65 (q, 2H, $SiCH_2$), 0.86–1.2 (m,17H, Si—C—Me and O—C—$CH_2CH_2CH_3$), 3.7 ppm (t, 4H, OCH_2); ^{13}CNMR ($CDCl_3$): −1.4 (1C, SiCH), 1.7 (6C, $SiMe_3$), 5.1, 12.8 (2C, Si-Et), 6.1, 18, 33.8, 61 ppm (8C, OBu); m/z (EI): 278 (2%, $[M]^+$), 348 (52%, $[M\text{-}Me]^+$), 333 (59%, [M-Et]+), 219 (75%), 216 (74%), 203 (100%), 187 (68%), 73 (50%).

Reaction of $TsiSiEtCl_2$ with $NaOCH_2Ph/PhCH_2OH$

$TsiSiEtCl_2$ (1 g, 2.78 mmol) was refluxed in 1.5 M $NaOCH_2Ph/PhCH_2OH$ (50 mL) for 72 h, and then added to n-hexane (50 mL). The organic layer was washed several times with water, and then separated. The organic layer was dried (Na_2SO_4), filtered, and evaporated to give a liquid an residue. The latter was subjected to TLC (silicagel, 7:1 n-hexane:dichloromethane as an eluent) to give $(Me_3Si)_2CHSiEt(OCH_2Ph)_2$.

^{1}HNMR ($CDCl_3$), −0.65 (s, 1H, SiCH), 0.12 (s, 18H, Me_3Si), 0.6–1.4 (m, 5H, Et), 4.3 (s, 4H, OCH_2), 7.2–8.1 ppm (m, 10H, aryl-H); ^{13}CNMR ($CDCl_3$): 0.03 (1C, SiCH), 1.6 (6C, $SiMe_3$), 5.1, 10.5 (2C, Si-Et), 49.2 (2C, OCH_2), 127.6–137.2 ppm (12C, aryl); m/z (El): 415 (10%, $[M\text{-}Me]^+$), 401 (8%, $[M\text{-}Et]^+$), 400 (22%), 323 (38%), 339 (20%), 91 (100%), 73 (53%).

Reaction of $TsiSiBuCl_2$ With $NaO^nPr/^nPrOH$

A solution of $TsiSiBuCl_2$ (1 g, 2.66 mmol) in 2 M $NaO^nPr/^nPrOH$ (50 ML) was refluxed for 48 h. The solution was added to n-hexane (50 Ml) and the organic layer washed several times with water. The organic layer was separated, dried (Na_2SO_4), filtered, and evaporated. The residue was purified by TLC (silicagel, 9:2 n-hexane:dichloromethane as an eluent) to give $(Me_3Si)_2CHSiBu(O^nPr)_2$.

^{1}HNMR ($CDCl_3$), −0.6 (s, 1H, CH), 0.12 (s, 18H, Me_3Si), 0.5–1.5 (m, 19H, Bu and O—C—CH_2CH_3), 4.2 ppm (t, 3H, OCH_2); m/z (El): 362 (2%, $[M]^+$), 347 (10%, $[M\text{-}Me]^+$), 305 (24%, $[M\text{-}Bu]^+$), 263 (50%), 187 (65%), 73 (100%). (Found: C, 56.9; H, 11.2. $C_{17}H_{42}O_2Si_3$ Calc.: C, 56.3;H,11.6%).

Reaction of $TsiSiBuCl_2$ With $NaO^iPr/PrOH$

A solution of $TsiSiBuCl_2$ (1 g, 2.66 mmol) in 2 M $NaO^iPr/^iPrOH$ (50 mL) was refluxed for 48 h. The solution was added to n-hexane (50 mL) and the organic layer washed several times with water. The organic layer was separated, dried (Na_2SO_4), filtered, and evaporated to give a liquid residue. The latter was purified by TLC (silicagel, 9:1 n-hexane:dichloromethane as an eluent) to give $(Me_3Si)_2CHSiBu(O^iPr)_2$.

^{1}HNMR ($CDCl_3$), −0.64 (s, 1H, CH), 0.13 (s, 18H, Me_3Si), 0.5–1.5 (m, 21H, Bu and O—C—CH_3), 4.1 ppm (m, 2H, OCH); m/z (EI): 347 (15%, $[M\text{-}Me]^+$), 305 (22%, $[M\text{-}Bu]^+$), 263(49%), 246(25%), 189 (62%), 73 (100%). (Found: C, 55.8; H, 12.1. $C_{17}H_{42}O_2Si_3$ Calc.: C, 56.3; H, 11.6%).

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