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MIGRATORY APTITUDE OF SUBSTITUENTS ON SILICON ATOMS OF DISILYLCARBENES

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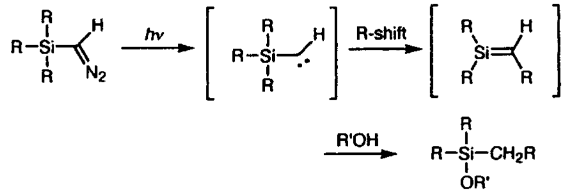
Photolysis of (dimethylphenylsilyl)(trimethylsilyl)diazomethane in *t*-BuOH yielded three different *t*-BuO-substituted (silylalkyl)silanes. The migratory aptitude of substituents from the silicon atoms to the carbenic center was found to be in the order Ph : Me (on phenyl-substituted Si) : Me (on TMS) = 3·8 : 1·0 : 1·0, the opposite of that reported for monosilylcarbenes. The photolysis of (1-phenyl-1-silacyclobutyl)(trimethylsilyl) diazomethane gave two silyl-substituted silacyclobutanes and one ring-expanded silacyclopentane. Again, the migratory aptitude of substituents was in the order Ph : ring-methylene : Me = 4·5 : 1·4 : 1·0, showing that the ring shifts faster than Me and also Ph shifts faster than any alkyl substituent.

INTRODUCTION

The 1,2-shift of substituents at the α-position of carbenes to form alkenes is one of the well known features of carbene reactions.[1] Silylcarbenes are not an exception and they undergo the substituent shift to form silenes which, in the presence of appropriate nucleophiles such as alcohols, finally produce (alkoxysilyl)alkanes [equation (1)].[2] Ando *et al.*[3] reported that the migratory aptitude of substituents on the silicon atom of monosilylcarbenes, which were photolytically generated from the corresponding diazomethanes [equation (2)], was in the order of Me : Ph = 47 : 19 and Me : $PhCH_2$ = 57 : 12. Also reported was the facile migration of a silyl group on a disilanyl substituent.[4] In their system, however, only two substituents can be compared at a time. On the other hand, Philip and Keating[5] examined a similar non-silicon system, i.e. 1-methyl-1-phenylethylcarbene, for which they found the relative migratory aptitude of substituents was Ph : Me = 50 : 9, the opposite of the order found by Ando *et al.*[3] for silylcarbenes.



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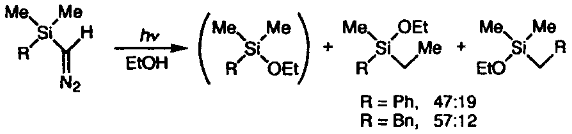
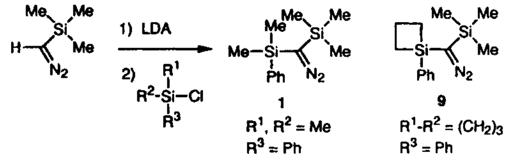


(2)

To compare more than two substituents at a time, both monosilylcarbenes bearing three different groups on a single silicon atom and disilylcarbenes bearing more than two different groups on the silicon atoms seem to be appropriate models for the purpose. We chose the latter model (carbenes **2** and **10**) and, contrary to our initial expectation, obtained a different result, on which we report here.

RESULTS AND DISCUSSION

Disilyldiazomethanes **1** and **9** were prepared by the reaction of trimethylsilyldiazomethane and chlorosilanes [equation (3)].[6,7] A solution of diazomethane **1** or **9** in a mixed solvent of *t*-BuOH and Et_2O (1 : 1) was placed in a Pyrex tube, bubbled with a stream of argon and irradiated at 0 °C for 3 h using a high-pressure mercury lamp. The product mixture was analyzed by both ^1H NMR and VPC methods.



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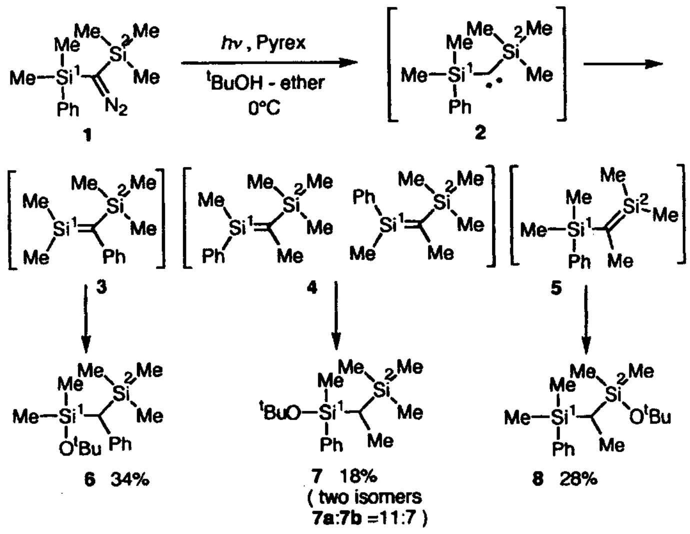
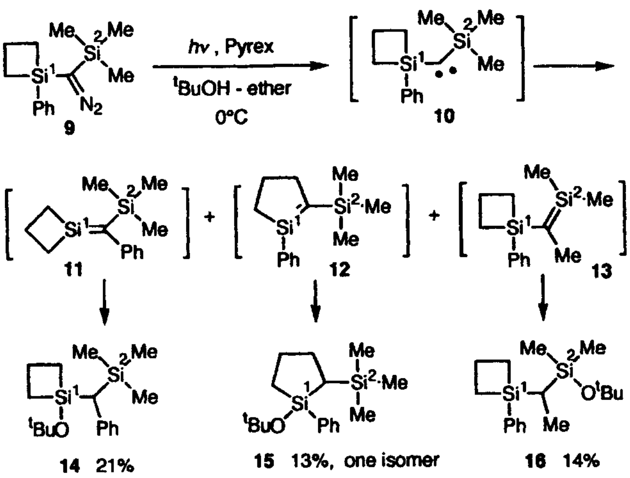
The photolysis reaction of (dimethylphenylsilyl)(trimethylsilyl)diazomethane (**1**) gave three products, dimethyl(1′,1′-dimethylethoxy)[(trimethylsilyl)(phenyl)methyl]silane (**6**), methyl(1′,1′-dimethylethoxy)[1-(trimethylsilyl)ethyl](phenyl)silane (mixture of diastereomers **7a** and **7b** in the ratio 11 : 7) and dimethyl(1′,1′-dimethylethoxy)[1-(dimethylphenylsilyl)ethyl]silane (**8**), in 34, 18 and 28% yields, respectively (Scheme 1). Their formation can be explained in terms of the intermediacy of silenes which were produced from disilylcarbene **2** via the 1,2-shift of substituents from one of the silicon atoms to the carbene center.The relative migratory aptitude of substituents on two silicon atoms, calculated from the product yields, is Ph : Me on Si-1 : Me on Si-2 = 3·8 : 1·0 : 1·0, showing that the phenyl group migrates faster than the methyl group. This represents the opposite aptitude to that reported for monosilylcarbenes.[3] The formation of two isomers **7a** and **7b** indicates that the 1,2-shift of a methyl groups from Si-1 produced both *E*- and *Z*-isomers of silene **4** in the same ratio 11 : 7, followed by a stereospecific *syn*-addition of *t*-BuOH to **4** to give the two isomers of **7**.

In addition to two different types of methyl substituents and a phenyl substituent, a strained silacycloalkyl substituent also seems worth comparing with methyl substituents to evaluate the effect of ring strain. The photolysis reaction of (1-phenyl-1-silacyclobutyl)-(trimethylsilyl)diazomethane (**9**) in the presence of *t*-BuOH gave three products, 1-(1′,1′-dimethylethoxy)-[(trimethylsilyl)(phenyl)methyl]silacyclobutane (**14**), 1-(1′,1′-dimethylethoxy)-1-phenyl-2-(trimethylsilyl)silacyclopentane (**15**) (one isomer, because silene **12** exists only in the Z-form and, therefore, the *syn* addition of *t*-BuOH produces only one adduct) and 1-[(1′,1′-dimethylethoxy)(dimethyl)silyl]ethyl-1-phenylsilacyclobutane (**16**), in 21, 13 and 14% yields, respectively (Scheme 2). The ring-enlarged silacyclopentane **15** was evidently formed by the rearrangement of the silacyclobutane ring of carbene **10** to produce silacyclopentene **12** followed by the addition of *t*-BuOH. Based on the product yields, the relative migratory aptitude of substituents on the two silicon atoms of **10** can be calculated to be Ph : ring-methylene : Me = 4·5 : 1·4 : 1·0, indicating that the ring-methylene on Si-1 shifts faster than the methyl group on Si-2 to some extent. However, the phenyl group on Si-1 again migrates faster than any of the alkyl substituents.

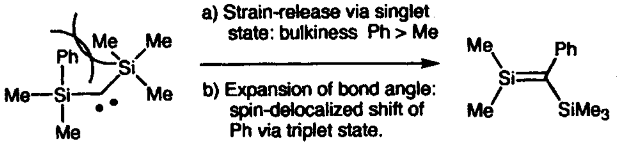
An intriguing result of the present study is undoubtedly the reversal of the order of migrating groups in comparison with Ando *el al.*'s observation[3] for monosilylcarbenes. A rational reason for this reversal is the steric effect: (a) to relieve the steric congestion in the disilylcarbene **2** or **10** whose ground state may be singlet,[8] a bulkier phenyl group migrates faster than a relatively small methyl group and, consequently, the transition state of the phenyl migration lies at a lower energy level than that of the methyl migration (Scheme 3); also in this transition state, a positive charge of the carbene *p*-orbital can be well delocalized; (b) another plausible explanation is that the steric congestion may alter the electronic configuration of the carbene center, lowering the energy gap between the singlet and triplet states, to favor the spin-delocalized migration of the phenyl group via the triplet state.



Scheme 1



Scheme 2



Scheme 3

EXPERIMENTAL

General. (Dimethylphenylsilyl)(trimethylsilyl)diazomethane (**1**) was prepared by the reaction of trimethylsilyldiazomethane (1·48 mmol), lithium diisopropylamide (LDA, 1·60 mmol) and chlorodimethylphenylsilane (1·24 mmol) in anhydrous diethyl ether at 0 °C. After the chromatography on an alumina column, **1** was obtained in 83% yield. (1-Phenyl-1-silacyclobutyl)(trimethylsilyl)diazo-methane (**9**) was prepared by reaction with chloro(phenyl)silacyclobutane similarly to that described above for **1** (37%).

Photolysis reaction of disilyldiazomethanes 1 and 9. A solution of diazomethane **1** or **9** in a mixed solvent of *t*-BuOH and Et_2O (1 : 1) was placed in a Pyrex tube, bubbled with a stream of argon and irradiated at 0 °C for 3 h using a high-pressure mercury lamp. The product mixture was analyzed by both ^1H NMR and VPC methods. The products were separated by silica gel chromatography with hexane as eluent and their spectral data are as follows.

Dimethyl(1,1-dimethylethoxy)-{[1-(trimethylsilyl)-1-phenyl]methyl}silane (6). ^1H NMR (300 MHz, $CDCl_3$), δ 0·03 (s, 3H), 0·05 (s, 9H), 0·17 (s, 3H) 1·29 (s, 9H), 1·45 (s, 1H), 7·00–7·06 (m, 3H), 7·16–7·21 (m, 2H); ^{13}C NMR (75·6 MHz, $CDCl_3$), δ −0·15, 2·33, 3·06, 9·96, 31·99, 72·58, 123·03, 127·73, 129·01, 142·64; IR (liquid film), 2900–3000 (m), 1600 (w), 1495 (w), 1365 (w), 1250 (m), 1195 (m), 1010–70 (m), 820–880 (m), 770 (w), 700 (w), 690 (w) cm^{-1}. Analysis (mixture of **6**, **7a** and **7b**): calculated for $C_{16}H_{30}OSi_2$, C 65·23, H 10·26; found, C 65·17, H 10·39%.

Methyl(1,1-dimethylethoxy)[1-(trimethylsilyl)ethyl] phenylsilane (7a, major diastereomer. ^1H NMR (300 MHz, $CDCl_3$) δ −0·01 (s, 9H), 0·11 (q, $J = 7·5$ Hz, 1H), 0·45 (s, 3H), 0·86 (d, $J = 7·5$ Hz, 3H), 1·19 (s, 9H), 7·32–7·38 (m, 3H), 7·53–7·61 (m, 2H). Diastereomer **7b** (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ −0·10 (s, 9H), −0·01 (q, $J = 7·5$ Hz, 1H), 0·48 (s, 3H), 0·98 (d, $J = 7·5$ Hz, 3H), 1·22 (s, 9H), 7·31–7.38 (m, 3H), 7·55–7·58(m, 2H).

Dimethyl(1,1-dimethylethoxy)[1-(dimethylphenylsilyl) ethyl]silane (8). ^1H NMR (300 MHz, $CDCl_3$), δ 0·08 (s, 6H), 0·12 (q, $J = 7·5$ Hz, 1H), 0·35 (s, 3H), 0·36 (s, 3H), 1·00 (d, $J = 7·5$ Hz, 3H), 1·26 (s, 9H), 7·34–7·37 (m, 3H), 7·55–7.58 (m, 2H); ^{13}C NMR (75·6 MHz, $CDCl_3$), δ −3·36, −1·61, 1·42, 2·08, 8·35, 9·21, 32·00, 72·13, 127·40, 128·35, 133·79, 140·57; IR (liquid film), 2920–3000 (m), 1250 (m), 1198 (m), 1108 (m), 1045 (m), 1020 (m), 830 (m), 812 (m), 775 (m), 698 (m) cm^{-1}; CIMS *m*/*z* (relative intensity, %) 295 (MH$^+$, 18), 279 (42), 223 (71), 161 (100). Analysis calculated for $C_{16}H_{30}OSi_2$, C 65·23, H 10·26; found, C 65·47; H 10·47%.

1-(1,1-Dimethylethoxy){[1-(trimethylsilyl)-1-phenyl] methyl}silacyclobutane (**14**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0·073 (s, 9H), 1·06 (m, 1H), 1·29 (m, 4H), 1·38 (s, 9H), 1·61 (s, 1H), 1·91 (m, 1H), 7·01–7·11 (m, 3H), 7·17–7·26 (m, 2H); ^{13}C NMR (75·6 MHz, $CDCl_3$), δ −0·70, 12·96, 21·45, 22·35, 29·86, 31·88, 73·62, 123·05, 127·76, 128·55,141·34; IR (liquid film), 2900–3000 (m), 1600 (w), 1495 (m), 1365 (m), 1250 (m), 1195 (m), 1125 (m), 1045 (m), 1025 (m), 865 (m), 840 (m), 700 (m) cm^{-1}; EIMS, *m*/*z* (relative intensity, %) 306 (M$^+$, 8), 250 (57), 235 (22), 207 (52), 179 (24), 159 (100); HRMS (EI), calculated for $C_{17}H_{30}OSi_2$ (M$^+$) 306·1827, found 306·1830. Analysis (mixture of **14**, **15** and **16**): calculated for $C_{17}H_{30}OSi_2$, C 66·60; H 9·86; found, C 66·62, H 1·03%.

1-(1,1-Dimethylethoxy)-2-(trimethylsilyl)-1-phenylsilacyclopentane (**15**). ^{1}H NMR (300 MHz, $CDCl_3$), δ −0·28 (s, 9H), 0·08 (m, 1H), 0·95 (m, 2H), 1·30 (m, 1H), 1·34 (s, 9H), 1·58 (m, 1H), 2·03 (m, 1H), 2·12 (m, 1H), 7·31–7·37 (m, 3H), 7·59–7·65 (m, 2H); ^{13}C NMR (75·6 MHz, $CDCl_3$), δ −1·11, 13·09, 17·62, 27·23, 28·47, 32·14, 72·88, 127·32, 129·08, 134·44, 139·43; IR (liquid film), 2900–3000 (m), 1365 (m), 1245 (m), 1195 (m), 1115 (m), 1050 (m), 1030 (m), 895 (w), 835 (m), 760 (w), 735 (w), 700, (m) cm^{-1}; CIMS, *m*/*z* (relative intensity, %) 307 (MH$^+$, 27), 251 (21), 235 (78), 173 (100); HRMS (CI), calculated for $C_{17}H_{30}OSi_2$ (MH$^+$) 307·1905, found 307·1900.

1-{1-]Dimethyl(1,1-dimethylethoxy)silyl]ethyl}-1-phenylsilacyclobutane (**16**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0·025 (s, 3H), 0·029 (s, 3H), 0·40 (q, $J = 7·5$ Hz, 1H), 1·14 (d, $J = 7·5$ Hz, 3H), 1·19 (s, 9H), 1·30 (m, including $J = 7·8$, 8·4, 9·3 and 10·2 Hz, 4H), 2·00 (ttd, $J = 8·4$, 9·3 and 12·6 Hz, 1H), 2·23 (ttd, $J = 7·8$, 10·2 and 12·6 Hz, 1H), 7·30–7·39 (m, 3H), 7·63–7·68 (m, 2H); ^{13}C NMR (75·6 MHz, $CDCl_3$), δ 1·31, 1·70, 8·49, 9·81, 13·37, 13·79, 18·09, 31·90, 71·02, 127·48, 128·76, 133·92, 134·98; IR (liquid film), 2900–3000 (m), 2830 (m), 1365 (m), 1250 (m), 1200 (m), 1050 (m), 1025 (m), 1000 (w), 838 (m), 775 (m), 700 (m) cm^{-1}; CIMS, *m*/*z* (relative intensity, %) 307 (MH$^+$, 27), 251 (42), 235 (18), 221 (19), 207 (25), 173 (100); HRMS (CI), calculated for $C_{17}H_{30}OSi_2$ (MH$^+$) 307·1905, found 307·1895.

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