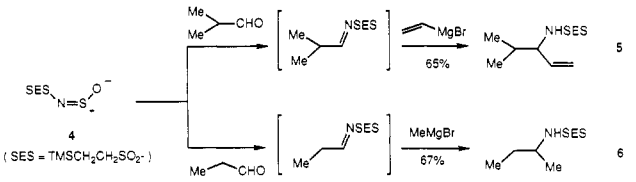
**Scheme I**




It is also possible to effect these reactions with other *N*-sulfinyl sulfonamides. We recently introduced the (β-(trimethylsilyl)ethyl)sulfonyl (SES) group as an easily removable amine-protecting function.[10] As shown in Scheme I, SES-protected sulfonamides **5** and **6** can be prepared by the Grignard addition procedure starting with *N*-sulfinyl compound **4**.[11]

There are a number of advantages of this procedure over existing methodology. The imines produced are highly electrophilic and react with all types (alkyl, aryl, allylic, acetylenic) of Grignard and organolithium compounds. The reaction products are N-protected primary amines rather than secondary amines as is often the case in the additions of organometallics to imines.[1-4] It is unnecessary to preform and isolate the imine in our method, and the entire procedure is easily conducted in one pot starting from any aldehyde. We believe that this is an efficient solution to the longstanding problem of addition of organometallics to imines.

## Experimental Section

**General Experimental Procedure.** To an oven-dried, two-necked 25-mL flask fitted with a syringe cap and an argon inlet was added 3 mL of dry $CH_2Cl_2$ followed by *N*-sulfinyl-*p*-toluenesulfonamide (0.45 mmol, 98 mg) in 2 mL of dry $CH_2Cl_2$. The alkyl aldehyde (0.3 mmol) was added via syringe, and the reaction mixture was stirred for 1–2 h at room temperature. The reaction mixture was kept between 20 and 30 °C while the organometallic reagent (0.9 mmol) was added slowly via syringe. The mixture was stirred for 1 h, was added to 50 mL of saturated NaCl solution, and was extracted with ethyl acetate (2 × 40 mL). The combined organic extract was dried over $MgSO_4$ and concentrated in vacuo, and the product was purified by preparative TLC on silica gel. Isolated yields of pure sulfonamides are shown in Table I.

The reaction of aromatic aldehydes followed the above procedure except that after addition of the aldehyde the reaction mixture was cooled to 0 °C, $BF_3{\cdot}Et_2O$ (0.06 mmol) was added via syringe, and the resulting solution was stirred for 5–6 h at 0 °C. The reaction mixture was then warmed to room temperature, and the organometallic reagent was added as above.

**Acknowledgment.** This work was supported by the National Institutes of Health (CA-34303).

**Registry No.** **3** (R = Et, R′ = Me), 23705-40-0; **3** (R = Et, R′ = Bu), 124070-38-8; **3** (R = Et, R′ = $-CH{=}CH_2$), 124070-39-9; **3** (R = Et, R′ = Ph), 70197-09-0; **3** (R = $Me_2CH$, R′ = Me), 110871-40-4; **3** (R = $Me_2CH$, R′ = $-CH{=}CH_2$), 124070-40-2; **3** (R = $Me_2CH$, R′ = $-C{\equiv}CBu$), 124070-41-3; **3** (R = $Me_2CH$, R′ = Ph), 110871-37-9; **3** (R = $Me_2CH$, R′ = $-CH_2CH{=}CH_2$), 124070-42-4; **3** (R = Ph, R′ = Me), 4809-56-7; **3** (R = Ph, R′ = Bu), 124070-43-5; **3** (R = Ph, R′ = $-C{\equiv}CBu$), 124070-44-6; **3** (R = Me, R′ = $-CH{=}CH_2$), 78388-18-8; **3** (R = Me, R′ = $CH_2TMS$), 124070-45-7; **3** (R = furanyl, R′ = $CH_2TMS$), 124070-46-8; **3** (R = naphthyl, R′ = $CH_2CH{=}CH_2$), 124070-47-9; **4**, 115534-34-4; **5**, 124070-48-0; **6**, 124070-49-1; $H_3CCH_2CHO$, 123-38-6; $Me_2CHCHO$, 78-84-2; MeCHO, 75-07-0; PhCHO, 100-52-7; $BuC{\equiv}CLi$, 17689-03-1; $TMSCH_2MgCl$, 13170-43-9; *N*-sulfinyl-*p*-toluenesulfonamide, 4104-47-6; 2-furancarboxaldehyde, 98-01-1; 2-naphthalenecarboxaldehyde, 66-99-9.

**Supplementary Material Available:** Preparative TLC elution solvents, physical properties, and $^1H$ and $^{13}C$ NMR, IR, and mass spectral data for the compounds in Table I and Scheme I (8 pages). Ordering information is given on any current masthead page.

(10) Weinreb, S. M.; Demko, D. M.; Lessen, T. A.; Demers, J. P. *Tetrahedron Lett.* **1986**, *27*, 2099.

(11) The *N*-sulfinyl compound was prepared from $Me_3SiCH_2CH_2SO_2NH_2$ by using the *N*-sulfinylbis(imidazole) procedure of Kim and Shin: Kim, Y. H.; Shin, J. M. *Tetrahedron Lett.* **1985**, *26*, 3821.

# Convenient Synthesis of Silylketenes from 1-*tert*-Butoxy-2-silylethynes

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## Introduction

Silkylketenes (**1**) exhibit unique characteristics among the aldoketenes. They are thermally stable and do not show any tendency to undergo thermal polymerization, yet are reactive toward appropriate counterparts.[1]

(Trimethylsilyl)ketene (**1a**)[2] is the only member of this family of compounds whose chemistry has been studied in detail.[3] Since the early work of Ruden[4] it is known that **1a** behaves as a powerful acylating agent toward hindered amines and alcohols and that it undergoes Wittig olefination reaction with stabilized phosphorus ylides leading to allenes. Further development of the chemistry of this compound by Brady and co-workers[5] has focused on the study of the reactivity of the ketene group and on its use in 2 + 2 cycloaddition reactions with electron-rich alkenes and aldehydes.[6]

Although alternative methods have been developed,[7] the usual preparation of **1a** follows the original procedure involving the silylation of ethoxyethyne and the thermal elimination of ethylene at 120 °C.[2,4] Two important drawbacks of this methodology are the limited stability of ethoxyethyne and the relatively high temperature required for the thermal generation of the ketene. Moreover, the ready attack of nucleophiles on the triple bond of

(1) For a review on organometallic derivatives of ketenes, see: Moreau, J.-L. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; pp 400–405.

(2) (a) Shchukovskaya, L. L.; Pal'chik, R. I.; Lazarev, A. N. *Dokl. Akad. Nauk. SSSR* **1965**, *164*, 357.

(3) For the preparation of other silylketenes, see: (a) Shchukovskaya, L. L.; Kol'tsov, A. I.; Lazarev, A. N; Pal'chik, R. I. *Dokl. Akad. Nauk. SSSR* **1968**, *179*, 892. (b) Kostyuk, A. S.; Dudukina, O. V.; Burlachenko, G. S.; Baukov, I. Y.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1969**, *39*, 467. (c) Brady, W. T.; Cheng, T. C. *J. Organomet. Chem.* **1977**, *137*, 287. (d) Danheiser, R. L.; Sard, H. *J. Org. Chem.* **1980**, *45*, 4810. (e) Jabry, Z.; Lasne, M.-C.; Ripoll, J.-L. *J. Chem. Res.*, Synop. **1986**, *188*.

(4) Ruden, R. A. *J. Org. Chem.* **1974**, *39*, 3607.

(5) (a) Brady, W. T.; Owens, R. A. *Tetrahedron Lett.* **1976**, 1553. (b) Brady, W. T.; Saidi, K. *Tetrahedron Lett.* **1978**, 721. (c) Brady, W. T.; Saidi, K. *J. Org. Chem.* **1979**, *44*, 733. (d) Brady, W. T.; Saidi, K. *J. Org. Chem.* **1980**, *45*, 727.

(6) For other synthetic applications of (trimethylsilyl)ketene, see: (a) Zaitseva, G. S.; Baukov, Y. I.; Mal'tsev, V. V.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1974**, *44*, 1415. (b) Zaitseva, G. S.; Bogdanova, G. S.; Baukov, Y. I.; Lutsenko, I. F. *J. Organomet. Chem.* **1976**, *121*, C21. (c) Taylor, R. T.; Cassell, R. A. *Synthesis* **1982**, 672.

(7) (a) Lutsenko, I. F.; Baukov, Y. I.; Kostyuk, A. S.; Saveyalava, N. I.; Krysina, V. K. *J. Organomet. Chem.* **1969**, *17*, 241. (b) Kostyuk, A. S.; Dudukina, O. V.; Burlachenko, G. S.; Baukov, Y. I.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1969**, *39*, 467.

0022-3263/90/1955-0395$02.50/0 

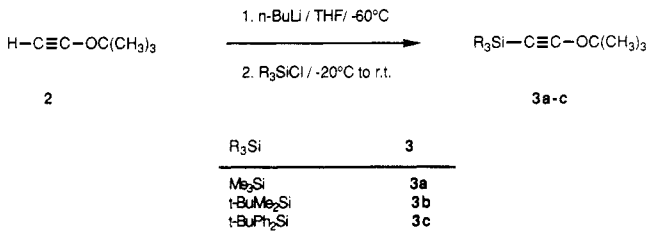
1-ethoxy-1-alkynes[8] renders problematic the in situ generation of **1a** from 1-ethoxy-2-(trimethylsilyl)ethyne.

Recent studies by our group[9] have shown that *tert*-butoxyethyne (**2**)[10] can be a convenient alternative for the widely used ethoxyethyne in many of its synthetic applications. The main differential features of **2** and its derivatives are the increased shielding of the triple bond, which prevents polymerization and nucleophilic attacks, and the enhancement of the rate of thermally induced elimination of olefin,[11] which allows the generation of ketenes at much lower temperatures.

In the present paper we report on the use of **2** as starting material for the preparation of silylketenes via the corresponding 1-*tert*-butoxy-2-silylalkynes (**3**). We also show that 1-*tert*-butoxy-2-(trimethylsilyl)ethyne can act as a convenient in situ source of (trimethylsilyl)ketene, which, in turn, can be efficiently trapped by nucleophiles.

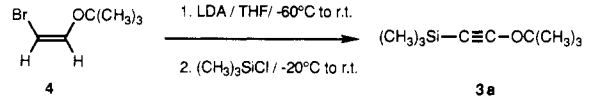
## Results and Discussion

The C-silylation of *tert*-butoxyethyne (**2**) was carried out by standard methodology, leading to the 1-*tert*-butoxy-2-silylethynes **3a–c** in 80–90% yield.



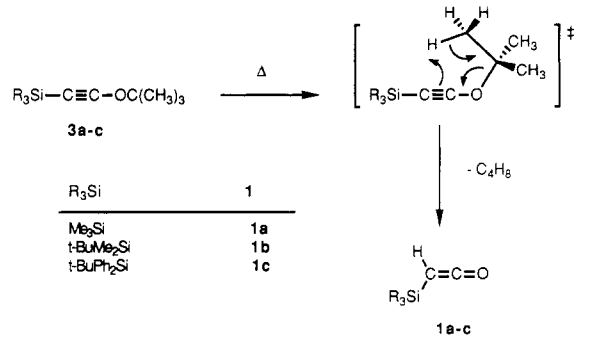

| $R_3Si$ | 3 |
|---|---|
| $Me_3Si$ | **3a** |
| t-$BuMe_2Si$ | **3b** |
| t-$BuPh_2Si$ | **3c** |

The silyl derivatives **3** can also be obtained by a one-pot $\beta$-elimination/silylation process from (*Z*)-1-bromo-2-*tert*-butoxyethene (**4**), the synthetic precursor of **2**, which in turn can be readily prepared from ethyl vinyl ether at the 0.5-mol scale.[10] Thus, **3a** was readily prepared from **4** in 74% overall yield in a single operation.



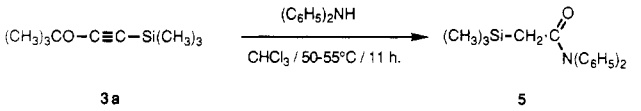

The thermally induced elimination of 2-methylpropene from **3a–c** should lead to the silylketenes **1a–c**. Owing to the differences of volatility which could be anticipated for these species, the experimental conditions were designed in each case to allow an easy isolation of the ketene product.

The preparation of the volatile **1a** was carried out by elimination with simultaneous distillation from a high-boiling solvent such as decalin.[12] Although the decomposition of **3a** was almost instantaneous at 100–110 °C, and previous experiments in other solvents ($CHCl_3$) had shown that no product other than **1a** was formed in the process, the isolated yield of **1a** was only 63%, very similar to that reported from 1-ethoxy-2-(trimethylsilyl)ethyne. At this point, we decided to take advantage from the very important steric shielding of the triple bond in **3a** by the bulky silyl and alkoxy groups, which could allow an in situ generation of **1a** in the presence of nucleophiles leading to trimethylsilylacetylation without nucleophilic addition to the triple bond of the precursor **3a**. In this context, it is important to recall that the easy nucleophilic addition of amines to ethoxyethyne does not take place at all in the case of **2**.[8,9b]




| $R_3Si$ | 1 |
|---|---|
| $Me_3Si$ | **1a** |
| t-$BuMe_2Si$ | **1b** |
| t-$BuPh_2Si$ | **1c** |

Thus, when a chloroform solution of **3a** was heated at 50–55 °C for 11 h in the presence of diphenylamine, *N,N*-diphenyl(trimethylsilyl)acetamide (**5**) was obtained in practically quantitative yield.




The preparation of **1b** and **1c** could be performed in a simpler way. Thus, when neat **3b** was heated at 80 °C for 2 h (observable gas evolution ceased after 90 min) and the residue was vacuum distilled, a quantitative yield of **1b** was obtained. On the other hand, the preparation of **1c** was achieved by heating under reflux for 2 h a solution of **3c** in benzene. After solvent evaporation and vacuum distillation, a 91% yield of **1c** was obtained.

Both **1b** and **1c** behave as very stable compounds at room temperature. In addition, it is worth noting the thermal stability of **1c**, which can be heated at 150–200 °C without any appreciable decomposition.

In conclusion, the reported methodology represents a convenient alternative to the preparation of silylketenes from 1-ethoxy-2-(trimethylsilyl)acetylene: The pyrolysis of the *tert*-butoxy derivatives can be conducted at lower temperatures, the readily available (*Z*)-1-bromo-2-*tert*-butoxyethene can be used as starting material, and, due to the steric shielding of the triple bond in the intermediate 1-*tert*-butoxy-2-silylethynes (**3**), the silylketenes can be in situ generated and trapped by nucleophiles. Silylketenes bearing bulky silyl groups can offer interesting possibilities for the stereoselective formation of C–C bonds,[5c] and the intermediate 1-*tert*-buxoxy-2-silylethynes can advantageously replace 1-ethoxy-2-(trimethylsilyl)ethyne in other synthetic applications.[13]

## Experimental Section

**Materials and Methods.** All $^1H$ and $^{13}C$ NMR $\delta$ values (ppm) refer to $Me_4Si$ as internal (**1c**, **3c**) or external (**1a**, **1b**, **3a**, **3b**, **5**) standard. Melting points and boiling points are uncorrected. THF was distilled from sodium benzophenone ketyl prior to use. (*Z*)-1-Bromo-2-*tert*-butoxyethene (**4**) and *tert*-butoxyethyne (**2**) were prepared by the previously described procedures.[10] Trimethylsilyl chloride was purified by distillation under $N_2$ prior to use; *tert*-butyldimethylsilyl chloride and *tert*-butyldiphenylsilyl chloride were used as received.

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(9) (a) Pericàs, M. A.; Serratosa, F.; Valentí, E. *Synthesis* **1985**, 1118. (b) Valentí, E.; Pericàs, M. A.; Seratosa, F.; Mañà, D., submitted for publication.

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(11) Moyano, A.; Pericàs, M. A.; Serratosa, F.; Valentí, E. *J. Org. Chem.* **1987**, *52*, 5532.

(12) Generation of (trimethylsilyl)ketene from neat **3a**, analogously to what reported (ref 4 and 5c) from 1-ethoxy-2-(trimethylsilyl)ethyne, generally led to poorer results.

(13) Kita, Y.; Akai, S.; Ajimura, N.; Yoshigi, M.; Tsugoshi, T.; Yasuda, H.; Tamura, Y. *J. Org. Chem.* **1986**, *51*, 4150.

**[(1,1-Dimethylethoxy)ethynyl]trimethylsilane (3a). Method A.** To a mixture of *n*-BuLi (25 mL, 1.6 M in hexane, 0.040 mol) and THF (30 mL) under Ar was added *tert*-butoxyethyne (**2**) (4.41 g, 0.045 mol) in THF (10 mL) at −50 °C with stirring. The mixture was allowed to warm up to room temperature for 45 min, and trimethylsilyl chloride (5.0 mL, 0.040 mol) was then added at −20 °C. The mixture was stirred for 60 min while warming up to room temperature and added to a mixture of petroleum ether (50 mL) and saturated aqueous $NH_4Cl$ (50 mL). The organic layer was separated, washed with phosphate buffer (pH 7) and water, and dried over $Na_2SO_4$. Evaporation of solvents and excess **2** at room temperature afforded **3a** (6.80 g, 100%), suitable as starting material for further transformations. The compound can be distilled at room temperature (0.5 mm Hg), by collecting the distillate at −78 °C to afford 5.43 g (0.032 mol, 80% yield) of spectroscopically pure **3a**, as colorless liquid.

**Method B.** To a solution of lithium diisopropylamide, prepared from *n*-BuLi (69 mL, 1.6 M in hexane, 0.11 mol) and diisopropylamine (17.5 mL, 0.124 mol), in THF (100 mL) under Ar was added (*Z*)-1-bromo-2-*tert*-butoxyethene (**4**) (8.95 g, 0.050 mol)[10] in THF (20 mL) at −60 °C. The mixture was stirred for 2 h while allowing to warm up to room temperature and then cooled to −20 °C, and trimethylsilyl chloride (7.6 mL, 0.060 mol) was then added. After 8 h of stirring at room temperature, the reaction mixture was poured onto saturated aqueous $NaHCO_3$ (100 mL), the organic layer was separated, and the aqueous layer was washed with petroleum ether (50 mL). The combined organic extracts were washed with 0.5 N HCl (2 × 100 mL), water (150 mL), and saturated brine (150 mL) and dried ($Na_2SO_4$). Solvent evaporation at room temperature afforded 6.33 g (0.037 mol, 74%) of **3a** suitable as starting material for further transformations: IR ($CCl_4$) $\nu_{max}$ 3000, 2970, 2180, 2120, 1400, 1370, 1270, 1250, 1210, 1160, 850, 700, 650 $cm^{-1}$; $^1H$ NMR (60 MHz, $CL_4$) $\delta$ 1.20 (s, 9 H, $(CH_3)_3CO$), 0.00 (s, 9 H, $(CH_3)_3Si$) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$) $\delta$ 106.55 (≡*C*O), 86.69 ($(CH_3)_3C$), 39.92 (≡*C*Si), 26.89 ($(CH_3)_3C$), 0.79 ($(CH_3)_3Si$) ppm; MS *m/e* (relative intensity) 170 (0.1), 155 (8), 114 (16), 99 (100), 73 (9), 57 (42).

**[(1,1-Dimethylethoxy)ethynyl](1,1-dimethylethyl)dimethylsilane (3b).** The compound was prepared by method A, as described for the preparation of **3a**. Starting from 3.92 g (0.040 mol) of **2**, 4.52 g (0.030 mol) of *tert*-butyldimethylsilyl chloride in THF (10 mL) was used in the silylation step. An additional 4-h stirring time at room temperature was introduced in this step. After workup and solvent evaporation, 6.73 g of crude **3b** were obtained. By filtration through a short pad (3.0 g) of $Et_3N$–$SiO_2$ (2.5% v/v), eluting with petroleum ether (250 mL), 6.28 g (0.0296 mol, 99%) of spectroscopically pure **3b** were obtained as a pale yellow oil: IR ($CCl_4$) $\nu_{max}$ 3000, 2970, 2940, 2910, 2890, 2870, 2180, 2120, 1480, 1470, 1420, 1400, 1380, 1270, 1260, 1160, 1010, 940, 850, 680, 620 $cm^{-1}$; $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 1.20 (s, 9 H, $(CH_3)_3CO$), 0.88 (s, 9 H, $(CH_3)_3CSi$), 0.00 (s, 6 H, $(CH_3)_2Si$) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$) $\delta$ 106.73 (≡*C*O), 86.67 ($(CH_3)_3CO$), 37.88 (≡*C*Si), 26.95 ($(CH_3)_3CO$), 26.18 ($(CH_3)_3CSi$), 16.79 ($(CH_3)_3CSi$), −3.87 ($(CH_3)_2Si$) ppm; MS *m/e* (relative intensity) 156 (4), 141 (2), 99 (100), 85 (3), 73 (5), 57 (2), 43 (8).

**[(1,1-Dimethylethoxy)ethynyl](1,1-dimethylethyl)diphenylsilane (3c).** The compound was prepared by method A, as described for the preparation of **3a**. Starting from 2.94 g (0.030 mol) of **2**, 5.50 g (0.020 mol) of *tert*-butyldiphenylsilyl chloride in THF (5 mL) was used in the silylation step. An additional 24-h stirring time at room temperature was introduced in this step. After workup and solvent evaporation, 6.99 g of crude **3c** was obtained. By dissolving the crude material in pentane and crystallization at −15 °C, 2.82 g of pure **3c** separated as pale yellow crystals. The mother liquor was filtered through a short pad (5.0 g) of $Et_3N$–$SiO_2$ (2.5% v/v), eluting with petroleum ether (250 mL) to afford, after evaporation, an additional 2.69-g fraction (combined yield 82%) of **3c**: mp 63–65 °C dec; IR ($CCl_4$) $\nu_{max}$ 3070, 3050, 2990, 2960, 2930, 2890, 2860, 2170, 2110, 1470, 1460, 1430, 1390, 1370, 1270, 1150, 1110, 1100, 1000, 700, 630, 610 $cm^{-1}$; $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 7.98–7.15 (m, 10 H, Ar H), 1.50 (s, 9 H, $(CH_3)_3CO$), 1.05 (s, 9 H, $(CH_3)_3CSi$) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$) $\delta$ 135.58 ($C_{ar}$-H), 134.95 ($C_{ar}$-Si), 129.04 ($C_{ar}$-H), 127.47 ($C_{ar}$-H), 109.62 (≡*C*O), 87.82 ($(CH_3)_3CO$), 36.32 (≡*C*Si), 27.19 ($(CH_3)_3CO$), 18.71 ($(CH_3)_3CSi$), 16.79 ($(CH_3)_3CSi$) ppm; MS *m/e* (relative intensity) 280 (0.4), 223 (100), 180 (4), 164 (3), 154 (2), 118 (8), 105 (7), 79 (2). Anal. Calcd for $C_{22}H_{28}OSi$: C, 78.52; H, 8.38. Found: C, 78.84; H, 8.38.

**(Trimethylsilyl)ethenone (1a).** 1-*tert*-Butoxy-2-(trimethylsilyl)ethyne (**3a**) (5.15 g, 0.0302 mol) was slowly added over a 2-h period to decalin (2 mL) at 100–110 °C, with simultaneous distillation. The collected (trimethylsilyl)ketene was further purified by distillation at 77–9 °C (lit.[4] bp 81–82 °C) to afford 2.16 g (63%) of pure **1a**: IR ($CCl_4$) $\nu_{max}$ 3050, 2980, 2130, 1280, 1260, 1060, 860, 630 $cm_{-1}$; $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 1.65 (s, 1 H, *H*C=C=O), 0.12 (s, 9 H, $(CH_3)_3Si$) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$) $\delta$ 179.45 (C=*C*=O), 0.54 ($(CH_3)_3Si$), −0.25 (*C*=C=O) ppm; MS *m/e* (relative intensity) 115 (44), 114 (4), 99 (25), 73 (100), 57 (21), 43 (25).

**In Situ Generation and Trapping of 1a: *N*,*N*-Diphenyl-2-(trimethylsilyl)acetamide (5).** A solution of **3a** (1.87 g, 0.011 mol) and diphenylamine (1.69 g, 0.010 mol) in acid-free chloroform (25 mL) was heated at 50–55 °C for 11 h. The solvent and excess **1a** were removed under vacuum to afford **5** (2.76 g, 98%). The product was further purified by vacuum distillation at 125 °C (0.1 mmHg) to afford 2.33 g (82%) of pure **5** as a viscous oil: IR ($CCl_4$) $\nu_{max}$ 3060, 3030, 1670, 1600, 1500, 1450, 1420, 1300, 1250, 1180, 1140, 1100, 1080, 1030, 1010, 860 $cm^{-1}$; $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 7.45–6.70 (m, 10 H, Ar H), 1.80 (s, 2 H, $CH_2$), 0.02 (s, 9 H, $(CH_3)_3CSi$) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$) $\delta$ 172.80 (*C*=O), 134.04 ($C_{ar}$-N), 129.04 ($C_{ar}$-H), 120.59 ($C_{ar}$-H), 117.57 ($C_{ar}$-H), 27.16 ($CH_2$), −0.93 ($CH_3$) ppm; MS *m/e* (relative intensity) 189 (17), 147 (100), 133 (5), 99 (8), 73 (42).

**[(1,1-Dimethylethyl)dimethylsilyl]ethenone (1b).** Neat **3b** (6.02 g, 0.0284 mol) was heated at 80 °C. A gas evolution was observed which ceased after 90 min. Heating was continued for 30 min, the reaction mixture was then cooled, and the product was distilled under vacuum at room temperature to afford 4.46 g (100%) of **1b**. Analytically pure **1b** was obtained by redistillation at 50 °C (16 mmHg) (88%): IR ($CCl_4$) $\nu_{max}$ 3040, 3020, 2960, 2930, 2900, 2880, 2860, 2110, 1470, 1390, 1360, 1270, 1260, 1250, 1220, 1060, 1010, 940, 840, 670 $cm^{-1}$; $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 1.60 (s, 1 H, *H*C=C=O), 0.90 (s, 9 H, $(CH_3)_3CSi$), 0.09 (s, 6 H, $(CH_3)_2Si$) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$) $\delta$ 179.96 (C=*C*=O), 25.86 ($(CH_3)_3CSi$), 17.60 ($(CH_3)_3CSi$), −3.29 (*C*=C=O), −4.56 ($(CH_3)_2Si$) ppm; MS *m/e* (relative intensity) 156 (3), 141 (1), 99 (100), 85 (2), 73 (4), 69 (5), 57 (2). Anal. Calcd for $C_8H_{16}OSi$: C, 61.48; H, 10.32. Found: C, 61.40; H, 10.54.

**[(1,1-Dimethylethyl)diphenylsilyl]ethenone (1c).** A solution of **3c** (1.68 g, 0.0050 mol) in benzene (50 mL) was heated under reflux for 2 h. After cooling, benzene was removed under reduced pressure and the residue was submitted to high vacuum distillation at 150 °C (0.08 mmHg) to afford 1.27 g of analytically pure **1c** (91%): IR ($CCl_4$) $\nu_{max}$ 3060, 3040, 3010, 2950, 2920, 2880, 2850, 2110, 1480, 1470, 1460, 1420, 1390, 1360, 1170, 1110, 1010, 1000, 820, 720, 700, 620, 610 $cm^{-1}$; $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 7.75–7.10 (m, 10 H, Ar H), 2.07 (s, 1 H, *H*C=C=O), 1.03 (s, 9 H, $(CH_3)_3CSi$) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$) $\delta$ 178.54 (C=*C*=O), 135.61 ($C_{ar}$-H), 133.78 ($C_{ar}$-Si), 129.62 ($C_{ar}$-H), 122.78 ($C_{ar}$-H), 27.15 ($(CH_3)_3CSi$), 19.09 ($(CH_3)_3CSi$), −3.63 (*C*=C=O) ppm; MS (*relative* intensity) 280 (0.5), 223 (100), 192 (5), 181 (6), 165 (9), 155 (3), 117 (12), 105 (11), 79 (3), 77 (4), 57 (5). Anal. Calcd for $C_{18}H_{20}OSi$: C, 77.09; H, 7.19. Found: C, 77.12; H, 7.52.

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**Supplementary Material Available:** $^1H$ and $^{13}C$ NMR spectra of compounds **3a** and **3b** (4 pages). Ordering information is given on any current masthead page.