Silver(I)-Catalysed Protiodesilylation of 1-(Trimethylsilyl)-1-alkynes

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A procedure for protiodesilylation of 1-(trimethylsilyl)-1-alkynes that involves the use of catalytic amounts of $AgNO_3$ and does not require the employment of KCN is described. This procedure allows for chemoselective deprotection of 1-(trimethylsilyl)-1-alkynes containing α-(trimethylsilyl)benzyl moieties, *tert*-butyldiphenylsilyl alkyl ethers or *tert*-butyldimethylsilyl aryl ether groups. However, it causes complete desilylation of 1-(trimethylsilyl)-1-alkynes characterised by a primary alcoholic group protected as a *tert*-butyldimethylsilyl ether. Interestingly, compounds that contain this last functional group can also furnish the corresponding alcohols by treatment with a catalytic amount of aqueous HNO_3.

Introduction

Several methods for the synthesis of 1-alkynes involve the preparation of 1-(trimethylsilyl)-1-alkynes followed by protiodesilylation of these silyl-protected compounds.[1] In general the protiodesilylation reaction can be effected by treatment of compounds **1** (Figure 1) with a large molar excess of a fluoride ion donor, typically $KF·2H_2O$ in DMF or methanol,[2] NH_4F in methanol[1a] or tetrabutylammonium fluoride (TBAF) in THF,[1c,1i,3] or with a molar excess of an oxygenated base in a protic solvent such as K_2CO_3 in methanol,[1d,4] $CaCO_3$ in methanol,[5] KOH in methanol[6] or sodium methoxide in methanol.[7,8] However, these procedures sometimes suffer from selectivity problems when used to remove trimethylsilyl groups from compounds **1** that are labile under basic conditions.[1k,9,10] For instance, treatment of silylalkyne **2** with KOH in methanol or with TBAF in THF provides allene **3** instead of the corresponding 1-alkyne.[1k]

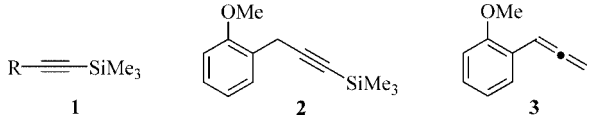
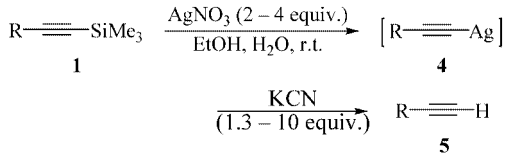


Figure 1. Chemical structures of compounds **1**, **2**, and **3**.

In 1967, Schmidt and Arens[10] reported a procedure allowing these problems to be overcome. This procedure, subsequently frequently employed for selective protiodesilylation of variously functionalised 1-(trimethylsilyl)-1-alkynes,[1i,1k,11] involves treatment of these compounds with a large molar excess of $AgNO_3$, usually in ethanol/water solution at room temperature, followed by treatment of the formed silver acetylides with a large molar excess of aqueous KCN (Scheme 1).



Scheme 1. Silver(I)-promoted deprotection of compounds **1**.

However, in spite of its synthetic utility, this procedure suffers from the disadvantages due to the use of large amounts of expensive $AgNO_3$ and toxic KCN, and so we decided to begin a study aimed at exploring the possibility of performing the protiodesilylation reaction of compounds **1** efficiently and selectively in the presence of a catalytic amount of a silver compound without use of a metal cyanide. Here we report the results of this study.

Results and Discussion

We first explored the silver-catalysed protiodesilylation of commercially available 1-(trimethylsilyl)ethynylbenzene (**1a**) under a variety of experimental conditions. In particular, as shown in Table 1, we performed this reaction at room temperature: *i)* in acetone containing a known amount of water or methanol, *ii)* in methanol, or *iii)* in acetone containing water and/or a carboxylic acid such as acetic acid or trifluoroacetic acid. We also examined the effects due to the nature and the molar amount either of the silver compound used as catalyst or of the carboxylic acid present in some silver-catalysed reactions carried out in acetone or in acetone and water.

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We found that $AgNO_3$, $AgOCOCF_3$, $AgBF_4$ and $AgOSO_2CF_3$ were active catalysts for the reaction, but Ag_2O, Ag_2CO_3, $AgHF_2$ and AgI proved to be completely inactive. On the other hand, $AgNO_3$ was the least expensive compound of the active catalysts examined, and use of 10 mol% of this salt allowed us to obtain phenylacetylene (**5a**) in GLC yields higher than those obtained by use of other silver compounds under similar experimental conditions (compare Entry 3 or 4 with Entries 9, 12 and 13, Table 1). In this preliminary experimentation we also found that: *i)* the reaction of **1a** in acetone containing 10 mol% $AgNO_3$ and 10–160 equiv. of water provided **5a** in 88–100% GLC yield, and *ii)* the reaction rate significantly increased when we used 100 equiv. of water instead of 10 equiv. (compare Entries 1 and 4, Table 1), but we noticed that a further increase in the amount of water gave rise to a decrease in the reaction rate even though, at least apparently, the reaction was still homogeneous (compare Entries 4 and 5, Table 1.

Moreover, we observed that protiodesilylation of **1a** could also be efficiently performed in acetone containing 10 mol% $AgNO_3$, 10 equiv. of water and 10 equiv. of trifluoroacetic acid (Entry 18, Table 1) or in dry methanol containing 10 mol% $AgNO_3$ (Entry 22, Table 1).

Having established the feasibility of this catalytic method, we explored its scope by applying the optimal reaction conditions to protiodesilylation of compounds **1b**, **1c**, **1d**, **1e** and **1a** on a 10 mmol scale (Figure 2).

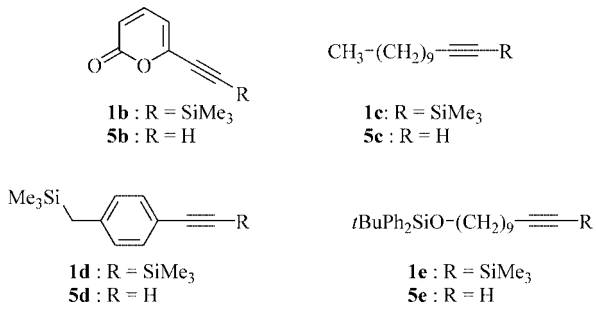
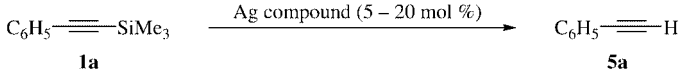


Figure 2. Chemical structures of compounds **1b**–**e** and **5b**–**e**.

Compounds **1b**[1b] and **1c**[12] were prepared by published procedures and compound **1d** was synthesised in 88% yield by treatment of (4-bromobenzyl)trimethylsilane (**6**) with 2 equiv. of (trimethylsilyl)acetylene (**7**) in piperidine at 80 °C for 21 h in the presence of 5 mol% $PdCl_2(PPh_3)_2$, 10 mol% PPh_3 and 10 mol% CuI (Scheme 2). On the other hand, silylalkyne **1e** was synthesised in 77% yield from the corresponding 1-alkyne **5e** by the procedure used for the preparation of **1c** from **5c**.[12]

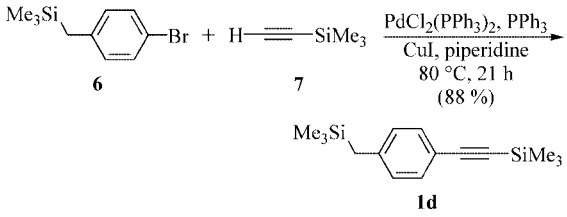
Table 1. Protiodesilylation of compound **1a** in the presence of a catalytic amount of a silver compound.



1a **5a**

Entry[a]	Ag catalyst	(mol %)	Protic co-solvent H_2O (equiv.)	MeOH (equiv.)	R-COOH (equiv.)	Solvent	Reaction time (h)	GLC conversion (%)	GLC yield (%)[b]
1	$AgNO_3$	10	10	–	–	acetone	85	100	88
2	$AgNO_3$	10	20	–	–	acetone	80	100	99
3	$AgNO_3$	10	40	–	–	acetone	47	100	100
4	$AgNO_3$	10	100	–	–	acetone	30	100	98
5	$AgNO_3$	10	160	–	–	acetone	47	100	100
6	$AgNO_3$	20	40	–	–	acetone	22	100	95
7	$AgNO_3$	5	100	–	–	acetone	65	100	95
8	$AgNO_3$	5	40	–	–	acetone	75	100	92
9	$AgOCOCF_3$	10	40	–	–	acetone	120	100	90
10	Ag_2O	10	40	–	–	acetone	45	–	–
11	Ag_2CO_3	10	40	–	–	acetone	45	–	–
12	$AgBF_4$	10	100	–	–	acetone	30	97	93
13	$AgOSO_2CF_3$	10	100	–	–	acetone	22	100	90
14	$AgHF_2$	10	100	–	–	acetone	100	–	–
15[c]	AgI	10	100	–	–	acetone	37[c]	–	–
16	–	–	100	–	(R = CF_3) 1.0	acetone	70	–	–
17	$AgNO_3$	10	–	–	(R = CF_3) 1.1	acetone	50	100	80
18	$AgNO_3$	10	10	–	(R = CF_3) 1.0	acetone	23	100	98
19	$AgNO_3$	10	10	–	(R = CH_3) 1.0	acetone	124	91	85
20	$AgNO_3$	10	–	40	–	acetone	124	79	70
21	$AgNO_3$	10	–	100	–	acetone	75	100	84
22	$AgNO_3$	10	–	solvent	–	MeOH	50	100	95

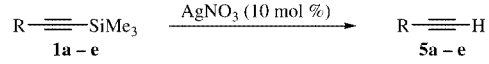
[a] Unless otherwise reported, all these reactions were performed in the dark at room temperature with 2.0 mmol of **1a** dissolved in 15 mL of acetone or methanol. [b] The GLC yield were evaluated with naphthalene as an internal standard. [c] This reaction was performed at room temperature for 21 h and at 55 °C for 16 h.



Scheme 2. Synthesis of compound **1d**.

We found that protiodesilylation at room temperature of compounds **1a**–**e** in acetone containing 10 mol% $AgNO_3$ and 100 equiv. of water occurred in high isolated yields (Entries 1, 3, 4, 6–8, Table 2) and that this reactions was very selective. In fact, under these conditions compound **1d** was converted into **5d** with complete preservation of its α-(trimethylsilyl)benzyl moiety (Entry 6, Table 2). Moreover, a selective reaction also occurred when **1e** underwent protiodesilylation at 45 °C in acetone containing 10 mol% $AgNO_3$ and 100 equiv. of water (Entry 7, Table 2). In fact, GLC and GLC-EI-MS analyses of the crude reaction product showed that it was made up of a 98:2 mixture of **5e** and **8** (Figure 3).

Table 2. $AgNO_3$-catalysed protiodesilylation of 1-(trimethylsilyl)-1-alkynes **1a**–**e**.[a]



Entry	1-silyl-1-alkyne **1**	Solvent	Protic co-solvent H_2O (equiv.)	Protic co-solvent CH_3COOH (equiv.)	Temperature/ Reaction Time (°C/h)	Product **5**	Isolated yield (%)
1	**1a**	acetone	100	–	20/31	**5a**	91
2	**1b**	acetone	10	1.0	20/21	**5b**	92
3	**1b**	acetone	100	–	20/21	**5b**	87
4	**1c**	acetone	100	–	20/24 then 55/24	**5c**	92
5	**1c**	MeOH	–	–	20/24 then 55/70	**5c**	88
6	**1d**	acetone	100	–	20/43	**5d**	94
7[b]	**1e**	acetone	100	–	45/4	**5e**[b]	94
8[c]	**1e**	acetone	100	–	20/30	**5e**[c]	93

[a] Unless otherwise reported, the reactions were performed in the presence of 10 mol% $AgNO_3$ with 10 mmol of compounds **1** dissolved in 75 mL of solvent. [b] The crude reaction product from this reaction proved to be made up of a 98:2 mixture of **5e** and **8**. [c] This reaction was carried out in the presence of 0.1 equiv. of HNO_3. The corresponding crude reaction product proved to be made up of a 98:2 mixture of **5e** and **8**.

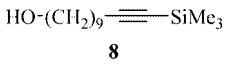


Figure 3. Chemical structure of compound **8**.

This same silver-catalysed reaction could also occur at room temperature with a longer reaction time, but with a result similar to that of Entry 7 of Table 2, when it was performed in acetone containing 100 equiv. of water and 0.1 equiv. of HNO_3 (Entry 8, Table 2).

Interestingly, protiodesilylation of **1b** by treatment with 10 mol% $AgNO_3$ in acetone containing 1 equiv. of trifluoroacetic acid occurred with a yield very similar to that obtained by treatment of **1b** with 10 mol% $AgNO_3$ in acetone containing 100 equiv. of water (compare Entries 2 and 3, Table 2). Moreover, the silver-catalysed protiodesilylation of **1c** could also be efficiently performed in methanol (Entry 5, Table 2).

These good results encouraged us to evaluate the chemoselectivity of our catalytic method more deeply and, in particular, to examine the silver-catalysed protiodesilylation of 1-(trimethylsilyl)alkynes containing a (*tert*-butyldimethylsilyl)oxy group, such as compounds **1f** and **1g** (Figure 4).

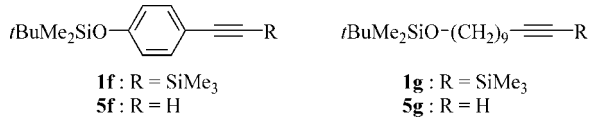
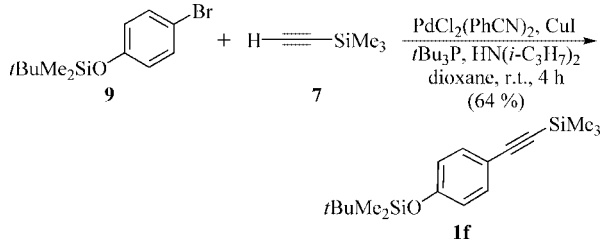


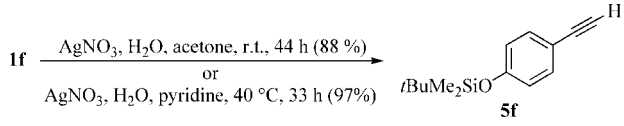
Figure 4. Chemical structures of compounds **1f**, **1g**, **5f**, and **5g**.

Compound **1f** was synthesised in 64% yield by treatment of **9**[13] with **7** in dioxane in the presence of diisopropylamine and catalytic amounts of $PdCl_2(PhCN)_2$, CuI and tri(*tert*-butyl)phosphane[14] (Scheme 3). On the other hand, **1g** was prepared in 71% yield from the corresponding 1-alkyne **5g**[15] by the same procedure as employed for the synthesis of **1c** from **5c**.[12]



Scheme 3. Synthesis of compound **1f**.

Interestingly, treatment of **1f** with 10 mol% $AgNO_3$ in acetone containing 100 equiv. of water at room temperature for 44 h proved to be chemoselective and provided **5f**[16] in 86% isolated yield (Scheme 4). This reaction also gave a small amount of compound **10** (Figure 5), probably originating from the complete protiodesilylation of **1f** due to the acidity developed during the $AgNO_3$-catalysed reaction.



Scheme 4. Chemoselective silver-catalysed protiodesilylation of compound **1f**.

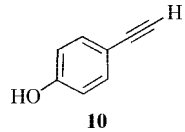
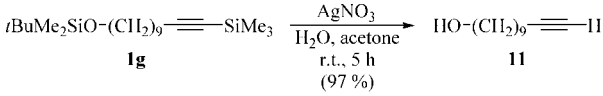


Figure 5. Chemical structure of compound **10**.

In order to avoid the formation of this byproduct, we performed the $AgNO_3$-catalysed protiodesilylation of **1f** in the presence of 0.3 equiv. of pyridine and found that this

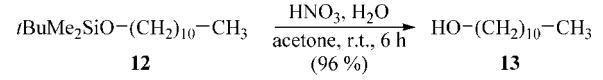
reaction, when carried out in acetone at 40 °C for 33 h in the presence of 60 equiv. of water, gave **5f** in 97% yield with complete chemoselectivity (Scheme 4).

Unfortunately, the catalytic protocol to convert compounds **1a**–**f** selectively into the corresponding 1-alkynes **5a**–**f** proved to be inapplicable to the chemoselective protiodesilylation of **1g**. In fact, we unexpectedly observed that treatment of **1g** with 10 mol% $AgNO_3$ in acetone containing 100 equiv. of water at room temperature for 5 h furnished 10-undecyn-1-ol (**11**) in 97% isolated yield (Scheme 5).



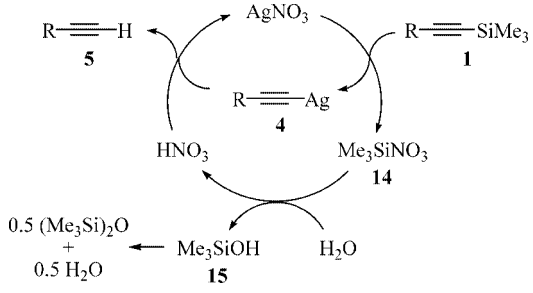
Scheme 5. Silver-catalysed protiodesilylation of compound **1g**.

A possible explanation of this result might be that HNO_3, formed during the removal of the (trimethylsilyl)ethynyl group, causes protiodesilylation of the *tert*-butyldimethylsilyoxy moiety of compound **1g** to give compound **11**. This interpretation was at least in part confirmed by the result of treatment of 1-[(*tert*-butyldimethylsilyl)oxy]undecane (**12**) with 10 mol% of concentrated HNO_3 in acetone containing 100 equiv. of water. In fact, this reaction, which was carried out at room temperature for 6 h, furnished 1-undecanol (**13**) in 96% isolated yield (Scheme 6). It should be noted that, to the best of our knowledge, there are no data reported in the literature on the deprotection of *tert*-butyldimethylsilyl ethers of aliphatic ynols or alkanols by a similar procedure. Moreover, it has recently been reported that the deprotection of *tert*-butyldimethylsilyl alkyl ethers does not proceed in 2 N H_2SO_4, HCl or *p*-toluenesulfonic acid in water at 40 °C despite the presence of excess amounts of the acids.[17]



Scheme 6. HNO_3-catalysed protiodesilylation of compound **12**.

In our opinion the results obtained in the $AgNO_3$-catalysed protiodesilylation of compounds **1** could be explained on the basis of the catalytic cycle reported in Scheme 7.



Scheme 7. Catalytic cycle for the protiodesilylation of compounds **1** in the presence of catalytic amounts of $AgNO_3$.

This cycle implies that treatment of compounds **1** with $AgNO_3$ in acetone and water initially provides silver acetylides **4** and trimethylsilyl nitrate (**14**). Hydrolysis of this last compound could afford trimethylsilanol (**15**) and HNO_3. The reaction of this acid with **4** would then give 1-alkynes **5** and would regenerate $AgNO_3$.

Conclusions

In summary, we have developed a procedure for deprotecting 1-(trimethylsilyl)-1-alkynes **1** involving the use of a catalytic amount of $AgNO_3$ in acetone and water and, unlike a previously reported procedure,[10] not requiring the use of KCN. This new procedure allows for selective deprotection of compounds **1** containing α-(trimethylsilyl)benzyl moieties, *tert*-butyldiphenylsilyl alkyl ethers or *tert*-butyldimethylsilyl aryl ether groups. In contrast, ω-(*tert*-butyldimethylsilyl)oxy-1-(trimethylsilyl)-1-alkynes undergo complete desilylation on treatment with a catalytic amount of $AgNO_3$ in acetone and water. Finally, it is worth mentioning that we have also found that *tert*-butyldimethylsilyl alkyl ethers undergo a very efficient desilylation reaction by treatment with a catalytic amount of HNO_3 in acetone and water at room temperature.

Experimental Section

General Remarks: Precoated Merck 60 F_{254} alumina silica gel sheets were used for TLC. GLC analyses were performed on a Dani GC 1000 instrument with a PTV injector, equipped with a Dani DDS 1000 data station. Two types of capillary columns were used: an Alltech AT-35 bonded FSOT column (30 m × 0.25 mm i.d.) and an Alltech AT-1 bonded FSOT column (30 m × 0.25 mm i.d.). Purifications by MPLC on silica gel (Merck 60 silica gel, particle size 0.015–0.040 nm) were performed on a Büchi B-680 system with a Knauer K-2400 differential refractometer as detector. GLC/EI-MS analyses were performed with a mass selective detector 5973 Network interfaced with an Agilent Technologies 6890N Network GC system. IR spectra were recorded with a Perkin–Elmer 1725 FT-IR spectrophotometer. NMR spectra were recorded with a Varian Gemini 200 MHz spectrometer, with TMS as the internal standard. All reactions involving air- and water-sensitive materials were performed in flame-dried glassware under argon by standard syringe, cannula and septa techniques. The following compounds were prepared by published procedures: $PdCl_2(PPh_3)_2$,[18] $PdCl_2(PhCN)_2$,[18] 6-[(trimethylsilyl)ethynyl]-2*H*-pyran-2-one (**1b**),[1b] 1-(trimethylsilyl)undec-1-yne (**1c**),[12] and 11-[(*tert*-butyldimethylsilyloxy]undec-1-yne (**5g**).[15]

1-(Trimethylsilyl)ethynyl-4-[(trimethylsilyl)methyl]benzene (1d): (4-Bromobenzyl)trimethylsilane (**6**, 3.57 g, 14.7 mmol) and (trimethylsilyl)acetylene (**7**, 2.88 g, 29.4 mmol) were sequentially added to a deaerated mixture of $PdCl_2(PPh_3)_2$ (515 mg, 0.735 mmol), PPh_3 (385 mg, 1.47 mmol) and CuI (280 mg, 1.47 mmol) in piperidine (100 mL) and the mixture was stirred under argon at 80 °C for 21 h. It was then poured into cold water (150 mL), cautiously treated at 0 °C with HCl (6 N, 170 mL) and extracted with Et_2O (6 × 70 mL). The organic extract was washed with water (4 × 60 mL), dried and concentrated under reduced pressure. The residue was purified by MPLC on silica gel with petroleum ether as eluent to give **1d** (3.37 g, 88%) as a pale yellow liquid. ^1H NMR (200 MHz, $CDCl_3$): δ = –0.03 (s, 9 H), 0.25 (s, 9 H), 2.08 (s, 2 H), 6.92 (d, J = 8.4 Hz,

2 H), 7.34 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –1.9 (3 C), 0.1 (3 C), 27.5, 92.8, 105.6, 118.3, 127.8 (2 C), 131.8 (2 C), 141.6 ppm. IR (film): $\tilde{\nu}$ = 2957, 2157, 1503, 1249, 1152, 847, 759 cm^{-1}. EI-MS: m/z (%) = 260 (8) $[M]^+$, 245 (6), 173 (14), 172 (100), 131 (4), 115 (5), 73 (50). $C_{15}H_{24}Si_2$ (260.53): calcd. C 69.15, H 9.29; found C 69.10, H 9.20.

11-[(*tert*-Butyldiphenylsilyl)oxy]undec-1-yne (5e): *tert*-Butyldiphenylsilyl chloride (6.49 g, 23.6 mmol) was added dropwise to a solution of undec-10-yn-1-ol (**11**, 3.32 g, 19.7 mmol) and imidazole (4.02 g, 59.0 mmol) in THF (40 mL) and the mixture was stirred under argon at room temperature for 4 h. It was then poured into cold water (100 mL) and extracted with Et_2O (6 × 80 mL). The organic extract was washed with water (2 × 40 mL), dried and concentrated under reduced pressure. The residue was purified by MPLC on silica gel with a 90:10 mixture of hexane and benzene as eluent to give **5e** (3.55 g, 84%) as a colourless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.05 (s, 9 H), 1.20–1.60 (m, 14 H), 1.91 (t, J = 2.7 Hz, 1 H), 2.17 (dt, J = 7.0, 2.7 Hz, 2 H), 3.65 (t, J = 6.4 Hz, 2 H), 7.35–7.39 (m, 6 H), 7.65–7.69 (m, 4 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 18.4, 19.2, 25.8, 26.9 (3 C), 28.5, 28.8, 29.1, 29.3, 29.6, 32.6, 64.0, 68.1, 84.7, 127.5 (4 C), 129.4 (2 C), 134.1 (2 C), 135.5 (4 C) ppm. IR (film): $\tilde{\nu}$ = 2931, 2856, 2118, 1427, 1111, 702, 614 cm^{-1}. EI-MS: m/z (%) = 349 (14), 271 (10), 200 (18), 199 (100), 183 (24), 181 (13), 123 (16). $C_{27}H_{38}OSi$ (406.69): calcd. 79.74, H 9.42; found C 79.74, H 9.40.

11-[(*tert*-Butyldiphenylsilyl)oxy]-1-(trimethylsilyl)undec-1-yne (1e): A hexane solution of *n*-butyllithium (1.6 M, 7.84 mL, 12.5 mmol) was added dropwise at –78 °C under argon to a stirred solution of compound **5e** (3.40 g, 8.40 mmol) in THF (75 mL). The mixture was stirred for 30 min, and chlorotrimethylsilane (82.06 mL, 16.7 mmol) was then added dropwise. After a further 20 min at –78 °C the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and allowed to warm up to 0 °C. It was then poured into water (200 mL) and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 50 mL) and the combined organic extracts were dried and concentrated under reduced pressure. The residue was purified by MPLC on silica gel with a 90:10 mixture of hexane and benzene as eluent to give **1e** (3.08 g, 77%) as a colourless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.15 (s, 9 H), 1.05 (s, 9 H), 1.20–1.60 (m, 14 H), 2.02 (t, J = 7.0 Hz, 2 H), 3.65 (t, J = 6.7 Hz, 2 H), 7.34–7.39 (m, 6 H), 7.65–7.70 (m, 4 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 0.3 (3 C), 19.3, 19.9, 25.8, 26.9 (3 C), 28.7, 28.8, 29.1, 29.3, 29.5, 32.6, 64.0, 84.2, 107.7, 127.5 (4 C), 129.4 (2 C), 134.1 (2 C); 135.5 (4 C) ppm. IR (film): $\tilde{\nu}$ = 2931, 2174, 1428, 1249, 1111, 842, 701 cm^{-1}. EI-MS: m/z (%) = 421 (20), 272 (24), 271 (100), 203 (14), 199 (13), 195 (22), 193 (23). $C_{30}H_{46}OSi_2$ (478.86): calcd. 75.25, H 9.68; found C 75.19, H 9.61.

{[4-(*tert*-Butyldimethylsilyloxy)phenyl]ethynyl}trimethylsilane (1f): Tri(*tert*-butyl)phosphane (214 μL, 0.86 mmol), a solution of (4-bromobenzyl)trimethylsilane (**6**, 4.10 g, 14.3 mmol) in dioxane (5 mL), (trimethylsilyl)acetylene (**7**, 2.37 mL, 17–1 mmol) and diisopropylamine (1.46 mL, 17.1 mmol) were sequentially added to a mixture of $PdCl_2(PhCN)_2$ (164 mg, 0.43 mmol) and CuI (54 mg, 0.29 mmol) in dioxane (5 mL) and the resulting mixture was stirred under argon at room temperature for 20 h. It was then diluted with AcOEt (100 mL) and filtered through Celite. The filtrate was concentrated under reduced pressure and the residue was purified by MPLC on silica gel with hexane as eluent to give **1f** (2.66 g, 64%) as a pale yellow liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.18 (s, 6 H), 0.23 (s, 9 H), 0.97 (s, 9 H), 6.75 (d, J = 8.8 Hz, 2 H), 7.35 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –4.4, 0.1 (2 C), 18.3, 25.7 (3 C), 92.5, 105.2, 115.9, 120.0 (2 C), 133.4 (2 C), 156.0 ppm. IR (film): $\tilde{\nu}$ = 2158, 1602, 1505, 1262, 910, 865, 841 cm^{-1}. EI-MS: m/z (%) = 304 (34) $[M]^+$, 289 (13), 249 (11), 248 (31), 247 (100), 233 (11), 73 (9).$C_{17}H_{28}OSi_2$ (304.58): calcd. C 67.04, H, 9.27; found C 66.98, H 9.24

11-[(*tert*-Butyldimethylsilyl)oxy]-1-(trimethylsilyl)undec-1-yne (1g): 11-[(*tert*-Butyldimethylsilyl)oxy]undec-1-yne (**5g**, 3.67 g, 12.7 mmol), which was prepared according to the literature[15] from 10-undecyn-1-ol (**11**), was converted into the title compound by the procedure employed for preparation of **1e** from **5e**. The crude reaction product was purified by MPLC on silica gel with hexane as eluent to give **1g** (3.20 g, 71%) as a colourless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.05 (s, 6 H), 0.15 (s, 9 H), 0.94 (s, 9 H), 1.20–1.60 (m, 14 H), 2.21 (t, J = 7.2 Hz, 2 H), 3.60 (t, J = 6.4 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –5.2 (2 C), 0.2 (3 C), 18.4, 19.9, 25.8, 26.0 (3 C), 28.6, 28.8, 29.0, 29.4, 29.5, 32.9, 63.3, 84.2, 107.7 ppm. IR (film): $\tilde{\nu}$ = 2930, 2857, 2175, 1249, 1098, 840, 774 cm^{-1}. EI-MS: m/z (%) = 297 (2), 209 (5), 149 (10), 148 (16), 147 (100), 133 (7), 73 (14). $C_{20}H_{42}OSi_2$ (354.73): calcd. C 67.72, H 11.93; found C 67.62, H 11.87.

1-[(*tert*-Butyldimethylsilyl)oxy]undecane (12): The crude reaction product obtained by treatment of undecan-1-ol (3.45 g, 20.0 mmol) with *tert*-butyldiphenylsilyl chloride according to the procedure employed for the synthesis of **5e** was purified by MPLC on silica gel with hexane as eluent to give **12** (5.39 g, 94%) as a colourless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 6 H), 0.90 (t, J = 6.4 Hz, 3 H), 0.92 (s, 9 H), 1.29 (br. s, 16 H), 1.53 (pseudo-t, J = 6.6 Hz, 2 H), 3.62 (t, J = 6.6 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –5.2, 14.2, 18.4, 22.8, 25.1, 26.0 (3 C), 29.4, 29.5, 29.7 (3 C), 32.0, 33.0, 63.4 ppm. IR (film): $\tilde{\nu}$ = 2927, 2856, 1463, 1255, 1102, 836, 774 cm^{-1}. EI-MS: m/z (%) = 230 (19), 229 (100), 97 (9), 89 (8), 83 (7), 75 (29), 73 (7). $C_{17}H_{38}OSi$ (286.57): calcd. C 71.25, H 13.37; found C 71.19, H, 13.34.

General Procedure for the $AgNO_3$-Catalysed Protiodesilylation of Compounds 1a–g in Acetone and Water: Water (18 mL, 1.0 mol) and $AgNO_3$ (0.17 g, 1.0 mmol) were added to a solution of compound **1** (10.0 mmol) in acetone (75 mL) and the resulting mixture was stirred in the dark at the temperature and for the period of time reported in Table 2 and in Schemes 4 and 5. It was then poured into a saturated aqueous NaCl solution (120 mL) and extracted with Et_2O (6 × 50 mL). The organic extract was washed with brine (3 × 30 mL), dried and concentrated under reduced pressure. The residue was purified by MPLC on silica gel or by fractional distillation. This procedure was employed for preparation of compounds **5a**–**e** (Entries 1, 3, 4, 6–10, Table 2), **5f** (Scheme 4) and **11** (Scheme 5). As shown in Table 2, where the experimental conditions and the yields of protiodesilylation of **5a**–**e** are summarized, compound **5b** was also prepared from the corresponding 1-silyl derivative **1b** by a modification of the general procedure. This modification involved the use of a solution of **1b** (10 mmol) and $AgNO_3$ (0.17 g, 1.0 mmol) in acetone (75 mL) and water (1.8 mL, 0.1 mol) and trifluoroacetic acid (0.77 mL, 0.01 mol, Entry 2, Table 2). On the other hand, protiodesilylation of **1f** (10.0 mmol) was also performed at 40 °C for 33 h in a solution of $AgNO_3$ (0.17 g, 1.0 mmol) in acetone (75 mL), water (10.8 mL, 0.6 mol) and pyridine (24.3 mL, 0.3 mol, Scheme 4). Compound **5e** was also prepared by treatment of **1e** (10 mmol) in acetone (75 mL) with 10 mol% $AgNO_3$, 100 equiv. of water and 0.1 equiv. of HNO_3 (Entry 8, Table 2), and compound **5f** was synthesised by treatment of **1f** in acetone (75 mL) with 10 mol% $AgNO_3$ in the presence of 60 equiv. of water (Scheme 4). The physical and spectral properties of compounds **5a**, **5c** and **11** were in good agreement with those of the corresponding commercially available products, those of **5b**[1b] were

in good agreement with those reported in the literature, and those of **5e** were in good agreement with those of the same compound we had synthesized from **11**.

1-Ethynyl-4-[(trimethylsilyl)methyl]benzene (5d): The crude reaction product from the $AgNO_3$-catalysed protiodesilylation of **1d** (Entry 6, Table 2) was purified by MPLC on silica gel with pentane as eluent to give **5d** (1.77 g, 94%) as a colourless liquid. ^1H NMR (200 MHz, $CDCl_3$): δ = –0.02 (s, 9 H), 2.09 (s, 2 H), 3.01 (s, 1 H), 6.94 (d, J = 7.0 Hz, 2 H), 7.35 (d, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –1.9 (3C), 27.5, 76.1, 84.1, 117.3, 127.9 (2 C), 131.9 (2 C), 141.9 ppm. IR (film): $\tilde{\nu}$ = 3296, 2955, 2107, 1505, 1249, 1152, 851 cm^{-1}. EI-MS: m/z (%) = 188 (37) $[M]^+$, 173 (11), 145 (8), 115 (10), 75 (6), 74 (11), 73 (100). $C_{12}H_{16}Si$ (188.35): calcd. C 76.53, H 8.56; found C 76.49, H 8.49.

1-[(*tert*-Butyldimethylsilyl)oxy]-4-ethynylbenzene (5f): The crude reaction product from the $AgNO_3$-catalysed protiodesilylation of **1f** in acetone and water (Scheme 4) was purified by MPLC on silica gel with hexane as eluent to give **5f** (2.04 g, 88%) as a colourless liquid. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.24 (s, 6 H), 1.02 (s, 9 H), 3.03 (s, 1 H). 6.82 (d, J = 8.8 Hz, 2 H), 7.42 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –4,4 (2 C), 18.2, 25.7 (3 C), 76.4, 83.7, 114.9, 120.1 (2 C), 133.5 (2 C), 156.2 ppm. IR (film): $\tilde{\nu}$ = 2929, 2109, 1602, 1505, 1264, 912, 841 cm^{-1}. EI-MS: m/z (%) = 232 (19) $[M]^+$, 177 (6), 176 (24), 175 (100), 159 (3), 145 (5), 115 (4). $C_{14}H_{20}OSi$ (232.40): calcd. C 72.35, H 8.67; found C 72.19, H 8.51.

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Note Added in Proof (March 10, 2005): While this manuscript was in press, Pale and co-workers published a letter concerning a subject very similar to that of our study [A. Orsini, A. Vitérisi, A. Bodlenner, J.-M. Weibel, P. Pale, *Tetrahedron Lett.* **2005**, *46*, 2259–2262].

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