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A mild access to silver acetylides from trimethylsilyl acetylenes

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Abstract—1-Trimethylsilyl-1-alkynes are selectively converted to the corresponding silver acetylides. Silver nitrate or triflate are used under neutral conditions, allowing other functional groups to remain unaffected.

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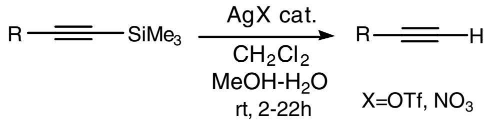
Although still in infancy, silver organic chemistry is gaining interest in the past 5 years.[1] Several reactions involving alkynes and silver salts as catalyst, have indeed been recently described.[2–5] A few examples also make use of silver acetylides in stoichiometric processes.[6–10]

Surprisingly, a single method is so far known to prepare silver acetylides.[10] This method is derived from the old test detecting the presence of terminal alkynes in a structure.[11] An aqueous ammoniacal solution of silver nitrate produces a complex, which reacts with alkynes in a mixture of alcohol and ammoniac, leading to the corresponding silver acetylide which precipitates. If these basic conditions do not interfere with the formation of simple alkyl substituted silver acetylides, such conditions are not always compatible with functionalized alkynes and so far, only a few silver acetylides have been described.[1,6–10]

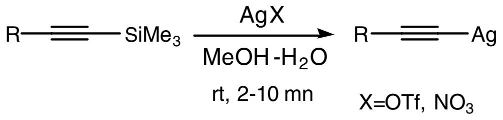
Following works on Pd/Ag-catalyzed cross-coupling reactions,[3–5] we recently set up a Ag-catalyzed selective deprotection of 1-trimethylsilyl-1-alkynes (Scheme 1).[12,13]



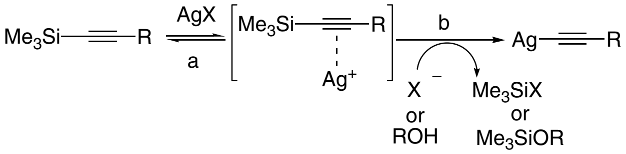
Scheme 1. The Ag-catalyzed deprotection of 1-trimethylsilyl-1-alkynes.

Based on mechanistic investigations of these Ag-catalyzed reactions,[14] we designed and reported here a novel access to silver acetylides from 1-trimethylsilyl-1-alkynes under very mild conditions (Scheme 2).

In both reactions, the first step is probably the formation of a π-complex between the silver salt and the 1-trimethylsilyl-1-alkyne (Scheme 3, step a).[14] This coordination would induce activation of the TMS group toward nucleophilic attack by either the silver counterion or a nucleophilic solvent. This cascade of events would lead to the formation of a silver acetylide (Scheme 3, step b). If these steps can be performed in a solvent in which the silver acetylide is insoluble, the latter should thus be recovered through a simple filtration, giving rise to a novel access to such organometallics.



Scheme 2. Formation of silver acetylides from 1-trimethylsilyl-1-alkynes.



Scheme 3. Mechanistic hypothesis for the formation of silver acetylides from 1-trimethylsilyl-1-alkynes.

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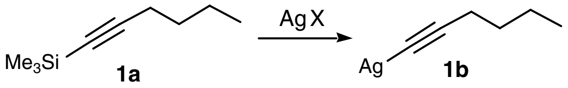
Based on these considerations, we submitted 1-trimethylsilyl-1-alkynes to various silver salts in various conditions.

The commercially available 1-trimethylsilyl-1-hexyne was first used as a model to set up the right conditions (Table 1). In dichloromethane, most of the silver salts were insoluble and no reaction took place (entries 1, 6, 11, 14 and 17). In acetone and protic solvents, silver nitrate was not fully soluble but enough to promote evolution and a white precipitate rapidly formed (entries 2–5). This precipitate proved spectroscopically (^{1}H, ^{13}C, ^{109}AgNMR and IR) identical to 1-hexynyl silver **1b** obtained with the conventional method.[10,14] Methanol and aqueous methanol proved to be the best reaction medium, giving **1b** in good yields (entry 3–4).[15] In contrast, silver triflate is soluble in most solvents; however, the formation of **1b** only occurred in protic solvents (entries 8–10 vs 6–7). The reaction ran equally well in methanol and in mixtures of methanol and water (up to 1-1) but was surprisingly sluggish in water (entries 8–9 vs 10). Other silver salts were not effective for this transformation (entries 11–19). It is worth noting that only 1 equiv of silver salt is required.

In order to study the scope of this new transformation, representative trimethylsilylated alkynes **2a**–**8a** bearing various protecting groups were synthesized[16,17] and submitted to the above-described conditions.[18] The expected silver acetylides **2b**–**8b** were obtained in good to excellent yields, demonstrating that this method is perfectly compatible with various functional groups (Table 2).

Table 1. Formation of 1-hexynyl silver **1b** from 1-trimethylsilyl-1-hexyne in the presence of silver salts in various conditions



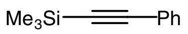
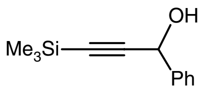
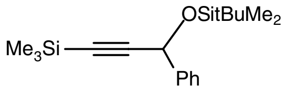
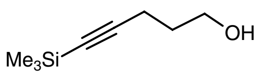
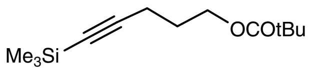
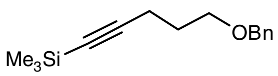
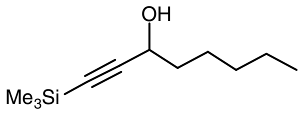
	Ag salt[a]	Solvent	Time	Yield[b]
1	$AgNO_3$	CH_2Cl_2	2 h	0[c]
2		Me_2CO	5 min	55
3		MeOH	10 min	76
4		aq MeOH	15 min	66
5		H_2O	25 min	11
6	AgOTf	CH_2Cl_2	2 h	0[d]
7		Me_2CO	2 h	0
8		MeOH	10 min	56
9		aq MeOH	15 min	56
10		H_2O	25 min	16
11	AgCl	CH_2Cl_2	2 h	0[c]
12		MeOH	2 h	0[c]
13		aq MeOH	2 h	0[c]
14	AgF	CH_2Cl_2	2 h	0[c]
15		MeOH	2 h	0[c]
16		aq MeOH	2 h	0[c]
17	$AgBF_4$	CH_2Cl_2	2 h	0[c]
18		MeOH	2 h	0[c]
19		aq MeOH	2 h	0[c]

[a] 1 equiv.
[b] Yield of isolated pure product.
[c] The silver salt was insoluble and the starting material was recovered.
[d] AgOTf was not completely dissolved and no reaction took place but if MeOH was added, hex-1-ynyl silver precipitated (60%).

2-Phenyl-1-trimethylsilylethyne **2a** was efficiently converted to the corresponding silver acetylide **2b** upon treatment with 1 equiv of silver nitrate or triflate in aqueous methanol (entries 1–2). Under the same conditions, 1-phenyl-3-trimethylsilylprop-2-ynol **3a** and its the *tert*-butyldimethylsilyl ether **4a** gave the corresponding silver acetylides **3b** and **4b** in good to excellent yields (entries 3–6). However, silver triflate seemed to induce some decomposition since a pink glueish solid difficult to handle and purify was formed instead of a grey-white crystalline solid when silver nitrate was used (entries 4 vs 3, 6 vs 5).

Similarly, 5-trimethylsilylpent-4-ynol **5a** quantitatively furnished the acetylide **5b** with silver nitrate but not with silver triflate (entry 7 vs 8). On the contrary, the pivalate and the benzyl derivatives **6a** and **7a** cleanly reacted with both silver salts, giving the corresponding acetylides **6b** and **7b** in good yields (entries 9, 11 vs 10, 12). Surprisingly compared to other free alcohols, 1-trimethylsily-

Table 2. Formation of various 1-trimethylsilyl-1-alkynes: reaction performed with 1 equiv of silver salt

	1-TMS Alkyne		Ag salt[a]	Yield[b]
1		**2a**	$AgNO_3$	78
2			AgOTf	82
3		**3a**	$AgNO_3$	71
4			AgOTf	[c]
5		**4a**	$AgNO_3$	90
6			AgOTf	[c]
7		**5a**	$AgNO_3$	99
8			AgOTf	[c]
9		**6a**	$AgNO_3$	75
10			AgOTf	53
11		**7a**	$AgNO_3$	76
12			AgOTf	89
13		**8a**	$AgNO_3$	82
14			AgOTf	77

[a] 1 equiv in aqueous methanol (H_2O–MeOH 25–75) at 20 °C.
[b] Yield of spectroscopically pure product.
[c] A glue-like solid precipitated, hampering the recovery of a pure clean silver acetylide.

loct-1-yn-3-ol **8a** also gave the corresponding acetylide **8b** whatever the silver salt (entries 13–14 vs 3–4, 7–8).

Silyl, ester and benzyl protecting groups are thus compatible with this method. In some cases, no protective group is even possible.

It is worth noting that Ag-catalyzed cyclization, a possible concurrent reaction when acetylenic alcohols were examined,[19] was not observed under these conditions.

In conclusion, we demonstrated here that 1-trimethylsilyl-1-alkynes can be cleanly converted to the corresponding silver acetylides in the presence of silver nitrate or triflate in protic solvents. Various functional groups, protected or not, are fully compatible with this new method. Further works in this area are now in progress.

Acknowledgements

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References and notes

1. Halbes, U.; Weibel, J. M.; Pale, P. *Chem. Soc. Rev.*, submitted for publication.
2. (a) Wei, C.; Li, Z.; Li, C.-J. *Org. Lett.* **2003**, *5*, 4473–4475; (b) Ji, J.-X.; Terry, T. L.; Au-Yeung, T. T. L.; Wu, J.; Chiu, W. Y.; Chan, A. S. C. *Adv. Synth. Catal.* **2004**, *346*, 42–44.
3. (a) Bertus, P.; Pale, P. *Tetrahedron Lett.* **1996**, *37*, 2019–2022; (b) Bertus, P.; Pale, P. *Tetrahedron Lett.* **1997**, *38*, 8193–8196; (c) Bertus, P.; Pale, P. *J. Organomet. Chem.* **1998**, *567*, 173–180; (d) Halbes, U.; Pale, P. *J. Organomet. Chem.* **2003**, *687*, 420–424.
4. Halbes, U.; Pale, P. *Tetrahedron Lett.* **2002**, *43*, 2039–2042.
5. (a) Halbes, U.; Bertus, P.; Pale, P. *Tetrahedron Lett.* **2001**, *42*, 8641–8644; (b) Halbes, U.; Pale, P. *Eur. J. Org. Chem.* **2002**, 2039–2042.
6. Inanaga, J.; Katsuki, T.; Takimoto, S.; Ouchida, S.; Inoue, K.; Nakano, A.; Okukado, N.; Yamaguchi, M. *Chem. Lett.* **1979**, 1021–1024.
7. Dillinger, S.; Bertus, P.; Pale, P. *Org. Lett.* **2001**, *3*, 1661–1664.
8. (a) Nada, T.; Koide, K. *Tetrahedron Lett.* **2003**, *44*, 443–445; (b) Shahi, S. P.; Koide, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 2525–2527.
9. Pouwer, R. H.; Williams, C. M.; Raine, A. L.; Harper, J. B. *Org. Lett.* **2005**, *7*, 1323–1325.
10. Davis, R. B.; Scheiber, D. H. *J. Am. Chem. Soc.* **1956**, *78*, 1675–1678.
11. Vogel, A. I. *Practical Organic Chemistry*, 3rd ed.; Longmans: London, 1967.
12. Orsini, A.; Viterisi, A.; Bodlenner, A.; Weibel, J. M.; Pale, P. *Tetrahedron Lett.* **2005**, *46*, 2259–2262.
13. See also Carpito, A.; Mannoci, L.; Rossi, R. *Eur. J. Org. Chem.* **2005**, 1859–1864.
14. Mechanistic studies are currently underway in our group. For a preliminary account, see: Halbes-Letinois, U.; Berger, S.; Pale, P. *J. Org. Chem.* **2005**, *70*, 9185–9190.
15. The conventional formation[10] starting from 1-hexyne gave in our hands yields from 49% to 63% depending on the conditions.
16. (a) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; (b) Colvin, E. W. *Silicon Reagent in Organic Synthesis*; Academic Press: London, 1988; (c) Winterfeldt, E. In *Modern Synthetic Methods*; Scheffold, R., Ed.; VCH: Weinheim, 1992; Vol. 6, pp 103–226.
17. Cossy, J.; Pale, P. *Tetrahedron Lett.* **1987**, *28*, 6039–6040.
18. Typical procedure for the formation of alkynyl silver from 1-trimethylsilyl-1-alkynes: To a solution of 1-trimethylsilyl-1-alkyne (1 equiv) in the appropriate solvent (see Table 1) (4 ml/mmol), was added silver nitrate or silver triflate (1 equiv) at room temperature. The starting materials rapidly disappeared and a white precipitate formed within 5–15 min. This solid was recovered by filtration and washed with cold methanol (stored at 0 °C). Subsequent drying led to the silver acetylide as a white powder.
19. (a) Pale, P.; Chuche, J. *Eur. J. Org. Chem.* **2000**, 1019–1025; (b) Dalla, V.; Pale, P. *New J. Chem.* **1999**, 803–805; (c) Dalla, V.; Pale, P. *Tetrahedron Lett.* **1994**, *35*, 3525.