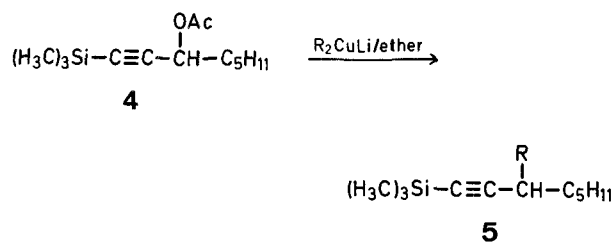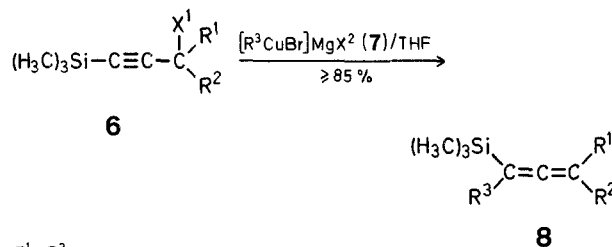The tendency of organocuprates to induce 1,3-substitution reactions in propynylic compounds is remarkably high. So we have found tha: even the bulky t-butylcuprate is capable to convert 1 ($R^1 = t$-C_4H_9, $R^2 = R^3 = H$, $X^1 = OTos$) exclusively into the allere 3 ($R^1 = R^4 = t$-C_4H_9, $R^2 = R^3 = H$), cf. Lit. [3].

In contrast with this observation, Brinkmeyer et al.[6] reported recently that the trimethylsilyl protected acetate 4 produced substituted alkynes 5 instead of allenes upon reaction with lithium dialkylcuprates.

$$\underset{4}{(H_3C)_3Si-C{\equiv}C-\overset{\overset{\displaystyle OAc}{|}}{C}H-C_5H_{11}} \quad \xrightarrow{R_2CuLi/ether}$$

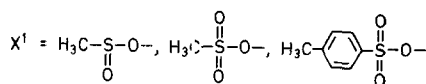$$\underset{5}{(H_3C)_3Si-C{\equiv}C-\overset{\overset{\displaystyle R}{|}}{C}H-C_5H_{11}}$$

Scheme A

In this paper we wish to present our results concerning the reaction of other trimethylsilyl protected propynyl ester with organocuprates. We have namely studied the interaction of trimethylsilyl protected propynyl sulfinates and sulfonates 6 with organoheterocuprates 7 in tetrahydrofuran medium. As is shown in Scheme B and in the Table the regiochemistry of the organocopper(I)-induced substitution in the esters just mentioned is completely different from the one given in Scheme A, in most cases studied.

$$\underset{6}{(H_3C)_3Si-C{\equiv}C-\overset{\overset{\displaystyle X^1}{|}}{\underset{\underset{\displaystyle R^2}{}}{C}}{\overset{\displaystyle R^1}{}}} \quad \xrightarrow[\geqslant 85\%]{[R^3CuBr]MgX^2 \ (7)/THF}$$

$$\underset{8}{\underset{R^3}{\overset{(H_3C)_3Si}{}}}C=C=C\underset{R^2}{\overset{R^1}{}}$$

R^1, R^2 = alkyl

R^3 = alkyl or C_6H_5

$X^1 = H_3C-\overset{O}{\underset{O}{\overset{||}{\underset{||}{S}}}}-O-$, $H_3C-\overset{O}{\underset{O}{\overset{||}{\underset{||}{S}}}}-O-$, $H_3C-\langle\rangle-\overset{O}{\underset{O}{\overset{||}{\underset{||}{S}}}}-O-$

$X^2 = Cl$ or Br

Scheme B

Our method constitutes an attractive route to a large variety of silylated allenes. To our knowledge, only a few syntheses of these compounds are known in the literature, e.g., the conjugate addition of 1-trialkylsilylpropynylcopper(I) compounds to dienoic esters[7] and the Claisen rearrangement of amide acetals derived from propargylic alcohols and dimethylacetamide diethyl acetal[8].

As is shown in the Table, most of the examples we studied dealt with propynyl esters 6 derived from methanesulfinic acid. From this Table it is also evident that such trimethylsilyl protected propynyl sulfinates were generally suitable starting compounds for the preparation of silylated allenes. (Table, entries 1–5, 8, 9, 12, 13–20a.)

In a few cases, however, the use of the sulfinate group as leaving group gave less satisfactory results, due to a
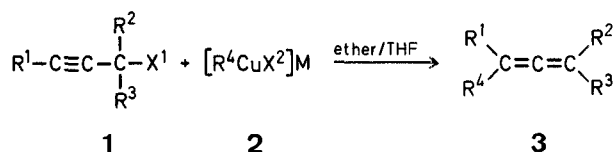
A New and General Route to 1-Trimethylsilyl-1,2-alkadienes

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The capability of organocopper(I) compounds 2 to induce 1,3-substitution reactions in various propynyl esters 1 with formation of allenes 3 is well-known. Crabbé et al.[1, 2] and van Dijck et al.[3], for instance, have investigated the behaviour of propynyl acetates in this type of reaction. We have found that allenic hydrocarbons were formed in excellent yields by reaction of propynyl tosylates with organocuprates[4]. The scope of this tosylate method is somewhat restricted, however, as tosylates derived from tertiary alcohols generally are rather difficult to prepare.
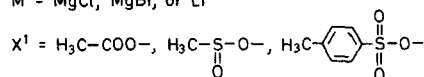
In a recent paper[5] we reported that the corresponding sulfinic esters, which are also very easily accessible from tertiary alcohols, reacted smoothly with organoheterocuprates via the 1,3-mode.

$$\underset{1}{R^1-C{\equiv}C-\overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle R^3}{|}}{C}}-X^1} + \underset{2}{[R^4CuX^2]M} \xrightarrow{ether/THF} \underset{3}{\underset{R^4}{\overset{R^1}{}}C=C=C\underset{R^3}{\overset{R^2}{}}}$$

R^1, R^2, R^3 = H, alkyl, or C_6H_5

R^4 = alkyl or C_6H_5

M = MgCl, MgBr, or Li

$X^1 = H_3C-COO-$, $H_3C-\overset{O}{\underset{O}{\overset{||}{\underset{||}{S}}}}-O-$, $H_3C-\langle\rangle-\overset{O}{\underset{O}{\overset{||}{\underset{||}{S}}}}-O-$

X^2 = alkyl, C_6H_5, or halogen

Table. Preparation of 1-Trimethylsilyl-1,2-alkadienes **8** from **6** and Organoheterocuprates **7** ($X^2 = Cl$ or Br)

Entry	R^1	R^2	R^3	X^1 in **6**	Yield [%]	b.p./torr	n_D^{20}	Molecular formula[a]
1	H	H	C_2H_5	H_3C—SO—O	90	40–41°/30	1.4455	$C_8H_{16}Si$ (140.3)
2	H	H	n-C_4H_9	H_3C—SO—O	88	66–67°/20	1.4507	$C_{10}H_{20}Si$ (168.3)
3	H	H	i-C_3H_7	H_3C—SO—O	95	47–48°/20	1.4470	$C_9H_{18}Si$ (154.3)
4	H	H	s-C_4H_9	H_3C—SO—O	94	59–60°/20	1.4518	$C_{10}H_{20}Si$ (168.3)
5	H	H	c-C_6H_{11}	H_3C—SO—O	90	100–102°/16	1.4845	$C_{12}H_{15}Si$ (187.3)
6a	H	H	t-C_4H_9	H_3C—SO—O	30[b]	69–70°/35	1.4564	$C_{10}H_{20}Si$ (168.3)
6b				Tos-O	85[c]			
7a	H	H	C_6H_5	H_3C—SO—O	40[d]	105–107°/15	1.5243	$C_{12}H_{16}Si$ (188.3)
7b				Mes-O	85[e]			
7c				Tos-O	85[e]			
8	H	t-C_4H_9	n-C_4H_9	H_3C—SO—O	91	110–111°/25	1.4546	$C_{14}H_{28}Si$ (224.5)
9	H	t-C_4H_9	s-C_4H_9	Mes-O	90	69–70°/25	1.4569	$C_{14}H_{28}Si$ (224.5)
10a	H	t-C_4H_9	t-C_4H_9	H_3C—SO—O	40[f]	95–96°/25	1.4601	$C_{14}H_{28}Si$ (224.5)
10b				Mes-O	98			
11a	H	t-C_4H_9	C_6H_5	H_3C—SO—O	80[g]	110–112°/25	1.5198	$C_{16}H_{24}Si$ (244.4)
11b				Mes-O	98			
12	CH_3	CH_3	C_2H_5	H_3C—SO—O	96	44–45°/25	1.4477	$C_{10}H_{20}Si$ (168.3)
13	CH_3	CH_3	n-C_3H_7	H_3C—SO—O	95	70–71°/25	1.4529	$C_{11}H_{22}Si$ (182.4)
14	CH_3	CH_3	n-C_4H_9	H_3C—SO—O	93	84–86°/25	1.4529	$C_{12}H_{24}Si$ (194.4)
15	CH_3	CH_3	i-C_3H_7	H_3C—SO—O	97	64–65°/25	1.4472	$C_{11}H_{22}Si$ (182.4)
16	CH_3	CH_3	s-C_4H_9	H_3C—SO—O	94	76–77°/25	1.4514	$C_{12}H_{24}Si$ (194.4)
17	CH_3	CH_3	t-C_4H_9	H_3C—SO—O	95	55–56°/30	1.4515	$C_{12}H_{24}Si$ (194.4)
18	CH_3	CH_3	C_6H_5	H_3C—SO—O	91	119–121°/24	1.5329	$C_{14}H_{29}Si$ (216.4)
19	—$(CH_2)_4$—		CH_3	H_3C—SO—O	90	80–81°/20	1.4822	$C_{12}H_{22}Si$ (192.3)
20a	—$(CH_2)_5$—		CH_3	H_3C—SO—O	91	85–86°/20	1.4866	$C_{13}H_{24}Si$ (194.4)
20b				Mes-O	98			
21	—$(CH_2)_5$—		C_6H_5	Mes-O	97	98–100°/0.4	1.5443	$C_{18}H_{26}Si$ (270.5)

[a] The microanalyses were in satisfactory agreement with the calculated values ($C \pm 0.2$, $H \pm 0.2$); the ^{1}H-N.M.R. spectra were also in accord with the proposed structures. Purity: 98% as determined by ^{1}H-N.M.R. and G.L.C. (conditions: SE-33, 10% on Chromosorb W). All I.R. spectra showed inter alia a strong absorbance at 1940 cm^{-1} ($>$C=C=C$<$).

[b] The alkyne $(H_3C)_3Si$—C≡C—CH_2—C_4H_9-t was preferentially formed in this case (relative amount 70%).

[c] The allene was contaminated with 15% of the alkyne $(H_3C)_3Si$—C≡C—CH_2—C_4H_9-t.

[d] Besides the allenic product 60% of the alkyne $(H_3C)_3Si$—C≡C—CH_2—C_6H_5 was obtained.

[e] In these cases small amounts ($\sim$15%) of $(H_3C)_3Si$—C≡C—CH_2—C_6H_5 were formed too.

[f] The allene of entry 10a was contaminated with 60% of the alcohol $(H_3C)_3Si$—C≡C—CH(OH)—C_4H_9-t.

[g] The allene of entry 11a was contaminated with 20% of the alcohol $(H_3C)_3Si$—C≡C—CH(OH)—C_4H_9-t.

competing 1,1-substitution or to attack of the cuprate on the sulfur atom of the sulfoxide group in the substrate. Entries 6a and 7a in the Table for instance show that the cuprates (t-C_4H_9CuBr)MgCl and (C_6H_5CuBr)MgBr induced besides the 1,3-substitution also the 1,1-substitution in considerable amounts in the parent compound **6** ($R^1 = R^2 = H$, $X^1 = H_3C$—SO—O).

The other undesired process, attack of the cuprate on the sulfur atom in **6**, took place when **6** ($R^1 = H$, $R^2 = t$-C_4H_9, $X^1 = H_3C$—SO—O) was treated with (t-C_4H_9CuBr)MgCl or (C_6H_5CuBr)MgBr (Table: entries 10a and 11a).

Interestingly, the ratio 1,3- versus 1,1-substitution was improved when sulfonic esters instead of methanesulfinic esters of the parent compound were reacted with the cuprates just mentioned (Table: entries 6b, 7b and 7c). The use of the sulfonate group as leaving group also appeared to be favourable for preventing the undesired formation of the alcohol **6** ($R^1 = H$, $R^2 = t$-C_4H_9, $X^1 = OH$) (compare entries 10a and 11a with entries 10b and 11b in the Table). Entries 20b and 21 in the Table are examples in which we used the methanesulfonic ester derived from 1-ethynylcyclohexanol. Generally, the thermal stability of tertiary sulfonates is very low and also in our case attempts to isolate the tertiary methanesulfonate in a pure state were unsuccessful. Nevertheless, entries 20b and 21 show that excellent

results were obtained when our tertiary sulfonate was treated in situ with organocuprates; this may also be of synthetic interest in other cases.

All operations with organometallic reagents were carried out in an atmosphere of dry nitrogen. The required propynyl alcohols were prepared from trimethylsilylacetylene and the appropriate ketone or aldehyde following the procedure given[9]. In the literature the following methods have been used to prepare trimethylsilylacetylene: (a) by reacting HC≡C—MgX (X = Cl or Br) with chlorotrimethylsilane in tetrahydrofuran (reported yields: 51%[10] and 64%[11]) and (b) by reacting HC≡C—Na with chlorotrimethylsilane in dioxan (yield: 85%[9]).

Trimethylsilylacetylene; Modified Procedure:

To a stirred solution of ethynylmagnesium bromide (2.3 mol) in tetrahydrofuran (3500 ml) is added chlorotrimethylsilane (2.2 mol) over 30 min, keeping the temperature of the reaction mixture at +10° by ice cooling. After the temperature of the resultant reaction mixture has risen to +25° the reaction vessel is closed and kept overnight without stirring. After 24 h, the reaction mixture is cautiously poured into a saturated aqueous solution of ammonium chloride (2000 ml) cooled at 0–5°. After separation of the aqueous layer, the organic layer is washed with cold (5°) aqueous saturated ammonium chloride solution (3 × 3000 ml, 3 × 4000 ml). Subsequently the organic layer is dried with magnesium sulfate and distilled; yield: 95%; b.p. 52°/760 torr; $n_D^{20} = 1.3900$.

Methanesulfinate Esters and Primary and Secondary Methanesulfonate Esters 6:

To a well stirred solution of alcohol 6 ($X^1 = OH$; 0.030 mol) and triethylamine (0.045 mol) in dichloromethane (100 ml), cooled at $-50°$, is added methanesulfinyl chloride (0.040 mol) or methanesulfonyl chloride (0.040 mol), respectively. Subsequently, the temperature of the resultant reaction mixture is slowly raised (15 min) to $+20°$. After being stirred for 30 min at $+20°$, the reaction mixture is poured into water (200 ml) and the dichloromethane layer separated. The aqueous layer is extracted with dichloromethane (2×50 ml). The combined extracts are washed with water (1×100 ml), dried with magnesium sulfate, and concentrated in vacuo. The purity of the sulfinates and sulfonates thus obtained is at least 95 % (based on ^{1}H-N.M.R.) and no further purifications are carried out; yield: 98–100 %.

Tosylates 6:

To a well-stirred solution of alcohol 6 ($R^1 = R^2 = H$, $X^1 = OH$; 0.040 mol) and tosyl chloride (0.050 mol) in diethyl ether (50 ml), freshly powdered potassium hydroxide (15.0 g) is added at $-50°$. Subsequently the temperature of the resultant reaction mixture is slowly raised within 15 min to $0°$. After stirring for 30 min at $0°$, the reaction mixture is poured into water (200 ml) and the ether layer is separated. The aqueous layer is extracted with ether (2×50 ml). After washing the combined extracts with water (1×100 ml) and drying with $MgSO_4$ the solvent is removed in vacuo. The purity of the tosylate is at least 95 % (based on ^{1}H-N.M.R.) and no further purification is carried out; yield: 98–100 %.

Methanesulfonate Ester from 1-Ethynylcyclohexanol:

To a solution of alcohol 6 [$R^1—R^2 = —(CH_2)_5—$, $X^1 = OH$; 0.030 mol] and lithium bromide (0.030 mol) in dry tetrahydrofuran (60 ml) is cautiously added a solution of n-butyllithium in hexane (0.030 mol) at $-60°$. After stirring of the reaction mixture for 30 minutes at this temperature, methanesulfonyl chloride (0.030 mol) is added. Stirring is continued during 60 min at $-60°$. The obtained tertiary sulfonate ester is used as a solution in tetrahydrofuran at $-60°$ (see below).

Heterocuprates 7:

To a stirred solution of the complex $LiCuBr_2$ (0.030 mol) in tetrahydrofuran (60 ml) is added a solution of the Grignard reagent (0.030 mol, $X = Cl$ or Br) in tetrahydrofuran (30 ml) at $0°$ when $R^3 = C_6H_5$, CH_3, or at $-50°$ in the other cases. Stirring is continued during 30 min at $0°$ and $-50°$, respectively.

Silylated Allenes 8:

A solution of the sulfinate ester (0.030 mol), the primary or secondary sulfonate ester (0.030 mol) in tetrahydrofuran (10 ml) is added to a stirred suspension of the heterocuprate 7 (0.030 mol) at $-60°$. In case of the tertiary methanesulfonate ester (Table: entries 20b)

and 21) the heterocuprate (precooled at $-60°$) is cautiously added to a solution of the sulfonate ester in tetrahydrofuran (see above) at $-60°$. After stirring for 30 min at $-60°$, the temperature of the reaction mixture is raised to $+20°$ within 45 min. Stirring is continued for 45 min at $+20°$ whereupon the reaction mixture is poured into a saturated solution of ammonium chloride in water (200 ml) containing sodium cyanide (2 g). The product is isolated by extraction with pentane (3×100 ml). The combined extracts are washed with water (3×100 ml) and dried with magnesium sulfate. The solvent is evaporated in vacuo and the residue distilled. The physical constants and yields of the products 8 are given in the Table.

When the desired allenes were contaminated with 1,1-substitution products (Table: entries 6b–7b), the latter were converted into the unprotected 1-alkynes by splitting off the trimethylsilyl group according to standard procedures[12,13] prior to distillation. The silylated allenes did not loose their trimethylsilyl group under the conditions mentioned in references 12 and 13.

1   J. L. Luche, E. Barreiro, J. M. Dollat, P. Crabbé, *Tetrahedron Lett.* 1975, 4615.

2   P. Crabbé, E. Barreiro, J. M. Dollat, J. L. Luche, *J. Chem. Soc. Chem. Commun.* 1976, 183.

3   L. A. van Dijck, B. J. Lankwerden, J. G. C. M. Vermeer, A. J. M. Weber, *Recl. Trav. Chim. Pays-Bas* 90, 801 (1971).

4   P. Vermeer, J. Meijer, L. Brandsma, *Recl. Trav. Chim. Pays-Bas* 94, 112 (1975).

5   P. Vermeer, H. Westmijze, H. Kleijn, L. A. van Dijck, *Recl. Trav. Chim. Pays-Bas* 97, 56 (1978).

6   R. S. Brinkmeyer T. L. McDonald, *J. Chem. Soc. Chem. Commun.* 1978, 876.

7   B. Ganem, *Tetrahedron Lett.* 1974, 4467.

8   K. A. Parker, R. W. Kosley Jr., *Tetrahedron Lett.* 1976, 341.

9   V. Jäger in Houben Weyl, *Methoden der Organischen Chemie*, 4th Edn., E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1977, Vol. 5/2a.

10 M. A. Cook, C. Eaborn, D. R. M. Walton, *J. Organometal. Chem.* 24, 301 (1970).

11 U. Krüerke, *J. Organometal. Chem.* 21, 83 (1970).

12 H. M. Schmidt, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* 86, 1138 (1967).

13 A. Zilverschoon, J. Meijer, P. Vermeer, L. Brandsma, *Recl. Trav. Chim. Pays-Bas* 94, 163 (1975).