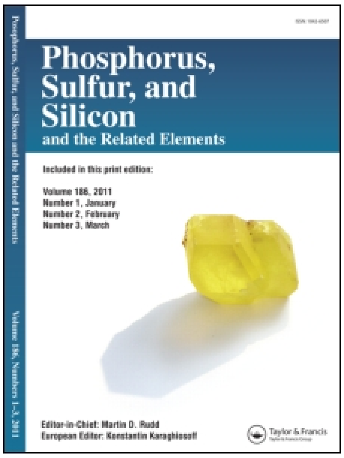

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STUDIES OF TRIPHENYLSILANETHIOL ADDITION TO ALKYNES: PREPARATION OF VINYL SULFIDES

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STUDIES OF TRIPHENYLSILANETHIOL ADDITION TO ALKYNES: PREPARATION OF VINYL SULFIDES

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The scope and limitations of triphenylsilanethiol (**1**) a solid hydrogen sulfide equivalent, were investigated in free radical reactions to terminal alkynes. The triphenylsilylthioenol ether intermediate thus obtained was deprotected with Cs_2CO_3 in the presence of various electrophiles to yield mixtures of E and Z vinyl sulfides. The ratio of E and Z isomers could be controlled by varying the concentration of the starting alkynes.

Keywords: radical; thiol; vinyl sulfide; silanethiol

Triphenylsilanethiol **1**,[1] a monoprotected form of H_2S is a white odorless solid with interesting characteristics. We have shown that this masked H_2S readily opened epoxides[2] to selectively furnished β-hydroxy mercaptans or could add to alkenes[3] to furnish thiols. We now wish to report on the use of triphenylsilanethiol **1** for radical addition reactions to alkynes to produce vinyl sulfides after a mild deprotection of the intermediate triphenylsilylsulfanyl and an alkylation step.

When a terminal alkyne was treated with **1** and AIBN in a refluxing benzene solution, the presence of an E/Z mixture of thioenol ether **2** could be detected by proton NMR owing to the characteristic AB pattern. Thioenol ether **2** was not isolated but directly converted *in situ* to a more stable methyl thioenol ether adduct. This was done in the same reaction flask by adding excess methyl iodide and cesium carbonate after the disappearance of starting material. Nucleophilic attack of the carbonate on the oxophilic silicone atom generated vinylthiolate **3** which was trapped by the elec-

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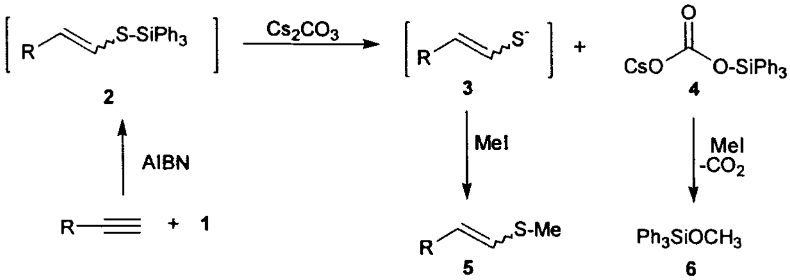
* Corresponding Author.

trophile providing **5** (Scheme 1). No change in the E/Z ratio was observed between the crude reaction mixture giving **2** and the isolated adduct **5.** The silyl carbonate **4** decomposed with the lost of CO_2 and the intermediate silanoate reacted with excess methyl iodide to give methoxytriphenylsilane **6.**

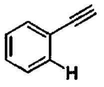
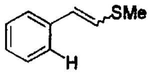
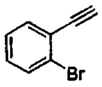
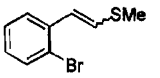
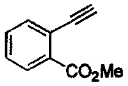
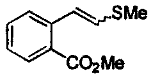
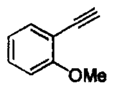
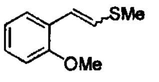


SCHEME 1

It is known that the addition of thiols to alkynes mainly yielded the kinetically favored cis adducts which could then isomerized to the thermodynamically more stable trans isomer either at elevated temperature or with an excess of free radicals[4]. However in our case, the selective formation of cis and trans isomer was also dependent on the concentration as well as the reaction time. Preliminary studies with phenylacetylene and **1** under various conditions led us to choose two sets of standard reaction conditions to favor either the trans or the cis adduct. When the reaction was run at a 2.0 M concentration with 8% equivalent of AIBN and 1.05 equivalent of **1** for 4 h, the trans adduct was favored (method A). On the other hand, when the reaction was run at 0.2 M concentration for a prolonged period of heating, the cis adduct was favored (method B). Table I shows the ratio outcome of the reaction of **1** with phenylacetylene derivatives and one aliphatic alkyne after deprotection of the triphenyl silyl group and quench with methyl iodide. At high concentration, phenylacetylene and the alkynes o-substituted aromatic with deactivating groups (NoCl, Br, CO_2Me) gave a similar E/Z ratio of ca. 4:1. The electron donating o-methyl ether on the other hand, gave an 8:1 selectivity. The aliphatic alkyne (entry 5) did behave differently. Decyne only showed a slight preference for the Z isomer.

Under diluted conditions, the cis isomer was the main product observed in an approximate a 1:4 ratio and obtained in a reasonable yield after a prolonged period of heating. This ratio is approximately the reverse of the one observed with Method A in the case of aryl alkynes.

TABLE I Radical addition of 1 on terminal alkynes after deprotection and alkylation

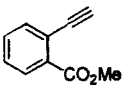
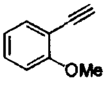
Entry	*Alkyne*	*Product*	*Mehod*[a]	*Time*[b]	*Ratio (E/Z)*	*Yield*
1-			A	4 h	4.2/1	68%
			B	22 h	1/3.4	56%
2-			A	4 h	3.6/1	77%
			B	18 h	1/3.7	52%
3-			A	4 h	3.7/1	75%
			B	18 h	1/4.6	69%
4-			A	5 h	8/1	79%
			B	15 h	0.8/1	75%
5-	Decyne		A	4 h	1/1.7	69%
			B	20 h	1/3.4	47%

[a] Method A: 2.0 M of alkyne, 8% equivalent AIBN and 1.05 equivalent of 1, Method B: 0.2 M of alkyne, 8% equivalent AIBN and 1.05 equivalent of 1.
[b] Time of reaction with 1 and alkyne before CS_2CO_3.

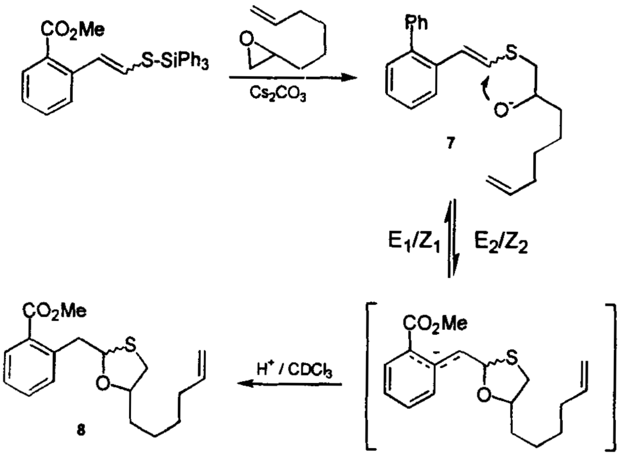
Table II highlights the effect of modifications on the reaction rate and ratio on two aromatic alkynes with time. At high concentration (2.0 M) and with 0.8 equivalent of AIBN, the reaction was complete within minutes, i.e. the starting material had reacted completely with **1** and a thermodynamic equilibration had started. With ten times less AIBN, the rate of addition of **1** was still rapid, but the cis isomer was favored in the first minutes of the reaction. This type of equilibrium was also described by Chatgilialoglu *et al.* with 5% AIBN (added every 2 h) at 0.25 M with tris(trimethylsilyl)silane, tributyltin hydride and thiophenol[5]. Under diluted conditions (0.2 M), the addition of **1** to alkynes was considerably slowed down and the Z isomer predominanted.

We then turned our attention to increase the scope of this reaction by varying the nature of the alkylating agent. Table III discloses the results for the addition of **1** on 2-ethynyl methyl benzoate, with four types of electrophiles[6]. Two ratios were measured for each electrophile used, to confirm that no change had occured between each step. Ratio-1 correspond to the E/Z ratio of intermediate **2** from an aliquot taken after 30 min of heating, and ratio-2 correspond the E/Z ratio of the final compound. The thiolate **2** obtained after deprotection with Cs_2CO_3 selectively displaced the iodide of 1-chloro-3-iodopropane to give the vinyl sulfide in good yield. The amount of trans adduct did not vary under the reaction conditions. The thiolate **2** also reacted in a 1,4-Michael type addition, with acyl chloride and in epoxide ring opening reaction. The isolated yield of vinyl sulfides varied from 68–78% for two steps in a one pot reaction. A change in the ratio was observed only in one case (entry 9). This may be rationalized by a reversible intramolecular addition of the alkoxide **7** to the conjugated olefin. Equilibration via ring opening of oxathiane returns **7**, but this time in a higher ratio (Scheme 2). In fact, some cyclized product **8** was formed form the alcohol **7**, on standing in a NMR tube.

TABLE II E/Z ratio of intermediate 2 as a function of time, concentration, initiator and 1

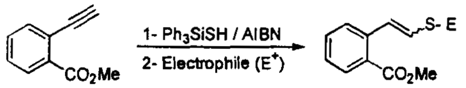
Alkyne	*Conc. (M)*	*AIBN (eq.)*	*Thiol 1 (eq.)*	*E/Z Ratio*[a]				
				5 min	*0.5h*	*1 h*	*4 h*	*24 h*
	2.0	0.80	1.25	1.1/1	5.4/1	5.9/1	5.8/1	
	2.0	0.08	1.25	1/4.1 (16%)	1.6/1	3.4/1	3.8/1	
	0.2	0.08	1.25	1/10.3 (75%)	1/7.8 (48%)	1/5.5 (31%)	1/3.5 (5%)	1/3.4
	2.0	0.80	1.25	4.4/1	7.5/1	8.4/1	8.3/1	
	2.0	0.08	1.25	1/1.2	4.4/1	7.3/1	7.3/1	
	0.2	0.08	1.25	1/5.1 (62%)	1/3.3 (21%)	1/1.4 (5%)	1.7/1	2.5/1

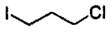
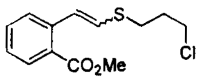
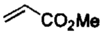
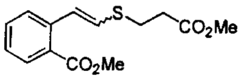
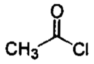
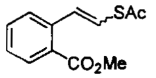
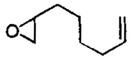
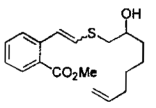
[a] Yield in parenthesis correspond to unreacted alkyne.



SCHEME 2

TABLE III Formation of vinyl sulfides with various electrophiles



Entry	*Electrophile*	*Product*	*Ratio-1*[a]	*Ratio-2*[b]	*Yield*
6-			4.3/1	4.3/1	78%
7-			3.4/1	3.3/1	74%
8-			3.9/1	3.9/1	68%
9-			4.1/1	7.2/1	70%

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[a] ^{1}H NMR ratio, determined on intermediate **2**; [b] ^{1}H NMR ratio, determined on the final product.

Thus, triphenylsilanethiol **1** is a useful solid H_2S equivalent in free-radical type reactions on terminal alkynes. The initial addition product **2** cannot react further to give symmetrical sulfide since the sulfur atom is protected by a triphenylsilyl group. This protecting group is readily removed under mild conditions to provide a stable vinyl thiolate that does not equilibrate. Various vinyl sulfides have been prepared from **3** with appropriate electrophiles, and either cis or trans isomers can be formed. The reaction was general and a variety of functional groups. are well tolerated.

References

[1] L. Birkafer; A. Ritter, H. Galler, *Chem. Ber.*, **96**, 3289 (1963).

[2] J. Brittain; Y. Gareau, *Tetrahedron Lett.*, **34**, 3363 (1993).

[3] B. Haché; Y. Gareau, *Tetrahedron Lett.*, **35**, 1837 (1994).

[4] D.K. Wedegaertner; R.M. Kopchnik; J.A. Kampmeier, *J. Am. Chem. Soc.*, **93**, 6890 (1971); H.J. Alkema; J.F. Arens, *Rec. Trav. Chim. Pays-Bas*, **79**, 1257 (1960).

[5] C. Chatgilialoglu; M. Ballestri; C. Ferreri; D. Cecchi, *J. Org. chem.*, **60**, 3831 (995); and references cited theirein.

[6] Method A was used to obtain sufficient quantities of both isomers to be fully characterized.