[(Trimethylsilyl)methyl]copper(I) Species: Versatile Reagents To Prepare Functionally Substituted Allylic Silanes

Henk Kleijn and Peter Vermeer*

Laboratory for Organic Chemistry, State University at Utrecht, Croesestraat 79, 3522 AD Utrecht, The Netherlands

Received November 27, 1984

Smooth S_N2' reactions in α-alkynyl and -allenyl oxiranes, in esters derived from α-allenic alcohols, and in the bis(methanesulfonate) derived from 1,4-dihydroxy-2-butyne were observed with the reagent [(trimethylsilyl)-methyl]copper(I). In this way, several allylic silanes bearing functional groups became available. Another route to functionally substituted allylic silanes was elaborated by adding [(trimethylsilyl)methyl]copper(I) or its homocuprate derivative to alkynes such as 2-alkynoic esters, ethoxyacetylene, 1-alkynyl sulfides, and 1-alkynyl sulfones. The addition reactions appeared to occur regiospecifically and in many cases also with high stereoselectivity. A 1,4-bis[(trimethylsilyl)methyl]-substituted butatriene derivative could be obtained by sequential addition of the bis[(trimethylsilyl)methyl]cuprate compound and methyl iodide to a 1-alkynyl sulfide. For one case it was shown that the addition of [(trimethylsilyl)methyl]copper(I) to 1-alkynyl sulfones can be used to prepare sulfur-free 1-alkenes bearing in the β-position the (trimethylsilyl)methyl group.

Organocopper(I) species are versatile reagents for organic synthesis.[1] They may be used as nucleophiles in substitution reactions and were applied in this manner to synthesize, e.g., allenes of high optical purity.[2] They also add, generally in a regio- and stereospecific way, to the carbon–carbon triple bond of compounds like 2-alkynoic esters,[3] ethoxyethyne,[4] 1-alkynyl sulfides,[5] sulfoxides,[6] and sulfones,[7] and 1-alkynes.[8] This addition reaction has opened up interesting routes to a large variety of (hetero-) substituted olefins.

Some time ago, Jarvis and Lappert reported on the structure of an interestingly functionalized alkylcopper(I) compound, viz. [(trimethylsilyl)methyl]copper(I).[9] It is a tetramer showing a square-planar arrangement of the four copper atoms that are held together by four bridging (trimethylsilyl)methyl ligands. The chemistry of this copper(I) compound, and of its "ate" derivative, has been explored to some extent. The compound adds to dimethyloxosulfonium methylide,[10] dimethyl acetylenedicarboxylate,[11] ethyl propiolate,[12] 1,1-diethoxy-2-propyne,[12] and ethoxyacetylene[12] and, very slowly, to 1-heptyne.[12] [(Trimethylsilyl)methyl]copper(I) has also been used to induce substitution reactions in propargylic esters; the products are α-allenic silanes.[13] [(Trimethylsilyl)-methyl]magnesium chloride has been reported to convert α,β-unsaturated ketones into γ-trimethylsilyl-substituted saturated ketones when catalytic amounts of cuprous salts were added.[14]

This paper gives our results obtained during our investigations on the synthetic merits of [(trimethylsilyl)-methyl]copper(I) and its "ate" derivative. The reagents were prepared in situ from [(trimethylsilyl)methyl]magnesium chloride and an equimolar or half the amount of the complex $LiCuBr_2$, respectively.

Results and Discussion

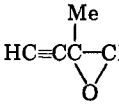
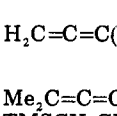
Table I gives a compilation of the reactions that we performed using [(trimethylsilyl)methyl]copper(I), Me_3SiCH_2Cu (**1a**), and the cuprate $(Me_3SiCH_2)_2CuMgCl$ (**1b**) as reagents. The reactions were carried out in tetrahydrofuran (THF); in all cases allylic silanes were produced, compounds that are well-known building blocks in organic synthesis.[15] Substitution as well as addition reactions were studied.

Substitution. For the substitution reactions we used **1a**. It is our experience that reagents of the type RCu generally give purer substitution products than the reagents R_2CuM do, especially when propargylic compounds are the substrates.[16] Moreover, cuprates R_2CuM are not suited reagents to convert sulfinates (e.g. **6**, **10**, and **12**) because of substantial attack by the cuprate on the sulfinate group itself.[17] Table I shows that **1a** is an appropriate reagent to convert α-acetylenic and -allenic oxiranes (**2** and **8**), α-allenic methanesulfinates (**6**, **10**, **12**) as well as the disulfonate **4** into the corresponding 1,3-substitution products (yields 80–97%). The reactions were complete within 1.0 h at 25 °C, and all had proceeded regiospecifically: in none of the products could other regio isomers be detected. Apparently our copper(I) compound **1a** prefers the 1,3-substitution mode, a preference that is often observed for such reactions.[18]

(1) For reviews of organocopper chemistry see: (a) Normant, J. F. *Synthesis* **1972**, 63. (b) Posner, G. H. *Org. React.* **1972**, *19*, 1. (c) *Ibid.* **1975**, *22*, 253. (d) Jukes, A. E. *Adv. Organomet. Chem.* **1974**, *12*, 215.
(2) Elsevier, C. J. Doctoral Dissertation, State University at Utrecht, 1984.
(3) For instance see: Anderson, R. J.; Corbin, V. L.; Cotterrell, G.; Cox, G. R.; Henrick, C. A.; Schaub, F.; Siddall, J. B. *J. Am. Chem. Soc.* **1975**, *97*, 1197.
(4) (a) Alexakis, A.; Cahiez, G.; Normant, J. F.; Villieras, J. *Bull. Soc. Chim. Fr.* **1977**, 693. (b) Westmijze, H. Doctoral Dissertation, State University at Utrecht, 1979.
(5) Vermeer, P.; de Graaf, C.; Meijer, J. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 24.
(6) Vermeer, P.; Meijer, J.; Eylander, C. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 240.
(7) (a) Truce, W. E.; Lusch, M. J. *J. Org. Chem.* **1974**, *39*, 3174. (b) Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 14.
(8) For a review see: Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.
(9) Jarvis, J. A. J.; Kilbourn, B. T.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 475.
(10) Schmidbaur, H.; Richter, W. *Z. Anorg. Allg. Chem.* **1977**, *429*, 222.
(11) Nishiyama, H.; Sasaki, M.; Itoh, K. *Chem. Lett.* **1981**, 905.
(12) Bourgain-Commerçon, M.; Foulon, J. P.; Normant, J. F. *Tetrahedron Lett.* **1983**, *24*, 5077.
(13) Montury, M.; Psaume, B.; Gore, J. *Tetrahedron Lett.* **1980**, *21*, 163.
(14) Taylor, R. T.; Galloway, J. G. *J. Organomet. Chem.* **1981**, *220*, 295.
(15) For instance see: (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981. (c) Magnus, P. D.; Sarkar, T.; Djuric, S. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 7, p 515. (d) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.
(16) We have very often observed that upon treatment of propargylic esters with cuprates R_2CuM substantial amounts of allenes arise in which hydrogen instead of the desired group R had been introduced.
(17) Vermeer, P.; Westmijze, H.; Kleijn, H.; van Dijck, L. A. *Recl. Trav. Chim. Pays-Bas* **1978**, 97, 56.
(18) For a possible explanation see the mechanism proposed for the conversion of 1-haloallenes by organocopper(I) species into alkynes: Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063.

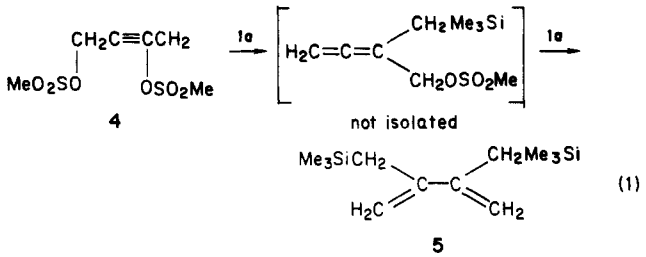
0022-3263/85/1950-5143$01.50/0

Table I. Substitution and Addition Reactions with Me_3SiCH_2Cu (1a) and $(Me_3SiCH_2)_2CuMgCl$ (1b)[a]

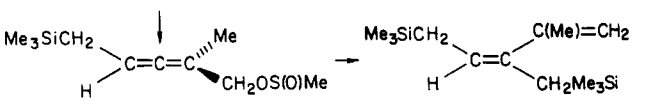
entry	substrate	Cu(I) reagent	product	yield, %
1	 (2)	1a	$Me_3SiCH_2CH{=}C{=}C(Me)CH_2OH$ (3)	90
2	$(MeSO_2OCH_2C{\equiv})_2$ (4)	1a	$H_2C{=}C(CH_2Me_3Si)(Me_3SiCH_2)C{=}CH_2$ (5)	90
3	$H_2C{=}C{=}C(OMe)C(Me)_2OS(O)Me$ (6)	1a	$H_2C{=}(CH_2Me_3Si)(MeO)C{=}CMe_2$ (7)	80
4	 (8)	1a	$H_2C{=}C(CH_2Me_3Si)(MeO)C{=}C(Me)CH_2OMe_3Si$ (9)[b,c]	97
5	$Me_2C{=}C{=}C(Me)CH_2OS(O)Me$ (10)	1a	$Me_2C{=}C(CH_2Me_3Si)C(Me){=}CH_2$ (11)	90
6	$TMSCH_2CH{=}C{=}C(Me)CH_2OS(O)Me$ (12)	1a	$Me_3SiCH_2CH{=}C(CH_2Me_3Si)C(Me){=}CH_2$ (13)[d]	95
7	$RC{\equiv}CCO_2Me$	1a,b	$Me_3SiCH_2C(R){=}CHCO_2Me$[e]	
	14a, R = Ph		15a, R = Ph	90–98
	b, R = (Z)-Et(Me)C=CH$(CH_2)_2$		b, R = (Z)-Et(Me)C=CH$(CH_2)_2$	98
8	$EtOC{\equiv}C{-}H$ (16)	1a	$Me_3SiCH_2C(OEt){=}CHE$[f]	
			17a, E = H	95
			b, E = Cl	90
			c, E = I	95
			d, E = $H_2C{=}CHCH_2$	98
			e, E = $Me_3SiC{\equiv}C$	95
			f, E = CO_2Me	70
			g, E = (E)-$Me_3SiCH_2C(OEt){=}CH$	98
9	$RC{\equiv}CSMe$	1a,b	$Me_3SiCH_2C(R){=}CHSMe$[g]	
	18a, R = H		19a, R = H	70
	b, R = Ph		b, R = Ph	95
10	$HC{\equiv}CSPh$ (20)	1b	$Me_3SiCH_2CH{=}CHSPh$ (21)[h]	90
11	$RC{\equiv}CSO_2Me$	1a	$Me_3SiCH_2C(R){=}CHSO_2Me$[i]	
	22a, R = Ph		23a, R = Ph	98
	b, R = n-C_4H_9		b, R = n-C_4H_9	98
12	$PhC{\equiv}CSO_2Ph$ (24)	1a	$Me_3SiCH_2C(Ph){=}C(E)SO_2Ph$[i]	
			25a, E = H	80
			b, E = $H_2C{=}CHCH_2$	90

[a] The reactions were performed in THF. [b] The alcohol formed initially was converted into the O-silylated compound 9 without prior purification. [c] The geometry of the tetrasubstituted double bond has not been determined. [d] The geometry of the trisubstituted double bond is presumably E. [e] The E/Z ratio for 15 was in the range 70/30 to 90/10. [f] In all cases pure E isomers were obtained. [g] E/Z ratio: for 19a, 85/15; for 19b, >98/2. [h] E/Z ratio for 21: 70/30. [i] Pure E isomers were formed.

The conversion of 4 into 5 consists of two successive 1,3-substitution reactions (eq 1). The allene that is initially formed reacts further with 1a to give the synthetically highly useful allyl bis(silane) 5.[19] For this conversion 2 equiv of 1a are required. Diene 5 has been used as a conjunctive reagent in tandem Diels–Alder reactions[20] and, by umpolung, in tandem [6.5] annulations.[21] The literature procedure to prepare this valuable compound is rather laborious, and the overall yield is at its best 53%.[22] Our new procedure is rapid and gives 5 in 90% yield. We hope that the expeditious and economically attractive route depicted in eq 1 will stimulate further applications of 5 in organic synthesis. Note that α-acetylenic oxiranes such as 2 may be used to synthesize highly functionalized 1,3-dienes like 13 (we prepared 13 from 2 through 3 and 12).



The geometries of the tetrasubstituted double bond of 9 and of the trisubstituted one of 13 have not been determined yet. In view of ^1H NMR and GLC analysis both compounds were formed with over 90% stereoselectivity. The double bond of 13 will be mainly E as it is reasonable to assume that the 1,3-substitution reaction in 12 will proceed by approach of 1a from the least hindered site (eq 2).[23] It is too premature to do a configurational assignment to 9 as it is not clear in which conformation compound 8 will preferentially react with 1a.



Addition. Table I shows that both 1a and 1b add smoothly to a variety of activated carbon–carbon triple bonds (entries 7–12; eq 3). The adducts were formed stereoselectively (X = CO_2Me, SR′) or even stereospecifically (X = OEt, SR′, SO_2R') by (predominant or

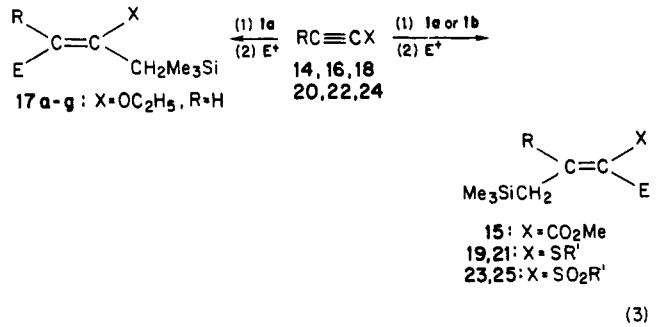
(19) Some hexamethylphosphoric triamide had to be added to prevent the formation of side products. The use of the disulfinate gave inferior results. Educt 4 was prepared in 90% yield following our procedure for the corresponding disulfinate: Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas*, **1980**, *99*, 340.

(20) Trost, B. M.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 4299.

(21) Trost, B. M.; Shimuzi, M. *J. Am. Chem. Soc.* **1983**, *105*, 6757.

(22) The literature procedure starts from 2,3-dibromopropene which is converted into 2-bromo-3-(trimethylsilyl)propene. The latter compound is treated sequentially with t-BuLi, cuprous bromide, and cupric chloride (total reaction time: 19.5 h). See: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1982**, *104*, 3733 (note 6 in ref 20).

(23) For a comparable stereochemistry see: Kleijn, H.; Vermeer, P. *J. Organomet. Chem.*, in press.



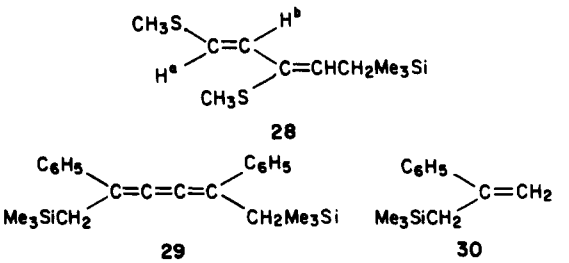
(3)

exclusive) cis addition of **1a** and **1b** (yields 70–98%). When **1b** was applied, only one of the two available Me_3SiCH_2 groups could be transferred with an acceptable rate, a phenomenon that is more observed in organocuprate chemistry. The conversion of ethoxyethyne (**16**) by **1a** into adduct **17a** (E = H) has already been described (yield 59% when THF was used as the solvent).[12] In the course of our study we found that the yield of this reaction can be improved up to 95%. We were especially interested in reactions of the intermediary adduct **17** (E = Cu) with electrophiles in order to get allylic silanes bearing some other functionalities. The adduct appeared to react smoothly and in excellent yields with *N*-chlorosuccinimide (→**17b**), iodine (→**17c**), allyl bromide (→**17c**), allyl bromide (→**17d**), (trimethylsilyl)ethynyl iodide (→**17e**), and carbon dioxide (→**17f**, after methylation according to Shaw et al.[24]); its oxidation by molecular oxygen gave the 1,3-diene **17g**. Adducts **17a** and **17b** were very prone to isomerize into the vinylic silanes $Me_3SiCH{=}C(OC_2H_5)CH_2E$ (E = H, Cl).

Another stereospecific route to the allylic silane **17e** (E = $Me_3SiC{\equiv}C$) was found in the reaction of iodide **17c** with $Me_3SiC{\equiv}CZnCl$ using tetrakis(triphenylphosphine)palladium as catalyst (yield 98%; cf. ref 25).

The 2-alkynoic esters **14a,b** reacted with **1a** and **1b** to give *Z*/*E* mixtures of the adducts **15a,b** in 90–98% yield (E = H). The *Z*/*E* ratio depended on whether **1a** or **1b** was used. In the case of **15a** the *Z*/*E* ratio amounted to 30/70 when **1a** was applied and 10/90 when **1b** was used as the reagent; adduct **15b** showed the *Z*/*E* ratio 27/73 when it was prepared from **14b** and **1b**. The addition of organocopper(I) species to 2-alkynoic esters is often accompanied with loss of stereospecificity.[26] The addition of **1** to 2-alkynoic esters constitutes an interesting entrance to natural product synthesis. Adduct **15b**, for instance, will be a valuable starting compound to synthesize the ethyl homologue of the recently discovered diterpene trixagol.[27,28]

Allylic silanes bearing in the γ-position an R'S group are available by reaction of **1a** and **1b** with 1-alkynyl sulfides (entries 9 and 10). The adduct was regio- and stereochemically pure starting from $C_6H_5C{\equiv}CSCH_3$ (**18b**, reagent **1b**); it was contaminated with a higher boiling compound starting from $HC{\equiv}CSCH_3$ (**18a**, reagents **1a** and **1b**). To the contaminant we assign structure **28** ($^3J(H^a,H^b)$ = 15.8 Hz; the configuration of $\Delta^{3,4}$ has not been determined yet). It will arise by subsequent addition of **19** (E = Cu, $CuCH_2Me_3SiMgCl$) to unreacted **18a**. The relative amount of **28** was 30% upon reaction of **18a** with an equimolar amount of **1a** and 20% upon reaction with an equimolar amount of **1b**; when 4.0 mol equiv of **18a** relative to the amount of **1b** was used, the percentage of **28** became 80%. Several attempts to prevent the formation of **28** by performing the reactions at lower temperatures (down to −60 °C) were unsuccessful. The purification of **19a** from **28** could easily be done by distillation at reduced pressure. Compound **28** itself is unstable, even when stored at −30 °C.



Reactions of organocopper(I) species with 1-alkynyl sulfides normally occur stereospecifically.[5] We were therefore rather surprised to find that the reactions of **18a** with **1a** as well as **1b** yield *E*/*Z* mixtures (ratio ca. 85/15). It is not clear whether the formation of both isomers occurs directly or that it is due to some isomerization in initially pure [α-(methylthio)vinyl]copper(I) compounds. Similarly, a mixture of isomeric adducts **21** (*E*/*Z* ca. 70/30) was obtained after reaction of $HC{\equiv}CSC_6H_5$ (**20**) with **1b**; the use of **1a** in this case gave highly impure adduct.

The interesting (*Z*)-butatriene **29** could be obtained by addition of excess of methyl iodide to adduct **19b** in which E was $CuCH_2Me_3Si$ (yield 75%).[29] Besides **29**, some **19b** in which E is CH_3 was also formed (yield 25%). As discussed elsewhere the conversion of [α-(methylthio)vinyl]cuprates into butatrienes will proceed through initial methylation of the methylthio group.[30]

Allylic silanes bearing in the γ-position a sulfonyl group could be prepared regio- and stereospecifically by reacting sulfones **22** and **24** with **1a** (yields 80–98%). Allylation of the intermediary vinylcopper(I) species was possible, albeit that the reaction is relatively slow when compared with the allylation of vinylcopper(I) species bearing hydrogen in the α-position.

Vinylic sulfones are versatile compounds. They undergo stereospecific reduction to olefins by reaction with sodium dithionite[31] and aluminum amalgam.[32] In the case of the allylic silane **25a** we attempted such a conversion. The sodium dithionite procedure (conditions: DMF/H_2O, $NaHCO_3$, 110 °C) led to α-methylstyrene. We think that the formation of α-methylstyrene took place by initial desilylation of **25a** followed by desulfonylation of the produced sulfone $C_6H_5(CH_3)C{=}CHSO_2C_6H_5$ (or its isomer $H_2C{=}C(C_6H_5)CH_2SO_2C_6H_5$). The aluminum amalgam reduction gave the desired compound 3-(trimethylsilyl)-2-phenylpropene (**30**) in 70% yield. The attempted preparation of **30** by treating phenylacetylene with **1a**, **1b**, or $(Me_3SiCH_2)_3Cu_2MgCl$ was not successful (solvent: THF).[33] Our sulfone route could therefore be an attractive

(24) Shaw, J. E.; Kunerth, D. C.; Sherry, J. J. *Tetrahedron Lett.* **1973**, 689.
(25) Negishi, E. In "Aspects of Mechanism and Organometallic Chemistry"; Brewster, J. H., Ed.; Plenum Press: New York, 1978; p 25 and references cited therein.
(26) For instance see ref 3. A stereocontrolled cis addition of $RCu{\cdot}BR'_3$ reagents to 2-alkynoic esters has been reported: Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Org. Chem.* **1979**, *44*, 1744.
(27) (a) De Pascual-T, J.; Caballero, E.; Caballero, C.; Medarde, M.; Barrero, A. F.; Grande, M. *Tetrahedron Lett.* **1978**, 3491. (b) *Ibid. Tetrahedron* **1982**, *38*, 1837.
(28) Armstrong, R. J.; Weiler, L. *Can. J. Chem.* **1983**, *61*, 2530.
(29) Van den Hoek, W. G. M.; Kroon, J.; Kleijn, H.; Westmijze, H.; Vermeer, P.; Bos, H. J. T. *J. Chem. Soc., Perkin Trans. 2* **1979**, 423.
(30) Westmijze, H.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1975**, 2923.
(31) Bremner, J.; Julia, M.; Launay, M.; Stacino, J.-P. *Tetrahedron Lett.* **1982**, *23*, 3265.
(32) Pascali, V.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1973**, 351.

alternative to the reported slow addition of **1a** and **1b** to inactivated 1-alkynes, a reaction that requires Et_2O as solvent (cf. ref 12).

Other interesting applications of vinylic sulfones are the stereoselective substitution of the sulfonyl group by Grignard compounds in the presence of transition-metal catalysts[34] and their (stereospecific) conversion into olefins by addition of cuprates.[35] Derivatization of vinylic sulfones is possible through α-lithiation.[36]

Conclusion

[(Trimethylsilyl)methyl]copper(I) compounds react with a wide variety of unsaturated compounds to give functionalized silanes under mild conditions, generally in good to excellent yields. This approach to prepare the synthetically very useful allylic silanes is therefore a valuable extension of the known methodologies to obtain such compounds.

Experimental Section

General Procedures. All reactions were performed under nitrogen. Tetrahydrofuran (THF) was distilled from $LiAlH_4$. (Trimethylsilyl)methyl chloride was purchased from Aldrich; its Grignard derivative was prepared in THF in the usual way and was stored under nitrogen and titrated prior to use by the method of Watson and Eastham.[37] The alkynes **2**, **14**, **16**, **18**, **22**, and **24** were prepared following standard procedures.[38-40] (*Z*)-6-Methyl-5-octen-1-yne, the starting material for ester **14b**, was obtained according to our procedure.[33] Sulfide **20** was prepared by reaction of $Me_3SiC{\equiv}CLi$ with an equimolar amount of PhSCl in Et_2O followed by subsequent desilylation of the product by sodium hydroxide in a mixture of methanol and water (yield 60%). Disulfonate **4** was prepared from 2-butyne-1,4-diol,[19] epoxide **8** from methoxypropadiene,[41] and sulfinates **6**, **10**, and **12** from the corresponding alcohols $H_2C{=}C{=}C(OMe)CH_2OH$,[42] $Me_2C{=}C{=}C(Me)CH_2OH$,[43] and **3**, respectively, by treatment of the alcohols with methanesulfinyl chloride using triethylamine as the base.[44] Cuprous bromide was prepared by the method of Keller and Wycoff.[45] Lithium bromide was dried at 220 °C under high vacuum and was used as a 3.0 M solution in THF.

The ^1H NMR spectra were recorded at 90 MHz with a Varian EM-390 spectrometer. The spectra were obtained from CCl_4, C_2Cl_4, or $CDCl_3$ solutions containing $CHCl_3$ or CH_2Cl_2 as the internal standard. The chemical shifts are expressed in parts per million (δ) downfield from Me_4Si, and the ^1H NMR peak areas are expressed as the number of hydrogen atoms (H). Mass spectra were recorded with a Kratos MS-80 spectrometer. The IR spectra were obtained with a Perkin-Elmer Model 457 spectrophotometer as neat liquid films or as KBr pellets and were calibrated with a polystyrene standard. Elemental analyses were performed by G. J. Rotscheid, ITC/TNO Zeist, The Netherlands. Analytical GLC was performed with a Pye-Unicam Model 104 gas chromatograph using a SE-33 column.

Preparation of the Copper(I) Reagents. A solution of $LiCuBr_2$ (15.0 mmol) in THF (35 mL)[46] was cooled to −60 °C, and [(trimethylsilyl)methyl]magnesium chloride (1.0 M solution in THF; 15.0 mmol to prepare **1a** and 30.0 mmol to prepare **1b**) was dropwise added. The mixture was stirred for 15 min at −60 °C and then used as such.

General Procedure To Prepare 3, 7, 11, and 13. To a stirred solution of **1a** (15.0 mmol) in THF (50 mL) was added, at −60 °C, substrate **2**, **6**, **10**, or **12** (13.0 mmol of each). The mixture was stirred for 0.5 h at 25 °C and then poured into an aqueous NH_4Cl solution containing NaCN (ca. 1 g). The products were isolated by extraction with pentane (3 × 30 mL). The combined extracts were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was stripped off in vacuo and the residue distilled at reduced pressure. The purity of the compounds was at least 95% (by GLC and ^1H NMR); physical constants and characteristic spectroscopic data for the compounds are as follows:

2-Methyl-5-(trimethylsilyl)-2,3-pentadien-1-ol (3): bp 100–102 °C (15 mmHg); $[n]^{20}_D$ 1.4792; IR (neat) 3360, 1958, 1260 cm^{-1}; ^1H NMR (CCl_4) δ 5.18 (m, J = 3.0, 3.0, 8.4 Hz, 1 H), 3.98 (d, J = 3.0 Hz, 2 H), 1.72 (d, J = 3.0 Hz, 3 H), 1.33 (d, J = 8.4 Hz, 2 H), 0.07 (s, 9 H); mass spectrum, m/z 170 (parent), 73 (base). Anal. Calcd for $C_9H_{18}OSi$: C, 63.49; H, 10.66. Found: C, 63.28; H, 10.52.

3-Methoxy-4-methyl-2-[(trimethylsilyl)methyl]-1,3-pentadiene (7): bp 70–72 °C (15 mmHg); $[n]^{20}_D$ 1.4551; IR (neat) 3080, 1660, 1615, 1250 cm^{-1}; ^1H NMR (CCl_4) δ 5.13 (br s, 1 H), 4.87 (d, J = 2.5 Hz, 1 H), 3.46 (s, 3 H), 1.80 (s, 3 H), 1.76 (s, 3 H), 1.72 (br s, 2 H), 0.12 (s, 9 H); mass spectrum, m/z 198 (parent), 73 (base). Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 65.34; H, 10.77.

2,4-Dimethyl-3-[(trimethylsilyl)methyl]-1,3-pentadiene (11): bp 65–68 °C (15 mmHg); $[n]^{20}_D$ 1.4557; IR (neat) 3080, 1630, 1250 cm^{-1}; ^1H NMR (CCl_4) δ 5.02 (br s, 1 H), 4.71 (br s, 1 H), 1.87 (s, 3 H), 1.78 (br s, 3 H), 1.69 (br s, 5 H), 0.09 (s, 9 H); mass spectrum, m/z 182 (parent), 73 (base); HR MS for $C_{11}H_{22}Si$ (calcd) 182.1490, (found) 182.1496.

2-Methyl-3-[(trimethylsilyl)methyl]-5-(trimethylsilyl)-1,3-pentadiene (13): bp 100 °C (15 mmHg); $[n]^{20}_D$ 1.4592; IR (neat) 3080, 1627, 1250 cm^{-1}; ^1H NMR (CCl_4) δ 5.16 (t, J = 8.5 Hz, 1 H), 5.06 (br s, 1 H), 4.80 (br s, 1 H), 1.90 (br s, 3 H), 1. 68 (s, 2 H), 1.65 (d, J = 8.5 Hz, 2 H), 0.15 (s, 18 H); mass spectrum, m/z 240 (parent), 73 (base).

Preparation of 2,3-Bis[(trimethylsilyl)methyl]-1,3-butadiene (5). Diester **4** (12.5 mmol) was added at −60 °C to a stirred solution of copper(I) compound **1a** in THF (50 mL) containing some hexamethylphosphoric triamide (15 mL). The temperature of the mixture was raised to 25 °C, and stirring at this temperature was continued for 1 h. The product was isolated as described above. The purity of the product was at least 98% (by GLC and ^1H NMR): bp 95–97 °C (15 mmHg); $[n]^{20}_D$ 1.4641; IR (neat) 3100, 1615, 1582, 1250 cm^{-1}; ^1H NMR (CCl_4) δ 5.06 (br s, 2 H), 4.87 (br s, 2 H), 1.87 (s, 4 H), 0.16 (s, 9 H); mass spectrum, m/z 226 (parent), 73 (base); HR MS for $C_{12}H_{26}Si_2$ (calcd) 226.1573, (found) 226.1595.

Preparation of 3-Methoxy-4-methyl-2-[(trimethylsilyl)methyl]-5-[(trimethylsilyl)oxy]-1,3-pentadiene (9). This 1,3-diene was prepared in a manner similar to **3**, **7**, **11**, and **13**. The resulting carbinol was converted into the corresponding silyl ether by treatment with chlorotrimethylsilane in the presence of triethylamine as base (solvent: Et_2O). The distilled product contained ca. 15% of an unknown impurity (by GLC and ^1H NMR): bp 72–75 °C (0.3 mmHg); $[n]^{20}_D$ 1.4542; IR (neat) 3080, 1660, 1250 cm^{-1}; ^1H NMR (CCl_4) δ 5.02 (m, 1 H), 4.81 (d, J = 2.5 Hz, 1 H), 4.12 (s, 2 H), 3.18 (s, 3 H), 1.42 (s, 3 H), 1.30 (br s, 2 H), −0.28 (s, 9 H), −0.40 (s, 9 H); mass spectrum, m/z 286 (parent), 73 (base); HR MS for $C_{14}H_{30}O_2Si_2$ (calcd) 286.1784, (found) 286.1767.

General Procedure for the Conversion of 2-Alkynoic Esters. The 2-alkynoic ester **14a** or **14b** (15.0 mmol) was added

(33) The corresponding copper(I) compound Me_3Cu_2MgCl is more reactive, see: Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 249.
(34) Fabre, J. L.; Julia, M.; Verpeaux, J. N. *Tetrahedron Lett.* **1982**, *23*, 2469.
(35) De Chirico, G.; Fiandanese, V.; Marchese, G.; Naso, F.; Sciacovelli, O. *J. Chem. Soc., Chem. Commun.* **1981**, 523.
(36) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3279.
(37) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.
(38) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971.
(39) Brandsma, L.; Verkruijsse, H. D. "Synthesis of Acetylenes, Allenes and Cumulenes. A Laboratory Manual"; Elsevier: Amsterdam, 1981.
(40) Jäger, V. In "Houben-Weyl, Methoden der Organischen Chemie"; Georg Thieme Verlag: Stuttgart, 1977; Vol. 2a.
(41) Schreurs, P. H. M.; Meijer, J.; Vermeer, P.; Brandsma, L. *Tetrahedron Lett.* **1976**, 2387.
(42) Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916.
(43) This alcohol was prepared following our procedure: Vermeer, P.; Meijer, J.; de Graaf, C.; Schreurs, H. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 46.
(44) See our procedure given in ref 17.
(45) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.
(46) The THF-soluble complex was obtained by stirring cuprous bromide (15.0 mmol) with lithium bromide (15.0 mmol) in THF (35 mL) for 15 min at 25 °C.

at −60 °C to a stirred solution of cuprate **1b** (15.0 mmol) in THF (65 mL). The mixture was stirred for 1 h at −30 °C and then poured into a saturated aqueous NH_4Cl solution containing NaCN (ca. 1 g). The product was extracted with pentane (2 × 30 mL); the combined extracts were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was stripped off in vacuo and the residue distilled at reduced pressure. The purity of the 2-alkenoic esters prepared in this manner was at least 95% (by GLC and ^1H NMR). Physical constants and spectroscopic data are as follows:

Methyl 4-(trimethylsilyl)-3-phenyl-2-butenoate (15a): *Z*/*E* ratio 10/90; bp 100–110 °C (0.5 mmHg); $[n]^{20}_D$ 1.5240; IR (neat) 1725, 1708, 1622, 1250 cm^{-1}; ^1H NMR (CCl_4) δ 7.1–7.5 (m, 5 H), 5.92 (s, 1 H, *Z*-**15a**), 5.73 (s, 1 H, *E*-**15a**), 3.72 (s, 3 H, *Z*-**15a**), 3.52 (s, 3 H, *E*-**15a**), 2.90 (s, 2 H, *Z*-**15a**), 2.08 (s, 2 H, *E*-**15a**), −0.05 (s, 9 H, *Z*-**15a** and *E*-**15a**); mass spectrum, *m*/*z* 248 (parent), 144 (base); HR MS for $C_{14}H_{20}O_2Si$ (calcd) 248.1233, (found) 248.1234.

Methyl 7-methyl-3-[(trimethylsilyl)methyl]-2,6-nonadienoate (15b): 2*Z*,6*Z*/2*E*,6*Z* ratio 27/73; bp 60–65 °C (0.01 mmHg); $[n]^{20}_D$ 1.4779; IR (neat) 1720, 1630, 1250 cm^{-1}; ^1H NMR (CCl_4) δ 5.40 (s, 1 H, 2*Z*,6*Z*-**15b**), 5.31 (s, 1 H, 2*E*,6*Z*-**15b**), 5.02 (br t, *J* = 7.2 Hz, 1 H, 2*E*,6*Z*-**15b** (corresponding proton for the 2*Z*,6*Z* isomer positioned at δ 4.95, which was determined by proton decoupling experiments)), 3.45 (s, 3 H, both isomers), 2.60–1.74 (several overlapping multiplets, total area 8 H), 1.62 (s, 2 H, 2*E*,6*Z*-**15b**), 1.58 (s, 3 H, both isomers), 0.87 (t, *J* = 6.9 Hz, 3 H, both isomers), 0.02 (s, 9 H); mass spectrum, *m*/*z* 268 (parent), 73 (base). Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51; Si, 10.46. Found: C, 66.25; H, 10.30; Si, 10.19.

Procedures for the Conversion of Ethoxyacetylene into Adducts 17a–g. Ethoxyacetylene (**16**; 15.0 mmol) was added at −60 °C to a stirred solution of copper(I) compound **1a** in THF (50 mL). The mixture obtained was stirred for 0.5 h at −30 °C. Adducts **17a–g** (purity >95% by ^1H NMR and GLC) were obtained as follows:

2-Ethoxy-3-(trimethylsilyl)-1-propene (17a). This adduct was formed by pouring the reaction mixture described above into a saturated aqueous NH_4Cl solution (150 mL) containing NaCN (ca. 1 g) and extracting it with pentane (see the procedure for the isolation of **15a,b**): bp 35–37 °C (15 mmHg); $[n]^{20}_D$ 1.4250; IR (neat) 3110, 1638, 1245 cm^{-1}; ^1H NMR (CCl_4) 3.65 (d, *J* = 1.5 Hz, 1 H), 3.60 (d, *J* = 1.5 Hz, 1 H), 3.59 (q, *J* = 7.2 Hz, 2 H), 1.54 (s, 2 H), 1.18 (t, *J* = 7.2 Hz, 3 H), 0.04 (s, 9 H).

(*E*)-1-Chloro-2-ethoxy-3-(trimethylsilyl)-1-propene (17b). This compound was obtained by cooling the THF solution of the vinylcopper(I) adduct down to −60 °C followed by addition of hexamethylphosphoric triamide (6 mL) and *N*-chlorosuccinimide (15.0 mmol). The resulting deep blue solution was stirred for 0.5 h at −60 °C and then poured into a saturated aqueous NH_4Cl solution containing NaCN (ca. 1 g). Workup was accomplished as described for **15a,b**: bp 70–71 °C (15 mmHg); $[n]^{20}_D$ 1.4500; IR (neat) 3110, 1618, 1249 cm^{-1}; ^1H NMR (CCl_4) 4.99 (s, 1 H), 3.60 (q, *J* = 7.0 Hz, 2 H), 1.79 (s, 2 H), 1.21 (t, *J* = 7.0 Hz, 3 H), 0.06 (s, 9 H).

(*E*)-2-Ethoxy-1-iodo-3-(trimethylsilyl)-1-propene (17c). In this case iodine (15.0 mmol) was added at −30 °C to the vinylcopper(I) compound. The mixture was then stirred for 1 h at 25 °C. Compound **17c** was isolated as described for **15a,b**. The vinylic iodide was unstable and had to be stored in the refrigerator at −30 °C: bp 50–51 °C (1 mmHg); $[n]^{20}_D$ 1.5017; IR (neat) 3100, 1600, 1251 cm^{-1}; ^1H NMR (CCl_4) 4.67 (s, 1 H), 3.75 (q, *J* = 7.0 Hz, 2 H), 1.95 (s, 2 H), 1.27 (t, *J* = 7.0 Hz, 3 H), 0.07 (s, 9 H).

(*E*)-5-Ethoxy-6-(trimethylsilyl)-1,4-hexadiene (17d). This skipped diene was synthesized by adding allyl bromide (15.0 mmol) to the vinylcopper(I) adduct at −30 °C followed by stirring the resulting mixture for 3 h at 25 °C. Diene **17d** was isolated as described for **15a,b**: bp 65–67 °C (15 mmHg); $[n]^{20}_D$ 1.4495; IR (neat) 3080, 1662, 1638, 1249 cm^{-1}; ^1H NMR (CCl_4) 5.71 (m, *J* = 6.0, 6.9, 17.4 Hz, 1 H), 5.07 (br d, *J* = 17.4 Hz, 1 H), 4.99 (br d, *J* = 9.6 Hz, 1 H), 4.13 (t, *J* = 7.5 Hz, 1 H), 3.57 (q, *J* = 7.0 Hz, 2 H), 2.59 (dd, *J* = 6.0, 7.5 Hz, 2 H), 1.50 (s, 2 H), 1.17 (t, *J* = 7.0 Hz, 3 H), −0.03 (s, 9 H); mass spectrum, *m*/*z* 198 (parent), 73 (base); HR MS for $C_{11}H_{22}OSi$ (calcd) 198.1440, (found) 198.1433.

(*E*)-4-Ethoxy-1,5-bis(trimethylsilyl)-3-penten-1-yne (17e). The enyne was prepared by adding (trimethylsilyl)ethynyl iodide (15.0 mmol) to the intermediary vinylcopper(I) compound at −30 °C followed by stirring the reaction mixture for 2 h at 25 °C. Isolation of the product was accomplished as described for **15a,b**. An alternative route to **17e** was as follows: A solution of [(trimethylsilyl)ethynyl]zinc chloride (5.0 mmol) in THF (20 mL) was prepared by adding at −30 °C a solution of *n*-BuLi (5.0 mmol) in *n*-hexane (3.5 mL) to a stirred solution of (trimethylsilyl)-acetylene (5.5 mmol) in THF (15 mL) followed after 5 min by zinc chloride (5.0 mmol, dissolved in 5 mL of dry THF). The mixture was stirred for 5 min at −20 °C. Subsequently were added at −20 °C tetrakis(triphenylphosphine)palladium[47] (10 mL of a 0.02 M solution in THF) and iodide **17c** (5.0 mmol). The mixture was stirred for 0.75 h at 25 °C and worked up in the usual way (yield of **17e** 98%; purity >95% (by GLC and ^1H NMR)): bp 115–117 °C (15 mmHg); $[n]^{20}_D$ 1.4720; IR (neat) 3060, 2138, 1605, 1250, 1235 cm^{-1}; ^1H NMR (CCl_4) 4.32 (s, 1 H), 3.68 (q, *J* = 7.0 Hz, 2 H), 1.89 (s, 2 H), 1.23 (t, *J* = 7.0 Hz, 3 H), 0.12 (s, 9 H), 0.02 (s, 9 H).

Methyl (*E*)-3-Ethoxy-4-(trimethylsilyl)-2-butenoate (17f). The ester was formed by adding lithium bromide (75.0 mmol) to the vinylcopper(I) adduct followed by passing an excess of dry carbon dioxide through the resulting solution for 0.5 h at 25 °C. The reaction mixture was poured into a saturated aqueous NH_4Cl solution (200 mL) containing NaCN (ca, 1 g) and the acid extracted with ether (3 × 30 mL). The ether was evaporated and the residue converted into the corresponding ester by adding it to a solution of sodium hydroxide (30.0 mmol) in a mixture of water and hexamethylphosphoric triamide (7 and 38 mL, respectively) and shaking the resulting mixture with methyl iodide (55.0 mmol) for 15 min at 25 °C. The ester was isolated by pouring the reaction mixture into a 0.2 N HCl solution (100 mL) and extracting the ester with pentane (3 × 30 mL). The combined extracts were washed with a saturated aqueous NH_4Cl solution (2 × 50 mL) and dried with $MgSO_4$. The solvent was evaporated in vacuo: bp 95–100 °C (15 mmHg); $[n]^{20}_D$ 1.4609; IR (neat) 1710, 1600, 1248 cm^{-1}; ^1H NMR (CCl_4) 4.76 (s, 1 H), 3.74 (q, *J* = 6.9 Hz, 2 H), 3.53 (s, 3 H), 2.34 (s, 2 H), 1.21 (t, *J* = 6.9 Hz, 3 H), −0.05 (s, 9 H); mass spectrum, *m*/*z* 216 (parent), 73 (base). Anal. Calcd for $C_{10}H_{20}O_3Si$: C, 55.52; H, 9.33. Found: C, 54.47; H, 9.07.

(*E*,*E*)-2,5-Diethoxy-1,6-bis(trimethylsilyl)-2,4-hexadiene (17g). This conjugated diene was easily obtained by passing dry oxygen through the THF solution of the vinylcopper(I) adduct for 2 h at 25 °C. The product was isolated as indicated for compounds **15a,b**: mp 45.0 °C; IR (KBr) 3080, 1600, 1248 cm^{-1}; ^1H NMR (CCl_4) 4.86 (s, 2 H), 3.64 (q, *J* = 7.0 Hz, 4 H), 1.56 (s, 4 H), 1.22 (t, *J* = 7.0 Hz, 6 H), 0.02 (s, 18 H).

Procedures for the Conversion of 1-Alkynyl Sulfides into 1-Alkenyl Sulfides. To a stirred solution of cuprate **1b** (15.0 mmol) in THF (65 mL) was added, at −60 °C, the 1-alkynyl sulfide (15.0 mmol in the case of **18**, 11.5 mmol in the case of **20**). The resulting mixture was stirred for 2 h at −30 °C in the case of sulfide **20** and for 1 h at 25 °C in the case of **18**. The adducts were isolated as described for **15a,b**. Crude **19a** contained ca. 20% of diene **28**. The adducts were purified by distillation at reduced pressure. Their purities were determined by GLC and ^1H NMR analysis and amounted to ca. 90% for **19a** (*E*/*Z* ca. 85/15), 95% for **19b**, and better than 95% for **21** (*E*/*Z* ca. 70/30).

(*E*/*Z*)-3-(Trimethylsilyl)-1-(methylthio)-1-propene (19a): bp 65–67 °C (15 mmHg); $[n]^{20}_D$ 1.4717; IR (neat) 1600, 1247 cm^{-1}; ^1H NMR (CCl_4) for the *E* isomer 5.70 (d, *J* = 14.4 Hz, 1 H), 5.38 (dt, *J* = 7.5, 14.4 Hz, 1 H), 2.09 (s, 3 H), 1.43 (d, *J* = 7.5 Hz, 2 H), −0.05 (s, 9 H); mass spectrum, *m*/*z* 160 (parent), 73 (base). Anal. Calcd for $C_7H_{16}SSi$: C, 52.43; H, 10.05. Found: C, 52.09; H, 10.04.

(*E*)-3-(Trimethylsilyl)-1-(methylthio)-2-phenyl-1-propene (19b): bp 80–85 °C (0.1 mmHg); $[n]^{20}_D$ 1.5455; IR (neat) 1600, 1248 cm^{-1}; ^1H NMR (CCl_4) 7.33 (s, 5 H), 5.72 (s, 1 H), 2.21 (s, 3 H), 2.00 (s, 2 H), −0.09 (s, 9 H) (s, 9 H); mass spectrum, *m*/*z* 236 (parent), 73 (base); HR MS for $C_{13}H_{20}SSi$ (calcd) 236.1055, (found) 236.1053.

(*E*/*Z*)-3-(Trimethylsilyl)-1-(phenylthio)-1-propene (21): bp 80–85 °C (0.1 mmHg); $[n]^{20}_D$ 1.5506; IR (neat) 3070, 3055, 1580, 1250 cm^{-1}. ^1H NMR (CCl_4) 7.0–7.5 (m, 5 H), 5.7–6.3 (m, 2 H),

(47) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

1.78 (d, J = 7.5 Hz, 2 H of the E isomer), 1.64 (d, J = 7.4 Hz, 2 H of the Z isomer), 0.1 (s, 9 H); mass spectrum, m/z 222 (parent), 73 (base).

General Procedure for the Conversion of 1-Alkynyl Sulfones into 1-Alkenyl Sulfones. To a stirred solution of copper(I) compound **1a** (15.0 mmol) in THF (50 mL) was added, at -60 °C, the 1-alkynyl sulfone **22** or **24** (15.0 mmol). The mixture was stirred for 2 h at -30 °C in the case of **22** and for 1.5 h at 25 °C in the case of **24**. The 1-alkenyl sulfones **23a**, **23b**, and **25a** were obtained by pouring the respective reaction mixtures into an aqueous NH_4Cl solution (150 mL) containing NaCN (ca. 1 g). The products were isolated by extraction with methylene chloride (3 × 50 mL), washing the combined extracts with water (3 × 50 mL) and drying with $MgSO_4$. The solvent was evaporated in vacuo at 25 °C. Sulfone **23a** was obtained as a pure, white crystalline compoune (purity >95% by ^1H NMR); sulfones **23b** and **25a** were oils and could be distilled under high vacuum (purity of **23b** >95% by GLC and ^1H NMR; purity of **25a** ca. 90% by ^1H NMR). The allylated compound **25b** was prepared by adding allyl bromide (38 mmol) to the intermediary vinylcopper(I) compound **25** (E = Cu) and stirring the mixture for 1 h at 25 °C. Its isolation was performed as described for the other sulfones. The allylated adduct was a white solid and contained ca. 10% of an unknown impurity (by ^1H NMR).

(*E*)-1-(Methylsulfonyl)-3-(trimethylsilyl)-2-phenyl-1-propene (23a): mp 129.7 °C; IR (KBr) 1605, 1592, 1280, 1245, 1132, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) 7.34 (s, 5 H), 6.18 (s, 1 H), 2.47 (s, 3 H), 2.00 (s, 2 H), -0.14 (s, 9 H); mass spectrum, m/z 268 (parent), 73 (base). Anal. Calcd for $C_{13}H_{20}O_2SSi$: C, 58.16; H, 7.51; S, 11.95; Si, 10.46. Found: C, 58.14; H, 7.42; S, 11.95; Si, 10.27.

(*E*)-1-(Methylsulfonyl)-2-[(trimethylsilyl)methyl]-1-hexene (23b): bp 115-120 °C (0.05 mmHg); $[n]^{20}_D$ 1.4817; IR (neat) 1603, 1300, 1248, 1123 cm^{-1}; ^1H NMR (CCl_4) 5.62 (s, 1 H), 2.60 (s, 3 H), 2.22 (br t, J = 7.5 Hz, 2 H), 1.49 (s, 2 H), 0.90-1.40 (m, 4 H), 0.68 (t, J = 6.5 Hz, 3 H), -0.15 (s, 9 H).

(*E*)-1-(Phenylsulfonyl)-3-(trimethylsilyl)-2-phenyl-1-propene (25a): bp 140-150 °C (0.2 mmHg); $[n]^{20}_D$ 1.5687; IR (neat) 3050, 1585, 1248 cm^{-1}; ^1H NMR (CCl_4) 7.0-8.0 (m, 10 H), 6.38 (s, 1 H), 2.05 (s, 2 H), -0.01 (s, 9 H); mass spectrum, m/z 330 (parent), 192 (base).

(*E*)-4-(Phenylsulfonyl)-6-(trimethylsilyl)-5-phenyl-1,4-hexadiene (25b): mp 43.2 °C; IR (neat) 3060, 1635, 1607, 1590, 1250 cm^{-1}; ^1H NMR (CCl_4) 6.8-8.1 (m, 10 H), 5.7-6.2 (m, J = 6.2, 10.8, 17.1 Hz, 1 H), 5.18 (br d, J = 17.1 Hz, 1 H), 5.15 (br d, J = 10.8 Hz, 1 H), 3.38 (d, J = 6.2 Hz, 2 H), 1.96 (s, 2 H), -0.13 (s, 9 H).

Preparation of (*Z*)-1,6-Bis(trimethylsilyl)-2,5-diphenyl-2,3,4-hexatriene (29). Excess of methyl iodide (70 mmol) was added at -30 °C to the mixed homocuprate **19** (E = $CuCH_2Me_3SiMgCl$; 15.0 mmol; 65 mL of THF). The mixture was stirred for 1 h at 25 °C and then poured into an aqueous NH_4Cl solution (200 mL) containing NaCN (ca. 1 g). The product was isolated as described for **15a,b** and purified by crystallization from methanol (purity >95% by ^1H NMR): mp 119.5 °C; Raman 2043, 1592, 1490, 1320, 1303, 1280, 1184, 1103, 1001 cm^{-1}; ^1H NMR (CCl_4) 7.50 (br d, J = 6.9 Hz, 4 H), 7.0-7.4 (m, 6 H), 2.12 (s, 4 H), -0.08 (s, 18 H); mass spectrum, m/z 376 (parent), 73 (base).

Preparation of 3-(Trimethylsilyl)-2-phenyl-1-propene (30). Aluminum amalgam (0.16 mol of Al in 2% aqueous $HgCl_2$)[48] was added to a stirred solution of 1-alkenyl sulfone **25a** (5.0 mmol) in a mixture of THF (190 mL) and water (10 mL). The mixture was refluxed for 2 h. After the reaction mixture was poured into an aqueous NH_4Cl solution (400 mL), the product was extracted with pentane (3 × 50 mL). The combined extracts were washed with water (3 × 50 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue distilled at reduced pressure to give **30** in 70% yield and with a purity of at least 95% (by GLC and ^1H NMR): bp 100-102 °C (15 mmHg); $[n]^{20}_D$ 1.5109; IR (neat) 3080, 1615, 1250 cm^{-1}; ^1H NMR (CCl_4) 7.1-7.5 (m, 5 H), 5.09 (br s, 1 H), 4.79 (br s, 1 H), 1.97 (s, 2 H), -0.11 (s, 9 H).

(48) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1345.

Synthesis of α-Arylsulfonoxy Ketones from Ketone Derivatives

Robert V. Hoffman,* C. Sean Carr, and Bryan C. Jankowski

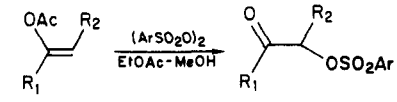
Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003

Received April 30, 1985

Silyl enol ethers, enamines, and enols can all be efficiently converted to α-arylsulfonoxy ketones by reaction with arylsulfonyl peroxides.

There has been increasing interest in the chemistry of α-sulfonoxy ketones. They have been used as precursors for α-keto carbocations,[1] as Favorski ring contraction substrates,[2] and as thiol-specific electrophiles.[3] In addition, Creary has described some interesting base-catalyzed reactions of these compounds.[1] The most common preparation of these materials begins with an α-hydroxy ketone that is condensed with a sulfonyl chloride in the presence of base.[4] This method is quite erratic,[5] and often it is necessary to first prepare the corresponding sulfinate ester, which is then oxidized to the sulfonate ester.[6] A recent paper by Koser describes the preparation of α-tosyloxy ketones by the reaction of ketones with [hydroxy(tosyloxy)iodo]benzene. This method is not regiospecific for unsymmetric ketones, although good yields are obtained.[7]

Work in these laboratories has shown that arylsulfonyl peroxides react with enol acetates in the presence of methanol to give α-arylsulfonoxy ketones in high yields (eq 1).[8] Many preparations for enol acetates have been



(1)

reported.[9] Enol acetates are most commonly prepared from ketones by one of several methods.[10] They can also

(1) Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3. This is an excellent summary of the solvolytic work done with these compounds.
(2) Conia, J. M.; Salaun, J. R. *Acc. Chem. Res.* **1972**, *5*, 33.
(3) Simons, S. S., Jr.; Pons, M.; Johnson, D. F. *J. Org. Chem.* **1980**, *45*, 3084 and references therein.
(4) (a) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235. (b) Crossland, R. K.; Servis, K. L. *Ibid.* **1970**, *35*, 3195.
(5) See for example: (a) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 4151. (b) Creary, X.; Geiger, C. C. *Ibid.* **1983**, *105*, 7123.
(6) Coates, R. M.; Chen, J. E. *Tetrahedron Lett.* **1969**, 2705.
(7) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.
(8) Hoffman, R. V. *Synthesis*, in press.
(9) An excellent compilation of methods: Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966.

0022-3263/85/1950-5148$01.50/0