Substitution Reactions of Organocuprates with β-(Phenylseleno)vinyl Sulfones Derived from the Selenosulfonation of Acetylenes. A Convenient and Stereospecific Preparation of Vinyl Sulfones and Olefins from Acetylenes[1,2]

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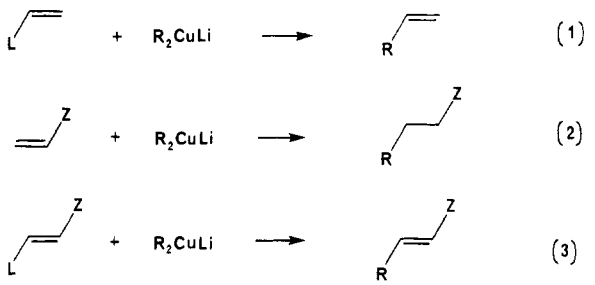
Received March 19, 1987

The free-radical selenosulfonation of acetylenes affords β-selenovinyl sulfones **1** which undergo substitution of the selenium moiety with organocuprates to provide a convenient and stereospecific preparation of vinyl sulfones **2** and therefore ultimately of di- and trisubstituted olefins **3**. The novel selenocuprates of general structure RCu(SePh)Li proved especially efficacious for this purpose and a ^{77}Se NMR study of MeCu(SePh)Li indicated that it is a homogeneous cuprate species. Vinyl cuprates also react with seleno sulfones **1** to afford conjugated dienyl sulfones. The substitutions generally proceed in high yield with retention of configuration. Grignard reagents in the presence of catalytic amounts of Cu(I) salts can be used instead of stoichiometric organocuprates but suffer from more stringent steric limitations and less predictable stereochemistry.

The first organocuprate, Me_2CuLi, was reported by Gilman and co-workers in 1952.[5] In the ensuing years, organocuprates proved to be invaluable reagents for C–C bond formation with myriad applications.[6] They effect substitution reactions with alkyl, aryl, or vinyl halides, as well as with sulfonates, acetates, and epoxides, usually in a highly stereospecific manner.[7] Organocuprates undergo 1,4-addition to enones and react similarly with other Michael acceptors.[8] In a process combining some of the features of both vinylic substitution and Michael addition, enones containing β-leaving groups are converted to β-alkylated substitution products by a formal addition–elimination sequence when treated with organocuprates.[9,10] These transformations are depicted in eq 1–3.



L= leaving group; Z= electron-withdrawing or delocalizing group

It occurred to us that β-selenovinyl sulfones **1** might be employed in a process analogous to eq 3, where L = SePh and Z = SO_2Ar, to afford β-alkylated vinyl sulfones. Although several Michael additions of organocuprates to other vinyl sulfones are known[11] to our knowledge the only reported instances of cuprate substitutions of C–Se compounds are those of seleno esters, which are thus converted to ketones.[12] However, the phenylseleno moiety is a reasonably effective leaving group,[13] and its departure is known to be assisted by complexation with "selenophilic" metal ions such as Cu(I).[14] The transformation of β-selenovinyl sulfones **1** to β-alkylvinyl sulfones **2** therefore seemed reasonable. The required starting materials **1** are readily available from the free-radical selenosulfonation of acetylenes, which is known to proceed in a highly regio- and stereoselective manner.[15] Futhermore, vinyl sulfones can be reductively desulfonylated by a number of literature methods,[16] in some cases stereospecifically.[16a-e] Our investigation of the reactions of β-selenovinyl sulfones with organocuprates[17] was therefore prompted by the expectation that such processes would permit the efficient and stereoselective conversion of acetylenes to di- and trisubstituted olefins **3** as shown in eq 4. Also, the vinyl sulfones

(1) We gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada.

(2) Taken in part from the Ph.D. Thesis of S. Collins, University of Calgary, 1983, and from the M.S. Thesis of K.-W. Law, University of Calgary, 1985.

(3) Recipient of an NSERC Postgraduate Scholarship and an Honorary Killam Scholarship.

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(5) Gilman, H.; Jones, R. G.; Woods, L. A. *J. Org. Chem.* **1952**, *17*, 1630.

(6) For reviews, see: (a) Posner, G. H. *An Introduction to Synthesis using Organocopper Reagents*; Wiley: New York, 1980. (b) Normant, J. F. *Pure Appl. Chem.* **1978**, *50*, 709. (c) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59.

(7) Posner, G. H. In *Organic Reactions*; Dauben, W. G., Ed.; Wiley: New York, 1975; Vol. 22, Chapter 2.

(8) Posner, G. H. In *Organic Reactions*; Dauben, W. G., Ed.; Wiley: New York, 1972; Vol. 19, Chapter 1.

(9) For a survey of such reactions, see ref 6a, p 66. See also: (a) Piers, E.; Cheng, K. F.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 1256. (b) Dieter, R. K.; Silks, L. A., III.; Fishpaugh, J. R.; Kastner, M. E. *J. Am. Chem. Soc.* **1985**, *107*, 4679.

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(11) For examples, see: (a) Posner, G. H.; Brunelle, D. J. *J. Org. Chem.* **1973**, *38*, 2747. (b) Hutchinson, D. K.; Hardinger, S. A.; Fuchs, P. L. *Tetrahedron Lett.* **1986**, *27*, 1425. (c) Hutchinson, D. K.; Fuchs, P. L. *Ibid.* **1986**, *27*, 1429. (d) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3277. (e) Julia, M.; Righini, A.; Verpeaux, J.-N. *Tetrahedron Lett.* **1979**, 2393. (f) Fiandanese, V.; Marchese, G.; Naso, F. *Tetrahedron Lett.* **1978**, 5131.

(12) Sviridov, A. F.; Ermolenko, M. S.; Yashunsky, D. V.; Kochetkov, N. K. *Tetrahedron Lett.* **1983**, *24*, 4355 and 4359.

(13) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans 2* **1977**, 1898.

(14) Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1980**, *102*, 860.

(15) (a) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077. (b) Back, T. G.; Collins, S.; Gokhale, U.; Law, K.-W. *Ibid.* **1983**, *48*, 4776. (c) Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438.

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(17) Preliminary communication: Back, T. G.; Collins, S.; Law, K.-W. *Tetrahedron Lett.* **1984**, *25*, 1689. For an application to marine sterol synthesis, see: Back, T. G.; Proudfoot, J. R.; Djerassi, C. *Tetrahedron Lett.* **1986**, *27*, 2187. For reactions of β-seleno sulfones with other carbon nucleophiles, see the following article.

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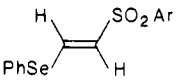
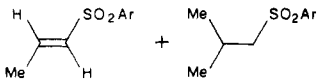
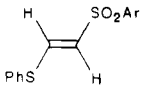
Table I. Reactions of Methylcuprates with 1a

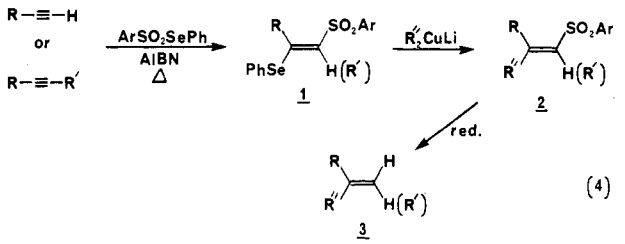


1a

entry	organocuprate (molar equiv)	conditions	products[a,b] (% yield)
1	Me_2CuLi (1:1)	0 °C, Et_2O, 2 h	 4 (68) + 5 (20)
2	MeCu(CN)Li (1.2)	−23 °C, THF, 2.5 h	4 (74)
3	MeCu(SPh)Li (1.2)	−23 °C, THF, 1 h	 6 (55) + 4 (31)
4	MeCu(SePh)Li (1.2)	0 °C, THF, 2 h	4 (90)

[a] Ar = *p*-tolyl. [b] All yields refer to isolated products.

2 are themselves products of interest with numerous synthetic applications.[11,16,18,19]

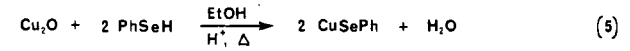


(4)

Results and Discussion

Alkyl Selenocuprates. Several classes of organocuprates have been reported, having differing reactivities and other properties. In many situations, a judicious choice of cuprate is required for optimum results. Among the most widely employed types of reagents are the dialkyl homocuprates (R_2CuLi),[6-8] heterocuprates of general structure RCuXLi where X is an appropriate ligand,[6-8] magnesium cuprates generated from Grignard reagents and catalytic (or stoichiometric) amounts of cuprous halides,[20] and various higher order cuprates.[21]

Our studies commenced with an investigation of the reactions of various methylcuprates with the simple, unsubstituted seleno sulfone **1a**. The results are shown in Table I. Lithium dimethylcuprate (Me_2CuLi) produced the desired vinyl sulfone **4** as the principal product, but this was accompanied by the dialkylated saturated sulfone **5**, evidently formed by the further addition of the cuprate to the initially produced **4**. This side reaction was suppressed with the cyanocuprate MeCu(CN)Li, but unfortunately this reagent proved ineffective with other, more substituted seleno sulfones **1** (where R, R′ ≠ H). The thiocuprate MeCu(SPh)Li behaved unexpectedly by preferentially transferring the PhS moiety[22] instead of the methyl group to the substrate, producing the β-thiovinyl sulfone **6** as the chief product. This undesired reaction would of course be prevented by employing the selenocuprate MeCu(SePh)Li instead of the corresponding thiocuprate. Although we were unable to find reports of selenocuprates in the literature, we discovered that they can be generated in situ in the conventional manner by adding 1 molar equiv of the appropriate alkyllithium to CuSePh in ether or THF. Cuprous phenylselenolate was in turn conveniently prepared by the acid-catalyzed reaction of benzeneselenol with cuprous oxide in ethanol (eq 5 and 6). When MeCu(SePh)Li was thus prepared and



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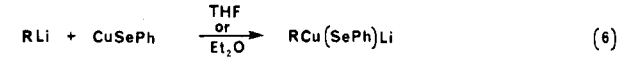

(6)

allowed to react with **1a**, the desired β-methyl sulfone **4** was obtained in excellent yield (entry 4, Table I) and was unaccompanied by the dialkylated byproduct **5**. This result suggested that selenocuprates would be the reagents of choice for the purpose at hand and prompted further study of their properties in this context.

Lipshutz and co-workers[23] demonstrated that the composition of organocuprates depends on factors such as the solvent, the presence of lithium salts, and the nature of the cuprous salt used in their formation. Under some conditions equilibrating mixtures of lower order cuprates, free alkyllithium, and higher order cuprates exist, instead of a unique organocuprate. In order to gain insight into the composition of a typical selenocuprate, we recorded the ^{77}Se NMR spectrum of MeCu(SePh)Li at −65 °C in THF solution. Only one signal, at δ 128 relative to dimethyl selenide was observed within the range δ −1500 to 2500. In a control experiment designed to confirm that

(18) For reviews, see: (a) Truce, W. E.; Klingler, T. C.; Brand, W. W. In *Organic Chemistry of Sulfur*; Oae, S.; Ed.; Plenum Press: New York, 1977; Chapter 10. (b) Durst, T. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 3, Chapter 11.9. (c) Field, L. *Synthesis* **1978**, 713. (d) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.

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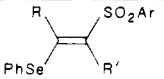
(20) Erdik, E. *Tetrahedron* **1984**, *40*, 641.

(21) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.

(22) Preferential thioarylation of 3-bromo-2-methyl-2-cyclopentenone with this reagent was also observed by Piers et al.; see ref 9a.

(23) (a) Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *J. Am. chem. Soc.* **1985**, *107*, 3197. (b) Lipshutz, B. H.; Whitney, S.; Kozlowski, J. A.; Breneman, C. M. *Tetrahedron Lett.* **1986**, *27*, 4273.

Table II. Substitution of β-Selenovinyl Sulfones 1 with Organocuprates



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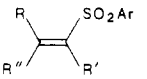
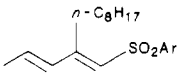
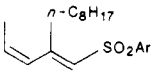


entry	starting material[a] no.	R	R′	organocuprate[b] R″	(equiv)	conditions[c] temp	(time, h)	product no.	(yield, %)[d]
1	**1a**	H	H	Me	(1.2)	0 °C	(2)	**4**	90
2	**1a**			*n*-Bu	(1.2)	0 °C	(0.5)	**7**	75
3	**1a**			*t*-Bu	(2.5)	rt	(3)	**8**	84
4	**1b**	*n*-C_8H_{17}	H	Me	(1.2)	0 °C	(3)	**9**	86
5	**1b**			*n*-Bu	(1.2)	0 °C	(2)	**10**	62
6	**1b**			Ph[e]	(2.0)	0 °C	(0.5)	**11**	45
7	**1b**			MeCH=CH[e]	(2.0)	rt[f]	(0.5)	**12**[g]	78
8	**1b**			(MeO)C=CH_2[e]	(2.0)	rt[f]	(0.5)	**13**	68
9	**1c**	Me_3Si	H	Me	(2.6)	rt	(17)	**14**	56
10	**1d**	*n*-Bu	*n*-Bu	Me	(2.6)	rt	(20)	**15**	92
11	**1d**			*n*-Bu	(2.6)	rt	(19)	**16**	80
12	**1d**			*sec*-Bu	(2.5)	rt[h]	(16)	**17**	76
13	**1e**	Ph	Me	Me	(1.2)	rt	(2)	**18**	41
14	**1f**	Ph	Ph	Me	(1.2)	rt	(3)	**19**	82
15	**1g**	$HOCH_2CH_2$	H	(MeO)C=CH_2[e]	(2.0)	rt[f]	(0.5)	**20**	79

[a] Ar = *p*-tolyl. [b] Organocuprates were prepared from equimolar amounts of R″Li and CuSePh unless otherwise noted. [c] All reactions were performed in THF solution. rt = room temperature. [d] Isolated yields are reported on homogeneous products (one spot on TLC and/or >97% pure on GC). [e] Organocuprates were prepared from 2R″Li + CuBr·SMe_2. [f] The reaction was first performed at −70 °C, then warmed to room temperature and continued for the indicated time. [g] The product was a 70:30 mixture of **12a** and **12b**. [h] HMPA (~10%) was added to the reaction mixture.

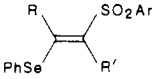


12a



12b

Table III. Substitution of β-Selenovinyl Sulfones with Cu(I)-Catalyzed Grignard Reagents[a]



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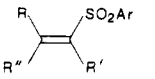


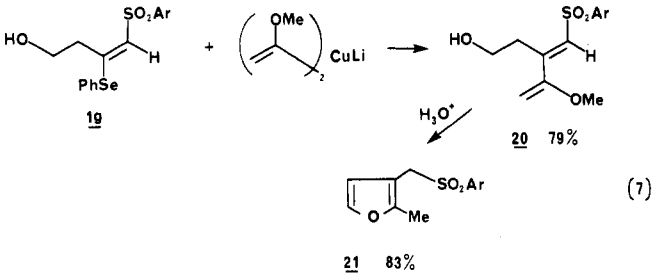
entry	starting material[b] no.	R	R′	catalyst CuX, X =	R″MgBr R″	(equiv)	h	product no.	(yield, %)[c]
1	**1b**	*n*-C_8H_{17}	H	Br	Me	(1.2)	2	**9**	89
2	**1b**			I	Me	(1.2)	3	**9**	82
3	**1b**			CN	Me	(1.2)	3	**9**	82
4	**1b**			SPh	Me	(1.2)	3	**9**	78
5	**1b**			SePh	Me	(3)	3.5	**9**	100
6	**1b**			Br	Et	(4)	1	**24**	35
7	**1b**			SePh	Et	(1.6)	1	**24**	49
8	**1c**	Me_3Si	H	SePh	Me	(5)	1	**14**	84
9	**1e**	Ph	Me	SePh	Me	(5)	48	**18**	39
10	**1e**			SePh	Et	(4)	4	**25**	13
11	**1g**	$HO(CH_2)_2$	H	SePh	Me	(5)	1	**26**	77
12	**1g**			SePh	Et	(1.6)	2	**27**	40

[a] All reactions were performed in THF solvent at room temperature in the presence of 0.02–0.10 mol equiv of CuX. [b] Ar = *p*-tolyl. [c] Isolated yields are reported.

this signal was due to the actual cuprate and not to an artifact of its decomposition, the cuprate solution was subsequently treated with seleno sulfone **1b** and observed to react normally (vide infra). We therefore conclude that MeCu(SePh)Li is a homogeneous cuprate species which survived intact during the NMR experiment.[24]

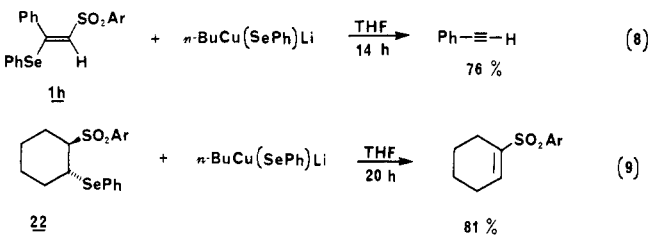
Reactions of Organocuprates with β-Selenovinyl Sulfones 1. The substitution reactions of organocuprates with a variety of other β-selenovinyl sulfones, derived from both terminal and internal acetylenes, were attempted next and the results are summarized in Table II. In general, selenocuprates were employed with excellent results, affording high yields of the desired products **4** and **7–20** and proving sufficiently robust to use even at room temperature. In the case of the phenylcuprate in entry 6 and vinylcuprates in entries 7, 8, and 15, superior results were obtained by generating the required reagents from 2 equiv of the corresponding organolithiums and 1 equiv of CuBr·SMe_2. In each case in Table II there was no evidence of any significant further addition to the products. The successful employment of vinylcuprates in the preparation of products **12**, **13**, and **20** demonstrates that the method constitutes a useful route to conjugated dienyl sulfones as well as to vinyl sulfones. Product **20** also illustrates that unprotected hydroxyl groups are tolerated in the substrate. This compound cyclized to the furan **21** when treated with aqueous acid in a subsequent step (eq 7).

(24) The selenocuprate was generated in situ in THF from equimolar amounts of MeLi and CuSePh, affording a clear, green-brown solution. The possibility that the NMR signal is due to the time-averaged resonances of separate, rapidly equilibrating species cannot be entirely ruled out, but appears improbable at the low temperature employed in the experiment. The selenocuprates may also exist as dimers or other aggregates of general formula $[RCu(SePh)Li]_n$; see ref 6a, pp 3–4.

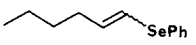


The substitution reaction proceeds in a highly stereospecific fashion with retention of configuration. This is clearly evident in products **4**, **7**, and **8** (entries 1–3) from their ^{1}H NMR spectra, which display coupling constants for the vinylic hydrogens $J_{trans} \simeq 15$ Hz. The other products in Table II also appeared to be homogeneous stereoisomers, as evidenced by ^{1}H NMR, TLC, and GC analysis, and retention of configuration was inferred by analogy with **4**, **7**, and **8** but was not proven conclusively.

During the course of our studies, several side reactions and limitations to the method came to light. Despite successful substitutions with the aryl derivatives **1e** and **1f** (entries 13 and 14), seleno sulfone **1h** failed to produce substantial amounts of the expected substitution product with *n*-BuCu(SePh)Li under the usual conditions. GC analysis of the product mixture indicated the formation of 76% of phenylacetylene, suggesting that elimination of $ArSO_2SePh$ can in some cases compete with substitution (eq 8). Further experiments established that saturated



β-seleno sulfones such as **22** undergo preferential elimination of PhSeH (eq 9) and that unactivated vinyl selenides lacking the presence of the sulfone moiety (e.g. **23**)



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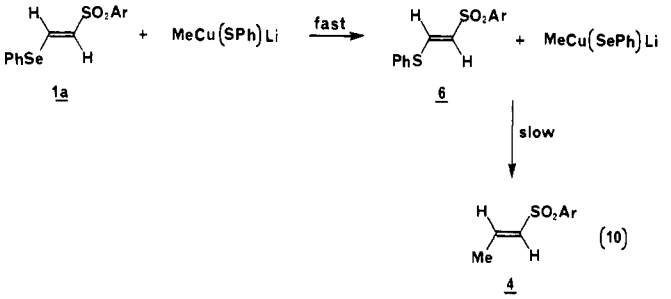
fail to react substantially under these conditions. Similarly, attempts to react seleno sulfone **1b** with lithium acetylides in the presence of various Cu(I) salts or with $(Me_3Si)_2CuLi$[25] failed to give synthetically useful results.

The possibility of performing similar substitution reactions with β-thiovinyl sulfones instead of their seleno counterparts was not explored directly, but the result in entry 3 in Table I suggests that such a process would not be facile. The reaction of MeCu(SPh)Li with seleno sulfone **1a** to afford the β-thio sulfone **6** is presumably accompanied by the simultaneous formation of MeCu(SePh)Li (eq 10). The poor yield of the methyl-substituted product **4** thus indicates that the selenocuprate does not readily react further with **6**.

Cu(I)-Catalyzed Reactions of Grignard Reagents with β-Seleno Sulfones 1. As an alternative to the use of stoichiometric amounts of cuprate reagents prepared from organolithium compounds, the employment of Grignard reagents in the presence of catalytic amounts of Cu(I) salts is often equally effective in both substitution



and addition reactions.[20] It has also been reported that vinyl (and other) selenides undergo substitution of the selenium moiety by Grignard reagents in the presence of nickel–phosphine complexes.[26] We therefore also examined the possibility of using Cu(I)-catalyzed Grignard reagents instead of stoichiometric organocuprates in the process shown in eq 4. The results are summarized in Table III.

A comparison of entries 1–5 and of 6 and 7 in Table III indicates that the best yields of substitution products are again obtained with CuSePh as the catalyst. Unfortunately, the reaction appears to be synthetically useful only in relatively unhindered cases. The often drastic reduction in yield in going from methyl- to ethylmagnesium bromide in the case of each β-seleno sulfone studied illustrates this point, and attempts to use still more hindered Grignard reagents failed completely.

An examination of the ^{1}H NMR spectra of product **9** obtained in entries 2–5 in Table III indicated that it was formed as a mixture of *E*/*Z* stereoisomers, as two separate vinylic methyl signals were discerned in the form of doublets exhibiting long-range coupling at δ 2.13 and 1.85 with $J = 1.1$ and 1.3 Hz, respectively. A comparison with the spectrum of the pure *Z* isomer obtained from the stereospecific selenocuprate reaction in entry 4 in Table II permitted their assignment as the *E* and *Z* isomers, respectively. Integration of the two doublets showed that the *E*/*Z* ratio was close to 50:50 with CuI, CuCN, or CuSPh catalyst and 25:75 with CuSePh. Surprisingly, the CuBr-catalyzed reaction (entry 1, Table III) provided a product of comparable purity (>97% *Z*) to that obtained from the use MeCu(SePh)Li in Table II. In the other examples in Table III, the products also appeared to form with a high degree of stereospecificity and their structures are tentatively assigned as those resulting from retention of configuration.

The sensitivity to steric effects and the less predictable stereochemistry are disadvantages of the Cu(I)-catalyzed Grignard reactions compared to the stoichiometric organocuprates employed in Table II.

Conclusions. The substitution of the selenium moiety of β-selenovinyl sulfones **1** with organocuprates proceeds efficiently with retention of configuration to afford vinyl sulfones **2**. Selenocuprates RCu(SePh)Li are especially useful in this process and vinylcuprates provide access to dienyl sulfones. Grignard reagents in the presence of Cu(I) catalysts can also be employed but are restricted to relatively unhindered examples and suffer from less predictable stereochemistry. Since β-selenovinyl sulfones **1** are readily available from acetylenes by free-radical selenosulfonation, and since the vinyl sulfones **2** can be reductively desulfonylated to olefins **3** by literature procedures, the overall sequence provides a means for the 2-alkylation of acetylenes. Acetylenes thus serve as the synthetic

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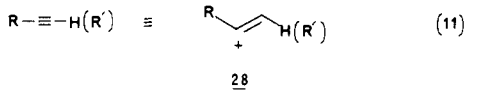
(26) Okamura, H.; Miura, M.; Kosugi, K.; Takei, H. *Tetrahedron Lett.* **1980**, *21*, 87.

equivalents of the cations **28** (eq 11) in the preparation of di- and trisubstituted olefins.



(11)

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Experimental Section

Melting points were obtained on an A.H. Thomas hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 467 or Nicolet 5DX spectrometer. NMR spectra were obtained on a Hitachi Perkin-Elmer R24B instrument at 60 MHz or on a Varian XL-200 instrument at 200 MHz. All ^1H NMR spectra were obtained in $CDCl_3$ solution unless otherwise noted and are reported in parts per million downfield from tetramethylsilane as internal standard. The ^{77}Se NMR spectrum of MeCu(SePh)Li was obtained on the Varian XL-200 instrument at 38.14 MHz in THF solution. A coaxial NMR tube was employed containing diphenyl diselenide in THF in the inner chamber as the standard. The chemical shift of the selenocuprate was 332 ppm upfield from the standard or 128 ppm downfield from dimethyl selenide.[27] High and low resolution mass spectra were recorded on a Varian Mat CH5 or Kratos M80 mass spectrometer. GC analyses were carried out on a Varian 3700 chromatograph equipped with a Varian CDS 111C electronic integrator and a flame ionization detector. Stainless steel columns (2 m × 0.3 cm) packed with 3% OV-101 or 3% OV-17 on Chromosorb W-HP were employed. Preparative TLC was carried out on Analtech 20 × 20 cm glass plates coated with 1 mm of silica gel GF. Elemental analyses were obtained by Drs. W. S. Lin and R. Yamdagni (University of Calgary).

β-Selenovinyl sulfones **1a–g**[15] and the seleno sulfone **22**[28] were prepared as described previously. Alkyl- and phenyllithiums were obtained in ether or hydrocarbon solutions from the Aldrich Co. while 1-propenyllithium was prepared in ether from 1-bromopropene and lithium powder containing 1% sodium. (1-Methoxyvinyl)lithium was generated by the procedure of Baldwin.[29] All organolithiums were titrated with 2,5-dimethoxybenzyl alcohol[30] or diphenylacetic acid[31] prior to use and transferred via syringe. Grignard reagents were obtained from the Aldrich Co. as ethereal solutions. THF was freshly distilled from $LiAlH_4$ for each experiment. 1-(Phenylseleno)-1-hexene (**23**) was prepared by the method of Raucher.[32] All other reagents were purchased from commercial sources and employed without further purification. Glassware was oven- or flame-dried and all experiments were performed under argon or nitrogen.

Cuprous Benzeneselenolate. Sodium borohydride (1.89 g, 50 mmol) was dissolved in 25 mL of 2 M aqueous sodium hydroxide and 25 mL of ethanol. Diphenyl diselenide (7.81 g, 25 mmol) was added in portions with stirring. The resulting yellow suspension was heated to reflux under nitrogen for 30 min until a clear solution was obtained. It was then cooled to 0 °C and acidified to pH 5–6 with concentrated hydrochloric acid. Cuprous oxide (3.6 g, 25 mmol) was added in one portion and the mixture was refluxed with mechanical stirring under nitrogen for 18 h. The brownish yellow precipitate was filtered, washed with ethanol and water, and dried overnight in vacuo to afford 11.7 g (89%) of the title compound. Anal. Calcd for C_6H_5CuSe: C, 32.81; H, 2.30. Found: C, 31.88, 32.79; H. 2.58, 2.13.

2-Methylpropyl *p*-Tolyl Sulfone (5). *p*-Toluenethiol (124 mg, 1.00 mmol) was added slowly to sodium methoxide prepared from sodium (23 mg, 1.0 mmol) and 5 mL of methanol. 1-Bromo-2-methylpropane (206 mg, 1.5 mmol) in 2 mL of methanol was then added. The resulting solution was refluxed for 3 h then cooled and filtered, and the solvent was removed in vacuo. The crude sulfide was dissolved in 10 mL of dichloromethane and treated with MCPBA (345 mg, 2.0 mmol) in portions. The resulting solution was refluxed for 10 h and then cooled, washed with 5% K_2CO_3 solution (3 × 10 mL), dried over anhydrous $MgSO_4$, and evapoated to dryness to give 172 mg (81%) of the title compound as a homogeneous (TLC, GC) oil. An analytical sample was obtained by distillation: bp (Kugelrohr) 55–60 °C (0.125 Torr); IR (film) 1593, 1301, 1145 cm^{-1}; ^1H NMR (60 MHz) δ 7.72 (d, J = 8 Hz, 2 H), 7.27 (d, J = 8 Hz, 2 H), 2.91 (d, J = 6.4 Hz, 2 H) 2.36 (s superimposed on m, 4 H), 1.03 (d, J = 6.5 Hz, 6 H); mass spectrum, m/e (relative intensity) 212 (M^+, 3), 92 (63), 91 ($C_7H_7^+$, 53), 57 ($C_4H_9^+$, 100). Anal. Calcd for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.59; S, 15.10. Found: C, 62.12; H, 7.66; S, 15.02.

Reactions of 1-(Phenylseleno)-2-(*p*-tolylsulfonyl)ethene (1a) with Methylcuprates (See Table I). With Me_2CuLi (Entry 1). Methyllithium (0.55 mmol) in ether was added to a stirred suspension of cuprous iodide (52 mg, 0.28 mmol) in 5 mL of ether at 0 °C. After 10 min, the solution was cooled to −50 °C and the seleno sulfone **1a** (84 mg, 0.25 mmol) in 10 mL of ether was added dropwise over 15 min. The solution was kept at −50 °C for 30 min and was then warmed to 0 °C for 2 h and quenched with wet ether. The mixture was filtered through Celite and the filtrate was concentrated in vacuo to afford a yellow oil which was separated by preparative TLC in 25% ethyl acetate–hexane to give 11 mg (20%) of 2-methylpropyl *p*-tolyl sulfone (**5**) as a homogeneous (TLC, GC) oil, identical (TLC, IR) with an authentic sample (vide supra) and 33 mg (68%) of (*E*)-1-(*p*-tolylsulfonyl)propene (**4**); mp 97–100 °C (lit.[33] mp 100 °C); IR (KBr) 1634, 1302, 1145 cm^{-1}; ^1H NMR (60 MHz) δ 7.60 (d, J = 8 Hz, 2 H), 7.23 (d, J = 8 Hz, 2 H), 7.2–6.8 (dq, J = 15.2, 6.6 Hz, 1 H), 6.35 (dq, J = 15.2, 1.4 Hz, 1 H), 2.37 (s, 3 H), 1.87 (dd, J = 6.6, 1.4 Hz, 3 H); mass spectrum; m/e (relative intensity) 196 (M^+, 96), 91 ($C_7H_7^+$, 100).

With MeCu(CN)Li (Entry 2). Methyllithium (1.2 mmol) in ether was added to a stirred suspension of cuprous cyanide (90 mg, 1.2 mmol) in 5 mL of THF at 0 °C. The resulting solution was cooled to −78 °C and the seleno sulfone **1a** (337 mg, 1.00 mmol) in 5 mL of THF was added dropwise over 5 min. The solution was warmed to −23 °C and stirred for 2.5 h at which time GC analysis of an aliquot indicated that no starting material remained. The solution was quenched and worked up as described in entry 1. Preparative TLC in 20% ethyl acetate–hexane furnished 145 mg (74%) of the vinyl sulfone **4**, mp 97–99 °C; IR identical with the authentic sample prepared in entry 1. None of the saturated sulfone **5** was detected.

With MeCu(SPh)Li (Entry 3). Methyllithium (1.2 mmol) in ether was added to a stirred suspension of cuprous benzenethiolate (172 mg, 1.20 mmol) in 10 mL of THF at 0 °C. After 15 min, the solution was cooled to −78 °C and the seleno sulfone **1a** (337 mg, 1.00 mmol) in 5 mL of THF was added. The mixture was warmed to −42 °C and stirred for 1 h, at which time GC analysis of a quenched aliquot showed some remaining starting material. The solution was warmed to −23 °C and after 1 h, GC analysis showed only a trace of starting material. The mixture was quenched and worked up as in entry 1. The solvent was removed in vacuo and the residue separated by preparative TLC in 25% ethyl acetate–hexane to give 221 mg of a solid which appeared homogeneous on TLC. Its ^1H NMR spectrum revealed the presence of two components: the unsaturated sulfone **4** and (*E*)-1-(phenylthio)-2-(*p*-tolylsulfonyl)ethene (**6**) in the ratio of 1:1.9 as determined by integration of the vinylic resonances. The yields of **4** and **6** were therefore 31% and 55%, respectively. Repeated recrystallization from ether–hexane afforded the pure vinyl sulfone **6**: mp 110 °C (lit.[34] mp 111–112 °C); IR (KBr) 1580, 1310, 1141 cm^{-1}; ^1H NMR (200 MHz) δ 7.71 (d, J = 14.5 Hz, 1 H) 7.63 (d, J = 8.3 Hz, 2 H) 7.4–7.2 (complex, 7 H), 5.91 (d, J = 14.5 Hz, 1 H), 2.35 (s, 3 H); mass spectrum, m/e (relative intensity) 290 (M^+, 20), 199 (18), 134 (100).

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(28) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249.
(29) Baldwin, J. E.; Höfle, G. A.; Lever, W. O., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7125. For the preparation of the related lithium bis(1-methoxyvinyl)cuprate, see: Chavdarian, C. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 3822.
(30) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87.
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(32) Raucher, S. *J. Org. Chem.* **1977**, *42*, 2950.
(33) Backer, H. J.; Strating, J.; Drenth, J. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 365.
(34) Modena, G.; Todesco, P. E. *Gazz. Chim. Ital.* **1959**, *89*, 866; *Chem. Abstr.* **1960**, *54*, 22452h.

With MeCu(SePh)Li (Entry 4). Methyllithium (1.2 mmol) in ether was added to a stirred suspension of cuprous benzeneselenolate (220 mg, 1.20 mmol) in 5 mL of THF at 0 °C. After 15 min, the solution was cooled to −78 °C and the seleno sulfone **1a** (337 mg, 1.00 mmol) was added in 6 mL of THF. The solution was allowed to warm to 0 °C and stirring was continued for 2 h. The mixture was quenched and worked up as in entry 1 and preparative TLC in 25% ethyl acetate–hexane afforded 90% of the product **4**, identical with the product obtained in entry 1.

Reactions of Organocuprates with β-Selenovinyl Sulfones (See Table II). The reactions in Table II employing CuSePh (entries 1–5 and 9–14) were performed as in the procedure for entry 4 in Table I. In most cases, cooling of the selenocuprate reagent to −78 °C prior to addition of the β-seleno sulfone proved unnecessary. The selenocuprate was usually generated at 0 °C and the β-seleno sulfone was added after 15 min, followed by stirring for the length of time and at the temperature indicated in Table II. Individual procedures are given for entries 6–8 and 15.

(*E*)-1-(*p*-Tolylsulfonyl)propene (4) (Entry 1). See entry 4, Table I.

(*E*)-1-(*p*-Tolylsulfonyl)-1-hexene (7) (Entry 2). The known[35] product **7** was purified by column chromatography on silica gel (elution with benzene) followed by Kugelrohr distillation: bp 90–92 °C (0.075 Torr). Its structure was confirmed by its IR, ^{1}H NMR, and mass spectra.

(*E*)-3,3-Dimethyl-1-(*p*-tolylsulfonyl)-1-butene (8) (Entry 3). The known[36] product **8** was purified by preparative TLC with 20% ethyl acetate–hexane to afford an oil with R_f 0.53. Its structure was confirmed by its IR, ^{1}H NMR, and mass spectra.

(*Z*)-2-Methyl-1-(*p*-tolylsulfonyl)-1-decene (9) (Entry 4). The product was purified by column chromatography on silica gel (elution with benzene), followed by Kugelrohr distillation: bp 120 °C (0.03 Torr); IR (film) 1615, 1600, 1308, 1152 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.79 (d, J = 8 Hz, 2 H), 7.32 (d, J = 8 Hz, 2 H), 6.16 (br s, 1 H), 2.56 (t, J = 7 Hz, 2 H), 2.43 (s, 3 H), 1.85 (d, J = 1.3 Hz, 3 H), 1.2 (complex, 12 H), 0.89 (t, J = 6 Hz, 3 H); mass spectrum, m/e (relative intensity) 308 (M^+, <0.1), 91 ($C_7H_7^+$, 20), 41 (100). Anal. Calcd for $C_{18}H_{28}O_2S$: C, 70.09; H, 9.15; S, 10.39. Found: C, 70.05; H, 9.15; S, 10.73.

(Z)-2-*n*-Butyl-1-(*p*-tolylsulfonyl)-1-decene (10) (Entry 5). The product was purified by preparative TLC in 14% ethyl acetate–hexane to afford a pale yellow oil with R_f 0.67: bp (Kugelrohr) 170–190 °C (0.15 Torr); IR (film) 1618, 1598, 1314, 1302, 1149 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.78 (d, J = 8.3 Hz, 2 H), 7.30 (d, J = 8.3 Hz, 2 H), 6.12 (s, 1 H), 2.54 (t, J = 7.5 Hz, 2 H), 2.43 (s, 3 H), 2.11 (t, J = 7.5 Hz, 2 H), 1.2 (complex, 16 H) 0.9 (complex, 6 H); mass spectrum, m/e (relative intensity) 350 (M^+, 1), 91 ($C_7H_7^+$, 31), 55 (100). Anal. Calcd for $C_{21}H_{34}O_2S$: C, 71.95; H, 9.78; S, 9.15. Found: C, 71.73; H, 9.94; S, 9.07.

(*E*)-2-Phenyl-1-(*p*-tolylsulfonyl)-1-decene (11) (Entry 6). Phenyllithium (1.00 mmol) in cyclohexane–ether (70:30) was added to a stirred suspension of CuBr·SMe$_2$ (103 mg, 0.50 mmol) in 1 mL of THF at −70 °C. The seleno sulfone **1b** (112 mg, 0.25 mmol) in 1 mL of THF was added after 15 min and the mixture was warmed to 0 °C and stirred for 0.5 h. The reaction was quenched with aqueous NH_4Cl solution, filtered through Celite, and concentrated in vacuo. The product was isolated by preparative TLC in benzene to afford 41 mg (45%) of the title compound as a pale yellow oil, R_f 0.48: IR (film) 1599, 1571, 1315, 1302, 1147 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.86 (d, J = 8 Hz, 2H), 7.3 (complex, 7 H), 6.47 (s, 1 H), 3.01 (t, J = 7 Hz, 2 H), 2.44 (s, 3 H), 1.2 (complex, 12 H), 0.86 (t, J = 7 Hz, 3 H); mass spectrum, m/e (relative intensity) 370 (M^+, 1), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{23}H_{30}O_2S$: C, 74.52; H, 8.18; S, 8.65. Found: C, 74.75; H, 8.51; S, 8.57.

(1*E*)-2-*n*-Octyl-1-(*p*-tolylsulfonyl)-1,3-pentadiene (12) (Entry 7). 1-Propenyllithium (16.0 mmol) in ether was added to CuBr·SMe$_2$ (1.65 g, 8.0 mmol) in 25 mL of THF at −70 °C. The seleno sulfone **1b** (1.80 g, 4.0 mmol) in 15 mL of THF was added after 15 min, the reaction was warmed to room temperature, and stirring was continued for 0.5 h. The reaction was worked up as in entry 6 and the crude product was purified by flash chromatography on silica gel. Elution with dichloromethane afforded the title compound (1.04 g, 78%) as a 70:30 mixture of 3*E*,3*Z* stereoisomers. A portion of this product was further separated into the pure isomers by preparative TLC in 1% ethyl acetate–benzene.

The *E* isomer **12a** had the following properties: R_f 0.36; IR (film) 1638, 1598, 1316, 1302, 1289, 1147 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.82 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2H), 6.20 (s, 1H), 5.78 (m, 2H), 2.58 (t, J = 7 Hz, 2H), 2.44 (s, 3 H), 1.75 (dd, J = 5.2, 2.2 Hz, 3 H), 1.2 (complex, 12 H), 0.88 (t, J = 7 Hz, 3 H) [Double irradiation at δ 1.75 sharpened the signal at δ 5.78 to a singlet and irradiation at δ 5.8 produced a broad singlet at δ 1.75.];[37] mass spectrum, m/e (relative intensity) 334 (M^+, 1), 91 ($C_7H_7^+$, 89), 81 (90), 41 (100); exact mass calcd for $C_{20}H_{30}O_2S$ 334.19665, found 334.1938.

The *Z* isomer **12b** had the following properties: R_f 0.21; IR (film) 1650, 1598, 1318, 1302, 1290, 1149 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.76 (d, J = 8 Hz, 2 H), 7.29 (d, J = 8 Hz, 2 H), 6.24 (s overlapping with m, 2 H), 5.69 (m, 1 H), 2.42 (s, 3 H), 2.21 (t, J = 7 Hz, 2 H), 1.49 (dd, J = 7.6, 1.7 Hz, 3 H), 1.2 (complex, 12H), 0.87 (t, J = 7 Hz, 3 H) [Double irradiation at δ 1.5 produced a doublet at δ 5.69 with J_{cis} = 11.6 Hz; irradiation at δ 5.7 gave a broad singlet at δ 1.49; and irradiation at δ 6.2 resulted in a doublet at δ 1.49 with J = 7.6 Hz.]; mass spectrum, m/e (relative intensity) 334 (M^+, 1.5) 91 ($C_7H_7^+$, 80) 81 (92), 41 (100); exact mass calcd for $C_{20}H_{30}O_2S$ 334.19665, found 334.1980.

(*E*)-3-Methoxy-2-*n*-octyl-1-(*p*-tolylsulfonyl)-1,3-butadiene (13) (Entry 8). Methoxyvinyllithium (2.00 mmol) in THF was added to CuBr·SMe$_2$ (206 mg, 1.00 mmol) in 3 mL of THF at −70 °C. After 30 min, the seleno sulfone **1b** (244 mg, 0.50 mmol) in 2 mL of THF was added, the solution was warmed to room temperature, and stirring was continued for 30 min. The reaction was worked up as in entry 6 and the product was purified by flash chromatography on silica gel. Elution with 50% dichloromethane–hexane afforded 119 mg (68%) of the title compound as a pale yellow oil: IR (film), 1616, 1602, 1580, 1317, 1148 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.82 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H), 6.75 (s, 1 H), 4.63 (d, J = 3 Hz, 1 H), 4.39 (d, J = 3 Hz, 1 H), 3.57 (s, 3 H), 2.73 (t, J = 8 Hz, 2 H), 2.43 (s, 3 H), 1.2 (complex, 12 H), 0.89 (t, J = 7 Hz, 3 H); mass spectrum, m/e (relative intensity) 350 (M^+, 2), 195 ($M^+ - ArSO_2$, 93), 91 ($C_7H_7^+$, 77), 41 (100); exact mass calcd for $C_{20}H_{30}O_3S$ 350.1916, found 350.1925.

(*Z*)-1-(*p*-Tolylsulfonyl)-2-(trimethylsilyl)propene (14) (Entry 9). The product was purified by preparative TLC in 10% ethyl acetate–hexane, R_f 0.35: mp 48.5–50 °C (from methanol); IR (film) 1596, 1319, 1148 cm^{-1}; ^{1}H NMR (60 MHz) δ 7.62 (d, J = 8 Hz, 2 H), 7.17 (d, J = 8 Hz, 2 H), 6.49 (q, J = 1.7 Hz, 1 H), 2.35 (s, 3 H), 1.93 (d, J = 1.7 Hz, 3 H), 0.40 (s, 9 H); mass spectrum, m/e (relative intensity) 253 ($M^+ - CH_3$, 50), 180 (17), 149 (100), 73 (Me_3Si^+, 64). Anal. Calcd for $C_{13}H_{20}O_2SSi$: C, 58.17; H, 7.51; S, 11.95. Found: C, 57.93; H, 7.85; S, 12.36.

(*Z*)-5-Methyl-6-(*p*-tolylsulfonyl)-5-decene (15) (Entry 10). The product was purified by preparative TLC in 10% ethyl acetate–hexane, R_f 0.52: bp (Kugelrohr) 230–250 °C (0.05 Torr); IR (film) 1618, 1596, 1311, 1301, 1287, 1146 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.73 (d, J = 8 Hz, 2 H), 7.28 (d, J = 8 Hz, 2 H), 2.41 (s overlapping with m, 7 H), 1.85 (s, 3 H), 1.3 (complex, 8 H), 0.9 (m, 6 H); mass spectrum, m/e (relative intensity) 308 (M^+, 4) 41 (100). Anal. Calcd for $C_{18}H_{28}O_2S$: C, 70.08; H, 9.15; S, 10.40. Found: C, 69.92; H, 9.17; S, 10.20.

5-*n*-Butyl-6-(*p*-tolylsulfonyl)-5-decene (16) (Entry 11). The product was purified by preparative TLC in 10% ethyl acetate–hexane, R_f 0.60: bp (Kugelrohr) 200 °C (0.2 Torr); IR (film) 1612, 1596, 1314, 1301, 1285, 1147 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.71 (d, J = 8 Hz, 2 H), 7.27 (d, J = 8 Hz, 2 H), 2.41 (s superimposed on m, 7 H), 2.13 (crude t, 2 H), 1.6–1.2 (complex, 12 H), 0.9 (complex, 9 H); mass spectrum, m/e (relative intensity) 350 (M^+ <1), 41 (100). Anal. Calcd for $C_{21}H_{34}O_2S$: C, 71.95; H, 9.78; S, 9.15. Found: C, 72.06; H, 9.99; S, 8.87.

(*E*)-5-*sec*-Butyl-6-(*p*-tolylsulfonyl)-5-decene (17) (Entry 12). The product was purified by preparative TLC in 10% ethyl acetate–hexane to give an oil, R_f 0.56: IR (film) 1598, 1312, 1301,

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(36) Hershberger, J.; Russell, G. A. *Synthesis* **1980**, 475.

(37) The failure to observe the expected vinylic coupling constant J_{trans} may be due to fortuitous magnetic equivalence of the trans vinylic hydrogens. In C_6D_6 solvent, this coupling constant was readily discerned: J_{trans} = 15.5 Hz.

1287, 1145 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.72 (d, J = 8 Hz, 2 H), 7.28 (d, J = 8 Hz, 2 H), 2.41 (s superimposed on m, 8 H), 1.6–1.2 (complex, 10 H), 1.05 (d, J = 7 Hz, 3 H), 0.9 (complex, 9 H); mass spectrum, m/e (relative intensity) 350 (M^+, 1). Anal. Calcd for $C_{21}H_{34}O_2S$: C, 71.95; H, 9.78; S, 9.15. Found: C, 71.85; H, 9.95; S, 8.84.

(*Z*)-2-Phenyl-3-(*p*-tolylsulfonyl)-2-butene (18) (Entry 13). The product was purified by preparative TLC in 14% ethyl acetate–hexane, R_f 0.38: mp 79.5–81.5 °C (from dichloromethane–hexane); IR (Nujol) 1634, 1594, 1313, 1158 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.5–7.0 (complex, 9 H), 2.37 (s, 3 H), 2.20 (s, 3 H), 2.08 (s, 3 H); mass spectrum, m/e (relative intensity) 286 (M^+, 21), 131 ($M^+ - SO_2Ar$, 68), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; S, 11.19. Found: C, 71.10; H, 6.36; S, 11.49.

(*Z*)-1,2-Diphenyl-1-(*p*-tolylsulfonyl)propene (19) (Entry 14). The product was purified by preparative TLC in 40% benzene–chloroform, R_f 0.28: mp 149.5–151 °C (from dichloromethane–hexane); IR (Nujol) 1633, 1587, 1311, 1301, 1145 cm^{-1}; ^{1}H NMR (200 MHz) 7.4–7.1 (complex, 14 H), 2.35 (s, 3 H), 1.86 (s, 3 H); mass spectrum, m/e (relative intensity) 348 (M^+, 7), 193 ($M^+ - SO_2Ar$, 93) 115 ($PhC{\equiv}CCH_2^+$, 100), 91 ($C_7H_7^+$, 69). Anal. Calcd for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.785; S, 9.20. Found: C, 75.56; H, 5.77; S, 9.25.

(*E*)-3-(1-Methoxyvinyl)-4-(*p*-tolylsulfonyl)-3-buten-1-ol (20) (Entry 15) and 2-Methyl-3-[(*p*-tolylsulfonyl)methyl]-furan (21). (Methoxyvinyl)lithium (2.00 mmol) was added to CuBr·SMe_2 (206 mg, 1.00 mmol) and the resulting cuprate was treated with seleno sulfone **1g** (191 mg, 0.50 mmol) via the procedure described in entry 8. Flash chromatography over silica gel and elution with chloroform afforded 111 mg (79%) of the title compound **20** as a yellow oil: IR (film) 3520, 1614, 1597, 1581, 1314, 1303, 1290, 1147 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.83 (d, J = 8 Hz, 2 H), 7.36 (d, J = 8 Hz, 2 H), 6.89 (s, 1 H), 4.69 (d, J = 3.5 Hz, 1 H), 4.45 (d, J = 3.5 Hz, 1 H), 3.82 (t, J = 6.3 Hz, 2 H), 3.58 (s, 3 H), 3.09 (t, J = 6.3 Hz, 2 H), 2.45 (s, 3 H); mass spectrum, m/e (relative intensity) 282 (M^+, <1), 267 ($M^+ - CH_3$, 3), 251 ($M^+ - OCH_3$, 6), 43 (100).

The above compound **20** (111 mg, 0.39 mmol) was dissolved in methanol and treated with 0.02 N aqueous HCl for 30 min at room temperature. Evaporation under reduced pressure followed by flash chromatography on silica gel and elution with dichloromethane afforded 81 mg (83%) of the furan **21**: mp 102 °C (from chloroform–hexane); IR (KBr) 1623, 1596, 1307, 1300, 1140 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.59 (d, J = 8 Hz, 2 H), 7.29 (d, J = 8 Hz, 2 H), 7.21 (d, J = 1.4 Hz, 1 H), 6.19 (d, J = 1.4 Hz, 1 H), 4.08 (s, 2 H), 2.43 (s, 3 H), 1.87 (s, 3 H); mass spectrum, m/e (relative intensity) 250 (M^+, 100). Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.40; H, 5.60; S, 12.80. Found: C, 62.59; H, 5.65; S, 12.70.

Reaction of Seleno Sulfone 1h with *n*-BuCu(SePh)Li. The selenocuprate was prepared form *n*-butyllithium (2.6 mmol) and CuSePh (2.6 mmol) in THF at 0 °C in the usual manner. The seleno sulfone **1h** (1.00 mmol) was added in THF and the mixture was stirred 14 h at room temperature. At this time, no significant amount of substitution product was evident and GC analysis with 1-phenylpropyne as an internal standard indicated the formation of 76% of phenylacetylene.

Reaction of *trans*-1-(Phenylseleno)-2-(*p*-tolylsulfonyl)-cyclohexane (22) with *n*-BuCu(SePh)Li. The selenocuprate was prepared from *n*-butyllithium (0.60 mmol) and CuSePh (0.60 mmol) in THF at 0 °C in the usual manner. The seleno sulfone **22** (196 mg, 0.50 mmol) in THF was added and the mixture was stirred 20 h at room temperature. After quenching with wet ether and filtration through Celite, the concentrated product was isolated by preparative TLC in 14% ethyl acetate–hexane to afford 96 mg (81%) of 1-(*p*-tolylsulfonyl)cyclohexene, R_f 0.36: mp 81–82.5 °C (lit.[28] mp 80–82 °C), identical (IR, ^{1}H NMR) with an authentic sample.

Cu(I)-Catalyzed Reactions of Grignard Reagents with β-Selenovinyl Sulfones (See Table III). All of the products in Table III were prepared in essentially the same manner and only one typical procedure (entry 5) will be described in detail.

2-Methyl-1-(*p*-tolylsulfonyl)-1-decene (9) (Entry 5). Methylmagnesium bromide (1.5 mmol) in ether was added to CuSePh (10 mg, 0.05 mmol) in 2 mL of THF. After 15 min, seleno sulfone **1b** (225 mg, 0.5 mmol) in 2 mL of THF was added and stirring was continued for 3.5 h. The reaction was quenched with aqueous NH_4Cl, diluted with ether, dried over $MgSO_4$, filtered through Celite, and evaporated. Preparative TLC in 10% ethyl acetate–hexane afforded 155 mg (100%) of the title compound as an oil which was identical in all respects (IR, ^{1}H NMR, and mass spectrum) with the product obtained in entry 4 in Table II, except that the ^{1}H NMR spectrum showed two vinyl methyl signals at δ 1.85 and 2.13 in the ratio of 4:1.

The same product, differing only in the ratio of E/Z isomers was obtained in entries 1–4.

(*Z*)-2-Ethyl-1-(*p*-tolylsulfonyl)-1-decene (24) (Entries 6 and 7). The product was purified by preparative TLC in 14% ethyl acetate–hexane, R_f 0.56: bp (Kugelrohr) 145 °C (0.33 Torr); IR (film) 1620, 1598, 1314, 1301, 1147 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.78 (d, J = 8 Hz, 2 H), 7.31 (d, J = 8 Hz, 2 H), 6.11 (br s, 1 H), 2.59 (m, 2 H), 2.43 (s, 3 H), 2.15 (m, 2 H), 1.2 (complex, 12 H), 1.01 (t, J = 7 Hz, 3 H), 0.89 (t, J = 7 Hz, 3 H); mass spectrum, m/e (relative intensity) 322 (M^+, 5), 91 ($C_7H_7^+$, 49), 41 (100). Anal. Calcd for $C_{19}H_{30}O_2S$: C, 70.76; H, 9.38; S, 9.94. Found: C, 70.98; H, 9.66; S, 9.83.

(*Z*)-1-(*p*-Tolylsulfonyl)-2-(trimethylsilyl)propene (14) (Entry 8). The product was purified by preparative TLC as described in entry 9 in Table II. It was identical in all respects with the previous sample.

(*Z*)-2-Phenyl-3-(*p*-tolylsulfonyl)-2-butene (18) (Entry 9). The product was purified by preparative TLC as described in entry 13 in Table II. It was identical in all respects with the previous sample.

(*Z*)-3-Phenyl-2-(*p*-tolylsulfonyl)-2-pentene (25) (Entry 10). The product was purified by preparative TLC in chloroform to afford the title compound as an oil, R_f 0.15: IR (film) 1623, 1595, 1307, 1155 cm^{-1}; ^{1}H NMR (60 MHz) δ 7.47–6.8 (complex, 9 H), 2.40 (s, superimposed on q, 5 H), 2.25 (s, 3 H), 0.98 (t, J = 8 Hz, 3 H); mass spectrum, m/e (relative intensity) 300 (M^+, 12), 129 (100), 91 ($C_7H_7^+$, 75); exact mass calcd for $C_{18}H_{20}O_2S$ 300.1184, found 300.1187.

(*Z*)-3-Methyl-4-(*p*-tolylsulfonyl)-3-buten-1-ol (26) (Entry 11). The product was purified by preparative TLC in 60% ethyl acetate–hexane to afford the title compound as a yellow oil, R_f 0.46: IR (film) 3506, 1623, 1597, 1311, 1287, 1146 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.79 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H), 6.28 (br s, 1 H), 3.83 (t, J = 6 Hz, 2 H), 2.88 (t, J = 6 Hz, 2 H), 2.44 (s, 3 H), 2.40 (s, 1 H, exchanged D_2O), 1.94 (d, J = 1.4 Hz, 3 H); mass spectrum, m/e (relative intensity) 210 (44), 91 ($C_7H_7^+$, 83), 84 (100). Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.98; H, 6.71; S, 13.34. Found: C, 59.72; H, 6.87; S, 13.48.

(*Z*)-3-Ethyl-4-(*p*-tolylsulfonyl)-3-buten-1-ol (27) (Entry 12). The product was purified by preparative TLC in 67% ethyl acetate–hexane to afford the title compound as a yellow oil, R_f 0.58: IR (film) 3412, 1619, 1597, 1311, 1301, 1287, 1145 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.80 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H), 6.24 (br s, 1 H), 3.81 (t, J = 6 Hz, 2 H), 2.89 (t, J = 6 Hz, 2 H), 2.44 (s, 3 H), 2.25 (m, 3 H, collapsed to q, J = 7 Hz, 2 H upon D_2O exchange), 1.05 (t, J = 7 Hz, 3 H); mass spectrum, m/e (relative intensity) 224 (49), 91 ($C_7H_7^+$, 91), 41 (100). Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13; S, 12.61. Found: C, 61.42; H, 7.23; S, 12.28.

Registry No. **1a**, 86409-89-4; **1b**, 86409-85-0; **1c**, 86409-87-2; **1d**, 87517-80-4; **1e**, 86409-90-7; **1f**, 81763-76-0; **1g**, 86409-86-1; **1h**, 81763-73-7; **4**, 32228-15-2; **5**, 91358-89-3; **6**, 15717-55-2; **7**, 71964-05-1; **8**, 74829-77-9; **9**, 108817-48-7; **10**, 108817-49-8; **11**, 108817-50-1; **12a**, 108817-51-2; **12b**, 108817-52-3; **13**, 108817-53-4; **14**, 108817-54-5; **15**, 108817-55-6; **16**, 91358-93-9; **17**, 108817-56-7; **18**, 108817-57-8; **19**, 108817-58-9; **20**, 108817-59-0; **21**, 108817-60-3; **22**, 76649-90-6; **24**, 108817-61-4; **25**, 108817-62-5; **26**, 108817-63-6; **27**, 108817-64-7; Me_2CHCH_2Br, 78-77-3; *p*-MeC_6H_4SH, 106-45-6; $PhC{\equiv}CH$, 536-74-3; 1-(*p*-tolylsulfonyl)cyclohexene, 67963-03-5.