Reaction of Epoxide 7 with $Al(CH_3)_3$–BuLi. Proceeding as previously described,[3] a solution of epoxide **7** (0.20 g, 0.9 mmol) in pentane (8 mL) was cooled at −50 °C then treated under N_2 with 2 M $Al(CH_3)_3$ in hexane (1.08 mL) and with 1.6 M BuLi in hexane (0.16 mL). The reaction mixture was then stirred at 0 °C for 5 h. Evaporation of the washed (water) ether extracts afforded an oily residue (0.205 g) consisting of practically pure **24** (^1H NMR and GC, entry 10, Table I).

Reaction of Epoxide 7 with $Al(CH_3)_3$–BuLi in the Presence of 12-Crown-4. Proceeding as previously described,[3] treatment of epoxide **7** (0.10 g, 0.46 mmol) with $Al(CH_3)_3$–BuLi [from 2 M $Al(CH_3)_3$ (1.5 mL) and 1.6 M BuLi (0.2 mL)] in the presence of 12-crown-4 (3.1 mmol), afforded after 4 h at rt a crude reaction product consisting of practically pure methyl alcohol **24** (GC, ^1H NMR, entry 11, Table I).

Reaction of Epoxide 8 with $(CH_3)_2CuLi$. As previously described for the corresponding reaction of epoxide **7**, treatment of epoxide **8** (0.218 g, 1.0 mmol) with $(CH_3)_2CuLi$ (3.0 mmol) in anhydrous ether (5 mL) at 0 °C for 20 h afforded a crude oily reaction product (0.22 g) consisting of a 90:10 mixture of methyl alcohols **25** and **26**[18] (GC, entry 8, Table II) which was subjected to semipreparative TLC with 85:15 petroleum ether/diisopropyl ether as the eluant. Extraction of the most intense band afforded pure ***t*-3-[(benzyloxy)methyl]-*t*-2-methyl-*r*-1-cyclohexanol** (**25**) (0.12 g) as a liquid: IR, see Table III; ^1H NMR δ 7.22–7.35 (m, 5 H), 4.49 (s, 2 H), 3.35 (m, 2 H), 2.20 (m, 1 H, $W^1/_2$ = 23.8 Hz), 0.87 (d, 3 H, J = 7.2 Hz), and see Table III. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.65; H, 9.31.

LAH Reduction of Epoxide 7. Following previously described procedures,[4] reduction of epoxide **7** (0.218 g, 1.0 mmol) in pentane (10 mL) with $LiAlH_4$ (0.078 g, 2 mmol) afforded a crude oily product (0.19 g) consisting of alcohol practically pure **28** (GC and ^1H NMR, entry 7, Table I), which was subjected to semipreparative TLC with 8:2:0.1 petroleum ether/AcOEt/MeOH as the eluant. Extraction of the most intense band afforded pure ***cis*-2-[(benzyloxy)methyl]cyclohexanol** (**28**) (0.16 g) as a liquid: IR, see Table III; ^1H NMR δ 7.26–7.35 (m, 5 H), 4.53 and 4.52 (ABdd, 2 H, J = 12.5 Hz), 3.57 (m, 2 H). Anal. Calcd for $C_{14}H_{20}O_2$: C, 85.66; H, 10.27. Found: C, 85.70; H, 10.32.

LAH Reduction of Epoxide 7 in the Presence of 12-Crown-4. Following a previously described procedure,[4] treatment of a solution of epoxide **7** (0.218 g, 1.0 mmol) in pentane (10 mL) with a suspension of $LiAlH_4$ (0.078 g, 2.0 mmol) previously left in contact with 12-crown-4 (0.36 mL, 2.2 mmol) for 15 h at rt, afforded after 3 h at rt a crude oily product consisting of alcohol **28** practically pure (GC and ^1H NMR, entry 8, Table I).

LAH Reduction of Epoxide 8. As above described for **7**, treatment of epoxide **8** (0.218 g, 1.0 mmol) in pentane (10 mL) with $LiAlH_4$ (0.078 g, 2.0 mmol) afforded a crude oily product (0.21 g) consisting of a 72:28 mixture of alcohols **29** and **30** which was subjected to semipreparative TLC with 8:2:0.1 petroleum ether/AcOEt/MeOH as the eluant. Extraction of the two most intense bands afforded pure **29**[5] (0.12 g) and ***trans*-2-[(benzyloxy)methyl]cyclohexanol** (**30**) (0.030 g) as a liquid: IR, see Table III; ^1H NMR δ 7.26–7.35 (m, 5 H), 4.54 (s, 2 H), 3.50 (m, 2 H), and see Table III. Anal. Calcd for $C_{14}H_{20}O_2$: C, 85.66; H, 10.27. Found: C, 85.49; H, 10.32.

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Registry No. 7, 138630-47-4; 8, 138749-89-0; 11, 138630-48-5; 12, 138630-49-6; 13, 138749-90-3; 14, 138749-91-4; 15, 138630-50-9; 16, 138630-51-0; 17, 138749-92-5; 18, 138749-93-6; 19, 138630-52-1; 20, 138630-53-2; 21, 138749-94-7; 22, 138749-95-8; 23, 138630-54-3; 24, 138630-55-4; 25, 138749-96-9; 26, 138749-97-0; 28, 138630-56-5; 29, 137946-43-1; 30, 138630-57-6; 31, 138630-58-7; 32, 25662-37-7; 33, 3309-97-5; 34, 137946-46-4; 40, 108743-93-7; 41, 76886-31-2; cyclohexene, 110-83-8.

Supplementary Material Available: Determination of the structure, configuration, and conformational analysis of epoxides **7** and **8** and of all the ring-opening products **11**–**31** (9 pages). Ordering information is given on any current masthead page.

Reactions of 2-Halovinyl Aryl Sulfoxides with Organometallic Reagents

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(*E*)- and (*Z*)-2-halovinyl aryl sulfoxides **1**–**4** were subjected to reactions with organocopper, organomagnesium, or organolithium reagents. The organometallic reagents gave different products: diorganocuprates led to formation of carbon–carbon bond, with production of alkenyl sulfoxides **5**–**10**, whereas formation of carbon–sulfur bond and production of diaryl or aryl alkyl sulfoxides **11**–**13** were observed in the reaction with the other organometallics. Possible mechanisms for the two observed processes are briefly discussed.

In a series of papers,[1] we have described the stereospecific cross-coupling reaction of (*E*)- or (*Z*)-2-bromovinyl phenyl sulfide[1b,g,2] with Grignard reagents in the presence of nickel or palladium complexes as catalyst. We have also reported a variety of syntheses which shows that the method represents a convenient stereospecific route to alkenes and dienes.[3] In earlier studies,[4] we had investigated the synthetic, mechanistic, and stereochemical aspects of the cross-coupling process between (*E*)- or (*Z*)-2-halovinyl phenyl sulfones and diorganocuprates. A similar investigation of the reactions of the corresponding sulfoxides appeared essential. In particular, a versatile route to

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[1] For earlier work concerning our sequential cross-coupling approach, see: (a) Fiandanese, V.; Marchese, G.; Naso, F.; Ronzini, L. *J. Chem. Soc., Chem. Commun.* **1982**, 647. (b) Fiandanese, V.; Marchese, G.; Naso, F.; Ronzini, L. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1115. (c) Fiandanese, V.; Miccoli, G.; Naso, F.; Ronzini, L. *J. Organometal. Chem.* **1986**, *312*, 343. (d) Fiandanese, V.; Marchese, G.; Naso, F.; Ronzini, L. *Synthesis* **1987**, 1034. (e) Fiandanese, V.; Marchese, G.; Mascolo, G.; Naso, F.; Ronzini, L. *Tetrahedron Lett.* **1988**, *29*, 3705. (f) Naso, F. *Pure Appl. Chem.* **1988**, *60*, 79. (g) Cardellicchio, C.; Fiandanese, V.; Naso, F. *Gazz. Chim. Ital.* **1991**, *121*, 11.

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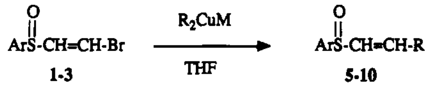
Table I. Reactions of 2-Bromovinyl Aryl Sulfoxides with Organocuprates



$$\mathrm{Ar\overset{O}{\overset{\|}{S}}\text{-}CH{=}CH\text{-}Br} \xrightarrow[\mathrm{THF}]{\mathrm{R_2CuM}} \mathrm{Ar\overset{O}{\overset{\|}{S}}\text{-}CH{=}CH\text{-}R}$$

1-3 5-10

	substrate				products		
entry[a]	no.	Ar	R_2CuM	temp (°C)	no(s).	*E*/*Z*	yield (%)[b]
1	1(*E*)	Ph	*n*-Bu_2CuLi[c]	−5	5(*E*) + 6(*Z*)	80:20	65
2	1(*E*)	Ph	*n*-$Bu_2CuMgBr$	0	5(*E*)	100:0	71
3	2(*Z*)	Ph	*n*-Bu_2CuLi[c]	−5	5(*E*) + 6(*Z*)	25:75	70
4	2(*Z*)	Ph	*n*-$Bu_2CuMgBr$	0	5(*E*) + 6(*Z*)	10:90	64
5	1(*E*)	Ph	Ph_2CuLi[d]	−5	7(*E*)	100:0	35
6	1(*E*)	Ph	$Ph_2CuMgBr$	0	7(*E*)	100:0	54
7	2(*Z*)	Ph	Ph_2CuLi[d]	−5	7(*E*) + 8(*Z*)	80:20	51
8	2(*Z*)	Ph	$Ph_2CuMgBr$	0	7(*E*)	100:0	52
9	2(*Z*)	Ph	$Ph_2CuMgBr$	−30	7(*E*) + 8(*Z*)	60:40	–[e]
10	2(*Z*)	Ph	$Ph_2CuMgBr$	−80	7(*E*) + 8(*Z*)	50:50	–[e]
11	3(*Z*)	2-Np	*n*-$Bu_2CuMgBr$	0	9(*Z*)	0:100	63
12	3(*Z*)	2-Np	*sec*-$Bu_2CuMgBr$	0	10(*Z*)	0:100	69

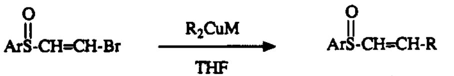
[a] Reaction time 0.5 h (except entries 9 and 10 which were 4 h). [b] Yields refer to isolated purified products. [c] Prepared from BuLi in hexane. [d] Prepared from PhLi in diethyl ether. [e] Conversion was only 25% (see text).

alkenyl sulfoxides by cross-coupling reactions with halovinyl sulfoxides with organometallic reagents was considered of interest owing to the wide use of unsaturated sulfoxides in organic synthesis.[5–10] Some relevant examples include their use as dienophiles[6] in Diels–Alder reactions, or Michael acceptors,[7] in asymmetric synthesis,[8] in Pummerer type reactions,[9] and in the preparation of trisubstituted olefins.[10]

In this paper we report on the reactions of (*E*)- and (*Z*)-2-halovinyl aryl sulfoxides with diorganocuprates and Grignard and organolithium reagents.

Results

(a) Reactions of 2-Halovinyl Aryl Sulfoxides 1–4 with Organocuprates. (*E*)- and (*Z*)-2-bromovinyl phenyl sulfoxides (1 and 2)[11] and (*Z*)-2-bromovinyl 2-naphthyl sulfoxide (3), obtained by *m*-chloroperoxybenzoic acid (*m*-CPBA) oxidation of the corresponding sulfides, reacted with cuprates in a cross-coupling process, giving aryl alkenyl sulfoxides 5–10, according to eq 1. The relevant data are reported in Table I.



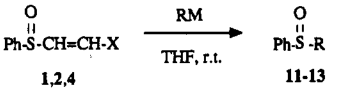
$$\mathrm{Ar\overset{O}{\overset{\|}{S}}\text{-}CH{=}CH\text{-}Br} \xrightarrow[\mathrm{THF}]{\mathrm{R_2CuM}} \mathrm{Ar\overset{O}{\overset{\|}{S}}\text{-}CH{=}CH\text{-}R} \quad (1)$$

1-3 5-10

1,2 Ar= Ph M=MgBr, Li 5-8 R=*n*-Bu, Ph
3 Ar= 2-Np M=MgBr 9, 10 R=*n*-Bu, *sec*-Bu

The reaction between *n*-Bu_2CuLi and the (*E*)-isomer 1 produced a mixture of (*E*)- and (*Z*)-sulfoxides 5[12] and 6 (80:20 *E*:*Z*, entry 1), while *n*-$Bu_2CuMgBr$ gave exclusively (*E*)-5 (entry 2). The cross-coupling of the (*Z*)-compound 2 afforded a mixture of the (*E*)- and (*Z*)-sulfoxides both with *n*-Bu_2CuLi (25:75 *E*:*Z*, entry 3) and with *n*-$Bu_2CuMgBr$ (10:90 *E*:*Z*, entry 4).

Table II. Reactions of 2-Halovinyl Phenyl Sulfoxides with Organomagnesium or Organolithium Compounds



$$\mathrm{Ph\text{-}\overset{O}{\overset{\|}{S}}\text{-}CH{=}CH\text{-}X} \xrightarrow[\mathrm{THF,\ r.t.}]{\mathrm{RM}} \mathrm{Ph\text{-}\overset{O}{\overset{\|}{S}}\text{-}R}$$

1,2,4 11-13

	substrate			products	
entry[a]	no.	X	RM	no.	yield (%)[b]
1	1(*E*)	Br	*n*-BuMgBr	11	79
2	2(*Z*)	Br	*n*-BuMgBr	11	84
3	4(*E*)	Cl	*n*-BuMgBr	11	81
4	1(*E*)	Br	*n*-PentMgBr	12	86
5	2(*Z*)	Br	*n*-PentMgBr	12	79
6	1(*E*)	Br	PhMgBr	13	91
7	2(*Z*)	Br	PhMgBr	13	93
8	1(*E*)	Br	PhLi[c]	13	43
9	2(*Z*)	Br	PhLi[c]	13	47

[a] Reaction time: 10 min. [b] Yields refer to isolated purified products. [c] In diethyl ether.

(*E*)-Bromide 1 gave exclusively (*E*)-sulfoxide 7[13] in the reactions with Ph_2CuLi (entry 5) and $Ph_2CuMgBr$ (entry 6), with a better isolated yield in the latter case.

A more complex situation was observed with the (*Z*)-isomer 2. The reaction with Ph_2CuLi gave a mixture of the (*E*)- and (*Z*)-sulfoxides 7 and 8[13] (80:20 *E*:*Z*, entry 7), whereas complete inversion of configuration was observed with $Ph_2CuMgBr$, leading exclusively to the (*E*)-isomer (entry 8). Mixtures of (*E*)-7 and (*Z*)-8 were obtained with the same reagent at lower temperatures (entries 9 and 10). However, in the latter two entries, after 4 h the conversion was only 25% and the starting vinyl bromide was recovered unchanged.

(*Z*)-Sulfoxide 3 was subjected to a cross-coupling reaction with *n*-$Bu_2CuMgBr$ and *sec*-$Bu_2CuMgBr$, yielding respectively (*Z*)-sulfoxides 9 and 10 (entries 11 and 12), without detectable quantities of the (*E*)-isomers.

The corresponding (*E*)-vinyl chloride 4[14] reacted completely with *n*-$Bu_2CuMgBr$, giving only a small amount of diphenyl disulfide together with many other unidentified byproducts.

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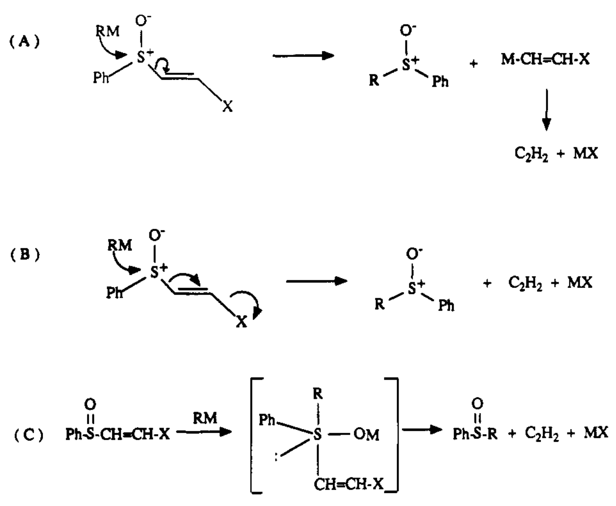
Scheme I

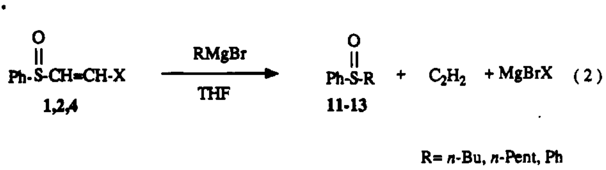


A 1:1 mixture of (*E*)-**1** and (*Z*)-**2** was treated with an insufficient amount of *n*-$Bu_2CuMgBr$, in order to evaluate the reactivity difference between the stereoisomers. Since the *E*/*Z* ratios remained unchanged after consumption of the organometallic reagent, we conclude that no significant difference exists between the reaction rates of the two stereoisomers.

(b) Reactions of 2-Halovinyl Phenyl Sulfoxides with Organomagnesium and Organolithium Compounds. As reported in Table II, the reactions of (*E*)- and (*Z*)-2-halovinyl sulfoxides with *n*-butyl-, *n*-pentyl-, or phenylmagnesium bromides at room temperature proceeded, leading respectively to *n*-butyl (**11**)[15] and *n*-pentyl phenyl sulfoxides (**12**),[16] and diphenyl sulfoxide (**13**)[17] in good isolated yields.

In order to ascertain the fate of the halovinyl moiety, the evolved gas from the reaction between phenylmagnesium bromide and (*Z*)-**2** (entry 7) was trapped in a liquid nitrogen-cooled bulb and analyzed by mass spectrometry, revealing it to be acetylene. In another experiment the evolved acetylene was trapped in cold (−80 °C) diethyl ether and titrated. The gas titrated was almost equimolecular with the produced sulfoxide (see the Experimental Section).

Therefore, the reactions are occurring according to eq 2.



$$\underset{\mathbf{1,2,4}}{\text{Ph-}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{-CH=CH-X}} \xrightarrow[\text{THF}]{\text{RMgBr}} \underset{\mathbf{11\text{-}13}}{\text{Ph-}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{-R}} + C_2H_2 + \text{MgBrX} \quad (2)$$

R= *n*-Bu, *n*-Pent, Ph

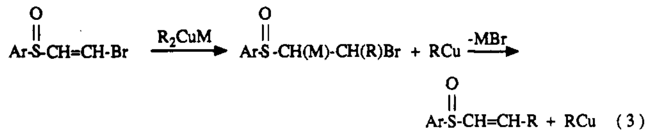
The reaction is not general for vinyl aryl sulfoxides. For instance, no significant formation of sulfoxide **13** was observed even after several hours when (*E*)-**7** or (*Z*)-**8** was reacted with phenylmagnesium bromide at room temperature.

Finally, (*E*)-**1** or (*Z*)-**2** was treated with organolithiums. Phenyllithium gave sulfoxide **13** together with diphenyl disulfide as a side product (entries 8 and 9). As a consequence of this reduction, the isolated yields were lower than those obtained with the organomagnesium reagents. Butyllithium was reacted with (*E*)-**1** or (*Z*)-**2** at room temperature and at −80 °C, but only diphenyl disulfide and a tarry residue were obtained.

Discussion

Although no detailed mechanistic investigation was undertaken for the present system, the results reported above show that the selectivity pattern of the reactions between halovinyl aryl sulfoxides and organometallic reagents depends upon the nature of the latter.

Diorganocuprates give a straightforward cross-coupling process, a behavior which has been observed in the reactions of the corresponding sulfones.[4] It seems reasonable to assume that the mechanism followed is the addition–elimination type, which was considered valid for the sulfones. This mechanism involves an initial nucleophilic attack by the reagent on the carbon atom followed by halogen expulsion as shown in eq 3.



$$\text{Ar-}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{-CH=CH-Br} \xrightarrow{R_2CuM} \text{Ar-}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{-CH(M)-CH(R)Br} + \text{RCu} \xrightarrow{-\text{MBr}} \text{Ar-}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{-CH=CH-R} + \text{RCu} \quad (3)$$

The stereochemical results indicating retention of configuration with dibutyl cuprates, the complete lack of stereospecificity with diphenyl cuprate, and the similar *E*/*Z* reactivity are all reminescent of the behavior of the sulfones.[4] It is also worth noting that cuprates appear to react with the sulfoxides in a manner similar to lithium enolates.[11]

In contrast, when organometallic reagents are used which do not possess the well-known marked tendency of the organocopper reagents to react with organic halides giving cross-coupling products,[19] the center of the attack becomes the sulfur atom. A few related processes can be found in the literature. Durst and co-workers[20] and Johnson and co-workers[21] independently synthesized optically active dialkyl sulfoxides, by reaction of optically active alkyl aryl sulfoxides with alkyllithium compounds, with a stereospecific displacement of the aryl group. Hojo and co-workers[22] obtained alkyl aryl or diaryl sulfoxides by reaction of aryl chloromethyl sulfoxides with alkyl or aryl Grignard reagents. Similarly, Kagan and co-workers[23] treated optically active 1-hexynyl methyl sulfoxide with *t*-BuLi and obtained methyl *tert*-butyl sulfoxide with inversion of configuration.

On the other hand, Oae and co-workers[24] have found that most frequently the reactions between alkyl or aryl heteroaryl sulfoxides and Grignard reagents lead to products of coupling between the residues originally bound to the sulfinyl group. The rationale offered for these reactions involved the formation of a hypervalent unstable sulfur species (σ-sulfurane), followed by ligand coupling.

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Against this background, we can explain our results by assuming that the Grignard reagent attacks the sulfur atom with a concomitant expulsion of a two-carbon fragment which then decomposes to give acetylene according to Scheme I (A). Alternatively, acetylene could be formed in a concerted manner (B). However, the similarity in reactivity of the (*E*)-1 and (*Z*)-2 compounds seems to rule out such a possibility. Indeed, by analogy with the dehydrohalogenation of vinyl halides,[25] configuration would be expected to play an important role in a concerted elimination.

Alternatively, the reaction could occur through an unstable σ-sulfurane according to Scheme I (C). A similar possibility was carefully evaluated by Durst and co-workers[20] for the reactions of alkyl aryl sulfoxides with alkyllithiums. Their results were best explained by invoking a transition state rather than a σ-sulfurane intermediate. We think that it could be possible to extend to our systems the same arguments used by these authors, reaching the conclusion that mechanism A (reaction through a transition state) should be preferred in respect to mechanism C (reaction through in intermediate).

Similar considerations could also apply to the formation of diphenyl sulfoxide in the reactions with phenyllithium. However, the formation of diphenyl disulfide and the result of the reaction with butyllithium indicate a more complex overall picture for these reagents.

Apart from the mechanistic aspects discussed above which undoubtedly deserve further attention, the results of the present investigation indicate that halovinyl sulfoxides are synthetically useful compounds with an interesting capability to lead to different classes of products, depending on the nature of the organometallic reagent.

Experimental Section

All reactions involving organometallic reagents were carried out under a N_2 atmosphere. THF was distilled twice from sodium wire and maintained under N_2. The purified reaction products were characterized by their ^{1}H NMR spectra, recorded at 200 MHz in $CDCl_3$, their IR spectra (film), and their mass spectra determined by GC/MS analysis (SE30, 25 m, capillary column and mass selective detector MSD 5970B, 70 eV). The *E*/*Z* ratios of the cross-coupling products in the reactions with diorganocuprates were determined by GLC analysis on a capillary column apparatus. The acetylene analysis was performed with a quadrupole mass spectrometer (40 eV).

Materials. The starting sulfoxides 1–4 were synthesized by *m*-CPBA oxidation of the corresponding sulfide, using the following procedure. Four millimoles of *m*-CPBA in 30 mL of $CHCl_3$ were added to 4 mmol of the sulfide in 10 mL of $CHCl_3$, at 0 °C. The mixture was stirred for 3 h at rt, and then the solvent was evaporated under vacuum. The residue was treated with a 1 M aqueous Na_2CO_3 and extracted three times with diethyl ether. The combined extracts were washed with water, dried (Na_2SO_4), and evaporated in vacuo to give the crude sulfoxide, which was purified by flash chromatography (eluent petroleum ether/diethyl ether, 1:1).

(*E*)-((2-Bromoethenyl)sulfinyl)benzene (1),[11] mp 56–57 °C (hexane), and **(*Z*)-((2-bromoethenyl)sulfinyl)benzene (2)**[11] [Kugelrohr distillation at 135–140 °C (6×10^{-5} Torr)] had spectral data (^{1}H NMR and MS) which are consistent with their structure.

(*Z*)-2-((2-Bromoethenyl)sulfinyl)naphthalene (3): mp 94–95 °C (heptane) was obtained from (*Z*)-2-((2-bromoethenyl)thio)naphthalene:[1g] yield 68%; ^{1}H NMR δ 8.24 (s, 1 H), 7.92–7.81 (m, 3 H), 7.64–7.50 (m, 3 H), 7.02 (d, $J = 6.7$ Hz, 1 H), 6.87 (d, $J = 6.7$ Hz, 1 H); MS (70 eV) *m*/*e* (relative intensity) 282 ((M + 2), 5), 280 (M^+, 5), 234 (97), 232 (100), 175 (66), 127 (84), 115 (74); IR 1065, 1041, 813, 800, 746, 702 cm^{-1}. Anal. Calcd for $C_{12}H_9BrOS$: C, 51.26; H, 3.23; Br, 28.42; S, 11.40. Found C, 51.28; H, 3.26; Br, 28.53; S, 11.66.

(*E*)-((2-Chloroethenyl)sulfinyl)benzene (4),[14] mp 37–38 °C (hexane), had spectral data (^{1}H NMR and MS) which are consistent with its structure.

Cross-Coupling Reactions of 2-Halovinyl Aryl Sulfoxides 1–4 with Organocuprates. General Procedure. A slurry of 0.57 g (3 mmol) of CuI in 10 mL of THF was stirred and cooled at 0 °C under N_2. A solution of 6 mmol of the organometallic reagent in THF (unless otherwise specified in Table I) was added. After 10 min, the flask was cooled to the reaction temperature (see Table I), and a solution of 2 mmol of the halovinyl sulfoxide in 15 mL of THF was added dropwise. Stirring was continued for an additional 30 min. The reaction mixture was then quenched with a saturated aqueous NH_4Cl solution and extracted three times with diethyl ether. The combined organic extracts were dried (Na_2SO_4), and the solvent was removed under vacuum. The products were separated by flash chromatography (silica gel, diethyl ether/petroleum ether, 1:1, as eluent) and purified by distillation or crystallization.

(*E*)-(1-Hexenylsulfinyl)benzene (5),[12] bp 115–117 °C (0.5 Torr), had spectral data (^{1}H NMR and MS) which agree with those reported.

(*Z*)-(1-Hexenylsulfinyl)benzene (6) [Kugelrohr oven temperature 120–125 °C (6×10^{-2} torr)]: ^{1}H NMR δ 7.60–7.42 (m, 5 H), 6.26–6.11 (m, 2 H), 2.61–2.40 (m, 2 H), 1.60–1.11 (m, 4 H), 0.87 (t, $J = 6.8$ Hz, 3 H). A shift reagent experiment with $Eu(fod)_3$ allowed a vinyl proton coupling to be determined, $J = 9.5$ Hz: MS (70 eV) *m*/*e* (relative intensity) 208 (M^+, 7), 191 (100), 149 (79), 135 (10), 123 (10), 110 (24), 78 (29); IR 1082, 1039, 746, 689 cm^{-1}. Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74; S, 15.39. Found: C, 68.79; H, 7.72; S, 15.52.

(*E*)-((2-Phenylethenyl)sulfinyl)benzene (7),[13] mp 61–62 °C (hexane/diethyl ether), and **(*Z*)-((2-phenylethenyl)sulfinyl)benzene (8)**[13] [Kugelrohr oven temperature 155–160 °C (3×10^{-3} Torr)] had MS data which agree with those reported.[13b] **(*E*)-7**: ^{1}H NMR δ 7.70–7.31 (m, 11 H), 6.82 (d, $J = 15.5$ Hz, 1 H). **(*Z*)-8**: ^{1}H NMR δ 7.55–7.05 (m, 10 H), 6.92 (d, $J = 10.6$ Hz, 1 H), 6.23 (d, $J = 10.6$ Hz, 1 H).

(*Z*)-2-(1-Hexenylsulfinyl)naphthalene (9) [Kugelrohr oven temperature 170–175 °C (3×10^{-5} Torr)]: ^{1}H NMR δ 8.01–7.99 (m, 1 H), 7.73–7.63 (m, 3 H), 7.38–7.25 (m, 3 H), 6.07–5.98 (m, 2 H), 2.51–2.34 (m, 2 H), 1.33–1.22 (m, 4 H), 0.75 (t, $J = 6.9$ Hz, 3 H). A shift reagent experiment with $Eu(fod)_3$ allowed a vinyl proton coupling to be observed, $J = 10.0$ Hz: MS (70 eV) *m*/*e* (relative intensity) 258 (M^+, 17), 241 (100), 166 (79), 160 (64), 128 (87), 115 (92); IR 1066, 1039, 909, 813, 732 cm^{-1}. Anal. Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02; S, 12.41. Found: C, 74.06; H, 7.19; S, 12.25.

(*Z*)-2-((3-Methyl-1-pentenyl)sulfinyl)naphthalene (10) [Kugelrohr oven temperature 155–160 °C (5×10^{-5} Torr)]: MS (70 eV) *m*/*e* (relative intensity) 258 (M^+, 13), 242 (21), 210 (51), 181 (100), 159 (26), 128 (42), 115 (46); IR 1065, 1038, 812, 747 cm^{-1}. Anal. Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02; S, 12.41. Found: C, 74.31; H, 7.14; S, 12.61. Column chromatography (petroleum ether/diethyl ether, 1:1) allowed the separation of two stereoisomers:[26] ^{1}H NMR δ (first eluted stereoisomer) 8.21–8.19 (m, 1 H), 7.94–7.82 (m, 3 H), 7.59–7.45 (m, 3 H), 6.20 (d, $J = 9.6$ Hz, 1 H), 5.95 (dd, $J = 9.6$, $J = 10.4$ Hz, 1 H), 3.21–2.99 (m, 1 H), 1.58–1.20 (m, 2 H), 1.08 (d, $J = 6.7$ Hz, 3 H), 0.93 (t, $J = 7.3$ Hz, 3 H); δ (second eluted stereoisomer) 8.22–8.20 (m, 1 H), 7.95–7.83 (m, 3 H), 7.60–7.50 (m, 3 H), 6.23 (d, $J = 9.6$ Hz, 1 H), 6.00 (dd, $J = 9.6$, $J = 10.4$ Hz, 1 H), 3.25–3.02 (m, 1 H), 1.57–1.21 (m, 2 H), 1.15 (d, $J = 6.7$ Hz, 3 H), 0.93 (t, $J = 7.3$ Hz, 3 H).

Reaction of 2-Halovinyl Phenyl Sulfoxides 1, 2, and 4 with Grignard or Organolithium Reagents. General Procedure. A solution of 3 mmol of the organometallic reagent in THF (unless otherwise specified in Table II) was added dropwise to a stirred solution of 2 mmol of the halovinyl sulfoxide in 20 mL of THF, under N_2. After 10 min, the reaction mixture was quenched with a saturated aqueous NH_4Cl and extracted three times with diethyl ether. The combined organic extracts were dried (Na_2SO_4), and the solvent was removed in vacuo. The products were purified by distillation or by column chromatography (silica gel, diethyl ether/petroleum ether, 1:1, as eluent) followed by crystallization.

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(*n*-Butylsulfinyl)benzene (11)[15] [Kugelrohr oven temperature 100–105 °C (4×10^{-2} Torr)] and **1,1′-sulfinylbisbenzene (13)**,[17] mp 70–71 °C (hexane), had spectral data (^1H NMR and MS) which are consistent with their structure.

(*n*-Pentylsulfinyl)benzene (12)[16] [Kugelrohr oven temperature 105–110 °C (6×10^{-2} Torr)]: ^1H NMR δ 7.65–7.43 (m, 5 H), 2.81–2.73 (m, 2 H), 1.79–1.24 (m, 6 H), 0.90–0.82 (m, 3 H); MS (70 eV) *m/e* (relative intensity) 196 (M^+, 1), 179 (35), 126 (100), 110 (20), 78 (46). Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33. Found: C, 67.02; H, 8.11; S, 16.16.

Acetylene Analysis. In the reaction between phenylmagnesium bromide and **(*Z*)-2**, the outlet of the reaction flask was connected to a 5-mL bulb, equipped with an inlet and an outlet, and cooled with liquid N_2. N_2 was flushed during the reaction time and after the quenching. A white crystalline solid was formed in the bulb. The bulb's inlet was then stoppered and most of the N_2 was removed at the same temperature by a vacuum pump connected to the outlet. The bulb was allowed to reach room temperature and the evolved gas was analyzed by mass spectrometry. Acetylene (M^+, 26) was found.

In another experiment, starting from 2 mmol of halovinyl sulfoxide, the reaction flask was flushed with N_2, and the gas was bubbled into cold diethyl ether (−80 °C). A cold methanolic solution of K_2HgI_4 (prepared by adding 5 g of HgI_2 to 25 mL of a 20% solution of KI in CH_3OH[27]) was added to the ethereal solution of acetylene, followed by 6 mL of a 0.5 N solution of NaOH. Titration of NaOH excess with 0.1 N H_2SO_4 gave the amount of acetylene trapped in diethyl ether (85% of the amount of the starting sulfoxide).

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Registry No. 1, 74031-48-4; 2, 74031-47-3; 3, 138286-19-8; 4, 134262-30-9; 5, 138286-20-1; 6, 138286-21-2; 7, 40110-66-5; 8, 40110-65-4; 9, 138286-22-3; 10 isomer 1, 138286-23-4; 10 isomer 2, 138286-24-5; 11, 13153-10-1; 12, 34756-51-9; 13, 945-51-7; (*E*)-PhSCH=CHBr, 17101-82-5; (*Z*)-PhSCH=CHBr, 17101-71-2; (*Z*)-(2-Np)SCH=CHBr, 134613-51-7; (*E*)-PhSCH=CHCl, 26620-11-1.

Supplementary Material Available: Spectral data of compounds 1, 2, 4, and 11 (1 page). Ordering information is given on any current masthead page.

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Preparation of 1,4-Diketones and Their Reactions with Bis(trialkyltin) or Bis(triphenyltin) Sulfide–Boron Trichloride

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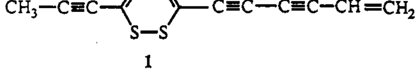
1,4-Diphenyl- and 1,4-bis(4-chlorophenyl)-1,4-butanediones (3 and 4), as well as 1-phenyl-, 1-(4-chlorophenyl)-, and 1-(4-methoxyphenyl)-1,4-pentanediones (7–9) react with bis(tributyltin), bis(tricyclohexyltin), and/or bis(triphenyltin) sulfide in the presence of boron trichloride to give, 2,5-diaryl- or 5-methyl-2-arylthiophenes. 1,8-Diphenyl-1,7-octadiyne-3,6-dione (10) and 1-phenyl-1,7-nonadiyne-3,6-dione (11), which were prepared in nine steps from 1,4-butanediol, react with the thionation reagents to give 2,5-bis(2-phenylethynyl)thiophene (**20g**) and 2-(2-phenylethynyl)-5-(1-propynyl)thiophene (**20f**), respectively.

1,4-Dicarbonyl compounds are useful synthetic intermediates, particularly in the synthesis of natural products. This report describes a nine-step procedure for the controlled and versatile synthesis of less readily available unsymmetrical alkynyl 1,4-diketones. Owing to the interest in the disulfide/dithione valence isomerization and in the synthesis of the potent antiviral natural products Thiarubrines A and B (1 and 2) and their derivatives,[1-7] we decided to attempt to develop mild experimental procedures for the difficult conversion of 1,4-diketones to the corresponding 1,4-dithiones[4,5,8-20] which could be cyclized



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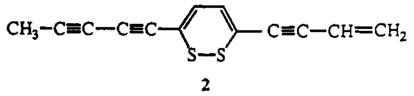

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