fact that nucleophilic attack of the thiophenoxide anions is probably not rate limiting in this case,[27] would minimize the effect of the interface on the reaction rate.

We emphasize, however, that the absence of significant intrinsic rate effects on the thiolysis of NPA by thiophenoxides in CTAB cannot be taken as general phenomenon, i.e., the lack of an effect of charged interfaces on the reactivity of SH groups. Indeed preliminary investigations[14] of the thiolysis of NPA by long-chain alkyl mercaptans, which is not limited by the same restrictions, show that the catalytic factors are much higher than those predicted on the basis of eq 9 with $k_{2M} = k_{2w}$.

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Registry No.—CTAB, 57-09-0; NPA, 830-03-5.

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# Addition of Organocopper(I) Reagents to α,β-Acetylenic Sulfoxides[1a]

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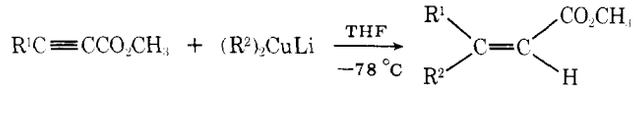
α,β-Acetylenic sulfoxides (**2**) reacted readily with monoalkylcopper reagents (**1**) at −78 °C in tetrahydrofuran to afford high yields of β-alkylated α,β-ethylenic sulfoxides (**3**). As in the analogous reaction with α,β-acetylenic esters, the addition was highly stereoselective, giving the product of a cis addition to the triple bond almost exclusively. The product sulfoxides were oxidized almost quantitatively with *m*-chloroperbenzoic acid to produce the corresponding sulfones (**12**) stereospecifically, thus providing a highly stereoselective synthesis of isomeric α,β-ethylenic sulfones. The structures of these compounds, and thus the cis nature of the addition reaction, were established on the basis of their $^1$H NMR spectra, and in the case of (*Z*)- and (*E*)-1-(ethanesulfonyl)-2-methyl-1-hexene (**14a** and **14b**) were confirmed unambiguously by an alternate stereospecific synthesis of each isomer. The reaction of (*E*)-2-iodo-1-(ethanesulfonyl)-1-hexene (**21**) with methylcopper bis(diisopropyl sulfide) gave **14a**, while (*E*)-2-iodo-1-(ethanesulfonyl)propene (**20**) and the corresponding *n*-butylcopper complex gave **14b**. In contrast to the clean addition of monoalkylcopper reagents to acetylenic sulfoxides, lithium di-*n*-butylcuprate reacted with **2a** and **2b** to also give ethyl *n*-butyl sulfoxide. This cleavage product presumably resulted from attack at the sulfoxide sulfur rather than additive attack on the triple bond.

The chemistry of organocopper(I) reagents represents an ever-expanding topic of investigation that has received a great deal of attention in recent years.[2] In particular, the conjugate addition reactions of organocopper(I) reagents with α,β-unsaturated carbonyl compounds and related substances have been actively investigated since 1966, when it was demonstrated that such species were the reactive intermediates in the copper-catalyzed conjugate additions of Grignard reagents to α,β-unsaturated ketones.[3] α,β-Acetylenic esters also undergo a facile conjugate addition reaction with lithium diorganocuprates,[4] with cis addition taking place exclusively.




In contrast, an investigation of the reaction of lithium dialkylcuprates with a number of α,β-ethylenic sulfur compounds[5] has shown that with these substrates conjugate addition, if it occurs at all, is more difficult than with α,β-ethylenic carbonyl compounds, and that competing side reactions are more prevalent.

At the time this work was initiated, no additions of organocopper(I) reagents to α,β-acetylenic sulfur compounds had

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**Table I. Addition of Monoalkylcopper Reagents (1) to α,β-Acetylenic Sulfoxides (2)**

| $R^1$ | Registry no. | $R^2$ | Registry no. | % cis addition | Product | Registry no. | % yield |
|---|---|---|---|---|---|---|---|
| $CH_3$ (**1a**) | 1184-53-8 | $CH_3$ (**2a**) | 25558-06-9 | | **4** | 65832-85-1 | 100 |
| $CH_3$ (**1a**) | | $n$-$C_4H_9$ (**2b**) | 54088-87-8 | >96[a] | **5a** | 54088-88-9 | 100 |
| $n$-$C_4H_9$ (**1b**) | 34948-25-9 | $CH_3$ (**2a**) | | 98.8[a] | **5b** | 54088-89-0 | 98 |
| $CH_3$ (**1a**) | | $C_6H_5$ (**2c**) | 65832-84-0 | 100[b] | **6a** | 65832-86-2 | 93 |
| $C_6H_5$ (**1c**) | 3220-49-3 | $CH_3$ (**2a**) | | 100[b] | **6b** | 65832-87-3 | 100 |
| $CH_3$ (**1a**) | | H (**2d**) | 36565-71-6 | 100[c] | **7** | 65832-88-4 | 81 |
| $n$-$C_4H_9$ (**1b**) | | $n$-$C_4H_9$ (**2b**) | | | **8** | 65832-89-5 | 97 |
| $n$-$C_4H_9$ (**1b**) | | $C_6H_5$ (**2c**) | | 100[b] | **9a** | 65832-90-8 | 97.5 |
| $C_6H_5$ (**1c**) | | $n$-$C_4H_9$ (**2b**) | | 100[b] | **9b** | 65832-91-9 | 100 |
| $n$-$C_4H_9$ (**1b**) | | H (**2d**) | | 100[b] | **10** | 65832-92-0 | 96.5 |
| $C_6H_5$ (**1c**) | | $C_6H_5$ (**2c**) | | | **11** | 57642-54-3 | 100 |

[a] Determined by GLC analysis after oxidation of the sulfoxide to the sulfone. [b] Determined by NMR. No indication in the sulfoxide, or the sulfone derived from it, of any of the trans addition product. [c] NMR of the sulfoxide was complicated by contamination with unidentified nonisomeric material and was ambiguous; NMR of the sulfone derived from it indicated only the product of cis addition.

**Table II. Oxidation of α,β-Ethylenic Sulfoxides (3) to α,β-Ethylenic Sulfones (12)**

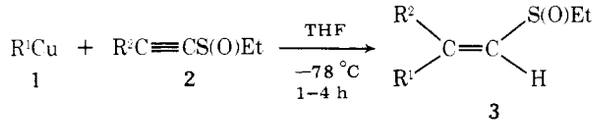
| Sulfoxide, mmol | Peracid,[a] mmol | Sulfone, % yield | Registry no. |
|---|---|---|---|
| **4**, 1.50 | 1.50 | **13**, 100 | 65832-93-1 |
| **5a**, 1.57 | 1.65[b] | **14a**, 99 | 54088-92-5 |
| **5b**, 2.57 | 2.75[c] | **14b**, 88 | 54088-91-4 |
| **6a**, 2.76 | 2.76 | **15a**, 100 | 58202-55-4 |
| **6b**, 1.44 | 1.44 | **15b**, 100 | 65832-94-2 |
| **7**, 1.07 | 1.07 | **16**, 66 | 65832-95-3 |
| **8**, 1.505 | 1.58[b] | **17**, 100 | 58202-53-2 |
| **9a**, 2.76 | 2.76 | **18a**, 100 | 58202-56-5 |
| **9b**, 1.44 | 1.44 | **18b**, 100 | 58202-54-3 |
| **10**, 0.817 | 0.817 | **19**, 95 | 65832-96-4 |

[a] 85% $m$-chloroperbenzoic acid. [b] 5% excess. [c] 7% excess.

been reported. It was anticipated, however, that, since acetylenic substrates are more subject to nucleophilic attack than their ethylenic analogues,[6] acetylenic organosulfur compounds would readily undergo conjugate addition reactions with organocopper reagents. This expectation has been justified and we have briefly described the results of our investigation of the addition of monoalkylcopper reagents and lithium diorganocuprates to α,β-acetylenic sulfoxides.[7] The data presented herein represent a more complete account of that work. During the course of this investigation a preliminary account of the conjugate addition of Grignard reagents to α,β-acetylenic sulfides in the presence of stoichiometric amounts of cuprous halides was reported by other workers.[8a] Subsequently they have published brief reports of similar additions to acetylenic sulfoxides[8b] and sulfones[8c] which completely support the findings to be presented here.

## Results and Discussion

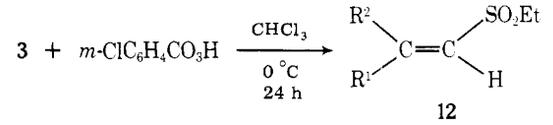
**RCu Additions.** Monoalkylcopper reagents (**1**) were found to react with α,β-acetylenic sulfoxides (**2**) in a highly stereoselective manner to produce excellent yields of β-alkylated α,β-ethylenic sulfoxides (**3**) (Table I). In all cases the product




of a cis addition of $R^1$ and H to the triple bond was formed almost exclusively. Addition took place even with a terminal acetylenic sulfoxide (**2d**) with no observable abstraction of the acetylenic proton by the organometallic reagent.

In all reactions involving the possible formation of geometrical isomers, the NMR spectra of the crude ethylenic sulfoxides showed the stereoselective formation of essentially only *one* isomer, it usually being clear, when each isomer was available (**5, 6, 9**), that the members of each (*E*)-(*Z*) pair were distinguishable by NMR. In the case of **6,** the NMR spectra of each isomer appeared very similar, and there was some doubt that the differences between the two spectra were real, possibly being due to solvent effects instead. When the two presumed isomers were combined to give an approximately 1:1 mixture, however, the NMR spectrum showed without question two distinctly different compounds.

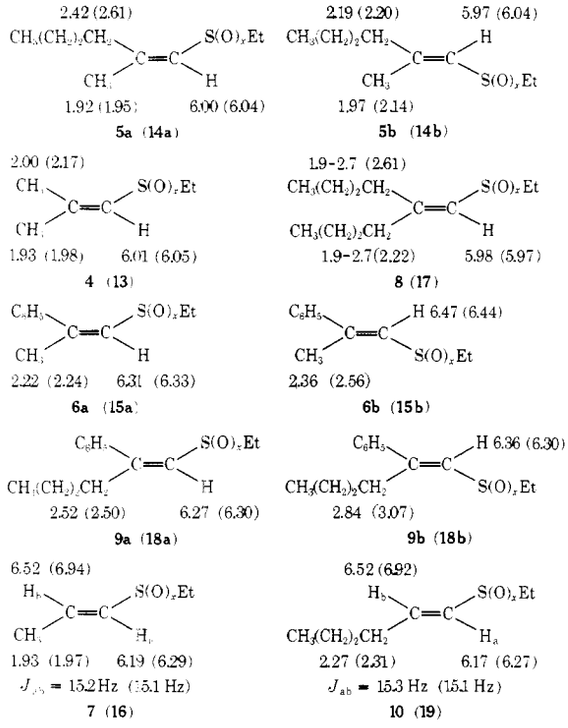
The direct GLC analysis of the sulfoxide products of these reactions (as well as the acetylenic sulfoxide starting materials) proved to be difficult due to thermal decomposition[9] of these compounds at the temperatures (>125 °C) necessary to elute them from even nonpolar (SE-30, SF-96) columns. The corresponding sulfones, however, were quite stable thermally and were readily obtained from the sulfoxides. Treatment of the sulfoxides, **3,** with 1.0 equiv of $m$-chloroperbenzoic acid in chloroform at 0 °C for 24 h produced almost quantitative yields of the α,β-ethylenic sulfones, **12** (Table II).




In all cases involving the oxidation of a *single* sulfoxide geometrical isomer, only *one* sulfone isomer (as shown by NMR and, in some cases, by GLC) was formed with retained configuration.

**Structural Assignments.** In order to determine the stereochemistry of the organocopper(I) addition reactions it was necessary to determine unambiguously the stereochemical structure of the olefinic products. This was carried out using three independent approaches. The structure of each isomer of sulfoxides **5, 6,** and **9** (and the corresponding sulfones **14, 15,** and **18**) was deduced from a comparison of the NMR spectra of the two isomers in each pair, primarily of the chemical shift values of their allylic methyl and methylene protons. In the case of the disubstituted olefins **7** and **10** (and the corresponding sulfones **16** and **19**) the stereochemistry was determined on the basis of the magnitude of the olefinic proton coupling constant. Finally, these structural assignments were confirmed in two cases by a stereospecific alternate synthesis of the isomeric sulfones **5a** and **5b.** These were shown to be identical to the sulfones derived from the sulfoxide products of the addition of respectively **1a** to **2b** and **1b** to **2a.**

**Table III. NMR Data for α,β-Ethylenic Sulfoxides (3) and Sulfones (12; the Sulfone δ Values are in Parentheses)[a]**



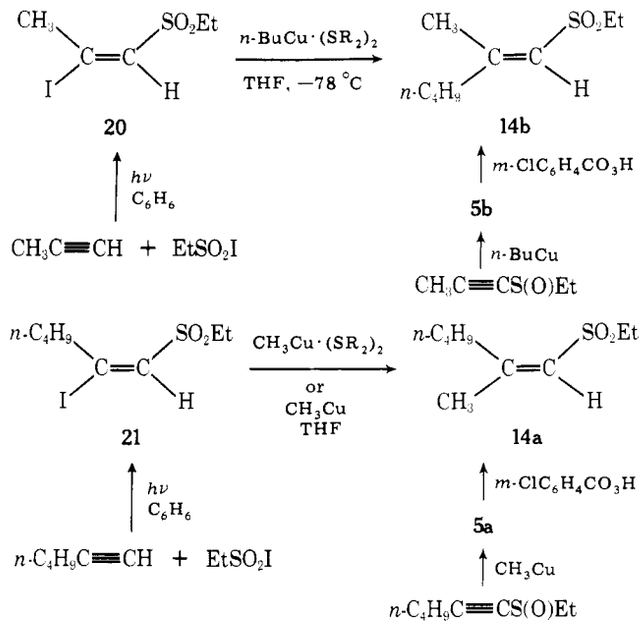

[a] 10–20% (v/v) in $CDCl_3$, ppm (δ) downfield from tetramethylsilane: sulfoxide, $x = 1$ (sulfone, $x = 2$).

The $^1$H-NMR absorptions due to the allylic methyl and methylene protons in the ethylenic sulfoxides, **3**, and the corresponding sulfones, **12**, were expected to appear further downfield when they were cis to the sulfur functionality than when they were trans to the sulfoxide or sulfone group.[10,11] Therefore, the (*E*) structure was assigned to sulfoxide **5b** and sulfone **14b**, which have their allylic methyl absorption at lower field and their allylic methylene signal at higher field than **5a** and **14a**, respectively (Table III). The values for the allylic methyl and methylene protons in these compounds also matched very closely those for the corresponding methyl groups in **4** and **13** and the corresponding methylene groups in **8** and **17**. In a similar fashion the (*E*) configuration was assigned to sulfoxides **6b** and **9b** and sulfones **15b** and **18b** and the (*Z*) configuration to **6a**, **15a**, **9a**, and **18a**. These assignments were further substantiated by an examination of the chemical shifts of the vinyl protons in these aromatic systems. Those vinyl protons cis to a phenyl group were expected to be deshielded to a greater extent by its induced magnetic field than those trans to it, which would be essentially unaffected by the diamagnetic anisotropy of the aromatic ring. The NMR spectra of the above mentioned aryl compounds were in complete agreement with this prediction in all of the structural assignments made above.

When addition product **3** and its derived sulfone **12** were disubstituted olefins, the olefinic protons were found to have an NMR coupling constant of approximately **15** Hz (this was especially evident with the sulfones **16** and **19**), indicating a trans arrangement about the double bond. The assignment of a trans geometry for these compounds was also supported by the presence of a strong band in the 960–980-cm$^{-1}$ region of the infrared spectra of sulfoxides **7** and **10**, while there was virtually no absorption in the 665–730-cm$^{-1}$ region that could be attributed to a cis olefin.

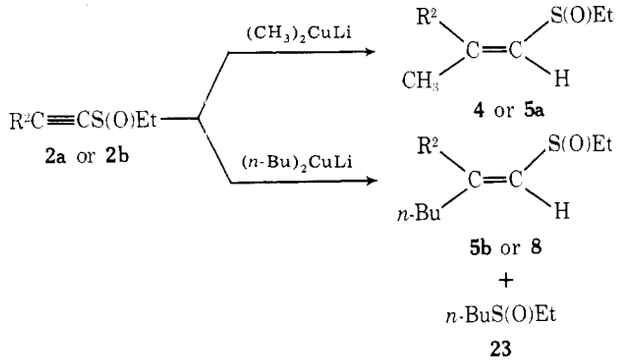
**Alternate Synthesis of 14a and 14b.** The addition of sulfonyl iodides to acetylenes to produce iodovinyl sulfones (e.g., **20** and **21**) has been shown to take place in a trans fashion exclusively.[12] Replacement of the halogen by an alkyl or aryl group would then lead to a sulfone of the same kind (**12**) as that obtained from sulfoxide **3**. Simple vinyl halides have been shown to undergo this type of displacement of halogen by lithium diorganocuprates, with almost complete retention of stereochemistry.[13,14] Although the reaction of iodovinyl sulfones with cuprous phenylacetylide[12,15] was under investigation in this laboratory concurrent with the present study, a similar reaction with simple alkyl or aryl organocopper(I) reagents had not been previously reported.

We have found that the reaction of **20** with an *n*-butylcopper bis(diisopropyl sulfide) complex leads to the highly stereospecific formation of **14b** in 88% yield.[7] The same reaction with lithium di-*n*-butylcuprate, or the similar reaction of **21** with lithium dimethylcuprate,[16] however, gave nonstereospecific coupling, resulting in 20:80 (with $(n\text{-Bu})_2$CuLi) and 64:36 (with $Me_2$CuLi after 3.5 h; 54:46 after 4.5 h) mixtures of **14a** and **14b**. The reaction of **21** with a methylcopper bis(diisopropyl sulfide) complex also gave highly stereospecific coupling, although it also gave, after 5 h at −78 °C, considerable amounts of recovered **21**, and a by-product, **22**. Fortunately, reacting *uncomplexed* methylcopper with **21** for 8 h at −78 °C resulted in almost complete consumption of the iodovinyl sulfone, although sizable quantities of **22** were still produced. Happily, the stereospecificity of this reaction was, if anything, slightly higher. The identity of **22** has been established by other workers in this laboratory as being *n*-BuCH=CHSO$_2$Et of predominantly the cis configuration.[17] This presumably arose through protonation of a vinyl copper species formed via copper–halogen exchange between the organocopper reagent and the iodovinyl sulfone, in a manner similar to that observed with simple vinyl halides.[13] Working up the reaction by adding an excess of methyl iodide prior to protonation[13] decreased slightly the amount of **22** formed but did not eliminate it. Another investigation in this laboratory based upon and performed subsequent to this work has uncovered experimental conditions, which efficiently prevent this undesired side reaction. A study of the reaction of organocopper(I) reagents with iodovinyl sulfones[15] has shown that methylcopper reacts smoothly with **21** at 0 °C in THF to give **14a** exclusively to the total exclusion of **22**.




**$R_2$CuLi Additions.** While monoalkylcopper reagents added cleanly to **2**, some lithium diorganocuprates also gave a by-product resulting from cleavage of the acetylenic sulfoxide.

Although lithium dimethylcuprate added normally to **2a** (83%) and **2b** (97.5%, >96% cis addition), lithium di-*n*-butylcuprate reacted to give appreciable quantities of ethyl-*n*-butyl sulfoxide (**23**) as well. Apparently the more reactive




lithium di-*n*-butylcuprate can attack the acetylenic sulfoxide at sulfur to displace an acetylide, as well as adding to the triple bond. The less reactive lithium dimethylcuprate, in contrast, was only capable of additive attack on the triple bond. It might be argued that this cleavage product could be arising from small amounts of *n*-butyllithium present in the reaction mixture, rather than from $(n\text{-Bu})_2\text{CuLi}$. Indeed, *n*-butyllithium did react with **2a** under the same conditions to give predominantly cleavage to **23**, as well as lesser amounts of 1-ethylsulfinylpropadiene (**24**) (resulting from isomerization of the starting acetylenic sulfoxide).

$$\underset{\textbf{2a}}{CH_3C{\equiv}CS(O)Et} + n\text{-BuLi} \xrightarrow[-78\ ^\circ C]{THF} \textbf{23} + \underset{\textbf{24}}{H_2C{=}C{=}CHS(O)Et}$$

In spite of this result, however, we do not favor this explanation for several reasons. An accidential slight excess of *n*-butyllithium was precluded in these reactions by using a 2% excess of cuprous iodide in the formation of the diorganocuprate. In addition it was considered highly improbable that an error in quantities could have occurred sufficiently large to produce the observed yields of **23** (on the order of 20% as determined by GLC after oxidation of the sulfoxide products to sulfones). Furthermore, it has been shown that alkyllithiums are *not* present in solutions of lithium diorganocuprates due to an equilibrium with the monoalkylcopper

## Experimental Section

**General.** Infrared spectra were recorded on either a Beckman IR-33 or a Perkin-Elmer Model 137B infracord infrared spectrometer. NMR spectra were recorded on a Varian A-60A instrument. Mass spectra were obtained on a Hitachi RMU-6A mass spectrometer. Microanalyses were performed by Dr. C. S. Yeh and staff, Purdue University. Analytical and preparative gas–liquid phase chromatography (GLC) were performed on a Wilkins (Varian) Aerograph Autoprep Model A-700 instrument having a thermal conductivity detector and using helium as a carrier gas. Column A: 8 ft × 0.25 in., 15% neopentyl glycol isophthalate on 60–80 mesh Chromasorb W; column B: 10 ft. × 0.25 in., 10% OV-17 on 60–80 mesh, acid washed, dimethyldichlorosilane treated (AW/DMCS) Chromosorb W; column C: 6.5 ft. × 0.375 in., 10% GE SF-96 on 60–80 mesh, AW/DMCS Chromosorb W.

Reagent grade tetrahydrofuran (THF) was distilled from lithium aluminum hydride under nitrogen immediately before use. Anhydrous methanol was stored over 3A molecular sieves. Cuprous iodide was purchased from Research Organic/Inorganic Chemical Corp. and was purified by the method of Posner and Sterling.[19] Diisopropyl sulfide and 85% *m*-chloroperbenzoic acid were obtained from Aldrich Chemical Co. and were used without further purification. Methyllithium (manufactured from methyl chloride by Foote Mineral Co.) was purchased from Matheson Coleman and Bell, and *n*-butyl- and phenyllithium were obtained from Alfa Inorganics (Ventron). They were stored in the cold under nitrogen and were standardized by a modified Gilman double titration method.[20]

Apparatus for experiments requiring dry conditions were either flame or oven dried and cooled under a stream of nitrogen. During work-up of the reactions, general drying of the solvent was performed over anhydrous magnesium sulfate and the solvent was removed on a rotary evaporator in vacuo at water aspirator pressure.

**Preparation of α,β-Acetylenic Sulfoxides (2).** These were prepared from the corresponding α,β-acetylenic sulfides[21] by oxidation with 1.0 equiv of *m*-chloroperbenzoic acid in chloroform at 0 °C for 24 h.[22]

1-(Ethanesulfinyl)-1-hexyne (**2b**) was obtained from 1-(ethylthio)-1-hexyne[23] in 86% yield: bp 72 °C (0.20 mm) (75 °C (0.17 mm)); IR (neat) 2205 (s, C≡C), 1078 $cm^{-1}$ (s, S→O); NMR ($CDCl_3$ δ 0.93 (distorted t, 3 H), 1.38 (t, $J$ = 7.25 Hz, 3 H), 1.15–2.0 (m, 4 H), 2.47 (broadened t, 2 H), 2.99 (q, $J$ = 7.25 Hz, 2 H). Anal. Calcd for $C_8H_{14}OS$: C, 60.72; H, 8.92; S, 20.26. Found: C, 61.02; H, 8.81; S, 20.01.

1-(Ethanesulfinyl)-2-phenylethyne (**2c**) was obtained crude, after removing traces of solvent in vacuo at 4 mm, in quantitative yield from 1-(ethylthio)-2-phenylethyne.[23] This was used as such in subsequent organocopper(I) reactions, the NMR indicating it contained no major impurities, since it was found to decompose with vigorous evolution of a gas upon attempted distillation at approximately 90 °C (0.2 mm): IR (neat) 2185 (s, C≡C), 1075, 1035 (s, S→O), 761, 692 (s, $C_6H_5$), 1607, 1583, 1499, 1452, 835 $cm^{-1}$; NMR ($CDCl_3$) δ 1.49 (t, $J$ = 7.25 Hz, 3 H), 3.13 (q, $J$ = 7.25 Hz, 2 H), 7.42 (m, 5 H).

**General Procedure for the Addition of $R^1Cu$ (1) to α,β-Acetylenic Sulfoxides (2).** A quantity of cuprous iodide 2% in excess of the number of moles of organolithium reagent to be used was weighed into a round-bottom flask containing a magnetic stirring bar and having a side arm fitted with a rubber septum stopper. After fitting with a gas inlet adapter tube (with stopcock) and oven drying, the flask was connected to a mercury bubbler via the adapter tube and was cooled while flushing with prepurified nitrogen introduced through the septum stopper via a syringe needle. A dry THF was then injected, the volume of which, in combination with the volume of organolithium solution to be used, resulted in an approximately 0.25 M solution of the organocopper(I) reagent. The resulting stirred suspension was placed in a cooling bath (0 °C for MeLi and PhLi, −10 °C for *n*-BuLi) and a solution of the organolithium reagent was injected over a 1–2-min period. The more stable organocopper(I) reagents (methyl and phenyl) were allowed to stir at 0 °C for 10 min and then cocled to −78 °C for 15 min, while the less stable *n*-butyl reagents were cooled in a dry ice–acetone bath immediately. Into this solution of RCu (25 mol % in excess of the acetylenic sulfoxide) was then rapidly injected a 0.25 M solution (precooled to −78 °C) of **2** in THF. After stirring at −78 °C for 1–4 h, the reaction was quenched by injecting 5–10 mL of anhydrous methanol (precooled in a syringe to −78 °C) and then pouring the resulting mixture into a saturated aqueous ammonium chloride solution. Extraction with dichloromethane (3 × 25 mL), drying, and evaporation in vacuo usually gave essentially pure ethylenic sulfoxide **3** (Table IV). During the aqueous workup, an orange, yellow, or yellow-grey to silver-grey solid was usually formed. During the extractions, this was found for the most part in the more dense dichloromethane layer. No attempt was made

**Table IV. Experimental Data for the Reaction of $R^1Cu$ (1) with $R^2C{\equiv}CS(O)Et$ (2)**

| $R^1Cu$ | CuI, mmol | $R^1Li$, mmol | Acetylene, mmol | Time, h | Product, % yield |
|---|---|---|---|---|---|
| **1a** | 3.37 | 3.30[a] | **2a,** 2.64 | 2.0 | **4**[f] |
| **1a** | 3.82 | 3.74[b] | **2b,** 2.99 | 1.5 | **5a**[f] |
| **1b** | 3.87 | 3.87[c] | **2a,** 3.1 | 2.0 | **5b,** 98 |
| **1a** | 7.575 | 7.425[a] | **2c,** 5.94 | 2.0 | **6a,** 93 |
| **1c** | 3.67 | 3.60[d] | **2a,** 2.88 | 4.0 | **6b**[f] |
| **1a** | 1.68 | 1.65[a] | **2d,** 1.32 | 2.0 | **7,** 81 |
| **1b** | 3.95 | 3.87[c] | **2b,** 3.1 | 1.0 | **8,** 97 |
| **1b** | 7.21 | 7.07[e] | **2c,** 5.66 | 2.0 | **9a,** 98 |
| **1c** | 3.67 | 3.60[d] | **2b,** 2.88 | 4.0 | **9b**[f] |
| **1b** | 2.00 | 1.96[e] | **2d,** 1.57 | 2.0 | **10,** 97 |
| **1c** | 7.72 | 7.56[d] | **2c,** 6.05 | 4.0 | **11**[f] |

[a] 1.65 M methyllithium in diethyl ether. [b] 1.78 M methyllithium in diethyl ether. [c] 1.76 M *n*-butyllithium in *n*-hexane. [d] 1.80 M phenyllithium in 70:30 benzene–diethyl ether. [e] 2.02 M *n*-butyllithium in *n*-hexane. [f] Quantitative.

to prevent this solid from being drawn off with the organic extracts, since it was easily removed later along with the drying agent by filtration. Purification for microanalysis was usually accomplished by molecular distillation at reduced pressure. (Satisfactory analyses could not be obtained for the sulfoxides **4, 5a, 5b,** and **6a,** although they were obtained for the corresponding sulfones.)

**1-(Ethanesulfinyl)-2-methylpropene (4):** IR (neat) 1646, 800 (m, $R_2C$=CHR), 1049, 1024 (s, S→O), 2965, 2940, 2900, 1453, 1385, 1265, 1173, 976, 859 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.25 (t, $J$ = 7.5 Hz, 3 H), 1.93 (d, $J$ = 1.25 Hz, 3 H), 2.00 (d, $J$ = 1.25 Hz, 3 H), 2.75 (q, $J$ = 7.5 Hz, 2 H), 6.01 (m, 1 H).

**(*Z*)-1-(Ethanesulfinyl)-2-methyl-1-hexene (5a):** IR (neat) 2985, 2960, 2895, 1464 (s, CH), 1637, 797 (m, $R_2C$=CHR), 1050, 1026 (s, S→O), 1389, 1262, 1170, 1101, 973, 932, 731 $cm^{-1}$; NMR ($CDCl_3$) 0.93 (distorted t, 3 H), 1.27 (t, $J$ = 7.5 Hz, 3 H), 1.1–1.8 (m, 4 H), 1.92 (d, $J$ = 1.4 Hz, 3 H), 2.42 (broadened t, 2 H), 2.72 (q, $J$ = 7.5 Hz, 2 H), 6.00 (m, 1 H).

**(*E*)-1-(Ethanesulfinyl)-2-methyl-1-hexene (5b):** IR (neat) 2985, 2960, 2900 (s, CH), 1642, 809 (m, $R_2C$=CHR), 1050, 1026 (s, S→O), 1465, 1390, 1265, 1170, 1117, 978, 936, 865, 740; NMR ($CDCl_3$) $\delta$ 0.92 (distorted t, 3 H), 1.24 (t, $J$ = 7.5 Hz, 3 H), 1.1–1.8 (m, 4 H), 1.97 (d, $J$ = 1.1 Hz, 3 H), 2.19 (broadened t, 2 H), 2.73 (q, $J$ = 7.5 Hz, 2 H), 5.97 (m, 1 H).

**(*Z*)-β-(Ethanesulfinyl)-α-methylstyrene (6a):** IR (neat) 1624 (w, shoulder, C=C), 1045, 1023 (s, S→O), 835 and/or 804 (m, $R_2C$=CHR), 767, 701 (s, $C_6H_5$), 3080, 3055, 3000, 2960, 2940, 2900, 1607, 1580, 1501, 1447, 1383, 1329, 1265, 1190, 1165, 1135, 1080, 972, 922, 729 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.22 (t, $J$ = 7.5 Hz, 3 H), 2.22 (d, $J$ = 1.4 Hz, 3 H), 2.74 (q, $J$ = 7.5 Hz, 2 H), 6.31 (q, $J$ = 1.4 Hz, 1 H), 7.32 (s, 5 H).

**(*E*)-β-(Ethanesulfinyl)-α-methylstyrene (6b)** was purified for microanalysis by molecular distillation at 70 °C (0.15 mm): IR (neat) 1615 (m, C=C), 1046, 1027 (s, S→O), 812 (s, $R_2C$=CHR), 753, 696 (s, $C_6H_5$), 3080, 3050, 3000, 2960, 2900, 1581, 1505, 1451, 1390, 1311, 1261, 1235, 1194, 1168, 1078, 975, 924 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.30 (t, $J$ = 7.5 Hz, 3 H), 2.36 (d, $J \approx$ 1.25 Hz, 3 H), 2.85 (q, $J$ = 7.5 Hz, 2 H), 6.47 (q, $J \approx$ 1.25 Hz, 1 H), 7.40 (m, 5 H). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; S, 16.50. Found: C, 68.10; H, 7.46; S, 16.35.

**(*E*)-1-(Ethanesulfinyl)propene (7)** was purified for microanalysis by molecular distillation at 52 °C (0.2 mm): IR (neat) 1646 (w, C=C), 1052, 1028 (s, S→O), 960 (s, *trans*-RCH=CHR), 3040, 3005, 2965, 2945, 2900, 1452, 1425, 1385, 1320, 1283, 1242, 1178, 1140, 1097, 813, 788, 760, 739, 620 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.25 (t, $J$ = 7.5 Hz, 3 H), 1.93 (d, $J \approx$ 5.2 Hz, 3 H), 2.74 (q, $J$ = 7.5 Hz, 2 H), 6.19 (d, $J \approx$ 15.2 Hz, 1 H), 6.52 (doublet, $J \approx$ 15.2 Hz, of distorted quartets, $J \approx$ 5.2 Hz, 1 H). Anal. Calcd for $C_5H_{10}OS$: C, 50.81; H, 8.53; S, 27.12. Found: C, 50.90; H, 8.59; S, 27.00.

**1-(Ethanesulfinyl)-2-(*n*-butyl)-1-hexene (8)** was purified for microanalysis by molecular distillation at 85 °C (0.15 mm): IR (neat) 2985, 2960, 2895 (s, CH), 1632, 820 (m, $R_2C$=CHR), 1050, 1029 (s, S→O), 1470, 1391, 1265, 1168, 1140, 1119, 976, 790, 735 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 0.93 (distorted t, 6 H), 1.27 (t, $J$ = 7.5 Hz, 3 H), 1.1–1.9 (m, 8 H), 1.9–2.7 (m, 4 H), 2.74 (q, $J$ = 7.5 Hz, 2 H), 5.98 (s, 1 H). Anal. Calcd for $C_{12}H_{24}OS$: C, 66.61; H, 11.18; S, 14.82. Found: C, 66.44; H, 11.33; S, 14.90.

**(*Z*)-1-(Ethanesulfinyl)-2-phenyl-1-hexene (9a)** was purified for microanalysis by molecular distillation at 86 °C (0.10 mm): IR (neat) 3080, 3050 (w, CH), 2980, 2955, 2895 (s, CH), 1624 (w, C=C), 1043, 1022 (s, S→O), 840 and/or 814 (m, $R_2C$=CHR), 772, 700 (s, $C_6H_5$), 1606, 1580, 1501, 1461, 1450, 1424, 1388, 1330, 1261, 1187, 1165, 1137, 1116, 1080, 970, 938, 920, 727 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 0.87 (distorted t, 3 H), 1.22 (t, $J$ = 7.5 Hz, 3 H), 1.1–1.6 (m, 4 H), 2.52 (broadened t, 2 H), 2.74 (q, $J$ = 7.5 Hz, 2 H), 6.27 (t, $J$ = 1.25 Hz, 1 H), 7.31 (m, 5 H). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.56. Found: C, 70.92; H, 8.69; S, 13.50.

**(*E*)-1-(Ethanesulfinyl)-2-phenyl-1-hexene (9b)** was purified for microanalysis by molecular distillation at 91 °C (0.2 mm): IR (neat) 3085, 3055 (m, CH), 2985, 2960, 2895 (s, CH), 1610, 822 (m, $R_2C$=CHR), 1050, 1029 (s, S→O), 757, 700 (s, $C_6H_5$), 1580, 1505, 1464, 1452, 1390, 1316, 1265, 1240, 1169, 1140, 1114, 976, 929, 880 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 0.87 (distorted t, 3 H), 1.32 (t, $J$ = 7.5 Hz, 3 H), 1.1–1.8 (m, 4 H), 2.84 (q, $J$ = 7.5 Hz, overlapping a broadened t, 4 H), 6.36 (s, 1 H), 7.37 (s, 5 H). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.56. Found: C, 71.35; H, 8.57; S, 13.28.

**(*E*)-1-(Ethanesulfinyl)-1-hexene (10)** was purified for microanalysis by molecular distillation at 58 °C (0.15 mm): IR (neat) 2990, 2960, 2900 (s, CH), 1644 (m, C=C), 1060, 1030 (s, S→O), 973 (s, *trans*-RCH=CHR), 1426, 1390, 1320, 1280, 1263, 1140, 930, 788 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 0.92 (distorted t, 3 H), 1.26 (t, $J$ = 7.5 Hz, 3 H), 1.1–1.8 (m, 4 H), 2.27 (d of overlapping, broadened t, 2 H), 2.73 (q, $J$ = 7.5 Hz, 2 H), 6.17 (d, $J$ = 15.3 Hz, 1 H), 6.52 (doublet, $J$ = 15.3 Hz, of distorted triplets, $J$ = 6.0 Hz, 1 H). Anal. Calcd for $C_8H_{16}OS$: C, 59.95; H, 10.06; S, 20.00. Found: C, 59.74; H, 10.18; S, 20.03.

**β-(Ethanesulfinyl)-α-phenylstyrene (11).** The crude product was recrystallized from cyclohexane to give 0.927 g (59.7%) of analytically pure light yellow crystals: mp 99–100.5 °C; IR (KBr) 1046, 1017 (s, S→O), 865 (m, $R_2C$=CHR), 765, 699 (s, $C_6H_5$), 3085, 3020, 2995, 2965, 2940, 2905, 1602, 1581, 1506, 1455, 1420, 1390, 1345, 1320, 1275, 1230, 1171, 1139, 1088, 971, 930, 808, 780, 732 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.26 (t, $J$ = 7.5 Hz, 3 H), 2.83 (q, $J$ = 7.5 Hz, 2 H), 6.82 (s, 1 H), 7.31 (s, 10 H). Anal. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29; S, 12.51. Found: C, 74.76; H, 6.18; S, 12.57.

**Oxidation of α,β-Ethylenic Sulfoxides (3) to α,β-Ethylenic Sulfones (12).** To a 0.15–0.17 M solution of α,β-ethylenic sulfoxide (used as it was isolated directly from an organocopper(I) addition reaction) in chloroform at 0 °C was added 1.0 equiv of solid 85% *m*-chloroperbenzoic acid. After stirring at 0 °C for 24 h, the reaction mixture was washed twice with a solution made up of equal volumes (usually 10–20 mL each) of a 10% $Na_2SO_3$ solution and a saturated $NaHCO_3$ solution. Drying and evaporation in vacuo usually gave an almost quantitative yield of essentially pure α,β-ethylenic sulfone (Table II). These compounds were purified for microanalysis by preparative GLC.

**1-(Ethanesulfonyl)-2-methylpropene (13)** had a GLC retention time of 11.6 min on column A at 190 °C and 45 mL/min and was collected for microanalysis from column B under similar conditions: IR (neat) 1660, 814 (s, $R_2C$=CHR), 1321, 1298, 1149 (s, $SO_2$), 3075, 3020, 2980, 2960, 2925, 1469, 1439, 1400, 1256, 1199, 1098, 1070, 1000, 892, 730 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.34 (t, $J$ = 7.5 Hz, 3 H), 1.98 (d, $J$ = 1.35 Hz, 3 H), 2.17 (d, $J$ = 1.25 Hz, 3 H), 3.00 (q, $J$ = 7.5 Hz, 2 H), 6.05 (m, 1 H). Anal. Calcd for $C_6H_{12}O_2S$: C, 48.62; H, 8.16; S, 21.63. Found: C, 48.80; H, 8.41; S, 21.47.

**(*Z*)-1-(Ethanesulfonyl)-2-methyl-1-hexene (14a)** had a GLC retention time of 21.3 min on column A at 190 °C and 45 mL/min and was collected for microanalysis from column B under similar conditions: IR (neat) 2990, 2960, 2900 (s, CH), 1649 (s, C=C), 1320, 1290, 1144 (s, $SO_2$), 805 (m, $R_2C$=CHR), 1473, 1403, 1398, 1249, 1065, 993, 889, 865, 832 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 0.93 (distorted t, 3 H), 1.32 (t, $J$ = 7.5 Hz, 3 H), 1.13–1.83 (m, 4 H), 1.95 (d, $J \approx$ 1.5 Hz, 3 H), 2.61 (broadened t, 2 H), 2.98 (q, $J$ = 7.5 Hz, 2 H), 6.04 (broadened s, 1 H). Anal. Calcd for $C_9H_{18}O_2S$: C, 56.80; H, 9.53; S, 16.85. Found: C, 57.04; H, 9.57; S, 16.71.

**(*E*)-1-(Ethanesulfonyl)-2-methyl-1-hexene (14b)** had a GLC retention time of 29.0 min on column A at 190 °C and 45 mL/min and was collected for microanalysis from column B under similar conditions: IR (neat) 2990, 2960 (s, CH), 2900 (m, CH), 1641 (s, C=C), 1312, 1284, 1135 (s, $SO_2$), 800 (m, $R_2C$=CHR), 3075, 1464, 1427, 1393, 1241, 1179, 1055, 986, 938, 878, 717 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 0.92 (distorted t, 3 H), 1.30 (t, $J$ = 7.0 Hz, 3 H), 1.1–1.85 (m, 4 H), 2.14 (d, $J \approx$ 1.5 Hz, 3 H), 2.20 (broadened t, 2 H), 2.99 (q, $J \approx$ 7.0 Hz, 2 H), 6.04 (m, 1 H). Anal. Calcd for $C_9H_{18}O_2S$: C, 56.80; H, 9.53; S, 16.85. Found: C, 56.72; H, 9.35; S, 16.63.

**(*Z*)-β-(Ethanesulfonyl)-α-methylstyrene (15a)** was collected for microanalysis from column C, retention time 9.7 min at 195 °C and 60 mL/min: IR (neat) 1636, 852 or 797 (m, $R_2C$=CHR), 1310, 1283, 1140 (s, $SO_2$), 770, 702 (s, $C_6H_5$), 3015, 2975, 2910, 1610, 1585, 1505, 1464, 1445, 1423, 1385, 1345, 1240, 1199, 1085, 1050, 1035, 981, 925, 736 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.20 (t, $J$ = 7.5 Hz, 3 H), 2.24 (d, $J$ = 1.45 Hz, 3 H), 2.67 (q, $J$ = 7.5 Hz, 2 H), 6.33 (q, $J$ = 1.45 Hz, 1 H), 7.37 (s, 5 H). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71; S, 15.24. Found: C, 63.05; H, 6.53; S, 15.03.

**(*E*)-β-(Ethanesulfonyl)-α-methylstyrene (15b)** was collected for microanalysis from column C, retention time 14.6 min at 195 °C and 60 mL/min: IR (neat) 1620 (m, C=C), 1310, 1283, 1135 (s, $SO_2$), 830 or 812 (s, $R_2C$=CHR), 760, 697 (s, $C_6H_5$), 3085, 3010, 2970, 2905, 1582, 1506, 1453, 1420, 1390, 1240, 1197, 1080, 1050, 1005, 983, 924, 620 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.40 (t, $J$ = 7.5 Hz, 3 H), 2.56 (d, $J \approx$ 1.25 Hz, 3 H), 3.09 (q, $J$ = 7.5 Hz, 2 H), 6.44 (q, $J \approx$ 1.25 Hz, 1 H), 7.42 (s, 5 H). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71; S, 15.24. Found: C, 62.67; H, 6.91; S, 15.07.

**(*E*)-1-(Ethanesulfonyl)propene (16)** was collected for microanalysis from column B, retention time 8.4 min at 185 °C and 30 mL/min: IR (neat) 3075, 3010, 2975, 2910 (w, CH), 1659, 964 (m, *trans*-RCH=CHR), 1320, 1300, or 1287, and 1137 (s, $SO_2$), 1452, 1426, 1390, 1247, 1056, 822, 789, 754, 711 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.32 (t, $J$ = 7.5 Hz, 3 H), 1.97 (dd, $J$ = 1.2, 6.5 Hz, 3 H), 2.98 (q, $J$ = 7.5 Hz, 2 H), 6.29 (doublet, $J$ = 15.1 Hz, of quartets, $J$ = 1.2 Hz, 1 H), 6.94 (doublet, $J$ = 15.1 Hz, of quartets, $J$ = 6.5 Hz, 1 H). Anal. Calcd for $C_5H_{10}O_2S$: C, 44.75; H, 7.51; S, 23.89. Found: C, 44.98; H, 7.54; S, 23.80.

**1-(Ethanesulfonyl)-2-(*n*-butyl)-1-hexene (17)** was collected

for microanalysis from column B, retention time 25.6 min at 185 °C and 120 mL/min, and retention time 34.2 min on column A at 192 °C and 45 mL/min, reduced to 17.5 min at 120 mL/min: IR (neat) 2985, 2960, 2900 (s, CH), 1633, 821 (m, $R_2C$=CHR), 1313, 1283, 1138 (s, $SO_2$), 1425, 1390, 1290, 1056, 985, 939, 880, 790, 717 $cm^{-1}$; NMR ($CDCl_3$) δ 0.93 (distorted t, 6 H), 1.36 (t, $J$ = 7.5 Hz, 3 H), 1.15–2.0 (m, 8 H), 2.22 (broadened t, 2 H), 2.61 (broadened t, 2 H), 3.00 (q, $J$ = 7.5 Hz, 2 H), 5.97 (s, 1 H). Anal. Calcd for $C_{12}H_{24}O_2S$: C, 62.02; H, 10.41; S, 13.80. Found: C, 62.20; H, 10.22; S, 14.00.

**(*Z*)-1-(Ethanesulfonyl)-2-phenyl-1-hexene (18a)** was collected for microanalysis from column C, retention time 8.9 min at 225 °C and 60 mL/min: IR (neat) 2980, 2960 (s, CH), 2895 (m, CH), 1630, 840 (m, $R_2C$=CHR), 1310, 1281, 1128 (s, $SO_2$), 780, 700 (s, $C_6H_5$), 3080, 3060, 1609, 1582, 1502, 1462, 1451, 1422, 1390, 1240, 1192, 1082, 1051, 1031, 1008, 980, 940, 730 $cm^{-1}$; NMR ($CDCl_3$) δ 0.88 (distorted t, 3 H), 1.20 (t, $J$ = 7.5 Hz, 3 H), 1.15–1.7 (m, 4 H), 2.50 (broadened t, 2 H), 2.63 (q, $J$ = 7.5 Hz, 2 H), 6.30 (t, $J \approx$ 1.25 Hz, 1 H), 7.35 (s, 5 H). Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; S, 12.70. Found: C, 66.50; H, 8.11; S, 12.45.

**(*E*)-1-(Ethanesulfonyl)-2-phenyl-1-hexene (18b)** was collected for microanalysis from column C, retention time 9.5 min at 225 °C and 60 mL/min: IR (neat) 2990, 2960 (s, CH), 2900 (m, CH), 1617, 830 (s, $R_2C$=CHR), 1315, 1285, 1140 (s, $SO_2$), 770 or 755, 700 (s, $C_6H_5$), 3090, 3060, 1583, 1507, 1466, 1455, 1423, 1392, 1242, 1089, 1056, 1020, 987, 930, 880, 620 $cm^{-1}$; NMR ($CDCl_3$) δ 0.87 (distorted t, 3 H), 1.42 (t, $J$ = 7.5 Hz, 3 H), 1.1–1.7 (m, 4 H), 3.07 (m, 2 H), 3.08 (q, $J$ = 7.5 Hz, 2 H), 6.30 (s, 1 H), 7.38 (s, 5 H). Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; S, 12.70. Found: C, 66.87; H, 8.05; S, 12.45.

**(*E*)-1-(Ethanesulfonyl)-1-hexene (19)** was collected for microanalysis from column B, retention time 21.6 min at 190 °C and 30 mL/min: IR (neat) 2990, 2965, 2900 (s, CH), 1647, 989 (m, *trans*-RCH=CHR), 1324, 1289, 1141 (s, $SO_2$), 3080, 1479, 1429, 1395, 1244, 1058, 935, 889, 835, 732 $cm^{-1}$; NMR ($CDCl_3$) δ 0.92 (distorted t, 3 H), 1.32 (t, $J$ = 7.5 Hz, 3 H), 1.1–1.8 (m, 4 H), 2.31 (m, 2 H), 2.98 (q, $J$ = 7.5 Hz, 2 H), 6.27 (doublet, $J$ = 15.1 Hz, of triplets, $J$ = 1.1 Hz, 1 H), 6.92 (doublet, $J$ = 15.1 Hz, of triplets, $J$ = 6.0 Hz, 1 H). Anal. Calcd for $C_8H_{16}O_2S$: C, 54.51; H, 9.15; S, 18.19. Found: C, 54.37; H, 9.33; S, 18.30.

**Alternate Synthesis of (*E*)-1-(Ethanesulfonyl)-2-methyl-1-hexene (14b).** Diisopropyl sulfide (3.6 mL, 0.5 mL/mmol of CuI)[24] was injected into an ice-cold suspension of 1.368 g (7.18 mmol) of cuprous iodide in 20.5 mL of THF. After cooling to −10 °C, 4.0 mL (7.04 mmol) of 1.76 M *n*-butyllithium in *n*-hexane were injected over a 2 min period, followed by immediate cooling to −78 °C. Into this solution of *n*-butylcopper bis(diisopropyl sulfide) (2.5 equiv) was injected a solution (precooled to −78 °C) of 0.733 g (2.82 mmol, 1.0 equiv) of (*E*)-2-iodo-1-(ethanesulfonyl)propene (**20**)[25] in 11.3 mL of THF. After 5 h at −78 °C, 5 mL of anhydrous methanol was injected and the resulting reaction mixture was then poured into 25 mL of saturated ammonium chloride solution. Extraction with dichloromethane (3 × 25 mL), drying, and evaporation gave 2.092 g of light yellow *solid*, whose NMR showed the desired product and also an extremely large isopropyl absorption, possibly due to some kind of copper–diisopropyl sulfide complex. Bubbling air through a pentane solution of this material resulted in the precipitation of a fine yellow solid, which was filtered off. Evaporation of the pentane filtrate then gave 0.471 g (88%) of crude 1-(ethanesulfonyl)-2-methyl-1-hexene. GLC analysis on column A at 190 °C and 45 mL/min indicated that this was 93% pure and was predominantly the desired (*E*) isomer ((*E*):(*Z*) = 97.5:2.5), with NMR, IR, and GLC retention time identical to the sulfone, **14b**, obtained by oxidation of the product of the addition of *n*-butylcopper to 1-(ethanesulfinyl)propyne.

**Reaction of Lithium Di-*n*-butylcuprate with (*E*)-2-Iodo-1-(ethanesulfonyl)propene (20).** A solution of 0.687 g (2.64 mmol) of **20** in 10.5 mL of THF, precooled to −78 °C, was added rapidly to a solution of 5.0 equiv of lithium di-*n*-butylcuprate at −78 °C, prepared from 2.563 g (13.46 mmol) of cuprous iodide in 38 mL of THF and 15.0 mL (26.40 mmol) of 1.76 M *n*-butyllithium in *n*-hexane. After 0.5 h at −78 °C a 5-mL aliquot was withdrawn in a precooled syringe and injected into 1 mL of anhydrous methanol at −78 °C. Pouring into 5 mL of saturated $NH_4Cl$, extraction with dichloromethane (3 × 5 mL), drying, and evaporation in vacuo gave a yellow liquid. GLC analysis on column A at 190 °C and 45 mL/min showed that 69.7% of this material was a mixture of 1-(ethanesulfonyl)-2-methyl-1-hexenes, **14a:14b** = 19.5:80.5. In addition, 22.4% of this crude product was made up of two materials with retention times of 8.05 and 9.9 min, in a ratio of 72.5:27.5. These are probably the cis and trans isomers, respectively, of 1-(ethanesulfonyl)propene, arising from a vinyl copper species formed by copper–halogen exchange between the organocuprate and the iodovinyl sulfone.

The remainder of the reaction mixture was treated after 5.5 h with 3.2 mL (4.86 g, 26.40 mmol) of 1-iodobutane (precooled to −78 °C) and then stirred at 0 °C for 4 h. Working up in the same manner as before gave a yellow liquid. GLC analysis showed a similar **14a:14b** ratio of 28:72, but the amount of by-product at 7.8 and 9.5 min was much smaller.

**Alternate Synthesis of (*Z*)-1-(Ethanesulfonyl)-2-methyl-1-hexene (14a).** A solution of 0.598 g (1.98 mmol) of (*E*)-2-iodo-1-(ethanesulfonyl)-1-hexene (**21**)[12] in 7.9 mL of THF (precooled to −78 °C) was added to 2.5 equiv of methylcopper bis(diisopropyl sulfide) at −78 °C, prepared in the same manner as the *n*-butylcopper complex from 1.038 g (5.45 mmol) of cuprous iodide and 2.725 mL of diisopropyl sulfide in 14.1 mL of THF and 3.0 mL (4.95 mmol) of 1.65 M methyllithium in diethyl ether. After stirring for 5 h at −78 °C, 5 mL of anhydrous methanol (precooled to −78 °C) was injected, and the reaction mixture then poured into 40 mL of saturated ammonium chloride. Extraction with dichloromethane (3 × 25 mL), drying, and evaporation in vacuo gave 1.51 g of white *solid*. Bubbling air through a pentane solution of this material, followed by filtration and evaporation of the filtrate in vacuo, gave 0.446 g of a pink liquid. GLC analysis of this material on column B at 190 °C and 45 mL/min showed that there was still starting iodovinyl sulfone **21** present. To the extent that 1-(ethanesulfonyl)-2-methyl-1-hexene was formed, however, the (*Z*) isomer was formed stereospecifically (**14a:14b** = 94.5:5.5). In addition, there was a pair of by-product peaks at 9.9 and 12.3 min, in a ratio of 2:98 (**14:21:22** = 50.2:33.4:16.4). The NMR also showed the desired (*Z*) isomer, **14a**, and the iodovinyl sulfone, **21**, and showed further vinyl absorption in the δ 6.2–6.5 region due to the by-product, **22**.

**Reaction of Methylcopper with (*E*)-2-Iodo-1-(ethanesulfonyl)-1-hexene (21).** A solution of 0.598 g (1.98 mmol) of **21** in 7.9 mL of THF (precooled to −78 °C) was added to 2.5 equiv of methylcopper at −78 °C prepared from 0.962 g (5.05 mmol) of cuprous iodide in 16.8 mL of THF and 3.0 mL (4.95 mmol) of 1.65 M methyllithium in diethyl ether. After stirring for 8 h at −78 °C, a 13.0-mL aliquot was withdrawn in a precooled syringe and injected into 5 mL of anhydrous methanol at −78 °C. Pouring into 40 mL of saturated ammonium chloride, extraction with dichloromethane (3 × 15 mL), drying, and evaporation in vacuo gave 0.203 g of material. GLC analysis on column B showed that essentially all of the iodovinyl sulfone had been consumed but that substantial amounts of by-product were still present (**14:21:22** = 71.9:4.9:23.2), although the formation of 1-(ethanesulfonyl)-2-methyl-1-hexene was still stereospecific (**14a:14b** = 96.3:3.7).

To the remainder of the reaction mixture was added a solution of 1.54 mL (3.515 g, 24.7 mmol) of methyl iodide in 5 mL of THF (precooled to −78 °C). After stirring for an additional 2 h, injection of 5 mL of precooled anhydrous methanol and work-up exactly as before gave 0.190 g of liquid. GLC analysis showed there was only a moderate decrease in the amount of by-product, with little change otherwise.

**Addition of Lithium Dimethylcuprate to 1-(Ethanesulfinyl)-propyne (2a).** A solution of 0.413 g (3.56 mmol) of **2a** in 14.2 mL of THF (precooled to −78 °C) was added to a solution of 1.25 equiv of lithium dimethylcuprate, prepared from 0.865 g (4.54 mmol) of cuprous iodide in 12.8 mL of THF and 5.0 mL (8.9 mmol) of 1.78 M methyllithium in diethyl ether. After stirring at −78 °C for 2 h, 5 mL of anhydrous methanol (precooled to −78 °C) was injected. Pouring into 25 mL of saturated ammonium chloride, extraction with dichloromethane (3 × 25 mL), drying, and evaporation in vacuo gave 0.393 g (83%) of essentially pure 1-(ethanesulfinyl)-2-methylpropene (**4**).

**Addition of Lithium Dimethylcuprate to 1-(Ethanesulfinyl)-1-hexyne (2b).** Lithium dimethylcuprate, prepared from 0.727 g (3.82 mmol) of cuprous iodide in 11.8 mL of THF and 4.2 mL (7.48 mmol) of 1.78 M methyllithium in diethyl ether, was reacted with 0.473 g (2.99 mmol) of **2b** in 12.0 mL of THF at −78 °C for 1.5 h. Quenching and workup exactly as in the previous reaction gave 0.507 g (97%) of essentially pure (*Z*)-1-(ethanesulfinyl)-2-methyl-1-hexene (**5a**). Oxidation of 0.253 g (1.45 mmol) of this material in 8.5 mL of chloroform with 0.310 g (0.263 g peracid, 1.53 mmol, 5% excess) of 85% *m*-chloroperbenzoic acid at 0 °C for 24 h gave, after workup, 0.284 g (103%) of sulfone. GLC analysis on column A showed that the 1-(ethanesulfonyl)-2-methyl-1-hexene formed was >95.6% (*Z*) isomer **14a**.

**Reaction of Lithium Di-*n*-butylcuprate with 1-(Ethanesulfinyl)propyne (2a).** Lithium di-*n*-butylcuprate, prepared from 0.751 g (3.94 mmol) of cuprous iodide in 11.1 mL of THF and 4.4 mL (7.74 mmol) of 1.76 M *n*-butyllithium in *n*-hexane, was reacted with 0.360 g (3.1 mmol) of **2a** in 12.4 mL of THF at −78 °C for 2 h. Addition of 5 mL of precooled anhydrous methanol and then pouring into 25 mL

of saturated ammonium chloride, followed by extraction with dichloromethane (3 × 25 mL), drying, and evaporation in vacuo, gave 0.516 g of yellow liquid. The NMR and IR spectra of this material were slightly different from those of the expected **5b**, the NMR possibly indicating the presence of another compound. Oxidation of this 0.516 g of material in 5.0 mL of chloroform with 0.601 g (0.511 g of peracid, 2.96 mmol) of 85% *m*-chloroperbenzoic acid in 12.0 mL of chloroform at 0 °C for 12 h and then at room temperature for 12 h gave, after workup, 0.557 g of yellow liquid. Again the IR and NMR were similar but not identical to those of the expected **14b**.

GLC analysis of this oxidation product, on column A at 190 °C and 45 mL/min, while showing the expected 1-(ethanesulfonyl)-2-methyl-1-hexenes (**14a:14b** = 3.2:96.8, at 20.9 and 29.1 min, respectively), also showed a second component at 12.1 min. A sample of this by-product, mp 47–48.5 °C, was isolated by collection from column A and was identified as ethyl *n*-butyl sulfone (lit.[26] mp 50–50.5 °C) by comparison of its IR, NMR, and mass spectra with those of an authentic sample.[27] The GLC area ratio of 1-(ethanesulfonyl)-2-methyl-1-hexenes to ethyl *n*-butyl sulfone was 81:19. The isolation of this sulfone by-product indicated that ethyl *n*-butyl sulfoxide (**23**) was being formed as a by-product in the di-*n*-butylcuprate addition reaction.

**Reaction of Lithium Di-*n*-butylcuprate with 1-(Ethanesulfinyl)-1-hexyne (2b).** Lithium di-*n*-butylcuprate, generated from 0.753 g (3.95 mmol) of cuprous iodide in 11.1 mL of THF and 4.4 mL (7.74 mmol) of 1.76 M *n*-butyllithium in *n*-hexane, was reacted with 0.491 g (3.1 mmol) of **2b** in 12.4 mL of THF at −78 °C for 1.0 h. Quenching and workup as in the previous experiment gave 0.615 g of liquid. Oxidation of 0.410 g of this material (⅔ of the total 0.615-g yield, theoretically 2.07 mmol of sulfoxide) with 0.442 g (0.376 g of peracid, 2.17 mmol, 5% excess) of 85% *m*-chloroperbenzoic acid in 13 mL of chloroform at 0 °C for 24 h gave, after workup, 0.460 g of liquid. GLC analysis on column as before showed this to be a mixture of 1-(ethanesulfonyl)-2-(*n*-butyl)-1-hexene (at 36.0 min) and ethyl *n*-butyl sulfone (at 10.3 min) in a ratio of 83:17.

**Reaction of 1-(Ethanesulfinyl)propyne (2a) with *n*-Butyllithium.** A solution of 0.409 g (3.52 mmol) of **2a** in 14.1 mL of THF was reacted with a solution of 2.0 mL (3.52 mmol) of 1.76 M *n*-butyllithium in *n*-hexane, dissolved in 12.1 mL of THF, at −78 °C for 2 h. Injection of 5 mL of precooled anhydrous methanol followed by workup gave 0.471 g of yellow liquid. The IR and NMR of this material indicated that it was predominantly ethyl *n*-butyl sulfoxide (**23**), with small amounts of ethanesulfinylpropadiene (**24**),[22a] and virtually no addition product **5b**. The propadiene **24** was indicated in the IR by a small, sharp peak at 1952 $cm^{-1}$ (C=C=C) and in the NMR by an apparent triplet ($J \approx 6.5$ Hz) at $\delta$ 6.15 (-**CH**=C=$CH_2$) and a doublet ($J$ = 6.5 Hz) at $\delta$ 5.30 (CH=C=**$CH_2$**). Oxidation of 0.235 g of this material (½ of the total 0.471-g yield, theoretically 1.76 mmol of sulfoxide) with 0.376 g (0.320 g of peracid, 1.85 mmol, 5% excess) of 85% *m*-chloroperbenzoic acid in 11 mL of chloroform at 0 °C for 24 h gave, after workup, 0.270 g of yellow liquid. The IR and NMR similarly showed that this was predominantly ethyl *n*-butyl sulfone, with a small amount of ethanesulfonylpropadiene[22a] (IR 1980 $cm^{-1}$ (C=C=C); NMR $\delta$ 6.22 (dd, -**CH**=C=$CH_2$), 5.52 (d, $J$ = 6.5 Hz, -CH=C=**$CH_2$**)). GLC analysis on column A showed ethyl *n*-butyl sulfone at 10.2 min.

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