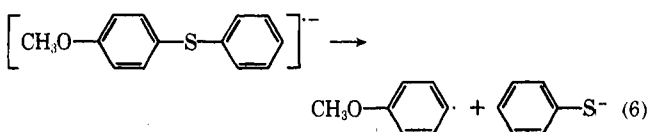


ortho methyl groups does not appear to affect combination of an aryl radical with the amide ion^{2b} or with picolyl anions.^{3b} Formation of *m*-xylene from its 2-iodo derivative represents reduction; the concomitant product of oxidation is diphenyl disulfide.

A companion experiment to run 5, Table I, was reaction of iodobenzene with *p*-methoxybenzenethiolate ion (120 min) to form phenyl *p*-methoxyphenyl sulfide in 71% yield. It is significant that no trace of bis(*p*-methoxyphenyl) sulfide was found as a product. Alkali metal cleavage of phenyl *p*-methoxyphenyl sulfide in ammonia or methylamine affords thiophenol and anisole,⁷ indicating that its radical anion undergoes fission as shown in eq 6.^{2e} If *p*-methoxyphenyl radical were formed in the presence of *p*-methoxybenzenethiolate ion, some bis(*p*-methoxyphenyl) sulfide should be formed. We conclude that in this system the phenyl *p*-methoxyphenyl sulfide radical anion transfers an electron to iodobenzene (eq 4) faster than it splits as in eq 6.



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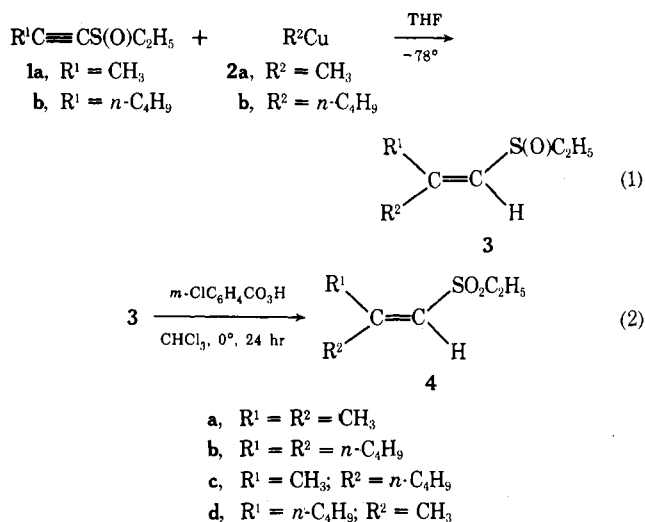
The Addition of Organocopper(I) Reagents to α,β -Acetylenic Sulfoxides^{1,2}

Summary: Monoalkylcopper(I) reagents (2) add to α,β -acetylenic sulfoxides (1) with almost exclusive *cis* stereoselectivity to form β -alkylated α,β -ethylenic sulfoxides (3) in high yield.

Sir: Organocopper(I) reagents add to a variety of α,β -unsaturated compounds,³ including α,β -ethylenic sulfones⁴ and α,β -acetylenic esters⁵ and acids.^{5c,6} Our continuing interest in nucleophilic additions to activated acetylenes,⁷ and in the ability of organosulfur functionalities to activate the triple bond toward conjugate addition, prompted an investigation of the reaction of organocopper(I) reagents with α,β -acetylenic sulfur compounds.

We have found that α,β -acetylenic sulfoxides (1)⁸ react readily with monoalkylcopper(I) reagents (2) to produce,

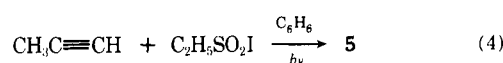
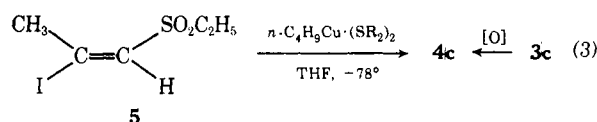
after work-up, high yields of the corresponding β -alkylated α,β -ethylenic sulfoxides (3). Furthermore, the addition reaction was shown to be highly stereoselective, producing the product of *cis* addition to the triple bond almost exclusively.



The following procedures are representative. Into a 50-ml flask, equipped with a stopple-covered, side arm, an adapter tube with stopcock connected to a mercury bubbler, and a magnetic stirring bar, is weighed 0.727 g (3.82 mmol, 2% in excess of the alkyllithium reagent to be used) of cuprous iodide. After oven drying, the flask is cooled while flushing with nitrogen, 12.9 ml of dry THF is injected, and to the resulting suspension at 0° is added 2.1 ml (3.74 mmol) of a 1.78 M solution of methyl lithium in diethyl ether over a 2-min period. The resulting suspension of methylcopper(I) (25% excess) is cooled to -78° for 15 min and a solution of 0.473 g (2.99 mmol) of ethyl 1-hexynyl sulfoxide (1b) in 12.0 ml (~0.25 M) of dry THF, pre-cooled to -78°, is injected rapidly. After stirring for 1.5 hr at -78° the reaction mixture is quenched by injecting 5 ml of methanol pre-cooled to -78° and then pouring into 25 ml of saturated aqueous ammonium chloride solution. Extraction with dichloromethane (3 × 25 ml), drying over MgSO₄, and evaporation *in vacuo* gives 0.549 g (>100%) of 3d. In a similar manner the reaction of 3.87 mmol (25% excess) of *n*-butylcopper(I) in THF (~0.25 M) with 0.360 g (3.1 mmol) of ethyl 1-propynyl sulfoxide (1a) in 12.4 ml of dry THF for 2 hr at -78° followed by quenching with pre-cooled methanol and work-up gives 0.531 g (98%) of the other geometrical isomer, 3c.

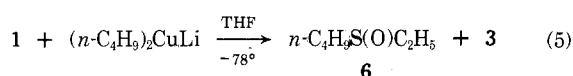
It was also shown that the α,β -ethylenic sulfoxides 3 can be oxidized almost quantitatively to the corresponding sulfones 4 (with no evidence of isomerization about the double bond) by treatment with 1 equiv of *m*-chloroperbenzoic acid in chloroform at 0° for 24 hr.¹⁰

The *cis* stereoselectivity of the organocopper(I) addition to α,β -acetylenic sulfoxides was established unambiguously¹¹ by an alternate stereospecific synthesis of sulfone 4c. The reaction of the iodovinyl sulfone 5 with 2.5 equiv of *n*-butylcopper-bis(diisopropyl sulfide) complex^{12,13} in dry



THF at -78° for 5 hr gives an 88% yield of **4c** with 97.5% stereospecificity. Compound **5** is in turn obtained *via* the known stereoselective addition of a sulfonyl iodide to an acetylene,¹⁴ in 56% isolated yield.

It is interesting to note that, while monoalkylcopper(I) reagents add cleanly to α,β -acetylenic sulfoxides, lithium dialkylcuprates may also give a product resulting from the cleavage of the acetylenic sulfoxide. While lithium dimethylcuprate adds normally to **1a** (83%) and **1b** (97.5%, >96% *cis* addition); the more reactive lithium di-*n*-butylcuprate reacts to give appreciable quantities of *n*-butyl ethyl sulfide (**6**) as well, apparently arising from attack by the organocopper(I) reagent at sulfur rather than on the triple bond.



Like results have been observed for additions of organocopper(I) reagents to α,β -acetylenic sulfones,⁸ ethyl 1-propynyl sulfone giving an 81% yield of adduct with lithium di-*n*-butylcuprate and a 90% yield with *n*-butylcopper. However, here a difference between the two types of organocopper(I) reagents is manifest in the stereochemistry of the product, *n*-butylcopper giving 92% *cis* addition while di-*n*-butylcuprate gives, on work-up, 81% of the product, which would correspond to overall *trans* addition.¹⁵

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- Glpc analysis of the product of **1a** and **2b**, after oxidation to the sulfone, on an Aerograph Autoprep A-700 chromatograph using an 8 ft \times 0.25 in. 15% neopentyl glycol isophthalate on 60–80 mesh Chromosorb W column at 190° and 45 ml/min shows 98.8% *cis* addition. Similarly, **1b** and **2a** give >96% *cis* addition. The direct glpc analysis of the sulfoxide products from these reactions, however, proves to be difficult owing to thermal decomposition at the temperatures necessary to elute them from even nonpolar (SE-30, SF-96) columns.
- The stereochemistry of the sulfoxide products and their corresponding sulfones is also indicated by their ^1H nmr spectra [in CDCl_3 , parts per million (δ) downfield from tetramethylsilane]. The allylic methyl group in **3c** appears further downfield (1.97; sulfone **4c**, 2.14) than in **3d** (1.92; sulfone **4d**, 1.95) and the allylic methylene group in **3c** appears further upfield (2.20; sulfone **4c** 2.22) than in **3d** (2.42; sulfone **4d**, 2.61).
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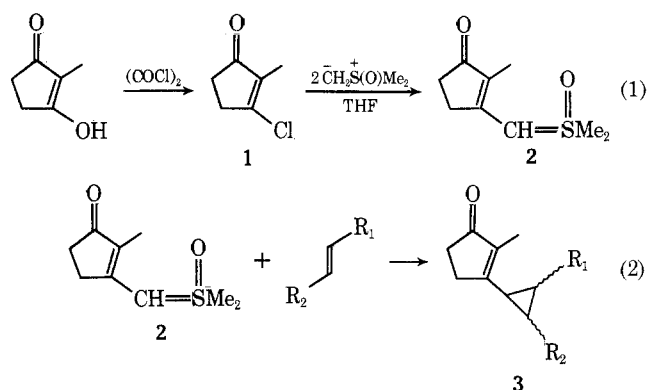
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A New and Efficient Approach to Functionalized Hydroazulenes *via* 2-Methylcyclopentenone 3-Dimethylsulfoxonium Methylide¹

Summary: A three-step sequence for the construction of functionalized hydroazulenes **5** is described starting from the novel cyclopentenone ylide **2**. The preparation of **2**, its reactions with Michael acceptors to produce vinyl cyclopropanes such as **3**, and the use of the divinylcyclopropane rearrangement to generate the bicyclo[5.3.0]decadienone system are described.

Sir: Recently, many sesquiterpenes possessing a hydroazulene skeleton have been isolated,² some of which have exhibited significant medicinal properties.³ Despite the many efforts in the area of hydroazulene synthesis,⁴ there are a very limited number of approaches which could accommodate a multitude of sensitive oxygen functionality. Our interest in sesquiterpene lactones possessing the guaiane and pseudoguaiane skeletons has resulted in the development of the synthetic scheme described in this communication. We have recently reported on the reactions and synthetic applications of carbonyl stabilized allyl sulfoxonium ylides.⁵ In this communication we wish to report on the preparation of 2-methylcyclopentenone 3-dimethylsulfoxonium methylide (**2**), its reactions with several Michael acceptors, and its utility in the synthesis of functionalized hydroazulenes.

Sulfoxonium ylide **2** was prepared in at least 50% overall yield from the commercially available 2-methyl-1,3-cyclopentanedione. The 1,3-dione was treated with excess oxalyl chloride to produce the 3-chloro-2-methyl-2-cyclopentenone (**1**).⁶ Treatment of the vinyl chloride **1** with 2 equiv of dimethylsulfoxonium methylide in tetrahydrofuran resulted in the formation of the crystalline ylide **2** (mp $170\text{--}173^\circ$).^{7,8}



This new allyl ylide reacted cleanly with Michael acceptors such as acrolein, crotonaldehyde, and methyl vinyl ketone to produce vinyl cyclopropanes **3a–c** (see Table I).^{5a}

Table I

	R ₁	R ₂	React temp, $^\circ\text{C}$	React time, hr	Yield, %
3a	CHO	H	R.T.	3	70
3b	CHO	CH ₃	56	8	50
3c	COCH ₃	H	56	4	75

Usually the reaction was carried out using 1.5 to 2.0 equiv of the Michael acceptor in acetonitrile. Cyclopropanes **3a–c** were isolated in a very pure state by evaporation of the acetonitrile and washing the ethyl acetate solution of the residue with water. Cyclopropane **3a** consisted of a 7:1 mixture