Reaction of α,β-Ethylenic Sulfur Compounds with Organocopper Reagents

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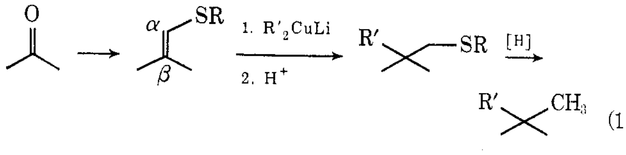
Received February 26, 1973

The results of lithium dimethyl- and di-*n*-butylcuprate(I) reactions with alkenyl sulfides **1–3** and the corresponding sulfonium salts, with 2-alkylidene-1,3-dithianes **5–7** and the corresponding bis sulfonium salts, and with alkenyl sulfones **11–24** are reported. In the series styryl methyl sulfide (**3**), styryl methyl sulfone (**12**), and styryl *p*-chlorophenylsulfone (**17**) there is an increasing amount of organocopper addition to the olefinic carbon β to sulfur. 2-Alkylidene-1,3-dithianes **5–7**, in contrast to 2-methylene-1,3-dithiane, are inert to organolithium and organocopper reagents. Alkenyl *p*-chlorophenyl sulfones undergo organocopper addition β to sulfur, and the resulting alkyl aryl sulfones can be selectively hydrogenolyzed at the alkyl–sulfur bond using 6% sodium amalgam in ethanol to form alkanes in high yields; this sequence allows effective conversion of aldehyde carbonyls to tertiary alkyl carbon atoms in which each of the three alkyl groups may be different and permits transformation of certain ketone carbonyl groups to quaternary carbon atoms.

Organocopper reagents undergo addition to the β carbon of a variety of α,β-unsaturated compounds, such as α,β-ethylenic and acetylenic ketones and esters,[2] α,β-ethylenic epoxides,[3] allylic[4] and propargylic[5] acetates, and acetylenic and allenic phosphine oxides and sulfides.[6] Several of these addition reactions have been used as one of the key steps in syntheses of such natural products of nootkatone,[7] fulvoplumierin,[8] juvenile hormone,[9] and various prostaglandins.[10] The recent development of effective methods for converting carbonyl compounds to α,β-ethylenic sulfides,[11] 2-alkylidene-1,3-dithianes (ketene thioacetals),[12] and α,β-ethylenic sulfones[13] has made these readily available substrates for study with organocopper reagents. Determining which type of α,β-unsaturated sulfur compound undergoes most effective organocopper β addition to form a sulfur-stabilized carbanion would be of general interest, and would specifically permit conversion of an aldehyde or ketone carbonyl group to a tertiary or quaternary carbon atom (eq 1, sequence illustrated with vinyl *sulfides*).[14] Such a transformation would increase significantly the versatility of carbonyl groups in organic synthesis.



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We report herein the results of organocopper interaction with alkenyl sulfides and sulfonium salts, with 2-alkylidene 1,3-dithianes and the corresponding bis sulfonium salts, and with various alkenyl sulfones.

Results and Discussion

Alkenyl Methyl Sulfides.—Alkenyl methyl sulfides **1–3** were prepared in high yields from the corresponding carbonyl compounds and lithium diethyl methylthiomethylphosphonate.[11] It was already known that alkenyl sulfide **4** undergoes reaction with lithium dimethylcuprate(I) to place a methyl group specifically on the carbon β to the carbonyl group and not β to the sulfur atom.[15] The inability of sulfide sulfur to activate a double bond toward organocopper β addition was established when sulfides **2** and **3** were recovered in high yield even after prolonged exposure to lithium dimethylcuprate(I). Although cyclohexylidene sulfide **2** is inert also to lithium di-*n*-butylcuprate(I),[16] styryl sulfide **3** undergoes replacement of the methythio group by the *n*-butyl group to form 1-phenyl-1-hexene in 90% yield.[17] This substitution of the methylthio by the *n*-butyl group most likely occurs *via* an addition–elimination mechanism; the higher reactivity of styryl sulfide **3** compared to cyclohexylidene sulfide **2**, therefore, is probably due to the relative stability of the benzylic species generated by organocopper addition to the carbon atom β to the phenyl group.

$n\text{-}C_6H_{13}CH{=}CHSCH_3$

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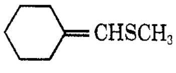

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$C_6H_5CH{=}CHSCH_3$

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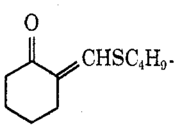

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An attempt was made to increase the electrophilicity of these alkenyl sulfides by converting them to the corresponding *S*-methyl sulfonium salts.[18] Treating alkenyl sulfide **1**, for example, with methyl fluoro-

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[1] NSF Trainee, 1970–present.

[2] G. H. Posner, *Org. React.*, **19**, 1 (1972).

[3] (a) J. Staroscik and B. Rickborn, *J. Amer. Chem. Soc.*, **93**, 3046 (1971); (b) D. M. Wieland and C. R. Johnson, *ibid.*, **93**, 3047 (1971).

[4] R. J. Anderson, C. A. Henrick, and J. B. Siddall, *J. Amer. Chem. Soc.*, **92**, 735 (1970).

[5] P. Rona and P. Crabbé, *J. Amer. Chem. Soc.*, **91**, 3289 (1969).

[6] (a) A. M. Aguiar and J. S. R. Irelan, *J. Org. Chem.*, **34**, 4030 (1969); (b) J. Berlan, M. Capman, and W. Chodkiewicz, *C. R. Acad. Sci.*, **273**, 295 (1971).

[7] M. Pesaro, G. Bozzato, and P. Schudel, *Chem. Commun.*, 1152 (1968).

[8] G. Buchi and J. A. Carlson, *J. Amer. Chem. Soc.*, **91**, 6470 (1969).

[9] E. J. Corey, J. A. Katzenellenbogen, S. A. Roman, and N. W. Gilman, *Tetrahedron Lett.*, 1821 (1971).

[10] (a) A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Amer. Chem. Soc.*, **94**, 925 (1972); (b) E. J. Corey and D. J. Beames, *ibid.*, **94**, 7210 (1972), and references cited therein.

[11] E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970).

[12] (a) F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 1926 (1972). (b) P. F. Jones and M. F. Lappert, *Chem. Commun.*, 526 (1972).

[13] G. H. Posner and D. J. Brunelle, *J. Org. Chem.*, **37**, 3547 (1972).

[14] (a) For preliminary communications, see G. H. Posner and D. J. Brunelle, *Tetrahedron Lett.*, 293 (1972), and G. H. Posner and D. J. Brunelle, *ibid.*, 935 (1973). (b) For two recent related studies of geminal dialkylation of carbonyls, see B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 2038 (1973), and E. J. Corey and J. I. Shulman, *ibid.*, **92**, 5522 (1970).

[15] R. M. Coates and R. L. Sowerby, *J. Amer. Chem. Soc.*, **93**, 1027 (1971).

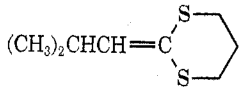
[16] Lithium di-*n*-alkylcuprates are more reactive than dimethylcuprate; see ref 2.

[17] The yield is based on 40% recovered starting material.

[18] For examples of vinyl sulfonium salts, see (a) J. Gosselck, L. Beress, H. Schenk, and G. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **4**, 1080 (1965); (b) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961).

sulfonate ("magic methyl") produced dimethyl 1-octenylsulfonium fluorosulfonate as an oil showing an nmr singlet at δ 3.10 for the *S*-methyl groups. Reaction with lithium dimethylcuprate(I), however, did not produce an ylide *via* β addition of an anionic methyl group but rather gave parent alkenyl sulfide **1** in 97% yield upon aqueous work-up. Expecting that two sulfur atoms would stabilize an adjacent carbanion better than one sulfur atom, we directed attention next to olefins in which two sulfide sulfur atoms are attached to the same carbon atom of the double bond.

2-Alkylidene-1,3-dithianes.—2-Methylene-1,3-dithiane has been reported to undergo addition of organolithium compounds to give 2-substituted 2-lithio-1,3-dithianes,[19] and much speculation has appeared on the potential utility of this reaction as a general method for extension of the carbon chain in alkyllithium reagents.[12,20,21] We have prepared 2-alkylidenedithianes **5**–**7** in high yields from the corresponding carbonyl compounds and 2-lithio-2-trimethylsilyl-1,3-dithiane.[12] In sharp contrast to 2-methylene-1,3-dithiane, however, none of these 2-alkylidenedithianes **5**–**7** reacts with either methyllithium or lithium dimethylcuprate(I)! In fact, lack of deuterium incorporation upon D_2O quenching shows that methyllithium and lithium dimethylcuprate(I) do not even abstract an allylic proton from these alkylidenedithianes to produce stable 2-lithio-2-alkenyl-1,3-dithianes. The more reactive butyl metallic species, *n*-BuLi and $(n\text{-Bu})_2CuLi$, also fail to react with ketene thioacetals **5** and **7**, as shown by lack of deuterium incorporation on D_2O work-up. This substantially lower reactivity of 2-alkylidene- *vs.* 2-methylene-1,3-dithianes toward organolithium reagents is possibly due to unfavorable steric interactions between the organolithium reagent and the alkyl groups attached to the double bond of the alkylidenedithiane. These results firmly establish that 2-alkylidene-1,3-dithianes do not undergo addition of organolithium (or organocopper) reagents so easily as originally anticipated.[12,20,21]



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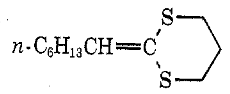

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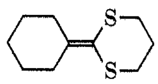

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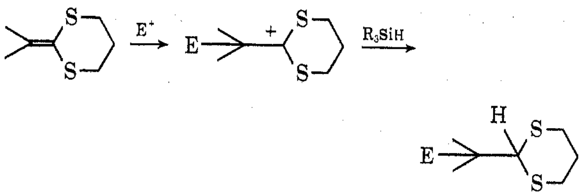
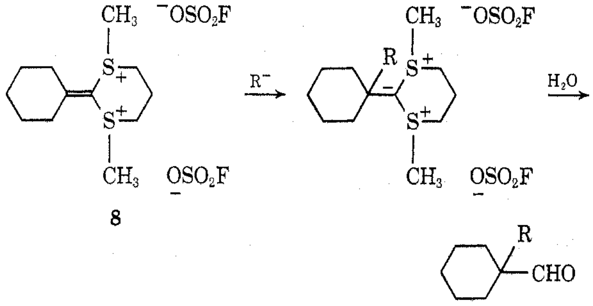
Because generation of a sulfur-stabilized carbanion failed to occur *via* anionic addition to these alkylidenedithianes, we next tried to take advantage of the known ability of sulfur to stabilize an adjacent carbonium ion.[20] Electrophilic addition of a proton (and bromonium, chloronium, and acylium ions) to several alkylidenedithianes followed by hydride attack has been reported[20] (eq 2). If electrophilic attack by an incipient alkyl carbonium ion could be achieved, followed by hydride attack, then the desired regiospecific addition of R and H across the double bond of alkylidene dithianes would be accomplished. Treating 2-cyclohexylidene-1,3-dithiane (**7**) with excess methyl fluorosulfonate gave a white precipitate (nmr singlet at δ 3.2 for *S*-methyl groups, 6 H) which was immediately treated *in situ* with triethylsilane; aqueous work-up gave parent dithiane **7** as the major product, which indicated that methylation, to the extent to which it had occurred, had taken place on sulfur (possibly forming a bis sulfonium salt) rather than on alkenyl carbon, and therefore that pursuing this approach would not be fruitful.



(2)

This apparent generation of 2-alkylidene-1,3-dithiane bis sulfonium salts[22,23] suggested that *anionic* addition to the alkylidene double bond of these salts might lead to an ylide type structure which could undergo several subsequent reactions, for example, hydrolysis to an aldehyde (eq 3).[24] Although the bis sulfonium salt of dithiane **5** reacted with lithium dimethylcuprate(I) to give 17 products, none of which was present in more than 20% yield by vpc analysis, 2-cyclohexylidene-1,3-dithiane bis sulfonium salt **8** reacted more cleanly. With methyllithium it gave parent 2-cyclohexylidene-1,3-dithiane (**7**) in 90% yield on aqueous work-up, and with lithium dimethylcuprate(I) it gave vinyl sulfide **9** in 55% yield and what appeared to be dimethylated vinyl sulfide **10** in 30% yield. Although the mechanism for formation of vinyl sulfides **9** and **10** is not



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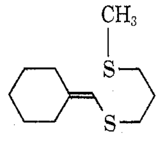

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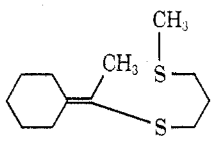

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[19] (a) R. M. Carlson and P. M. Helquist, *Tetrahedron Lett.*, 173 (1969); (b) D. Seebach, *Synthesis*, 17 (1969).

[20] F. A. Carey and J. R. Neergaard, *J. Org. Chem.*, **36**, 2731 (1971).

[21] Conjugated ketene thioacetals have recently been shown to undergo Michael-type addition of alkyllithium reagents: D. Seebach, M. Kolb, and B.-T. Grobel, *Angew. Chem.*, **85**, 42 (1973).

[22] These salts were prepared from 2 equiv of magic methyl but could not be purified by chromatography or by distillation and therefore were used *in situ*.

[23] Bis sulfonium salts have been reported: (a) I. Stahl, M. Hetschko, and J. Gosselck, *Tetrahedron Lett.*, 4077 (1971); (b) C. P. Lillya, E. F. Miller, and P. Miller, *Int. J. Sulfur Chem.*, **1**, 89 (1971); (c) C. P. Lillya and P. Miller, *J. Amer. Chem. Soc.*, **88**, 1559 (1966); (d) J. Gosselck, G. Schmidt, L. Beress, and H. Schenk, *Tetrahedron Lett.*, 331 (1968).

[24] S-Alkylation of thioketals with $Et_3O^+BF_4^-$ and with methyl fluorosulfonate followed by hydrolysis produces carbonyl compounds: (a) T. Oishi, K. Kamemoto, and Y. Ban, *Tetrahedron Lett.*, 1085 (1972); (b) M. Fetizon and M. Jarion, *Chem. Commun.*, 382 (1972).

clear,[25] isolation of vinyl sulfide **9** in 55% yield from one initial experiment prompted a thorough study of the effect of solvent, temperature, time, and organometallic reagent on the relative distribution of sulfides **9** and **10** (Table I); hydrolysis of vinyl sulfide **9** was expected to give, and did indeed produce, cyclohexanecarboxaldehyde.[11]

TABLE I

REACTION OF BIS SULFONIUM SALT **8** WITH 10 EQUIV OF METHYLMETALLIC REAGENTS

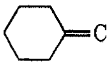
Organo-metallic	Solvent	Temp, °C	Time, hr	% yield[a] of products **9**	**10**	**7**
CH_3Li	Et_2O	−78	3			81
		0	1			
CH_3Cu	Et_2O	−78	2			23
		25	6			
	Pyridine	0	2.5			
$(CH_3)_2CuLi$	Et_2O	0	1	55	30	15
$(CH_3)_2CuLi$	Et_2O	−78	2	50	32	9
		−20	2			
		0	2			
$(CH_3)_2CuLi$	1:1 Toluene:Et_2O	0	2	77	8	10
$(CH_3)_2CuLi$	THF[b]	0	3	65	30	5

[a] Yield was determined by analytical vpc using an internal standard. [b] THF = tetrahydrofuran.

Several conclusions can be drawn from the data in Table I: (1) neither methylcopper nor methyllithium is effective in converting sulfonium salt **8** into either sulfide **9** or **10**; (2) a toluene–ether solvent mixture or tetrahydrofuran as solvent increase the amount of vinyl sulfide **9** at the expense of dimethylated sulfide **10**. Most of the yields reported in Table I are average values of several experiments in which yield variation ranged from 5 to 15%, owing presumably to the heterogeneity of the reaction mixture and to the use of unpurified[22] sulfonium salt **8**.

Recent preparation of thioacetal bis sulfoxides[26] and bis sulfones[27] and their conversion to carbonyl compounds prompted us to investigate 2-alkylidene-1,3-dithiane bis sulfoxides and bis sulfones. Various attempts at oxidation of 2-cyclohexylidene-1,3-dithiane (**7**) with 1-chlorobenzotriazole[26a] failed to give pure bis sulfoxide; direct treatment of unpurified bis sulfoxide with lithium dimethylcuprate(I) gave unclear results. Oxidation of cyclohexylidenedithiane **7** with hydrogen peroxide in acetic acid[18b] did not produce any **7**-bis sulfone, nor did condensation of 2-lithio-1,3-dithiane bis sulfone with cyclohexanone, presumably owing to the stability of the disulfolane anion (pK_a = 13).[28] Consequently, attention was directed to alkenyl monosulfones, compounds which were known to undergo nucleophilic addition of alkoxides and thioalkoxides.[29]

Alkenyl Methyl Sulfones.—Alkenyl methyl sulfones **11–13** were prepared in high yields from the corresponding carbonyl compounds and lithium diethyl methylsulfonomethylphosphonate.[13] It was anticipated that the sulfonyl group would facilitate organocopper β addition primarily by stabilizing the adjacent carbanion produced by such addition (eq 4a).[30] If alkenylsulfonomethyl carbanion formation were to occur before organocopper addition to the double bond, however, then such organometallic addition would be severely retarded by the negative charge already on the alkenyl sulfone (eq 4b). In experimental fact, cyclohexylidene sulfone **11** is deuterated in the methyl group when exposed first to lithium dialkylcuprates(I) and then *in situ* to D_2O, and no addition to the double bond is observed. Likewise, methyllithium and lithium dimethylcuprate(I) do not add to styryl sulfone **12**, but lithium di-*n*-butylcuprate does; besides 35% of methyl-deuterated styryl sulfone **12**, β adduct **14** is formed in 50% yield. The occurrence of *n*-butyl addition β to sulfur in styryl sulfone **12** but not in styryl sulfide **3** is probably due to the larger stabilization of adjacent negative charge by the methylsulfonyl than by the methylthio group.



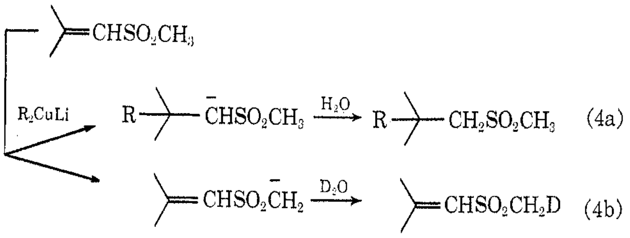
11

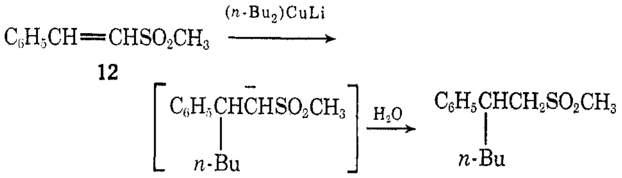
$C_6H_5CH{=}CHSO_2CH_3$

12

$n\text{-}C_6H_{13}CH{=}CHSO_2CH_3$

13

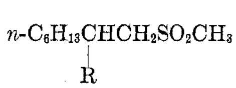




$$C_6H_5CH{=}CHSO_2CH_3 \xrightarrow{(n\text{-}Bu_2)CuLi} \left[\begin{array}{c} C_6H_5CH\bar{C}HSO_2CH_3 \\ | \\ n\text{-}Bu \end{array}\right] \xrightarrow{H_2O} \begin{array}{c} C_6H_5CHCH_2SO_2CH_3 \\ | \\ n\text{-}Bu \end{array}$$

12 **14**

Lithium dimethyl- and di-*n*-butylcuprate(I) addition to alkenyl sulfone **13** also takes place specifically β to sulfur to give adducts **15** and **16** in 70–75% yields.



$$\begin{array}{c} n\text{-}C_6H_{13}CHCH_2SO_2CH_3 \\ | \\ R \end{array}$$

15, R = CH_3
16, R = Bu-*n*

Isolation of 10–20% starting alkenyl sulfone **13** is due presumably to the intermediacy of a small amount of alkenylsulfonymethyl anion which is protonated upon aqueous work-up (eq 4b).

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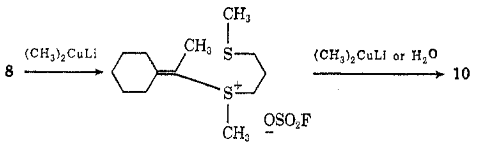
[25] A possible mechanism for formation of dithiane **10** may be outlined as follows.



[26] (a) P. R. Heaton, J. M. Midgley, and W. B. Whalley, *Chem. Commun.*, 750 (1971); (b) H. Nieuwenhuyse and R. Low, *Tetrahedron Lett.*, 4141 (1971).

[27] S. J. Daum and R. L. Clarke, *Tetrahedron Lett.*, 165 (1967).

[28] E. J. Corey, H. Konig, and T. Lowry, *Tetrahedron Lett.*, 515 (1962).

[29] M. F. Shostakovskii, E. N. Prilzhaeva, L. V. Tsymbal, V. A. Azovskaya, and N. G. Starova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2239 (1959); *Chem. Abstr.*, **54**, 10847e (1959).

[30] The pK_a of most aliphatic sulfones is about 23, roughly comparable to that of aliphatic esters: R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953).

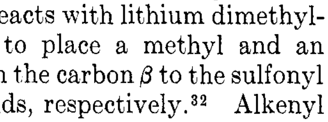
In order to prevent the organocopper reagents from acting as bases which remove a proton from the methyl group adjacent to sulfonyl sulfur, and to increase the stabilizing effect of the sulfonyl group on adjacent carbanions, attention was turned to alkenyl *aryl* sulfones.

Alkenyl Aryl Sulfones.—Alkenyl *p*-chlorophenyl sulfones **17–20** were prepared in high yields from the corresponding aldehydes, even from 3-ethoxycarbonylcyclohexanecarboxaldehyde, and lithium diethyl *p*-chlorophenylsulfonomethylphosphonate.[13,31] The *p*-chlorophenyl group was selected primarily because the *p*-chloro substituent would help stabilize the carbanion formed *via* organocopper addition to the β carbon atom of the alkenyl aryl sulfones and because *p*-chlorothiophenol (from which the phosphonate is made) is commercially available at a reasonable price. *p*-Chlorophenyl styryl sulfone (**17**) reacts with lithium dimethyl- and di-*n*-butylcuprates(I) to place a methyl and an *n*-butyl group specifically on the carbon β to the sulfonyl group in 100 and 75% yields, respectively.[32] Alkenyl styryl sulfone **17** then culminates the series of styryl sulfur compounds (**3**, **12**, and **17**) and allows successful addition of methyl and *n*-alkyl groups to the β carbon of an α,β-ethylenic sulfur compound. Interestingly, attempts to introduce *sec*- and *tert*-alkyl groups using the new lithium *tert*-butoxy-*sec*- and *tert*-alkylcuprates(I)[33,34] failed completely; styryl sulfone **17** was recovered in good yield in all cases. Addition of lithium dialkylcuprates(I) to the β carbon of α,β-ethylenic *p*-chlorophenyl sulfones **18–20** also proceeded in excellent yields, as described previously.[14a] That such organocopper β addition to alkenyl aryl sulfone **19**, for example, produced a sulfonyl-stabilized anionic species was shown by quenching the reaction mixture with excess D_2O or excess methyl iodide and isolating α-deuterated or α-methylated sulfone in good yield (eq 5).

$C_6H_5CH{=}CHSO_2C_6H_4Cl\text{-}p$ **17**

$C_6H_5CH(CH_3)CH{=}CHSO_2C_6H_4Cl\text{-}p$ **18**

$n\text{-}C_6H_{13}CH{=}CHSO_2C_6H_4Cl\text{-}p$ **19**



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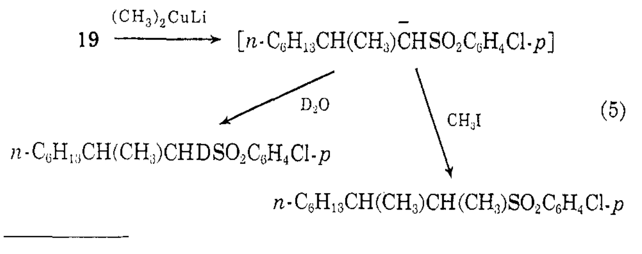
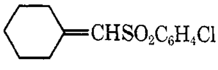


$$19 \xrightarrow{(CH_3)_2CuLi} [n\text{-}C_6H_{13}CH(CH_3)\overset{-}{C}HSO_2C_6H_4Cl\text{-}p] \quad (5)$$

$$\xrightarrow{D_2O} n\text{-}C_6H_{13}CH(CH_3)CHDSO_2C_6H_4Cl\text{-}p$$

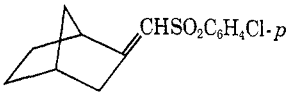
$$\xrightarrow{CH_3I} n\text{-}C_6H_{13}CH(CH_3)CH(CH_3)SO_2C_6H_4Cl\text{-}p$$

$(CH_3)_2C{=}CHSO_2C_6H_4Cl\text{-}p$ **21**



22

$n\text{-}C_5H_{11}C(CH_3){=}CHSO_2C_6H_4Cl\text{-}p$ **23**



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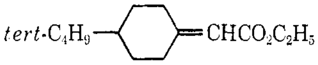
Preparation of α,β-ethylenic *p*-chlorophenyl sulfones from most ketones was difficult even under forcing conditions and use of special cosolvents (*e.g.*, hexamethylphosphoramide).[11] Although acetone and cyclohexanone were converted in good yields to the corresponding alkenyl *p*-chlorophenyl sulfones **21** and **22**, the yields of alkenyl sulfones **23** and **24** (from 2-heptanone and 2-norbornanone) dropped to 30–40%, and to 0% from 5-nonanone and benzophenone. These results, together with the good yield of alkenyl *methyl* sulfone from 2-heptanone,[14a] suggest a steric interference between the bulky diethyl *p*-chlorophenylsulfonomethylphosphonate anion and di-*n*-alkyl or other large ketones.[35] Attempts to condense lithium diethyl *p*-chlorophenyl*thio*methylphosphonate with most ketones also failed.[36] This difficulty in preparing alkenyl *p*-chlorophenyl sulfones from most ketones limits the generality of the scheme outlined in eq 1 for conversion of ketone carbonyls to quaternary carbon atoms.

Lithium dimethyl- and di-*n*-butylcuprate(I) addition to the double bond of alkenyl sulfone **21** proceeds in 72 and 89% yields, respectively, whereas methyl and *n*-butyl addition to cyclohexylidenemethyl sulfone **22** proceeds in 30 and 50% yields, respectively. Organocopper conjugate addition to α,β-ethylenic carbonyl compounds is known to be retarded by disubstitution on the β carbon, and, although lithium dimethylcuprate(I) adds to isopropylideneacetates in modest yields, cyclohexylideneacetate **25** is essentially inert to lithium dimethylcuprate(I).[2] It is not unexpected, therefore, that organocopper reagents add well to alkenyl sulfone **21** but poorly to cyclohexylidenemethyl sulfone **22**. Because six-membered rings are so prominent in many types of natural products and are so useful as synthetic intermediates, several variations of organometallic reagent, solvent, time, temperature, and work-up procedure were tried in order to optimize the yield of alkyl sulfones **26** (Table II).



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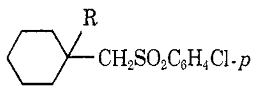

26a, $R{=}CH_3$
b, $R = C_4H_9\text{-}n$

The data in Table II indicate that the optimum conditions for methyl addition to sulfone **22** involve using lithium dimethylcuprate(I) in diethyl ether at room temperature for 72 hr and hydrogen sulfide work-up, which gives adduct **26** ($R = CH_3$) in 27% yield. Addition of the *n*-butyl group is best achieved in diethyl

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[31] On occasion we have observed that column chromatography of some α,β-ethylenic sulfones causes isomerization to β,γ-ethylenic sulfones which are thermodynamically more stable [D. E. O'Connor and W. I. Lyness, *J. Amer. Chem. Soc.*, **86**, 3840 (1964)]; in fact, reaction of acetophenone with lithium diethyl *p*-chlorophenylsulfonomethylphosphonate forms allylic sulfone i in 20% yield.

$C_6H_5C({=}CH_2)CH_2SO_2C_6H_4Cl\text{-}p$
i

[32] Organocopper addition to styryl *p*-chlorophenyl *sulfoxide* was found to be substantially slower than addition to the corresponding sulfone.

[33] G. H. Posner and C. E. Whitten, *Tetrahedron Lett.*, 1815 (1973).

[34] G. H. Posner and J. J. Sterling, *J. Amer. Chem. Soc.*, **95**, 3076 (1973).

[35] Compare, for example, the sensitivity of the bisulfite carbonyl addition reaction to apparently slight changes in structure of carbonyl compounds. Some methyl but not di-*n*-alkyl ketones undergo bisulfite addition: L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd ed, Reinhold, New York, N. Y., 1956, p 202.

[36] Had *p*-chlorophenyl alkenyl *sulfides* been formed, these could have been oxidized to the corresponding sulfones (ref 18b).

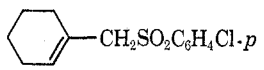
TABLE II

REACTION OF CYCLOHEXYLIDENEMETHYL SULFONE **22** WITH 10 EQUIV OF ORGANOMETALLIC REAGENTS[a]

Organometallic	Solvent	Time, hr	Temp, °C	% isolated yield of **26**[b]
$(CH_3)_2CuLi$	Et_2O	5	0	11
$(CH_3)_2CuLi$	Pentane	5	0	10
$(CH_3)_2CuLi$	THF	5	0	0
$(CH_3)_2CuLi$	Toluene	5	0	10
$(CH_3)_2CuLi$	Toluene	24	25	18
$(CH_3)_2CuLi$	2:1 Pentane:Et_2O	12	25	20
$(CH_3)_2CuLi$	Et_2O	72	25	27[c]
CH_3Li	Et_2O	3	25	5
$CH_3Li \cdot TMED$[d]	Et_2O	3	0	0[e]
$(n\text{-}Bu)_2CuLi$	Et_2O	12	25	0
$(n\text{-}Bu)_2CuLi$	Et_2O	16	10	0
$(n\text{-}Bu)_2CuLi$	Et_2O	5	0	38
$(n\text{-}Bu)_2CuLi$	Et_2O	2	−20	48
		5	0	
$(n\text{-}Bu)_2CuLi$	2:1 Et_2O:Pentane	5	0	30

[a] Typical work-up involved use of aqueous ammonium chloride. [b] Substantial amounts of starting material were recovered in all 5-hr reactions. [c] H_2S work-up. [d] TMED = tetramethylenediamine. [e] Cyclohexenylmethyl *p*-chlorophenyl sulfone was formed in 45% yield.

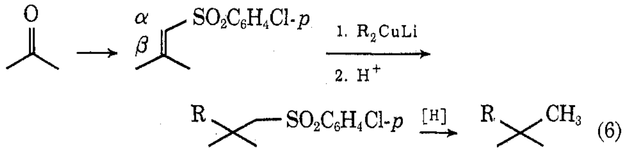
ether for 2 hr at −20° and then 5 hr at 0° followed by aqueous ammonium chloride work-up to give adduct **26** ($R = C_4H_9\text{-}n$) in 50% yield. Cyclohexylidenemethyl sulfone **22** is inert to methyllithium but reacts with the methyllithium–tetramethylethylenediamine complex to form β,γ-alkenyl sulfone **27** in 45% yield upon aqueous ammonium chloride work-up.[31]



27

In an attempt to increase the electrophilicity of cyclohexylidenemethyl sulfones, cyclohexylidenemethyl *p-fluoro*phenyl sulfone was prepared from lithium diethyl *p*-fluorophenylsulfonomethylphosphonate (*p*-fluorothiophenol is commercially available) and cyclohexanone.[13] It was hoped that the larger electron-withdrawing inductive effect of fluorine compared to that of chlorine ($\sigma_I = 0.52$ *vs.* 0.47)[37] might outweigh the larger electron-releasing resonance effect of fluorine compared to that of chlorine ($\sigma_R = -0.44$ *vs.* -0.24);[37] the relative importance of inductive and resonance effects in stabilization of *p*-halophenylsulfonylmethyl carbanions could not be evaluated beforehand because search of the literature failed to show any data for the relative acidities of *p*-halophenylsulfonic acids or of *p*-halophenyl methyl sulfones. Lithium dimethyl- and di-*n*-butylcuprate(I) add to cyclohexylidenemethyl *p-fluoro*phenyl sulfone in significantly lower yield than to *p-chloro*phenyl sulfone **22**. It would thus appear that *p*-chlorophenylsulfonylmethyl anions may be more stable than the corresponding *p*-fluorophenyl anions and that *p*-chlorophenyl methyl sulfones may be more acidic than *p*-fluorophenyl methyl sulfones. Attempts to prepare cyclohexylidenemethyl *m,p*-dichlorophenyl sulfone failed.

Hydrogenolysis of Alkyl Aryl Sulfones.—The successful β addition of lithium dimethyl- and di-*n*-butylcuprate(I) to the double bond of alkenyl *p*-chlorophenyl sulfones to form alkyl *p*-chlorophenyl sulfones now required selective *alkyl*–sulfur bond hydrogenolysis to permit overall conversion of an aldehyde or ketone carbonyl to a tertiary or quaternary carbon atom (eq 6). No general method had been reported for such



selective hydrogenolysis, and indeed treating alkyl aryl sulfones with lithium in methylamine causes cleavage of the *aryl*–sulfur bond.[38] An indirect route which seemed workable was lithium aluminum hydride reduction of alkyl aryl sulfones to the corresponding sulfides[39] followed by alkyl–sulfur bond hydrogenolysis,[38] but overall yields in these two steps are not high. An early report[40] that sodium amalgam in refluxing ethanol caused cleavage of methyl phenyl sulfone to benzenesulfinic acid suggested the possibility of using this method for selective hydrogenolysis of alkyl *p*-chlorophenyl sulfones. As summarized in Table III, 6% sodium amalgam in refluxing ethanol for about 12 hr does indeed cause *alkyl*–sulfur bond hydrogenolysis to form alkane and *p*-chlorobenzenesulfinic acid consistently in high yields.[14a]

The overall sequence (eq 6) described herein allows effective conversion of aldehyde carbonyls to tertiary alkyl carbon atoms in which each of the three alkyl groups may be different and permits transformation of certain ketone carbonyl groups to quaternary carbon units. The maximum efficiency of this sequence is exemplified by the conversion of heptanal to 2-methyloctane in 82% overall yield and benzaldehyde to isopropylbenzene in 89% overall yield.[14a]

Experimental Section

General.—Infrared spectra were obtained with Perkin-Elmer 337 and 457 infrared spectrophotometers as liquid films, KBr pellets, or in $CHCl_3$ or CCl_4 solution. Nmr spectra were obtained with a Varian A-60 or a Jeol MH-100 spectrometer in CCl_4 or $CDCl_3$ solution, with TMS internal standard. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6 mass spectrometer. Melting points, determined with a Mel-Temp melting point apparatus, and boiling points are uncorrected. Analytical vpc were performed on a Varian Aerograph series 1200 gas chromatograph, using a 7 ft × 0.125 in. 5% SE-30 on Chrom G column (column A), a 10 ft × 0.25 in. 10% FFAP on Chrom W column (column B), a 10 ft × 0.25 in. 10% Carbowax 20M on Chrom W column (column C), or an 18 ft × 0.125 in. 20% Reoplex on Anachrom AS column (column D). Preparative vpc was performed on a Varian Aerograph Model 90-P gas chromatograph, using a 20 ft × 0.375 in. 20% Carbowax on Chrom W column (column E), a 20 ft × 0.375 in. 20% QF-1 on Chrom W column (column F), or a 20 ft × 0.375 in. 20% SE-30 on Chrom W column (column G). Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Chemalytics, Inc., Tempe, Ariz.

All reactions involving organometallic compounds were performed in three-neck round-bottom flasks equipped with serum

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[37] J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure," McGraw-Hill, New York, N. Y., 1968, p 243.

[38] W. E. Truce, D. P. Tate, and D. N. Burdge, *J. Amer. Chem. Soc.*, **82**, 2872 (1960).

[39] F. G. Bordwell and W. H. McKellin, *J. Amer. Chem. Soc.*, **73**, 2251 (1951).

[40] R. E. Dabby, J. Kenyon, and R. F. Mason, *J. Chem. Soc.*, 4881 (1952).

TABLE III

SODIUM AMALGAM REDUCTIONS OF ALKYL ARYL SULFONES IN REFLUXING ETHANOL

Alkyl aryl sulfone	Registry no.	Reflux time, hr	Hydrocarbon product	Registry no.	Vpc % yield[a] (column, temp in °C)	Bp, °C (mm)	n_D (temp, °C)
n-$C_6H_{13}CH(CH_3)CH_2SO_2Ar$[b]	40582-87-4	4	n-$C_6H_{13}CH(CH_3)_2$	3221-61-2	85 (D, 70)		1.4024 (20)[c]
n-$C_6H_{13}CH$(n-Bu)CH_2SO_2Ar	40582-88-5	12	n-$C_6H_{13}CH$(n-Bu)CH_3	1632-70-8	72 (B, 110)		1.4192 (20[d]
$C_6H_5CH(CH_3)CH_2SO_2Ar$	40582-89-6	5	$C_6H_5CH(CH_3)_2$	6031-02-3	99 (B, 110)		
C_6H_5CH(n-Bu)CH_2SO_2Ar	40582-90-9	15	C_6H_5CH(n-Bu)CH_3	5099-92-7	92 (B, 130)		1.4862 (28)[e]
26a		15	1,1-Dimethylcyclohexane		70 (D, 62)[f]		
26b		15	1-n-Butyl-1-methylcyclohexane		55 (B, 110)	188–189 (760)[g]	
n-$C_4H_9C(CH_3)_2CH_2SO_2Ar$	40582-91-0	15	n-$C_4H_9C(CH_3)_3$	590-73-8	70 (D, 20)	105 (760)[h]	
$C_6H_5CH(CH_3)CH(CH_3)CH_2SO_2Ar$	40582-92-1	18	$C_6H_5CH(CH_3)CH(CH_3)_2$	4481-30-5	100 (B, 130)	187 (760)[i]	1.4915 (20)[i]
$C_6H_5CH(CH_3)CH$(n-Bu)CH_2SO_2Ar	40582-93-2	15	$C_6H_5CH(CH_3)CH$(n-Bu)CH_3	40582-96-5	80 (B, 140)	244–245 (760)[j]	1.4862 (27.5)

[a] Yield based on added internal standard; see Experimental Section for details. [b] Ar = p-ClC_6H_4. [c] Lit. n^{20}_D 1.4032: F. C. Whitmore and H. A. Southgate, *J. Amer. Chem. Soc.*, **60**, 2571 (1938). [d] Lit. n^{20}_D 1.4198: D. H. Gibson and R. Pettit, *ibid.*, **87**, 2620 (1965). [e] Lit. n^{20}_D 1.4902: H. N. Stephens and F. L. Roduta, *ibid.*, **57**, 2380 (1935). [f] Yield based on 60% pure **26a**; product identified by comparison of nmr, vpc retention time, and mass spectra with those of an authentic sample. [g] Lit. bp 191.5°: S. I. Khromov, E. S. Balenkova, P. A. Akishin, and B. A. Kazanskii, *Dokl. Akad. Nauk SSSR*, **97**, 103 (1954); *Chem. Abstr.*, **49**, 8828*a* (1955). [h] Lit. bp 107°: C. R. Noller, *J. Amer. Chem. Soc.*, **51**, 598 (1929). [i] Lit. bp 188–189°, n^{16}_D 1.4972: M. Konowalloff and J. Egeroff, *Chem. Zentr.*, **1**, 776 (1899); A. Klages, *Ber.*, **36**, 3691 (1903). [j] *Anal.* Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.06; H, 12.01.

stoppers and a nitrogen-filled balloon. Prior to the introduction of reactants, the apparatus was dried with a Bunsen burner flame while being purged with N_2. Freshly opened bottles of commercial anhydrous diethyl ether, pentane, or toluene were used without purification. Tetrahydrofuran (THF) was dried over $LiAlH_4$ and stored under N_2 prior to use. Methyllithium and n-butyllithium were obtained in *ca.* 2.0 and 1.8*M* ether and pentane solutions, respectively, from Alfa Inorganics, Inc., Bevery, Mass., and were titrated[41] prior to use.

Preparations of Starting Materials. Alkenyl Methyl Sulfides.—1-Octenyl methyl sulfide (1), cyclohexylidenemethyl methyl sulfide (2), and methyl styryl sulfide (3) were prepared from heptanal, cyclohexanone, and benzaldehyde, in yields of 89, 67, and 77%, according to the procedure of Corey and Shulman,[11] using lithium diethyl methylthiomethylphosphonate.

2-Alkylidene-1,3-dithianes.—2-(2-Methyl)propylidene-1,3-dithiane (5) and 2-cyclohexylidene-1,3-dithiane (7) were prepared in 78 and 72% yields according to the procedure of Carey and Court,[12] from isobutyraldehyde and cyclohexanone, using 2-lithio-2-trimethylsilyl-1,3-dithiane.

2-Heptylidene-1,3-dithiane (6).—Analogous to the procedure of Carey and Court,[12] dithiane 6 was prepared from 20.0 mmol of heptanal, 9.1 ml of 2.2 *M* n-BuLi, and 20.0 mmol of 2-trimethylsilyl-1,3-dithiane, giving, after distillation, 3.378 g (78%) of dithiane 6: bp 92–95° (0.05 mm); nmr (CCl_4) δ 0.90 (distorted t, 3, CH_3), 1.3 [broad d, 8, $(CH_2)_4$], 2.2 (m, 4, CH_2 α to olefin and CH_2 β to S), 2.8 (distorted t, 4, CH_2's α to S), 6.85 (t, J = 7 Hz, 1, vinyl).

Anal. Calcd for $C_{11}H_{20}S_2$: C, 61.05; H, 9.32; S, 29.63. Found: C, 60.89; H, 9.21; S, 29.69.

Dimethyl 1-Octenyl Sulfonium Fluorosulfonate.—Methyl fluorosulfonate ("magic methyl," 0.200 g, 1.50 mmol) was added to a solution of 1.00 mmol of alkenyl sulfide 1 in 10 ml of anhydrous ether at 0° and under N_2, slowly forming a brown oil on the sides of the flask. The ether was evaporated to yield the crude product: nmr ($CDCl_3$) δ 0.89 (distorted t, 3, CH_3), 1.1–1.7 (m, 8, methylenes), 3.10 [s, 6, $S(CH_3)_2$], 6.3–7.2 (m, 2, vinyl protons). The vinyl sulfonium salt decomposed during purification attempts by column chromatography.

Dimethyl 2-Cyclohexylidene-1,3-dithiane Bis Sulfonium Fluorosulfonate (8).—Methyl fluorosulfonate (0.3422 g, 3.00 mmol) was added to 1.00 mmol (0.200 g) of dithiane 7 in 20 ml of anhydrous ether at 0° and under N_2, and the solution was stirred at 25° overnight. Sulfonium salt 8, isolated by filtration, showed a singlet in the nmr ($CDCl_3$) at δ 3.2 which integrated for six protons; it is therefore probably a bis and not a monosulfonium salt. The organocopper solution, prepared as in the general procedure, was added *via* syringe to the unpurified sulfonium salt 8.

Attempted Formation of Bis Sulfoxide of 2-Cyclohexylidene-1,3-dithiane (7).—To a stirred solution of 10.00 mmol (2.00 g) of dithiane 7 in 100 ml of CH_2Cl_2 at −78° and under N_2 was added a solution of 20.00 mmol of 1-chlorobenzotriazole[26a] in CH_2Cl_2, reacting at −78° for 4 hr, then allowing the temperature to rise to −50° and quenching with 3% NaOH when that temperature was reached. Work-up involved extraction into three 50-ml portions of ether, treatment with Norit, drying over $MgSO_4$, filtration and evaporation. Upon evaporation, a gummy residue formed. Column chromatography over 100 g of silica did not yield pure product. The procedure was repeated, reacting only at −78°, and using MeOH as solvent, but no pure bis sulfoxide was formed.

Attempted Formations of Bis Sulfone of 2-Cyclohexylidene-1,3-dithiane (7). A.—Analogous to the procedure of Wittig and Schlosser[18b] for oxidation of alkenyl sulfides, 0.7 ml of 30% H_2O_2 was added to a stirred slurry of 1.00 mmol (0.200 g) of dithiane 7 in 2.6 ml of glacial acetic acid at 0°. An additional 2.0 ml of HOAc was added, and the mixture was stirred overnight. Work-up by extraction into ether and washing with H_2O and 10% $NaHCO_3$ yielded only 0.029 g of oily residue, which was not identified.

B.—To a solution of 5.0 mmol (0.6012 g) of 1,3-dithiane in 10 ml of glacial acetic acid at 20° was added 3.5 ml of 30% H_2O_2. The solution was stirred for 5 min, and 10 ml of HOAc was added. The solution was stirred at 20° for 2 hr, then at 50° for 12 hr. After 12 hr, a thick precipitate had formed, which was separated by suction filtration to give 0.719 g of the bis sulfone of 1,3-dithiane (1,3-disulfolane,[28] 79%): mp 308.5–310° after recrystallization from 1:1 methanol–acetone; ir (KBr) 1340, 1145, and 1109 cm^{-1} (SO_2).

To 5.00 mmol (0.9212 g) of 1,3-disulfolane in a three-neck flask under N_2 was added 15 ml of dry THF, and the slurry was cooled to −78°; then 3.8 ml (5.0 mmol) of 1.32 *M* n-BuLi was added at that temperature. A Gilman test with Michler's ketone taken after 15 min was negative to alkyllithium.[42] The heterogeneous mixture was stirred at −78° for 1 hr; then 5.00 mmol (0.490 g) of cyclohexanone was added, the mixture was stirred at that temperature for an additional 1 hr and then allowed to warm to 0°, and stirring was continued for 1 hr. Acetic acid (3.0 ml) was added in 3 ml of THF, and the mixture was stirred at 0° for 30 min, then warmed to 25° for 90 min. The white precipitate (which had been present during the entire course of reaction) was removed by filtration, washed with 10 ml of ether and 10 ml of H_2O, and dried to yield 0.710 g of white solid identified by melting point (305–309°) as 1,3-disulfolane (77% recovery).

Alkenyl Methyl Sulfones.—Cyclohexylidenemethyl methyl sulfone (11), methyl *trans*-styryl sulfone (12), and methyl 1-octenyl sulfone (13) were prepared as previously described[13] from cyclohexanone, benzaldehyde, and heptanal, by condensation with lithium diethyl methylthiomethylphosphonate in yields of 97, 87, and 97%, respectively.

Alkenyl Aryl Sulfones.—p-Chlorophenyl *trans*-styryl sulfone (17), p-chlorophenyl 1-octenyl sulfone (19), and p-chlorophenyl cyclohexylidenemethyl sulfone (22) were prepared as previously described[13] from benzaldehyde, heptanal, and cyclohexanone by condensation with lithium diethyl (p-chlorophenyl)sulfonomethylphosphonate, in yields of 90, 80, and 72%, respectively.

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[41] G. M. Whitesides, C. P. Casey, and J. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).

[42] H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, **47**, 2002 (1925).

p-Chlorophenyl 3-Phenyl-1-butenyl Sulfone (18).—From 22.00 mmol of diethyl (p-chlorophenyl)sulfonomethylphosphonate (**28**), 20.0 mmol of n-BuLi, and 20.0 mmol of 2-phenylpropionaldehyde (2.684 g, Aldrich), crude alkenyl sulfone **18** was formed and was recrystallized from ethanol to give 4.877 g (80%) of sulfone **18**: mp 61.5–62.5°; nmr ($CDCl_3$) δ 1.37 (d, $J = 7$ Hz, 3, CH_3), 3.65 (p, $J = 7$ Hz, 1, benzylic CH), 6.28 (d of d, $J = 15$, 1 Hz, 1, vinyl proton α to SO_2), 7.0–8.0 (m, 10, aromatic and vinyl protons).

Anal. Calcd for $C_{16}H_{15}SO_2Cl$: C, 62.64; H, 4.93; S, 10.45; Cl, 11.56. Found: C, 62.98; H, 5.14; S, 10.48; Cl, 11.57.

p-Chlorophenyl 2-(3-Ethoxycarbonylcyclohexyl)ethenyl Sulfone (20).—Phosphonate **28** (20.00 mmol), 11.05 ml (20.0 mmol) of 1.81 *M* n-BuLi, and 20.00 mmol (3.690 g) of 3-ethoxycarbonylcyclohexanecarboxaldehyde (Aldrich) in 120 ml of dry THF were allowed to stir at −78° for 45 min, then warmed to 25° and stirred overnight.[13] Standard work-up yielded 7.174 g of yellow oil (theoretical 6.888 g), which was purified by column chromatography using 100 g of silica and benzene eluent to give 3.785 g (55%) of sulfone **20**: nmr ($CDCl_3$) δ 1.0–2.1 (broad m with t superimposed, $J = 7.5$ Hz, 13, cyclohexyl protons and CH_3 of ester), 4.1 ($J = 7.5$ Hz, 2, CH_2 of ester), 6.34 (d, $J = 16$ Hz, 1, vinyl proton α to SO_2), 6.7–7.2 (m, 1, vinyl proton β to SO_2), 7.55 and 7.88 (pair of d, $J = 9$ Hz, 4 aromatic).

p-Chlorophenyl 2-Methyl-1-propenyl Sulfone (21).—Phosphonate **28** (20.00 mmol), 11.0 ml (20.0 mmol) of 1.81 n-BuLi, and 2.0 ml (∼28 mmol) of acetone in 100 ml of dry THF were allowed to stir at −78° for 1 hr, then overnight at 25°.[13] Standard work-up yielded 5.129 g of crude sulfone **21**, which was distilled to give 4.618 g of sulfone **21** (100%), which crystallized to a white solid: mp 39–39.5°; bp 125–130° (0.03 mm); nmr δ 1.90 (d, $J = 1.3$ Hz, 3, CH_3), 2.17 (d, $J = 1.3$ Hz, 3, CH_3), 6.25 (p, $J = 1.3$ Hz, 1, vinyl proton), 7.57 and 7.93 (pair of d's, $J = 9$ Hz, 4, aromatic protons).

Anal. Calcd for $C_{10}H_{11}SO_2Cl$: C, 52.06; H, 4.81; S, 13.90; Cl, 15.38. Found: C, 52.10; H, 4.76; S, 13.81; Cl, 15.32.

p-Chlorophenyl 2-Methyl-1-heptenyl Sulfone (23).—Phosphonate **28** (10.00 mmol), 7.5 ml (10.0 mmol) of 1.31 *M* n-BuLi, and 10.00 mmol of 2-heptanone in 50 ml of dry THF were stirred at −78° for 2 hr, then at 25° overnight.[13] Standard work-up yielded 3.448 g (theoretical 2.860 g) of crude sulfone **23**, which was found to be 42% pure by nmr integration. Purification of the crude product by column chromatography over Alcoa F-20 alumina was attempted, but isomerization of the double bond was found to occur. The nmr spectrum showed about a 50:50 mixture of allylic and vinylic sulfones: δ 0.7–1.7 (m, aliphatic chain), 1.8–2.4 (s superimposed on m, CH_3 and CH_2 of vinyl sulfone), 3.85 (s, CH_2 α to SO_2 in allylic sulfone), 4.83 and 5.05 (broad s's, vinylidene protons of allylic sulfone), 6.22 (m, vinyl proton of vinyl sulfone), 7.0–7.8 (m, aromatic).

Attempts were made to increase the yield of vinyl sulfone **23** by several methods. (a) Repeating the reaction in anhydrous ether at 25° yielded neither starting materials nor desired product. (b) Reaction in cyclohexane at 25° yielded only a very small amount of vinyl sulfone **23**; unreacted phosphonate was recovered. (c) The reaction was repeated forming the phosphonate anion at −20°, then cooling to −78°, and reacting as usual; only 8% formation of vinyl sulfone **23** was detected. (d) The reaction was repeated forming the phosphonate anion as −78°, then adding 1.0 equiv of tetramethylethylenediamine after 30 min at −78°. After an additional 30 min, 2-heptanone was added, and the reaction was completed as usual; standard work-up indicated only 17% formation of vinyl sulfone **23** and 70% recovered phosphonate.

p-Chlorophenyl 2-Norbornylidenemethyl Sulfone (24).—According to the standard procedure,[13] 20.00 mmol of phosphonate, 20.0 mmol of n-BuLi, and 20.00 mmol of 2-norbornanone were allowed to react at −78° for 2 hr, then at 25° overnight. Standard work-up yielded 7.110 g of yellow oil (theoretical 5.650 g). Column chromatography over 150 g of silica using hexane, 1:1 hexane–benzene, and benzene eluents yielded 3.148 g of yellow semisolid, which was recrystallized from ethanol to yield 2.023 g (36%) of white crystalline sulfone **24**: mp 81.5–82.5°; nmr spectrum indicated approximately a 50:50 mixture of *E* and *Z* isomers, δ 1.1–2.2 (m, 7, norbornyl ring protons), 2.28–2.50 (m, 2, allylic methylene), 2.78 and 3.90 (two broad s's, total of 1, allylic bridgehead protons in *E* and *Z* isomers), 5.98 and 6.12 (s and t, $J = 3$ Hz, total of 1, vinyl proton in *E* and *Z* isomers), 7.3–7.8 (m, 4, aromatic).

Anal. Calcd for $C_{14}H_{15}SO_2Cl$: C, 59.46; H, 5.35; S, 11.34; Cl, 12.54. Found: C, 59.46; H, 5.02; S, 11.04; Cl, 12.55.

Attempted Formations of Vinyl Sulfones from 5-Nonanone and Benzophenone.—Reactions were carried out as previously described,[13] treating the anion of phosphonate **28** with 5-nonanone or benzophenone at −78° for 2 hr. Standard work-up of each reaction gave no desired vinyl sulfone and recovery of 99% starting materials.

Attempted Formation of p-Chlorophenyl Vinyl Sulfides from 2-Heptanone and 5-Nonanone.—According to the procedure previously described,[11] lithium diethyl(p-chlorophenyl)thiomethyl phosphonate was treated with 5-nonanone and 2-heptanone at −78° for 2 hr. Heating for 5 hr at 50°, followed by standard work-up, yielded only starting materials. No vinyl sulfide was detected by nmr.

Cyclohexylidenemethyl p-Fluorophenyl Sulfone.—Chloromethyl p-fluorophenyl sulfide (61.3 mmol), which had been prepared in 81% yield from p-fluorothiophenol analogous to Fancher's[43] procedure, was treated with triethyl phosphite (102 mmol) to form diethyl (p-fluorophenyl)thiomethylphosphonate (94% yield), which was oxidized according to the procedure previously described,[13] to form diethyl p-fluorophenylsulfonomethylphosphonate (71% yield, mp 85–85.5°).

Analogous to the standard procedure, 10.00 mmol of the phosphonate was treated with 10.0 mmol of n-BuLi at −78° for 2 hr, then 10.0 mmol of cyclohexanone was added, and the solution was stirred at −78° for 1 hr, then at 25° overnight. Standard work-up yielded 2.579 g of colorless oil (theoretical 2.544 g), which was purified by column chromatography over 100 g of silica using hexane, 3:1 hexane–benzene, and benzene eluents. The benzene fractions were combined and evaporated to yield 2.454 g of white solid which was recrystallized from ethanol to yield 1.3225 g of pure cyclohexylidenemethyl p-fluorophenyl sulfone (52%): mp 63.5–65.5°; nmr ($CDCl_3$) δ 1.6 (broad s, 6, cyclohexyl protons), 2.15 (broad m, 2, cyclohexyl protons γ to SO_2), 2.70 (broad m, 2, cyclohexyl protons γ to SO_2), 6.20 (s, 1, vinyl proton), 7.0–7.5 and 7.8–8.2 (m, 4, aromatic).

Anal. Calcd for $C_{13}H_{15}SO_2F$: C, 61.40; H, 5.94; S, 12.61; F, 7.47. Found: C, 61.25; H, 5.94; S, 12.84; F, 7.59.

Reactions of α,β-Ethylenic Sulfur Compounds with Organocopper Reagents. General Procedure for Organocopper Reactions.—To a three-neck flask, fitted with two serum stoppers and a T-joint to which a nitrogen-filled balloon was attached, was added 10.0 equiv of cuprous iodide, and a magnetic stirring bar. The flask was evacuated while being flamed, then purged with nitrogen from the balloon. This procedure was repeated three times, to exclude oxygen and water. Enough anhydrous diethyl ether was added *via* a dry syringe that upon addition of MeLi–ether solution (n-BuLi–pentane or hexane), a 0.25 *M* $Li(CH_3)_2Cu$ [$Li(n\text{-}Bu)_2Cu$] solution resulted. The CuI–ether mixture was stirred and cooled to 0° [−40° for $Li(n\text{-}Bu)_2Cu$], and 20 equiv of MeLi–ether solution was added (20 equiv of BuLi–pentane or hexane) *via* a dry syringe. The resulting 0.25 *M* $Li(CH_3)_2Cu$ [$Li(n\text{-}Bu_2Cu)$] solution was adjusted to the reaction temperature, and 1 equiv of substrate was added in *ca.* 10% ether solution. The reaction was stirred and maintained at the appropriate temperature for the specified time, then quenched by pouring into 50 ml of saturated NH_4Cl solution. The organic layer was extracted three times with equal portions of ether, dried over $MgSO_4$, filtered, and rotoevaporated to give the crude product.[44]

Cyclohexylidenemethyl Methyl Sulfide (2).—The reaction was carried out as in the general procedure, treating 1.0 mmol of sulfide **2** with 10 mmol of $Li(CH_3)_2Cu$. Vpc analysis (column C at 120°) indicated 100% starting material after 1 hr at 0°, 97% starting material after 2 hr at 0°, and 97% starting material after 40 hr at 25°. The nmr spectrum was identical with that of starting material.

Reaction of 1.00 mmol of sulfide **2** with 5 mmol of $Li(n\text{-}Bu)_2Cu$ was carried out as in the general procedure. Vpc analysis indicated 95% starting material after 1 hr at 0° and 94% starting material after 15 hr at 25°. The nmr spectrum was identical with that of starting material.

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[43] German Patent 1,112,735 (1958) to L. W. Fancher (Stauffer Chemical Co.); *Chem. Abstr.*, **56**, 11499 (1962).

[44] New compounds were purified and subjected to microanalysis; some new liquid sulfone products could not be purified sufficiently for microanalysis and therefore were identified spectroscopically (nmr, ir, mass) and by hydrogenolysis to known compounds.

Methyl Styryl Sulfide (3).—Reaction was carried out as in the general procedure, with 10 mmol of $Li(CH_3)_2Cu$ reacting with 1.00 mmol of sulfide **3** at 25° for 15 hr. Starting material (93%) was recovered and identified by nmr.

In reaction of 1.00 mmol of sulfide **3** with 10 mmol of $Li(n\text{-}Bu)_2Cu$ at 25° for 15 hr, starting material was detected in 40% recovery by vpc analysis (column A at 120°), along with *trans*-1-phenyl-1-hexene, in 50% yield. The hydrocarbon product was separated from sulfide **3** by preparative vpc (column G at 190°), and identified by comparison to literature nmr and ir spectra for *trans*-1-phenyl-1-hexene.[45]

2-Cyclohexylidene-1,3-dithiane (7).—The reaction was carried out as in the general procedure, treating 1.00 mmol of dithiane **7** with 10 mmol of $Li(CH_3)_2Cu$ at 25° for 50 hr. Vpc analysis (column A at 200°) indicated no reaction.

In reaction of 1.00 mmol of dithiane **7** with 10 mmol of MeLi or *n*-BuLi at 25° for 22 hr, vpc analysis (column A at 200°) indicated no reaction; the nmr spectra were identical with those of starting material.

2-(2-Methyl)propylidene-1,3-dithiane (5).—The reactions were carried out as in the general procedure, treating 1.00 mmol of dithiane **5** with 10 mmol of $Li(CH_3)_2Cu$ or $Li(n\text{-}Bu)_2Cu$ for 50 hr at 25°. Vpc analysis (column A at 150°) and nmr indicated no reaction and complete recovery of starting material.

In reaction of 1.00 mmol of dithiane **5** with 10 mmol of MeLi at 25° for 24 hr, vpc analysis and nmr indicated no reaction and complete recovery of starting material.

2-Heptylidene-1,3-dithiane (6).—The reaction was carried out as in the general procedure, treating 1.00 mmol of dithiane **6** with 10 mmol of $Li(CH_3)_2Cu$ at −78° for 2 hr, then at 25° for 15 hr. The reaction was quenched with D_2O and worked up as usual. The nmr spectrum indicated no reaction and no deuteration, with 95% recovery of starting material.

In reaction of 1.00 mmol of dithiane **6** with 10 mmol of MeLi at 25° for 15 hr, with D_2O quench, no reaction or deuteration was observed in the nmr spectrum.

Dimethyl 1-Octenyl Sulfonium Fluorosulfonate.—The reaction was carried out by adding 10 mmol of a solution of $Li(CH_3)_2Cu$, formed as in the general procedure, to an ether suspension of 1.00 mmol of the sulfonium salt formed as above, and stirring at 25° for 2 hr. After the usual work-up, methyl 1-octenyl sulfide (**1**) was recovered (97%) and identified by nmr.

Dimethyl 2-Cyclohexylidene-1,3-dithiane Bis Sulfonium Fluorosulfonate (8).—(A) To 1.00 mmol of bis sulfonium salt **8**, formed as above, was added 2.0 mmol of triethylsilane, and the reaction was stirred for 12 hr. Work-up by washing with H_2O and $NaHCO_3$ yielded only 0.067 g of material, the nmr of which was identical with that of dithiane **7**. (B) To 1.00 mmol of bis sulfonium salt **8**, formed as above, was added 10 ml of H_2O, and the reaction mixture was stirred for 1 hr; addition of H_2O caused complete disappearance of the white precipitate. Work-up by washing with H_2O and $NaHCO_3$, drying, and evaporation yielded only 0.090 g of liquid, which could not be identified. (C) The organocopper reactions were carried out by forming an 0.5 *M* solution of 10 mmol of $Li(CH_3)_2Cu$ as in the general procedure, and adding it *via* a dry syringe to the suspension of 1.00 mmol of bis sulfonium salt **8**, with solvent and temperature adjusted to the conditions listed in Table I, and allowing reaction to proceed for the required time. Work-up as in the general procedure, followed by analytical vpc (column A, 200°), gave the results shown. In reactions with MeLi and MeCu, no products were seen by vpc other than starting materials. The products from reaction with $Li(CH_3)_2Cu$ were separated by preparative vpc (columns F and G at 240°), to yield cyclohexylidenemethyl (3-methylthio)propyl sulfide (**9**): nmr ($CDCl_3$) δ 1.5 (broad s, 6, cyclohexyl protons), 1.6–2.3 (m with s at 2.02 superimposed, 9, methyl superimposed on methylenes), 2.3–2.8 (m, 4, methylenes α to S), 5.40 (s, 1, vinyl proton); mass spectrum (70 eV) *m/e* (rel intensity) 216 (77), 201 (28), 123 (32), 121 (88), 95 (71), 89 [100, $(CH_2)_3SCH_3$], 73 (63); hydrolysis with NBS in 80% acetonitrile[46] yielded cyclohexanecarboxaldehyde, identified by comparison of ir and nmr spectra with those in the literature.[47]

Also isolated was 1-(cyclohexylidene)ethyl (3-methylthio)propyl sulfide (**10**): nmr ($CDCl_3$) δ 1.5 (broad s, cyclohexyl protons), 1.6–2.3 (m with 2 s's superimposed, methyl groups superimposed on methylenes), 2.4–2.8 (m, methylenes α to S); mass spectrum (70 eV) *m/e* (rel intensity) 230 (18), 216 (3), 141 (37), 121 [100, $S(CH_2)_3SCH_3$], 109 (18), 107 (22), 85 (27), 79 (18).

Dimethyl 2-(2-Methyl)propylidene-1,3-dithiane Bis Sulfonium Fluorosulfonate.—To 1.00 mmol of the bis sulfonium salt formed from dithiane **5** as above was added at −78° 10 mmol of $Li(CH_3)_2Cu$, formed as in the general procedure, and the reaction was stirred at −78° for 1 hr, at −20° for 1 hr, and at 0° for 2 hr. The reaction mixture was worked up as in the general procedure to give 0.264 g of yellow oil. Vpc analysis (column A, with temperature programming 160–240°) indicated 20 peaks, with the largest five representing 55% of the total; no product was present in more than 20%; only a small amount of starting material was evident in the nmr and vpc.

Cyclohexylidenemethyl Methyl Sulfone (11).—The reaction was carried out as in the general procedure, treating 1.00 mmol of sulfone **11** with 10 mmol of $Li(CH_3)_2Cu$ for 48 hr at 25°. Vpc analysis (column A at 135°) indicated no reaction.

In reaction of 1.00 mmol of sulfone **11** with 5 mmol of $Li(n\text{-}Bu)_2Cu$ at 0° for 17 hr, vpc analysis of an aliquot (column A at 135°) indicated a 98% recovery of starting material; the reaction was quenched with D_2O at that time, and worked up as usual. The nmr spectrum indicated partial deuteration of the sulfonyl methyl, from broadening of the singlet; a mass spectral study indicated only deuterated sulfone.

Methyl *trans*-Styryl Sulfone (12).—The reaction was carried out as in the general procedure, using 10 mmol of $Li(CH_3)_2Cu$, treating with 1.00 mmol of sulfone **12** at 25° for 36 hr; vpc analysis (column A, 150°) indicated 80% recovery of starting material in an aliquot removed at that time. The reaction was quenched in D_2O and worked up as usual. The nmr spectrum indicated starting material, with partial deuteration, evidenced by broadening of the sulfonyl methyl singlet.

In reaction of 1.00 mmol of sulfone **12** with 10 mmol of MeLi for 24 hr at 25°, starting material was recovered (90%), identified by nmr.

In reaction of 1.00 mmol of sulfone **12** with 5 mmol of $Li(n\text{-}Bu)_2Cu$ at 25° for 5 hr, a mixture of 35% starting sulfone **12** and 50% methyl 2-phenylhexyl sulfone was obtained. The product was isolated by column chromatography over silica gel, and identified by nmr ($CDCl_3$): δ 0.9–2.0 (m, 9, *n*-butyl group), 2.32 (s, 3, sulfonyl CH_3), 3.3 (m, 3, benzylic methine, sulfonyl methylene), 7.2–7.6 (m, 5, aromatic).

Methyl 1-Octenyl Sulfone (13).—The reaction was carried out as in the general procedure, treating 1.00 mmol of sulfone **13** with 10 mmol of $Li(CH_3)_2Cu$ at 25° for 9 hr, giving 70% of methyl 2-methyloctyl sulfone and 20% starting material, identified by nmr. The methylated product could not be separated from sulfone **13** by vpc, tlc, or column chromatography.

In reaction of 2.00 mmol of sulfone **13** with 20 mmol of $Li(n\text{-}Bu)_2Cu$ for 9 hr at 0°, 75% of methyl 2-butyloctyl sulfone was formed, and 11% starting material was recovered. The product was purified by column chromatography over silica gel, and identified by nmr ($CDCl_3$): δ 0.90 (pair of distorted t, 6, methyl groups), 1.3 (broad s, 17, methylenes and methine), 2.9 (s superimposed on d, 5, $CH_2SO_2CH_3$).

***p*-Chlorophenyl *trans*-Styryl Sulfone (17).**—The reaction was carried out as in the general procedure, using 10 mmol of $Li(CH_3)_2Cu$, treating with 1.00 mmol of sulfone **17** for 2 hr at 0°. The standard work-up yielded 0.296 g of solid *p*-chlorophenyl 2-phenylpropyl sulfone (100%): mp 101.5–102°; nmr ($CDCl_3$) δ 1.38 (m, 3, methyl), 3.34 (m, 3, methine and methylene), 6.9–7.7 (m, 9, aromatic).

Anal. Calcd for $C_{15}H_{15}SO_2Cl$: C, 61.11; H, 5.13; S, 10.88; Cl, 12.03. Found: C, 61.08; H, 5.21; S, 10.56; Cl, 12.04.

In reaction of 1.00 mmol of sulfone **17** with 5 equiv of $Li(n\text{-}Bu)_2Cu$ for 1 hr at 0°, *p*-chlorophenyl 2-phenylhexyl sulfone was formed (75%), identified by nmr ($CDCl_3$): δ 0.8–2.0 (m, 9, butyl group), 3.0–3.5 (m, 3, methylene and methine), 6.9–8.0 (m, 9, aromatic); mp 69–72°.

***p*-Chlorophenyl (3-Phenyl)-1-butenyl Sulfone (18).**—The reaction was carried out as in the general procedure, treating 1.00 mmol of sulfone **18** with 10 mmol of $Li(CH_3)_2Cu$ for 1 hr at 0°, to give *p*-chlorophenyl 2-methyl-3-phenylbutyl sulfone (97%). Recrystallization from ethanol (83%) gave mp 86.5–88.5°; nmr ($CDCl_3$) δ 1.04 (pair of overlapping d, 6, methyl groups), 2.0–3.2 (m, 4, methines and methylene), 7.0–7.8 (m, 9, aromatic).

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[45] G. H. Posner, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1968; *Diss. Abstr.*, **29**, 1613B (1968).

[46] B. W. Erickson, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1970.

[47] (a) R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **44**, 45 (1966); (b) G. J. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, **87**, 2864 (1965); (c) J. F. King and B. Vig, *Can. J. Chem.*, **40**, 1023 (1962).

Anal. Calcd for $C_{18}H_{19}SO_2Cl$: C, 63.24; H, 5.93; S, 9.93; Cl, 10.98. Found: C, 63.43; H, 5.93; S, 10.00; Cl, 11.20.

In reaction of 2.00 mmol of sulfone **18** with 20 mmol of Li(n-Bu)$_2$Cu at 0° for 5 hr, 0.692 g of p-chlorophenyl 2-butyl-3-phenylbutyl sulfone was formed (95%): nmr ($CDCl_3$) δ 0.8–2.2 (m, 13, methyl, butyl, and methine protons), 2.7–3.1 (m, 3, sulfonyl methylene and benzylic methine), 6.7–7.6 (m, 9, aromatic).

p-Chlorophenyl 1-Octenyl Sulfone (19).—The reaction was carried out as in the general procedure, treating 1.00 mmol of sulfone **19** with 5 mmol of Li(CH_3)$_2$Cu for 4 hr at 0° to form 0.294 g of p-chlorophenyl 2-methyloctylsulfone (97%): nmr ($CDCl_3$) δ 0.87 (distorted t, 3, CH_3), 1.0–1.4 (m, d superimposed on m, 13, β-methyl and methylenes), 1.7–2.1 (m, 1, β-methine), 2.9–3.1 (m, 2, sulfonyl methylene), 7.55 and 7.92 (pair of d, J = 9 Hz, 4, aromatic).

In reaction of 1.00 mmol of sulfone **19** with 5 mmol of Li(n-Bu)$_2$Cu at 0° for 2 hr, 0.321 g of p-chlorophenyl 2-butyloctyl sulfone was formed (93%): nmr ($CDCl_3$) δ 0.87 (m, 6, methyl), 1.1–1.6 (m, 16, methylenes), 1.8–2.1 (m, 1, β-methine), 2.9–3.1 (broad d, J = 5.5 Hz, 2, sulfonyl methylene), 7.56 and 7.93 (pair of d, J = 9 Hz, 4, aromatic).

In reaction of 1.00 mmol of sulfone **19** with 10 mmol of Li(CH_3)$_2$Cu for 3 hr at 0°, followed by quenching with 50 mmol of CH_3I and stirring for 12 hr at 25° before work-up, 0.621 g of p-chlorophenyl 1,2-dimethyloctyl sulfone was formed (90%): nmr ($CDCl_3$) δ 0.7–1.4 (m, 19, methylenes and methyls), 1.7–2.2 (m, 1, β-methine), 2.9–3.1 (m, 1, α-methine), 7.3–7.9 (m, 4, aromatic).

In reaction of 2.00 mmol of sulfone **19** with 10 mmol of Li(CH_3)$_2$Cu for 3 hr at 0°, followed by quenching with 1.0 ml of D_2O, and stirring at 25° for 1 hr before work-up, 0.551 g of p-chlorophenyl 2-methyloctyl sulfone was formed with 95% d_1 and 5% d_2, as characterized by nmr ($CDCl_3$): δ 0.84 (distorted t, 3, methyl), 1.0–2.4 (d superimposed on broad s, 13, β-methyl and methylenes), 1.8–2.2 (m, 1, β-methine), 2.8–3.1 (m, 1, sulfonyl methine), 7.42 and 7.76 (pair of d, J = 8 Hz, 4, aromatic).

p-Chlorophenyl 2-(3-Ethoxycarbonylcyclohexyl)ethenyl Sulfone (20).—The reaction was carried out as in the general procedure, treating 5.00 mmol of sulfone **20** with 25 mmol of Li(CH_3)$_2$Cu at 0° for 3 hr, to form 1.673 g of p-chlorophenyl 2-(3-ethoxycarbonylcyclohexyl)propyl sulfone (90%). The crude product was purified by column chromatography over F-1 alumina to give 1.020 g of the pure sulfone (55%): nmr ($CDCl_3$) δ 0.8–2.8 (m, 17, cyclohexyl and methyl), 2.9–3.2 (m, 2, sulfonyl methylene), 3.5–3.7 (m, 1, methine α to ester), 4.0–4.3 (split q, 2, OCH_2), 7.56 and 7.88 (pair of d, J = 8 Hz, 4, aromatic); ir ($CHCl_3$) 1730 (C=O), 1155 and 1090 cm^{-1} (SO_2).

In reaction of 2.00 mmol of sulfone **20** with 10 mmol of Li(n-Bu)$_2$Cu for 2 hr at 0°, 0.792 g of p-chlorophenyl 2-(3-ethoxycarbonylcyclohexyl)hexyl sulfone was formed (97%): nmr ($CDCl_3$) δ 0.8–2.8 (m, 23, cyclohexyl and n-butyl protons), 2.9–3.2 (m, 2, sulfonyl methylene), 3.5–3.7 (m, 1, methine α to ester), 4.0–4.3 (split q, 2, OCH_2), 7.55 and 7.90 (pair of d, J = 8 Hz, 4, aromatic).

p-Chlorophenyl 2-Methyl-1-propenyl Sulfone (21).—The reaction was carried out as in the general procedure, treating 1.00 mmol of sulfone **21** with 10 mmol of Li(CH_3)$_2$Cu for 5 hr at 0°, to give 0.225 g of colorless semisolid, which was shown to be p-chlorophenyl neopentyl sulfone (72%): nmr ($CDCl_3$) δ 1.20 (s, 9, t-Bu), 3.05 (s, 2, CH_2), 7.57 and 7.92 (pair of d's, J = 9 Hz, 4, aromatic); recrystallization from ethanol gave mp 142–145°; ir ($CHCl_3$) 1340 (CH_3 bend), 1155 and 1090 (SO_2), 1015, 910 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 246 (4.6), 177 (11), 159 (18), 111 (22), 71 (100).

In reaction of 4.00 mmol of sulfone **21** with 20 mmol of Li(n-Bu)$_2$Cu for 2 hr at 0°, 1.155 g of p-chlorophenyl 2,2-dimethylhexyl sulfone was formed (100%): nmr ($CDCl_3$) δ 0.88 (distorted t, 3, CH_3), 1.18 (s, 6, *gem*-dimethyl), 1.1–1.6 (m, 6, methylenes), 3.05 (s, 2, sulfonyl methylene), 7.57 and 7.92 (pair of d's, J = 9 Hz, 4, aromatic); ir ($CHCl_3$) 1340 (CH_3 bend), 1155 and 1090 (SO_2), 1015 cm^{-1}.

p-Chlorophenyl Cyclohexylidenemethyl Sulfone (22).—The reactions were carried out with 1.00 mmol of sulfone **22** reacting with 10 mmol of Li(CH_3)$_2$Cu in the appropriate solvent, reacting for the times and temperatures listed in Table II. The yields were determined by multiplying the mass balance and the nmr yield (nmr yields were determined by integration). In quenching a reaction of 1.00 mmol of sulfone **22** after 72-hr reaction with 10 mmol of Li(CH_3)$_2$Cu at 25° by bubbling H_2S through the reaction mixture, 0.1220 g of crude product was obtained, which was found to be 60% pure by nmr ($CDCl_3$), having a singlet for the sulfonyl methylene at δ 3.07. The product could not be separated from the starting materials by tlc or vpc.

Reactions of 1.00 mmol of sulfone **22** with 10 mmol of Li(n-Bu)$_2$Cu formed in the appropriate solvent were carried out as in the general procedure, at the times and temperatures shown in Table II. Yields were determined by multiplying mass balance and nmr (integration) yield. Treating 5.0 mmol of sulfone **22** with 50 mmol of Li(n-Bu)$_2$Cu in toluene for 2 hr at −20°, then 5 hr at 0°, 1.482 g of crude p-chlorophenyl (1-butylcyclohexyl)methyl sulfone were obtained, which was 50% pure. Purification by preparative tlc over silica gel gave pure butylated sulfone: nmr ($CDCl_3$) δ 0.90 (distorted t, J = 5 Hz, 3, methyl), 1.1–1.8 (m, 16, methylenes), 3.04 (s, 2, sulfonyl methylene), 7.42 and 7.78 (pair of d, J = 9 Hz, 4, aromatic).

In reaction of 1.00 mmol of sulfone **22** with 10 mmol of MeLi for 3 hr at 25°, starting material was recovered (95%), identified by nmr.

In reaction of 1.00 mmol of sulfone **22** with 10 mmol of 1:1 MeLi–tetramethylenediamine for 3 hr at 25°, 0.244 g of liquid were obtained, which was identified by nmr as a mixture of 50% p-chlorophenyl 1-cyclohexenemethyl sulfone (**27**) and 35% starting sulfone **22** (CH_2SO_2 at δ 3.72, vinyl proton at δ 5.40).

p-Chlorophenyl 2-Methyl-1-heptenyl Sulfone (23).—The reaction was carried out as in the general procedure, treating 1.00 mmol of sulfone **23** with 10 mmol of Li(CH_3)$_2$Cu at 0° for 12 hr, then at 25° for 12 hr before work-up, to give 0.293 g of crude product. The nmr spectrum ($CDCl_3$) indicated that p-chlorophenyl 2,2-dimethylheptyl sulfone had been formed (50%), and starting material recovered (25%); methylated sulfone was evident from a large singlet at δ 1.17 (*gem*-dimethyl) and a smaller singlet at δ 3.06 (CH_2SO_2). The product could not be separated from the starting material by tlc or vpc.

p-Chlorophenyl 2-Norbornylidenemethyl Sulfone (24).—The reactions were carried out as in the general procedure, treating 1.00 mmol of sulfone **24** with 10 mmol of Li(CH_3)$_2$Cu for 24 hr at 25°, or with 10 mmol of Li(n-Bu)$_2$Cu for 5 hr at 0°, to give 0.080 and 0.154 g of crude products, respectively. The nmr spectra of the products showed that the desired reaction had not occurred from the absence of the expected singlet at δ ~3 for CH_2SO_2; starting material was not recovered from the reactions.

Cyclohexylidenemethyl p-Fluorophenyl Sulfone.—The reactions were carried out as in the general procedure, treating 1.00 mmol of the p-fluorophenyl sulfone with 10 mmol of Li(CH_3)$_2$Cu at 0° for 5 hr, or with 10 mmol of Li(n-Bu)$_2$Cu at 0° for 2 hr. The nmr spectra of the crude products showed 95 and 80% starting material recovery, respectively.

General Procedure for Sodium Amalgam Reductions of Alkyl Aryl Sulfones.—To 5.0 g of 6% sodium amalgam in a round-bottom flask were added 1.00 mmol of alkyl aryl sulfone in 20 ml of anhydrous ethanol, and the mixture was stirred and refluxed for 4–20 hr. At that time, the solution was washed with 30 ml of 3% NaOH and extracted with three 20-ml portions of pentane, and the combined pentane layers were washed twice with 20-ml portions of H_2O. After drying ($MgSO_4$), an aliquot was removed for vpc analysis to give yields listed in Table III, and the remainder of solution was evaporated to give crude products, which were identified by nmr, ir, and mass spectra. Boiling points and refractive indices were obtained after purification by bulb-to-bulb distillation or preparative vpc (column E).

Acknowledgment.—We thank the National Science Foundation for financial support (GP-33667) and Mr. K. Chang for technical assistance.

Registry No.—**1**, 40582-68-1; **6**, 40582-69-2; **7**, 37891-71-7; **8**, 40582-71-6; **9**, 40582-72-7; **10**, 40582-73-8; **12**, 15436-11-0; **13**, 35324-47-1; **17**, 16215-12-6; **18**, 40582-76-1; **19**, 35324-49-3; **20**, 40582-78-3; **21**, 40582-79-4; **22**, 35324-50-6; **23**, 40582-81-8; **24**, 40582-82-9; **26a**, 40582-85-2; **26b**, 40582-86-3; **27**, 40582-83-0; **28**, 40137-12-0; CH_3Li, 917-54-4; CH_3Cu, 1184-53-8; (CH_3)$_2$CuLi, 15681-48-8; CH_3Li–TMED, 39296-37-2; (n-Bu)$_2$CuLi, 24406-16-4; heptanal, 111-71-7; 2-trimethylsilyl-1,3-dithiane, 13411-42-2; dimethyl 1-octenyl sulfonium, fluorosulfonate, 40582-98-7; methyl fluorosulfonate, 421-20-5; 2-phenylpropionaldehyde, 3805-10-5; 3-ethoxycarbonylcyclohexanecarboxaldehyde, 40582-99-8; 2-heptanone, 110-43-0;

2-norbornanone, 497-38-1; cyclohexylidenemethyl *p*-fluorophenyl sulfone, 40583-00-4; chloromethyl *p*-fluorophenyl sulfide, 459-27-8; cyclohexanone, 108-94-1; methyl 2-butyloctyl sulfone, 40583-02-6; *p*-chlorophenyl 1,2-dimethyloctyl sulfone, 40583-03-7; *p*-chlorophenyl 2-(3-ethoxycarbonylcyclohexyl)propyl sulfone, 40583-04-8; *p*-chlorophenyl 2-(3-ethoxycarbonylcyclohexyl)hexyl sulfone, 40583-05-9; *p*-chlorophenyl neopentyl sulfone, 40583-06-0.

Asymmetric Additions of Organolithium Reagents to Allylic Alcohols

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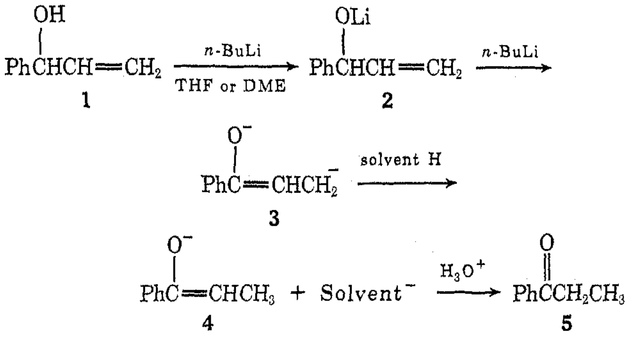
Received March 15, 1973

The reaction of α-vinylbenzyl alcohol (**1**) with *n*-butyllithium in hexane–TMEDA affords 1-phenyl-2-methyl-1-hexanol (**6**) and 5-benzyldecane (**7**) in an 3:1 ratio. The hydroxyl group in **1** induces the *n*-butyllithium to attack the double bond in a highly stereospecific manner, such that only one pair of enantiomers (**6a** and **6b**) are formed from **1** (*dl*). Addition to the double bond of **1** is also observed with *tert*-butyllithium except that in this case the addition is exclusively to the terminal end of olefin. The corresponding methyl ether of α-vinylbenzyl alcohol (**12**) does not react with *n*-butyllithium in an addition manner, but rather undergoes 1,2 and 1,4 Wittig rearrangements.

The reaction of 2 equiv of *n*-butyllithium in hexane–THF or hexane–DME (dimethoxyethane) with α-vinylbenzyl alcohol (**1**) gives a good yield of propiophenone (**5**).[1] The mechanism of this rearrangement has been established to be that shown in Scheme I.

SCHEME I



The dianion intermediate **3** never reaches a large concentration, because, soon after it forms, it abstracts a proton from the solvent. Organic dianions have proven to be useful synthetic intermediates;[2] consequently, we sought ways to increase the effective yield of this highly reactive species and possibly others like it.

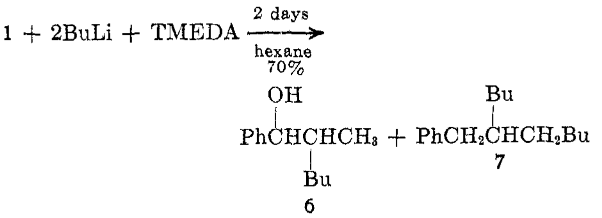
An ideal solvent for running these reactions would be pure hexane, since it has no acidic hydrogens; however, *n*-butyllithium loses much of its metalation powers in nonoxygenated solvents.[3] Thus, it was not surprising to find that α-vinylbenzyl alcohol was recovered "unchanged" when treated with excess *n*-butyllithium in pure hexane. Since tertiary amines are known[3,4] to enhance the reactivity of alkyllithium compounds, we repeated the later reaction in the presence of $N,N,$-N^1,N^1-tetramethylethylenediamine (TMEDA) and found that a completely different reaction had occurred—the butyllithium added to the double bond.

Although one would not normally expect an electron-rich organometallic reagent to add to nonconjugated olefins, there are several reported cases that this kind of reaction can occur.[5] Most of the reported organometallic additions to olefins have involved allylic alcohols. There appears to be a complex formed between lithium alkoxides and alkyllithium reagents which can subsequently deliver the RLi to an adjacent olefin in an intramolecular fashion. It is known that the solubility of lithium butoxide in *n*-heptane increases proportionately with increasing *n*-butyllithium concentration.[6] This suggests that a complex is formed between butoxide and lithium alkyl by the interaction of an oxygen unshared electron pair with a vacant hybridized orbital of lithium.[6,7]

The role that TMEDA plays is not clear. Some organolithium additions to allylic alcohols are known to occur in the absence of this reagent. It seems reasonable that the increased reactivity of organolithium reagents in the presence of TMEDA is due to complexation of the lithium atom with one or more amine sites.[8] Since the TMEDA does not interfere with addition of RLi to the allylic alkoxide, the alkoxide must either join with TMEDA to give a tetrahedral complex of the RLi or displace one of the amino groups of the bidentate ligand.

Results

The reaction of 2 equiv of *n*-butyllithium with 1 equiv of α-vinylbenzyl alcohol in hexane in the presence of 1–4 equiv of TMEDA for 2 days produced a 70% yield of three products: 1-phenyl-2-methyl-1-hexanol (**6**), 68%, 5-benzyldecane (**7**), 22%, and an unidentified component, 10%. When only 0.5 equiv of TMEDA was used over a reaction period of 1 day, the yield



$$\mathbf{1} + 2\text{BuLi} + \text{TMEDA} \xrightarrow[\text{hexane}\ 70\%]{\text{2 days}} \underset{\mathbf{6}}{\text{PhCH(OH)CH(Bu)CH}_3} + \underset{\mathbf{7}}{\text{PhCH}_2\text{CH(Bu)CH}_2\text{Bu}} \quad (1)$$

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