comparison of the areas under their emission curves with those of the standard.

Acknowledgment. This research was generously supported by funds from the Kansas Commission on Advanced Technology and Oread Laboratories, Inc.

Registry No. **3**, 7149-49-7; **3** (2,3-diacid), 2169-87-1; **3** (2,3-dialcohol), 31554-15-1; **4**, 103836-27-7; **4** (bis(diethyl acetal)), 103836-43-7; **5**, 103836-28-8; **5** (bis(diethyl acetal)), 103836-44-8; **6a**, 103851-02-1; **6b**, 103851-03-2; **7a**, 103836-29-9; **7b**, 103836-30-2; **7c**, 103836-31-3; **7d**, 103836-32-4; **7e**, 103836-33-5; (±)-**7f**, 103851-04-3; (±)-**7g**, 103836-34-6; **7h**, 103836-35-7; **7i**, 103836-36-8; D,D-**7j**, 103836-37-9; D,D-**7k**, 103836-38-0; **8a**, 103836-39-1; **8b**, 103836-40-4; **9a**, 103836-41-5; **9b**, 103836-42-6; 2-$Br_2CHC_6H_4CHBr_2$, 13209-15-9; $(H_3C)_3CNH_2$, 75-64-9; $(H_3C)_3CSH$, 75-66-1; $H_3C(CH_2)_2NH_2$, 107-10-8; EtOH, 64-17-5; CH_2O, 50-00-0; $H_3C(CH_2)_3NH_2$, 109-73-9; maleic anhydride, 108-31-6; glycine, 56-40-6; DL-alanine, 302-72-7; glycylglycine, 556-50-3; D-alanyl-D-alanine, 923-16-0; 1-cyano-2H-benz[*f*]isoindole, 103836-45-9.

A Comparison of the Reactions of [(Phenylthio)(trimethylsilyl)methyl]lithium with α,β-Unsaturated Ketones and Those of Other Acyl Anion Equivalents Containing Sulfur[1]

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The factors influencing the site of attack of [(phenylthio)(trimethylsilyl)methyl]lithium (1) with enones were investigated. Cyclohexenone (2) was chosen as a model compound, and conjugate addition occurred in THF–HMPA or DME; this mode of addition was also promoted by a potassium counterion. When the reaction was carried out with other enones, conjugate addition in THF–HMPA or DME was only observed if the β-position or the α,β-unsaturated ketone was not disubstituted. 1,4-Addition of 1 could be accomplished by preparation of the cuprate. The use of this approach was illustrated by a preparation of 4,4-dimethylcyclopent-2-en-1-one (**28**). For determination of the influence of DME on the regiochemical control of the addition of other sulfur-containing anions to enones, the study was extended to the anions derived from 1,3-dithian (**29**), bis(phenylthio)methane (**30**), bis(phenylthio)(trimethylsilyl)methane (**35**), and bis(trimethylsilyl)(phenylthio)methane (**36**). With these anions, DME did not promote conjugate addition to any significant extent.

α-Silyl sulfides have been used as formyl anion equivalents for the preparation of aldehydes.[2] The utility of these α-silyl sulfides has been expanded to the synthesis of alkenes[3] and ketones.[4] The observation that [(phenylthio)(trimethylsilyl)methyl]lithium (1) added in a 1,4-manner to cyclohexenone (2), when 1,2-dimethoxyethane (DME) was used as the solvent,[5] prompted us to investigate the general application of these reaction conditions. Indeed, the conjugate addition of formyl and acyl anion equivalents to α,β-unsaturated carbonyl compounds (Scheme I) has been the subject of many investigations as the products,[6-8] 1,4-dicarbonyl compounds, are extremely useful synthetic intermediates.

Scheme I

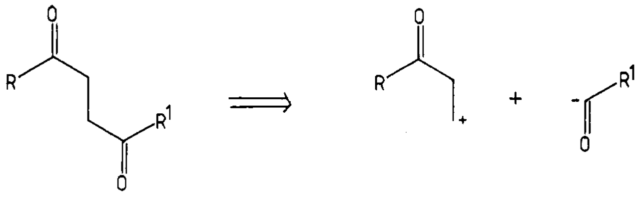

Table I. Reactions of [(Phenylthio)(trimethylsilyl)methyl]lithium (1) with Cyclohexenone (2) in Various Solvents with Temperature Variations

			yields,[a] %		
entry	solv	temp, °C	recovered (3)	1,2-addn (6)	1,4-addn (7)
1	THF	rt[b]	10	90	0[c]
2		0	10	90	0
3		−23	15	75	10
4		−78	10	80	10
5	DME	rt[b]	28	0	72
6		0	26	0	74
7		−23	30	0	70
8		−78	36	0	64
9	Et_2O	rt[b]	65	35	0
10		0	55	45	0
11		−23	70	30	0
12		−78	56	44	0
13	hexane	0	100	0	0

[a] By NMR and confirmed by GLC.[12] [b] Room temperature. [c] None detected, i.e., <5%.

In addition to defining the scope and limitations of DME

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[1] Parts of this work were carried out at the University of Southampton, for which an SRC postdoctoral fellowship is gratefully acknowledged, and the University of Liverpool.

[2] Kocienski, P. J. *Tetrahedron Lett.* **1980**, *21*, 1559. Ager, D. J.; Cookson, R. C. *Tetrahedron Lett.* **1980**, *21*, 1677. Ager, D. J. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1131.

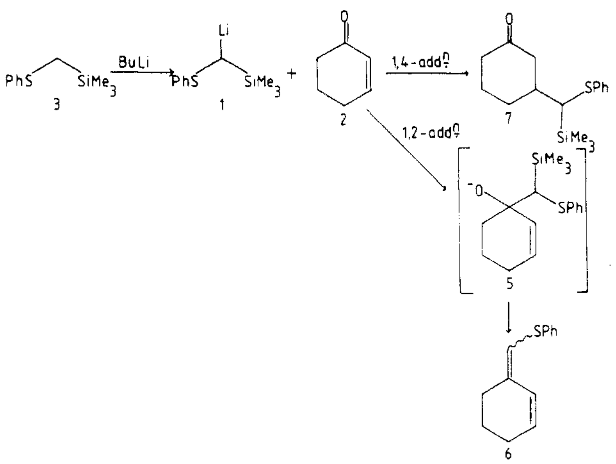
[3] Ager, D. J. *Tetrahedron Lett.* **1981**, *22*, 2923. Cohen, T.; Sherbine, J. P.; Matz, J. R.; Hutchings, R. R.; McHenry, B. M.; Willey, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 3245. Ager, D. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 183.

[4] Ager, D. J. *Chem. Soc. Rev.* **1982**, *11*, 493. Ager, D. J. *Tetrahedron Lett.* **1980**, *21*, 4759. Ager, D. J. *Tetrahedron Lett.* **1983**, *24*, 95. Ager, D. J. *J. Chem. Soc., Chem. Commun.* **1984**, 486. Ager, D. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 195.

[5] Ager, D. J. *Tetrahedron Lett.* **1981**, *22*, 2803.

[6] (a) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231. (b) Meyers, A. I.; Brinkmeyer, R. S. *Tetrahedron Lett.* **1975**, 1749. (c) Seebach, D.; Kolb, M.; Grobel, B.-T. *Chem. Ber.* **1973**, *106*, 2277. (d) Rustemeier, K.; Breitmaier, E. *Chem. Ber.* **1982**, *115*, 3898. (e) Seebach, D. *Synthesis* **1969**, 17. (f) Rao, A. V. R.; Venkatswamy, G.; Javeed, M.; Deshpande, V. H.; Rao, B. R. *J. Org. Chem.* **1983**, *48*, 1552. (g) Corey, E. J.; Crouse, D. *J. Org. Chem.* **1968**, *33*, 298. (h) Blumbach, J.; Hammond, D. A.; Whiting, D. A. *Tetrahedron Lett.* **1982**, *23*, 3949. (i) Mukaiyama, T.; Narasaka, K.; Furusato, M. *J. Am. Chem. Soc.* **1972**, *94*, 8641. (j) Seebach, D.; Burstinghaus, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 57. (k) Burstinghaus, R.; Seebach, D. *Chem. Ber.* **1977**, *110*, 841.

Scheme II



for the promotion of conjugate additions with the formyl anion equivalent **1** and α,β-unsaturated ketones, the use of this solvent to achieve similar regioselectivity with other sulfur-containing formyl and acyl anion equivalents was also a goal for this investigation. This aspect of the work arose from Krief's comprehensive review,[9] in which the use of DME as a solvent to provide 1,4-addition is cited in only three cases: 1-lithio-1,1-bis(methylseleno)ethane with cyclohexenone (**2**)[7c] and the lithium enolate of methyl bis(ethylthio)acetate with **2** and methyl vinyl ketone.[10]

The major factors which can affect the regiochemical outcome of the reaction of a nucleophile with an enone are (a) metal counterion, (b) temperature, (c) substitution on the anion, (d) stabilizing effects of these substituents, (e) nature of the anion, and (f) solvent.[9,11] The nature of the enone can also play a role in determining the mode of addition. In this investigation, an attempt was made to vary only one of the factors in any particular experiment so that trends and variations were readily apparent.

Reaction of [(Phenylthio)(trimethylsilyl)methyl]lithium (1) with Cyclohexenone (2). The results of the reaction, under a wide variety of conditions, are summarized in Table I. The amount of starting material recovered, in this case (phenylthio)(trimethylsilyl)methane (**3**), has been included in the tables, to indicate whether the anion was tending to act as a base rather than a nucleophile.[12]

The presence of the silyl group within the anion **1**, modified the overall reaction outcome when 1,2-addition occurred. The β-silyl alkoxide **5** eliminated, under the reaction conditions, to produce a mixture of the *E*- and *Z*-unsaturated sulfides.[13]

With other nucleophiles, it has been noted that the 1,2-adduct can, under strongly basic conditions, isomerize to the thermodynamically more stable 1,4-isomer.[8] The reaction was worked up after a variety of time periods (5, 10, 15, 30, 60, or 120 min) to determine if this was occurring when **1** was condensed with **2**. Even under a wide variety of reaction conditions, the product ratio was found to be invarient from that given in Table I. The observations suggest that an equilibrium does not exist between the 1,2- and 1,4-adducts and the elimination to **6** must be more rapid than any isomerization.

In THF, 1,2-addition was the only mode of attack observed, as noted in previous investigations.[5,14] When ether was used as solvent, the same regioselectivity was observed but the yields were markedly decreased due to incomplete anion formation.[2] By contrast, DME led to the 1,4-adduct **7** exclusively. Thus, the effect of solvent on the reaction of **1** with **2** is very dramatic. It should be noted that 1-butylcyclohex-2-en-1-ol (**4**) was the sole product in hexane, as deprotonation of **3** does not occur under these conditions.

Variations in temperature had little, or no effect on the major reaction pathway observed in any of the solvents used.

Additives have been shown to change the mode of addition with other formyl anion equivalents.[7] The effects of additives on the regiochemical outcome of the condensation of the α-silyl anion **1** and the enone **2** are summarized in Table II.

Although a small amount of 1,4-addition was observed in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), with THF as the solvent, 1,2-addition was still the major pathway. The product distribution did not vary whether the anion was prepared in THF and then TMEDA added or whether it was prepared in TMEDA–hexane and then diluted with THF.[15]

By contrast, hexamethylphosphoric triamide (HMPA) in THF-promoted conjugate addition, in a manner previously observed with other sulfur-containing anions.[7] A small, but detectable, amount of 1,2-addition also occurred under these conditions. Variations in temperature had very little effect on the product distribution, although slightly higher, overall yields were observed at lower temperatures.

Although diazabicyclo[2.2.2]octane (Dabco) led to the conjugate addition product **7**, the yield was low and the major reaction pathway seemed to be deprotonation of the enone.[16] In a similar manner, pyridine had little effect

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(7) (a) Brown, C. A.; Yamaichi, A. *J. Chem. Soc., Chem. Commun.* **1979**, 100. (b) Vedejs, E.; Nader, B. *J. Org. Chem.* **1982**, *47*, 3193. (c) Lucchetti, J.; Dumont, W.; Krief, A. *Tetrahedron Lett.* **1979**, 2695. (d) Wartski, L.; El-Bouz, M. *Tetrahedron* **1982**, *38*, 3285. (e) El-Bouz, M.; Wartski, L. *Tetrahedron Lett.* **1980**, *21*, 2897. (f) Lucchetti, J.; Krief, A. *Organomet. Chem.* **1980**, *194*, C49. Dumont, W.; Lucchetti, J.; Kreif, A. *J. Chem. Soc., Chem. Commun.* **1983**, 66. (g) Seebach, D.; Locker, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 957. (h) Mpango, G. P.; Mahalanabis, K. K.; Mahdavi-Damghani, Z.; Snieckus, V. *Tetrahedron Lett.* **1980**, *21*, 4823. (i) Grotjahn, D. B.; Andersen, N. H. *J. Chem. Soc., Chem. Commun.* **1981**, 306. (j) Taschner, M. J.; Kraus, G. A. *J. Org. Chem.* **1978**, *43*, 4235. (k) Ziegler, F. E.; Schwartz, J. A. *J. Org. Chem.* **1978**, *43*, 985. (l) Ziegler, F. E.; Schwartz, J. A. *Tetrahedron Lett.* **1975**, 4643. (m) Tobin, P. S.; Basu, S. K.; Grosserode, R. S.; Wheeler, D. M. S. *J. Org. Chem.* **1980**, *45*, 1250. (n) Grosserode, R. S.; Tobin, P. S.; Wheeler, D. M. S. *Synth. Commun.* **1976**, *6*, 377. (o) Mpango, G. P.; Snieckus, V. *Tetrahedron Lett.* **1980**, *21*, 4827. (p) Lucchetti, J.; Krief, A. *Synth. Commun.* **1983**, *13*, 1153.

(8) (a) Wilson, S. R.; Misra, R. N.; Georgiadis, G. M. *J. Org. Chem.* **1980**, *45*, 2460. (b) Ostrowski, P. C.; Kane, V. V. *Tetrahedron Lett.* **1977**, 3549. (c) Wilson, S. R.; Misra, R. N. *J. Org. Chem.* **1978**, *43*, 4903. (d) Lucchetti, J.; Krief, A. *J. Chem. Soc., Chem. Commun.* **1982**, 127.

(9) Krief, A. *Tetrahedron* **1980**, *36*, 2531.

(10) Gregge, R. J.; Herrman, J. L.; Richman, J. E.; Romanet, R. F.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2599.

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(12) Deprotonation was essentially complete, except in ether (see ref 2). When deprotonation was not quantitative, 1-butylcyclohex-2-en-1-ol (**4**) was formed as a byproduct. This byproduct, on occasions, complicated interpretation of the NMR spectra; product distributions were confirmed by GLC analysis (±5% of NMR results). The spectra of the individual products were obtained by isolation—see Experimental Section.

(13) In some experiments, the presence of a hydroxyl group was apparent from the IR spectrum. This was mainly due to the formation of **4** but, in some cases, may have arisen small amounts of the β-hydroxysilane. Rapid filtration through a short silica column effected removal of the hydroxyl absorption in the IR.

(14) Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 939.

(15) In all experiments, the hexane from the butyllithium solution was not removed (see Experimental Section).

Table II. Reactions of 1 with 2 in the Presence of Various Additives

				yield,[a] %		
entry	solv	additive	temp, °C	recovered (3)	1,2-addn (6)	1,4-addn (7)
1	THF	TMEDA	rt	8	87	5
2			0	21	71	8
3			−23	19	71	10
4		HMPA	rt	15	5	80
5			0	25	5	70
6			−23	10	5	85
7			−78	0	5	95
8		Dabco	rt	87	0[b]	13
9			0	62	0	38
10			−23	87	0	13
11			−78	90	0	10
12		pyr	rt	16	84	0
13			0	38	41	21
1j			−23	42	45	13
15			−78	34	41	25
16		KO-*t*-Bu	0[c]	52	0	10
17			−23[d]	5	0	5
18			−78[e]	14	5	64
19			−78⟹rt[f]	15	4	44
20		MgCl$_2$	rt	14	86	0
21	DME	TMEDA	rt	43	17	40
22			0	32	43	25
23			−23	45	9	46
24			−78	49	9	42
2k		HMPA	rt	35	0	65
26			0	29	0	71
27			−23	35	0	65
28			−78	35	0	65
29		Dabco	rt	76	24	0
30			0	83	17	0
31			−23	80	20	0
32		pvr	rt	26	30	44
33		KO-*t*-Bu	0[g]	0	0	17
34	Et$_2$O	TMEDA	0	18	82	0
35			−23	16	84	0
36			−78	7	93	0
37		HMPA	−23	10	4	81
38		KO-*t*-Bu	rt[h]	42	0	25
39			0[i]	70	0	25
40			−23[i]	60	20	15
41			−78[i]	50	40	6
42	C$_6$H$_{14}$	TMEDA	rt	19	81	0
43			0	24	76	0
44		HMPA	0[k]	13	0	18
45		Dabco	0	68	5	27
46		pvr	0	81	0	19
47		KO-*t*-Bu	0[l]	78	0	6

[a] By NMR and confirmed by GLC.[12] [b] None detected, i.e., <5%. [c] 38% Thioanisole (8) was also formed. If the enone 2 was added after 0.25 h, the ratio by 3:6:7:8 became 61:0:8:31. [d] 90% Thioanisole (8) was also formed. [e] 17% 7 also formed. If the enone 2 was added after 0.25 h, the ratio of 3:6:7:8 became 9:5:76:10. [f] Cold bath removed upon addition of 3. 37% 8 also formed. If the enone 2 was added after 0.25 h, the ratio of 3:6:7:8 became 23:5:54:18. [g] 83% 8 also formed. 2 was added after 0.5 h. [h] 33% 8 also formed. [i] 5% 8 also formed. [j] 4% 8 also formed. [k] 69% 8 also formed. [l] 16% 8 also formed.

on the regiochemical outcome of the addition, but the amount of recovered (phenylthio)(trimethylsilyl)methane (3) was increased significantly. These additives, Dabco and pyridine, are forming a complex with the organolithium 1 increasing its effective size and, thus, promoting 1 to react as a base rather than a nucleophile.

Potassium *tert*-butoxide was used to effect a change of counterion. As with other systems,[9] conjugate addition was promoted by the potassium ion, but desilylation became a competing pathway, particularly at higher temperatures. In these experiments, the potassium *tert*-butoxide was added prior to the *n*-butyllithium and further studies showed that the reactive anion was attacking the silyl group of 3, rather than deprotonating the methylene group. Desilylation of 3 leads to the anion of thioanisole which did not react with the enone 2 but was protonated upon workup to yield thioanisole (8).[17] Although this problem could be circumvented by the addition of potassium *tert*-butoxide to a solution of 1, variable product ratios were observed, presumably due to incomplete counterion exchange.

The addition of a magnesium salt did not promote formation of 7, and the 1,2-adduct 6 was the observed product.

When DME was used as the solvent, rather than THF, the same trends were followed for each additive, but the organolithium 1 had a greater tendency to act as a base.

With ether as solvent, TMEDA led to 1,2-addition, while HMPA gave conjugate addition. In these cases, the additive promoted deprotonation of 3 and was added con-

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[16] Anion formation was certainly complete as a deuterium oxide quench gave >90% of the deuterated analogue of 3.

[17] It is also possible that the anion of thioanisole reacted as a base with the solvent.

Table III. Reaction of 1 with Various Enones

					yield,[a] %		
entry	solv	additive	temp, °C	enone	**3**	1,2-adduct	1,4-adduct
1	THF	none	rt	**9**	29	71 ((**14**)	0[b]
2				**10**	5	95 (**15**)	0
3				**11**	15	85 (**16**)	0
4				**12**	0	100 (**20**)	0
5			0	**13**	10	90 (**21**)	0
6			−78	**9**	24	76 (**14**)	0
7				**10**	13	87 (**15**)	0
8				**11**	12	88 (**16**)	0
9				**12**	5	95 (**20**)	0
10		TMEDA	rt	**10**	0	100 (**15**)	0
11				**11**	20	80 (**16**)	0
12				**12**	5	95 (**20**)	0
13			0	**13**	5	95 (**21**)	0
14			−78	**9**	13	87 (**14**)	0
15				**10**	5	95 (**15**)	0
16		HMPA	rt	**9**	54	7 (**14**)	39 (**17**)
17				**10**	29	44 (**15**)	27 (**18**)
18				**11**	41	54 (**16**)	5 (**19**)
19				**12**	53	47 (**20**)	0
20				**13**	40	60 (**21**)	0
21			−78	**9**	29	51 (**14**)	20 (**17**)
22				**10**	37	29 (**15**)	34 (**18**)
23				**11**	47	48 (**16**)	5 (**19**)
24				**12**	46	54 (**17**)	0
25	DME	none	rt	**9**	57	11 (**14**)	32 (**17**)
26				**10**	0	60 (**15**)	40 (**18**)
27				**11**	33	63 (**16**)	4 (**19**)
28				**12**	50	50 (**20**)	0
29				**13**	5	95 (**21**)	0
30			−78	**9**	45	15 (**14**)	40 (**17**)
31			−78	**10**	10	57 (**15**)	33 (**18**)
32				**11**	14	64 (**16**)	12 (**19**)
33				**12**	48	52 (**20**)	0
34				**13**	54	46 (**21**)	0
35		TMEDA	0	**9**	37	49 (**14**)	14 (**17**)
36			−78	**9**	56	18 (**14**)	25 (**17**)
37		HMPA	0	**9**	38	16 (**14**)	46 (**17**)
38			−78	**9**	36	15 (**14**)	49 (**17**)

[a] By NMR.[12] [b] None detected.

currently with the base.[17] The use of potassium *tert*-butoxide resulted in significant amounts of recovered silane **3** which may be attributed to incomplete reaction through low solubility.

As deprotonation of (phenylthio)(trimethylsilyl)methane (**3**) cannot be accomplished in hexane (vide supra), the additives were used to aid this process. The highly basic TMEDA–hexane system led exclusively to the 1,2-adduct **6**. HMPA promoted attack of the butyllithium at silicon, rather than deprotonation, which resulted in the production of thioanisole (**8**) together with a small amount of the 1,4-adduct **7**.

The observations outlined above suggest that the reaction of [(phenylthio)(trimethylsilyl)methyl]lithium (**1**) with cyclohexenone (**2**) to provide **7** is under complexation control.[11] In an association-controlled reaction, there is a strong covalent bond between the nucleophile and the metal ion. Thus, hard metals, such as the alkalis, give rise to 1,2-addition because of favorable interactions with the hard carbonyl oxygen atom, whereas soft metals, such as copper, promote 1,4-addition (vide infra). With complexation control, there is a "loose" ion pair between the nucleophile and metal counterion. The formation of a complex between the metal ion and the carbonyl oxygen of the enone results in an increase of the orbital coefficients at the carbonyl carbon atom compared to the "free" enone—the effect is most pronounced with lithium—which promotes 1,2-addition, especially in ethereal solvents. In addition, a nucleophile with a low-energy HOMO, that is a hard anion,[19] leads to 1,2-addition, while a soft anion with a high-energy HOMO promotes 1,4-addition. With complexation control, a solvent (or additive) which strongly solvates the metal ion will promote conjugate addition as this would leave a free, uncomplexed oxygen on the enone. The regiochemistry observed with **1** and **2** is in accord with related systems[7] and suggests that the formation of **7** in DME is due to solvation of the lithium ion by this solvent.

With the affect of all the variants now established, attention turned to the problem of promoting conjugate addition with other enones.

Reactions of 1 with Other Enones. The enones used in this part of the study were but-3-en-2-one (**9**), pent-3-en-2-one (**10**), 4-methylpent-3-en-2-one (**11**), 3-methylcyclohex-2-en-1-one (**12**), and 3,5,5-trimethylcyclohex-2-en-1-one (**13**). The results have been collected in Table III.

As with cyclohexenone (**2**), TMEDA promoted 1,2-addition, while HMPA favored formation of the 1,4-adduct. However, the presence of a β-substituent on the α,β-unsaturated ketone hindered this mode of addition, and in the cases of the cyclic enones **12** and **13**, this pathway was totally inhibited. The product distribution with DME as solvent were similar to those obtained with THF. Variations in temperature gave no significant modification to the reaction outcome. Overall, the trends observed with

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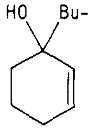
(18) If **1** was prepared in TMEDA–hexane and then diluted with ether prior to the addition of **2**, **6** was produced quantitatively.

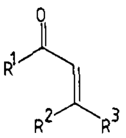
(19) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.



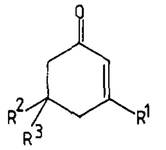
4

$C_6H_5SCH_3$

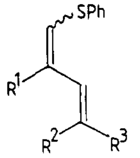
8



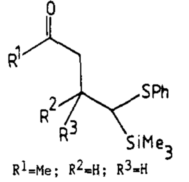
(9) R^1=Me; R^2=H; R^3=H
(10) R^1=Me; R^2=H; R^3=Me
(11) R^1=Me; R^2=Me; R^3=Me



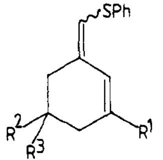
(2) R^1=H; R^2=H; R^3=H
(12) R^1=Me; R^2=H; R^3=H
(13) R^1=Me; R^2=Me; R^3=Me



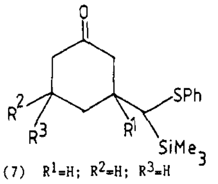
(14) R^1=Me; R^2=H; R^3=H
(15) R^1=Me; R^2=H; R^3=Me
(16) R^1=Me; R^2=Me; R^3=Me



(17) R^1=Me; R^2=H; R^3=H
(18) R^1=Me; R^2=H; R^3=Me
(19) R^1=Me; R^2=Me; R^3=Me



(6) R^1=H; R^2=H; R^3=H
(20) R^1=Me; R^2=H; R^3=H
(22) R^1=Me; R^2=Me; R^3=Me



(7) R^1=H; R^2=H; R^3=H
(21) R^1=Me; R^2=H; R^3=H
(23) R^1=Me; R^2=Me; R^3=Me

2 were followed, but the steric effects of a β-substituent on the enone promoted 1,2-addition in accord with previous studies.[9]

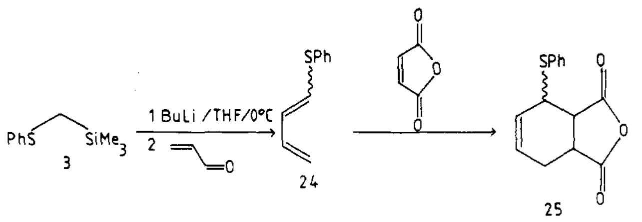
It is evident that DME acts in a very similar manner to THF–HMPA to promote 1,4-addition of **1**. The advantages of using DME, rather than HMPA for safety reasons and convenience, are readily apparent. However, the mode of addition does depend heavily upon the substitution on the enone.

1,2-Addition was promoted by a variety of reaction conditions and provides a useful method for the preparation of sulfur-substituted 1,3-dienes. An example of such a sequence is outlined in Scheme III. Reaction of (phenylthio) (trimethylsilyl)methane (**3**) with butyllithium in THF followed by acrolein gave 1-(phenylthio)-1,3-butadiene (**24**), which could be isolated (52%)[20] or treated directly with a dienophile to achieve the Diels–Alder reaction (41% for **25**).[21]

As with other systems, a simple change of solvent cannot be used to ensure conjugate addition of **1**, particularly with sterically congested enones. To achieve this goal, a cuprate had to be used.

Cuprate Additions of 1. The cuprate **26** was prepared by reaction of [(phenylthio)(trimethylsilyl)methyl]lithium (**1**) with 0.5 equiv of copper(I) iodide in THF at −78 °C for 1 h. These conditions were found to be optimum. Shorter reaction times, for the formation of the cuprate, resulted in an increase of the amount of 1,2-addition observed, while longer reaction times, or the use of higher temperatures, resulted in dimerization to yield 1,2-bis(phenylthio)-1,2-bis(trimethylsilyl)ethane (**27**). Indeed, when cuprate formation was attempted at −23 °C, the only reaction observed was dimerization.[22]

Scheme III



Scheme IV

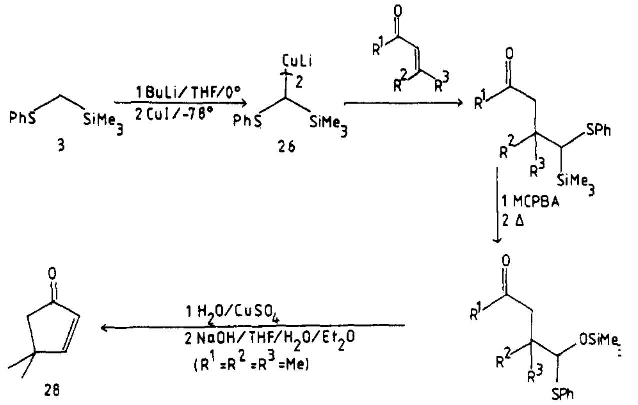


Table IV. Addition of [(Phenylthio)(trimethylsilyl)methyl]lithium (1) in THF to Enones in the Presence of Copper(I)

entry	enone	additive	3[b]	yield,[a] % 1,2-addn	yield,[a] % 1,4-addn	isolated yield of 1,4-adduct,[c] %
1	2	CuI	d			83
2		PhSCu	21	6	72 (7)	66
3	9	CuI	49	10 (14)	41 (17)	37
4	10	CuI	15	18 (15)	67 (18)	63
5	11	CuI	14	11 (16)	75 (19)	69
6	12	CuI	18	12 (20)	70 (22)	68
7		PhSCu	26	5 (20)	69 (22)	63
8	13	CuI	28	12 (21)	60 (23)	52

[a] By NMR. [b] When CuI was used, 1 equiv of **3** was isolated in addition to quantity shown. [c] After column chromoatography. [d] Not measured.

Use of the cuprate **26** resulted in a large increase in the yield of the 1,4-adduct with β-substituted α,β-unsaturated ketones (see Table IV). In an attempt to decrease the time required for the formation of **26**, the mixed cuprate derived from reaction of **1** with (phenylthio)copper[23] was prepared. However, the optimum yields were still obtained with relatively extended reaction times (0.75–1 h).

As 1,4-dicarbonyl compounds have proven useful for the preparation of 2-cyclopentenones by an Aldol reaction, the adduct **19** was converted to 4,4-dimethylcyclopent-2-en-1-one (**28**). The sulfide **19** was oxidized to the sulfoxide with *m*-chloroperoxybenzoic acid in dichloromethane. The sila-Pummerer rearrangement was achieved in THF under reflux to afford the *O*-(trimethylsilyl)(phenylthio)acetal, which was hydrolyzed to the aldehyde in the presence of copper(II).[2] The aldehyde was not isolated but was cyclized under basic conditions to the cyclopentenone **28**. If the carbon α to the aldehyde group was not fully substituted, attempted cyclization resulted in a complex mix-

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[20] Evans, D. A.; Bryan, L. A.; Sims, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 2891.

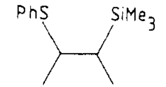
[21] Gundermann, K.-D.; Holtman, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 668.

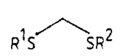
[22] For examples of dimerization with α-heterosubstituted organometallics promoted by copper(I) see: Muhaiyama, T.; Narasaka, K.; Furusato, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 652. Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *4*, 1077 and reference 9.

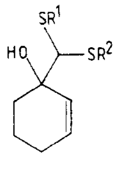
[23] Posner, G. H.; Brunelle, D. J.; Sinoway, L. *Synthesis* **1974**, 662.

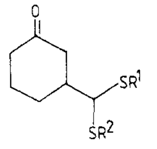
ture.[24] Although *O*-silylthioacetals can be hydrolyzed under basic conditions, such as those which effect cyclization, removal of the thiophenoxide is advantageous as this prevents subsequent reaction of this nucleophile with the enone product.

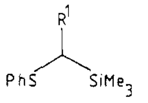
Reactions of Other Sulfur-Containing Anions with Cyclohexenone (2). The aim of this part of the study was to determine the affect of DME on the regioselectivity of the reaction of α-thioanions with enones. The two formyl anion equivalents employed were derived from 1,3-dithian (**29**) and bis(phenylthio)methane (**30**). Reaction with cyclohexenone (**2**) would then result in the 1,2-adducts **31** and **32** and/or the 1,4-adducts **33** and **34**, respectively. The other two anions used were obtained from bis(phenylthio)(trimethylsilyl)methane (**35**)[25] and bis(trimethylsilyl)(phenylthio)methane (**36**). In the case of 1,2-addition, the presence of the silyl moiety would be expected to provide the dienes **37** and **38** through a Peterson elimination, while 1,4-addition would yield the ketones **39** and **40**, respectively. The results are summarized in Table V.

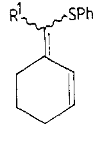

27

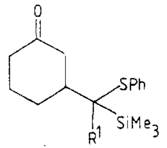

(29) $R^1,R^2=-(CH_2)_3-$
(30) $R^1=R^2=Ph$


(31) $R^1,R^2=-(CH_2)_3-$
(32) $R^1=R^2=Ph$


(33) $R^1,R^2=-(CH_2)_3-$
(34) $R^1=R^2=Ph$


(35) $R^1=SPh$
(36) $R^1=SiMe_3$


(37) $R^1=SPh$
(38) $R^1=SiMe_3$


(39) $R^1=SPh$
(40) $R^1=SiMe_3$

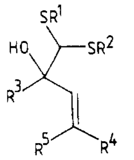
1,3-Dithian (**29**) preferred to undergo 1,2-addition, except when HMPA was used as additive.[7] DME did not promote conjugate addition with this anion.

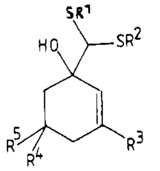
In contrast, some 1,4-addition was detected with [bis(phenylthio)methyl]lithium in THF. This mode of addition was increased significantly in THF–HMPA. When the reaction was carried out with THF/HMPA at -78 °C, only conjugate addition was observed (Table V, entry 18). However, when the reaction was quenched 5 min after the addition of the enone, a ratio for **32**:**34** of 17:83 was observed. This suggests that an equilibration mechanism between the kinetic 1,2- and thermodynamic 1,4-adducts is operating in this system.[8] With TMEDA as the additive, 1,2-addition was the preferred reaction pathway. When DME was used as solvent, both 1,2- and 1,4-addition were observed. Additives in this solvent gave the same trends seen with THF. For [bis(phenylthio)methyl]lithium, DME proved inferior to THF–HMPA for the promotion of conjugate addition.

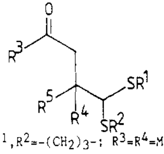
The greater tendency of the anion derived from **30** to provide 1,4-addition, when compared with 1,3-dithian (**29**), presumably arises from increased anion stability. The acyclic system of **30** allows rotation to optimize orbital overlap in the carbanion. In addition, there is increased stability of the charge buildup through the aromatic moieties. Thus, the lithium is more susceptible to complexation than for 2-lithio-1,3-dithiane with the solvent and additive, because of the increased carbanion stability, allowing conjugate addition to occur. The anion derived from **30** is larger than **29**; an increase in the size of the nucleophile promotes 4-addition.[9]

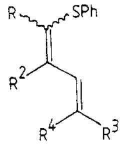
The trends of a larger and more stable nucleophile to favor conjugate addition were adequately illustrated with the organolithiums derived from **35** and **36**, where no 1,2-addition was observed, even in THF. The size of the anions did, however, lead to significant amounts of recovered sulfide through proton abstraction from the enone rather than nucleophilic attack. As conjugate addition was observed in THF, DME did not have a marked effect on the regiochemical outcome of these reactions.

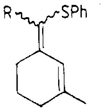
Reactions of Other Sulfur-Containing Anions with Other Enones. The number of examples was kept to a minimum as other studies have been conducted in this area, and the major aim was to determine the effect of DME on the regiochemical outcome of these reactions. The results of the additions are summarized in Table VI.

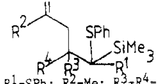

(41) $R^1,R^2=-(CH_2)_3-$; $R^3=Me$; $R^4=R^5=H$
(42) $R^1,R^2=-(CH_2)_3-$; $R^3=R^4=Me$; $R^5=H$
(43) $R^1,R^2=-(CH_2)_3-$; $R^3=R^4=R^5=Me$
(47) $R^1=R^2=Ph$; $R^3=Me$; $R^4=R^5=H$
(48) $R^1=R^2=Ph$; $R^3=R^4=Me$; $R^5=H$
(49) $R^1=R^2=Ph$; $R^3=R^4=R^5=Me$


(44) $R^1,R^2=-(CH_2)_3-$; $R^3=Me$; $R^4=R^5=H$
(45) $R^1,R^2=-(CH_2)_3-$; $R^3=R^4=R^5=Me$
(50) $R^1=R^2=Ph$; $R^3=Me$; $R^4=R^5=H$
(51) $R^1=R^2=Ph$; $R^3=R^4=R^5=Me$


(46) $R^1,R^2=-(CH_2)_3-$; $R^3=R^4=Me$; $R^5=H$
(52) $R^1=R^2=Ph$; $R^3=Me$; $R^4=R^5=H$
(53) $R^1=R^2-Ph$; $R^3=R^4=Me$; R^5-H


(54) $R^1=SPh$; $R^2=Me$; $R^3=R^4=H$
(55) $R^1=SPh$; $R^2=R^3=Me$; $R^4=H$
(59) $R^1=SiMe_3$; $R^2=R^3=Me$; $R^4=H$
(60) $R^1=SiMe_3$; $R^2=R^3=R^4=Me$


(56) $R^1=SPh$
(61) $R^1=SiMe_3$


(57) $R^1=SPh$; $R^2=Me$; $R^3=R^4=H$
(58) $R^1=SPh$; $R^2=R^3=Me$; $R^4=H$
(62) $R^1=SiMe_3$; $R^2=Me$; $R^3=R^4=H$
(63) $R^1=SiMe_3$; $R^2=R^3=Me$; $R^4=H$
(64) $R^1=SiMe_3$; $R^2=R^3=R^4=Me$

In THF, and the absence of additives, the disubstituted nucleophiles formed from **29** and **30** underwent 1,2-addition exclusively. When a third anion-stabilizing group was present, **35** and **36**, conjugate addition was the favored reaction pathway with acyclic enones. For example, no diene **54** could be detected from the condensation of the organolithium derived from **35** with **9**. With β-substituted cyclic enones, the trisubstituted enones led to 1,2-addition, which, because of the presence of the silyl group, eliminated to give the substituted diene as the final product. Direct attack of the nucleophile on the carbonyl carbon atom is, presumably, a direct result of the steric congestion at the β-position of the enone and the large size of the organolithium. The preference for **35** and **36** to add in a conjugate manner with acyclic enones is a reflection of the stability of the carbanions and their size. Temperature variations had little effect on the regiochemical outcome of any of the reactions conducted in THF.

When DME was employed as solvent, 1,3-dithian (**29**) still preferred the 1,2-addition mode, although a small

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(24) Cf.: Cavill, G. W. K.; Goodrich, B. S.; Laing, D. G. *Aust. J. Chem.* **1970**, *23*, 83.

(25) The cuprate derived from **35** has been used to accomplish 1,4-additions. Cohen, T.; Nolan, S. M. *Tetrahedron Lett.* **1978**, 3533.

Table V. Reactions of α-Thiocarbanions with Cyclohexenone (2)

					yield,[a] %		
entry	solv	additive	temp, °C	sulfide	recovered sulfide	1,2-aedduct	1,4-adduct
1	THF	none	rt	**29**	0	100 (**31**)	0
2				**30**	0	65 (**32**)	35 (**34**)
3				**35**	39	0	61 (**39**)
4				**36**	53	0	47 (**40**)
5			0	**30**	6	63 (**32**)	31 (**34**)
6			−78	**30**	0	72 (**32**)	28 (**34**)
7				**36**	37	0	63 (**40**)
8		TMEDA	rt	**29**	0	100 (**31**)	0
9				**30**	10	81 (**32**)	9 (**34**)
10			0	**30**	15	80 (**32**)	5 (**34**)
11			−78	**29**	0	100 (**31**)	0
12				**30**	10	77 (**32**)	13 (**34**)
13		HMPA	rt	**29**	16	26 (**31**)	58 (**33**)
14				**30**	20	0	80 (**34**)
15				**35**	34	0	66 (**34**)
16				**36**	29	0	71 (**40**)
17			0	**30**	0	5 (**32**)	95 (**34**)
18			−78	**30**	10	0	90 (**34**)
19	DME	none	rt	**29**	30	70 (**31**)	0
20				**30**	0	60 (**32**)	40 (**34**)
21				**35**	50	0	50 (**39**)
22				**36**	57	0	43 (**40**)
23			0	**30**	15	50 (**32**)	35 (**34**)
24			−78	**29**	31	69 (**31**)	0
25				**30**	5	50 (**32**)	45 (**34**)
26		TMEDA	rt	**30**	44	33 (**32**)	23 (**34**)
27			0	**30**	8	32 (**32**)	60 (**34**)
28			−78	**30**	23	12 (**32**)	65 (**34**)
29		HMPA	0	**30**	14	10 (**32**)	76 (**34**)
30		KOBu-*t*	0	**30**	76	0 (**32**)	24 (**34**)

[a] By NMR.

amount of the conjugate addition product **46** was detected when the reaction was performed at −78 °C (Table VI, entry 39). Bis(phenylthio)methane (**30**) provided small amounts of the 1,4-products with the enones **9** and **10**, which are not significantly hindered at the β-position. The major reaction pathway, however, was still direct attack of the organolithium at the carbonyl group. Variations in temperature proved invariant for determining the site of attack of the nucleophile on the enone.

In a similar manner, the change of solvent from THF to DME had no effect on the regiochemical outcome of the trisubstituted anions derived from **35** and **36**. The only dramatic affect of DME on the mode of addition of a nucleophile to an enone in this study was observed with [(phenylthio)(trimethylsilyl)methyl]lithium (**1**).

As stated above, the more stable an anion, the greater the tendency for conjugate addition to occur. This is clearly illustrated in Tables V and VI, where anions bearing three hetero groups preferred 1,4-addition, unless the β-position of the enone was sterically crowded. In addition, [bis(phenylthio)methyl]lithium showed a larger preference to undergo 1,4-addition than did 2-lithio-1,3-dithian. The phenyl substituents stabilize the anion derived from **30** by an inductive effect; they are, also, much larger in size than the methylenes of **29**. Both factors promoted conjugate addition. With the (phenylthio)(trimethylsilyl)methane (**3**) reactions, although the silyl group does stabilize an α-anion, the effect is not as large as for a sulfur group.[9] This effect is, however, offset by the increase in the relative size of the silyl group, compared to phenylthio, around the reaction center. Certainly, the interplay between electronic and steric factors in **1** is subtle, particularly as this anion reacts as a "hard" anion with alkyl halides.[2]

Overall, DME does not promote 1,4-addition of a sulfur-containing nucleophile to an enone, except under limited circumstances. With [(phenylthio)(trimethylsilyl)methyl]lithium (**1**), conjugate addition was observed in DME with enones not hindered at the β-position. The availability of the Peterson elimination from the 1,2-adduct, within this system, suggests that the 1,2- and 1,4-adducts are not in equilibrium.

Experimental Section

All reactions involving organometallic reagents were performed under an atmosphere of dry nitrogen. All ethereal solvents, tetrahydrofuran (THF), diethyl ether, and 1,2-dimethoxyethane (DME), were dried by distillation from sodium–benzophenone just prior to use. Petroleum ether refers to that fraction with boiling point 60–90 °C, which was distilled from phosphorus pentoxide and stored over 4A molecular sieve.

NMR spectra were obtained in deuteriochloroform solution at 90 or 220 MHz with tetramethylsilane as internal standard; if the molecule contained a silyl group, dichloromethane was used as the internal standard. Infrared spectra were recorded in chloroform solution.

Preparation of Starting Materials. 1,3-Dithian (**29**) was obtained from Aldrich Chemical Co. Bis(phenylthio)methane (**30**) was prepared from diiodomethane after the method of Corey.[26] (Phenylthio)(trimethylsilyl)methane (**3**) was prepared as previously described,[2] as were bis(phenylthio)(trimethylsilyl)methane (**35**) and bis(trimethylsilyl)(phenylthio)methane (**36**).[27]

General Procedure. Butyllithium (3.6 mL of a 1.4 M solution in hexane, 5 mmol) was added to the sulfide (5 mmol) in the reaction solvent (15 mL) at 0 °C. After 1 h, the reaction temperature was adjusted as necessary and any additives included (5 mmol; 2 mL of HMPA were used rather than 5 mmol). The enone (5 mmol) was added and the reaction mixture allowed to come to room temperature overnight. The mixture was poured into saturated aqueous ammonium chloride (25 mL) and extracted with ether (3 × 25 mL). The combined extracts were washed with 2 M sodium hydroxide (25 mL) and saturated sodium chloride solution (25 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The NMR spectrum of the product mixture was re-

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(26) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097.
(27) Ager, D. J. *J. Org. Chem.* **1984**, *49*, 168.

Table VI. Reactions of α-Thioanions with Enones

						yield,[a] %		
entry	solv	additive	temp, °C	sulfide	enone	sulfide	1,2-adduct	1,4-adduct
1	THF	none	rt	**29**	**9**	26	74 (**41**)	0
2					**10**	6	94 (**42**)	0
3					**11**	0	100 (**43**)	0
4					**12**	0	100 (**44**)	0
5				**30**	**9**	45	55 (**47**)	0
6					**10**	0	100 (**48**)	0
7					**11**	12	88 (**49**)	0
8					**12**	13	87 (**50**)	0
9				**35**	**9**	39	0	41 (**57**)
10					**12**	59	48 (**56**)	0
11				**36**	**9**	53	0	47 (**62**)
12					**10**	54	14 (**59**)	32 (**63**)
13					**11**	67	28 (**60**)	5 (**64**)
14					**12**	78	22 (**61**)	0
15			−78	**30**	**9**	24	76 (**47**)	0
16					**12**	5	95 (**50**)	0
17				**36**	**9**	67	0	33 (**62**)
18		HMPA	rt	**30**	**12**	10	95 (**50**)	0
1.			−78		**12**	13	87 (**50**)	0
20		TMEDA	rt		**12**	0	100 (**50**)	0
21			−78		**12**	16	84 (**50**)	0
22	DME	none	rt	**29**	**9**	36	64 (**41**)	0
23					**10**	6	94 (**42**)	0
24					**11**	11	89 (**43**)	0
25					**12**	8	92 (**44**)	0
26					**13**	5	95 (**45**)	0
27				**30**	**9**	21	69 (**47**)	10 (**52**)
28					**10**	14	67 (**48**)	19 (**53**)
29					**11**	10	90 (**49**)	0
30					**12**	11	89 (**50**)	0
31					**13**	9	91 (**51**)	0
32				**35**	**9**	87	0	13 (**57**)
33					**10**	58	10 (**55**)	32 (**58**)
34					**12**	64	36 (**56**)	0
35				**36**	**9**	89	0	11 (**62**)
36				**36**	**10**	62	14 (**59**)	24 (**63**)
37					**11**	70	30 (**60**)	0
38					**12**	64	36 (**61**)	0
39			−78	**29**	**10**	12	83 (**42**)	5 (**46**)
40					**11**	0	100 (**43**)	0
41					**12**	0	100 (**44**)	0
42				**30**	**10**	16	68 (**48**)	16 (**53**)
43					**11**	16	84 (**49**)	0
44					**12**	10	90 (**50**)	0

[a] By NMR.

corded. For characterization of the compounds, certain examples were subjected to column chromatography. The isolated yields and spectroscopic data for these compounds are listed below.[28]

General Procedure for Cuprate Additions of [(Phenylthio)(trimethylsilyl)methyl]lithium (1). Butyllithium (7.1 mL of a 1.4 M solution in hexane, 10 mmol) was added to (phenylthio)(trimethylsilyl)methane (**3**) (1.96 g, 10 mmol) in THF (50 mL) at 0 °C. The reaction was stirred at this temperature for 0.5 h and cooled to −78 °C and copper(I) iodide (0.95 g, 5 mmol) added. After 1 h, the enone (5 mmol) was added and the mixture allowed to warm to room temperature overnight. The reaction mixture was poured into 1:1 concentrated aqueous ammonia/saturated aqueous ammonium chloride (150 mL), stirred for 1 h, and extracted with ether (3 × 30 mL). The combined extracts were washed with 2 M hydrochloric acid (25 mL), saturated aqueous sodium hydrogen carbonate solution (25 mL), and saturated aqueous sodium chloride (25 mL), dried (Na_2SO_4), and evaporated under reduced pressure to give, after column chromatography (SiO_2, eluting with light petroleum-ether), the 1,4-adduct. See Table IV for yields. Spectroscopic data are listed below.

3-[(Phenylthio)methylene]-1-cyclohexene (6).[14] Table I, entry 1, gave the vinyl sulfide as a colorless liquid (0.78 g, 77%): IR ν_{max} 1660 (conj C=C), 1585 cm^{-1} (Ar C=C); NMR δ 7.5–7.0 (5 H, m, Ph), 6.8–5.8 (3 H, m, CH=C), 2.7–1.6 (6 H, m, CH_2's).

3-[(Phenylthio)(trimethylsilyl)methyl]cyclohexanone (7). Table I, entry 5 (0.95 g, 65%), and Table IV, entry 1 (1.21 g, 83%), gave **7** as rhomboids: mp 58–59 °C (petroleum ether); IR ν_{max} 1705 (C=O), 1580 (Ar C=C), 1255 cm^{-1} ($SiMe_3$); NMR δ 7.5–7.0 (5 H, m, Ph), 2.6–1.2 (10 H, m, alkyls), 0.13 (9 H, s, $SiMe_3$); MS, *m/z* (relative intensity) 292 (8, M^+), 219 (26, M − $SiMe_3$), 110 (53, PhSH), 73 (100, Me_3Si^+). Anal. Calcd for $C_{16}H_{24}OSSi$: C, 65.7; H, 8.25. Found: C, 65.8; H, 8.35.

2-Methyl-1-(phenylthio)-1,3-butadiene (14).[29] Table III, entry 1 (0.54 g, 61%), as a colorless liquid: IR ν_{max} 1620 (C=C), 1585 cm^{-1} (Ar C=C); NMR δ 7.3–6.6 (6 H, m, Ph and C=CHS), 5.95–5.60 (1 H, m, *C*H=CH$_2$), 4.95–4.35 (2 H, m, C=C*H*$_2$), 1.42 and 1.38 (3 H, ratio 1:1, d, *J* = 1 Hz, Me); MS, *m/z* (relative intensity) 176 (11, M^+), 109 (100, $PhS^{+\cdot}$).

2-Methyl-1-(phenylthio)-1,3-pentadiene (15). Table III, entry 2 (0.79 g, 83%), as a colorless liquid: IR ν_{max} 1650 (C=C), 1585 cm^{-1} (Ar C=C); NMR δ 7.7–7.0 (6 H, m, Ph and =CHS), 6.8–5.3 (2 H, m, CH=CH), 1.6–1.3 (6 H, m, Me's); MS, *m/z* (relative intensity) 190 (5, M^+), 109 (100, PhS^+); exact mass calcd for $C_{12}H_{14}S$ 190.08160, found 190.08013.

2,4-Dimethyl-1-(phenylthio)-1,3-pentadiene (16). Table III, entry 3 (0.70 g, 69%), as a colorless oil: IR ν_{max} 1650 (C=C), 1590

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(28) Some compounds, such as **46**, were only produced in small amounts. They were not isolated, but their presence and structure were inferred from the NMR spectra by analogy with other systems.

(29) Kreh, D. W.; Krug, R. C. *J. Org. Chem.* **1967**, *32*, 4057.

(30) Smith, R. A. J.; Lal, R. A. *Aust. J. Chem.* **1979**, *32*, 353.

cm^{-1} (Ar C=C); NMR δ 7.6–6.9 (6 H, m, Ph and =CHS), 6.48 (1 H, br s, CH=C), 1.52 (3 H, br s, C=CMe), 1.40 and 1.38 (6 H, br s, C=CMe_2); MS, m/z (relative intensity) 204 (7, M + 1), 109 (100, PhS^+); exact mass calcd for $C_{13}H_{16}S$ 204.097 27, found 204.098 17.

1-(Phenylthio)-1-(trimethylsilyl)-4-pentanone (17). Table IV, entry 3 (0.49 g, 37%), as a colorless oil: IR ν_{max} 1710 (C=O), 1590 (Ar C=C), 1260 cm^{-1} ($SiMe_3$); NMR δ 7.5–7.0 (5 H, m, Ph), 2.82 (1 H, t, J = 7.5 Hz, CHSSi), 2.6–1.3 (7 H, m, overlaid with s at 2.11, alkyls), 0.16 (9 H, s, $SiMe_3$); MS, m/z (relative intensity) 266 (5, M^+), 109 (21, PhS^+), 73 (100, Me_3Si^+); exact mass calcd for $C_{14}H_{22}OSSi$ 266.116 06, found 266.115 32.

2-Methyl-1-(phenylthio)-1-(trimethylsilyl)-4-pentanone (18). Table IV, entry 4 (0.88 g, 63%), as a colorless liquid: IR δ_{max} 1710 (C=O), 1590 (Ar C=C), 1260 cm^{-1} ($SiMe_3$); NMR δ 7.5–7.1 (5 H, m, Ph), 2.47 (1 H, d, J = 7 Hz, CHSSi), 2.3–1.8 (3 H, m, –CH_2CHMe–), 2.01 (3 H, s, COMe), 1.30 and 1.21 (3 H; 2d's J = 7.5 Hz, CH*Me*), 0.21 (9 H, s, $SiMe_3$); MS, m/z (relative intensity) 280 (9, M^+), 206 (15, M – (Me_3SiH)), 109 (44, PhS^+), 73 (100, Me_3Si^+); exact mass calcd for $C_{15}H_{24}OSSi$ 280.131 71, found 280.132 17.

2,2-Dimethyl-1-(phenylthio)-1-(trimethylsilyl)-4-pentanone (19). Table IV, entry 5 (1.01 g, 69%), as a colorless liquid: IR ν_{max} 1710 (C=O), 1585 (Ar C=C), 1255 cm^{-1} ($SiMe_3$); NMR δ 7.6–7.0 (5 H, m, Ph), 2.39 (1 H, s, CHSSi), 2.18 (2 H, s, $COCH_2$), 2.05 (3 H, s, COMe), 1.31 (6 H, s, CMe_2), 0.08 (9 H, s, $SiMe_3$); MS, m/z (relative intensity) 294 (4, M^+), 279 (11, M – Me), 109 (61, PhS^+), 73 (100, Me_3Si^+); exact mass calcd for $C_{16}H_{26}OSSi$ 294.147 36, found 294.148 01.

1-Methyl-3-[(phenylthio)methylene]-1-cyclohexene (20). Table III, entry 4 (0.92 g, 85%), as a colorless oil: IR ν_{max} 1660 (C=C), 1590 cm^{-1} (Ar C=C); NMR δ 7.5–7.1 (5 H, m, Ph), 6.48, 5.96, 5.90, and 5.78 (2 H, br s's, olefinic), 2.4–1.5 (9 H, m, overlaid with s at δ 1.78, CH_2's and Me); MS, m/z (relative intensity) 216 (43, M^+), 140 (62, M + 1 – PhS^+), 109 (100, PhS^+), 77 (95, Ph^+), exact mass calcd for $C_{14}H_{16}S$ 216.097 27, found 216.095 13.

3-[(Phenylthio)methylene]-1,5,5-trimethyl-1-cyclohexene (21). Table III, entry 5 (0.95 g, 78%): IR ν_{max} 1660 (C=C), 1585 cm^{-1} (Ar C=C); NMR δ 7.5–7.0 (5 H, m, Ph), 6.4 and 5.71 (1 H, br s's, =CHS), 5.89 (1 H, br s, CH=C), 3.06 (2 H, d, J = 8 Hz, CH_2CO), 1.75 (2 H, d, J = 6 Hz, CH_2C=), 1.68 (3 H, br s, =CMe), 0.88 (6 H, br s, CMe_2); MS, m/z (relative intensity) 244 (18, M^+), 229 (15, M – Me), 109 (100, PhS^+); exact mass calcd for $C_{16}H_{20}S$ 244.128 57, found 244.129 03.

3-Methyl-3-[(phenylthio)(trimethylsilyl)methyl]cyclohexanone (22). Table IV, entry 6 (1.05 g, 69%): IR ν_{max} 1705 (C=O), 1580 (Ar C=C), 1255 cm^{-1} ($SiMe_3$); NMR δ 7.5–7.0 (5 H, m, Ph), 2.47 (1 H, s, CHSSi), 2.3–1.3 (8 H, m, CH_2's), 1.32 (3 H, s, Me), 0.19 (9 H, s, $SiMe_3$); MS, m/z (relative intensity) 306 (3, M^+), 110 (79, PhS^+), 73 (100, Me_3Si^+); exact mass calcd for $C_{17}H_{26}OSSi$ 306.147 36, found 306.148 11.

3-[(Phenylthio)(trimethylsilyl)methyl]-3,5,5-trimethylcyclohexanone (23). Table IV, entry 8 (0.87 g, 52%); IR ν_{max} 1705 (C=O), 1580 (Ar C=C), 1260 cm^{-1} ($SiMe_3$); NMR δ 7.5–7.0 (5 H, m, Ph), 2.38 (1 H, s, CHSSI), 2.2–1.4 (6 H, m, overlaid with s at δ 1.74, CH_2's and Me), 0.96 and 0.94 (6 H, 2s, 5-Me's), 0.14 (9 H, s, $SiMe_3$); MS, m/z (relative intensity) 334 (17, M^+), 225 (46, M – PhS), 109 (100, PhS^+), 73 (91, Me_3Si^+); exact mass calcd for $C_{19}H_{30}OSSi$ 334.178 66, found 334.179 29.

1-[2-(1,3-Dithianyl)]cyclohex-3-en-1-ol (31).[8a] Table V, entry 1 (0.87 g, 81%), as a slightly yellow oil: IR ν_{max} 3550 br (OH), 1640 cm^{-1} (C=C); NMR δ 5.70 (2 H, m, olefinic), 4.07 (1 H, s, SCHS–), 3.05–2.7 (4 H, m, SCH_2's), 2.25–1.3 (9 H, m, other alkyls and OH).

1-[Bis(phenylthio)methyl]cyclohex-3-en-1-ol (32). Table V, entry 9 (1.13 g, 69%), as an oil: IR ν_{max} 3400 br (OH), 1590 cm^{-1} (Ar C=C); NMR δ 7.5–7.1 (10 H, m, Ph's), 5.98 (1 H, m, CH=C), 5.78 (1 H, d, J = 10 Hz, CH=C), 4.48 (1 H, s, CHS), 1.9–1.4 (7 H, m, CH_2's and OH); MS, m/z (relative intensity) 328 (1, M^+), 310 (7, M – H_2O), 218 (17, M – SPh), 110 (100, PhSH), 77 (50, Ph^+); exact mass calcd for $C_{19}H_{20}O_2S$ 328.095 55, found: 328.095 69.

3-[2-(1,3-Dithianyl)]cyclohexanone (33). This was prepared in a separate reaction[7a] as a colorless liquid: IR ν_{max} 1715 (C=O), NMR δ 4.08 (1 H, d J = 6 Hz, CHS_2) 2.88 (4 H, m, CH_2S), 2.2–1.5 (11 H, m, other alkyls); MS, m/z (relative intensity) 216 (6, M^+), 119 (100, $^+\overline{CHSCH_2CH_2CH_2S}$); exact mass calcd for $C_{10}H_{16}OS_2$ 216.064 25, found 216.063 72.

3-[Bis(phenylthio)methyl]cyclohexanone (34).[25] Table V, entry 18 (1.16 g, 71%), as rhomboids: mp 49–51 °C (petroleum ether) (lit.[25] 52.5–53.5 °C); IR ν_{max} 1710 (C=O), 1585 cm^{-1} (Ar C=C); NMR δ 7.5–7.0 (10 H, m, Ph's), 4.25 (1 H, 3d, J = 5 Hz, CHS), 2.6–1.3 (9 H, m, alkyls).

3-[Bis(phenylthio)(trimethylsilyl)methyl]cyclohexanone (39). Table V, entry 15 (1.16 g, 58%), as a viscous oil: IR ν_{max} 1710 (C=O), 1585 (Ar C=C), 1255 cm^{-1} ($SiMe_3$); NMR δ 7.5–7.0 (10 H, m, Ph's), 2.4–1.3 (9 H, m, alkyls), 0.22 (9 H, s, $SiMe_3$); MS, m/z (relative intensity) 400 (2, M^+), 110 (59, PhSH), 73 (100, Me_3Si^+); exact mass calcd for $C_{22}H_{28}OS_2Si$ 400.135 08, found 400.138 10.

3-[Bis(trimethylsilyl)(phenylthio)methyl]cyclohexanone (40). Table V, entry 16 (1.18 g, 65%), as an oil: IR ν_{max} 1710 (C=O), 1580 (Ar C=C), 1250 cm^{-1} ($SiMe_3$); NMR δ 7.5–7.0 (5 H, m, Ph), 2.3–1.2 (9 H, m, alkyls), 0.19 (18 H, s, $SiMe_3$); MS, m/z (relative intensity) 364 (4, M^+), 109 (16, PhS^+), 73 (100, Me_3Si^+); exact mass calcd for $C_{19}H_{32}OSSi_2$ 364.171 24, found 364.170 03.

2-(1,3-Dithianyl)but-3-en-2-ol (41). Table VI, entry 1 (0.39 g, 41%), as a liquid, which could not be purified completely due to degradation: IR ν_{max} 3400 br cm^{-1} (OH); NMR δ 6.07 (1 H, dd, J = 12.5, 16 Hz, *CH*=CH_2), 5.41 (1 H, d, J = 16 Hz, trans =CH), 5.20 (1 H, d, J = 12.5 Hz, cis =CH), 4.15 (1 H, s, CHS), 3.0–2.7 (4 H, m, CH_2S), 2.6 (1 H, br s, exchanged in D_2O, OH), 1.81 (2 H, m, CH_2), 1.42 (3 H, s, Me); MS, m/z (relative intensity) 190 (2, M^+), 172 (3, M – H_2O), 119 (100, $^+\overline{CHSCH_2CH_2CH_2S}$); exact mass calcd for $C_8H_{14}OS_2$ 190.048 60, found 190.049 13.

2-(1,3-Dithianyl)pent-3-en-2-ol (42). Table VI, entry 2 (0.73 g, 72%), as a liquid which could not be purified completely due to degradation: IR ν_{max} 3400 br cm^{-1} (OH); NMR δ 5.85–5.6 (2 H, m, olefinic), 4.11 (1 H, s, CHS), 2.9–2.7 (4 H, m, CH_2S), 2.6 (1 H, br s, exchanged with D_2O, OH), 1.99 (2 H, m, CH_2), 1.68 (3 H, d, J = 6 Hz, =CH*Me*), 1.38 (3 H, s, Me); MS, m/z (relative intensity) 204 (2, M^+) 1.86 (3, M – H_2O), 119 (100, $^+\overline{CHSCH_2CH_2CH_2S}$); exact mass calcd for $C_9H_{16}OS_2$ 204.064 25, found 204.063 82.

2-[2-(1,3-Dithianyl)]-4-methylpent-3-en-2-ol (43). Table VI, entry 3 (0.63 g, 58%), as a slightly yellow liquid, which could not be purified completely without degradation: IR ν_{max} 3350 br (OH), 1660 cm^{-1} (C=C); NMR δ 5.55 (1 H, br s, CH=C), 4.34 (1 H, s, CHS), 2.93 (4 H, m, CH_2S), 2.6 (1 H, br s, exchanged with D_2O, OH), 2.08 (2 H, m, CH_2), 1.91, 1.84, and 1.48 (3 × 3 H, 3s, Me's); MS, m/z (relative intensity) 218 (1, M^+), 200 (6, M – H_2O), 121 (100).

1-[2-(1,3-Dithianyl)]-3-methylcyclohex-2-en-1-ol (44). Table VI, entry 4 (0.79 g, 69%), as a colorless liquid, which could not be purified completely due to degradation: IR ν_{max} 3400 br (OH), 1650 cm^{-1} (C=C); NMR δ 5.48 (1 H, br s, CH=C), 4.09 (1 H, s, CHS), 2.85 (4 H, m, CH_2S), 2.5 (1 H, br s, exchanged with D_2O, OH), 2.5–1.6 (11 H, m overlaid with br s at δ 1.72, alkyls); MS, m/z (relative intensity) 230 (1, M^+), 212 (100, M – H_2O), 119 (76, $^+\overline{CHSCH_2CH_2CH_2S}$).

1-[2-(1,3-Dithianyl)]-3,5,5-trimethylcyclohex-2-en-1-ol (45). Table VI, entry 26 (0.54 g, 42%), as a slightly yellow oil, which could not be purified complete due to degradation: IR ν_{max} 3400 br (OH), 1660 cm^{-1} (C=C); NMR δ 5.41 (1 H, br s, CH=C), 4.04 (1 H, s, CHS), 2.9–2.7 (4 H, m, CH_2S), 2.6–1.5 (10 H, m, overlaid with br s at δ 1.76, CH_2's and C=CMe), 1.05 and 1.03 (6 H, 2s, CMe_2); MS, m/z (relative intensity) no M^+, 240 (41, M – H_2O), 119 (100, $^+\overline{CHSCH_2CH_2CH_2S}$).

2-[Bis(phenylthio)methyl]but-3-en-2-ol (47).[6i] Table VI, entry 15 (0.36 g, 24%), as a slightly yellow oil which could not be purified completely due to degradation: IR ν_{max} 3400 br (OH), 1585 cm^{-1} (Ar C=C); NMR δ 7.5–7.1 (10 H, m, Ph's), 6.16 (1 H, dd, J = 18 and 11 Hz, *CH*=CH_2), 5.42 (1 H, d, J = 18 Hz, trans, olefinic), 5.17 (1 H, d, J = 11 Hz, cis, olefinic), 4.26 (1 H, s, CHS), 3.3 (1 H, br s, exchanged with D_2O, OH, 1.47 (3 H, s, Me).

2-[Bis(phenylthio)methyl]pent-3-en-2-ol (48). Table VI, entry 6 (0.82 g, 52%), as a slightly yellow oil which could not be purified completely without degradation: IR ν_{max} 3400 br (OH), 1580 cm^{-1} (Ar C=C); NMR δ 7.5–7.0 (10 H, m, Ph's), 5.9–5.7 (2 H, m, olefinics), 4.38 (1 H, s, CHS), 3.0 (1 H, br s, exchanged with

D_2O, OH), 1.64 (3 H, d, *J* = 6 Hz, =CMe), 1.48 (3 H, s, Me): MS, *m/z* (relative intensity) 316 (1.5, M^+), 110 (100, PhSH), 109 (53, PhS^+); exact mass calcd for $C_{18}H_{20}OS_2$: 316.095 55, found 316.093 92.

2-[Bis(phenylthio)methyl]-4-methylpent-3-en-2-ol (49).[30] Table VI, entry 7 (0.69 g, 42%), as a slightly yellow oil which could not be purified completely without degradation: IR ν_{max} 3400 br (OH), 1580 cm^{-1} (Ar C=C); NMR δ 7.5–7.0 (10 H, m, Ph's), 5.51 (1 H, s, olefinic), 4.27 (1 H, s, CHS), 3.4 (1 H, br s, exchanged with D_2O, OH), 1.91, 1.58, and 1.37 (9 H, 3s, Me's).

1-[Bis(phenylthio)methyl]-3-methylcyclohex-2-en-1-ol (50). Table VI, entry 7 (0.89 g, 52%), as a slightly yellow oil which could not be purified completely due to degradation: IR ν_{max} 3400 br (OH), 1580 cm^{-1} (Ar C=C); NMR δ 7.5–7.1 (10 H, m, Ph's), 5.44 (1 H, br s, olefinic), 4.49 (1 H, s, CHS), 2.8 (1 H, br s, exchanged with D_2O, OH), 2.1–1.5 (9 H, m, overlaid with br s at 1.67, alkyls); MS, *m/z* (relative intensity) no M^+, 232 (10, M – PhSH), 110 (100, PhSH), 109 (49, PhS^+).

1-[Bis(phenylthio)methyl]-3,5,5-trimethylcyclohex-2-en-2-ol (51). Table VI, entry 31 (0.76 g, 41%), as a yellow oil which could not be purified completely due to degradation: IR ν_{max} 3400 br (OH), 1585 cm^{-1} (Ar C=C); NMR δ 7.6–7.0 (10 H, m, Ph's), 5.15 (1 H, s, olefinic), 4.25 (1 H, s, CHS), 2.4–1.8 (5 H, m, CH_2's and OH), 1.81, 1.09, and 1.00 (9 H, 3s, Me's); MS, *m/z* (relative intensity) no M^+, 260 (5, M – PhSH), 231 (13, $(PhS)_2CH^+$), 138 (15, M – $(PhS)_2CH_2$), 122 (100, M – $(PhS)_2CH$ + OH), 110 (100, PhSH).

3-[Bis(phenylthio)methylene]-1-methyl-1-cyclohexene (56). Table VI, entry 10 (0.66 g, 41%), as a yellow oil: IR ν_{max} 1660 (C=C), 1580 cm^{-1} (Ar C=C); NMR δ 7.5–7.0 (10 H m, Ph's), 5.68 (1 H, br s, olefinic), 2.1–1.5 (9 H, m, overlaid with br s at δ 1.62, alkyls); MS, *m/z* 324 (2, M^+), 109 (100, PhS^+), 109 (100, PhS^+); exact mass calcd for $C_{20}H_{20}S_2$ 324.100 64, found 324.101 11.

1,1-Bis(phenylthio)-1-(trimethylsilyl)-4-pentanone (57). Table VI, entry 9 (0.62 g, 33%), as an oil; IR ν_{max} 1710 (C=O), 1590 (Ar C=C), 1260 cm^{-1} ($SiMe_3$); NMR δ 7.5–7.0 (10 H, m, Ph's), 2.21 (2 H, t, *J* = 7 Hz, $COCH_2$), 2.06 (3 H, s, COMe), 1.38 (2 H, t, *J* = 7 Hz, CH_2CS_2Si), 0.23 (9 H, s, $SiMe_3$); MS, *m/z* (relative intensity) no M^+, 265 (3, M – PhS), 109 (56, PhS^+), 73 (100, Me_3Si^+).

1,1-Bis(phenylthio)-2-methyl-1-(trimethylsilyl)-4-pentanone (58). Table VI, entry 33 (0.29 g, 15%), as a viscous oil; IR ν_{max} 1705 (C=O), 1585 (Ar C=C), 1260 cm^{-1} ($SiMe_3$); NMR δ 7.5–6.9 (10 H, m, Ph), 2.29 (2 H, t, *J* = 7 Hz, $COCH_2$), 2.09 (3 H, s, COMe), 1.8 (1 H, m, CH), 1.15 (3 H, d, *J* = 7.5 Hz, CH*Me*), 0.16 (9 H, s, $SiMe_3$); MS, *m/z* (relative intensity) no M^+, 279 (2, M – PhS), 109 (41, PhS^+), 73 (100, Me_3Si^+).

1,1-Bis(trimethylsilyl)-1-(phenylthio)-4-pentanone (61). Table VI, entry 11 (0.61 g, 36%), as an oil: IR ν_{max} 1710 (C=O), 1585 (Ar C=C), 1260 cm^{-1} ($SiMe_3$); NMR δ 7.6–7.1 (5 H, m, Ph), 2.65 (2 H, t, *J* = 7 Hz, $COCH_2$), 2.16 (3 H, s, COMe), 1.25 (2 H, t, *J* = 7 Hz, CH_2CSi_2), –0.11 (18 H, s, $SiMe_3$); MS, *m/z* (relative intensity) no M^+, 229 (2, M – PhS), 109 (21, PhS^+), 73 (100, Me_3Si^+).

1,1-Bis(trimethylsilyl)-2-methyl-1-(phenylthio)-4-pentanone (63). Table VI, entry 12 (0.28 g, 16%), as an oil: IR ν_{max} 1710 (C=O), 1585 (Ar C=C), 1260 ($SiMe_3$); NMR δ 7.7–7.0 (5 H, m, Ph), 2.86 (2 H, t, *J* = 7 Hz, $COCH_2$), 2.12 (3 H, s, COMe), 1.55 (1 H, q, *J* = 7.5 Hz, C*H*Me), 0.82 (3 H, d, *J* = 7.5 Hz, CH*Me*), 0.01 (18 H, s, $SiMe_3$); MS, *m/z* (relative intensity) no M^+, 243 (2, M – PhS), 110 (15, PhSH), 73 (100, Me_3Si^+).

1,2-Bis(phenylthio)-1,2-bis(trimethylsilyl)ethane (27). This compound was isolated, as a byproduct from the cuprate experiments, as an oil: IR ν_{max} 1585 (Ar C=C), 1260 cm^{-1} ($SiMe_3$); NMR δ 7.5–7.1 (10 H, m, Ph), 2.46 (2 H, s, CH), 0.19 (18 H, s, $SiMe_3$); MS, *m/z* (relative intensity) 390 (7, M^+), 280 (14, M – PhSH), 110 (31, PhSH), 73 (100, Me_3Si^+); exact mass calcd for $C_{20}H_{30}S_2Si_2$ 390.132 75, found 390.132 51.

1-*n*-Butylcyclohex-2-en-1-ol (4). Cyclohexenone (0.46 mL, 0.46 g, 4.8 mmol) was added to a solution of *n*-butyllithium (3.6 mL of a 1.4 M solution in hexane, 5 mmol) in THF (25 mL), at 0 °C. After 1 h, saturated aqueous ammonium chloride solution (25 mL) was added and the mixture extracted with ether (3 × 20 mL). The combined extracts were washed with saturated aqueous sodium chloride (25 mL), dried (Na_2SO_4), and evaporated under reduced pressure to give the allyl alcohol (4): IR ν_{max} 3400 (br) cm^{-1} (OH); NMR δ 5.8–5.5 (2 H, m, olefinic), 2.2–0.8 (16 H, m, alkyls and OH).

Preparation of 1-(Phenylthio)-1,3-butadiene (24). *n*-Butyllithium (14.3 mL of a 1.4 M solution in hexane, 20 mmol) was added to (phenylthio)(trimethylsilyl)methane (**3**) (3.92 g, 20 mmol) in THF (60 mL) at 0 °C. After 0.5 h, acrolein (1.34 mL, 1.12 g, 20 mmol) was added. Stirring was continued for 1 h, when saturated aqueous ammonium chloride (50 mL) was added. The mixture was extracted with ether (3 × 30 mL), washed with saturated sodium chloride solution (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure to give the diene **24**: bp 65–73 °C (0.1 mmHg) (bulb to bulb) (lit.[20] 50–53 °C (0.04 mmHg); IR ν_{max} 1660 (C=C), 1585 cm^{-1} (Ar C=C); NMR δ 7.5–7.0 (5 H, m, Ph), 6.4–6.2 and 5.4–4.9 (5 H, m, olefinics).

The crude diene **24**, obtained after evaporation of the solvent, was reacted with maleic anhydride to provide the adduct **25** (41% from **3**), mp 85–86 °C (lit.[21] mp 87 °C).

Conversion of 2,2-Dimethyl-1-(phenylthio)-1-(trimethylsilyl)-4-pentanone (19) to 4,4-Dimethylcyclopent-2-en-1-one (28). 2,2-Dimethyl-1-(phenylthio)-1-(trimethylsilyl)-4-pentanone (**19**) (5.88 g, 20 mmol) in dichloromethane (20 mL) was added over 0.5 h to *m*-chloroperoxybenzoic acid (4.05 g of 85% peracid, 20 mmol) in dichloromethane (150 mL) at –23 °C.[2] After being stirred for 1.5 h at this temperature, the mixture was poured into 2 M sodium hydroxide (250 mL) and extracted with dichloromethane (2 × 100 mL). The extracts were washed with saturated aqueous sodium chloride solution (100 mL), dried (Na_2SO_4), and evaporated under reduced pressure to a yellow liquid which was taken up in THF (20 mL) and heated under reflux for 3 h. The mixture was cooled, diluted with ether (100 mL), and washed with 0.5 M copper sulfate solution (3 × 30 mL). The washing were back-extracted with ether (2 × 10 mL). The combined organic solutions were diluted with tetrahydrofuran (50 mL), added to 1 M potassium hydroxide (50 mL), and heated under reflux for 48 h. The mixture was cooled and the aqueous phase saturated with sodium chloride and extracted with ether (3 × 25 mL). The combined extracts were washed with saturated aqueous sodium chloride (2 × 25 mL), dried (Na_2SO_4), and evaporated under reduced pressure to give the enone **28** (0.86 g, 39%): bp 50–55 °C (15 mmHg) (bulb to bulb) (lit.[31] 60–62 °C (20 mmHg)); IR ν_{max} 1705 (C=O); NMR δ 7.28 (1 H, d, *J* = 6 Hz, olefinic), 6.82 (1 H, d, *J* = 6 Hz, olefinic), 2.14 (2 H, s, CH_2), 1.14 (6 H, s, Me).

Registry No. **1**, 30536-77-7; **2**, 930-68-7; **3**, 17873-08-4; **4**, 88116-46-5; **6**, 71341-87-2; **7**, 79409-24-8; **9**, 78-94-4; **10**, 3102-33-8; **11**, 141-79-7; **12**, 1193-18-6; **13**, 78-59-1; **14**, 16061-69-1; **15**, 104115-15-3; **16**, 104115-16-4; **17**, 104130-08-7; **18**, 104115-17-5; **19**, 104115-18-6; **20**, 104115-19-7; **21**, 104115-20-0; **22**, 104115-21-1; **23**, 104115-22-2; **24**, 53097-28-2; **28**, 22748-16-9; **29**, 505-23-7; **30**, 3561-67-9; **31**, 53178-46-4; **32**, 104115-23-3; **33**, 71491-60-6; **34**, 69814-21-7; **35**, 37891-39-7; **36**, 62761-90-4; **39**, 104115-24-4; **40**, 104115-25-5; **41**, 104115-26-6; **42**, 104115-27-7; **43**, 104115-28-8; **44**, 81793-30-8; **45**, 104130-09-8; **46**, 104115-29-9; **47**, 39121-62-5; **48**, 104115-30-2; **49**, 70626-92-5; **50**, 104130-10-1; **51**, 104115-31-3; **52**, 39121-54-5; **53**, 104115-32-4; **55**, 104115-33-5; **56**, 104115-34-6; **57**, 104115-35-7; **58**, 104115-36-8; **59**, 104115-37-9; **60**, 104115-38-0; **61**, 104115-39-1; **62**, 104115-40-4; **63**, 104115-41-5; **64**, 104115-42-6; TMEDA, 110-18-9; HMPA, 680-31-9; Dabco, 280-57-9; Pyr, 110-86-1; KO-*t*-Bu, 865-47-4; $MgCl_2$, 7786-30-3; CuI, 7681-65-4; PhSCu, 1192-40-1; DME, 110-71-4; acrolein, 107-02-8.

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