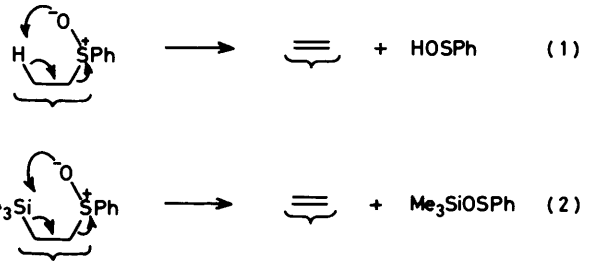
Cycloelimination of β-Silylethyl Sulphoxides: Alkene, Alkyne, and Vinylsilane-forming Reactions †

By Ian Fleming,* Jon Goldhill, and David A. Perry, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The cycloelimination (1)→(3) of trimethylsilyl sulphenate from a β-silylethyl sulphoxide is slightly faster than the corresponding cycloelimination (2)→(3) of sulphenic acid itself. The former type of reaction can be used to form acetylenes [*e.g.* (24)→(25)]. However, this pathway is only followed when there is no hydrogen on the β-carbon; when there is such a hydrogen, the elimination of sulphenic acid (8)→(10) takes place, because the silyl group substantially speeds up the abstraction of the hydrogen atom adjacent to it.

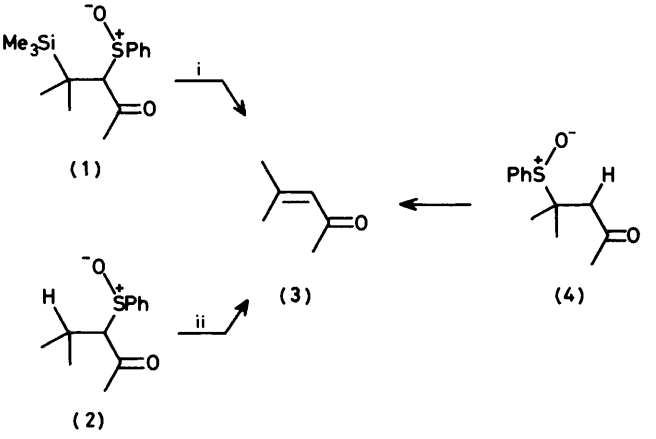
THE elimination of benzenesulphenic acid from sulphoxides [equation (1)] is well-known and synthetically useful.[1-3] We have now investigated the possibility that a β-silylethyl sulphoxide might undergo an analogous reaction [equation (2)]. Some of our results have been reported earlier in a preliminary communication.[4]



RESULTS AND DISCUSSION

It is known, in the corresponding α-eliminations, that the sila-Pummerer reaction is faster than the normal Pummerer reaction.[5] It is also very well established now that the displacement of silicon from carbon by oxygen nucleophiles is usually faster than the corresponding displacement of hydrogen from carbon.[6,7] These analogies suggest that the reaction in equation (2) should be faster than that in equation (1), as it proves to be; the β-silyl sulphoxide (1) gives 4-methylpent-3-en-2-one (3) about three times faster than the analogous compound (2).

Although unlikely, it was just possible that the rate of the reaction (2)→(3) that we were measuring was not the rate of the elimination step, but the rate of decomposition of the sulphenic acid by-product. We were following the reaction simply by ^{1}H n.m.r. spectroscopy, but, if the elimination step were rapid and reversible, neither the rate of disappearance of the signals from the sulphoxide (2) nor the rate of appearance of the signals from the enone (3) would be a measure of the rate of elimination. We therefore took some trouble to establish that the rates we were measuring were appropriate. The addition of trimethyl phosphite, which would act as a sulphenic acid scavenger,[2,8] had no effect on the rate of the reaction (1)→(3), but it did speed up slightly the reaction (2)→(3). However, this was probably a solvent effect, since the amount of phosphite added was quite large. More informative was a brief study of the elimination (4)→(3). This reaction was much faster; it was complete in less than 10 min at 90 °C, whereas t for the reaction (2)→(3) was 4.6 h at 90 °C. Furthermore, there was no trace in the ^{1}H n.m.r. spectrum of the reaction mixture of the distinctive signals of the sulphoxide (2), nor was it detectable by t.l.c. Clearly sulphenic acid does not add to 4-methylpent-3-en-2-one



i, CCl_4, 90 °C, $t_{\frac{1}{2}}$ 1.4 h; ii, CCl_4, 90 °C, $t_{\frac{1}{2}}$ 4.6 h

with the regiochemistry (3)→(2) to any measurable extent, and the reaction (2)→(3) is irreversible.

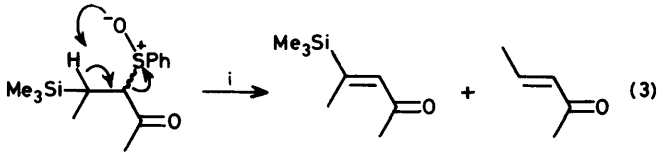
Having established that the reaction in equation (2) is fast and clean, we used it to make the α,β-unsaturated ketone (7), as we have reported elsewhere:[9] the β-silylethyl sulphoxide elimination (5)→(7) was cleaner than our more usual way of converting β-silylketones into α,β-unsaturated ketones, the corresponding desilylbromination (6)→(7).[10]

However, the β-silylethyl sulphoxide elimination is not generally applicable. In spite of the greater rate of the

(5) X = SOPh
(6) X = Br
(7)

† No reprints available.

reaction in equation (2) than that in equation (1), the sulphoxide elimination in equation (3) almost entirely takes place with loss of the *hydrogen* atom from the sulphoxide (8), and only a trace of pent-3-en-2-one (11) could be detected (t.l.c.) when the reaction was carried out at 65 °C. At a higher temperature (120 °C) the chemoselectivity was not quite so completely in favour of hydrogen loss, and 12% of pent-2-en-3-one was detectable (^{1}H n.m.r.). In the other direction, at room temperature, the corresponding selenoxide (9) gave no detectable pent-3-en-2-one, even by t.l.c.



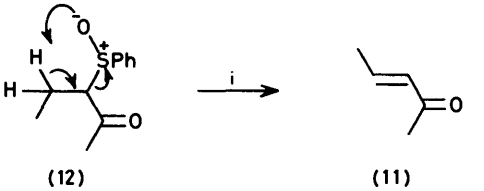
(8) (10) (11) trace

(9) Se for S

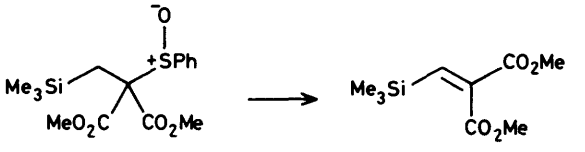
i, CCl_4, 70 °C, $t_{\frac{1}{2}}$ 3 min

The explanation for this seemingly contradictory pair of observations was easy to find. The presence of the silyl group in the β-sulphoxide (8) greatly increases the rate of elimination of the hydrogen atom adjacent to it. Thus the half-life for the reaction (8)→(10) is *ca.* 3 min at 70 °C, but the half-life for the corresponding reaction (12)→(11) without silicon is 4.4 h at this temperature. Similarly, with two α-carbonyl groups and one β-silyl group, the sulphoxide (13) was highly unstable; it started to decompose to the β-silylmethylenemalonate (14) even at −20 °C, in a reaction which had gone to completion by the time the product was worked up. The analogue of compound (13) without the β-silyl group has a half-life of 20—25 min at 60 °C.

The effect the silyl group has is very reasonable. It is well known that conjugatively electron-withdrawing groups such as carbonyl speed up the elimination when they are attached to the β-carbon of an ethyl sulphoxide, as in (4).[2] It is also known that a conjugatively electron-donating substituent, such as a methyl or hydroxy-group, slows down the elimination of a hydrogen adjacent



(12) (11)

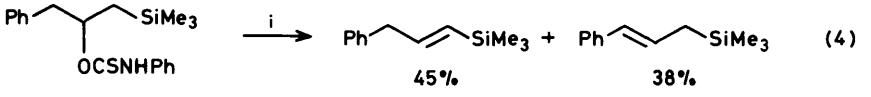


(13) (14)

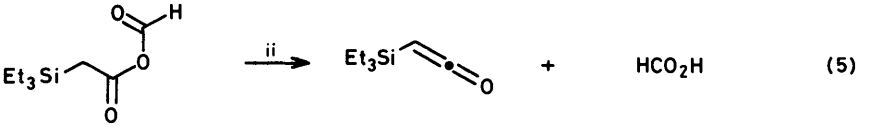
i, CCl_4, 70 °C, $t_{\frac{1}{2}}$ 260 min

to it, with the result that allylic alcohols are produced by default from β-hydroxyethyl sulphoxides.[11] Since the silyl group is conjugatively electron-withdrawing, it should, and evidently does, speed up the elimination of a hydrogen adjacent to it. This explains, incidentally, a number of other reactions of a related kind, in which hydrogen, and not silicon, is removed in a cycloelimination [equations (4)—(6)].[12-14]

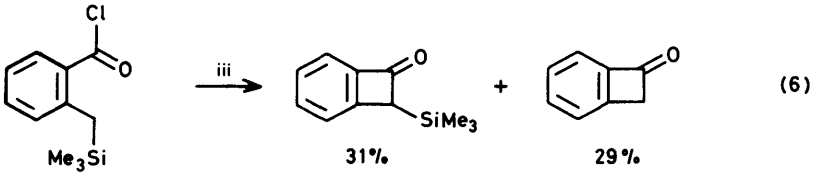
Because a hydrogen α to a silyl group is more easily removed than a hydrogen that is not, it is possible to direct the cycloelimination into the silicon-containing branch of the ester (15); this gave the esters (16) and (17)



(4)



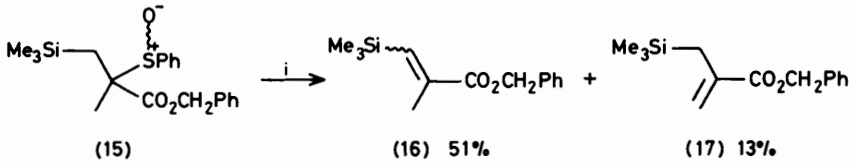
(5)



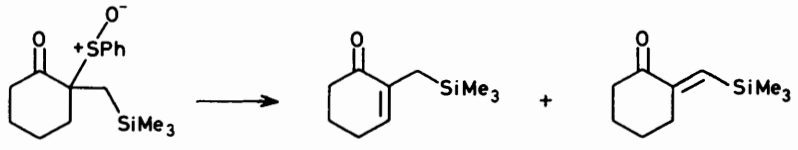
(6)

i, 125 °C, 1 h; ii, 140 °C; iii, 600 °C

in the ratio 4 : 1. However, the activation provided by the silyl group in the ketone (18) is not enough to direct the elimination exocyclic to the ring; the major product (74%) was the cyclohexenone (19), but the amount of the minor product (20) (22%) was greater than the amount (5%) known [2] to be produced when there is no silyl group in the molecule.



(15) (16) 51% (17) 13%

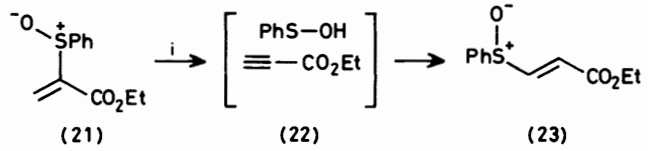


(18) (19) 74% (20) 22%

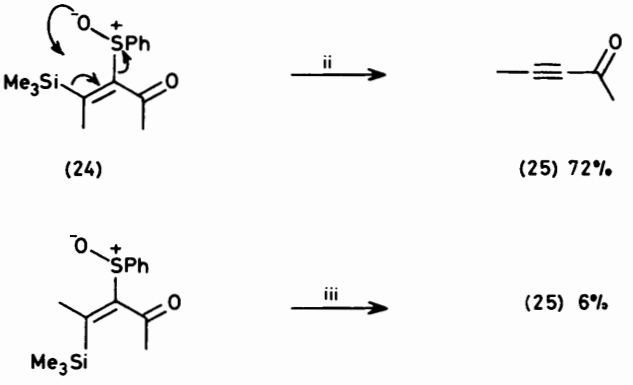
i, Room temp., 24 h

Finally, we have investigated the possibility that acetylenes might be produced by a sulphoxide elimination. As far as we are aware, this has never been observed, although the corresponding selenoxide eliminations have been reported.[15] In reviewing the literature on this subject, we discovered that no one seemed to have given this type of reaction a fair chance; the compounds tested had always had alternative reactions available to them.[16] Accordingly, we heated the sulphoxide (21), and found that the major product was the isomeric sulphoxide (23). Almost certainly this was produced by an acetylene-forming elimination (21)→(22), followed by a readdition (22)→(23), with the regioselectivity known for that reaction.[17] However, the readdition was so fast and efficient that we were unable to detect the acetylenic intermediate (22). In contrast, the β-silylvinyl sulphoxide (24) cleanly gave the acetylenic ketone (25) at 120 °C; evidently the silyl sulphenyl ester does not consume the product. Furthermore, the reaction is *syn*-stereospecific, since the geometrical isomer (26) was thermally stable at 160 °C, and gave only traces of the acetylenic ketone even at 220—230 °C. The silicon–sulphoxide elimination [structure (24)] which forms an acetylene does have a diagonal analogue in a boron sulphoxide elimination.[18]

The Synthesis of the Compounds used in this Work and the Proof of Stereochemistry for the Ketones (24) *and* (26).— The sulphoxides (1) and (8) were prepared by conjugate addition of dimethyl cuprate to the appropriate β-trimethylsilylenones [9] followed by sulphenylation and oxidation, as in the sequence converting compound (10) into the β-sulphoxide (1). The sulphoxide (13) was prepared by sulphenylation of β-trimethylsilylmethylmalonate,[10] followed by oxidation, and the sulphoxides (15) and (18) were prepared similarly. The sulphides (28) and (29) were prepared by base treatment of the benzenesulphenyl chloride adduct (27) of the enone (10).[9] Subsequent treatment with peracid gave the sulphoxides (24) and (26), respectively. Interestingly, when zinc bromide was added to the adduct (27) instead of base, a quite different result was obtained, namely the formation of the β-sulphides (30). This amounts, overall, to the electrophilic substitution of a vinylsilane.[19] The sulphoxides corresponding to (30) gave penta-3,4-dien-2-one (31) when heated, thus illustrating one of the ways in which vinyl sulphoxides can avoid the acetylene-forming reaction.



(21) (22) (23)

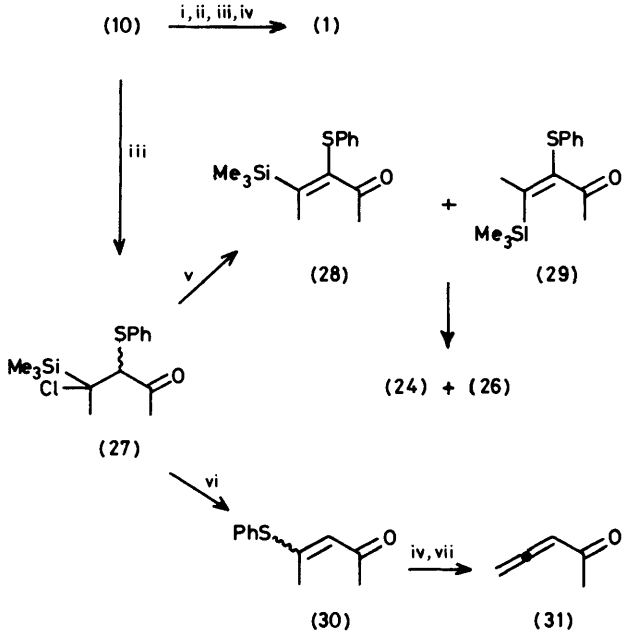


(24) (25) 72%

(26)

i, 120 °C, toluene; ii, 120 °C; iii, 220—230 °C

The proof of the stereochemistry of the isomers (24) and (26) was not trivial. A chemical-shift argument was actually misleading, and nuclear Overhauser experiments were inconclusive. Shift reagent studies were fairly convincing, but the problem was most satisfactorily solved using selective line-broadening [20] with tris(di-



Reagents: i, Me_2CuLi; ii, Me_3SiCl; iii, PhSCl; iv, MCPBA; v, DBU; vi, $ZnBr_2$; vii, heat

pivaloylmethanato)gadolinium(III) [Gd(dpm)$_3$]. The details of the assignment are given in the Experimental section.

EXPERIMENTAL

Light petroleum refers to the fraction with b.p. 30—40 °C.

The Preparation of Sulphoxides from Silyl Enol Ethers.—Benzenesulphenyl chloride (1M-solution in pentane or dichloromethane) was added dropwise to a stirred solution of the silyl enol ether in dichloromethane (*ca.* 0.2M) under nitrogen at −78 °C until a pale yellow colouration persisted (1.0 equiv. required). *m*-Chloroperbenzoic acid (MCPBA) (1.2 equiv. as a 0.5M-solution in CH_2Cl_2) was then added slowly to the stirred solution. After 3 min the mixture was poured into 10% sodium carbonate solution and extracted with dichloromethane. The extract was dried ($MgSO_4$) and evaporated under reduced pressure to give the sulphoxides.

Using this procedure 4-methyl-2-trimethylsiloxy-4-trimethylsilylpent-2-ene [9] (5 mmol) gave *4-methyl-3-phenylsulphinyl-4-trimethylsilylpentan-2-one* (1) (69%) as a mixture of diastereoisomers (*ca.* 3 : 1 by n.m.r.), R_F 0.33 (light petroleum–diethyl ether, 1 : 1), $\nu_{max.}$ (film) 1 692 (CO) and 1 050 cm^{-1} (SO); δ (CCl_4) 7.54 (5 H, s), 3.74 and 3.31 (1 H, s, CHS), 1.92 (3 H, s, MeCO), 1.49 and 1.41 (3 H, s, CMe_2, major diastereoisomer), 1.41 and 1.34 (3 H, s, CMe_2, minor diastereoisomer), and 0.17 (9 H, s) (Found: M^+ − Me, 281.1042. $C_{15}H_{24}O_2SSi$ requires M − Me, 281.1031); *m/z* 281 (0.34%), 198 (20), 98 (15), and 73 (100). Similarly, 4-methyl-2-trimethylsiloxy-4-trimethylsilyloct-2-ene [9] gave 4-methyl-3-phenylsulphinyl-4-trimethylsilyloctan-2-one (5), and 2-trimethylsiloxy-4-trimethylsilylpent-2-ene [9] gave 3-phenylsulphinyl-4-trimethylsilylpentan-2-one (8), which were heated directly.

The Preparation of Sulphoxides from Sulphides.—MCPBA (1.2 equiv.) in dry dichloromethane (*ca.* 0.5M) was added dropwise to a stirred solution of the sulphide in dry dichloromethane (*ca.* 0.2M) under nitrogen at −78 °C. After 3 min, basic aqueous work-up, as described above, gave the sulphoxides.

Using this procedure 4-methyl-3-phenylthiopentan-2-one (prepared by the method of Held *et al.*[21]) gave 4-methyl-3-phenylsulphinylpentan-2-one (2) as a mixture of diastereoisomers (*ca.* 3 : 4 by n.m.r.). Similarly, 4-methyl-4-phenylthiopentan-2-one (prepared by the method of Tilak and Vaidya [22]) gave 4-methyl-4-phenylsulphinylpentan-2-one (4), δ (CCl_4) 7.51 (5 H, s), 2.72 (1 H, s, CH_AH_BCO), 2.44 (1 H, s, CH_AH_BCO), 2.12 (3 H, s), 1.29 (3 H, s), and 1.12 (3 H, s), and 3-phenylthiopentan-2-one [23] (prepared by the method of Held *et al.*[21]) gave 3-phenylsulphinylpentan-2-one (12) as a mixture of diastereoisomers (*ca.* 2 : 3 by n.m.r.), δ (CCl_4) 7.58 (5 H, m), 3.8—3.3 (1 H, m, CHS), 2.12 and 1.98 (3 H, s, MeCO), 1.90 (2 H, m, containing *J* 7 Hz), and 0.99 and 0.95 (3 H, t, *J* 7 Hz). These sulphoxides were too unstable for further characterisation and were heated directly. Ethyl (2-phenylthio)propenoate (prepared by the method of Montiero and Gemal [24]) gave *ethyl 2-phenylsulphinylpropenoate* (21), R_F 0.50 (Et_2O), $\nu_{max.}$ (film) 1 720 and 1 055 cm^{-1}; δ (CCl_4) 7.9—7.3 (5 H, m), 6.76 (1 H, s), 6.71 (1 H, s), 4.84 (2 H, q, *J* 7 Hz), and 1.31 (3 H, t, *J* 7 Hz) (Found: M^+, 224.0501. $C_{11}H_{12}O_3S$ requires M, 224.0507). (*Z*)-3-Phenylthio-4-trimethylsilylpent-3-en-2-one (28) (preparation as described below) gave (Z)-3-*phenylsulphinyl-4-trimethylsilylpent-3-en-2-one* (24) as prisms, m.p. 88—89 °C (from hexane) (decomp., remelts 75—82 °C) (Found: C, 59.8; H, 7.1; S, 11.4. $C_{14}H_{20}O_2SSi$ requires C, 59.9; H, 7.2; S, 11.4%), R_F 0.32 (diethyl ether–light petroleum, 1 : 1); δ ($CDCl_3$) 7.51 (5 H, s), 2.15 (3 H, s, MeCO), 2.01 (3 H, s, MeC=C), and 0.43 (9 H, s) (Found: M^+, 280.0949. $C_{14}H_{20}O_2SSi$ requires M, 280.0954); *m/z* 280 (0.79%), 265 (10), 198 (12), and 73 (100). (*E*)-3-Phenylthio-4-trimethylsilylpent-3-en-2-one (29) (preparation as described below) gave (E)-3-*phenylsulphinyl-4-trimethylsilylpent-3-en-2-one* (26), R_F 0.40 (diethyl ether–light petroleum, 1 : 1); $\nu_{max.}$ (film) 1 695 cm^{-1}; δ ($CDCl_3$) 7.53 (5 H, s), 2.37 (3 H, s, MeC=C), 2.12 (3 H, s, MeCO), and 0.17 (9 H, s) (Found: M^+, 280.0942. $C_{14}H_{20}O_2SSi$ requires M, 280.0954); *m/z* 280 (0.04%), 265 (55), and 73 (100).

The Preparation and Thermolysis of 3-Phenylseleninyl-4-trimethylsilylpentan-2-one (9).—Benzeneseleninyl chloride (2 mmol) in dry dichloromethane (5 ml) was added dropwise to 2-trimethylsiloxy-4-trimethylsilylpent-2-ene [9] (2 mmol) in dry dichloromethane (10 ml) under argon at −23 °C until an orange colour persisted. Evaporation of the solvent under reduced pressure gave the crude phenylseleninyl ketone which was purified by chromatography on silica (diethyl ether–light petroleum, 1 : 9 as eluant) at the expense of extensive decomposition. This compound was dissolved in dry [$^2H_2$]dichloromethane (1 ml) under argon and ozonised oxygen was passed in a slow stream at −78 °C until a blue-green colour developed. Argon was then passed through to flush out the excess of ozone and the solution was warmed to room temperature. The only product which could be detected by t.l.c. and n.m.r. was 4-trimethylsilylpent-3-en-2-one (10) [9] as a mixture of (*E*)- and (*Z*)-isomers, R_F 0.35 and 0.45 (diethyl ether–light petroleum, 1 : 9), $\nu_{max.}$ (film) 1 690 and 1 580 cm^{-1}; δ (CCl_4) 6.73 and 6.43 (1 H, q, *J* 2 Hz), 2.21 (3 H, s), 2.20 and 2.05 (3 H, d, *J* 2 Hz), and 0.19 (9 H, s).

The Preparation and Thermolysis of Dimethyl (Phenylsulphinyltrimethylsilylmethyl)malonate (13).—Dimethyl malonate (0.22 mol) in dry dioxan (2 ml) was added dropwise to a stirred suspension of sodium hydride (11.52 g of a 50% emulsion, washed with hexane, 0.24 mol) in dry hexamethyl-

phosphoric triamide (HMPA) (50 ml) and dry dioxan (200 ml) at reflux under nitrogen. After hydrogen evolution had ceased trimethylsilylmethyliodide (0.2 mol) in dry dioxan (25 ml) was added and the reaction maintained at reflux. After 2.5 h the mixture was cooled, poured into water, and extracted with hexane. The extracts were washed with brine, dried ($MgSO_4$), and evaporated to give, after distillation, *dimethyl trimethylsilylmethylmalonate* (29.96 g, 68%), b.p. 46—48 °C at 0.08 mmHg (Found: C, 49.9; H, 8.05. $C_9H_{18}O_4Si$ requires C, 49.6; H, 8.25%), $\nu_{max.}$ (film) 1 736 cm^{-1}; δ (CCl_4) 3.75 (6 H, s, 2 × OMe), 3.36 (1 H, t, *J* 8 Hz), 1.19 (2 H, d, *J* 8 Hz), and 0.08 (9 H, s, $SiMe_3$); *m/z* 202 (56%), 159 (66), and 73 (63). This malonic ester (1.09 g, 5 mmol) in dry tetrahydrofuran (THF) (3 ml) was added dropwise to a stirred solution of lithium di-isopropylamide (LDA) (5 mmol) in dry THF (15 ml) at 0 °C under nitrogen. After 40 min phenyl benzenethiosulphonate [25] (1.25 g, 5 mmol) in dry THF (3 ml) was added rapidly and the reaction mixture was allowed to warm to room temperature and left for 2 d. The products were poured into hydrochloric acid (3M) and extracted with diethyl ether. The extract was washed twice with brine, dried ($MgSO_4$), and evaporated *in vacuo* to give, after column chromatography on silica (CH_2Cl_2 as eluant), *dimethyl phenylthio(trimethylsilylmethyl)malonate* (81%), $\nu_{max.}$ (film) 3 050, 1 730, and 1 575 cm^{-1}; δ (CCl_4) 7.7—7.3 (5 H, m), 3.68 (6 H, s, 2 × OMe), 1.52 (2 H, s), and 0.10 (9 H, s) (Found: M^+, 326.1006. $C_{15}H_{22}O_4SSi$ requires *M*, 326.1008); *m/z* 326 (0.4%), 311 (6), 217 (17), 113 (100), and 73 (47). MCPBA (1.0 mmol) in dry dichloromethane (4 ml) was added slowly to a stirred solution of the α-phenylthiomalonic ester (1 mmol) in dry dichloromethane (3 ml) at −20 °C. After 20 min the mixture was poured into aqueous sodium hydrogen carbonate and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and evaporated. The products were purified twice by preparative t.l.c. (CH_2Cl_2 and ethyl acetate–hexane, 1 : 4) to give *dimethyl trimethylsilylmethylenemalonate* (14) (59%), R_F 0.35 (CH_2Cl_2), 0.5 (ethyl acetate–hexane, 1 : 4); $\nu_{max.}$ (film) 1 730, 1 610, 1 440, and 1 240 cm^{-1}; δ (CCl_4) 7.12 (1 H, s, HC=C), 3.78 (6 H, s, 2 × OMe), and 0.14 (9 H, s) (Found: M^+ − Me, 201.0583. $C_9H_{16}O_4Si$ requires *M* − Me, 201.0583); *m/z* 201 (100%), 184 (12), 151 (24), 89 (52), and 73 (30).

The Preparation and Thermolysis of Benzyl 2-Phenylsulphinyl(2-trimethylsilylmethyl)propionate (15).—3-Trimethylsilylpropionic acid (3 mmol), benzyl alcohol (4 mmol), molecular sieves (4A, *ca.* 1 g) and toluene-*p*-sulphonic acid (*ca.* 10 mg) were heated in toluene (10 ml) under reflux for 6 h. The solution was then cooled, filtered through Celite, evaporated under reduced pressure and purified by column chromatography (CH_2Cl_2 as eluant) to give benzyl 3-trimethylsilylpropionate (70%), R_F 0.6 (CH_2Cl_2), $\nu_{max.}$ (film) 3 040, 1 740, 1 500, and 1 250 cm^{-1}; δ (CCl_4) 7.25 (5 H, s), 5.01 (2 H, s, CH_2Ph), 2.28 (2 H, t, *J* 8.5 Hz, CH_2CO), 0.82 (2 H, t, *J* 8.5 Hz, CH_2Si), and 0.00 (9 H, s). This ester (354 mg, 1.5 mmol) in dry THF (2 ml) was added dropwise to a stirred solution of LDA (1.6 mmol) in dry THF (5 ml) at −78 °C under nitrogen. After 30 min this solution was quenched by transfer into diphenyl disulphide (350 mg, 1.6 mmol) in dry THF (5 ml) at room temperature under nitrogen. After 15 min the products were partitioned between diethyl ether and hydrochloric acid (3M). The organic layer was washed with aqueous sodium hydrogen carbonate and with brine, dried ($MgSO_4$), evaporated, and purified by t.l.c. (dichloromethane–hexane, 1 : 1) to give benzyl 2-phenylthio-3-trimethylsilylpropionate (62%), δ (CCl_4) 7.35 (5 H, br s), 5.0 (2 H, s, CH_2Ph), 3.8 (1 H, dd, *J* 10 and 6 Hz, CHS), 0.9—1.4 (2 H, m, CH_2Si), and 0.12 (9 H, s). This α-methylthio-ester (322 mg, 0.936 mmol) in dry THF (3 ml) was added dropwise to a solution of LDA (1.2 mmol) in dry THF (5 ml) at −78 °C under nitrogen. After 30 min methyl iodide (0.125 ml, 2 mmol) was added and the mixture allowed to warm to room temperature. The products were partitioned between diethyl ether and brine, and the organic layer was washed with brine, dried ($MgSO_4$), evaporated and purified by t.l.c. (dichloromethane–hexane, 1 : 1) to give benzyl 2-methyl-2-phenylthio-3-trimethylsilylpropionate (78%), R_F 0.4 (dichloromethane–hexane, 1 : 1), $\nu_{max.}$ (film) 3 050, 1 750, 1 585, and 1 250 cm^{-1}; δ (CCl_4) 7.2 (5 H, m), 5.04 (1 H, d, *J* 12 Hz, CH_AH_BPh), 4.90 (1 H, d, *J* 12 Hz, CH_AH_BPh), 1.52 (1 H, d, *J* 14 Hz, CH_AH_BSi), 1.44 (3 H, s, Me), 1.03 (1 H, d, *J* 14 Hz, CH_AH_BSi), and −0.02 (9 H, s). MCPBA (88 mg, 0.51 mmol) in dry dichloromethane (3 ml) was added slowly to a stirred solution of this ester (182 mg, 0.51 mmol) in dry dichloromethane (3 ml) at −20 °C. After 10 min the products were poured into aqueous sodium hydrogen carbonate and extracted with dichloromethane. The extract was dried ($MgSO_4$) and evaporated to give the sulphoxide, R_F 0.1 (CH_2Cl_2). T.l.c. showed a gradual decomposition at room temperature. After 24 h the products were purified by t.l.c. (CH_2Cl_2) to give three products identifiable by n.m.r. These were: (*Z*)-benzyl 2-methyl-3-trimethylsilylprop-2-enoate (16) (18 mg, 13%), R_F 0.7 (CH_2Cl_2), δ (CCl_4) 7.42 (5 H, br s), 6.20 (1 H, br s, CHSi), 5.22 (2 H, s, CH_2Ph), 2.16 (3 H, s, Me), and 0.17 (9 H, s); (*E*)-benzyl 2-methyl-3-trimethylsilylprop-2-enoate (16) (38%), R_F 0.6—0.7 (CH_2Cl_2), δ (CCl_4) 7.36 (5 H, s), 6.86 (1 H, s, CHSi), 5.18 (2 H, s, CH_2Ph), 2.08 (3 H, s, Me), and 0.24 (9 H, s), mixed with benzyl 2-methylene-3-trimethylsilylpropanoate (17) (12%), R_F 0.6—0.7 (CH_2Cl_2), δ (CCl_4) 5.21 (2 H, s, CH_2Ph), 1.90 (2 H, s, CH_2Si), and 0.04 (9 H, s, $SiMe_3$).

The Preparation and Thermolysis of 2-Phenylsulphinyl-2-trimethylsilylmethylcyclohexanone (18).—Freshly prepared *N*-cyclohexylidenecyclohexylamine (18.4 g, 100 mmol) in dry THF (20 ml) was added slowly to a stirred solution of LDA (105 mmol) in dry THF (200 ml) at 0 °C under nitrogen. After 30 min trimethylsilylmethyl iodide (16.3 ml, 105 mmol) was added, and the solution then stirred for a further 45 min. The products were partitioned between brine and diethyl ether and the organic layer shaken with a buffered acetic acid solution [sodium acetate trihydrate (25 g), acetic acid (50 ml) and H_2O (50 ml)] for 5 min. The organic layer was washed twice with saturated brine, then repeatedly with aqueous sodium hydrogen carbonate; it was dried ($MgSO_4$), evaporated under reduced pressure, and distilled to give 2-*trimethylsilylmethylcyclohexanone* (82%), b.p. 73—75 °C at 4.5 mmHg, $\nu_{max.}$ (film) 1 710 and 1 250 cm^{-1}; δ (CCl_4) 2.2—1.36 (9 H, m), 1.16 (1 H, dd, *J* 15 and 7 Hz, CH_AH_BSi), 0.37 (1 H, dd, *J* 15 and 6 Hz, CH_AH_BSi), and 0.03 (9 H, s) (Found: M^+, 184.1278. $C_{10}H_{20}OSi$ requires *M*, 184.1273); *m/z* 184 (11%), 169 (56), and 75 (100). This ketone (9.2 g, 50 mmol) was converted into its thermodynamic silyl enol ether by the method of House *et al.* [26] (reaction time 66 h) to give, after column chromatography (CH_2Cl_2 as eluant), 1-trimethylsiloxy-2-(trimethylsilylmethyl)cyclohexene (9.0 g, 71%). This silyl enol ether (2.0 mmol) in dry THF (2 ml) was added dropwise to a stirred solution of methyl-lithium (2.0 ml of a 1.1M-solution in diethyl ether, 2.2 mmol) in dry THF (5 ml) at room temperature under nitrogen.[27] After 5 min, diphenyl disulphide (2.0 mmol) in dry HMPA (2 ml) was added rapidly and the reaction stirred for 2 h. The products were

partitioned between diethyl ether and aqueous sodium hydrogen carbonate, and the organic layer washed with hydrochloric acid (3M) and with brine, dried ($MgSO_4$), and evaporated. Purification by t.l.c. (CH_2Cl_2) gave *2-phenylthio-2-(trimethylsilylmethyl)cyclohexanone* (135 mg, 23%), R_F 0.55 (CH_2Cl_2), $\nu_{max.}$ (CCl_4) 3 075, 1 700, and 1 250 cm^{-1}; δ (CCl_4) 7.32 (5 H, br s), 3.1—3.5 (1 H, m, axial CHCO), 1.5—2.6 (7 H, m), 1.31 (1 H, d, *J* 14.5 Hz, CH_AH_BSi), 0.81 (1 H, d, *J* 14.5 Hz, CH_AH_BSi), and 0.00 (9 H, s) (Found: M^+, 292.1328. $C_{16}H_{24}OSSi$ requires *M*, 292.1317); *m/z* 292 (7%), 277 (15), and 183 (100). MCPBA (0.212 mmol) in dry dichloromethane (2 ml) was added slowly to a stirred solution of the α-phenylthio-ketone (62 mg, 0.212 mmol) at −20 °C. After 10 min the products were poured into aqueous sodium hydrogen carbonate and extracted with chloroform. The extract was dried ($MgSO_4$), evaporated under reduced pressure, and purified by t.l.c. (CH_2Cl_2) to give a mixture of *2-trimethylsilylmethylcyclohex-2-enone* (19) (74%), R_F 0.35 (CH_2Cl_2), $\nu_{max.}$ (CCl_4) 3 060, 1 680, and 1 250 cm^{-1}; δ (CCl_4) 6.52 (1 H, m), 2.8—1.8 (6 H, m), 1.68 (2 H, d, *J* 2 Hz, CH_2SO), and 0.00 (9 H, s); *m/z* 182 (M^+, 30%), 167 (*M* − Me, 70), and 73 ($SiMe_3$, 100), and 2-trimethylsilylmethylenecyclohexanone (20).[9]

Thermolysis of Ethyl 2-Phenylsulphinylpropenoate (21).—The sulphoxide (21) (2 mmol) (as prepared above) in toluene (5 ml) was heated under reflux at 120 °C under argon for 1.5 h. Evaporation under reduced pressure followed by column chromatography (diethyl ether–light petroleum, 1 : 1 as eluant) gave *ethyl 3-phenylsulphinylpropenoate* (23) (*ca.* 60%), R_F 0.27 (diethyl ether–light petroleum, 1 : 1), $\nu_{max.}$ (film) 1 730, 1 620, and 1 055 cm^{-1}; δ (CCl_4) 7.95—7.4 (5 H, m), 7.55 (1 H, d, *J* 15 Hz), 6.64 (1 H, d, *J* 15 Hz), 4.22 (2 H, q, *J* 7 Hz), and 1.35 (3 H, t, *J* 7 Hz) (Found: M^+, 224.051. $C_{11}H_{12}O_3S$ requires *M*, 224.0507); *m/z* 224 (19.8%), 175 (95), and 130 (100); and *ethyl 3-phenylsulphonylpropenoate* (*ca.* 20%), R_F 0.42 (diethyl ether–light petroleum, 1 : 1), $\nu_{max.}$ (film) 1 730, 1 330, and 1 150 cm^{-1}; δ (CCl_4) 8.1—7.45 (5 H, m), 7.33 (1 H, d, *J* 15.5 Hz), 6.76 (1 H, d, *J* 15.5 Hz), 4.24 (2 H, q, *J* 7 Hz), and 1.33 (3 H, t, *J* 7 Hz) (Found: M^+, 240.0462. $C_{11}H_{12}O_4S$ requires *M*, 240.0456); *m/z* 240 (1.47%), 195 (38), and 141 (25).

Preparation of 3-Phenylthio-4-trimethylsilylpent-3-en-2-one (28) *and* (29).—Benzenesulphenyl chloride (5 mmol) was added to the enone (10) [9] (5 mmol) in dry dichloromethane (10 ml) at room temperature. N.m.r. showed that the instantaneous reaction initially gave 3-chloro-4-phenylthio-4-trimethylsilylpentan-2-one, but that this slowly rearranged to 4-chloro-3-phenylthio-4-trimethylsilylpentan-2-one (27) after *ca.* 2 h. The latter compound (27) was isolated by evaporation under reduced pressure, R_F 0.35 (diethyl ether–light petroleum, 1 : 9); δ (CCl_4) 7.7—7.2 (5 H, m), 4.01 (1 H, s, CHS), 2.37 (3 H, s, MeCO), 1.76 (3 H, s, MeCSi), and 0.35 (9 H, s). The adduct (27) (10 mmol) was dissolved in carbon tetrachloride (10 ml, AnalaR) and diazabicyclo-[5.4.0]undec-5-ene (DBU) (11 mmol) in carbon tetrachloride (10 ml, AnalaR) was added at 0 °C. A precipitate appeared immediately and heat was evolved. The mixture was shaken for 5 min, poured into dilute hydrochloric acid (2M) and extracted with dichloromethane. The extract was dried (Na_2SO_4), evaporated under reduced pressure and the product purified by column chromatography (diethyl ether–light petroleum, 1 : 9 as eluant) to give (Z)-*3-phenylthio-4-trimethylsilylpent-3-en-2-one* (28) (25%, after a period in CCl_4 solution in the light to allow the isomers to equilibrate), R_F 0.39 (diethyl ether–light petroleum, 1 : 9), $\nu_{max.}$ (film) 1 695, 1 588, and 1 250 cm^{-1}; δ ($CDCl_3$) 7.23 (5 H, s), 2.21 (3 H, s, MeCO), 2.00 (3 H, s, MeC=C), and 0.27 (9 H, s), and (E)-*3-phenylthio-4-trimethylsilylpent-3-en-2-one* (29) (75%), R_F 0.55 (diethyl ether–light petroleum), $\nu_{max.}$ (film) 1 691, 1 587, and 1 250 cm^{-1}; δ ($CDCl_3$) 7.20 (5 H, s), 2.17 (3 H, s, MeCO), 2.13 (3 H, s, MeC=C), and 0.17 (9 H, s) (Found: M^+, 264.1001. $C_{14}H_{20}OSSi$ requires *M*, 264.1004); *m/z* 264 (0.12%), 249 (23), and 125 (62).

Pent-3-yn-2-one (25).—The sulphoxide (24) (0.309 mmol) was distilled bulb-to-bulb, oven temperature 120 °C at 14 mmHg, and the distillate collected at the temperature of liquid nitrogen. Redistillation gave pent-3-yn-2-one (25) [28] (72% by n.m.r.). The other isomer, the sulphoxide (26), distilled over unchanged at 160 °C at 0.1 mmHg, but on heating (220—230 °C at 14 mmHg) gave pent-3-yn-2-one (25) (6.4% by n.m.r.), $\nu_{max.}$ (film) 2 225 and 1 680 cm^{-1}; δ (CCl_4) 2.28 (3 H, s, MeCO) and 2.06 (3 H, s); the 2,4-dinitrophenylhydrazone had m.p. 150—151 °C (from EtOH), (lit.,[28] 149 °C).

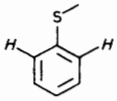
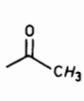
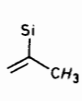
4-Phenylthiopent-3-en-2-one (30).—The adduct (27) (3 mmol) was heated in dry ethanol-free chloroform (10 ml) with a trace of anhydrous zinc bromide (*ca.* 2 mg) at 60 °C under reflux for 8 h. Evaporation under reduced pressure and chromatography on coarse silica gave (*E*)-4-phenylthiopent-3-en-2-one [(*E*)-(30)] [29] (45%), 0.28 (diethyl ether–light petroleum, 3 : 7), $\nu_{max.}$ (film) 1 681 and 1 580 cm^{-1}; δ (CCl_4) 7.49 (5 H, s), 5.66 (1 H, br s), 2.48 (3 H, br s, MeC=C), and 2.04 (3 H, s, MeCO), and (*Z*)-4-phenylthiopent-3-en-2-one [(*Z*)-(30)] [6,29] (45%), R_F 0.44 (diethyl ether–light petroleum, 3 : 7); δ (CCl_4) 7.7—7.1 (5 H, m), 6.24 (1 H, br s), 2.40 (3 H, s, MeCO), and 1.86 (3 H, br s, MeC=C).

Penta-3,4-dien-2-one (31).—Oxidation of both isomers of the sulphide (30) with MCPBA as described above gave the corresponding isomers of the known 4-phenylsulphinylpent-3-en-2-one [29] which behaved identically on heating. Bulb-to-bulb distillation at 160—210 °C at 14 mmHg gave only a small yield of penta-3,4-dien-2-one (31) [30] together with much unchanged starting material; the mixture was separated by redistillation at a lower temperature, $\nu_{max.}$ (film) 1 960, 1 935, and 1 690 cm^{-1}; δ (CCl_4) 5.67 (1 H, t, *J* 6.5 Hz, C=CHCO), 5.17 (2 H, d, *J* 6.5 Hz, $C=CH_2$), and 2.25 (3 H, s, MeCO).

Determination of the Kinetics of Sulphoxide Thermolysis.—The sulphoxide, together with *ca.* 0.5 equiv. of dichloromethane, was dissolved in carbon tetrachloride so that the concentration was 0.17—0.70M when the volume was made up to 1.5 ml in an n.m.r. tube, which was then sealed. It was then heated in a constant temperature oil-bath, accurate to ±1 °C, and the n.m.r. spectrum was recorded at convenient intervals until little or no starting material remained. With the sulphoxides (1), (2), and (4) the extent of reaction was determined by repeated integration of the signal at δ 6.0 [vinyl proton of 4-methylpent-3-en-2-one (3)] and δ 5.35 (dichloromethane). With sulphoxides (8) and (12) the total integral over the vinyl proton region was recorded, and as before compared to the integral for the dichloromethane peak. The amount of enone formed (x, in arbitrary dimensionless units), and the maximum value of x attained (a, estimated by graphical extrapolation), were plotted according to the familiar integrated first-order rate equation: $\ln a/a - x = kt$. The plot of $\ln a/(a - x)$ against t was linear over at least two or three half-lives, indicating that good first-order kinetics were observed. The values of k_1 given in the text were calculated using linear regression.

Proof of the Stereochemistry of the Isomers (24) *and* (26).— The two isomers of 4-phenylthiopent-3-en-2-one, (28) and (29), precursors of compounds (24) and (26) respectively, complexed the lanthanoid shift reagent $Eu(fod)_3$ in deuteriochloroform solution at the carbonyl group, causing downfield shifts of all the protons as given in the Table.[31] Direct

Chemical shifts of the ^1H n.m.r. spectra of compounds (24), (26), (28), and (29) on complexing with $Eu(fod)_3$

		Functional group			
					$(CH_3)_3Si-$
Compound					
(28)	Initial δ [b]	7.23	2.21	2.00	0.27
	G [c]	2.74	5.02	3.47	0.89
(29)	Initial δ	7.20	2.17	2.13	0.17
	G [c]	0.81	1.82	0.73	0.73
	G [c]	2.43	5.46	2.25	2.25
	(corrected) [d]	(±0.36)	(±0.82)	(±0.34)	(±0.34)
(24)	Initial δ	7.51	2.15	2.01	0.43
	G [c]	6.56	5.28	1.79	1.46
(26)	Initial δ	7.53	2.12	2.37	0.17
	G [c]	14.58	13.36	1.62	1.62

[a] The methyl singlets were differentiated by generation of the kinetic enolate of the sulphides by treatment with LDA in THF at −78 °C for 1.5 h. Quenching with D_2O led to a *ca.* 30% reduction in the integral of one signal, assumed to be the acetyl group. Oxidation of each monodeuteriated sulphide to its sulphoxide allowed the same identification to be made with these compounds. [b] δ values are in p.p.m. [c] G is the induced shift in p.p.m. per equiv. of $Eu(fod)_3$ added. [d] The correction is for the lower binding constant shown by compound (29), and makes the G values comparable to those for compound (28).

comparison of induced shifts for the various functional groups was made difficult because of the different binding constants for the two isomers. The ratio of binding constants was estimated as being 3 ± 0.6 by a competitive binding experiment using a mixture of the two isomers, and this figure was used to correct the induced shifts to allow direct comparisons to be made. The functional groups *syn* to the acetyl groups were found to move substantially faster in the n.m.r. spectra on addition of the shift reagent. In contrast, no useful comparison could be made when the same experiment was attempted with the sulphoxides (24) and (26), since these more polar compounds appeared to bind the europium ion as bidentate ligands; the two groups attached to the β-position at the enone could not then be differentiated. The less Lewis-acidic lanthanoid reagent $Gd(dpm)_3$ binds to compounds (24) and (26) only at the sulphoxide group and causes a relaxation effect which is inversely proportional to the sixth power of the distance of the metal ion (with no angular dependence).[20] Addition of one six-hundredth of an equivalent of this reagent to the sulphoxides (24) or (26) causes substantial line broadening of all of the singlets in the n.m.r. spectra except those due to groups assigned as being *anti* to the sulphoxide group. These results support and complement those from the shift-reagent experiments.

[1/1894 *Received 7th December*, 1981]

REFERENCES

[1] C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, 1960, **82**, 1810.
[2] B. M. Trost, T. N. Salzmann, and K. Hiroi, *J. Am. Chem. Soc.*, 1976, **98**, 4887.
[3] D. N. Jones, D. R. Hill, D. A. Lewton, and C. Sheppard, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1574.
[4] I. Fleming and D. A. Perry, *Tetrahedron Lett.*, 1981, **22**, 5095.
[5] A. G. Brook and D. G. Anderson, *Can. J. Chem.*, 1968, **46**, 2115; P. G. Kocienski, *Tetrahedron Lett.*, 1980, 1559; D. J. Ager and R. C. Cookson, *ibid.*, 1980, 1677; D. J. Ager, *ibid.*, 1981, 587.
[6] C. Eaborn and R. W. Bott in ' Organometallic Compounds of Group IV Elements, Volume 1, " The Bond to Carbon," Part 1,' ed. A. G. MacDiarmid, Dekker, New York, 1968, p. 359.
[7] E. W. Colvin, ' Silicon in Organic Synthesis,' Butterworths, London, 1981; I. Fleming in ' Comprehensive Organic Chemistry,' ed. D. H. R. Barton and W. D. Ollis, Pergamon, 1979, vol. 3, ed. D. N. Jones, p. 544.
[8] D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, 1974, **7**, 147.
[9] I. Fleming and D. A. Perry, *Tetrahedron*, 1981, **37**, 4027.
[10] I. Fleming and J. Goldhill, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1493.
[11] J. Nokami, K. Ueta, and R. Okawara, *Tetrahedron Lett.*, 1978, 4903.
[12] F. A. Carey and J. R. Toler, *J. Org. Chem.*, 1976, **41**, 1966.
[13] Y. I. Baukof, G. S. Burlachenko, A. S. Kostyuk, and I. Flutsenko, *Dokl. Vses. Konf. Khim. Atsetilena*, 4th 1972, 130 (*Chem. Abstr.*, 1973, **79**, 78904).
[14] B. L. Chenard, C. Slapak, D. K. Anderson, and J. S. Swenton, *J. Chem. Soc., Chem. Commun.*, 1981, 179.
[15] H. J. Reich and W. W. Willis, *J. Am. Chem. Soc.*, 1980, **102**, 5967.
[16] E. Block, R. E. Penn, and L. K. Revelle, *J. Am. Chem. Soc.*, 1979, **101**, 2200; J. Nokami, K. Nishiuchi, S. Wakabayashi, and R. Okawara, *Tetrahedron Lett.*, 1980, 4455.
[17] E. Block and J. O'Connor, *J. Am. Chem. Soc.*, 1974, **96**, 3929; J. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.*, 1973, **8**, 197 and 205.
[18] M. Naruse, K. Utimoto, and H. Nozaki, *Tetrahedron*, 1974, **30**, 2159.
[19] T. H. Chan and I. Fleming, *Synthesis*, 1979, 761.
[20] D. H. Welti, M. Linder, and R. R. Ernst, *J. Am. Chem. Soc.*, 1978, **100**, 403.
[21] P. Held, M. Gross, and A. Jumar, *Z. Chem.*, 1970, 187.
[22] B. D. Tilak and V. M. Vaidya, *Tetrahedron Lett.*, 1963, 487.
[23] P. Blatcher and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1074.
[24] H. J. Montievo and A. L. Gemal, *Synthesis*, 1975, 437.
[25] B. M. Trost and G. S. Massiot, *J. Am. Chem. Soc.*, 1977, **99**, 4405.
[26] H. O. House, L. C. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 1969, **34**, 2324.
[27] H. O. House, M. Gall, and M. D. Olmstead, *J. Org. Chem.*, 1971, **36**, 2361.
[28] E. A. Braude, E. R. H. Jones, F. Sondheimer, and J. B. Toogood, *J. Chem. Soc.*, 1949, 607.
[29] S. Danishefsky, T. Harayama, and R. K. Singh, *J. Am. Chem.* Soc., 1979, **101**, 7008.
[30] R. Couffignal and M. Gaudemar, *Bull. Soc. Chim. Fr.*, 1969, 898.
[31] J. K. M. Sanders and D. H. Williams, *J. Am. Chem. Soc.*, 1971, **93**, 641; J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Am. Chem. Soc.*, 1972, **94**, 5325.