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α-ALKYLATION AND α-ALKYLIDENATION OF CARBONYL COMPOUNDS BY *O*-SILYLATED ENOLATE PHENYLTHIOALKYLATION†

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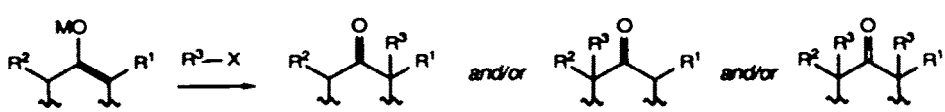
Abstract—For many reactions next to a carbonyl group, the use of *O*-silylated enolate chemistry offers improvements in yield and selectivity over the corresponding reactions of Group I metal enolates. In the case of α-alkylation of carbonyl compounds, Lewis-acid ($TiCl_4$ or $ZnBr_2$) promoted phenylthioalkylation of *O*-silylated enolates **3** by α-chlorosulphides **4** (R^3=H, Me, Pr^n, Pr^i, Bu^t, and Me_3Si), followed by reductive sulphur removal by Raney nickel, **5** → **6**, is found to be a reliable method for this synthetically important C-C bond forming step. An alternative sulphur elimination pathway *via* the sulphoxide, **5** → **7**, allows the regio- and stereocontrolled α-alkylidenation of carbonyl compounds. The phenylthioalkylation reaction is applicable to ketones, aldehydes, esters, and lactones.

The α-alkylation of carbonyl compounds by nucleophilic displacement of an alkyl halide with an enolate is a fundamental reaction in organic synthesis.[1] However, with simple ketones the basicity of Group I metal enolates (*i.e.* **1** for M=Li, Na, K) often results in competitive enolate equilibration, leading to loss of regiospecificity and multiple alkylation (see **Scheme 1**). The accessibility[1c,d] of a kinetically-generated specific lithium enolate of a ketone does not, therefore, necessarily guarantee site-specific monoalkylation, as in **1** → **2**.[2] Steric problems in forming the new carbon-carbon bond at highly congested reaction sites, competing elimination of the alkyl halide, and carbonyl condensation reactions, particularly with aldehydes, are additional restrictions on the method. While alternative methods for directed α–alkylation are available based on reactive enolate equivalents, particularly azaenolates,[3] together with the classical approach of using β-dicarbonyl compounds (as well as using other activating and blocking groups in the carbonyl component), the use of specific enolates with less electropositive metals might have distinct advantages.[4]

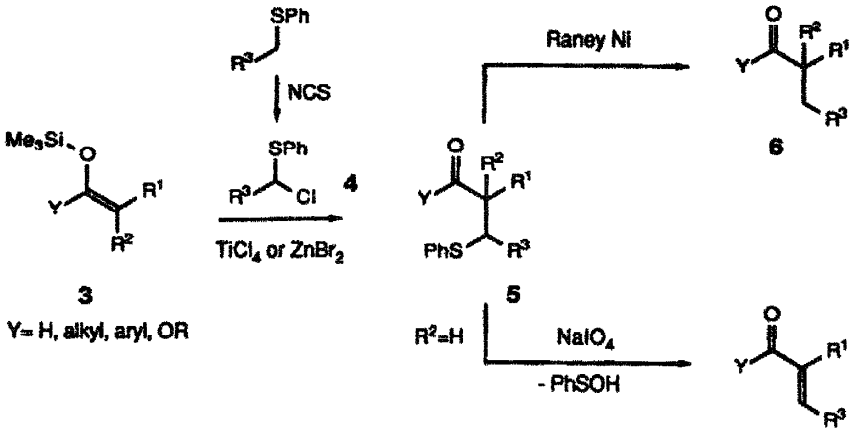


1 **2**

Scheme 1

O-Silylated enolates **3** are versatile synthetic intermediates,[5] which can function as specific enol equivalents for the controlled formation of C-C bonds next to the carbonyl group in modifications of many classical enolate reactions (*cf.* aldol, Michael), as well as in entirely new reactions. These covalent enolate derivatives, which are very easily prepared,[5] are only weakly nucleophilic and show no reaction with alkyl halides under normal conditions. However, regiocontrolled alkylation by certain S_N1-reactive alkyl halides is easy if a suitable Lewis-acid catalyst (most commonly $TiCl_4$ or $ZnBr_2$) is used. This permits *tert*-alkylation,[6] which fails completely with basic metal enolates, as well as alkylation by some reactive primary and secondary alkyl halides.[7] To extend this reaction to all primary alkyl halides,[9] the introduction of an α-phenylthio activating group on the halide reactant, *i.e.* **4**, provided a simple and effective solution.[8] Under

Lewis-acid catalysis, *O*-silylated enolates of carbonyl compounds can then be alkylated regiospecifically in high yield by α-chloroalkylphenylsulphides,[10] as in 3 + 4 → 5 (Scheme 2). The versatile phenylthio group introduced in the alkylation product may then be used in various ways; the simplest case is reductive removal, 5 → 6, leading overall to controlled monoalkylation. The other obvious means of removal involves oxidation to the sulphoxide (or sulphone) and β-elimination to give the α-alkylidenated carbonyl compound, as in 5 → 7. The phenylthio group (or its oxidised derivatives) may also be used, in suitable situations, to give a new carbonyl group by Pummerer-type rearrangement, to direct α-deprotonation, or the C-S bond may be reductively cleaved to give an organolithium.



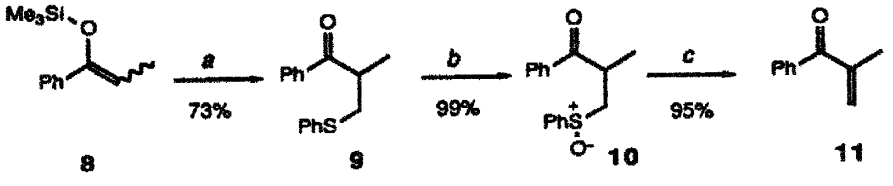
Scheme 2

Since the phenylthioalkylation reaction[8] was first described in 1979, it has been applied to a wide range of *O*-silylated enolates with α-chlorosulphides containing a variety of other functional groups (halides, ketones, esters, silylethers, alkenes, *etc.*)[11] leading to many useful products. It has also been applied[12] to the γ-alkylation of α,β-unsaturated carbonyl compounds by using the corresponding *O*-silylated dienolates. Analogous alkylation methods for silyl enol ethers using thioacetals,[7b,9a-c] vinylsulphides,[9d] β-chlorosulphides,[9e-h] and α-nitrosulphides[9i] have also been devised. We now report the full details of our original method.

RESULTS AND DISCUSSION

Phenylthiomethylation of ketones

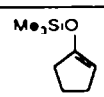
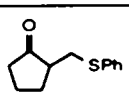
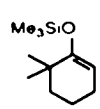
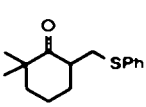
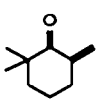
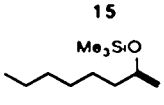
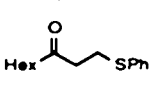
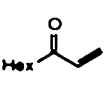
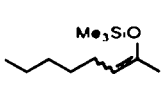
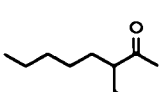
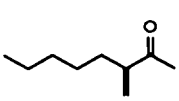
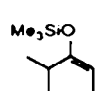
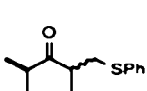
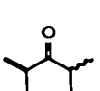
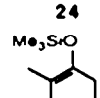
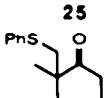
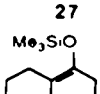
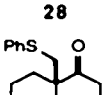
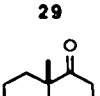
The simplest class of phenylthioalkylation reaction is phenylthiomethylation.[8a,b] Using lithium enolates, Reich and Renga[13] had previously described benzylthiomethylation reactions with $BnSCH_2Br$, but yields were only moderate at best and the reaction was not shown to be regiospecific with unsymmetrical ketones. The corresponding Lewis-acid promoted phenylthiomethylation of the silicon enolate proved to be a significant improvement.[8b] The reagent, chloromethylphenylsulphide, is readily available in high yield by



Scheme 3. (a) $PhSCH_2Cl$, 1.4 eq., $TiCl_4$, 1.1 eq., CH_2Cl_2, -23°C, 1 h; (b) $NaIO_4$, MeOH-H_2O, 9:1, 20°C, 16 h; (c) CCl_4-$CHCl_3$, 9:1, 65°C, 10 d.

chlorination of thioanisole with sulphuryl chloride.[14] Reaction of a mixture of the silyl enol ether **8** and $PhSCH_2Cl$ (1.4 equiv.) with $TiCl_4$ (1.1 equiv.) in dichloromethane (-23°C, 1 h) gave, after aqueous workup and chromatography, the α-phenylthiomethylketone **9** in 73% yield (**Scheme 3**). A catalytic amount (1-5 mol%) of anhydrous $ZnBr_2$ (CH_2Cl_2, 20°C, 16 h) could also be used successfully, but the yield was lower for ketone examples than that obtained with $TiCl_4$. In comparison, benzylthiomethylation of the corresponding lithium enolate is reported[13] to proceed in 60% yield. Mechanistically, this, and other phenylthioalkylations, probably involve generation of an intermediate thiocarbocation, $PhS^{+}{=}CHR$,[15] or an undissociated complex between the reagent and the Lewis acid, as the reacting electrophile. The results (see **Table 1**) for a range of ketone-derived silyl enol ethers by the $TiCl_4$ method indicated that alkylation worked well for acyclic and cyclic ketones. The reaction was regiospecific using 2-octanone, with **18** → **19** and **21** → **22**, and 2-methylcyclohexanone, with **24** → **25** and **27** → **28**. In each case, the starting silyl enol ether was formed regioselectively by using kinetic (*less*-substituted silyl enol ether) or thermodynamic (*more*-substituted silyl enol ether) control.[16]

Table 1. Synthesis of α-phenylthiomethylketones by $TiCl_4$-promoted alkylation of silyl enol ethers by $PhSCH_2Cl$; reductive and oxidative sulphur removal products.

Silyl Enol Ether	Method [a] (% regioisel.) [b]	Alkylation Product [c,d]	% Yield	Elimination Product [e]	% Yield	Reduction Product [f]	% Yield
 **12**	A	 **13**	65	 **14**	82		
 **15**	A	 **16**	77	 **17**	66		
 **18**	A (85)	 **19**	63	 **20**	71		
 **21**	B (92)	 **22**	75	 **23**	96		
 **24**	A (99)	 **25**	87			 **26**	99
 **27**	B (88)	 **28**	71			 **29**	98
 **30**	B (90)	 **31** [g]	80			 **32** [g]	92

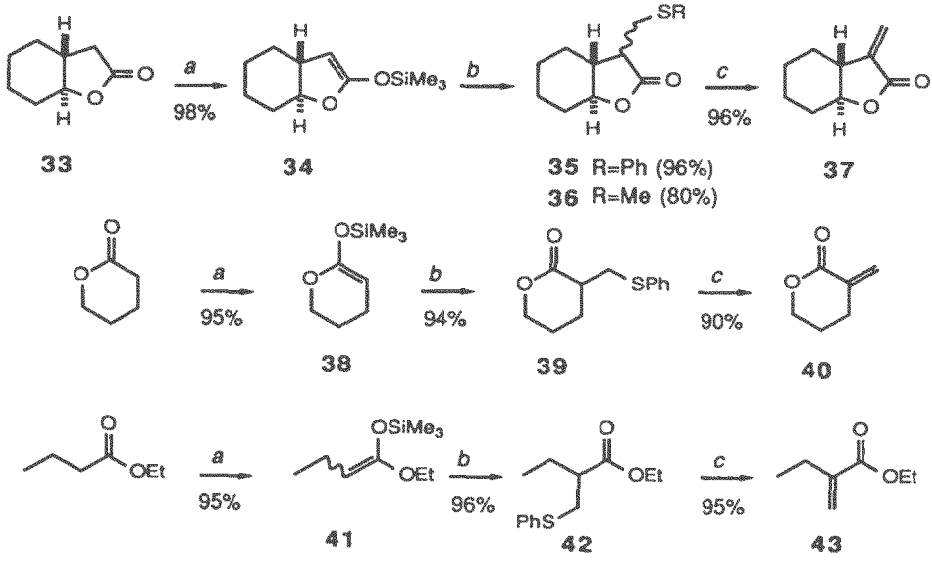
[a] Method A: LDA, THF, -78°C; Me_3SiCl, -78→20°C. Method B: Me_3SiCl, Et_3N, DMF, 110°C, 3 d. [b] determined by ^1H-NMR and/or gc. [c] $TiCl_4$, 1.1 eq., CH_2Cl_2, -23°C, 1 h. [d] the ratio of regioisomeric alkylation products was the same as the regioisomer ratio of the starting silyl enol ether. [e] $NaIO_4$, 1 eq., MeOH-H_2O, 9:1, 20°C, 16 h; CCl_4, 65°C, 0.5-16 h. [f] W-2 Ra Ni, Me_2CO-EtOH, 9:1, 20°C, 2 h. [g] 4:1 ratio of *cis*/*trans* fused isomers.

The α-phenylthiomethylated ketones could be used in various ways. We first focussed our attention on oxidative removal of the sulphur by sulphoxide cycloelimination to give the α-methyleneketone, which makes the overall transformation comparable to a Mannich reaction.[17] Unmasking of the α-methylene function (**Scheme 3** and **Table 1**) was straightforward; sulphoxide formation with $NaIO_4$ (MeOH-H_2O, 9:1 v/v, 20°C) was essentially quantitative and elimination of PhSOH took place in high yield (66-96%) on warming in CCl_4 or $CHCl_3$. The rate of sulphoxide elimination was found to be structure-dependent; the sulphoxide derived from **13** eliminated at 20°C with $t_{1/2}$ *ca* 48 h, while complete elimination from **10** required 10 days at 65°C. While higher temperatures could clearly also be used, a more rapid elimination method involves oxidation of the sulphide through to the sulphone with mCPBA and *in situ* elimination with DBU.[11c]

In three cases (**25** → **26**, **28** → **29**, and **31** → **32**), the phenylthio group was removed reductively by stirring with W-2 Raney nickel[18] in acetone (20°C, 2 h). This demonstrates the utility of our method for regiocontrolled α-methylation of ketones. In particular, bridgehead methylation in 1-decalone by conventional specific enolate chemistry leads to a significant proportion (23:62) of methylation on the other side of the carbonyl group.[19] Whereas phenylthiomethylation of silyl enol ether **30** gave the bridgehead alkylated isomers **31**, as a 4:1 mixture of *cis* and *trans* ring fusion, without enolate equilibration taking place. The *cis*-stereoselectivity of phenylthiomethylation in this example closely parallels that obtained[19,20] for the direct methylation of the corresponding lithium enolate.

Phenylthiomethylation of lactones and esters

The phenylthiomethylation/sulphoxide-elimination sequence also works well for esters and lactones.[8a] The α-methylene γ- or δ-lactone is a key feature of many cytotoxic sesquiterpenes and various methods have been devised for the synthesis of this unit.[21] Methods for the protection of the α-methylene unit include sulphide formation by Michael addition of thiols, which is then liberated under controlled conditions *via* the sulphonium salt[22] or sulphoxide.[23] Consequently, alkylation of a lactone enolate with an



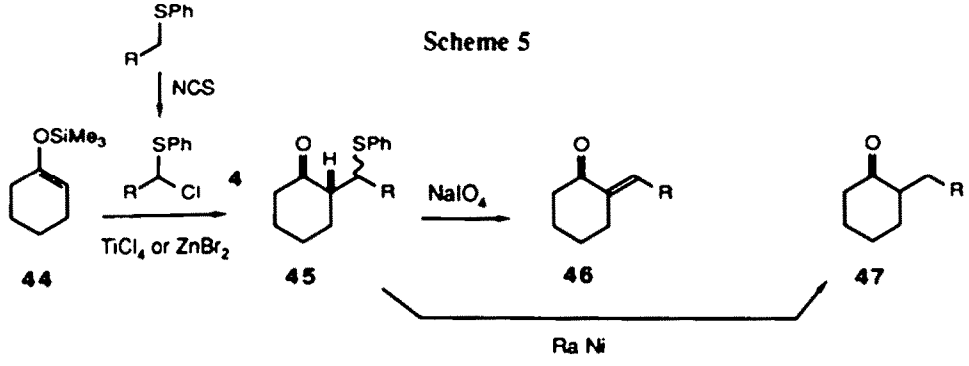
Scheme 4. (a) LDA, THF, -78°C, 0.5 h; Me_3SiCl, -78→20°C; (b) $PhSCH_2Cl$, 1.4 eq., $ZnBr_2$, 0.02 eq., CH_2Cl_2, 20°C, 16 h; (c) $NaIO_4$, MeOH-H_2O, 9:1, 16 h; CCl_4, 70°C, 4-16 h.

α-thioalkyl halide should lead directly to a masked α-methylene lactone. However, the lithium enolates of lactones are alkylated in only poor yield (0-20%) by $PhSCH_2I$,[23] $MeSCH_2Cl$,[24] $MeSCH_2I$,[24] and $BnSCH_2Br$.[13] In contrast, the corresponding *O*-silylated enolates may be easily phenylthiomethylated by the catalytic $ZnBr_2$ method (**Scheme 4**) in near quantitative yield. For instance, reaction of the *O*-silylated enolate **34** (prepared from **33** by LDA/Me_3SiCl in 98% yield) with $PhSCH_2Cl$ in CH_2Cl_2, in the presence of $ZnBr_2$ (0.02 equiv., 20°C, 16 h), gave the α-phenylthiomethyl-γ-lactone **35** in 96% yield. Oxidation to the sulphoxide ($NaIO_4$) and thermolysis cleanly gave the α-methylene-γ-lactone **37**. The overall yield for this lactone α-methylenation sequence was 90%, which makes it highly competitive with other reported methods.[22] The same sequence was performed on δ-valerolactone in 81% overall yield. In one case, an analogous methylthiomethylation reaction on **34** with $MeSCH_2Cl$ gave the sulphide **36**, which had previously[24] been converted to **37** by sulphonium salt formation with MeI followed by β-elimination with mild base. Ester enolates cannot be directly alkylated with $BnSCH_2Br$ in useful yield;[13] however, the $ZnBr_2$ method when applied to **41** gave the α-phenylthioester **42** in high yield, which could be routinely converted into the α-methylene ester **43**.

Phenylthioalkylation of carbonyl compounds

Our two-step alkylation method is applicable to the general introduction of primary alkyl groups by using α-chloroalkylphenylsulphides, *i.e.* **4** for R≠H, as the electrophilic reagent (**Scheme 5**).[8c] The α-

Scheme 5

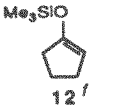
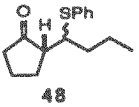
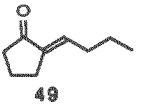
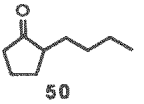
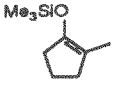
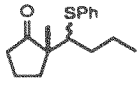
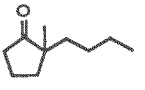
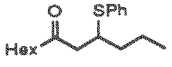
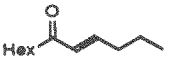
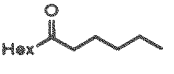
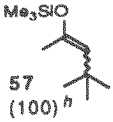
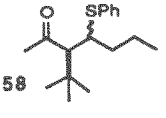
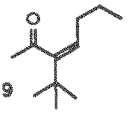
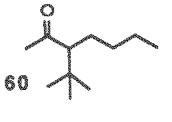
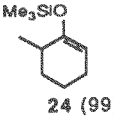
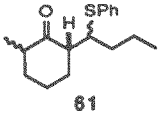
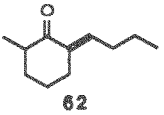
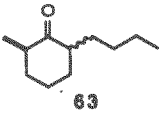
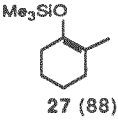
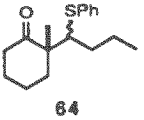
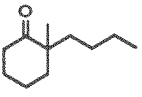
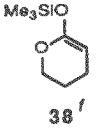
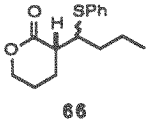
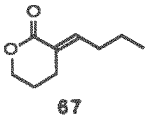
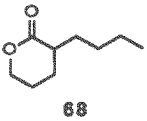
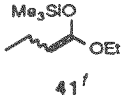
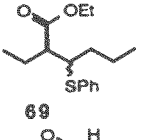
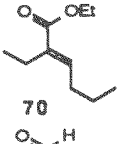
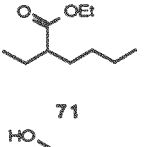
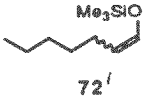
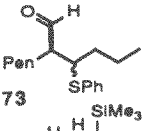
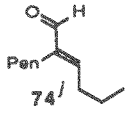
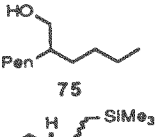
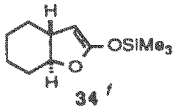
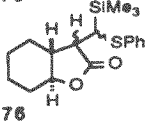
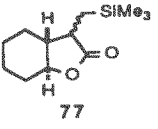


R	Method[a]	45(%)	46(%)[b]	47(%)[c]
Me	$TiCl_4$	78	92	95
Pr^n	$TiCl_4$	83	89	90
Pr^i	$TiCl_4$	66	94	91
Bu^t	$ZnBr_2$	78	95	93
Me_3Si	$ZnBr_2$	84		92

[a] $TiCl_4$, 1.1 eq., CH_2Cl_2, -23°C, 1 h. or $ZnBr_2$, 0.02 eq., CH_2Cl_2, 20°C, 16 h.
[b] $NaIO_4$, 1 eq., MeOH-H_2O, 9:1, 20°C, 16 h; CCl_4, 60°C, 5-60 h.
[c] W-2 Ra Ni, Me_2CO-EtOH, 9:1, 20°C, 2 h.

chlorosulphides **4**, for R=Me, Pr^n, Pr^i, and Bu^t, were readily prepared by NCS chlorination (CCl_4, 20°C, 6 -16 h, >95% yield) of the corresponding phenylsulphide (obtained by NaSPh displacement of the bromide or tosylate). The product was simply isolated by filtration and solvent evaporation. These moisture-sensitive α-chlorosulphides could be stored for several months under nitrogen at -15°C without significant deterioration. Reaction of silyl enol ether **44** with **4** in CH_2Cl_2, either in the presence of an equivalent of

Table 2. Synthesis of α-phenylthioalkylcarbonyl compounds by Lewis acid-promoted alkylation of *O*-silylated enolates by PhSCH(Cl)Pr^n and PhSCH(Cl)SiMe$_3$; reductive and oxidative sulphur removal products.

O-Silyl Enolate (% regiosel.) [a]	Lewis Acid [b]	Alkylation Product [c]	% Yield	Elimination Product [d]	% Yield	Reduction Product [e]	% Yield
 **12** [f]	$TiCl_4$	 **48**	90	 **49**	87	 **50**	94
 **51** (93) [g]	$ZnBr_2$	 **52**	82			 **53**	96
 **18** (85) [f]	$TiCl_4$	 **54**	79	 **55**	87	 **56**	85
 **57** (100) [h]	$TiCl_4$	 **58**	82	 **59**	85	 **60**	98
 **24** (99) [f]	$TiCl_4$ $ZnBr_2$	 **61**	89 82	 **62**	81	 **63**	95
 **27** (88) [g]	$TiCl_4$ $ZnBr_2$	 **64**	63 71			 **65**	94
 **38** [f]	$ZnBr_2$	 **66**	96	 **67**	81	 **68**	96
 **41** [f]	$ZnBr_2$	 **69**	98	 **70**	89	 **71**	90
 **72** [i]	$TiCl_2(OPr^i)_2$ $ZnBr_2$	 **73**	86 40	 **74** [j]	97	 **75**	91
 **34** [f]	$ZnBr_2$	 **76**	97			 **77**	95

[a] determined by ^{1}H-NMR and/or gc. [b] $TiCl_4$, 1.1 eq., CH_2Cl_2, -23°C, 1 h. $ZnBr_2$, 0.02 eq., 20°C, 0.5-16 h. $TiCl_4$-$Ti(OPr^i)_4$, 1:1, CH_2Cl_2, -78°C, 1 h. [c] the ratio of regioisomeric alkylation products was the same as the regioisomer ratio of the starting silyl enol ether. [d] $NaIO_4$, 1 eq., MeOH-H_2O, 9:1, 20°C, 16 h; CCl_4, 60°C, 1-60 h. [e] W-2 Ra Ni, Me_2CO-EtOH, 9:1, 20°C, 2 h. [f] prepared by: LDA, THF, -78°C; Me_3SiCl, -78→20°C. [g] prepared by: Me_3SiCl, Et_3N, DMF, 110°C, 3 d. [h] prepared from mesityl oxide by: MeMgI(cat.CuCl), Et_2O, -23°C; Me_3SiCl, Et_3N, HMPA. [i] prepared by: Me_3SiCl, Et_3N, DMF, 110°C, 3 h. [j] 70:30 ratio of *E*/*Z* isomers.

$TiCl_4$ (-23°C, 1 h) or a catalytic amount of $ZnBr_2$ (20°C, 16 h), gave the α-phenylthioalkylcyclohexanone **45** for R=Me, Pr^n, Pr^i, and Bu^t. In these, and subsequent phenylthioalkylations of prochiral enolates, the products were obtained as mixtures of diastereomers with no significant reaction diastereoselectivity evident. Raney nickel desulphurisation gave the corresponding α-alkylated cyclohexanone, **45** → **47**, in good overall yield. Ethylation, *n*-butylation, *iso*-butylation, and remarkably *neo*-pentylation were achieved in this way. In each of these cases, the sulphur was also removed oxidatively using $NaIO_4$, **45** → **46**, to give, effectively, the *E*-isomer of a directed aldol condensation after dehydration. Consequently, the α-chlorosulphides **4** are shown to serve as useful equivalents of both alkyl halides and aldehydes.

The phenylthiobutylation reaction using **4**, for R=Pr^n, was carried out successfully (see **Table 2**) on the *O*-silylated enolates of a range of carbonyl compounds: symmetrical (**12**) and unsymmetrical ketones (**51**, **18**, **57**, **24**, **27**); aldehydes (**72**); esters (**41**); lactones (**38**).[8c] In each case, reductive and oxidative sulphur removal was carried out on the intermediate α-phenylthiobutyl carbonyl compound. $TiCl_4$ and $ZnBr_2$ were again found to be the most effective Lewis acids for the alkylation step, but which was better depended on the substrate. With the more reactive ketene acetals of esters and lactones, $ZnBr_2$ was clearly the best Lewis acid and gave high yields. The $ZnBr_2$-catalysed reaction of esters and lactones was generally considerably faster than that of ketones; in many cases the reaction was exothermic and required cooling. For the aldehyde silyl enol ether **72**, a 1:1 mixture of $TiCl_4$ and $Ti(OPr^i)_4$, *i.e.* $Ti(OPr^i)_2Cl_2$, was best with $ZnBr_2$ giving a lower yield. For the silyl enol ethers of ketones, both $ZnBr_2$ and $TiCl_4$ were successful. $ZnBr_2$ has clear advantages of mildness, catalytic use, and ease of operation, but $TiCl_4$ may occasionally be superior in being more apt to give regiospecific alkylation.[7a] Both Lewis acids were successful, however, in promoting regiospecific phenylthiobutylation of the two isomeric silyl enol ethers, **24** and **27**, from 2-methylcyclohexanone. In contrast, the corresponding lithium enolates are not easily *n*-butylated without competing equilibration.[2c,25] A more testing case is introduction of a trimethylsilylmethyl group (*cf. neo*-pentylation). Reaction of ketone enolates with Me_3SiCH_2I proceed only in low yield, although metallated imines can be used with success.[26] Using the appropriate α-chlorosulphide **4**, R=$SiMe_3$, the $ZnBr_2$ method gave **45** (**Scheme 5**) and **76** (**Table 2**) in 84% and 97% yields and reductive desulphurisation gave the corresponding α-trimethylsilylmethyl- ketone **47** and lactone **77**.

These results show that the phenylthioalkylation reaction is equally effective for regiocontrolled alkylation at the more-substituted and less-substituted α-carbon of unsymmetrical ketones. It also works in the regiospecific alkylation of sterically hindered enolates, such as those having an adjacent quaternary carbon as in **57**, and can be used for the introduction of the more difficult primary alkyl groups like *neo*-pentyl and trimethylsilylmethyl. Only in the case of aldehydes is Raney nickel desulphurisation accompanied by competitive reduction of the carbonyl group, *cf.* **73** → **75**. It is, therefore, a reliable and widely applicable[11] method for the controlled α-alkylation of carbonyl compounds.

α–Alkylidenation of carbonyl compounds

The oxidative sulphur removal pathway makes available a method for the regiospecific α-alkylidenation of carbonyl compounds, where the intermediate sulphide serves to mask the unsaturation, and unmasking is efficiently achieved under mild conditions. In this respect, the method may have advantages over the conventional directed aldol condensation. For the majority of cases in **Scheme 5** and

Table 2, extensive elimination of PhSOH occurred at room temperature during the $NaIO_4$ oxidation step. Only in cases **45** → **46**, R=Bu^t, **69** → **70**, and **58** → **59**, was the sulphoxide isolated unscathed and elimination was carried out by warming in CCl_4 (60°C, 1-60 h). Elimination in these β-phenylsulphinyl carbonyl compounds, as opposed to α-phenylsulphinyl compounds,[27] is clearly favoured by the acidity of the proton next to the carbonyl group and breaking of the C-S bond in the cyclic transition state does not lead to development of positive charge adjacent to the carbonyl group. The ease of elimination was also found to increase with the degree of substitution of the double formed. The α,β-unsaturated carbonyl compounds were usually formed with high *E*-stereoselectivity, *i.e.* favouring the thermodynamic isomer, even though the starting sulphide was an *erythro/threo* mixture and sulphoxide elimination is *syn*-stereospecific. Possibly this results from the reversibility of PhSOH elimination[28] coupled with epimerisation adjacent to the carbonyl group. In the case of **45** → **46**, for R=Bu^t, equilibration to the thermodynamically preferred *E*-isomer was slow enough that the kinetic formation of the *Z*-isomer and its subsequent isomerisation to the *E*-isomer could be followed by ^{1}H-NMR.

EXPERIMENTAL

DMF and dichloromethane were distilled from calcium hydride. THF was freshly distilled from sodium/benzophenone ketyl prior to use. Commercial grade titanium tetrachloride was distilled under nitrogen before use. Commercial grade zinc bromide could be used after drying at 200°C at 0.5 mm Hg, although 'Gold Label' grade (99.999%) gave best results. For desulphurisation purposes, W-2 Raney nickel[18] could be stored at 0°C under EtOH for up to 2-3 months. ^{1}H NMR spectra were recorded at 90 MHz on a Varian EM-390 or 60 MHz on a Varian EM-360. Mass spectra were obtained by electron impact (70 eV). Gas chromatography columns used were 10% SE-30 Ultraphase on Chromasorb W or 15% silicone grease on Chromasorb B.

Preparation of O-silylated enolates—Silyl enol ethers **21**, **27**, **30**, **51**, and **72** were prepared from the parent ketone or aldehyde by a modification[16b] of the thermodynamic method (Me_3SiCl, Et_3N, DMF) of House *et al.*[16a] Silyl enol ethers **8**, **12**, **15**, **18**, **24**, **44**, and **34** and ketene alkylsilylacetals **34**, **38**, and **41** were prepared by a modification[16b] of the kinetic method (LDA, THF; Me_3SiCl) of House *et al.*[16a] Silyl enol ether **57** was prepared by CuCl catalysed addition of MeMgI to mesityl oxide and enolate trapping with Me_3SiCl. Ratios of regioisomers were determined by ^{1}H-NMR and/or gc and are given in **Tables 1** and **2**. Details of new compounds are as follows:

34: (kinetic, 98%) b.p. 58-59°C/0.2 mm Hg; Found C 61.9, H 9.45, $C_{11}H_{20}O_2Si$ requires C 62.2, H 9.50%; IR(film) 1651, 1249; ^{1}H NMR δ(CCl_4) 3.79 (1H, s), 3.45-3.79 (1H, m), 1.05-2.64 (9H, m), 0.25 (9H, s); MS 212(100%), 211, 197, 183. **38**: (kinetic, 95%) b.p. 28-29°C/0.1 mm Hg; Found C 56.1, H 9.50, $C_8H_{16}O_2Si$ requires C 55.8, H 9.35%; IR(film) 1686, 1250; ^{1}H NMR δ(CCl_4) 3.97 (2H, t, J=5 Hz), 3.67 (1H, t, J=3 Hz), 1.53-2.10 (4H, m), 0.16 (9H, s); MS m/e 172(100%). *2,2-Dimethyl-4-trimethylsilyloxypent-3-ene* **57**: Powdered dry cuprous chloride (1.5 g, 15 mmol) was added, under nitrogen, to a stirred solution of methylmagnesium iodide (150 ml of a 1 M solution in Et_2O, 150 mmol) at -23°C. After 10 min, mesityl oxide (11.5 ml, 100 mmol) in ether (20 ml) was added over 10 min, followed, after a further 10 min, by chlorotrimethylsilane (30 ml, 236 mmol), triethylamine (37.5 ml, 270 mmol), and HMPA (19 ml, 110 mmol). After 0.5 h, the mixture was warmed to room temperature, poured into satd. NH_4Cl solution (200 ml) and extracted with ether (3x150 ml). The organic phase was washed with brine, dried ($MgSO_4$), and evaporated *in vacuo*. Fractional distillation gave **57**, 15.9 g, 85% (b.p. 62-65°C/21 mm Hg) as an *E/Z* isomer mixture: IR(film) 1666, 1255; ^{1}H NMR δ(CCl_4) 4.76, 4.28 (1H, 2x s), 1.80, 1.73 (3H, 2x s), 1.15, 1.12 (9H, 2x s), 0.23, 0.20 (9H, 2x s); HRMS M^+ 186.1438, $C_{10}H_{22}OSi$ requires 186.1440; m/e 186, 171, 73(100%), 57.

Preparation of α-chlorosulphides 4—Chloromethylphenylsulphide was prepared by the method of Trost and Kunz.[14] α-Chlorosulphides **4**, R=alkyl or $SiMe_3$, were prepared by N-chlorosuccinimide chlorination of the corresponding alkylphenylsulphide (prepared from the alkyl bromide, chloride, or tosylate using NaSPh in EtOH) after the method of Tuleen and Stephens.[29] Powdered NCS (10.68 g, 80 mmol) was added in a single portion to a stirred solution of the sulphide (80

mmol) in CCl_4 at 20°C. After 6-18 h, the mixture was filtered and the filtrate evaporated *in vacuo* to give the moisture-sensitive α-chlorosulphide **4** (stored in the freezer under nitrogen), which was used without purification in the phenylthioalkylation reactions.

1-Chloroethylphenylsulphide **4**, R=Me: (6 h, 97%) ^{1}H NMR δ(CCl_4) 7.20-7.68 (5H, m), 5.32 (1H, q, J=7 Hz), 2.01 (3H, d, J=7 Hz); *cf* lit.[29] *1-Chlorobutylphenylsulphide* **4**, R=Pr^n: (6 h, 98%) IR(film) 3060, 1583, 1480, 1440; ^{1}H NMR δ($CDCl_3$) 7.14-7.69 (5H, m), 5.25 (1H, t, J=7 Hz), 1.94-2.19 (2H, m), 1.42-1.83 (2H, m), 0.93 (3H, t, J=7 Hz); HRMS M^+ 200.0426, $C_{10}H_{13}ClS$ requires 200.0426; m/e 200, 165, 164, 110(100%), 109. *1-Chloro-2-methylpropylphenylsulphide* **4**, R=Pr^i: (8 h, 98%) ^{1}H-NMR δ($CDCl_3$) 7.18-7.69 (5H, m), 5.19 (1H, d, J=4 Hz), 1.95-2.80 (1H, m), 1.16 (6H, d, J=6.5 Hz); HRMS M^+ 200.0428, $C_{10}H_{13}ClS$ requires 200.0426; m/e 200, 165, 110(100%). *1-Chloro-2,2-dimethylpropylphenylsulphide* **4**, R=Bu^t: (16 h, 95%) ^{1}H NMR δ($CDCl_3$) 7.22-7.67 (5H, m), 4.98 (1H, s), 1.26 (9H, s). *Chlorotrimethylsilylmethylphenylsulphide* **4**, R=$SiMe_3$: (18 h, 96%) ^{1}H NMR δ($CDCl_3$) 6.93-7.41 (5H, m), 4.57 (1H, s), 0.03 (9H, s); HRMS M^+ 230.0339, $C_{10}H_{15}ClSSi$ requires 230.0353; m/e 230, 121(100%), 110.

Phenylthioalkylation: $TiCl_4$ method—A solution of titanium tetrachloride (0.6 ml, 5.5 mmol) in dry CH_2Cl_2 (5 ml) was added at -23°C by syringe to a stirred solution of *O*-silylated enolate (5 mmol) and α-chloroalkylphenylsulphide **4** (6-7 mmol), at -23°C, in CH_2Cl_2 (5 ml) under nitrogen. After 1 h, the resulting deep red solution was poured into satd. $NaHCO_3$ solution (25 ml) and extracted repeatedly with ether. The organic phase was dried ($MgSO_4$) and evaporated *in vacuo* to give, after chromatography on SiO_2, the phenylthioalkylated carbonyl compound. Ratios of regioisomers were determined by ^{1}H NMR and/or gc and were in close agreement with isomer ratios in the substrates.

$ZnBr_2$ method—Powdered anhydrous zinc bromide (15-20 mg, *ca* 0.1 mmol) was added to a stirred solution of *O*-silylated enolate (5 mmol) and α-chloroalkylphenylsulphide **4** (6 mmol) in dry CH_2Cl_2 at 20°C under nitrogen. Typical reaction times are as follows: 16 h for **4**, R=H (ester and lactone examples); 30 min for **4**, R≠H (ester and lactone examples); 16 h for **4**, R≠H (ketone examples). After the prescribed time, the solvent was evaporated *in vacuo* and the residue chromatographed on SiO_2 to give the phenylthioalkylated carbonyl compound.

$Ti(OPr^i)_2Cl_2$ method—Titanium tetra-*iso*-propoxide (0.42 ml, 4 mmol) was added to a stirred solution of titanium tetrachloride (0.44 ml, 4 mmol) in dry CH_2Cl_2 (5 ml) at 20°C under nitrogen. After 10 min, this mixture was then transferred by syringe to a stirred solution of the *O*-silylated enolate (4 mmol) and the α-chloroalkylphenylsulphide **4** (5 mmol) in CH_2Cl_2 (5 ml) at -78°C under nitrogen. After 1h, the reaction was worked up as in the $TiCl_4$ method.

1-Phenyl-2-phenylthiomethylpropanone **9**: ($TiCl_4$, 73%) IR(film) 3060, 1680, 1598, 1580, 1482, 1450; ^{1}H NMR δ($CDCl_3$) 7.82 (2H, d, J=8 Hz), 7.10-7.58 (8H, m), 3.52-3.87 (1H, m), 3.41 (1H, dd, J=7, 12 Hz), 2.97 (1H, dd, J=6.5, 12 Hz), 1.31 (3H, d, J=7 Hz); HRMS M^+ 256.0915, $C_{16}H_{16}OS$ requires 256.0922; m/e 256, 147, 123, 105(100%), 77. *2-Phenylthiomethylcyclopentanone* **13**: ($TiCl_4$, 65%) IR(film) 1735; ^{1}H NMR δ($CDCl_3$) 7.02-7.47 (5H, m), 3.45 (1H, dd, J=3.5, 12 Hz), 2.77 (1H, dd, J=8, 12 Hz), 1.48-2.57 (7H, m); HRMS M^+ 206.0774, $C_{12}H_{14}OS$ requires 206.0765; m/e 206, 123, 110(100%), 109, 97, 69. *2,2-Dimethyl-6-phenylthiomethylcyclohexanone* **16**: ($TiCl_4$, 77%) IR(film) 3060, 1710, 1586, 1482, 1440; ^{1}H NMR δ($CDCl_3$) 7.05-7.45 (5H, m), 3.49 (1H, dd, J=3.5, 12 Hz), 2.26-3.01 (3H, m), 1.24-2.03 (5H, m), 1.18 (3H, s), 1.10 (3H, s); HRMS M^+ 248.1240, $C_{15}H_{20}OS$ requires 248.1235; m/e 248, 139, 123, 110, 69(100%). *1-Phenyl-thiononan-3-one* **19**: ($TiCl_4$, 63%) IR(film) 1710; ^{1}H NMR δ($CDCl_3$) 7.02-7.56 (5H, m), 3.12 (2H, t, J=7 Hz), 2.70 (2H, t, J=7 Hz), 2.35 (2H, t, J=7 Hz), 1.08-1.76 (8H, m), 0.88 (3H, t, J=6 Hz); HRMS M^+ 250.1385, $C_{15}H_{22}OS$ requires 250.1391; m/e 250, 137, 123, 110 (100%), 109. *3-Phenylthiomethyloctan-2-one* **22**: ($TiCl_4$, 75%) IR(film) 1710, ^{1}H NMR δ($CDCl_3$) 6.98-7.36 (5H, m), 3.09 (1H, dd, J=8, 12.5 Hz), 2.84 (1H, dd, J=6, 12.5 Hz), 2.50-2.80 (1H, m), 2.06 (3H, s), 1.06-1.77 (8H, m), 0.87 (3H, t, J=6 Hz); HRMS M^+ 250.1392, $C_{15}H_{22}OS$ requires 250.1392; m/e 250, 141, 123, 110(100%), 71. *2-Methyl-6-phenylthiomethylcyclohexanone* **25**: ($TiCl_4$, 87%) IR(film) 1710; ^{1}H NMR δ($CDCl_3$) 7.00-7.54 (5H, m), 3.46 (1H, dd, J=4, 13 Hz), 1.20-2.88 (9H, m) 0.99 (3H, d, J=6 Hz); HRMS M^+ 234.1083, $C_{14}H_{18}OS$ requires 234.1079; m/e 234, 125, 110(100%). *2-Methyl-2-phenyl-thiomethylcyclohexanone* **28**: ($TiCl_4$, 71%) IR(film) 1715; ^{1}H NMR δ($CDCl_3$) 7.03-7.50 (5H, m), 3.16 (2H, s), 2.24-2.50 (2H, m), 1.56-2.04 (6H, m), 1.20 (3H, s); HRMS M^+ 234.1074, $C_{14}H_{18}OS$ requires 234.1079; m/e 234, 125, 110(100%). *9-Phenylthiomethyl-1-decalone* **31**: ($TiCl_4$, 80%) IR(film) 3060, 1705, 1584, 1480, 1440; ^{1}H NMR δ($CDCl_3$) 7.05-7.48 (5H, m), 3.32 (2H, s), 1.00-2.48 (15H, m); HRMS M^+ 274.1386, $C_{17}H_{22}OS$ requires 274.1394; m/e 274(100%). *2-Phenylthiomethyl-3,4-trans-tetramethylene-γ-butyrolactone* **35**: ($ZnBr_2$, 96%) IR(film) 3060, 1770, 1584, 1483, 1442; ^{1}H NMR δ($CDCl_3$) 7.12-7.60 (5H, m), 4.04 (0.5H, dt, J=4, 10 Hz), 3.73 (0.5H, dt, J=4, 10 Hz), 3.54 (1H, dd, J=4, 14 Hz) 1.96-3.21 (2H, m), 1.08-1.96 (9H, m); HRMS M^+ 262.1029, $C_{15}H_{18}O_2S$ requires 262.1028; m/e 262(100%). *2-Methylthiomethyl-3,4-trans-tetramethylene-γ-butyrolactone* **36**: ($ZnBr_2$, 80%) IR(film) 177; ^{1}H NMR δ($CDCl_3$) 4.10 (0.5H, dt, J=4, 10 Hz), 3.79 (0.5H, dt, J=4, 10 Hz), 2.38-3.13 (3H, m), 2.17 (1.5H, s), 2.14(1.5H, s), 1.14-2.36(9H, m); HRMS M^+ 200.0877, $C_{10}H_{16}O_2S$ requires 200.0871; m/e 200(100%), 152,

139. *2-Phenylthiomethyl-δ-valerolactone* **39**: ($ZnBr_2$, 94%) IR(film) 3060, 1728, 1585, 1482, 1440; δ($CDCl_3$) 7.02-7.64 (5H, m), 4.24 (2H, t, J=6 Hz), 3.64 (1H, dd, J=4, 14 Hz), 2.96(1H, dd, J=8, 13 Hz), 2.16-2.83(1H, m), 1.44-2.2(4H, m); HRMS M^+ 222.0718, $C_{12}H_{14}O_2S$ requires 222.0714; m/e 222, 123(100%). *Ethyl 2-phenylthiomethyl-butanoate* **42**: ($ZnBr_2$, 96%) IR(film) 3060, 1730; ^1H NMR δ($CDCl_3$) 7.10-7.64(5H, m), 4.18 (2H, q, J=7 Hz), 3.25 (1H, dd, J=8.5, 14 Hz), 3.02 (1H, dd, J=6, 14 Hz), 2.44-2.73 (1H, m), 1.73 (2H, quint, J=7 Hz), 1.28 (3H, t, J=7 Hz), 0.91 (3H, t, J=7 Hz); HRMS M^+ 238.1012, $C_{13}H_{18}O_2S$ requires 238.1028; m/e 238, 123(100%), 110, 109. *2-(1-Phenylthioethyl)cyclohexanone* **45**, R=Me: ($TiCl_4$, 78%) IR(film) 1706, 1587, 1480; ^1H NMR δ($CDCl_3$) 6.90-7.68 (5H, m), 3.44-4.11 (1H, m), 1.36-2.73 (9H, m), 1.27 (1.5H, d, J=7.5 Hz), 1.20 (1.5H, d, J=8 Hz); HRMS M^+ 234.1081, $C_{14}H_{18}OS$ requires 234.1079; m/e 234, 137, 125, 110(100%), 97. *2-(1-Phenylthiobutyl)cyclohexanone* **45**, R=Pr^n: ($TiCl_4$, 83%) IR(film) 1708, 1585; ^1H NMR δ($CDCl_3$) 7.04-7.63 (5H, m), 3.30-3.84 (1H, m), 1.20-2.71 (13H, m), 0.92 (3H, t, J=6 Hz); HRMS M^+ 262.1388, $C_{16}H_{22}OS$ requires 262.1391; m/e 262(100%), 165, 153, 123, 110, 109. *2-(1-Phenylthio-2-methylpropyl)cyclohexanone* **45**, R=Pr^i: ($TiCl_4$, 66%) IR(film) 1707; ^1H NMR δ($CDCl_3$) 7.03-7.66 (5H, m), 3.69 (0.5H, dd, J=5, 7 Hz), 3.33 (0.5H, dd, J=5, 6 Hz), 1.50-2.89 (10H, m), 1.09 (3H, d, J=7 Hz), 0.94 (3H, d, J=6.5 Hz); HRMS M^+ 262.1396, $C_{16}H_{22}OS$ requires 262.1391; m/e 262, 218, 153(100%), 123, 110, 109. *2-(1-Phenylthio-2,2-dimethylpropyl)cyclohexanone* **45**, R=Bu^t: ($ZnBr_2$, 78%) IR(film) 1708, 1580; ^1H NMR δ($CDCl_3$) 6.97-7.48 (5H, m), 4.05 (0.5H, d, J=3.5 Hz), 3.10 (1H, d, J=2 Hz), 1.46-2.81 (9H, m); HRMS M^+ 276.1530, $C_{17}H_{24}OS$ requires 276.1547; m/e 276, 220, 219(100%). *2-(Phenylthiotrimethylsilylmethyl)cyclohexanone* **45**, R=Me_3Si: ($ZnBr_2$, 84%) IR(film) 1715, 1585, 1251; ^1H NMR δ($CDCl_3$) 7.10-7.56 (5H, m), 3.38 (0.5H, d, J=1.5 Hz), 3.15 (0.5H, d, J=4.5 Hz), 1.40-2.82 (9H, m), 0.13 (9H, s); HRMS M^+ 292.1320, $C_{16}H_{24}OSSi$ requires 292.1323; m/e 292, 277, 183(100%). *2-(1-Phenylthiobutyl)cyclopentanone* **48**: ($TiCl_4$, 90%) IR(film) 1730, 1580; ^1H NMR δ($CDCl_3$) 7.04-7.61 (5H, m), 3.49-3.78 (1H, m), 1.20-2.59 (11H, m), 0.88 (1.5H, t, J=6 Hz), 0.82 (1.5H, t, J=6 Hz); HRMS M^+ 248.1234, $C_{15}H_{20}OS$ requires 248.1235; m/e 248, 139, 138, 110(100%), 109, 55. *2-Methyl-2(1-phenylthiobutyl)cyclopentanone* **52**: ($ZnBr_2$, 82%) IR(film) 1730; ^1H NMR δ($CDCl_3$) 7.04-7.60 (5H, m), 3.16-3.37 (1H, m), 1.24-2.55 (10H, m), 1.16 (1.5H, s), 1.06 (1.5H, s), 0.72-1.00 (3H, m); HRMS M^+ 262.1394, $C_{16}H_{22}OS$ requires 262.1391; m/e 262(100%), 139, 110. *4-Phenylthiododecan-6-one* **54**: ($TiCl_4$, 79%) IR(film) 1735, ^1H NMR δ($CDCl_3$) 7.10-7.53 (5H, m), 3.48-3.77 (1H, m), 2.57-2.79 (2H, m), 2.34 (2H, t, J=8 Hz), 1.05-1.88 (12H, m), 0.71-1.05 (6H, m); HRMS M^+ 292.1848, $C_{18}H_{28}OS$ requires 292.1861; m/e 292, 165, 123, 110(100%), 55. *3-tert-Butyl-4-phenylthioheptan-2-one* **58**: ($TiCl_4$, 82%) IR(film) 3055, 1715, 1580; ^1H NMR δ($CDCl_3$) 7.17-7.56 (5H, m), 3.28 (1H, dt, J=2, 11 Hz), 2.84 (1H, d, J=2 Hz), 2.29 (3H, s), 1.16-2.19 (4H, m), 0.80-1.08 (3H, m), 0.83 (9H, s); HRMS M^+ 278.1717, $C_{17}H_{26}OS$ requires 278.1705; m/e 278, 222(100%), 165. *2-Methyl-6-(1-phenylthiobutyl)cyclohexanone* **61**: ($TiCl_4$, 98%; $ZnBr_2$, 82%) IR(film) 1710, 1580; ^1H NMR δ($CDCl_3$) 7.14-7.69 (5H, m), 3.47-3.80 (1H, m), 1.26-2.83 (12H, m), 0.80-1.22 (6H, m); HRMS M^+ 276.1553, $C_{17}H_{24}OS$ requires 276.1548; m/e 276, 165, 123, 110, 109, 55(100%). *2-Methyl-2-(1-phenylthiobutyl)cyclohexanone* **64**: ($TiCl_4$, 63%; $ZnBr_2$, 71%) IR(film) 1710, 1580; ^1H NMR δ($CDCl_3$) 7.02-7.57 (5H, m), 3.38-3.63 (1H, m), 2.08-2.47 (2H, m), 1.20-2.05 (10H, m), 1.12 (1.5H, s), 1.05 (1.5H, s), 0.70-0.99 (3H, m); HRMS M^+ 276.1561, $C_{17}H_{24}OS$ requires 276.1548; m/e 278, 165, 123, 110, 109, 55(100%). *2-(1-Phenylthiobutyl)-δ-valerolactone* **66**: ($ZnBr_2$, 96%) IR(film) 1730; ^1H NMR δ($CDCl_3$) 7.09-7.62 (5H, m), 4.15-4.46 (2H, m), 3.74-4.09 (1H, m), 2.51-3.00 (1H, m), 1.24-2.33 (8H, m), 0.76-1.09 93H, m); HRMS M^+ 264.1177, $C_{15}H_{20}O2S$ requires 264.1184; m/e 264, 155(100%). *Ethyl 2-ethyl-3-phenylthiohexanoate* **69**: ($ZnBr_2$, 98%) IR(film) 3060, 1730, 1585; ^1H NMR δ($CDCl_3$) 7.02-7.57 (5H, m), 4.10 (1H, q, J=7.5 Hz), 4.04 (1H, q, J=7.5 Hz), 3.05-3.40 (1H, m), 2.26-2.57 (1H, m), 1.33-1.96 (6H, m), 1.18 (1.5H, t, J=7.5 Hz), 1.16 (1.5H, t, J=7.5 Hz), 0.83 (6H, t, J=7 Hz); HRMS M^+ 280.1501, $C_{16}H_{24}O_2S$ requires 280.1497; m/e 280(100%). *2-(1-Phenylthiobutyl)heptanal* **73**: ($TiCl_2(OPr^i)_2$, 86%; $ZnBr_2$, 40%) IR(film) 3055, 1720, 1580; ^1H NMR δ($CDCl_3$) 9.69 (0.5H, d, J=2 Hz), 9.60 (0.5H, d, J=2.5 Hz), 7.06-7.53 (5H, m), 3.23-3.52 (1H, m), 2.18-2.55 (1H, m), 1.05-1.92 (12H, m), 0.70-1.04 (6H, m); HRMS M^+ 278.1691, $C_{17}H_{26}OS$ requires 278.1704; m/e 278(100%), 165, 151. *2-Phenylthiotrimethylsilylmethyl-3,4-trans-tetramethylene-γ-butyrolactone* **76**: ($ZnBr_2$, 97%) IR(film) 1775, 1585, 1483, 1440, 1250; ^1H NMR δ($CDCl_3$) 6.89-7.34 (5H, m), 3.15-3.68 (1H, m), 3.00 (0.33H, d, J=2.5 Hz), 2.83 (0.33H, J=2 Hz), 2.34 (0.33H, d, J=2 Hz), 2.40-2.93 (1H, m), 0.80-2.29 (9H, m), 0.04, 0.03, 0.00 (9H, 3x s); HRMS M^+ 334.1414, $C_{18}H_{26}O_2SSi$ requires 334.1422; m/e 334, 319, 252(100%), 225, 224.

Reductive sulphur removal—W-2 Raney nickel[18] (*ca* 1.5 g of a slurry in EtOH) was added to a solution of the sulphide (1 mmol) in acetone (10 ml) and the mixture was vigorously stirred at 20°C. After 2 h, the mixture was diluted with CH_2Cl_2 and the nickel cautiously removed by filtration through celite (CARE: pyrophoric if allowed to dry out). Evaporation of the filtrate *in vacuo* gave, after chromatography on SiO_2, the α-alkylated carbonyl compound.

26 (99%) and **29** (98%) were identical with authentic samples. *9-Methyl-1-decalone* **32**: (92%) 4:1 ratio of *cis/trans* isomers from integration of methyl singlets in the ^1H NMR at δ1.18 (*cis*) and δ1.08 (*trans*), *cf* lit.[20] *2-Ethylcyclohexanone* **47**, R=Me: (95%) IR(film) 1710; ^1H NMR δ($CDCl_3$) 1.03-2.38 (11H, m), 0.86 (3H, t, J=6.5 Hz); *cf* lit.[30] *2-Butylcyclo-*

hexanone **47**, R=Pr^n: (90%) IR(film) 1710; ^{1}H NMR δ($CDCl_3$) 1.06-2.57 (15H, m), 0.90 (3H, t); *cf* lit.[31] *2-(2-Methylpropyl)cyclohexanone* **47**, R=Pr^i: (91%) IR(film) 1708; ^{1}H NMR δ(CCl_4) 1.40-2.56 (12H, m), 0.91 (6H, d, J=6 Hz); *cf* lit.[32] *2-(2,2-Dimethylpropyl)cyclohexanone* **47**, R=Bu^t: (93%) IR(film) 1708; ^{1}H NMR δ(CCl_4) 1.29-2.57 (11H, m), 0.84 (9H, s); HRMS M$^+$ 168.1511, $C_{11}H_{20}O$ requires 168.1514; m/e 168, 153, 112, 119, 57(100%). *2-Trimethylsilylmethylcyclohexanone* **47**, R=$SiMe_3$: (92%) IR(film) 1710, 1250, ^{1}H NMR δ(CCl_4) 1.36-2.40 (9H, m), 1.16 (1H, dd, J=6, 15 Hz), 0.37 (1H, dd, J=7, 15 Hz), 0.03 (9H, s); *cf* lit.[26] *2-Butylcyclopentanone* **50**: (94%) IR(film) 1730; ^{1}H NMR δ(CCl_4) 1.02-2.40 (13H, m), 0.92 (3H, t, J=6 Hz); *cf* lit.[33] *2-Butyl-2-methylcyclopentanone* **53**: (96%) IR(film) 1730; ^{1}H NMR δ(CCl_4) 1.58-2.37 (6H, m), 0.75-1.50 (9H, m), 0.93 (3H, s). *Dodecan-6-one* **56**: (85%) IR(film) 1715; ^{1}H NMR δ(CCl_4) 2.00-2.39 (4H, m), 1.04-1.70 (14H, m), 0.75-1.04 (6H, m); *cf* lit.[34] *3-tert-Butylheptan-2-one* **60**: (98%) IR(film) 1715; ^{1}H NMR δ(CCl_4) 2.08-2.40 (1H, m), 2.07 (3H, s), 1.06-1.70 (6H, m), 0.90 (9H, s), 0.85-1.06 (3H, m); *cf* lit.[35] *2-Butyl-6-methylcyclohexanone* **63**: (95%) IR(film) 1710; ^{1}H NMR δ(CCl_4) 1.10-2.55 (14H, m), 0.75-1.10 (6H, m); *cf* lit[25]. *2-Butyl-2-methylcyclohexanone* **65**: (94%) IR(film) 1710; ^{1}H NMR δ(CCl_4) 2.04-2.41 (2H, m), 1.10-2.04 (12H, m), 0.75-1.10 (3H, m), 0.93 (3H, s); *cf* lit.[25] *2-Butyl-δ-valerolactone* **68**: (96%) IR(film) 1728; ^{1}H NMR δ($CDCl_3$) 4.29 (2H, t, J=5 Hz), 1.07-2.69 (11H, m), 0.90 (3H, t, J=6 Hz); *cf* lit.[36] *Ethyl 2-ethylhexanoate* **71**: (90%) IR(film) 1730; ^{1}H NMR δ($CDCl_3$) 4.17 (2H, q, J=7 Hz), 1.40-2.35 (9H, m), 1.23 (3H, t), 0.87 (6H, t, J=6 Hz); *cf* lit.[37] 2-Butylheptan-1-ol **75**: (91%) IR(film) 3500; ^{1}H NMR δ(CCl_4) 3.28-3.53 (2H, m), 1.10-2.25 (16H, m), 0.70-1.10 (6H, m). *2-Trimethylsilyl-methyl-3,4-trans-tetramethylene-γ-butyrolactone* **77**: (95%) IR(film) 1780; δ($CDCl_3$) 3.96 (0.5 H, dt, J=4.5, 10.5 Hz), 3.65 (0.5H, dt, J=4.5, 10 Hz), 2.55 (1H, m), 1.14-2.33 (9H, m), 0.54-1.06 (2H, m), 0.02, 0.00 (9H, 2x s); HRMS M$^+$ 226.1387, $C_{12}H_{22}O_2Si$ requires 226.1289; m/e 226, 211, 139(100%).

Oxidative sulphur removal—Sodium metaperiodate (214 mg, 1 mmol) was added to a stirred solution of the sulphide (1 mmol) in MeOH (9 ml) at 20°C, followed by the addition of water (1 ml). After stirring in the dark for 16 h, the reaction mixture was diluted with CH_2Cl_2 (20 ml) and poured into water (15 ml). The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo* to give the sulphoxide and/or sulphoxide elimination products. This mixture was warmed in CCl_4 (or $CHCl_3$) at 60-70°C to complete the elimination of PhSOH (followed by tlc or ^{1}H NMR). Thermolysis reaction times are indicated below. The α-alkylidene carbonyl compounds were purified by chromatography on SiO_2 or, for volatile products, distillation into a cold trap at 0.1 mm Hg. In the sulphoxide thermolysis, **45**→**46** for R=Bu^t, in CCl_4 at 60°C, ^{1}H NMR initially showed a mixture of *E* (δ6.32, t, J=2 Hz) and *Z* (δ5.19, t, J=2 Hz) enones and sulphoxide, where the isomer ratio was time-dependent: *E/Z*=1:4 (2 h); 2:1 (24 h); 6:1 (32 h); >10:1 (48 h).

1-Phenyl-2-phenylsulphinylpropanone **10**: 99%; ^{1}H NMR δ(CCl_4) 7.96 (1H, dd, J=2, 8 Hz), 7.82 (1H, dd, J=3, 6 Hz), 7.13-7.67 (8H, m), 3.77-4.32 (1H, m), 2.48-3.51 (2H, m), 1.39 (1.5H, d, J=7 Hz), 1.18 (1.5H, d, J=7 Hz); HRMS M+ 272.0873, $C_{16}H_{16}O_2S$ requires 272.0871; m/e 272, 258, 147, 126, 105(100%), 77. *1-Phenyl-2-methylpropenone* **11**: (CCl_4-$CHCl_3$, 9:1, 65°C, 10 d; 95%) ^{1}H NMR δ($CDCl_3$) 7.18-7.81 (5H, m), 5.83-5.96 (1H, m), 5.55-5.64 (1H, m), 2.08 (3H, m); *cf* lit.[13] *2-Methylenecyclopentanone* **14**: (CCl_4, 60°C, 3 h; 82%) IR(film) 1660; ^{1}H NMR δ(CCl_4) 5.79-5.94 (1H, m), 5.13-5.28 (1H, m), 1.72-2.81 (6 H, m); *cf* lit.[38] *2,2-Dimethyl-6-methylenecyclohexanone* **17**: (CCl_4, 60°C, 4 h; 66%) IR(film) 1660, 1640; ^{1}H NMR δ(CCl_4) 5.52-5.63 (1H, m), 4.93-5.04 (1H, m), 1.39-1.97 (6H, m), 1.06 (6H, s). *Non-1-en-2-one* **20**: (CCl_4, 60°C, 1 d; 71%) IR(film) 1690, 1630; ^{1}H NMR δ($CDCl_3$) 6.20 (1H, dd, J=2, 16 Hz), 6.14 (1H, dd, J=2, 9 Hz), 5.62 (1H, dd, J=9, 16 Hz), 2.35 (2H, t, J=6 Hz), 0.90-1.65 (8H, m), 0.87 (3H, t, J=6 Hz); *cf* lit.[38] *3-Methyleneoctan-2-one* **23**: (CCl_4, 60°C, 3 d; 96%) IR(film) 1695, 1630; ^{1}H NMR δ($CDCl_3$) 6.04 (1H, s), 5.71 (1H, s), 2.30 (3H, s), 2.23 (2H, t, J=7 Hz), 1.18-1.71 (8H, m), 0.96 (3H, t, J=6 Hz); *cf* lit.[38] **37** (CCl_4, 70°C, 14 h; 96%) and **40** (CCl_4, 70°C, 4 h; 90%) had IR and ^{1}H NMR spectra identical with lit.[39,40] values and authentic samples. *Ethyl 2-methylenebutanoate* **43**: (CCl_4, 70°C, 16 h; 95%) IR(film) 1710; ^{1}H NMR δ($CDCl_3$) 6.18 (1H, m), 5.52 (1H, m), 4.25 (2H, q, J=7.5 Hz), 2.34 (2H, q, J=7 Hz), 1.33 (3H, t, J=7.5 Hz), 1.08 (3H, t, J=7 Hz); *cf* lit.[41] *(E)-2-Ethylidenecyclohexanone* **46**, R=Me: (CCl_4, 60°C, 5 h; 92%) IR(film) 1670; ^{1}H NMR δ($CDCl_3$) 6.73 (1H, qt, J=2, 7 Hz), 2.23-2.64 (4H, m), 1.63-2.02 (4H, m), 1.72 (3H, d, J=7 Hz); *cf* lit[42]. *(E)-2-Butylidenecyclohexanone* **46**, R=Pr^n: (CCl_4, 60°C, 5 h; 89%) IR(film) 1670; ^{1}H NMR δ($CDCl_3$) 6.61 (1H, tt, J=2, 6.5 Hz), 1.13-2.64 (12H, m), 0.92 (3H, t, J=7 Hz); *cf* lit.[43] *(E)-2-(2-Methylpropylidene)cyclohexanone* **46**, R=Pr^i: (CCl_4, 60°C, 6 h; 94%) IR(film) 1665; ^{1}H NMR δ(CCl_4) 6.29 (1H, dt, J=2, 10 Hz), 1.46-2.77 (9H, m), 0.98 (6H, d, J=7 Hz); *cf* lit.[44] *(E)-2-(2,2-Dimethylpropylidene)cyclohexanone* **46**, R=Bu^t: (CCl_4, 60°C, 60 h; 95%) IR(film) 1670; ^{1}H NMR δ(CCl_4) 6.32 (1H, t, j=2 Hz), 1.93-2.68 (4H, m), 1.39-1.87 (4H, m), 1.07 (9H, s); HRMS M$^+$ 166.1359, $C_{11}H_{18}O$ requires 166.1358; m/e 166, 151(100%), 57. *(E)-2-Butylidenecyclopentanone* **49**: (CCl_4, 60°C, 4 h; 87%) IR(film) 1685; ^{1}H NMR δ($CDCl_3$) 6.54 (1H, tt, J=2, 8 hz), 1.15-2.73 (10H, m), 0.93 (3H, t, J=6.5 Hz); *cf* lit.[43] *(E)-Dodec-4-en-6-one* **55**: (CCl_4, 60°C, 3 h; 87%) IR(film) 1680; ^{1}H NMR δ($CDCl_3$) 6.83 (1H, dt, J=7, 16 Hz), 6.06 (1H, d, J=16 Hz), 1.97-2.68

(4H, m), 1.10-1.83 (10H, m), 0.70-1.10 (6H, m). *(Z)-3-tert-Butylhept-3-en-2-one* **59**: (CCl_4, 60°C, 60 h; 85%) IR(film) 1680; ^{1}H NMR δ($CDCl_3$) 5.29 (1H, t, J=7 Hz), 2.28 (3H, s), 1.10-2.18 (4H, m), 1.09 (9H, s), 0.92 (3H, t); HRMS M^+ 168.1516, $C_{11}H_{20}O$ requires 168.1514; m/e 168, 153, 57, 55(100%). *(E)-2-Butylidene-6-methylcyclohexanone* **62**: (CCl_4, 60°C, 4 h; 81%) IR(film) 1680; ^{1}H NMR δ($CDCl_3$) 6.63 (1H, tt, J=2, 7 Hz), 1.32-2.79 (11H, m), 1.29 (3H, d, J=6 Hz), 0.94 (3H, t, J=6 Hz). *(E)-2-Butylidene-δ-valerolactone* **67**: (CCl_4, 45°C, 1 h; 81%) IR(film) 1717; ^{1}H NMR δ($CDCl_3$) 6.78 (1H, tt, J=2, 7 Hz), 4.03-4.42 (2H, m), 1.21-2.60 (8H, m), 0.85 (3H, t, J=6 Hz); *cf* lit.[45] *Ethyl 2-ethylhex-2-enoate* **70**: (CCl_4, 60°C, 2 d; 89%) E/Z=70:30; IR(film) 1715; ^{1}H NMR δ($CDCl_3$) 6.76 (0.7H, t, J=7.5 Hz), 5.83 (0.3 H, t, J=7 Hz), 4.19 (2H, q, J=7.5 Hz), 1.40-2.94 (6H, m), 1.31 (3H, t, J=7.5 Hz), 0.70-1.22 (6H, m); *cf* lit.[46] *(E)-Butylideneheptanal* **74**: (CCl_4, 60°C, 5 h; 97%) IR(film) 1685, 1635; ^{1}H NMR δ(CCl_4) 9.37 (1H, s), 6.34 (1H, t, J=7 Hz), 2.04-2.53 (4H, m), 1.13-1.80 (8H, m), 0.75-1.13 (6H, m).

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