Pergamon

Tetrahedron Vol. 50, No. 31, pp. 9377-9398, 1994
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0040-4020/94 $7.00+0.00

0040-4020(94)00533-8

Allylation with Substituted Vinylthionium Ions from $SnCl_4$ Ionisation of 1,3- and 3,3-Bis(alkyl/phenylthio)propenes

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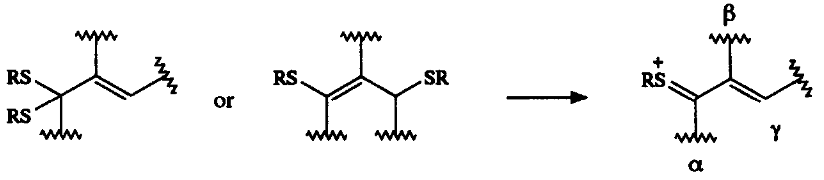
***Abstract*:** α- and γ-substituted vinylthionium ions from $SnCl_4$ ionisation of a range of substituted 1,3- and 3,3-bis(alkyl/phenylthio)propenes allylate enol silyl ethers in good yield. Levels of regioselectivity are sterically dependent and in the case of methyl as γ-substituent may be controlled by the steric bulk of the sulfur substituent. As with the Pummerer methodology, γ-addition generally gave (E)-vinyl sulfides exclusively implying the intermediacy of a 'free' vinylthionium ion. In appropriate cases, the allylated products may be hydrolysed and cyclised to the Robinson annulation products, desulfurised to the olefin or eliminated to the diene. Allyltrimethylsilane and indole are also allylated in good yield. Vinylthionium ions with a γ-phenylthio or methoxy group also undergo the reaction. In the methoxy case the reaction is highly sensitive to the number of equivalents of Lewis acid used and found to be truly catalytic in $TiCl_4$. A mechanistic rationale for this is presented. The study concludes with a pentannulation sequence involving intramolecular capture of a vinylthionium ion generated by the methodology.

1. Introduction.

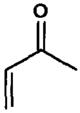
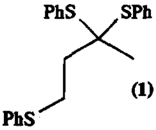
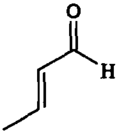
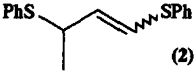
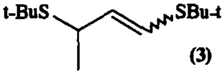
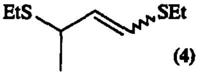
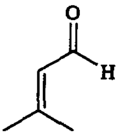
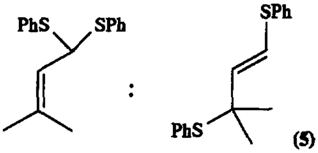
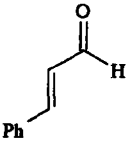
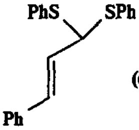
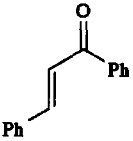
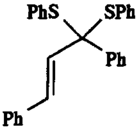
In the preceding paper[1], we described the scope and limitations of a masked Michael reaction involving enol silyl ethers and Pummerer-generated β- and γ-substituted vinylthionium ions from the appropriate allyl phenyl sulfoxides. We concluded, in the light of this study as well as previous research[2], that the Pummerer methodology is severely limited for α- and γ-substituted cases. In this paper we report on a comprehensive study of complementary methodology for generating α-, β-, and γ-substituted vinylthionium ions involving $SnCl_4$ ionisation of substituted 1,3- and 3,3-bis(alkyl/phenylthio)propenes[3,4]. Scheme 1.



Scheme 1

Table 1

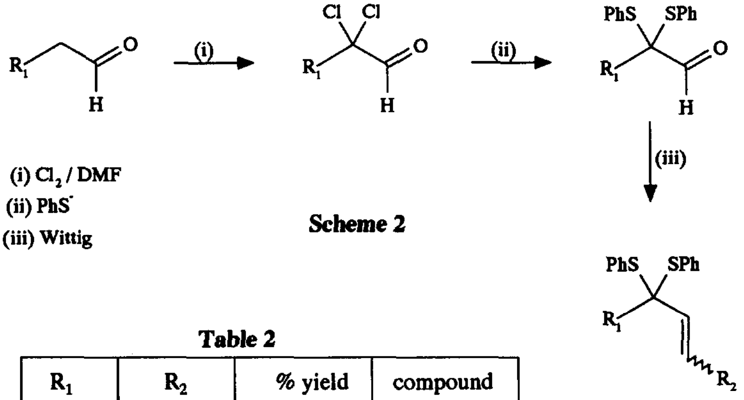
Synthesis of 1,3- and/or 3,3-bis(alkyl/phenylthio)propenes using thiol / P_2O_5 / enone(al).

ENONE(AL)	THIOL	PRODUCT	E : Z	YIELD %
	PhSH	 (1)	-	-
	PhSH	 (2)	96 : 4	50
"		 (3)	85 : 15	75
"	EtSH	 (4)	65 : 35	68
	PhSH	 (5) 40 : 60	100 : 0	58
		 (6)	100 : 0	83
		 (7)	100 : 0	8

2. Preparation of substituted 1,3- and 3,3-bis(alkylthio/phenylthio)alkenes.

Thioacetalisation of substituted enones using P_2O_5 and thiol in CH_2Cl_2 gave varying degrees of conjugate addition[5,6] depending on the γ-substituent. While but-2-enal(methacrolein) consistently gave 1,3-bis(alkyl/phenylthio)but-1-enes exclusively with a range of thiols, cinnamaldehyde gave exclusive thioacetalisation to the 3,3-bis(phenylthio) derivative with thiophenol. By comparison, 3-methylbut-2-enal bearing two methyl groups at the γ-position gave a 40:60 mixture of the 1,3- and 3,3-isomers. Table 1 summarises the results.

For 3,3-bis(phenylthio) substrates unsubstituted or methyl substituted at the γ-position, Wittig olefination[7] of the appropriate 2,2-bis(phenylthio)aldehyde emerged as the method[8] of choice for exclusive formation of these isomers. The aldehydes[9-12] used in the Wittig reaction were prepared by thiophenoxide substitution[13] of 2,2-dichloroaldehydes from chlorination[14] of the aldehyde in DMF. Scheme 2 and Table 2.



(i) Cl_2 / DMF
(ii) PhS^-
(iii) Wittig

Scheme 2

Table 2

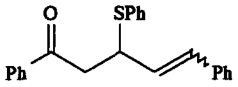
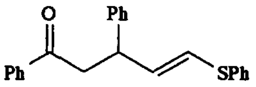
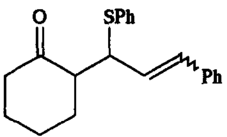
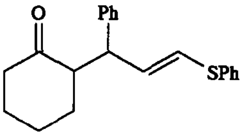
R_1	R_2	% yield	compound
Me	H	45	**(8)**
Et	H	71	**(9)**
Et	Me	53	**(10)**

3. Lewis acid promoted reactions of enol silyl ethers with substituted 1,3- and 3,3-bis(alkyl/phenylthio)alkenes.

Of particular interest in this part of the study was the influence of vinylthionium ion substitution as well as substrate structure (1,3 vs 3,3) on the regioselectivity of allylation. As a direct comparison with the Pummerer methodology, 1-phenyl-3,3-bis(phenylthio)propene (**6**) and the enol silyl ethers of acetophenone (**11**) and cyclohexanone (**12**) were chosen as reactants to probe optimum reaction conditions. Three equivalents of either $SnCl_4$ or $TiCl_4$ were required at -78°C in CH_2Cl_2 for complete conversion of starting material. This observation has been noted for thioacetals by other workers[15]. Yields were higher than those obtained using the Pummerer methodology. The ratios of α:γ adducts from the $SnCl_4$ reactions compared with those from the Pummerer methodology, [(**13a**):(**13b**) = 57:43 vs 75:25 / enol silyl ether (**11**) and (**14c**):(**14b**) = 70:30 vs 50:50 / enol silyl ether (**12**)], indicated that the Lewis acid reactions may involve Lewis acid complexed thioacetals rather than 'free' vinylthionium ions as intermediates. Table 3.

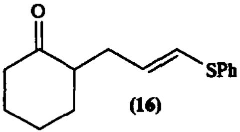
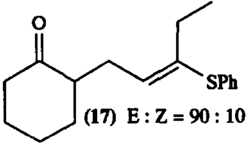
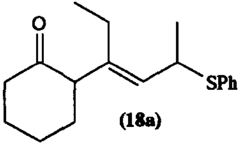
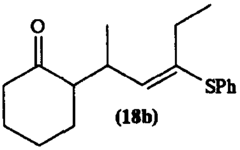
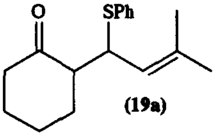
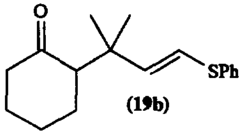
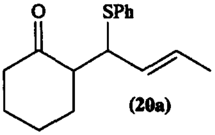
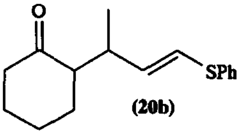
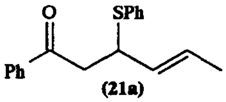
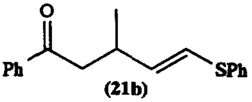
Table 3

Reaction of (11) and (12) with (6) / $SnCl_4$ (3eq) / CH_2Cl_2 / -78°C.

Enol Silyl Ether	Products α : γ	Yield %
(11)	 **(13a)** :  **(13b)** 57 : 43	62
(12)	 **(14a)** :  **(14b)** 70 : 30	93

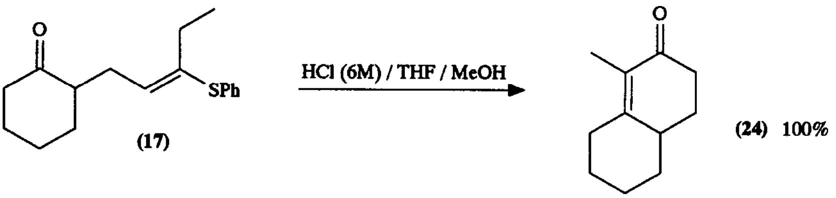
Reaction of the other vinylthionium ion precursors synthesised, **(2)**, **(5)**, **(9)** and **(10)** under these reaction conditions resulted in a drastic reduction in yield with only the α-adducts being isolated. A study of the reaction conditons using 1,3-bis(phenylthio)but-1-ene **(2)** as substrate revealed optimum conditions to be one equivalent of $SnCl_4$ at -20°C, affording a 66% yield of α:γ adducts (57:43). The higher temperature was necessary for complete disappearance of starting material. Furthermore, the ratio of α:γ adducts increased with the number of Lewis acid equivalents indicating that the γ-adduct, containing a vinyl sulfide functionality, is consumed at high Lewis acid concentrations. Literature precedent exists for this proposal[16]. This observation, thus explains the low overall yields at -78°C with three equivalents of Lewis acid. Moreover, it provides a means of obtaining the α-adducts exclusively. Using these optimised conditions, substituted 1,3- and 3,3-bis(alkyl/phenylthio)propenes **(2)**-**(10)** described previously were reacted with the enol silyl ethers **(11)** and **(12)**. The results are summarised in Table 4. All yields quoted were of columned products, and for the sake of consistency the enol silyl ethers of cyclohexanone **(12)** was mainly used. Both regio- and stereoisomer (E:Z and diastereomer where appropriate) ratios were calculated from the 200 MHz ^{1}H NMR spectra. Regarding the results, some trends and comparisons with the Pummerer methodology may be drawn. 1,3-Bis(phenylthio)propene, which has been used previously as an acyl anion equivalent[4b], gave the same Michael product **(16)** (entry 1) as that from allyl phenyl sulfoxide under Pummerer conditions. The yield from the $SnCl_4$ reaction was much lower (20% with 45% recovered starting material and one equivalent of Lewis acid) because of subsequent reaction of the vinyl sulfide of the γ-adduct with excess Lewis acid. As with the Pummerer reaction, the Lewis acid-mediated variation involves γ-attack (Michael) on the vinylthionium ion as its transoid conformer. Indeed, the Pummerer methodology gives the highest yield (65%) of **(16)** of all the methodologies including Cohen's[17] γ-alkylation of the lithium enolate of cyclohexanone by 3-chloro-1-phenylthiopropene (40%). In this regard, it is important to note that reaction of 3-chloro-1-phenylthiopropene, prepared by N-chlorosuccinimide chlorination of allyl phenyl sulphide as a mixture of E/Z isomers (E:Z =90:10), also reacted with enol silyl ether **(12)** and $SnCl_4$ to give **(16)** as a mixture of E/Z isomers approximating that of the starting chloride. Hence, this reaction, together with

Table 4

ENTRY	E⁺	Nu	PRODUCT(S)	α : γ	YIELD%
1	(15)	(12)	 (16)	0 : 100	20
2	(9)	"	 (17) E : Z = 90 : 10	0 : 100	48
3	(10)	"	 (18a)  (18b)	40 : 60	56
4	(5)	"	 (19a)  (19b)	92 : 8	95
5	(2)	"	 (20a)  (20b)	57 : 43	66
6	(2)	(11)	 (21a)  (21b)	16 : 84	68

Cohen's alkylation mentioned previously, approximates an S_N2 transition state, while the $SnCl_4$ ionisation of the bis-sulfide **(15)** as well as the Pummerer option must both proceed via an S_N1 mechanism involving the transoid vinylthionium ion resulting in stereocontrolled addition to produce the all (E)-isomer.

Entry 2 involving the thioketal **(9)** provides a solution to the poor yields obtained from masked Michael addition of enol silyl ethers to α-substituted allyl sulfoxides under Pummerer conditions described previously[2]. In the latter, Hünig's base competed as nucleophile as a result of the higher temperature required for the proton abstraction step of vinylthionium ion formation. In this case the product **(17)** of exclusive γ-attack was obtained as a 90:10 E:Z mixture in 48% yield. **(17)** could be hydrolysed to the Robinson annulation product **(24)** in quantitative yield in a one pot reaction. This result is in good agreement with results obtained with similar compounds prepared by Takeda[18] from enol silyl ethers and γ-(phenylthio)allylstannanes. Scheme 3.

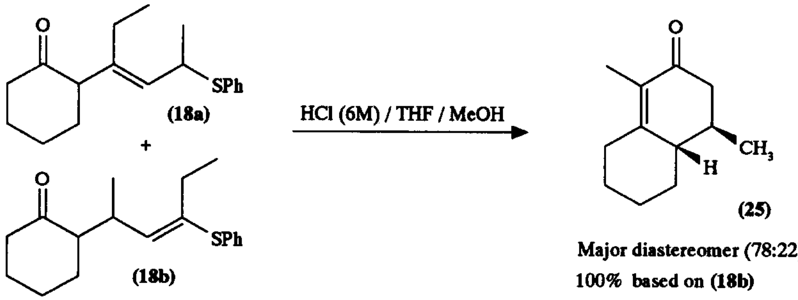


(17)

(24) 100%

Scheme 3

Entry 3 reveals that introduction of a methyl group at the γ-terminus understandably results in loss of regioselectivity of product formation. A significant percentage (40%) of α-attack was observed giving the final product **(18a)** as that of formal 1,3-sigmatropic rearrangement. Rearrangements of this nature have been observed with analogous selenium-substituted compounds[19]. Hydrolysis of **(18a)** and **(18b)** (HCl/MeOH/THF) gave a quantitative yield of the Robinson annulation product **(25)** based on the expectancy that only **(18b)** would react. However, neither unreacted **(18a)** nor any derivative thereof could be isolated. The major diastereomer of **(25)** was assigned as the ($4R^*$, $4aS^*$) diastereomer using the modelling programme ALCHEMY in conjunction with the Karplus equation[20]. Scheme 4.



(18a)

(18b)

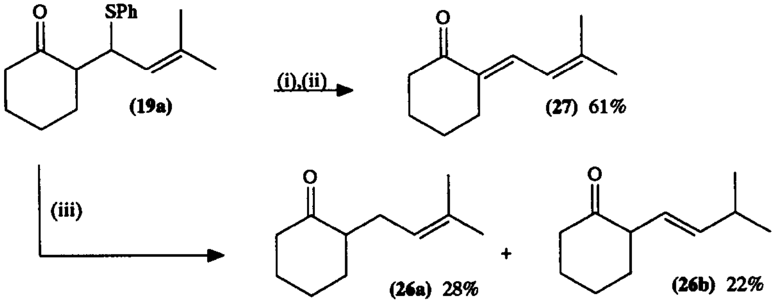
(18a) : (18b) = 40 : 60

(25)

Major diastereomer (78:22)
100% based on (18b)

Scheme 4

Entry 4 illustrates the situation at the other end of the spectrum in which the γ-terminus of the vinylthionium ion is sterically congested resulting in virtually exclusive α-attack to give **(19a)**:**(19b)** = (92:8). In this instance, complications in product distribution from having a 40:60 mixture of the 3,3- and 1,3-isomers as reactants did not arise indicating the intermediacy of a 'free' vinylthionium ion, inductively stabilised by the methyl groups. **(19a)** could be either reductively desulfurised with Raney nickel[21,22] to give **(26a,b)** or oxidatively eliminated to the diene **(27)** by treatment with oxone[23] followed by DBU[24]. Scheme 5 summarises.

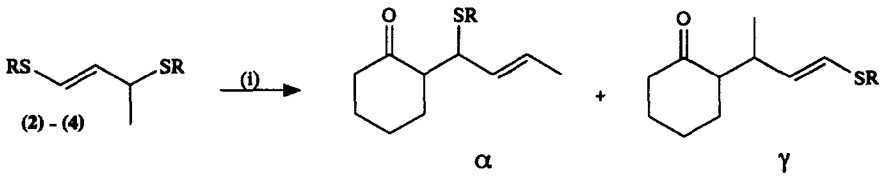


(i) Oxone / Wet Alumina / $CHCl_3$
(ii) DBU / THF
(iii) Raney Ni / EtOH

Scheme 5

The situation with methyl as a γ-substituent of a vinylthionium ion (no α-substituent) however, (entry 5) was less regioselective. Experimentally, the allyl sulfide (2) was more accessible than its crotyl thioacetal counterpart. We may recall in the Pummerer methodology, that the crotyl sulfoxide 1-phenylsulfinylbut-2-ene gave buta-1,3-dienyl phenyl sulfide as a major by-product via deprotonation of the γ-methyl group of the vinylthionium intermediate. Furthermore, the masked Michael adduct was obtained in low yield (17%) as a mixture of regioisomers (α:γ = 1:4). By comparison, entry 5 in the table reveals that use of the tin tetrachloride methodology on the same crotyl system gives a much superior yield (66%) and with the α-regioisomer predominating (57:43). Once again, this may reflect the involvement of a Lewis acid complexed species as the electrophile for carbon-carbon bond formation resulting in hinderance at the γ-position. However, with the enol silyl ether of acetophenone (entry 6) the (α:γ) ratio changed to (16:84) in a respectable overall yield of 68%. The α:γ selectivity could be controlled by appropriate choice of sulfur substituent on steric grounds. While the relatively bulky t-butyl group directed attack at the γ-position (α:γ = 15:85), the less demanding ethyl substituent resulted in a preference for α-attack (α:γ = 76:24) with the phenyl group intermediate. Presumably thiomethyl would be even more α-selective. Diastereomeric ratios of these adducts were always approximately 1:1. Table 5.

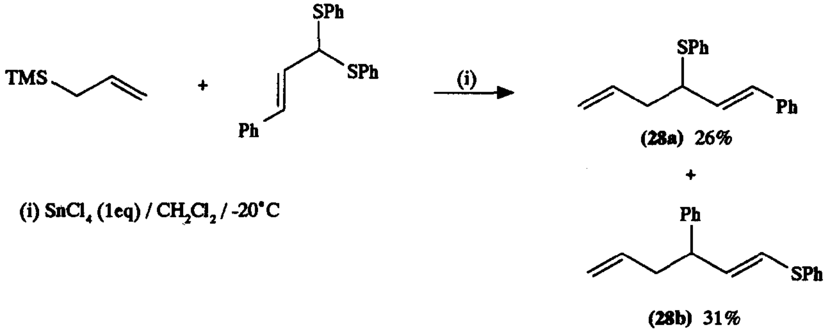
Table 5



(i) (12) / $SnCl_4$ / -20°C / CH_2Cl_2.

R	α : γ ratio	Yield%	Compound
Et	76 : 24	67	**(22a,b)**
Ph	57 : 43	66	**(20a,b)**
t-Bu	15 : 85	64	**(23a,b)**

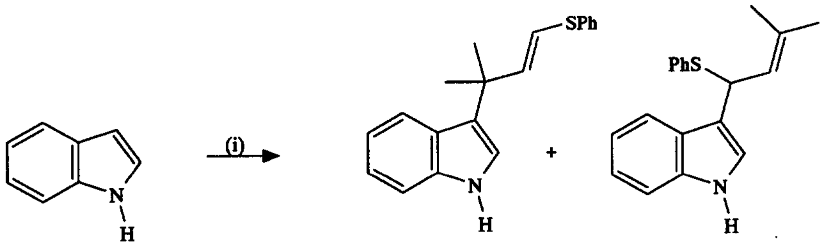
A further aspect which emerges from table 4 is the regioselectivity dependence on the structure of nucleophile (compare entries 5 and 6). To explore this aspect, the regiochemical outcome of reaction of two contrasting nucleophiles with two of the electrophilic substrates was determined. Allyltrimethylsilane (1.3 eq) was reacted with the thioacetal (**6**) derived from cinnamaldehyde, using $SnCl_4$ (1 eq) at -20°C in CH_2Cl_2 as before to give a 57% overall yield of a mixture of α:γ adducts (**28a,b**) in a ratio of 45:55 respectively. Similar experimental conditions with the enol silyl ether of cyclohexanone (**12**) with (**6**) gave an α:γ ratio of 60:40. Thus, in this instance there is reasonable parity. Scheme 6.



(i) $SnCl_4$ (1eq) / CH_2Cl_2 / -20°C

Scheme 6

By comparison, the other reaction chosen involving indole[25] as nucleophile and the 40:60 mixture of isomers of (**5**) gave the 3-substituted product (**29**) as a 59% yield of a 10:90 mixture of α:γ adducts as compared to a 92:8 ratio with the enol silyl ether of cyclohexanone (**12**). Experimentally, optimum yields were obtained by adding the indole last to (**5**) and $SnCl_4$(1 eq.) in CH_2Cl_2 at -20°C containing calcium carbonate (1 eq.). The reason for this dramatic inversion of regioselectivity is unclear although initial α-attack on nitrogen followed by [3,3] sigmatropic rearrangement seems mechanistically plausible. Had the α-adduct been formed, it would have been an attractive precursor for a Diels-Alder type dimerisation to the potent non-steroidal fertility regulating agent Yuehchukene[26], a reaction with literature precedent[27]. Scheme 7



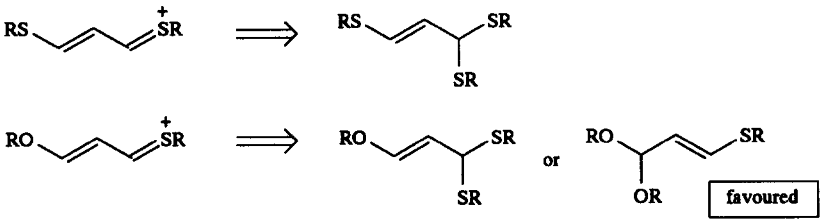
(29a) 53% **(29b)** 6%

(i) $SnCl_4$ (1eq) / $CaCO_3$ / CH_2Cl_2 / -20°C

Scheme 7

4. Synthesis and reactivity of γ-heterosubstituted vinylthionium ions.

A further aspect studied was the use of Lewis acid-generated γ-heterosubstituted vinylthionium ions as allylating agents as a comparison with the Pummerer-generated γ-phenylthio case mentioned previously[1]. With alkoxy as a γ-substituent, as with the carbon-substituted vinylthionium ions, a particular point of interest centred around the regioselectivity of enol silyl ether attack. Moreover, this aspect was considered likely to be governed by the choice of precursors since work on the alkyl-substituted vinylthionium ions had hinted at the involvement of Lewis acid bound intermediates as opposed to 'free' vinylthionium ions. In practice, the acetal/vinyl sulfide rather than the thioacetal/vinyl ether was found to be synthetically more accessible as starting material for the γ-alkoxy intermediate. Scheme 8.

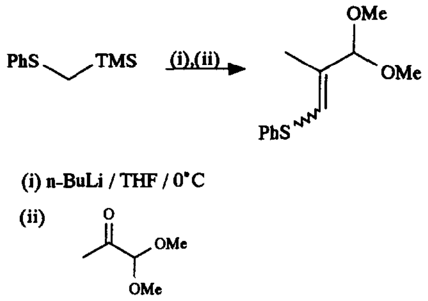


Scheme 8

1,3,3-Tris(phenylthio)propene **(30)** was prepared in a three step synthesis from acrolein in 40% overall yield as described in the preceding paper via the following route: conjugate additon of thiophenol in the presence of triethylamine; N-chlorosuccinimide chlorination α- to the sulfide which eliminated to the vinyl sulfide on stirring at 0 °C overnight, followed by thioacetalisation as before using thiophenol and P_2O_5 in CH_2Cl_2. **(30)**

was isolated as a pure (E)-isomer which was stable at room temperature indefinitely.

For preparation of 3,3-dimethoxy-1-phenylthiopropene, direct acetalisation of 3-phenylthioprop-2-enal or α-chlorination, acetalisation followed by dehydrochlorination of 3-phenylthiopropanal, proved unsuccessful. Eventually, the methyl analogue (31) was prepared in high yield and as a 7:3 mixture of E:Z isomers via Peterson olefination[28] of pyruvaldehyde dimethyl acetal. Scheme 9.

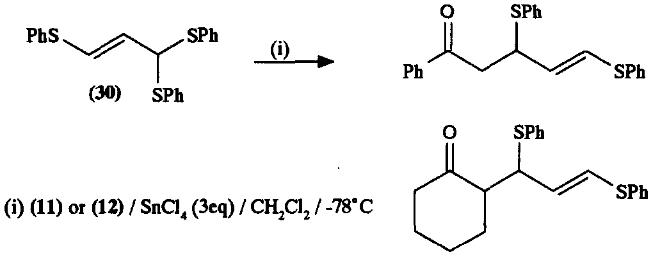


(31) 92%

E:Z = 7:3

Scheme 9

Reaction of (30) with the enol silyl ethers (11) and (12) with three equivalents of Lewis acid ($TiCl_4$ or $SnCl_4$) at -78 °C in CH_2Cl_2 gave both of the expected masked Michael adducts (32) and (33) in improved yields compared to the Pummerer reaction. In this case, excess Lewis acid for swift consumption of starting material proved not to be detrimental to the chemical yield. Furthermore, the products were obtained exclusively as (E)-isomers in all cases as with the Pummerer result. (33) was obtained as a 2:1 mixture of diastereomers identical to that obtained from the Pummerer route, indicating that a 'free' vinylthionium ion is involved in this instance. Scheme 10.



(32) 67%

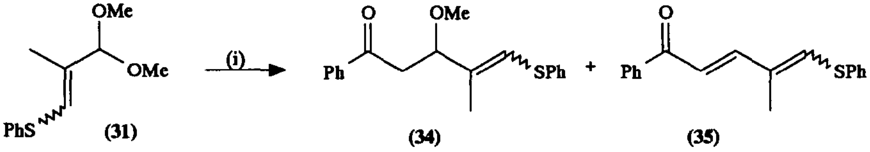
(33) 73%

(40:60)

Scheme 10

This methodology provides a useful alternative to introduction of the 1,3-bis(phenylthio)propenyl unit via alkylation of its carbanion[4b,4c]. Attempts to hydrolyse the adduct (33) with $HgCl_2$ in wet CH_3CN[4b], boron trifluoride/mercuric oxide[29a], copper(II) chloride / copper(II) oxide / ethanol[29b], $TiCl_4$ / H_2O[29c], $AgNO_3$ / H_2O[4c] or HCl/MeOH/THF[18] all failed, giving only unreacted starting material or multiple intractable products. This was disappointing since the sequence would have constituted overall conjugate additon to propargyl aldehyde.

By comparison, reaction of 3,3-dimethoxy-2-methyl-1-phenylthiopropene (31) with the enol silyl ether (11) proved to be highly sensitive to the number of equivalents of Lewis acid used. $TiCl_4$ was chosen as the latter in view of the Mukaiyama reaction[30]. Addition proceeded regioselectively at the acetal carbon to give a 5:1 E:Z mixture of **(34)** in moderate yield, with no evidence of attack at the α-carbon of the vinyl sulfide. Understandably, high concentrations of $TiCl_4$ (> 2 equivalents) resulted in β-elimination to the diene **(35)** as an E,E-isomer, but the reaction outcome could be selectively controlled by the concentration of Lewis acid. Scheme 11, Table 6.



(i) (11) / $TiCl_4$ (1.5eq) / CH_2Cl_2 / -78°C

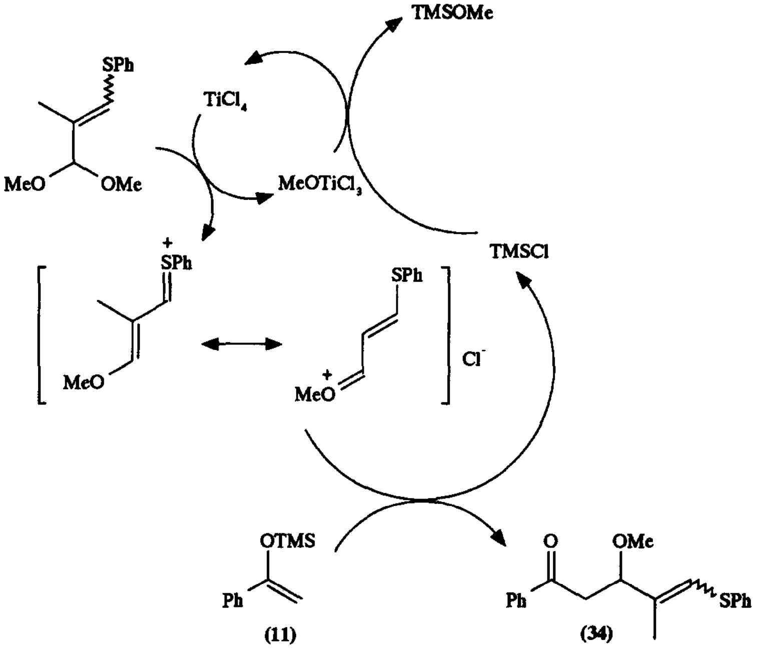
Scheme 11

Table 6

$TiCl_4$ (eq.)	Product Distribution[a] (34)	Product Distribution[a] (35)	Combined Yield %
0.1	100	0	74
0.5	94	6	66
1.0	75	25	60
1.5	55	45	56
2.0	12	88	57
2.5	0	100	59

a: determined as independent yields from chromatography.

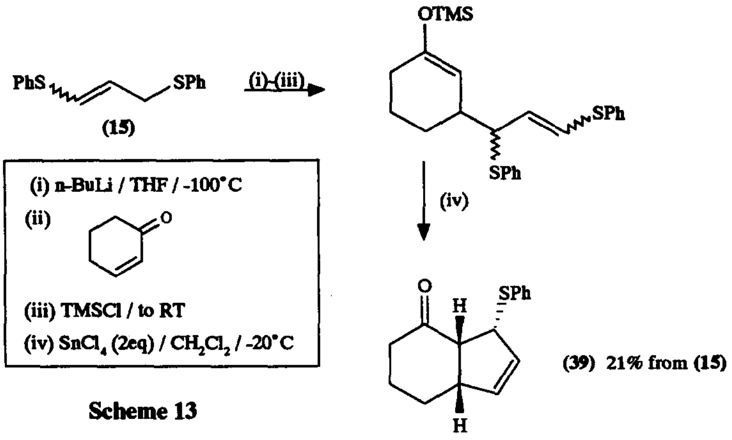
Of interest here is the complete conversion of starting material in high yield using only 0.1 equivalents of $TiCl_4$, when Mukaiyama-type reactions[30] usually require a stoichiometric amount of $TiCl_4$. Since TMSCl and $Ti(OPr)_4$ did not catalyse this reaction, the catalytic cycle shown in Scheme 12 is proposed in which $TiCl_4$ is regenerated. The involvement of a 'free' vinylthionium ion is supported by the increase in E:Z ratio of starting material to product from 7:3 to 5:1. Scheme 12. Reaction of **(31)** with two prochiral enol silyl ethers, viz. **(12)** and that of pentan-3-one **(36)**, revealed a reluctance of the product to β-eliminate in both cases. Once again, reaction could be promoted by a catalytic amount of $TiCl_4$ (0.5 eq) in CH_2Cl_2 at -78°C but excess Lewis acid or treatment with base (DBU)[31] failed to produce any diene. In the case of cyclohexanone, the product **(37)** was isolated in 82% yield as a single regio- and diastereoisomer and as an E:Z mixture of 9:1 as evidenced by 200 MHz ^1H and 50 MHz ^{13}C NMR data in conjunction with NOE analysis. Since it has been shown[32] that 1-trimethylsilyloxycyclohexene reacts with simple acetals in the presence of Lewis acids to give



Scheme 12

predominantly erythro diastereomers via an acyclic transition state, we tentatively assign (**37**) as the erythro configuration. Similarly, the enol silyl ether of pentan-3-one (**36**) as a 3:1 Z:E mixture reacted with (**31**) and $TiCl_4$ (0.5 eq.) in CH_2Cl_2 at -78°C to afford the β-methoxy adduct (**38**) as a 3:1 mixture of diastereomers and 85:15 E:Z ratio of geometrical isomers in 77% isolated yield. Use of a 7:1 Z:E mixture of enol silyl ether gave the same diastereomer ratio of 75:25, a feature observed by Noyori[32] for the reaction of enol silyl ethers and acetals with TMSOTf.

As a finale to the study, the methodology was applied to a pentannulation strategy, for which there has been several contributions in recent years[4b,33]. The approach chosen utilised conjugate addition[4b] of the anion of 1,3-bis(phenylthio)propene (**15**) to cyclohexanone followed by trapping[34] to the enol silyl ether. Attempts to purify the latter by column chromatography failed but cyclisation could be accomplished in a one pot reaction using $SnCl_4$ (2 eq.) at -20°C in CH_2Cl_2 (to replace the THF) to afford the annulated cis-3-phenylthio-3, 3a, 5, 6, 7, 7a-hexahydro-4H-inden-4-one (**39**) in 21% overall yield (isolated). The yield was not optimised and it may be possible to improve on it using more $SnCl_4$. The product (**39**) was isolated almost exclusively (ratio > 85 :15) as a single diastereomer as determined by ^1H and ^{13}C NMR. Its relative configuration was established as (3R*, 3aR*, 7aS*) as shown in Scheme 13 by comparing the coupling constants (specifically $J_{H3a\text{-}H3}$ and $J_{H3a\text{-}H7a}$) with those obtained from computer modelling using ALCHEMY[20] as mentioned before in conjunction with the Karplus equation. The ring junction stereochemistry was assigned as cis on the basis of an NOE experiment. Hence, this annulation complements existing strategies using bifunctional[35] reagents. Scheme 13.



Scheme 13

Thus, to summarise, the $SnCl_4$ based methodology resolves most of the problems associated with using Pummerer-generated α- and γ-substituted vinylthionium ions, and gives respectable to excellent yields particularly with substrates bearing electron donating substituents that can stabilise the vinylthionium ion intermediate. The Pummerer methodology, however, is still superior for the prototype masked Michael addition using allyl phenyl sulfoxide. Substitution at either the α- or γ- terminus of the vinylthionium ion generally favours attack at the γ- or α- terminus respectively on steric grounds and levels of regioselectivity are dependent on the steric bulk of the substituent. In the case of the synthetically useful methyl substituent at the γ- position, the regioselectivity may be controlled to a reasonable degree by the steric bulk of the sulfur substituent. Addition reactions generally gave (E)-vinyl sulfides regardless of the stereochemical integrity of the starting allylating agent. This compares well with the result from the Pummerer methodology and is considered useful for the synthesis of stereo-defined olefins using nickel catalysed cross coupling[36]. Futhermore, the methodology shows promise for using γ-heterosubstituted vinylthionium ions in regio- and diastereoselective alkylation reactions as well as annulation strategies.

EXPERIMENTAL

Infrared spectra were recorded on a Jasco FT / IR-5000 spectrometer as 50 mg. ml^{-1} solutions in $CHCl_3$ or CH_2Cl_2. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC-200 at 200.13 and 50.32 MHz respectively. Elemental analyses were performed on solid samples where appropriate. Liquid samples were invariably evaluated using high resolution mass spectrometry (HRMS) on a Kratos high resolution mass spectrometer. All solvents were dried where appropriate using standard methods and distilled before use. Column chromatography was carried out using Merck Kieselgel 60 (particle size 0.063-0.200 mm) or (0.040-0.063 mm) for flash chromatography. Preparative medium pressure chromatography was carried out using ICN Silica Gel Woelm (particle size 0.036-0.063 mm). Enol silyl ethers (**11**), (**12**) and (**36**) (Z:E = 3:1) were prepared using the method of Dunogues[37]. Acrolein, crotonaldehyde, 3-methyl-2-butenal, cinnamaldehyde, trans-4-phenyl-3-buten-2-one were all purchased from ALDRICH chemical company.

The following compounds were synthesised according to literature procedures: 2,2-bis(phenylthio)propanal[13,14], 2,2-bis(phenylthio)butanal, 1,3-bis(phenylthio)propene[5] (**15**), (E)-1,3,3-tris(phenylthio)prop-1-enal[1] (**30**).

1. Synthesis of 1,3-bis(alkyl/phenylthio)alkenes and 3,3-bis(phenylthio)alkenes.

A) General procedure using conjugate addition of thiols to enones.

The α,β-unsaturated carbonyl compound (1.0 eq.) was dissolved in dichloromethane under nitrogen , cooled to 0°C and phosphorus pentoxide (2.2 eq.) added using a powder funnel. Thiophenol (or aliphatic thiol), (2.2 eq), was then added from a syringe, and stirring was continued for 45 minutes at 0°C. The reaction was quenched with a potassium hydroxide solution (1M) and then extracted with dichloromethane. CAUTION: A vigorous reaction occurs if the reaction is quenched too rapidly . The combined organic extracts were dried with magnesium sulfate and evaporated in vacuo. The resulting material was purified by column chromatography (eluting with hexane:CH_2Cl_2 9:1) to yield 1,3- and/or 3,3-bis(alkylthio/phenylthio)propenes. The following compounds were thus prepared:

a) *1,3-Bis(phenylthio)but-1-ene* (**2**). Obtained in 50% as a 96:4 E:Z mixture; ν_{max} 3024, 1584, 1439, 1212 cm^{-1}; δ_H 1.33 (3H, d, J 6.9 Hz), 3.77 (1H, dq, J 7.0, 7.2 Hz), 5.78 (1H, dd, J 7.7, 14.9 Hz), 5.90 (1H, d, J 14.9 Hz), 6.90-7.44 (10H, m); δ_C 19.9, 46.1, 122.4, 126.00, 127.2, 128.5, 128.6, 128.6, 132.5, 133.2, 134.1, 135.8; m/z 163 (100), 129 (29), 109 (34), 85 (45), 65 (29), 51 (29), 45 (36), 39 (25); HRMS (m/z) calcd. for $C_{16}H_{16}S_2$ (M$^+$) 272.0693, found 272, 0679.

b) *1,3-Bis(t-butylthio)but-1-ene* (**3**) 75% yield as a 90:10 E:Z mixture; ν_{max} 2968, 2902, 2868, 1601, 1164, 951 cm^{-1}; δ_H 1.34 (21H, m), 3.57 (1H, dq, J 7.3, 7.3 Hz, E-isomer), 3.91 (1H, dq, J 7.1, 9.9 Hz, Z-isomer), 5.68 (1H, dd, J 9.7, 9.7 Hz, Z-isomer), 5.87 (1H, dd, J 8.3, 15.0 Hz, E-isomer), 6.03 (1H, d, J 9.5 Hz, Z-isomer), 6.19 (1H, d, J 15.0 Hz, E-isomer); δ_C 22.1, 22.6, 30.9, 31.5, 31.6, 36.7, 40.5, 43.6, 43.9, 118.9 (Z-isomer), 119.5 (E-isomer), 136.7 (Z-isomer), 139.8 (E-isomer); m/z 143 (24), 87 (100), 57 (72), 41 (54); HRMS (m/z) calcd. for $C_{12}H_{24}S_2$ (M$^+$) 232.1319, found 232.1307.

c) *1,3-Bis(ethylthio)but-1-ene* (**4**) 68% yield as a 65:35 E:Z mixture; ν_{max} 2974, 1603, 1452, 1191, 942 cm^{-1}; δ_H 1.26 (9H, m,) 2.45 (2H, m), 2.69 (2H, m), 3.42 (1H, dq, J 6.9, 8.9 Hz, E-isomer), 3.85 (1H, dq, J 6.8, 10.0 Hz, Z-isomer), 5.43 (1H, m, E & Z-isomers), 5.99 (1H, d, J 9.4 Hz, Z-isomer), 5.99 (1H, d, J 15.0 Hz, E-isomer); δ_C 14.4, 14.7, 15.1, 15.4, 20.3, 20.7, 24.7, 24.9, 26.3, 28.1, 37.9, 42.3, 123.3 (E-isomer), 125.1 (Z-isomer), 130.8 (E-isomer), 132.5 (Z-isomer); m/z 176 (15), 115 (100), 87 (14), 85 (23), 59 (20), 45 (28); HRMS (m/z) calcd. for $C_8H_{16}S_2$ (M$^+$) 176.0693, found 176.0681.

d) *1,1-Bis(phenylthio)-3-methylbut-2-ene* (**5a**) and *1,3-bis(phenylthio)-3-methylbut-1-ene* (**5b**) 58% yield as a 40:60 mixture; ν_{max} 3080, 1584, 1439, 1365 cm^{-1}; δ_H (**5a**) 1.32 (3H, d, J 1.3 Hz), 1.62 (3H, d, J 1.2 Hz), 5.11 (1H, d, J 10.4 Hz), 5.21 (1H, dq, J 10.4 Hz), 7.0-7.5 (10H, m); δ_H (**5b**) 1.38 (6H, s), 5.75 (1H, d, J 15.3 Hz), 6.02 (1H, d, J 15.3 Hz), 7.0-7.5 (10H, m); δ_C 17.8 (CH_3,(**5a**)), 25.3 (CH_3, (**5a**)), 27.6 (CH_3, (**5b**)), 50.3 (**5b**), 54.2 (**5a**), 120.5, 123.0, 126.3, 127.7, 128.4, 128.6, 128.7, 128.8, 128.9, 132.1, 133.2, 134.0, 135.4, 135.5, 137.4, 140.2; m/z 177 (28, M$^+$-SPh), 143 (24), 99 (100), 65 (46), 51 (26), 39 (34); HRMS (m/z) calcd. for $C_{17}H_{18}S_2$ M$^+$ 286.0850, found 286.0840.

e) *(E)-1-phenyl-3,3-bis(phenylthio)propene* (**6**) 83% yield; ν_{max} 3070, 1582, 1025 cm^{-1}; δ_H 5.01 (1H, d, J 8.1 Hz), 6.19 (1H, dd, J 7.9, 15.7 Hz), 6.33 (1H, d, J 15.7 Hz), 7.19-7.50 (15H, m); δ_C 58.5, 126.5, 126.8, 127.8, 128.0, 128.5, 128.8, 132.0, 133.2, 133.6, 136.0; HRMS (m/z) calcd. for $C_{21}H_{18}S_2$ (M$^+$) 334.0850, found 334.0850.

f) *(E)-3,3-Bis(phenylthio)-1,3-diphenylpropene* (**7**) Yield 8%; ν_{max} 3068, 1582, 1481, 1025 cm^{-1}; δ_H 5.85 (1H, d, J 10.0 Hz), 6.59 (1H, d, J 10.0 Hz), 6.78-7.57 (20H, m); δ_C 53.3, 125.8, 127.5, 127.7, 127.8, 127.9, 128.0, 128.5, 128.8, 128.9, 129.2, 133.7, 133.9, 134.2, 134.4, 135.8, 137.2, 139.1, 139.7;

B). General procedure using Wittig reaction of 2,2-bis(phenylthio)aldehydes.

The relevant phosphonium salt (1 eq.) was dissolved in dry THF, under a nitrogen atmosphere, at room temperature. n-Butyllithium (1.1 eq. as a 1.6 M solution in hexane) was then added from a glass syringe. The reaction mixture turned orange indicating formation of the desired ylide. After this was stirred for 0.5 h, the 2,2-bis(phenylthio)aldehyde, dissolved in a little THF, was added dropwise over 5 minutes. Stirring at room temperature was continued for a further 0.5 h and then a reflux condenser was fitted and the reaction mixture was heated at reflux for 12 h. At this stage the reaction mixture was poured into a saturated sodium hydrogen carbonate solution and extracted with hexane (3 x 30 ml). The combined hexane fractions were then dried over magnesium sulfate and evaporated in vacuo to yield the crude product. This was purified by column chromatography (elution with hexane:CH_2Cl_2 9:1) to give the 3,3-bis(phenylthio)propenes as colourless oils. The following compounds were thus prepared:

a) *3,3-Bis(phenylthio)but-1-ene* (**8**) 45% yield; δ_H 1.54 (3H, s), 4.82 (1H, dd, J 0.6, 17.2 Hz), 4.98 (1H, dd, J 0.5, 10.3 Hz), 5.96 (1H, dd, J 10.5, 17.2 Hz), 7.17-7.40 (6H, m), 7.50-7.60 (4H, m); δ_C 25.8, 61.9, 113.7, 128.4, 129.1, 132.8, 136.9, 140.8; m/z 163 (100.0, M^{+}-SPh), 135 (56), 130 (41), 109 (35), 65 (32), 59 (31), 53 (30), 51 (31); HRMS (m/z) calcd. for $C_{16}H_{16}S_2(M^+)$ 272.0693, found 272.0690.

b) *3,3-Bis(phenylthio)pent-1-ene* (**9**) 71% yield; ν_{max} 2976, 1628, 1584, 1087, 920 cm^{-1}; d_H 1.15 (3H, t, J 7.2 Hz), 1.77 (2H, q, J 7.3 Hz), 4.81 (1H, dd, J 0.6, 17.4 Hz), 4.99 (1H, dd, J 0.6, 10.7 Hz), 5.83 (1H, dd, J 10.8, 17.3 Hz), 7.1-7.6 (10H, m,); d_C 9.3, 29.9, 68.9, 114.6, 128.3, 128.7, 132.5, 136.4, 139.5; m/z 177 (100, M^{+}-SPh), 135 (92), 109 (50), 67 (40), 65 (55), 41 (64), 39 (35); HRMS (m/z) calcd. for $C_{17}H_{18}S_2$ (M^+) 286.0850, found 286.0832.

c) *4,4-Bis(phenylthio)hex-2-ene* (**10**) 53% yield. Double bond **not** unequivocally assigned as (E)- by NOE. ν_{max} 2936, 1584, 1477, 1025 cm^{-1}; δ_H 1.06 (3H, t, J 7.3 Hz), 1.68 (3H, dd, J 1.6, 7.3 Hz), 1.84 (2H, q, J 7.2 Hz), 5.30 (1H, dq J 1.7, 11.8 Hz), 5.53 (1H, dq, J 7.3, 11.8), 7.15-7.32 (6H, m,), 7.58-7.68 (4H, m); δ_C 9.6, 15.0, 32.6, 68.0, 128.3, 128.6, 129.0, 130.1, 132.4, 136.2; m/z 201 (62), 110 (43), 109 (40), 81 (55), 79 (76), 77 (42), 65 (55), 53 (57), 51 (42), 41 (100), 39 (79); HRMS (m/z) calcd. for $C_{18}H_{20}S_2$ (M^+) 300.1006, found 300.1030.

2. General Procedure for the Reaction of Enol Silyl Ethers with 1,3- and 3,3-Bis(alkylthio/phenylthio)alkenes.

The 1,3- and/or 3,3-bis(alkylthio/phenylthio)alkene (0.33 mmol, 1.0 eq.) was dissolved in dry dichloromethane (3 ml) and cooled to -20°C under a nitrogen atmosphere. The enol silyl ether (0.43 mmol, 1.3 eq.) was then added using a syringe, followed by tin tetrachloride (0.33 mmol, 1.0 eq.) which was added dropwise. The reaction mixture was stirred for 1h at -20 °C and then quenched rapidly with a saturated sodium hydrogen carbonate solution (2 ml). Further dilution of the reaction mixture with saturated sodium hydrogen carbonate solution (15 ml), extraction with dichloromethane (3 x 20 ml), drying of the combined organic fractions with magnesium sulfate, and evaporation in vacuo gave the crude product material. Column chromatography (eluting with hexane:CH_2Cl_2 8:2) then yielded the pure α- and/or γ-alkylation products.The following compounds were prepared:

a) *1,5-Diphenyl-3-phenylthiopent-4-en-1-one* (**13a**) and *(E)-1,3-diphenyl-5-phenylthiopent-4-en-1-one* (**13b**)[1]. $SnCl_4$ (3 eq.) was used. Yield of (**13a**):(**13b**) as a 57:43 mixture was 62%. Their spectral data was consistent with that obtained from the Pummerer route[1].

b) *2-(3-Phenyl-1-phenylthioallyl)cyclohexanone* **(14a)** and *(E)-2-(1-phenyl-3-phenylthioallyl) cyclohexanone* **(14b)**.

$SnCl_4$ (3 eq.) was used. Yield of **(14a)**:**(14b)** as a 70:30 mixture was 93%. **(14a)**/**(14b)** were both obtained as a 1:1 mixture of diastereomers. Their spectral data was consistent with that obtained from the Pummerer route[1].

c) *(E)-2-(3-Phenylthioallyl)cyclohexanone* **(16)**[2]. Yield was 22%.

d) *(E)-2-(3-Phenylthiopent-2-enyl)cyclohexanone* **(17)**.

Yield was 48%; ν_{max} 2940, 1711, 1584, 911 cm^{-1}; δ_H 1.04 (3H, t, J 7.4 Hz), 2.22 (2H, q, J 7.4 Hz), 1.26-2.69 (11H, m), 5.75 (1H, dd, J 6.8, 8.2 Hz), 7.13-7.41 (5H, m); δ_C 13.3, 24.4, 25.1, 27.8, 28.7, 33.6, 42.0, 50.4, 126.2, 128.8, 130.0, 133.2, 135.4, 136.8, 212.1; m/z 165 (100, M^{+}-SPh), 135 (92), 109 (30), 77 (33), 67 (36), 65 (35), 57 (45), 55 (37), 41 (83), 39 (33); HRMS (m/z) calcd. for $C_{17}H_{22}OS$ (M^+) 274.1391, found 274.1376.

e) *2-(1-Ethyl-3-phenylthiobut-1-enyl)cyclohexanone* **(18a)** and *(E)-2-(1-Methyl-3-phenylthiopent-2-enyl)cyclohexanone* **(18b)**.

Yield was 56% of **(18a)** and **(18b)** as a 40:60 mixture and as a 70:30 and 60:40 mixture of diastereomers respectively; ν_{max} 2970, 1709, 1584, 1479 cm^{-1}; δ_H (mixture of **(18a)** and **(18b)**) 0.91-1.19 (6H, m,), 1.42-2.47 (11H, m), 2.95 (1H, m, CH **(18b)**), 3.33 (1H, m, CH **(18a)**), 5.57 (1H, d, J 10.5 Hz, CH vinyl **(18a)**, major diastereomer), 5.65 (1H, d, J 9.6 Hz, CH vinyl **(18a)** minor diastereomer), 5.78 (1H, d, J 10.0 Hz, CH vinyl **(18b)** major diastereomer), 5.83 (1H, d, J 9.3 Hz, CH vinyl **(18b)** minor diastereomer), 7.09-7.39 (5H, m); m/z 191 (66), 179 (85), 149 (45), 81 (51), 79 (54), 57 (46), 55 (58), 41 (100); HRMS (m/z) calcd. for $C_{18}H_{24}OS$ (M^+) 288.1548, found 288.1538.

f) *2-(3-Methyl-1-phenylthiobut-2-enyl)cyclohexanone* **(19a)**.

Yield was 95%, (α:γ) ratio > 92:8; ν_{max} 2940, 1711, 1584, 1127 cm^{-1}; δ_H (minor diastereomer) 1.26 (3H, d, J 1.3 Hz), 1.61 (3H, d, J 1.2 Hz), 1.65-2.65 (9H, m), 4.18 (1H, dd, J 6.4, 10.6 Hz), 5.20 (1H, dq, J 1.3, 10.6 Hz), 7.21-7.47 (5H, m); δ_H (major diastereomer) 1.42 (3H, d, J 1.3 Hz), 1.64 (3H, d, J 1.2 Hz), 1.65-2.65 (9H, m), 4.36 (1H, dd, J 6.2, 10.6 Hz), 5.04 (1H, dq, J 1.3, 10.6 Hz), 7.21-7.47 (5H, m). Discernible peaks for γ-adduct; δ_H 6.07 (1H, d, J 15.1 Hz, vinylic H), 6.17 (1H, d, J 15.1 Hz, vinylic H); d_C (minor diastereomer) 17.6, 24.1, 25.5, 27.6, 30.7, 41.8, 47.9, 55.4, 124.0, 210.4; δ_C (major diastereomer) 17.8, 24.4, 25.7, 27.4, 30.1, 41.8, 46.5, 54.6, 122.3, 210.8; other signals: 127.3, 128.4, 128.5, 128.8, 133.8, 134.1, 135.2; m/z 165 (38), 149 (100), 147 (28), 93 (27), 79 (31), 69 (28), 41 (39), 39 (28); HRMS (m/z) calcd. for $C_{17}H_{22}OS$ (M^+) 274.1391, found 274.1384.

g) *2-(1-Phenylthiobut-2-enyl)cyclohexanone* **(20a)** and *(E)-2-(1-methyl-3-phenylthioprop-2-enyl) cyclohexanone* **(20b)**.

Yield of **(20a)** and **(20b)** was 66% as a 57:43 mixture and as a 60:40 and 50:50 mixture of diastereomers respectively; ν_{max} 2940, 1711, 1584, 1129 cm^{-1}; δ_H **(20a)** 1.59 (3H, m), 1.65-2.91 (9H, m), 3.87 (1H, dd, J 5.9, 9.2 Hz, minor diastereomer), 4.13 (1H, dd, J 5.7, 7.7 Hz, major diastereomer), 5.41 (2H, m), 7.12-7.48 (5H, m); δ_H **(20b)** 1.06 (3H, d, J 6.7 Hz), 1.65-2.91 (9H, m), 5.84 (1H, dd, J 8.3, 15.0 Hz, major diastereomer), 5.98 (1H, dd, J 7.2, 15.1 Hz, minor diastereomer), 6.16 (1H, d, J 15 Hz, major diastereomer), 6.17 (1H, d, J 15.1 Hz, minor diastereomer), 7.11-7.48 (5H, m), δ_C (**(20a)**; both diastereomers; isolated from column chromatography) 17.5, 17.7, 24.1, 24.3, 27.3, 27.5, 29.9, 30.6, 41.6, 50.3, 52.1, 54.3, 54.9, 126.9, 128.4, 128.4, 128.6, 128.6, 132.4, 132.9, 210.2, 210.5; m/z 151 (100, M^{+}-SPh), 135 (76), 133 (51), 109 (61), 107 (85), 93 (54), 91 (64), 81 (83), 79 (96); HRMS (m/z) calcd. for $C_{16}H_{20}OS$ (M^+) 260.1235, found 260.1240.

h) *1-Phenyl-3-phenylthiohex-4-en-1-one* **(21a)** and *(E)-3-Methyl-1-phenyl-5-phenylthiopent-4-en-1-one* **(21b)**.
Yield of **(21a)** and **(21b)** was 68% as a 16:84 mixture. Spectral data showed good agreement with literature[2]

values; δ_H **(21a)** 1.56 (3H, m), 2.81-3.33 (2H, m), 4.28 (1H, m), 5.41 (2H, m), 7.11-7.98 (10H, m); δ_H **(21b)** 1.13 (3H, d, J 6.5 Hz), 2.81-3.33 (3H, m), 5.91 (1H, dd, J 6.8, 15.1 Hz), 6.18 (1H, d, J 15.1 Hz), 7.11-7.98 (10H, m).

i) *2-(1-Ethylthiobut-2-enyl)cyclohexanone* **(22a)** and *(E)-2-(1-methyl-3-ethylthioprop-2-enyl) cyclohexanone* **(22b)**.

Yield of **(22a)** and **(22b)** was 67% as a 76:24 mixture and as a 50:50 and 60:40 mixture of diastereomers respectively; ν_{max} 2940, 1709, 1452, 1220, 969 cm^{-1}; δ_H **(22a)** 1.22 (3H, m), 1.70 (3H, m), 1.55-2.40 (9H, m), 2.47 (2H, m), 3.57 (1H, dd, J 6.4, 8.6 Hz, major diastereomer), 3.69 (1H, dd, J 6.7, 9.4 Hz, minor diastereomer), 5.26 (1H, ddq, J 1.5, 9.4, 15.1 Hz), 5.45 (1H, m). Discernible signals for **(22b)**; δ_H 5.93 (1H, d, J 15.2 Hz, vinyl H, minor diastereomer), 5.94 (1H, d, J 15.2, vinyl H, major diastereomer); m/z 115 (100), 55 (31), 45 (35); HRMS (m/z) calcd. for $C_{12}H_{20}OS$ (M$^+$) 212.1235, found 212.1248.

j) *(E)-2-(1-Methyl-3-(t-butylthio)prop-2-enyl)cyclohexanone* **(23b)**.

Yield of **(23a)** and **(23b)** was 64% as a 15:85 mixture and as a 70:30 and 45:55 mixture of diastereomers respectively; ν_{max} 2968, 1709, 1460, 1127 cm^{-1}; δ_H **(23b)** 1.02 (3H, d, J 6.8 Hz), 1.32 (9H, s), 1.38-2.54 (9H, m), 2.80 (1H, m), 5.71 (1H, dd, J 8.6, 14.9 Hz, major diastereomer), 5.87 (1H, dd, J 7.5, 15.0 Hz, minor diastereomer), 6.09 (1H, d, J 15.0 Hz, minor diastereomer), 6.11 (1H, d, J 14.9 Hz, major diastereomer); δ_C (**(23b)**, 2 diastereomers), 16.0, 18.8, 24.2, 24.7, 27.5, 28.0, 28.7, 30.7, 31.0, 31.4, 35.9, 36.6, 41.9, 42.0, 42.2, 43.6, 55.1, 55.9, 119.7 (minor diastereomer vinyl), 120.4 (major diastereomer vinyl), 139.6 (major diastereomer vinyl), 140.4 (minor diastereomer vinyl), 211.6 (minor), 212.5 (major); m/z 151 (39, M^{+}-SC(CH$_3$)$_3$), 87 (82), 57 (93), 41 (100); HRMS (m/z) calcd. for $C_{14}H_{24}OS$ M$^+$ 240.1548, found 240.1549.

3. Transformation of Addition products

a) *Vinyl sulfide hydrolysis and Robinson annulation to 1-methyl-4,4a,5,6,7,8-hexahydro-3H-napthalen-2-one* **(24)**[38].

Vinyl sulfide **(17)** (33 mg, 0.12 mmol) was refluxed in THF/MeOH/HCl (6M) (1.6 ml/1.6 ml/0.8 ml) for 6 hr. The solution was diluted with water (5 ml) and extracted with ether (3 x 20 ml). The combined ether extracts were washed with KF solution (10%), dried ($MgSO_4$) and evaporated. The residue was chromatographed (hexane:CH_2Cl_2 = 1:1) to give **(24)** (20 mg, 100%) as a colourless oil; ν_{max} 2936, 1659, 1615, 1201 cm^{-1}; δ_H 1.21-1.68 (4H, m), 1.78 (3H, s), 1.84-2.17 (5H, m), 2.21-2.52 (3H, m), 2.86 (1H, m); δ_C 10.6, 25.5, 26.6, 28.7, 31.3, 34.8, 36.3, 38.7, 159.8, 167.7, 199.7.

b) *Vinyl sulfide hydrolysis and Robinson annulation to (4R*, 4aS*)-1,4-dimethyl-4,4a,5,6,7,8-hexahydro-3H-napthalen-2-one* **(25)**.

Using the aforementioned hydrolysis procedure with **(18a)/(18b)** as a 40:60 mixture (104 mg, 0.36 mmol) and THF/MeOH/HCl(6M) (5 ml/5 ml/2.5 ml) gave **(25)** (39 mg, 0.22 mmol, 100% based on **(18b)** as a 78:22 mixture of diastereomers; ν_{max} 3022, 1713, 1657, 1448, 1365 cm^{-1}; δ_H 1.05 (3H, d, J 6.5 Hz), 1.19-1.53 (4H, m), 1.78 (3H, s), 1.80-2.02 (4H, m), 2.12 (1H, dd, J 11.6, 15.4 Hz), 2.14-2.23 (1H, m), 2.42 (1H, dd, 4.2, 15.4 Hz), 2.86 (1H, m); δ_C (major diastereomer) 10.5, 19.7, 25.6, 26.6, 31.5, 32.8, 34.2, 44.5, 46.1, 128.1, 158.8, 199.6; δ_C (minor diastereomer) 10.4, 17.6, 26.1, 27.8, 28.8, 31.0, 33.2, 42.0, 44.8; HRMS (m/z) calcd. for $C_{12}H_{18}O$ (M$^+$) 178.1358, found 178.1349.

c) *Raney nickel desulfurisation to 2-(3-methylbut-2-enyl)cyclohexanone* **(26a)** *and (E)-2-(3-methylbut-1-enyl)cyclohexanone* **(26b)**[39].

(19a) (110 mg, 0.40 mmol) was dissolved in acetone (5 ml) and W-2 Raney nickel[40] (as a slurry in ethanol) was added, with vigorous stirring, at 2 h intervals until t.l.c. indicated the absence of starting material. The reaction mixture was then diluted with dichloromethane (20 ml) and filtered through celite to remove the nickel (CAUTION: pyrophoric if allowed to dry out). Evaporation of the filtrate in vacuo and subsequent column chromatography (hexane:CH_2Cl_2 = 8:2) gave 2-(3-methylbut-2-enyl)cyclohexanone **(26a)** and (E)-2-(3-methylbut-1-enyl)cyclohexanone **(26b)** (34 mg, 0.20 mmol, 50%) in a 55:45 ratio respectively. ^{1}H NMR showed good agreement with literature values[39]; ν_{max} **(26a)**/**(26b)** 3022, 2940, 1711, 1450, 1365, 1226 cm^{-1}; δ_H **(26a)** 1.60 (3H, s), 1.69 (3H, d, J 1.2 Hz), 1.63-2.48 (11H, m), 5.08 (1H, m); δ_H **(26b)** 0.98 (6H, d, J 6.7 Hz), 1.63-2.48 (9H, m), 2.96 (1H, m), 5.39 (1H, dd, J 6.4, 19.0 Hz), 5.59 (1H, dd, J 6.8, 19.0 Hz).

d) *Oxidative phenylthio elimination to 2-(3-methylbut-2-enylidene)cyclohexanone* **(27)**.

(19a) (97 mg, 0.35 mmol, 1.0 eq.), in chloroform (0.5 ml), was added to a vigorously stirred suspension of wet alumina (0.5 g) and Oxone (0.65 g, 1.06 mmol, 3 eq.) in chloroform (2 ml)[23]. The mixture was then heated at reflux for 12 h. On cooling to room temperature the chloroform was evaporated in vacuo and the residue redissolved in THF (3 ml) and cooled to 0°C. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.1 ml, 0.67 mmol, 1.9 eq.) was then added and the reaction mixture stirred for 2 h. The reaction mixture was diluted into an ammonium chloride solution (1 M, 20 ml) and extracted with dichloromethane (3 x 20 ml). Drying with magnesium sulfate, in vacuo evaporation of solvent, and column chromatography (hexane:CH_2Cl_2 = 8:2) gave the pure product **(27)** (35 mg, 0.21 mmol, 61%) as a colourless oil. ^{1}H NMR showed good agreement with literature values[41]; ν_{max} 3022, 1713, 1667, 1622, 1568, 1259 cm^{-1}; δ_H 1.80 (4H, m), 1.92 (6H, s), 2.44 (2H, t, J 6.6 Hz), 2.59 (2H, m), 6.07 (1H, dm, J 12.2 Hz), 7.39 (1H, dt, J 2.1, 12.2 Hz).

4. Alternative nucleophiles for masked Michael addition.

a) *Allyltrimethylsilane with* **(6)** *to give 1-phenyl-3-phenylthiohexa-1,5-diene* **(28a)** *and (E)-3-phenyl-1-phenylthiohexa-1,5-diene* **(28b)**.

(E)-1-Phenyl-3,3-bis(phenylthio)propene **(6)** (114 mg, 0.34 mmol, 1.0 eq.), was dissolved in dichloromethane (3 ml) and cooled to -20°C under a nitrogen atmosphere. Allyltrimethylsilane (0.07 ml, 0.44 mmol, 1.3 eq.) and tin tetrachloride (0.04 ml, 0.34 mmol, 1.0 eq.) were then added dropwise, in that order. After stirring for 1 h at -20°C the reaction was quenched by pouring into a saturated sodium hydrogen carbonate solution (30 ml). This was then extracted with hexane (3 x 30 ml), the combined hexane fractions dried with magnesium sulfate, and then evaporated in vacuo to give the crude product material. This was purified by column chromatography (hexane) to yield a 45:55 mixture of **(28a)** (E:Z = 65:35) and **(28b)** (52 mg, 0.20 mmol, 57%) as a colourless oil; ν_{max} 3070, 1729, 1642, 1584, 1481, 1025 cm^{-1}; δ_H (**(28a)** and **(28b)**) 2.52 (2H, m), 3.49 (1H, m, **(28b)**), 3.78 (1H, m, Z-isomer of **(28a)**), 3.94 (1H, m, E-isomer of **(28a)**), 5.04 (2H, m), 5.63-6.29 (3H, m), 7.08-7.44 (10H, m); δ_C (mixture of **(28a)** and **(28b)** 40.0, 40.4, 45.1, 49.1, 116.5, 116.6, 122.1, 123.3, 126.2, 126.3, 126.5, 127.4, 127.6, 128.4, 128.5, 128.7, 128.8, 129.0, 135.7, 136.1, 136.1, 138.5; m/z 225 (11), 147 (11), 116 (19), 115 (100), 91 (20); HRMS (m/z) calcd. for $C_{18}H_{18}S$ (M^+) 266.1129, found 266.1122.

b) *Indole with* **(5)** *to give (E)-3-(1,1-dimethyl-3-phenylthioprop-2-enyl)indole* **(29)**.

A 40:60 mixture of 1,1-bis(phenylthio)-3-methylbut-2-ene **(5a)** and 1,3-bis(phenylthio)-3-methylbut-1-ene **(5b)** (544 mg, 1.90 mmol, 1.0 eq.) was dissolved in dry, distilled dichloromethane (5 ml) and dry calcium carbonate (190 mg, 1.90 mmol, 1.0 eq.) was then added. The resulting suspension was cooled to -20°C under a nitrogen atmosphere and tin tetrachloride (0.22 ml, 1.87 mmol, 1.0 eq) was added from a syringe. The solution turned dark red. At this stage, indole (221 mg, 1.89 mmol, 1.0 eq.) dissolved in dichloromethane

(1 ml) was added dropwise, over 5 minutes, from a syringe. The reaction mixture was stirred at -20°C for a further 1 h during which time the solution turned bright yellow. The reaction was quenched by pouring into a saturated sodium hydrogen carbonate solution (30 ml) and then extracted with dichloromethane (3 x 30 ml). The combined extracts were dried with magnesium sulfate and evaporated in vacuo to yield the crude product. This was purified by column chromatography (hexane:CH_2Cl_2 7:3) to give (E)-3-(1,1-dimethyl-3-phenylthioprop-2-enyl)indole **(29)** (329 mg, 1.12 mmol, 59%), as a pinkish, waxy solid, unstable in air, as the major product (90%). About 10% of the product material could be attributed to the corresponding α-product: ν_{max} **(29)** 3466, 3046, 2970, 1651, 1582, 1475, 1243, 911 cm^{-1}; δ_H 1.51 (6H, s), 6.21 (1H, d, J 16.3 Hz), 6.37 (1H, d, J 16.3 Hz), 7.07 (1H, d, J 2.5 Hz), 7.12-7.32 (6H, m), 7.51 (2H, m), 7.83 (1H, m), 8.02, (1H, br.s); δ_H discernible signals for α-adduct 1.45 (3H, s), 1.69 (3H, s), 5.33 (1H, d, J 10.1 Hz), 5.65 (1H, dm, J 10.4 Hz); δ_C **(29)** 28.1, 50.7, 111.3, 114.6, 119.8, 120.0, 120.1, 122.3, 123.0, 128.2, 128.4, 128.5, 133.4, 133.5, 136.6, 137.3, HRMS (m/z) sample decomposed prior to data collection.

5. Substrates for γ-heterosubstituted vinylthionium ions.

a) *(E)-1,3,3-Tris(phenylthio)propene* **(30)**[1].

b) *3,3-Dimethoxy-2-methyl-1-phenylthiopropene* **(31)**

Phenylthiotrimethylsilylmethane[42] (2.51 g, 12.8 mmol, 1.0 eq.) was dissolved in dry, distilled THF (30 ml) and cooled to 0°C under a nitrogen atmosphere. n-Butylithium (8 ml of a 1.6 M solution in hexane, 12.8 mmol, 1 eq.) was then added and the reaction mixture allowed to warm to room temperature over a period of 1 h. After again cooling to 0 °C, neat pyruvaldehyde dimethyl acetal (1.72 ml, 14.2 mmol, 1.1 eq.) was added and the reaction mixture was again left to warm to room temperature. Stirring at 0°C was continued for 12 h after which the reaction mixture was diluted with an ice-cold, saturated sodium hydrogen carbonate solution (50 ml) and extracted with hexane (3 x 30 ml). The combined extracts were dried with magnesium sulfate and evaporated in vacuo to yield 3,3-dimethoxy-2-methyl-1-phenylthiopropene **(31)** (2.64 g, 11.8 mmol, 92%) as a colourless oil. 200 MHz ^1H NMR showed the material to be an exceptionally pure 70:30 mixture of the (E)- and (Z)- isomers respectively; ν_{max} 2938, 1584, 1481, 1104, 1071 cm^{-1}; δ_H (E-isomer) 1.63 (3H, s), 3.13 (6H, s), 4.47 (1H, s), 6.29 (1H, s), 7.03-7.23 (5H, m); δ_H (Z-isomer) 1.70 (3H, s), 3.22 (6H, s), 5.02 (1H, s), 6.06 (1H, s), 7.03-7.23 (5H, m); δ_C 13.7 (E-isomer), 18.0 (Z-isomer), 52.9 (E), 54.2 (Z), 102.5 (Z) 105.0 (E), 122.3 (Z), 123.6 (E), 125.8, 126.3, 126.5, 128.5, 128.7, 128.9, 129.3, 133.1, 135.6, 136.8; m/z 193 (83, M^+- OMe), 161 (100), 115 (43), 75 (47); HRMS (m/z) calcd. for $C_{12}H_{16}O_2S$ (M^+) 224.0871, found 224.0869.

6. Reaction of enol silyl ethers with (30) and (31).

The general procedure described in section 2 was followed except $SnCl_4$ (3 eq.) was used with **(30)** and $TiCl_4$ (0.1 - 3 eq.) at -78 °C for **(31)**. The following compounds were prepared:

a) *(E)-1-Phenyl-3,5-bis(phenylthio)pent-4-en-1-one* **(32)**.

Yield of **(32)** was 67%. Spectral characteristics were identical to those reported[1].

b) *(E)-2-(1,3-Bis(phenylthio)prop-2-enyl)cyclohexanone* **(33)**.

Yield of **(33)** was 73% as a 40:60 mixture of diastereomers. Spectra characteristics were identical to those reported[1].

c) *3-Methoxy-4-methyl-1-phenyl-5-phenylthiopent-4-en-1-one* **(34)**.

Yield of **(34)** using $TiCl_4$ (0.1 eq.) was 74% as an E:Z mixture of 5:1. Found: C, 73.16; H, 6.44. $C_{19}H_{20}O_2S$

requires C, 73.04; H, 6.45% ; ν_{max} 3020, 2938, 1688, 1599, 1582, 1481, 1216, 1096 cm^{-1}; δ_H (E-isomer) 1.83 (3H, d, J 1.1 Hz), 2.97 (1H, dd, J 4.5, 16.1 Hz), 3.26 (3H, s), 3.41 (1H, dd, J 8.2, 16.1 Hz), 4.35 (1H, dd, J 4.5,8.2 Hz), 6.33 (1H, m), 7.15-7.60 (8H, m), 7.93-8.01 (2H, m); δ_H (Z-isomer) 1.87 (3H, d, J 1.4 Hz), 2.99 (1H, dd, J 4.8, 15.7 Hz), 3.26 (3H, s), 3.43 (1H, dd, J 8.4, 15.9 Hz), 5.03 (1H, dd, J 4.8, 8.4 Hz), 6.22 (1H, m), 7.15-7.60 (8H, m), 7.93-8.01 (2H, m); δ_C (E-isomer) 13.2, 43.1, 56.4, 81.8, 122.1, 126.3, 128.2, 197.6; δ_C (Z-isomer) 17.7, 42.2, 56.4, 75.8, 121.6, 126.2, 128.2, 197.3. Other signals: 128.5, 128.6, 128.9, 129.0, 133.0, 133.1, 135.9, 136.6, 137.1, 138.6.

d) *(E,E)-4-Methyl-1-phenyl-5-phenylthiopenta-2,4-dien-1-one* **(35)**.

Yield of **(35)** was 64% with TiCl$_4$ (3 eq.) m.p. 102-104 °C (Hexane/CH$_2$Cl$_2$); ν_{max} 3028, 1657, 1601, 1584, 1301, 1021 cm^{-1}; δ_H 2.03 (3H, d, J 0.8 Hz), 6.87 (1H, d, J 15.1 Hz), 6.89 (1H, d, J 0.7 Hz), 7.24-7.58 (9H, m), 7.93-8.00 (2H, m); δ_C 13.9, 118.8, 127.6, 128.2, 128.4, 129.3, 130.1, 132.1, 132.4, 134.3, 138.5, 139.2, 148.3, 190.5; (m/z > 10%) 28, 39, 51, 65, 77, 91, 105, 127, 128, 141, 171; HRMS (m/z) calcd. for $C_{18}H_{16}OS$ (M$^+$) 280.0922, found 280.0889.

e) *2-(1-Methoxy-2-methyl-3-phenylthioprop-2-enyl)cyclohexanone* **(37)**.

Yield of **(37)** with TiCl$_4$ (0.5 eq.) was 82% as a single diastereomer and an E:Z mixture of 9:1; ν_{max} 2940, 1711, 1584, 1129, cm^{-1}; δ_H (E-isomer) 1.73 (3H, d, J 1.1 Hz), 1.61-2.50 (9H, m), 3.30 (3H, s), 4.14 (1H, d, J 5.2 Hz), 6.26 (1H, q, J 1.0 Hz), 7.14-7.37 (5H, m); δ_C (E-isomer) 14.6, 24.0, 27.1, 41.9, 42.0, 53.0, 57.0, 82.3, 120.5, 126.0, 128.6, 128.9, 135.9, 136.3, 210.6; (m/z) 193 (100), 161 (78), 149 (28), 110 (27), 77 (28), 45 (39), 41 (40), 39 (27); HRMS (m/z) calcd. for $C_{17}H_{22}O_2S$ (M$^+$) 290.1340, found 290.1318.

f) *5-Methoxy-4,6-dimethyl-7-phenylthiohept-6-en-3-one* **(38)**.

Yield of **(38)** with TiCl$_4$ (0.5 eq.) and enol silyl ether **(36)** (E:Z = 1:3) was 77% as an (E:Z) mixture of (85:15) and as a mixture of diastereomers (75:25); ν_{max} 2984, 1715, 1584, 1462, 1091 cm^{-1}; δ_H (E-isomer) 1.02 (3H, t, J 7.3 Hz), 1.16 (3H, d, J 6.8 Hz), 1.75 (3H, d, J 1.1 Hz), 2.37-2.57 (2H, m), 2.83 (1H, m), 3.14 (3H, s, minor diastereomer), 3.24 (3H, s, major diastereomer), 3.72 (1H, d, J 10.3 Hz, minor diastereomer), 3.77 (1H, d, J 8.1 Hz, major diastereomer), 6.18 (1H, q, J 0.9 Hz, major diastereomer), 6.26 (1H, m, minor diastereomer), 7.17-7.34 (5H, m); δ_H (Z-isomer) 0.93 (3H, m), 1.06 (3H, m), 1.79 (3H, d, J 1.4 Hz), 2.37-2.60 (2H, m), 2.83 (1H, m), 3.18 (3H, s, major diastereomer), 3.27 (3H, s, minor diastereomer), 4.41 (1H, d, J 8.6 Hz, minor diastereomer), 4.58 (1H, d, J 10.3 Hz, major diastereomer), 6.21 (1H, m, minor diastereomer), 6.33 (1H, m, major diastereomer), 7.17-7.34 (5H, m); δ_C (E-isomer, major diastereomer) 7.6, 13.2, 13.6, 35.9, 49.6, 56.7, 86.8, 122.9, 126.4, 128.9, 129.1, 135.5, 136.0, 213.0; δ_C (Z-isomer, major diastereomer) 12.2, 14.2, 22.8, 29.8, 48.2, 56.4, 81.7, 124.2, 126.4, 128.7, 128.9, 135.0, 213.8; (m/z) 193 (100), 161 (87), 110 (28), 57 (57), 45 (36), 41 (24), 39 (20); HRMS (m/z) calcd. for $C_{16}H_{22}O_2S$ (M$^+$) 278.1340, found 278. 1318.

7. Stereoselective pentannulation to (3R*, 3aR*, 7aS*)-3-phenylthio-3, 3a, 5, 6, 7, 7a-hexahydro-4H-inden-4-one (39).

1,3-Bis(phenylthio)propene **(115)** (290 mg, 1.12 mol, 1.0 eq.) was dissolved in dry, distilled THF (5 ml) and cooled to -100°C under a nitrogen atmosphere. n-Butyllithium (0.70 ml of a 1.6 M solution in hexane, 1.12 mmol, 1.0 eq.) was added dropwise and the reaction mixture was stirred for 0.5 h at -100°C. The solution turned an orange/red colour indicating formation of the desired anion. Next, neat cyclohexenone (0.12 ml, 1.24 mmol, 1.1 eq.) was added over 5 minutes. Stirring at -100°C was continued for a further 0.5 h at which stage t.l.c. showed no starting materials and a single new spot. Chlorotrimethylsilane (0.29 ml, 2.32 mmol, 2.1 eq.) was then added and the reaction mixture was left to warm to room temperature over 1.5 h. At this stage the solution had become colourless, indicating formation of the desired intermediate enol silyl ether. The solvents were evaporated in vacuo and the residue was redissolved in dichloromethane (5 ml) and cooled to -20°C under a nitrogen atmosphere. Tin tetrachloride (0.26 ml, 2.24 mmol, 2.0 eq.) was added dropwise and the reaction mixture was stirred for 1 h at -20°C. Quenching with saturated sodium hydrogen carbonate solution (30 ml), extraction with dichloromethane (3 x 30 ml), drying of the combined dichloromethane fractions over magnesium sulfate, and in vacuo evaporation of solvents gave the crude product. This was purified by column chromatography (hexane:CH_2Cl_2 7: 3)) to yield mainly (3R*, 3aR*, 7aS*)-3-phenylthio-3, 3a, 5, 6, 7, 7a-hexahydro-4$\underline{H}$-inden-4-one (**39**) (58 mg, 0.24 mmol, 21%) as a colourless oil. ^{1}H NMR showed the product to be predominantly a single diastereomer, i.e. > 85:15 ratio (calculated from ^{13}C NMR spectrum) of two diastereomers; ν_{max} 2940, 1700, 1481, 1439, 1226, 909 cm^{-1} ; δ_H (major diastereomer) 1.23-2.19 (4H, m), 2.53 (2H, m), 2.88 (1H, m), 3.25 (1H, dd, J 7.9, 8.4 Hz), 4.42 (1H, dd, J 1.5, 8.8 Hz), 5.90 (1H, ddd, J 0.6, 1.5, 5.7 Hz), 5.94 (1H, ddd, J 0.9, 2.2, 5.6 Hz), 7.14-7.45 (5H, m); δ_C (major diastereomer) 23.6, 29.8, 42.8, 46.3, 53.8, 55.8, 126.7, 128.8, 129.0, 130.4, 133.1, 136.2, 211.9. Discernible peaks for minor diastereomer; δ_C 24.0, 31.1, 40.8, 46.0, 47.7, 127.7, 208.6; HRMS (m/z) calcd. for $C_{15}H_{16}OS$ (M$^+$) 244.0922, found 244.0917.

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(*Received in UK* 18 *April* 1994; *revised* 10 *June* 1994; *accepted* 17 *June* 1994)