Alkylation of Enol Silyl Ethers by Pummerer-generated Vinylthionium Ions: a Novel Masked Michael Reaction

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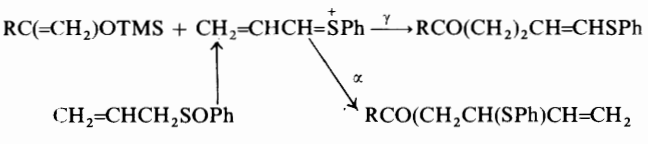
Reaction of the enol silyl ethers (**3**) and (**4**) with the allyl sulphoxides (**2**), (**7**), (**10**), and (**14**) under Pummerer conditions using trimethylsilyl trifluoromethanesulphonate (TMSOTf) and di-isopropylethylamine (Hunig's base) affords the *E*-masked Michael adducts (**5**), (**6**), (**8**), (**9**), (**12**), (**13**), and (**15**) in good yields. The vinylthionium ion intermediate is competitively intercepted by Hunig's base in the reaction to afford, for the allyl sulphoxide (**7**), the quaternary ammonium triflate salt (**18**), which is the sole product in the absence of silyl ether. The amine interception occurs with other pyramidal amines (triethylamine, quinuclidine, and diethyltrimethylsilylamine). The adduct (**18**) can be alkylated in moderate yield by less reactive enolates, *e.g.* malonate, using palladium(0) as catalyst.

A few years ago we were interested in developing the novel bifunctional[1] compound 2-methylene-3-trimethylsilylpropyl phenyl sulphoxide (**1**) into a versatile reagent in synthesis. We rationalised that although the compound would have various possibilities as a nucleophilic reagent, its electrophilic chemistry would need to be developed. We thought that a solution might be provided *via* the Pummerer chemistry of the allyl sulphoxide group in which a vinylthionium ion, if it could be generated without inference from the allyl silane, could offer the compound a rich electrophilic chemistry.

The Pummerer reaction has proved to be extremely versatile for functionality transfer from sulphur to carbon extending to O,[2] N,[3] S,[4] and halogen[5] nucleophile incorporation. In the realm of carbon–carbon bond formation most success has been achieved using intramolecular[6] olefinic interception of the Pummerer thionium ion intermediate, and in this respect the β-keto sulphoxide functionality has proved to be the electrophilic partner of choice. Far fewer examples exist, however, for intermolecular[7] interception by a carbon nucleophile, and the main problem to be overcome is competition for the thionium ion by other nucleophiles in the medium. We considered that an enol silyl ether might be an attractive nucleophilic partner for carbon–carbon bond formation with the allyl sulphoxide (Scheme 1) and our line of thinking was encouraged by a paper

$$Me_3SiCH_2C(=CH_2)CH_2SOPh$$

(1)



Scheme 1.

by Mukaiyama[8] describing enol silyl ethers as suitable nucleophilic partners for β-keto sulphoxides under Pummerer conditions using stannous triflate as Lewis acid and *N*-trimethylsilylimidazole as base. In this paper we describe our studies[9] on the alkylation of enol silyl ethers by Pummerer-generated vinylthionium ions.

Results and Discussion

We screened a variety of Lewis acids ($TiCl_4$, TMSOTf, $BF_3{\cdot}Et_2O$, $SnCl_4$) and bases (Pr^i_2NEt, NEt_3, pyridine) for the reaction, and found that the best combination was TMSOTf and Hunig's base (Pr^i_2NEt), which were also compatible with the enol silyl ether. In contrast to Mukaiyama's study in which the enol silyl was used as limiting reagent, we found that the highest yields were obtained using the enol silyl ether in slight excess (1.5 equiv.). The sulphoxide was added slowly to a mixture of the other reagents so that the vinylthionium ion could be intercepted as it was formed. Reactions were carried out in dry dichloromethane at −78 °C, and by t.l.c. were extremely fast at this temperature. With allyl phenyl sulphoxide (**2**) and the enol silyl ethers of cyclohexanone and acetophenone (**3**) and (**4**), adducts (**5**) and (**6**) were obtained as their *E* isomers as evidenced by ^1H n.m.r. (*J* 14.8, 14.9 Hz respectively) in 63 and 62% yield respectively. Furthermore, alkylation took place exclusively at the less hindered and electronically more favourable γ positon. Over prolonged periods in $CDCl_3$ the *E* isomer began to isomerise to the *Z* isomer in the n.m.r. tube while recording spectra (e.g. ^{13}C) but the reason for this is not clear. Similarly, 2-methylallyl phenyl sulphoxide (**7**) also underwent reaction with the enol silyl ethers (**3**) and (**4**) to afford the *E* isomers (**8**) and (**9**) exclusively as γ-adducts in 64 and 72% yield respectively. In the formation of (**8**), cyclohexanone enol silyl ether was prepared *in situ* by using an extra equivalent of TMSOTf and Hunig's base, indicating that the reaction may use the appropriate carbonyl compound as starting material. The *E*-geometry of (**9**) was ascertained from an n.O.e. experiment. In formation of all four adducts (**5**), (**6**), (**8**), and (**9**), one may conclude that the relatively bulky enol silyl ether reacts with the vinylthionium ion in its *transoid* conformation; this is a general characteristic of all alkylation reactions studied. Products other than (**8**) were crystalline solids, and all four gave satisfactory, reproducible spectroscopic and analytical data. These masked Michael adducts,[10] so called because the vinyl sulphide may serve as a masked carbonyl function, are attractive chemodifferentiated synthetic intermediates in view of the contrasting chemistries of the two functionalities. In particular, vinyl sulphide hydrolysis or ozonolysis would yield 1,5- and 1,4-dicarbonyl compounds respectively. Yields of the adducts compare very favourably with those obtained[11] by synthesis *via* alkylation of γ-chloro vinyl sulphides.

Table 1.

Sulphoxide	Enol silyl ether	Product(s)	Yield (%)
(a) CH_2=CHCH$_2$SOPh (**2**)	$CH_2(CH_2)_3CH$=$COTMS$ (**3**)	$OCCH_2(CH_2)_3CHCH_2CH$=CHSPh (**5**)	63
(b) (**2**)	PhC(=CH_2)OTMS (**4**)	PhCO(CH$_2$)$_2$CH=CHSPh (**6**)	62
(c) CH_2=C(Me)CH$_2$SOPh (**7**)	(**3**)	$OCCH_2(CH_2)_3CHCH_2C$(Me)=CHSPh (**8**)	64
(d) (**7**)	(**4**)	PhCO(CH$_2$)$_2$C(Me)=CHSPh (**9**)	72
(e) MeCH=CHCH$_2$SOPh (**10**)	(**4**)	CH_2=CHCH=CHSPh (**11**)	39
		PhCOCH$_2$CH(SPh)C=CHMe (**12**)	17 (α:γ:1:4)
		PhCOCH$_2$CH(Me)C=CHSPh (**13**)	
(f) CH_2=CHCH(Me)SOPh (**14**)	(**4**)	PhCO(CH$_2$)$_2$CH=C(Me) ~ SPh (**15**)	13

In broadening the scope of the reaction, we turned our attention to the methylated allyl sulphoxides (**10**) and (**14**). As a result of a recent paper by Miller[12] we were aware that use of the crotyl derivative but-2-enyl phenyl sulphoxide (**10**) might lead to deprotonation of the vinylthionium intermediate to buta-1,3-dienyl phenyl sulphide (**11**). In fact, the reaction of (**10**) with the silyl enol ether of acetophone (**4**), gave the butadiene in 39% yield after column chromatography along with the α and γ regioadducts (**12**) and (**13**) (1:4) in 17% yield. Presumably some α adduct (**12**) is formed owing to steric hindrance at the γ terminus. The low yield and chromatographic similarity of the two structural isomers (**12**) and (**13**) resulted in them being spectroscopically identified as a mixture. However, in the ^{1}H n.m.r. spectrum of (**12**) both the proton α to the phenylthio group (δ 4.28) and the vinyl protons (δ 5.41) were clearly distinguishable, while for (**13**) the two vinyl sulphide protons with J_{trans} 15.1 Hz could also be clearly made out, along with the highfield methyl doublet (J_{vic} 6.5 Hz) at δ 1.13.

Reaction of (**4**) with the α-methylated allyl sulphoxide (**14**) under the Pummerer conditions was expected to require a higher temperature as a result of a higher activation energy for the ylide formation step. Indeed, a temperature of −20 °C (40 min) was required for completion (monitored by t.l.c.), producing the γ adduct (**15**) as a mixture of isomers (E/Z = 5:2) in 13% yield. Presumably the presence of the α-methyl group encourages some reaction to occur *via* the *cisoid* conformation for steric reasons. Once again the isomeric mixture of (**15**) could not be separated chromatographically, but the ^{1}H n.m.r. spectrum revealed that the vinyl proton for both isomers was a triplet of quartets due to both vicinal (CH_2) and allylic (CH_3) couplings at δ 5.78 and 5.85 for E and Z isomers respectively. All reactions performed are summarised in Table 1.

We were perturbed by the moderate yields obtained, and could not account for the low mass balance at first. On turning our attention to esters as the nucleophilic partner we discovered the reason for the low yields. The enol silyl ether of ethyl acetate, made *in situ* with TMSOTf and Hunig's base, reacted with (**2**) to give the α-silyl vinyl sulphide adduct (**16**) in 33% yield along with the starting sulphoxide (**2**). The α-silylation process[13] presumably takes place after the alkylation reaction. However, with the enol silyl ether of dimethyl malonate (also made *in situ*) and allyl sulphoxide (**7**), the γ-adduct (**17**) (24%) was accompanied by a polar compound that could be eluted from the chromatography column. We discovered the compound to be the quaternary ammonium addition product (**18**), formed

$EtO_2CCH(TMS)CH_2CH$=CHSPh
(**16**)

$(MeO_2C)_2CHCH_2C$(Me)=CHSPh
(**17**)

between Hunig's base and the triflate salt of the vinylthionium ion intermediate.[14] Hence we rationalise the fluctuation in yields as being due to competing attack by the amine base, and as a function of reactivity of enol silyl ether and temperature of reaction. Further investigation revealed that a nearly quantitative yield of the salt (**18**) could be obtained by running the reaction in the absence of enol silyl ether at 0 °C for 5 min (Scheme 2). Longer reaction times resulted in a lower

$$CH_2=C(Me)Ch_2SOPh \longrightarrow Pr^i_2(Et)\overset{+}{N}CH_2C(Me)=CHSPH \quad OTf^- \quad (\mathbf{18})$$

yield of product. The salt was fairly unstable to column chromatography, but could be purified to analytical purity by washing with ethyl acetate. The salt gave satisfactory analytical and spectrosopic data and showed a quartet (δ 120.7 p.p.m., q, $^1J_{C,F}$ = 320 Hz) for the triflate ion in the ^{13}C n.m.r. spectrum due to fluorine coupling.

At this point we embarked upon a survey of bases which might intercept the vinylthionium intermediate (Table 2). Triethylamine was found to react smoothly at −78 °C with (**7**) and trimethylsilyl triflate to afford (**19**), which explains why triethylamine as base gives lower yields of masked Michael adduct that Hunig's base. DBN, in which the nitrogens are sp^2-like, failed to undergo the reaction, nor was any alkylation product produced in the presence of enol silyl ether. Since DBN is more basic than the pyramidal amines, this result suggests that for steric reasons it may have difficulty in deprotonating the trimethylsilyloxy sulphonium ion to the ylide. Alternatively it may be that it irreversibly reacts with TMSOTf to give an *N*-silylammonium salt which cannot be desilylated by sulphoxide.

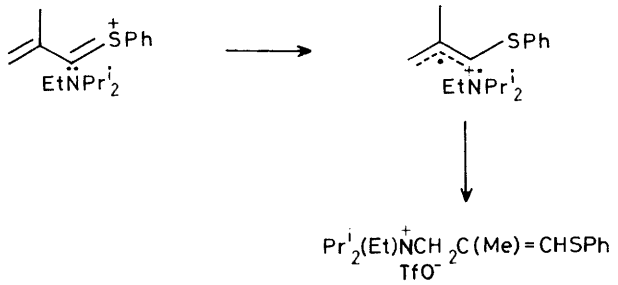
The importance of the base being pyramidal was further emphasised by the observation that even the very hindered base quinuclidine undergoes addition with the vinylthionium ion derived from (**7**) to afford α and γ regioisomers. Column chromatography of the mixture resulted in some isomerisation of the γ-adduct to α, and the latter (**20**) was obtained in crystalline form after recrystallisation. *N,N*-Diethyltrimethylsilylamine also reacts with TMSOTf and (**2**) to afford the

Table 2.

	Base	Product	Yield (%)
(a) CH_2=C(Me)CH_2SOPh	Pr^i_2NEt	(**18**)	91
(b) CH_2=C(Me)CH_2SOPh	NEt_3	$PhSCH{=}C(Me)CH_2\overset{+}{N}Et_3\ OTf^-$ (**19**)	92
(c) CH_2=C(Me)CH_2SOPh	Quinuclidine (Q)	$PhSCH{=}C(Me)CH_2\overset{+}{Q}\ OTf^-$ γ-(**20**)	
		$CH_2{=}C(Me)C(SPh)CH\overset{+}{Q}\ OTf^-$ α-(**20**)	83 (α:γ = 3:2)
(d) CH_2=CHCH_2SOPh	$(Et)_2NTMS$	$Et_2NCH_2CH{=}CHSPh$ (**21**)	96

synthetically useful masked Mannich derivative (**21**) after a mildly acidic work-up which desilylates the quaternary ammonium salt. Details of the amine interceptions are presented in Table 2.

Mechanistically a number of features deserve mentioning. First, although it is known that strongly electrophilic alkenes do react with tertiary amines to afford quaternary ammonium salts, to our knowledge this is the first example[15] of Hunig's base participating as a nucleophile in a formal Michael addition. Perusal of the literature[16] revealed that tertiary amines react readily with one-electron oxidants. The mechanism proposed involves one-electron transfer from the nitrogen lone pair to form a planar aminium radical cation. It appears plausible to us, therefore, that one strong mechanistic possibility is that Hunig's base and the vinylthionium ion undergo a SET[17] (single electron transfer) reaction to generate an intimate (radical ion–radical) pair which rapidly combine at the less hindered positions of the allyl radical to afford product (Scheme 3).



Scheme 3.

The only evidence obtained by us in support of such a mechanism has been the isolaton of 1,3-bis(phenylthio)propene (**22**) in very low yield from the reaction between ethyl acetate and (**2**) to give the α-silyl vinyl sulphide (**16**). We consider the formation of (**22**) as most likely proceeding *via* a radical coupling pathway involving the phenylthioallyl radical in preference to one occurring *via* the vinylthionium ion.

$PhSCH_2CH{=}CHSPh$
(**22**)

The efficiency of the base interception reaction in the absence of enol silyl ether encouraged us to explore the possibility of accomplishing the alkylation reaction *via* the quaternary ammonium adduct using (π-allyl)palladium chemistry. Systems with tertiary amine as leaving group[18] and phenylthio as an allylic substituent[19] have been studied individually in this context but, until this study, never together. Treatment of the Hunig's base adduct (**18**) with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in dichloromethane at room temperature followed by an excess (5 equiv.) of dimethyl sodiomalonate as a solid furnished the desired γ-adduct (**17**) in 60% yield and as a (6:1) mixture of *E*:*Z* isomers as indicated by ^{1}H 200 MHz n.m.r. spectroscopy. Although not an attractive solvent for the dimethyl malonate salt, dichloromethane is superior to THF for the alkylation reaction because the salt (**18**) is fairly insoluble in THF. The reaction requires much gentler conditions than other (π-allyl)palladium alkylations on account of the good leaving ability of the tertiary amine group. Alkylation occurs exclusively γ, consistent with previous results,[19] albeit with less stereocontrol compared with the enol silyl ether reaction.

With the malonate alkylation in hand, to complete the comparative study we focused our attention on the alkylation of the salt (**18**) by the lithium enolates of cyclohexanone and acetophenone. A number of problems were encountered from the outset. Firstly, as stated previously, the salt (**18**) is fairly insoluble in THF, an ideal solvent for enolate formation, and so a number of solvent systems had to be screened, including dimethoxyethane and DMF. The best solvent system finally turned out to be a THF–CH_2Cl_2 ≃ 1:1 system, chosen so that the (π-allyl)palladium complex could be generated in dichloromethane and added to the enolate in THF. Secondly, acetophone lithium enolate failed altogether to react. Cyclohexanone enolate, which was used in equimolar proportions to minimise subsequent aldol reactions, underwent alkylation with (**18**) to afford the γ-adduct (**8**) in 34% yield as an *E*/*Z* mixture (5:4). Alkylation of cylohexanone enolate with the Hunig's base adduct from allyl phenyl sulphoxide (**2**) could be done exclusively in THF since the quaternary ammonium salt is a viscous oil soluble in that solvent. The alkylation reaction proceeded to afford exclusively the γ-adduct (5) in 36% yield as an *E*/*Z* mixture in the ratio 3:2. The similarity in yields for the two reactions suggests that dichloromethane is not detrimental to the alkylation reaction in the presence of the enolates (Table 3).

Conclusion.—In this comparative study it has been shown that under Pummerer conditions allyl sulphoxides may serve as potent electrophilic partners for enol silyl ethers. The moderate yields of masked Michael adducts obtained compare favourably with the yields of other Michael addition reactions particularly in view of the excellent regio- and stereo-control, and these adducts are considered to be of considerable synthetic utility. The competitive interception of the intermediate vinylthionium ion by Hunig's base proves to be a disappointing feature of the Michael reaction, but has been put to good advantage using (π-allyl)palladium mediated alkylation reactions. In this regard, reaction with reactive carbonyl partners is preferred *via* their enol silyl ethers while less reactive enolates, *e.g.* malonate, react more favourably *via* the palladium(0) route. Apart from the

Table 3. Palladium(0) catalysed alkylation

	Amine salt	Enolate	Product *E*/*Z*	Yield (%)
(a)	(**18**)	$(MeO_2C)_2CHNa$	(**17**)	60
(b)	(**18**)	Cyclohex-1-enyl OLi	(**8**), 5/4	34
(c)	$PhSCH{=}CHCH_2\overset{+}{N}(Et)Pr^i_2\ OTf^-$	Cyclohex-1-enyl OLi	(**5**), 3/2	36

scope of this novel reaction for carbon–carbon bond formation, the nitrogen interception aspect opens up the way for a general heteroatom–carbon bond formation reaction for use in synthesis. Finally, the application of the reaction to the bifunctional reagent (**1**) will be reported in a subsequent paper.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded on a Pye Unicam SP-300 spectrophotometer and mass spectra recorded on either a Finnegan-MAT 8200 or AEI MS9 spectrometer. ^1H and ^{13}C N.m.r. spectra were recorded on Bruker AC-200 (200 MHz) or AM-500 spectrometers. Tetramethylsilane was used as standard and deuteriochloroform used as a solvent unless otherwise stated. 500 MHz ^1H N.m.r. spectra and elemental analyses were obtained from the CSIR, Pretoria.

All solvents were purified before use. In particular, tetrahydrofuran was distilled from sodium–benzophenone directly into the reaction flask. Column chromatography was performed using Merck Kieselgel 60 (70—230 mesh) using wet packed columns while flash chromatography[20] utilised dry-packed columns of Merck Kieselgel 60 (0.015—0.04 mm particle size). Allyl sulphoxides were made by thiophenoxide displacement of the corresponding bromide followed by oxidation with hydrogen peroxide in acetic acid. The enol silyl ethers of cyclohexanone and acetophenone were prepared using Fleming's method with chlorotrimethylsilane, triethylamine, and zinc chloride in DMF–benzene.[21] The enol silyl ether of dimethyl malonate was prepared *in situ* using trimethysilyl trifluoromethanesulphonate (TMSOTf) and di-isopropylethylamine in dichloromethane at −78 °C. Lithium enolates were prepared in tetrahydrofuran using lithium di-isopropylamide as base. Diethyltrimethylsilylamine was purchased from Aldrich Chemical Company.

(E)-2-(3-*Phenylthioallyl*)*cyclohexanone* (**5**): *Sulphoxide as Limiting Reagent.*—To a stirred solution of 1-trimethylsilyloxycyclohexene (**3**) (768 mg, 4.5 mmol) in dichloromethane (5 ml) at −78 °C were added di-isopropylethylamine (0.68 ml, 3.9 mmol) followed by allyl phenyl sulphoxide (**2**) (508 mg, 3 mmol) over a period of 10 min. The reaction mixture was stirred for 1 h at −78 °C and then quenched with 0.1M hydrochloric acid (2 ml). The mixture was then diluted with water (10 ml) and extracted with dichloromethane (3 × 25 ml). The combined extracts were dried and the solvent evaporated to furnish an oil which was chromatographed (hexane–CH_2Cl_2, 7:3) to afford (**5**) as a white crystalline solid (465 mg, 63%), m.p. 59—61 °C (hexane) (Found: C, 73.2; H, 7.35. $C_{15}H_{18}OS$ requires C, 73.13; H, 7.36%); $\nu_{max.}$(KBr) 1 700 (CO), 1 600 (C=C), 1 580, 1 470, and 1 430 cm^{-1} (C=C Ar); δ_H(200 MHz) 1.38 (1 H, m), 1.67 (2 H, m), 1.87 (1 H, m), 2.11 (3 H, m), 2.37 (3 H, m), 2.63 (1 H, m, *J* 1.3, 5.5, 6.9, and 13.8 Hz), 5.94 (1 H, m, *J* 6.9, 8.0, and 14.9 Hz), 6.20 (1 H, dd, *J* 1.3 and 14.9 Hz), and 7.15—7.35 (5 H, m); δ_C(50 MHz) 24.9, 27.8, 32.9, 33.4, 42.0, 50.1, 122.8, 126.0, 128.4, 128.8, 134.1, 136.1, and 211.9; *m*/*z* 246 (M^+, 37%), 149 (69%), 137 (100%), 125 (31%), 116 (43%), 110 (30%), 91 (31%), and 67 (40%).

(E)-1-*Phenyl*-5-*phenylthiopent*-4-*en*-1-*one* (**6**): *Enol Silyl Ether as Limiting Reagent.*—To a stirred solution of 1-phenyl-1-trimethylsilyloxyethylene (**4**) (688 mg, 3.6 mmol) in dichloromethane (5 ml) at −78 °C were added di-isopropylethylamine (0.78 ml, 4.5 mmol), TMSOTf (0.9 ml, 4.5 mmol), and allyl phenyl sulphoxide (**2**) (743 mg, 4.5 mmol) slowly in that order. Reaction time and work-up procedure were as for (**5**) to yield, after flash chromatography (hexane–CH_2Cl_2, 7:3), (**6**) as a white crystalline solid (596 mg, 62%), m.p. 77—78 °C (hexane) (Found: C, 75.55; H, 6.1. $C_{17}H_{16}OS$ requires C, 76.08; H, 6.01%); $\nu_{max.}$(KBr) 1 675 (CO), 1 635, 1 575, 1 470, and 1 430 cm^{-1}; δ_H(200 MHz) 2.61 (2 H, q, *J* 6.7 and 7.3 Hz), 3.10 (2 H, t, *J* 7.3 Hz), 6.01 (1 H, dt, *J* 6.7 and 14.9 Hz), 6.24 (1 H, d, *J* 14.9 Hz), 7.16—7.32 (5 H, m), 7.41—7.61 (3 H, m), and 7.93—7.99 (2 H, m); δ_C(50 MHz) 27.4, 37.7, 122.6, 126.2, 127.9, 128.6, 128.7, 128.9, 133.1, 134.5, 136.0, 136.7, and 198.9; *m*/*z* 268 (M^+, 29%), 159 (50%), 149 (11%), 116 (16%), 110 (14%), 105 (100%), 91 (13%), 77 (61%), 51 (19%), and 28 (50%).

(E)-2-(2-*Methyl*-3-*phenylthioallyl*)*cyclohexanone* (**8**): In situ *Preparation of Enol Silyl Ether.*—To a stirred solution of cyclohexanone (0.4 ml, 4 mmol) in dry dichloromethane (5 ml) at −78 °C were added di-isopropylethylamine (1.6 ml, 9 mmol), TMSOTf (1.8 ml, 9 mmol), and 2-methylallyl phenyl sulphoxide (**7**) (540 mg, 3 mmol) slowly in that order. The reaction mixture was stirred for 1 h at −78 °C before being quenched with water (5 ml). Extraction in the usual way, drying of the combined extracts ($MgSO_4$), and evaporation of solvent furnished an oil which was purified by flash chromatography (hexane–CH_2Cl_2, 7:3) to furnish (**8**) (499 mg, 64%) as a liquid (Found: C, 73.75; H, 8.25. $C_{16}H_{20}OS$ requires C, 73.80; H, 7.74%); $\nu_{max.}$($CHCl_3$) 1 700 (CO), 1 580 (C=C) and 1 505 and 1 470 cm^{-1} (C=CAr); δ_H(200 MHz) 1.33 (1 H, m), 1.65 (2 H, m), 1.81 (3 H, q, *J* 0.5 and 1.1 Hz), 1.87 (1 H, m), 2.09 (3 H, m), 2.32 (1 H, m), 2.44 (2 H, m), 2.74 (1 H, dd, *J* 4.8 and 14.8 Hz), 5.93 (1 H, q, *J* 1.1 Hz), and 7.10—7.28 (5 H, m); δ_C(50 MHz) 17.8, 24.7, 27.8, 33.2, 38.8, 41.9, 48.2, 117.6, 125.6, 127.9, 128.8, 136.9, 139.5, and 212.1; *m*/*z* 260 (M^+, 45%), 163 (31%), 151 (100%), 135 (32%), 130 (31%), 110 (18%), and 91 (27%).

(E)-4-*Methyl*-1-*phenyl*-5-*phenylthiopent*-4-*en*-1-*one* (**9**): *Sulphoxide as Limiting Reagent.*—To a stirred solution of 1-phenyl-1-trimethylsilyloxyethylene (**4**) (886 mg, 4.5 mmol) in dichloromethane (5 ml) at −78 °C were added di-isopropylethylamine (0.78 ml, 4.5 mmol), TMSOTf (0.9 ml, 4.5 mmol), and 2-methylallyl phenyl sulphoxide (**7**) (552 mg, 3.1 mmol) slowly in that order. Reaction time and work-up procedure were as for compound (**5**) to yield, after flash chromatography (hexane–CH_2Cl_2, 7:3), (**9**) as a white crystalline solid (623 mg, 72%), m.p. 50—52 °C (hexane) (Found: C, 76.65; H, 6.6. $C_{18}H_{18}$ OS requires C, 76.56; H, 6.42%); $\nu_{max.}$(KBr) 1 660 (CO), 1 575 (C=C), 1 470, and 1 435 cm^{-1}; δ_H(200 MHz) 1.91 (3 H, d, *J* 1.0 Hz), 2.62 (2 H, t, *J* 7.6 Hz), 3.16 (2 H, t, *J* 7.6 Hz), 6.01 (1 H, d, *J* 1.0 Hz), 7.13—7.39 (5 H, m), 7.42—7.6 (3 H, m), and 7.95—8.01 (2 H, m); δ_C(50 MHz) 18.0, 33.3, 36.5, 116.6, 125.5, 127.8, 128.4, 128.7, 132.8, 136.5, 136.7, 140.6, and 198.8; *m*/*z* 282 (M^+, 14%), 173 (33%), 105 (100%), 81 (10%), 77 (38%), and 51 (12%).

(E)-1-*Phenyl*-3-*phenylthiohex*-4-*en*-1-*one* (**12**) *and* (E)-3-*Methyl*-1-*phenyl*-5-*phenylthiopent*-4-*en*-1-*one* (**13**).—To a stirred

solution of 1-phenyl-1-trimethylsilyloxyethylene (**4**) (287 mg, 1.50 mmol) in dichloromethane (3 ml) at −78 °C were added TMSOTf (0.3 ml, 1.65 mmol) and di-isopropylethylamine (0.3 ml, 1.72 mmol) followed slowly by (*E*)-but-2-enyl phenyl sulphoxide (**10**), (165 mg, 0.92 mmol). The reaction was followed by t.l.c. and was completed in 10 min at −78 °C. After work-up, column chromatography [hexane followed by CH_2Cl_2–hexane (3:7)] afforded buta-1,3-dienyl phenyl sulphide (**11**) (59 mg, 39%); δ_H(60 MHz) 4.9—5.4 (2 H, m), 6.2—6.4 (3 H, m), and 7.0—7.5 (5 H, m); and an inseparable mixture of isomeric (**12**) and (**13**) (44 mg, 17%) in the ratio 1:4 respectively. Compound (**12**): δ_H(200 MHz) 1.56 (3 H, m, J_{gem} 4.8 Hz), 2.81—3.33 (2 H, m), 4.28 (1 H, m) 5.41 (2 H, m), 7.11—7.32 (5 H, m), 7.38—7.60 (3 H, m), and 7.84—7.98 (2 H, m); Compound (**13**): δ_H(200 MHz) 1.13 (3 H, d, *J* 6.5 Hz), 2.81—3.33 (3 H, m), 5.91 (1 H, dd, *J* 6.8 and 15.1 Hz), 6.18 (1 H, dd, *J* 0.7 and 15.1 Hz), 7.11—7.32 (5 H, m), 7.38—7.60 (3 H, m), and 7.84—7.98 (2 H, m); δ_C(50 MHz) 20.0, 33.4, 45.0, 120.9, 126.1, 128.0, 128.5, 128.6, 128.9, 133.0, 136.0, 137.1, 140.1, and 198.7. For the mixture of (**12**) and (**13**) $\nu_{max.}$($CHCl_3$) 1 670, 1 580, 1 560, 1 470, and 1 440 cm^{-1}; *m/z* 282 (M^+, 10%), 173 (52%), 105 (100%), and 77 (32%) (Found: M^+, 282.1078. $C_{18}H_{18}OS$ requires *M*, 282.1078).

(E)- *and* (Z)-1-*Phenyl*-5-*phenylthiohex*-4-*en*-1-*one* (**15**).—To a stirred solution of 1-phenyl-1-trimethylsilyloxyethylene (**4**) (204 mg, 1.06 mmol) in dichloromethane (3 ml) at −78 °C were added di-isopropylethylamine (0.2 ml, 1.15 mmol), TMSOTf (0.2 ml, 1.10 mmol), and 1-methylallyl phenyl sulphoxide (**14**) (113 mg, 0.63 mmol) slowly in that order. The reaction was followed by t.l.c. and required a reaction temperature of −20 °C (40 min) to go to completion. After work-up and column chromatography (CH_2Cl_2–hexane, 3:7), (**15**) was obtained (23 mg, 13%) as a mixture of *E*/*Z* isomers (5:2). *E* Isomer: δ_H(200 MHz) 1.85 (3 H, q, *J* 1.4 and 1.4 Hz), 2.51 (2 H, q, *J* 7.4 and 7.4 Hz), 3.01 (2 H, t, *J* 7.4 Hz), 5.78 (1 H, tq, *J* 1.4 and 7.4 Hz), 7.02—7.23 (5 H, m), 7.31—7.55 (3 H, m), 7.82—7.93 (2 H, m). *Z* Isomer: δ_H(200 MHz) 1.83 (3 H, q, *J* 1.3 and 1.3 Hz), 2.69 (2 H, q, *J* 7.2 and 7.3 Hz), 3.03 (2 H, t, *J* 7.2 Hz), 5.85 (1 H, tq, *J* 1.3 and 7.3 Hz), 7.02—7.23 (5 H, m), 7.31—7.55 (3 H, m), and 7.82—7.93 (2 H, m). For the *E*/*Z* mixture $\nu_{max.}$($CHCl_3$) 1 700, 1 670, 1 580, 1 570, 1 470, 1 440, and 1 430 cm^{-1}; *m/z* 282 (M^+, 16%), 173 (53%), 105 (100%), and 77 (38%) (Found: M^+, 282.1077. $C_{18}H_{18}OS$ requires *M*, 282.1078.

Ethyl(E)-5-*Phenylthio*-2-*trimethylsilylpent*-4-*enoate* (**16**).—To a stirred solution of ethyl acetate (264 mg, 3 mmol) in dry dichloromethane (3 ml) at −78 °C were added TMSOTf (1.1 ml, 6.1 mmol) and Hunig's base (1.1 ml, 6.3 mmol) and the solution was stirred at −78 °C for 30 mins. Allyl phenyl sulphoxide (**2**) (337 mg, 2.1 mmol) was added in dichloromethane (2 ml) slowly at −78 °C and the solution warmed to −40 °C over 1 h. Since t.l.c. indicated sulphoxide was still present at −40 °C, a further aliquot of TMSOTf (0.5 ml, 2.8 mmol) and Hunig's base (0.5 ml, 2.9 mmol) were added and the solution stirred for a further 30 mins at −20 °C. After work-up (0.1M HCl/CH_2Cl_2), and column chromatography (hexane–CH_2Cl_2, 7:3), (**16**) (210 mg, 33%) was obtained as a clear oil after microdistillation (Found: C, 61.45; H, 7.7. $C_{16}H_{24}O_2SSi$ requires C, 62.29; H, 7.84%); $\nu_{max.}$($CHCl_3$) 1 700, 1 580, 1 480, 1 440, 860, and 840 cm^{-1}; δ_H(200 MHz) 0.00 (9 H, s), 1.13 (3 H, t, *J* 7.1 Hz), 2.01 (1 H, dd, *J* 3.2 and 11.6 Hz), 2.12 (1 H, m), 2.54 (1 H, m), 4.02 (2 H, dq, *J* 0.9 and 7.1 Hz), 5.84 (1 H, dt, *J* 6.7 and 15.5 Hz), 6.09 (1 H, dt, *J* 1.1 and 15.5 Hz), and 7.06—7.21 (5 H, m); δ_C(50 MHz) − 2.7, 14.4, 29.9, 37.2, 59.8, 122.0, 126.0, 128.4, 128.8, 135.4, 136.2, and 174.3; *m/z* 308 (M^+, 9%), 199 (51%), 149 (27%), 81 (100%), and 73 (62%).

Dimethyl 2-(E)-2-*Methyl*-3-*phenylthioallylpropanedioate* (**17**).—To a stirred solution of dimethyl malonate (240 mg, 1.85 mmol) in dichloromethane (3 ml) at −78 °C was added di-isopropylethylamine (0.6 ml, 3.4 mmol) and TMSOTf (0.65 ml, 3.6 mmol) and the solution was stirred for 15 min. 2-Methylallyl phenyl sulphoxide (**7**) (235 mg, 1.3 mmol) dissolved in dichloromethane (2 ml) was then added slowly and the solution stirred for 1 h after which the reaction was quenched with saturated aqueous sodium hydrogen carbonate (10 ml). The solution was extracted with dichloromethane (3 × 25 ml) and the extract washed with 0.1M HCl (20 ml) and saturated brine (20 ml), dried, and evaporated to furnish, after column chromatography (hexane–CH_2Cl_2, 5:5), unchanged sulphoxide (46 mg) and (**17**) as a yellow oil (73 mg, 24% based on reacted sulphoxide) (Found: C, 60.8; H, 6.55. $C_{15}H_{18}O_4S$ requires C, 61.20; H, 6.16%); $\nu_{max.}$(CH_2Cl_2) 1 725 (CO), 1 580 (C=C), and 1 470 and 1 430 cm^{-1} (C=CAr); δ_H(200 MHz) 1.86 (3 H, d, *J* 1.1 Hz), 2.77 (2 H, dd, *J* 0.8 and 7.8 Hz), 3.65 (1 H, t, *J* 7.8 Hz), 3.73 (6 H, s), 6.04 (1 H, dd, *J* 0.8 and 1.1 Hz), and 7.18–7.28 (5 H, m); δ_C(50 MHz) 17.6, 38.0, 50.1, 52.5, 119.7, 125.9, 128.2, 128.8, 136.3, and 169.1; *m/z* 294 (M^+, 4%), 185 (4%), 125 (12%), 110 (14%), 85 (13%), 77 (21%), and 55 (100%).

N-*Ethyl*-N,N-*di-isopropyl*-N-(E)-2-*methyl*-3-*phenylthioallyl*-*ammonium Trifluoromethanesulphonate* (**18**).—To a stirred solution of 2-methylallyl phenyl sulphoxide (**7**) (180 mg, 1 mmol) in dry dichloromethane (5 ml) at 0 °C were added di-isopropylethylamine (0.36 ml, 2.1 mmol) and TMSOTf (0.4 ml, 2.2 mmol). The reaction was stirred at 0 °C for 5 min before being quenched (1M HCl; 10 ml) and extracted (3 × 25 ml of CH_2Cl_2). Drying and evaporation of solvent furnished the product in high purity (by ^1H n.m.r.). The salt may be purified further by washing with ethyl acetate to give a white solid (**18**) (402 mg, 91%), m.p. 107—109 °C (Found: C, 51.25; H, 6.75; N, 3.4. $C_{19}H_{30}F_3NO_3S_2$ requires C, 51.68; H, 6.85; N, 3.17%); $\nu_{max.}$ (KBr) 1 600, 1 570, 1 460, 1 400, 1 380, 1 250, and 1 020 cm^{-1}; δ_H(200 MHz) 1.42 (3 H, t, *J* 7.3 Hz), 1.52 (6 H, d, *J* 6.6 Hz), 1.54 (6 H, d, *J* 6.6 Hz), 2.03 (3 H, d, *J* 0.9 Hz), 3.46 (2 H, q, *J* 7.3 Hz), 4.01 (2 H, s), 4.02 (2 H, q, *J* 6.6 Hz), 6.92 (1 H, q, *J* 0.9 Hz), and 7.24—7.46 (5 H, m); δ_C(50 MHz) 9.9, 18.4, 18.8, 20.4, 51.1, 62.2, 66.0, and 120.7 (q, $^1J_{C,F}$ 320 Hz) 122.2, 127.4, 129.4, 129.7, 133.4, and 137.5; *m/z* 164 (M^+ − 278, 100%), 114 (56%), and 77 (81%).

N,N,N-*Triethyl*-N-(E)-2-*methyl*-3-*phenylthioallylammonium Trifluoromethanesulphonate* (**19**).—To a stirred solution of 2-methylallyl phenyl sulphoxide (**7**) (180 mg, 1 mmol) in dry dichloromethane (3 ml) at −78 °C were added triethylamine (0.3 ml, 2.2 mmol) and TMSOTf (0.3 ml, 1.6 mmol). The reaction was stirred for 1 h before being quenched (1M HCl; 10 ml) and extracted (3 × 25 ml of CH_2Cl_2). The combined extracts were dried and evaporated to furnish (**19**) as an oil (380 mg, 92%) which was unstable towards both column chromatography and vacuum distillation but shown to be essentially pure by ^1H n.m.r.; $\nu_{max.}$($CHCl_3$) 1 600, 1 580, 1 480, 1 400, 1 260, and 1 020 cm^{-1}; δ_H(200 MHz) 1.30 (3 H, t, *J* 7.1 Hz), 1.96 (3 H, s), 3.24 (2 H, q, *J* 7.1 Hz), 3.91 (2 H, s), 6.72 (1 H, s), and 7.32 (5 H, m); δ_C(50 MHz) 7.5, 19.5, 52.8, 64.1, and 120.5 (q, $^1J_{C,F}$ 320 Hz) 120.7, 127.4, 129.2, 129.7, 133.3, and 137.8; *m/z* 272 (11%), 180 (24%), 163 (M^+ − 250, 100%), 147 (27%), 135 (38%), 130 (38%), and 110 (68%).

N-(2-*Methyl*-1-*phenylthioallyl*)*quinuclidinium Trifluoromethanesulphonate* (**20**).—To a stirred solution of 2-methylallyl phenyl sulphoxide (**7**) (180 mg, 1.0 mmol) and quinuclidine (240 mg, 2.2 mmol) in dichloromethane (3 ml) at 0 °C was added TMSOTf (0.3 ml, 1.7 mmol). After 15 min the reaction was quenched with HCl (1M; 10 ml), extracted (3 × 25 ml of CH_2Cl_2), and the extract washed (1 × 50 ml of 1M H_2SO_4),

dried, and evaporated to give an oil (350 mg, 83%). This was shown by ^{1}H (200 MHz) n.m.r. to consist of the α and γ regioadducts of (**20**) in the ratio (3:2). Column chromatography (MeOH–$CHCl_3$, 5:95) afforded a white solid (220 mg, 52%) consisting of a mixture of α and γ regioadducts of (**20**) in the ratio (5:1). This was recrystallised from ethyl acetate to afford the pure α-regioisomer (**20**), m.p. 131—135 °C (EtOAc) (Found: C, 50.8; H, 5.75; N, 3.1. $C_{18}H_{24}F_3NO_3S_2$ requires C, 51.05; H, 5.71; N, 3.31%); $\nu_{max.}$(KBr) 1 600, 1 575, 1 460, 1 435, 1 370, 1 160, 1 020, and 635 cm^{-1}; δ_H(200 MHz) 1.80—1.95 (6 H, m), 1.94 (3 H, s), 2.02 (1 H, m), 3.35—3.65 (6 H, m), 5.25 (1 H, s), 5.34 (1 H, s), 5.42 (1 H, s), 7.24—7.32 (3 H, m), and 7.43—7.48 (2 H, m); δ_C(50 MHz) 19.5, 20.2, 23.8, 53.2, 87.2, 120.6, (q, $^1J_{C-F}$ 320 Hz) 125.2, 129.0, 129.8, 131.0, 131.9, and 135.4; *m/z* 215 (41%), 163 (M^+ − 260, 100%), 135 (55%), 109 (46%), 83 (36%), and 57 (79%).

N,N-*Diethyl*-N-(E)-3-*phenylthioallylamine* (**21**).—To a stirred solution of allyl phenyl sulphoxide (**2**) (180 mg, 1.1 mmol) in dichloromethane (3 ml) at 0 °C was added diethyltrimethylsilylamine (0.5 ml, 2.6 mmol) and TMSOTf (0.3 ml, 1.6 mmol). After 5 min the reaction was quenched (1M HCl) and extracted (3 × 25 ml CH_2Cl_2) to afford after work-up and column chromatography ($CHCl_3$), (**21**) as an oil (233 mg, 96%) (Found: C, 69.8; H, 8.5; N, 6.55. $C_{13}H_{19}NS$ requires C, 70.54; H, 8.65; N, 6.33%); $\nu_{max.}$($CHCl_3$) 1 600, 1 575, 1 470, 1 435, 1 290, 1 220, 1 165, and 1 020; δ_H(200 MHz) 1.08 (6 H, t, *J* 7.1 Hz), 2.58 (4 H, q, *J* 7.1 Hz), 3.22 (2 H, dd, *J* 1.2 and 6.7 Hz), 5.97 (1 H, dt, *J* 6.7 and 15.0 Hz), 6.36 (1 H, dt, *J* 1.2 and 15.0 Hz), and 7.31 (5 H, m); δ_C(50 MHz) 9.7, 46.6, 54.0, 119.5, 127.6, 129.3, 130.6, 133.0, and 134.1; *m/z* 221 (M^+, 73%), 206 (11%), 149 (100%), 116 (37%), 112 (71%), 109 (10%), 86 (24%), and 77 (7%) (Found: M^+, 221.1238. $C_{13}H_{19}NS$ requires *M*, 221.1238).

Palladium(0)-*catalysed Alkylation of Dimethyl Malonate by Compound* (**18**).—The tetra-alkylammonium salt (**18**) was prepared as described before from 2-methylallyl phenyl sulphoxide (**7**) (180 mg, 1 mmol), di-isopropylethylamine (0.4 ml, 2.3 mmol) and TMSOTf (0.3 ml, 1.7 mmol). The crude salt was dissolved in dry THF (5 ml), tetrakis(triphenylphosphine)-palladium(0) (40 mg, 0.04 mmol) was added and the solution was stirred at room temperature for 30 mins. In a separate flask sodium hydride (50% dispersion in mineral oil; 220 mg, 4.6 mmol) was added to dimethyl malonate (600 mg, 4.5 mmol) in dry THF (5 ml) under nitrogen and the solution was stirred for 30 min at room temperature. All the THF was then removed under reduced pressure to leave dimethyl sodiomalonate. The latter was rapidly transferred as a solid to the palladium complex in dichloromethane and the mixture was stirred for 40 min at room temperature. After this 1M HCl was added (10 ml) to quench the reaction and the organic products were extracted into dichloromethane (3 × 25 ml). Drying and evaporation of the combined extracts afforded an oil which was chromatographed (hexane–CH_2Cl_2, 5:5) to give (**17**) (178 mg, 60%) as an oil and a mixture of isomers (*E*/*Z*, 6:1). By comparison with the pure *E* isomer of (**7**) the following data was obtained; for the *Z* isomer: δ_H(200 MHz) 1.87 (3 H, d, *J* 1.4 Hz), 2.93 (2 H, d, *J* 7.9 Hz), 3.65 (1 H, t, *J* 7.9 Hz), 3.73 (6 H, s), 6.04 (1 H, dd, *J* 0.8 and 1.4 Hz), and 7.18—7.28 (5 H, m); δ_C(50 MHz) 23.0, 32.6, 49.7,52.5, 120.2, 125.9, 128.3, 128.8, 136.4, 137.2, and 169.1. For the *E*/*Z* mixture $\nu_{max.}$($CHCl_3$) 1 725, 1 620, 1 580, 1 470, and 1 430 cm^{-1}; *m/z* 294 (M^+, 100%), 185 (39%), 163 (63%), 153 (45%), 125 (51%), and 85 (19%).

Palladium(0)-*catalysed Alkylation of Cyclohexanone with Compound* (**18**).—The salt (**18**) (204 mg, 1.15 mmol) was prepared as described previously and dissolved in dichloromethane (5 ml). Tetrakis(triphenylphosphine)palladium(0) (40 mg, 0.04 mmol) was added and the solution was stirred for 0.5 h at room temperature. In a separate flask di-isopropylamine (0.2 ml, 1.4 mmol) was added to dry THF (3 ml) under nitrogen and the solution was cooled to −78 °C. Butyl-lithium (1.6M; 0.8 ml, 1.3 mmol) was added, and the solution stirred for 5 min before cyclohexanone was introduced (0.15 ml, 1.5 mmol); the solution was then left to warm to 0 °C over a period of 0.5 h. The solution of the enolate was syringed into the π-allylpalladium complex slowly at room temperature, causing a brown colour to develop. The mixture was then left for 40 min before being quenched (10 ml; 1M HCl) and worked up. The oil obtained was chromatographed (CH_2Cl_2–hexane, 3:7) to afford (**8**) (102 mg, 34%) as an *E*/*Z* mixture (5:4 by ^{1}H n.m.r.). By comparison with the pure *E* isomer of (**8**) the following data were obtained for the *Z* isomer: δ_H(200 MHz) 1.43 (1 H, m), 1.65 (2 H, m), 1.85 (3 H, s), 1.87 (1 H, m), 2.09 (3 H, m), 2.32 (1 H, m), 2.44 (2 H, m), 2.63 (1 H, dd), 6.00 (1 H, s), and 7.1—7.3 (5 H, m); δ_C(50 MHz) 23.4, 24.6, 27.7, 32.9, 38.9, 41.7, 48.7, 118.0, 125.6, 128.9, 128.8, 137.1, 140.8, and 212.3. For the *E*/*Z* mixture $\nu_{max.}$($CHCl_3$) 1 700, 1 580, 1 470, and 1 430 cm^{-1}; *m/z* 260 (M^+, 48%), 178 (48%), 163 (39%), 151 (100%), and 135 (62%).

Palladium(0)-*catalysed Alkylation of Cyclohexanone to afford* E/Z (**5**).—To a solution of allyl phenyl sulphoxide (**2**) (148 mg, 0.9 mmol) in dry dichloromethane (3 ml) at 0 °C were added di-isopropylethylamine (0.35 ml, 2 mmol) and TMSOTf (0.25 ml, 1.4 mmol). After 5 min the reaction was quenched (1M HCl; 10 ml) and extracted (3 × 25 ml CH_2Cl_2) to yield, after drying, and evaporation of the combined extracts, the crude salt which was dissolved in dry THF (5 ml). Tetrakis(triphenylphosphine)-palladium(0) catalyst (50 mg, 0.05 mmol) was added and the solution stirred for 0.5 h at room temperature. In a separate flask the enolate of cyclohexanone was prepared in THF as described in the previous experiment from di-isopropylamine (0.15 ml, 1.1 mmol), butyl-lithium (1.6M; 0.7 ml, 1.1 mmol) and cyclohexanone (0.1 ml, 1 mmol). The solution of the enolate was syringed into the π-allylpalladium complex slowly at room temperature, causing a black colour to appear. The solution was left stirring for 0.5 h before being quenched (10 ml, 1 M HCl) and worked up as before with hexane. Chromatography (CH_2Cl_2–hexane, 3:7) furnished (**5**) (80 mg, 36%) as an *E*/*Z* mixture (3:2 by ^{1}H n.m.r.). By comparison with the pure *E* isomer the following data was obtained for the *Z* isomer: δ_H(200 MHz) 6.24 (1 H, dd, *J* 9.3 Hz *cis* coupling) for α-vinyl H; δ_C(50 MHz) 24.8, 27.8, 29.2, 33.4, 41.9, 50.3, 124.3, 126.1, 128.7, 130.8, 134.1, 136.1, and 212.1. For the *E*/*Z* mixture $\nu_{max.}$($CHCl_3$) 1 700, 1 570, 1 470, and 1 430, cm^{-1}; *m/z* 246 (42%), 149 (64%), 137 (100%), 116 (39%), and 67 (35%).

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