Pergamon

Tetrahedron, Vol. 52, No. 6, pp. 2155-2166, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)01030-0

Allylated Ketosulphides of Benzothiazole as Intermediates for Stereoselective Synthesis of Allyl Ketones, Allyl Thiiranes and Dienes

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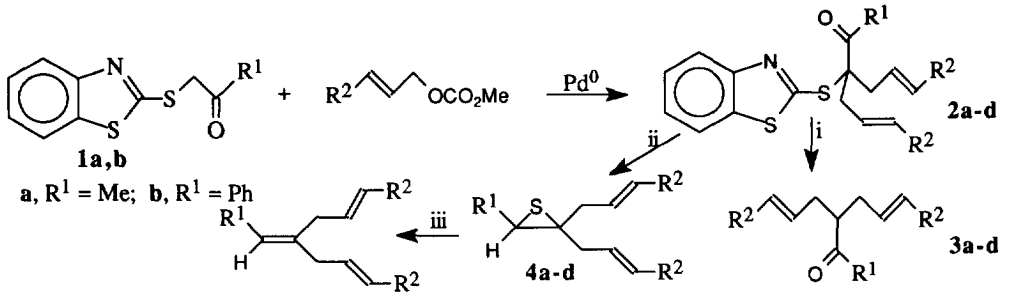
Abstract: α-Ketosulphides of benzothiazole **1** react with allylic carbonates in the presence of palladium acetate in dichloromethane under mild conditions affording α- and α,α-diallylated ketosulphides **2** in high yields. Reductive desulphurization of **2a-d** with tributyltin hydride gives diallylated ketones **3a-d**, whereas reduction of mono-allylated **2e-k** with sodium borohydride in isopropanol affords allyl episulphides **4e-k** prevalently as (Z)-isomers which can be transformed stereoselectively into dienes.

Palladium catalysed allylic substitution is a versatile process encompassing a wide range of allylic systems and their nucleophilic partners.[1-4] Among allylic systems, the use of carbonates as leaving groups has gained in popularity since the development of these reagents by Tsuji.[3] Contrary to active methylene compounds as malonates, β-ketoesters, silyl enol ethers or enamines,[5] simple ketones cannot be allylated satisfactorily with allylic carbonates. On the other hand the introduction of two allylic groups at the α-position of ketones, which can be done in principle by regioselective consecutive allylation is generally difficult since the generation of an anion at the same carbon after the first allylation is inhibited and as a consequence α,α'-dialkylated products are obtained.[6] In a preliminary communication[7] we reported that α-ketosulphides of benzothiazole **1** react with an excess of allylic carbonates in the presence of catalytic quantities of palladium acetate and triphenylphosphine in dichloromethane under mild conditions to afford, depending on the structure of the allylic carbonate, mono and α,α-diallylated ketosulphides **2** in high yields. The diallylated ketosulphides may be easily transformed into allylated ketones **3a-d**, episulphides and trienes as depicted in Scheme 1.



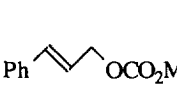
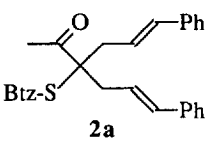
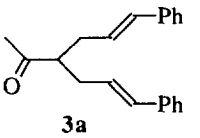
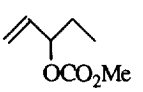
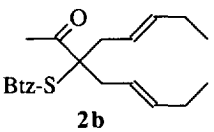
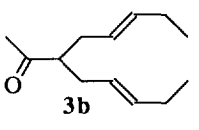
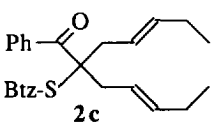
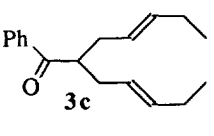
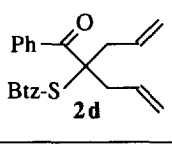
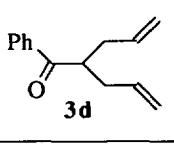
i= Bu_3SnH/toluene; ii= $NaBH_4$/isopropanol; iii= Ref. 8,9

Scheme 1

Beside the conversion of diallylated ketosulphides of benzothiazole into ketones and episulphides, this paper reports the stereoselective synthesis of monoallylated ketosulphides of benzothiazole which proved to be useful intermediates for the synthesis of, prevalently, (Z)-episulphides which, in turn, can be transformed into (E,Z)-dienes.

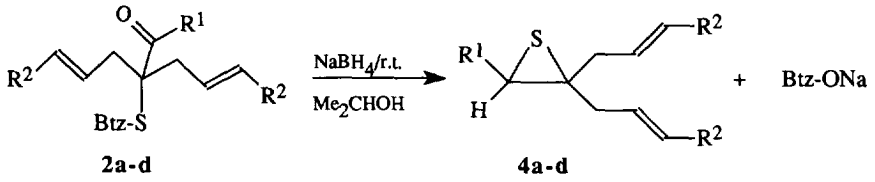
Ketones **1a,b** react with an excess of allylic carbonates in the presence of catalytic quantities of palladium acetate and triphenyl phosphine to give diallylated ketosulphides **2a-d**. In some cases stereoselective allylation was observed (Table 1, products **2a-c**) as previously reported.[7] Compounds **2a-d** are easily transformed into ketones **3a-d** by reaction with tributyltin hydride[8] in toluene (Table 1).

Table 1. Pd^0-Mediated Allylation of Ketosulphides of Benzothiazole and their Desulphurization to α,α-Diallyl Ketones.

Ketone	Carbonate	Product	Yield(%)	Allylated Ketone	Yield(%)
1a		 **2a**	78	 **3a**	94
1a		 **2b**	77	 **3b**	87
1b	"	 **2c**	82	 **3c**	90
1b		 **2d**	86	 **3d**	88

Btz= Benzothiazole-2-yl

Reduction with sodium borohydride in isopropanol of **2a-d** affords directly episulphides **4a-d** (Scheme 2). This reaction is characteristic for β-hydroxy sulphides of benzothiazole[7] since different β-hydroxy sulphides did not give episulphides. Table 2 summarises these results.

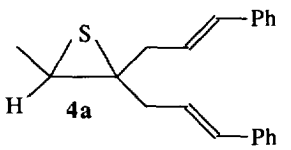
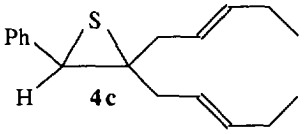
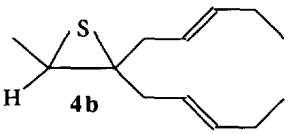
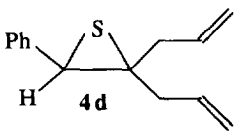


2a-d **4a-d**

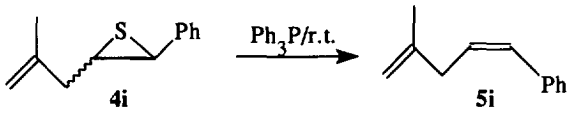
Scheme 2

Stereoselective desulphurization of **4a-d** with triphenyl phosphine, 2-selenoxo benzothiazole or aminium salts affords trienes as previously reported.[7,9]

Table 2. Conversion of Allylated Ketones into Episulphides

Ketone	Episulphide	Yield(%)	Ketone	Episulphide	Yield(%)
2a	 **4a**	85	**2c**	 **4c**	90
2b	 **4b**	78	**2d**	 **4d**	85

Since γ,δ-unsaturated ketones and dienes with definite stereochemistry of the double bonds are useful intermediates and can be obtained, the former by reductive desulphurization of monoallylated ketosulphides of benzothiazole with tributyltin hydride[8], and the latter by stereospecific reaction of the corresponding episulphides with 2-selenoxobenzothiazole[10] or triphenylphosphine[11], we tried mono-allylation of **1a-b** with stoichiometric quantities of carbonates under careful controlled reaction conditions. Whereas allylation with β-metallyl carbonate gives exclusively monoallylated ketosulphides **2i,j**, others carbonates lead to a mixture of di- and mono-allylated ketosulphides **2e-h** which can be easily separated by silica gel chromatography. Finally allylation of ketosulphide Btz-S-CH(CH_3)$COCH_3$ **1c** yields compound **2k** (Table 3). The carbonyl reduction of these compounds with sodium borohydride in isopropanol leads directly to mono-allylated episulphides **4e-j** whereas **2k** yields the episulphide **4k**. The stereochemistry of these episulphides is interesting since a prevalence of the Z-isomers is observed in some cases. For example compound **4i**, by reaction with triphenyl phosphine or with 2-selenoxobenzothiazole which are known[10,11] to desulphurize episulphides stereospecifically, gives almost exclusively (Z)-1-phenyl-4-methyl-1,4-pentadiene **5i** (Scheme 3).



Scheme 3

Generally it was observed that allyl subtituted ketosulphides bearing a phenyl substituent led prevalently to (Z)-episulphides whereas methyl substituted ones give almost an equal quantity of the two stereoisomers. For example, by desulphurization of **4e**, one may obtain almost pure (1Z,4E)-1,5-diphenyl-1,4-pentadiene.[9]

Actually we have not a plausible explanation for the observed stereochemistry in the formation of episulphides and work is in progress to explain this. However beside the possible synthesis of γ,δ unsaturated ketones, ketosulphides of benzothiazole may be used for a new stereospecific synthesis of dienes and trienes.

Table 3. Synthesis of Monoallylated Ketones and Episulphides.

Ketone	Product (Yield %)[a]	Episulphide (Z:E ratio)[b]	Ketone	Product (Yield %)	Episulphide (Z:E ratio)
1b	**2e** (65)	**4e** (90:10)	**1b**	**2i** (91)	**4i** (98:2)
1b	**2f** (58)	**4f** (95:5)	**1a**	**2j** (88)	**4j** (90:10)
1a	**2g** (45)	**4g** (60:40)	**1c**	**2k** (93)	**4k** (65:35)
1b	**2h** (60)	**4h** (70:30)			

[a] The yields of compounds **2e-h** refer to isolated products upon chromatographic separation from bisallylated ketosulphides. [b]Evaluated by ^1H NMR.

EXPERIMENTAL

Melting points(uncorrected) were determined on a Reichert Microscope.The purity of the reaction products was tested by GLC recorded on HP 5890A capillary gas-chromatograph (SE 30; 30m; 0.25 mm. i.d.). GC-MS analyses were performed on an HP 5970 instrument, and microanalyses on a mod. 1106 Carlo Erba Elemental Analyzer. IR spectra were recorded on a Perkin Elmer 681 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 500 spectrometer; chemical shifts are reported in parts per million (δ), solvent $CDCl_3$, coupling constants in Hz. Precoated TLC alumina sheets silica gel 60 F254 (Merck) and for column chromatography, silica gel 30-60 mesh (Baker) were used. Solvents were dried and distilled under nitrogen immediately prior to use.

1-(Benzothiazol-2-thio)-propanone (1a). This product was prepared as reported.[12] M.p.65-67 °C. Lit.[12] 69 °C. ^{1}H-NMR δ: 2.39 (3H, s, CH_3); 4.22 (2H, s, CH_2CO); 7.28-7.35 (1H, m, Ar), 7.38-7.42 (1H, m, Ar); 7.73-7.77 (1H, m, Ar); 7.80-7.85 (1H, m, Ar). IR (KBr) 1724, 1463, 1359, 758 cm^{-1}.

2-(Benzothiazol-2-thio)-1-phenyl-ethanone (1b). Mp: 107-109 °C.[13] ^{1}H-NMR δ: 4.95 (2H, s, CH_2CO); 7.25-7.32 (1H, m, Ar); 7.38-7.41 (1H, m, Ar); 7.49-7.53 (2H, m, Ph); 7.60-7.64 (1H, m, Ph); 7.75-7.78 (1H, m, Ar); 7.80-7.83 (1H, m, Ar); 8.06-8.08 (2H, m, Ph). IR (KBr) 1682, 753, 690 cm^{-1}.

3-(Benzothiazol-2-thio)-2-butanone (1c)
To benzothiazole-2-thiol (12.6 g, 75 mmol) dissolved in 80 ml of ethanol containing 75 mmol of sodium ethylate was added dropwise 3-chloro-2-butanone (7.5 ml, 75 mmol). This solution refluxed for 2h, evaporated to a small volume, and was poured into water. The oily product obtained gave, after extraction with ethyl acetate, drying (Na_2SO_4) and removal of the solvent, a solid. Mp. 45-47 °C (ethanol), 72% yield. ^{1}H-NMR δ: 1.59 (3H, d, J= 7.3 Hz, CH_3CH); 2.37 (3H, s, CH_3CO); 4.76 (1H, q, J= 7.3 Hz, $CHCH_3$); 7.28-7.31 (1H, m, Ar); 7.39-7.42 (1H, m, Ar); 7.72- 7.76 (1H, m, Ar); 7.82-7.86 (1H, m, Ar). IR (KBr pellet): 1720, 1377, 1349, 758 cm^{-1}.

Allylation of sulphides 1a-c with allylic carbonates: general procedure.
To palladium acetate (0.05 mmol) and triphenyl phosphine (0.25 mmol) dissolved in 5 ml of dichloromethane were added, at r.t. under nitrogen and stirring, the allylic carbonate (3.15 mmol) and the ketosulphide (1.05 mmol) both dissolved in 10 ml of the same solvent. After 1-3 hours, depending on the sulphide and carbonate, silica gel was added to the reaction solution and the resulting suspension, evaporated to dryness, was placed on the top of a column filled with silica gel and chromatographed (eluent petroleum ether:ethyl acetate 10:1) to give the diallylated ketosulphide **2a-d**. According to this procedure, the products reported in Table 1 were synthesized as pale yellow oils.The same reaction but performed with stoichiometric quantities af the allylic carbonates affords monoallylated ketosulphides **2e-k** together with, in some cases, diallylated ketosulphides.

3-(Benzothiazol-2-thio)-3-[3-phenyl-2(E)-propen-1-yl]-6-phenyl-5(E)-hexen-2-one (2a).
^{1}H-NMR δ: 2.51 (3H, s, CH_3); 2.92-3.03 (4H, m, allylic CH_2); 6.21 (2H, dt, J= 15.7 and 7.3 Hz, PhCH=C<u>H</u>); 6.46 (2H, d, J= 15.7 Hz, PhC<u>H</u>=CH); 7.18-7.45 (12H, m, Ar), 7.72-7.78 (1H, m, Ar), 7.89-

7.95 (1H, m, Ar). ^{13}C-NMR δ: 26.2, 37.4, 67.4, 121.0, 122.5, 123.5, 125.1, 126.2, 126.3, 127.6, 128.5, 134.5, 135.9, 136.9, 153.4, 161.3, 205.7. IR (liquid film): 3081, 3028, 1708, 1427, 966, 693 cm^{-1}.

3-(Benzothiazol-2-thio)-3-[2(E)-penten-1-yl]-5(E)-octen-2-one (2b).
^{1}H-NMR δ: 0.93 (6H, t, J=7.4, CH_3, ethyl); 1.94-2.03 (4H, m, CH_2, ethyl); 2.40 (3H, s, CH_3CO); 2.67 (4H, dd, J= 7.1 and 1.0 Hz, allylic CH_2); 5.37 (2H, dtt, J= 15.2, 7.1 and 1.5 Hz, C<u>H</u>=CHEt); 5.52 (2H, dtt, J= 15.2, 6.3 and 1.0 Hz, CH=C<u>H</u>Et); 7.24-7.32 (1H, m, Ar); 7.35-7.42 (1H, m, Ar); 7.70-7.75 (1H, m, Ar); 7.85-7.90 (1H, m, Ar). ^{13}C-NMR δ: 13.6, 25.6, 26.1, 36.5, 67.6, 120.8, 122.3, 122.4, 124.8, 125.9, 135.9, 137.2, 153.4, 161.7, 205.7. IR (liquid film): 3031, 2962, 2931, 1709, 1457, 1428, 758 cm^{-1}.

2-(Benzothiazol-2-thio)-2-[2(E)-penten-1-yl]-1-phenyl-4(E)-hepten-1-one (2c).
^{1}H-NMR δ: 0.92 (6H, t, J= 7.3 Hz, CH_3); 1.92-2.02 (4H, m, CH_2, ethyl); 2.85-2.95 (4H, m, allylic CH_2); 5.38-5.50 (4H, m, vinyl protons)[by irradiation at δ=2.90: 5.42 (2H, d, J= 15.3 Hz); 5.47 (2H, dt, J= 15.3 and 5.5 Hz)]; 7.22-7.50 (5H, m, Ar); 7.66-7.73 (1H, m, Ar); 7.85-7.91 (1H, m, Ar); 8.05-8.12 (2H, m, Ar). ^{13}C-NMR δ: 13.6, 25.7, 37.7, 66.1, 120.8, 122.3, 122.5, 124.9, 125.9, 127.8, 128.6, 128.8, 128.9, 136.2, 137.5, 153.2, 161.1, 199.6. IR (CCl_4): 3067, 2970, 1685, 1461, 1430, 1132, 1085, 995 cm^{-1}.

2-(Benzothiazol-2-thio)-1-phenyl-2-(2-propen-1-yl)-4-penten-1-one (2d).
^{1}H-NMR δ: 2.97 (4H, d, J= 7.1 Hz, allylic CH_2); 5.02-5.08 (2H, m, CH=C<u>H</u>$_2$); 5.11-5.16 (2H, m, CH=C<u>H</u>$_2$); 5.82 (2H, ddt, J= 17.0, 10.2 and 7.2 Hz, C<u>H</u>=CH_2); 7.27-7.33 (1H, m, Ar); 7.35-7.42 (3H, m, Ph); 7.44-7.48 (1H, m, Ar); 7.68-7.72 (1H, m, Ar); 7.87-7.90 (1H, m, Ar); 8.06-8.10 (2H, m, Ph).^{13}C-NMR δ: 38.6, 64.9, 119.9, 120.9, 121.6, 124.5, 125.0, 127.9, 128.9, 133.3, 133.5, 136.2, 137.5, 153.1, 160.1, 199.1. IR (liquid film): 1677, 1598, 1580, 993, 926 cm^{-1}.

2-(Benzothiazol-2-thio)-1,5-diphenyl-4(E)-penten-1-one (2e).
Yellowish oil. ^{1}H-NMR δ: 2.90-2.99 (1H, m, allylic CH_2); 3.10-3.19 (1H, m, allylic CH_2); 5.95 (1H, t, J= 7.1 Hz, C<u>H</u>CO); 6.21 (1H, dt, J= 15.8, 7.2 Hz, PhCH=C<u>H</u>); 6.49 (1H, dt, J= 15.8, 1.3 Hz, PhC<u>H</u>=CH); 7.13-7.48 (9H, m, Ar); 7.54-7.59 (1H, m, Ar); 7.70-7.74 (1H, m, Ar); 7.82-7.86 (1H, m, Ar); 8.09-8.14 (2H, m, Ar). ^{13}C-NMR δ: 35.8, 51.3, 121.1, 121.7, 124.5, 125.1, 126.1, 126.2, 127.4, 128.4, 128.6, 128.7, 128.8, 133.6, 133.7, 135.8, 137.0, 152.9, 164.6, 196.3.

2-(Benzothiazol-2-thio)-1-phenyl-4(E)-hepten-1-one (2f).
^{1}H-NMR δ: 0.84 (3H, t, J= 7.5 Hz, C<u>H</u>$_3$); 1.85-1.97 (2H, m, C<u>H</u>$_2$CH$_3$); 2.68-2.77 (1H, m, allylic proton); 2.96-3.03 (1H, m, allylic proton); 5.35-5.50 (2H, m, vinyl protons); 5.82 (1H, t, J= 7.3 Hz, C<u>H</u>CO); 7.20-7.48 (4H, m, Ar); 7.54-7.60 (1H, m, Ar); 7.70-7.74 (1H, m, Ar); 7.77-7.83 (1H, m, Ar); 8.08-8.12 (2H, m, Ar). GC-MS m/e (%): 353 (M^+, 2), 324 (5), 248 (100), 216 (51), 186 (26), 105 (75), 77 (26), 51 (5).

3-(Benzothiazol-2-thio)-5(E)-octen-2-one (2g).
^{1}H-NMR δ: 0.93 (3H, t, J= 7.5 Hz, CH_3, ethyl); 1.95-2.04 (2H, m, CH_2, ethyl); 2.36 (3H, s, C<u>H</u>$_3$CO); 2.54-2.61 (1H, m, allylic CH_2); 2.65-2.73 (1H, m, allylic CH_2); 4.73 (1H, t, J= 7.1 Hz, C<u>H</u>CO); 5.40 (1H, dtt, J= 15.2, 7.0, 1.5 Hz, vinyl proton); 5.62 (1H, dtt, J= 15.2, 6.3, 1.3 Hz, vinyl proton); 7.27-7.31 (1H, m,

Ar); 7.37-7.42 (1H, m, Ar); 7.71-7.75 (1H, m, Ar); 7.81-7.85 (1H, m, Ar). ^{13}C-NMR δ: 13.5, 25.5, 28.4, 33.9, 56.4, 121.1, 121.7, 123.5, 124.6, 126.1, 135.7, 136.7, 153.0, 164.6, 204.6. GC-MS m/e (%): 291 (M^+, 3), 248 (13), 220 (15), 192 (15), 180 (13), 167 (100), 149 (10), 108 (14), 77 (5), 43 (50).

2-(Benzothiazol-2-thio)-1-phenyl-4-penten-1-one (2h).
^{1}H-NMR δ: 2.75-2.80 (1H, m, allylic CH_2); 2.93-3.00 (1H, m, allylic CH_2); 5.03-5.07 (1H, m, CH=CH_2); 5.11-5.16 (1H, m, CH=CH_2); 5.83 (1H, ddt, J= 17.1, 10.1, 6.9 Hz, CH=CH_2); 5.88 (1H, t, J= 7.0 Hz, CHCO); 7.25-7.30 (1H, m, Ar); 7.35-7.40 (1H, m, Ar); 7.41-7.47 (2H, m, Ph); 7.52-7.57 (1H, m, Ph); 7.68-7.72 (1H, m, Ar); 7.79-7.83 (1H, m, Ar); 8.05-8.12 (2H, m, Ph). IR (liquid film): 1682, 1596, 1580, 995, 925 cm^{-1}. GC-MS m/e (%): 325 (M^+, 2), 284 (2), 220 (56), 188 (35), 136 (4), 105 (100), 77 (41), 51 (10).

2-(Benzothiazol-2-thio)-4-methyl-1-phenyl-4-penten-1-one (2i).
^{1}H-NMR δ : 1.79-1.82 (3H, m, CH_3); 2.69 (1H, dd, J= 14.6 and 7.1 Hz, allylic CH_2); 2.95 (1H, dd, J= 14.6 and 7.6 Hz, allylic CH_2); 4.78-4.81 (2H, m, vinyl protons); 5.99 (1H, t, 7.6 Hz, CHCO); 7.25-7.35 (1H, m, Ar); 7.37-7.42 (1H, m, Ar); 7.43-7.49 (2H, m, Ph); 7.52-7.60 (1H, m, Ph); 7.70-7.75 (1H, m, Ar); 7.77-7.82 (1H, m, Ar); 8.09-8.15 (2H, m, Ph).^{13}C-NMR δ : 22.5, 40.0, 48.9, 113.0, 114.5, 121.1, 121.6, 125.5, 126.0, 128.7, 128.8, 133.5, 135.8, 141.2, 152.7, 164.6, 196.5. IR (liquid film): 1738, 1686, 1652, 901 cm^{-1}.

3-(Benzothiazol-2-thio)-5-methyl-5-hexen-2-one (2j).
^{1}H-NMR δ: 1.80 (3H, s, CH_3); 2.38 (3H, s, CH_3CO); 2.52 (1H, dd, J= 14.6 Hz and 8.2 Hz, allylic CH_2); 2.72 (1H, dd, J= 14.6, 7.4 Hz, allylic CH_2); 4.80-4.83 (1H, m, vinyl proton); 4.85-4.87 (1H, m, vinyl proton); 4.87 (1H, t, J= 7.8 Hz, CHCO); 7.26-7.31 (1H, m, Ar); 7.36-7.43 (1H, m, Ar); 7.71-7.74 (1H, m, Ar); 7.80-7.85 (1H, m, Ar). IR (liquid film): 1718, 1651, 1376, 1357, 902 cm^{-1}. GC-MS m/e (%): 277 (M^+, 13), 244, (32), 207 (33), 180 (29), 167 (100), 136 (21), 108 (23), 67 (19), 65 (10), 43 (64).

3-(Benzothiazol-2-thio)-3,5-dimethyl-5-hexen-2-one (2k).
^{1}H-NMR δ: 1.66 (3H, s, CH_3CS), 1.75 (3H, s, CH_3), 2.45 (3H, s, CH_3CO), 2.65 (1H, d, J= 14.1 Hz, allylic CH_2), 2.76 (1H, d, J=14.1 allylic CH_2), 4.74-4.77 (1H, m, vinyl proton), 4.91-4.95 (1H, m, vinyl proton), 7.27-7.33 (1H, m, Ar), 7.36-7.43 (1H, m, Ar), 7.70-7.75 (1H, m, Ar), 7.85-7.91 (1H, m, Ar). IR (liquid film): 1713, 1644, 1376, 1353 cm^{-1}. GC-MS m/e (%): 291 (M^+, 1), 248 (29), 207 (51), 168 (100), 167 (73), 136 (7), 108 (12), 81 (11), 43 (48).

Desulphurization of diallylated ketosulphides (2a-d) to allylated ketones (3a-d): general procedure.
To the ketosulphide (0.61 mmol) and tributyltin hydride (0.82 mmol) dissolved in 10 ml of anhydrous toluene was added under nitrogen a catalytic quantity of 2,2'-azobis(2-methylpropionitrile). This solution was refluxed until the disappearance of the ketosulphide monitored by tlc (petroleum ether:ethyl acetate 20:1). Silica gel chromatography with the above eluent afforded pure allylated ketones as oils in 85-94% yield.

3-[3-phenyl-2-(E)-propen-1-yl]-6-phenyl-5(E)-hexen-2-one (3a).
^{1}H-NMR δ: 2.16 (3H, s, CH_3); 2.37-2.45 (2H, m, allylic CH_2); 2.50-2.59 (2H, m, allylic CH_2); 2.75-2.83 (1H, m, CHCO); 6.12 (2H, dt, J= 15.8 and 7.3 Hz, CH=CHPh); 6.41 (2H, d, J= 15.8 Hz, CH=CHPh); 7.17-7.34 (10H, m, Ph). ^{13}C-NMR δ: 29.9, 34.5, 52.7, 126.1, 126.9, 127.3, 132.4, 134.5, 137.2, 211.1. GC-MS m/e (%) 290 (M^+,1), 272 (47), 247 (10), 204 (25), 173 (53), 143 (22), 117 (41), 115 (54), 91 (100) 43 (70). IR (liquid film): 2926, 1709, 1649, 1599, 1450, 1428, 966, 694 cm^{-1}.

3-[2(E)-penten-1-yl]-5(E)-octen-2-one (3b).
^{1}H-NMR δ: 0.92 (6H, t, J= 7.5 Hz, CH_3); 1.92-2.00 (4H, m, CH_2, ethyl); 2.07 (3H, s, CH_3CO); 2.08-2.13 (2H, m, allylic protons, by irradiation at δ= 5.26 ppm a dd with J=13.4 and 6.1 Hz was observed); 2.18-2.23 (2H, m, allylic protons, by irradiation at δ= 5.26 ppm a dd with J=13.4 and 7.7 Hz was observed); 2.52 (1H, tt, J= 7.7 and 6.1 Hz, CHCO); 5.26 (2H, dtt, J= 15.2, 7.1 and 1.5 Hz, CH=CHEt); 5.46 (2H, dtt, J= 15.2, 6.4 and 1.3 Hz, CH=CHEt). ^{13}C-NMR δ: 13.8, 25.5, 29.6, 34.1, 53.2, 125.6, 134.7, 211.9. GC-MS m/e (%) 194 (M^+,1), 165 (2), 151 (2), 135 (6), 125 (100), 95 (22), 81 (24), 69 (15), 67 (16) 55 (16), 53 (10), 43 (98), 41 (48). IR (liquid film): 2963, 2932, 1714, 1600, 1461, 968 cm^{-1}.

2-[2(E)-penten-1-yl]-1-phenyl-4(E)-hepten-1-one (3c).
^{1}H-NMR δ: 0.86 (6H, t, J= 7.4 Hz, CH_3); 1.87-1.93 (4H, m, CH_2, ethyl); 2.16-2.24 (2H, m, allylic CH_2); 2.35-2.43 (2H, m, allylic CH_2), 3.42-3.50 (1H, m, CHCO); 5.29 (2H, dtt, J= 15.2, 7.0 and 1.3 Hz, vinyl protons); 5.44 (2H, dtt, J= 15.2, 6.3 and 1.1 Hz, vinyl protons), 7.40-7.45 (2H, m, Ph); 7.48-7.52 (1H, m, Ph); 7.88-7.92 (2H, m, Ph). ^{13}C-NMR δ: 13.7, 25.5, 34.7, 46.8, 125.8, 128.2, 128.5, 132.7, 134.6, 137.6, 203.5. GC-MS m/e (%) 256 (M^+,4), 212 (2), 187 (97), 157 (9), 145 (10), 105 (100), 81 (14), 77 (52), 51 (10), 41 (36). IR (liquid film): 3027, 2963, 2932, 1682, 1597, 1448, 1230, 968, 704 cm^{-1}.

1-phenyl-2-(2-propen-1-yl)-4-penten-1-one (3d).
^{1}H-NMR δ: 2.25-2.35 (2H, m, allylic CH_2 , by irradiation at δ= 5.72 ppm, a dd with a J= 13.7 and 6.1 Hz was observed. By further irradiation at δ= 3.57 ppm a dd with J=13.7 and 7.4 Hz was observed); 2.47-2.57 (2H, m, allylic CH_2, by irradiation at δ= 5.72 ppm, a dd with J=13.7 and 7.3 Hz was observed, whereas by irradiation at δ= 3.57 ppm a dd with J= 13.7 and 6.6 Hz was observed); 3.57 (1H, tt, J= 7.3, 6.1 Hz, CHCO); 4.90-5.05 (4H, m, $CH=CH_2$); 5.72 (2H, ddt, J= 17.1, 10.0 and 7.1 Hz, $CH=CH_2$); 7.40-7.48 (2H, m, Ph); 7.50-7.58 (1H, m, Ph); 7.88-7.95 (2H, m, Ph). ^{13}C-NMR δ: 35.8, 45.5, 116.9, 128.2, 128.6, 132.9, 135.4, 137.0, 202.6. GC-MS m/e (%) 200 (M^+,2), 159 (10), 157 (14), 105 (100), 91 (4), 77 (46), 51 (15). IR (liquid film): 3078, 2979, 2916, 1682, 1641, 1597, 1448, 1241, 1209, 917 cm^{-1}.

Conversion of diallylated ketosulphides (2a-d) into episulphides (4a-d) and monoallylated ones (2e-k) into episulphides (4e-k): general procedure.
To a solution of ketosulphide (1.4 mmol) in 10 ml of isopropanol was added under stirring sodium borohydride (1.4 mmol). The suspension was stirred at r.t. until the disappearance of the ketosulphide (6-48 h) (tlc, petroleum ether:ethyl acetate 10:1). Evaporation of the resulting suspension followed by silica gel chromatography gave the episulphide as an oil. Some episulphides partially desulphurize, in the injector of the mass spectrometer, to give the corresponding alkene spectra beside that of episulphides.

3-methyl-2,2bis[3-phenyl-2(E)-propen-1-yl]thiirane (4a).
^{1}H-NMR δ: 1.64 (3H, d, J= 6.2 Hz, CH_3); 2.53 (1H, ddd, J= 14.4, 7.1 and 1.3 Hz, allylic proton); 2.65-2.80 (3H, m, allylic protons); 3.02 (1H, q, J= 6.2 Hz, $CH_3C\underline{H}$); 6.23 (1H, dt, J=15.8 and 7.1 Hz, PhCH=C<u>H</u>); 6.26 (1H, dt, J= 15.8 and 7.1 Hz, PhCH=C<u>H</u>); 6.45 (1H, d, J= 15.8 Hz, Ph<u>CH</u>=CH); 6.52 (1H, d, J= 15.8 Hz, Ph<u>CH</u>=CH); 7.21-7.42 (10H, m, Ph). ^{13}C-NMR δ: 17.2, 37.6, 43.3, 43.4, 126.1, 126.2, 126.6, 126.9, 127.3, 127.4, 128.5, 128.6, 132.9, 137.2. GC-MS (thiirane) m/e (%) 306 (M^+,6), 273 (50), 272 (100) 181 (19), 169 (23), 155 (42), 117 (86), 115 (62), 91 (94), 77 (18) 39 (17). GC-MS (olefin) m/e (%) 274 (M^+,31), 245 (7), 205 (51), 183 (90), 170 (42), 155 (100), 143 (53), 141 (58), 115 (76), 91 (97), 77 (21), 65 (14), 51 (10).

3-methyl-2,2bis[2(E)-penten-1-yl]thiirane (4b).
^{1}H-NMR δ: 0.97 (6H, 2t quite overlapped, J= 7.4 Hz, CH_3, ethyl); 1.52 (3H, d, J= 6.1 Hz, <u>CH</u>$_3$CH(S)); 1.92-2.09 (4H, m, CH_2, ethyl); 2.23 (1H, dd, J= 14.3 and 6.8 Hz, C<u>H</u>$_2$C(S)); 2.36-2.50 (3H, m, C<u>H</u>$_2$C(S)); 2.86 (1H, q, J= 6.1 Hz, $CH_3C\underline{H}$(S)); 5.33-5.44 (2H, m, vinyl protons)[by irradiation at δ= 2.00 ppm: 5.37 (1H, dt, J= 15.3 and 6.7 Hz); 5.40 (1H, dt, J= 15.3 and 6.8 Hz)]; 5.45-5.60 (2H, m, vinyl protons)[by irradiation at δ= 2.00 ppm: 5.49 (1H, dt, J= 15.3 and 1.1 Hz); 5.55 (1H, dt, J= 15.3 and 1.3 Hz)]. ^{13}C-NMR δ: 13.8, 13.9, 17.1, 25.5, 25.6, 36.8, 42.6, 43.3, 54.1, 125.3, 125.6, 135.3, 135.4. GC-MS (thiirane) m/e (%) 210 (M^+,6), 181 (18), 177 (26), 147 (22), 141 (41), 121 (20), 109 (22), 107 (54), 99 (22), 93 (57), 91 (34), 81 (34), 79 (48), 69 (39), 55 (43), 41 (100). GC-MS (olefin) m/e (%) 178 (M^+,8), 149 (58), 135 (33), 107 (85), 93 (100), 79 (84), 67 (60), 55 (41), 41 (84). IR (liquid film): 3027, 2962, 2931, 1460, 1444, 968 cm^{-1}.

3-phenyl-2,2bis[2(E)-penten-1-yl]thiirane (4c).
^{1}H-NMR δ: 0.91 (3H, t, J= 7.4 Hz, CH_3); 1.01 (3H, t, J= 7.4 Hz, CH_3); 1.86-1.98 (3H, m, allylic protons); 2.03-2.12 (2H, m, CH_2, ethyl); 2.20 (1H, dd, J= 14.3 and 7.4 Hz, <u>H</u>$_2$CCH=CHEt); 2.43 (1H, dd, J= 14.0 and 7.0 Hz, <u>H</u>$_2$CCH=CHEt); 2.60 (1H, ddd, J= 14.0, 7.0 and 1.0 Hz, <u>H</u>$_2$CCH=CHEt); 3.99 (1H, s, PhC<u>H</u>(S)); 5.19-5.26 (1H, m, vinyl proton); 5.30 (1H, dt, J= 15.3 and 6.1 Hz, vinyl proton); 5.49 (1H, dtt, J= 15.3, 7.0 and 1.3 Hz, vinyl proton); 5.60 (1H, dtt, J= 15.3, 6.3 and 1.1 Hz, vinyl proton); 7.22-7.37 (5H, m, Ph). ^{13}C-NMR δ: 13.8, 13.9, 25.6, 25.7, 37.1, 43.0, 50.1, 55.1, 125.2, 125.6, 127.2, 127.9, 129.1, 135.3, 135.9, 136.3. GC-MS (thiirane) m/e (%) 272 (M^+,18), 239 (11), 197 (24), 171 (29), 145 (94), 129 (51), 115 (33), 91 (89), 77 (22), 69 (69), 55 (16), 41 (100). GC-MS (olefin) m/e (%) 240 (M^+,14), 211 (5), 171 (71), 141 (19), 129 (47), 115 (29), 91 (100), 77 (12), 55 (12), 41 (34). IR (liquid film): 3026, 2961, 1653, 1449, 969, 699 cm^{-1}.

3-phenyl-2,2bis(2-propen-1-yl)thiirane (4d).
^{1}H-NMR δ: 1.97 (1H, dd, J= 14.5 and 6.4 Hz, allylic proton); 2.30 (1H, dd, J= 14.5 and 7.6 Hz, allylic proton); 2.53 (1H, dd, J= 14.2 and 6.6 Hz, allylic proton); 2.69 (1H, ddt, J= 14.2, 7.3 and 1.1 Hz, allylic proton); 4.04 (1H, s, C<u>H</u>Ph); 4.90-4.96 (1H, m, C<u>H</u>$_2$=CH); 4.99-5.03 (1H, m, C<u>H</u>$_2$=CH); 5.15-5.20 (2H, m, C<u>H</u>$_2$=CH); 5.65 (1H, dddd, J= 17.8, 10.2 , 7.6 and 6.4 Hz, CH$_2$=C<u>H</u>); 5.91 (1H, ddt, J= 17.6, 9.6 and 7.1 Hz, CH$_2$=C<u>H</u>); 7.23-7.39 (5H, m, Ph). ^{13}C-NMR δ: 39.3, 44.0, 49.9, 53.7, 117.6, 118.2, 127.3,

128.0, 129.1, 134.7, 135.3, 135.8. GC-MS m/e (%) 216 (M^+,20), 215 (18), 169 (100), 143 (28), 142 (29), 141 (62), 117 (42), 91 (38), 77 (12), 41 (25).

(E) and (Z)-2-[3-phenyl-2(E)-propen-1-yl]-3-phenyl-thiirane (4e).

Spectral data of the Z isomer. ^{1}H-NMR δ: 2.17-2.27 (1H, m, allylic proton); 2.32-2.42 (1H, m, allylic proton); 3.26 (1H, dt, J= 6.9, 7.4 Hz, C<u>H</u>(S)CHPh); 4.23 (1H, d, J= 6.9 Hz, CH(S)C<u>H</u>Ph); 6.11 (1H, dt, J= 15.8, 6.8 Hz, PhCH=C<u>H</u>); 6.25 (1H, dt, J= 15.8, 1.3 Hz, PhC<u>H</u>=CH); 7.18-7.47 (10H, m, Ph). GC-MS m/e (%): 252 (M^+, 1), 220 (27), 178 (3), 165 (3), 142 (14), 129 (100), 65 (10), 51 (9), 39 (9).

(E) and (Z)-2-[2(E)-penten-1-yl]-3-phenyl-thiirane (4f).

Spectral data of Z isomer. ^{1}H-NMR δ: 0.91 (3H, t, J= 7.4 Hz, CH_3); 1.90-2.15 (4H, m, allylic CH_2); 3.15 (1H, dt, J= 7.0, 7.6 Hz, PhCH(S)C<u>H</u>); 4.16 (1H, d, J= 7.0 Hz, PhC<u>H</u>(S)CH); 5.25-5.40 (2H, m, vinyl protons) [by irradiation at δ= 1.93 ppm: doublet at δ= 5.33 ppm, with J= 15.1 Hz, CH=C<u>H</u>Et]; 7.24-7.42 (5H, m, Ar). GC-MS m/e (%): 204 (M^+, 3), 172 (12), 143 (42), 129 (100), 128 (74), 115 (37), 91 (71), 67 (19), 51 (14), 41 (30).

(E) and (Z)-2-[2(E)-penten-1-yl]-3-methyl-thiirane (4g).

Spectral data of the mixture of E and Z isomers. ^{1}H-NMR δ: 0.94-1.00 (3H, 2t quite overlapped, J= 7.4 Hz, CH_3, ethyl, E and Z isomers); 1.46-1.50 (3H, 2d quite overlapped, J= 6.1 Hz, C<u>H</u>3CHS, E and Z isomers); 1.96-2.05 (2H, m, CH_2, ethyl); 2.18-2.45 (2H, m, allylic CH_2); 2.60 (0.4H, q, J= 5.9 Hz, CH3CH(S)C<u>H</u>, E isomer); 2.63-2.66 (0.4H, m, CH3C<u>H</u>(S)CH)[by irradiation at δ= 1.48 ppm: d, δ=2.65 ppm, J= 5.3 Hz, E isomer]; 2.94 (0.6H, q, J= 7.0 Hz, CH3CH(S)C<u>H</u>, Z isomer); 3.01-3.09 (0.6H, m, CH3C<u>H</u>(S)CH)[by irradiation at δ= 1.48 ppm : d, δ= 3.05 ppm, J= 7.0 Hz, Z isomer]; 5.35-5.64 (2H, m, vinyl protons). GC-MS (Z isomer) m/e (%): 142 (M^+, 76), 127 (13), 113 (4)), 87 (30), 85 (31), 81 (37), 79 (47), 67 (100), 55 (45), 45 (45), 41 (85), 39 (57). GC-MS (E isomer) m/e (%): 142 (M^+, 83), 127 (15), 113 (31), 87 (42), 85 (32), 81 (43), 79 (48), 67 (100), 55 (47), 45 (50), 41 (91), 39 (51).

(E) and (Z)-2-(2-propen-1-yl)-3-phenyl-thiirane (4h)

Spectral data of the mixture of E and Z isomers. ^{1}H-NMR δ: 1.95-2.05 (0.7H, m, allylic CH_2, Z isomer); 2.18-2.27 (0.7H, m, allylic CH_2, Z isomer); 2.42-2.50 (0.3H, m, allylic CH_2, E isomer); 2.60-2.69 (0.3H, m, allylic CH_2, E isomer); 3.08 (0.3H, ddd, J= 6.6, 6.0 and 5.3 Hz, C<u>H</u>(S)CHPh, E isomer); 3.18 (0.7H, ddd, J= 7.9, 7.0 and 6.1 Hz, C<u>H</u>(S)CHPh, Z isomer); 3.62 (0.3H, d, J= 5.3 Hz, CH(S)C<u>H</u>Ph, E isomer); 4.19 (0.7H, d, J= 7.0 Hz, CH(S)C<u>H</u>Ph, Z isomer); 4.94-5.02 (1.4H, m, CH=C<u>H</u>2, Z isomer); 5.07-5.18 (0.6H, m, CH=C<u>H</u>2, E isomer); 5.73 (0.7H, ddt, J= 17.7, 9.7, 6.5 Hz, C<u>H</u>=CH2, Z isomer); 5.91 (0.3H, ddt, J= 17.1, 10.3, 6.5 Hz, C<u>H</u>=CH2, E isomer); 7.25-7.45 (5H, m, Ph). GC-MS (Z isomer) m/e (%): 176 (M^+, 4), 147 (4), 143 (20), 135 (39), 129 (100), 121 (36), 115 (28), 91 (36), 85 (10), 77 (11), 65 (9), 51 (12), 39 (15). GC-MS (E isomer) m/e (%): 176 (M^+, 3), 143 (42), 135 (35), 129 (100), 121 (25), 115 (18), 91 (36), 85 (12), 77 (10), 51 (14), 39 (16).

(Z)-2-(2-methyl-2-propen-1-yl)-3-phenyl thiirane (4i).
^{1}H-NMR δ: 1.64-1.68 (3H, m, CH_3); 1.91 (1H, dd, J= 15.8 and 8.0 Hz, allylic CH_2); 2.20 (1H, dd, J= 15.8 and 5.6 Hz, allylic CH_2); 3.26 (1H, ddd, J= 8.0, 7.0 and 5.6 Hz, PhCH(S)C<u>H</u>); 4.17 (1H, d, J= 7.0 Hz, PhC<u>H</u>(S)CH); 4.67-4.71 (1H, m, vinyl proton), 4.72-4.76 (1H, m, vinyl proton); 7.24-7.39 (5H, m, Ph). ^{13}C-NMR δ: 22.7, 38.6, 40.2, 42.3, 111.2, 127.4, 127.9, 129.2, 135.4, 143.5. This episulphide loses sulphur in the injector of the mass spectrometer and therefore the spectrum of the corresponding alkene is reported: GC-MS m/e (%) 158 (18), 143 (100), 129 (56), 128 (68), 115 (52), 91 (21), 80 (16), 77 (12), 65 (10), 51 (11). Beside the NMR data, the (Z)-geometry of this episulphide was also estabilished by its conversion to the corresponding (Z)-olefin **5i** by reaction with 3-methyl-2-selenoxobenzothiazole which converts stereospecifically episulphides into olefins. Thus, 3-methyl-2-selenoxobenzothiazole (0,9 mmol) and **4i** (0,9 mmol), dissolved in 5 ml of dichloromethane containing trifluoroacetic acid (1.82 mmol), were refluxed for 2h. After filtration of the selenium and evaporation of the solvent, the residue was chromatographed on silica gel (eluent petroleum ether: ethyl acetate 5:1) to give a pale yellow oil in a 72% yield which had an identical mass spectrum of the above olefin. ^{1}H-NMR δ: 1.74-1.78 (3H, m, allylic CH_3); 2.97 (2H, d, J= 7.6 Hz, allylic CH_2); 4.77-4.82 (2H, m, C=C<u>H</u>$_2$); 5.74 (1H, dt, J= 11.5 and 7.6 Hz, C<u>H</u>=CHPh); 6.54 (1H, d, J= 11.5 Hz, CH=C<u>H</u>Ph); 7.20-7.40 (5H, m, Ph). These data identify this olefin as (Z)-1-phenyl-4-methyl-1,4-pentadiene.

(E) and (Z)-2-(2-methyl-2-propen-1-yl)-3-methyl-thiirane (4j).
Spectral data of Z isomer. ^{1}H-NMR δ: 1.47 (3H, d, J= 5.8 Hz, C<u>H</u>$_3$CH(S)); 1.79 (3H, br. s, allylic CH_3); 2.32 (1H, dd, J= 16.1, 6.9 Hz, allylic proton); 2.41 (1H, dd, J= 16.1, 6.2 Hz, allylic proton); 3.00-3.09 (2H, m, C<u>H</u>(S)C<u>H</u>CH$_3$) [by irradiation at δ= 1.47 ppm: 2.99-3.04 (1H, m, C<u>H</u>(S)CHCH$_3$); 3.05 (1H, d, J= 6.9 Hz, CH(S)C<u>H</u>CH$_3$)]; 4.82 (2H, br. s, vinyl protons). GC-MS m/e (%): 128 (M^+, 100), 113 (90), 99 (24), 95 (44), 85 (28), 79 (36), 67 (53), 55 (44), 53 (28), 44 (35), 41 (28), 39 (46).

(E) and (Z)-2-(2-methyl-2-propen-1-yl)-2,3-dimethyl-thiirane (4k).
Spectral data of the mixture of E and Z isomers: ^{1}H-NMR δ: 1.44 (1.05H, s, C<u>H</u>$_3$C(S)CH, E isomer); 1.47 (1.95H, s, C<u>H</u>$_3$C(S)CH, Z isomer); 1.50-1.52 (3H, 2d quite overlapped, J= 6.1 Hz, C(S)CHC<u>H</u>$_3$); 1.72 (1.05H, br s, allylic CH_3, E isomer); 1.78 (1.95H, br s, allylic CH_3, Z isomer); 2.26 (0.35H, d, J= 14.2 Hz, allylic proton, E isomer); 2.39 (0.65H, d, J= 14.8 Hz, allylic proton, Z isomer); 2.52 (0.65H, d, J= 14.8 Hz, allylic proton, Z isomer); 2.54 (0.35H, d, J= 14.2 Hz, allylic proton, E isomer), 2.83-2.91 (1H, m, C(S)C<u>H</u>CH$_3$); 4.73-4.76 (0.35H, m, vinyl proton, E isomer); 4.77-4.79 (0.65H, m, vinyl proton, Z isomer); 4.80-4.83 (0.35H, m, vinyl proton, E isomer); 4.84-4.88 (0.65H, m, vinyl proton, Z isomer). Both of the isomers gave only a signal in the mass-spectrometer. GC-MS m/e (%): 142 (M^+, 53), 127 (77), 113 (32), 93 (35), 82 (53), 67 (94), 59 (71), 55 (47), 53 (64), 45 (44), 41 (94), 39 (100).

Acknowledgement : Work supported in part by C.N.R. (Rome) under the " Progetto Finalizzato Chimica Fine II" Programme and the Ministry of the University, Scientific and Technological Research (MURST)

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(*Received in UK* 16 *October* 1995; *revised* 17 *November* 1995; *accepted* 23 *November* 1995)