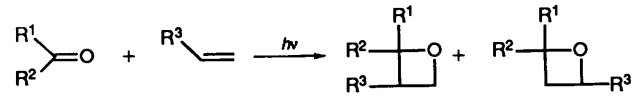
Alkenyl Sulphides and Ketene *S,S*-Dithioacetals as Olefin Components in the Paterno-Büchi Reaction: a Regioselective Synthesis of Oxetanes

N. Khan,[a] T. H. Morris,[a] E. H. Smith *[,a] and R. Walsh[b]
[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK*
[b] *Pharmaceutical Research Laboratories, Rhône-Poulenc-Rorer, Dagenham, Essex RM10 7XS, UK*

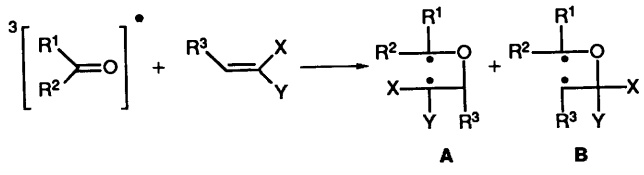
Under photolysis benzophenone reacts with alkenyl methyl sulphides to give 3-methylthiooxetanes regio- and stereo-selectively. Under the same conditions ketene *S,S*-dithioacetals polymerise.

There are a limited number of synthetic routes to oxetanes. The most simple conceptually, and the most convergent, is by way of the photocycloaddition of a carbonyl compound and an olefin, the Paterno–Büchi reaction.[1] Although this reaction is restricted in the carbonyl component mainly to aldehydes and ketones, the combination of these with a large range of olefins provides a process of wide scope. A serious disadvantage, however, is that the reaction is only occasionally regiospecific (for example in the combinations of the aldehydes with dienes,[2a] aldehydes with styrenes,[2b] ketones with dienes,[2c] ketones with enynes[2d] and ketones with alkenyl cyanides[2e]) (Scheme 1). It



Scheme 1

is the interaction of the light with the carbonyl component, specifically the excitation of an electron from an n-orbital of the carbonyl oxygen to a π^*-orbital of the carbonyl double bond, which provides the impetus for the reaction. Commonly the resultant singlet excited state species undergoes intersystem crossing to that of the triplet state. The latter is trapped by the olefin to give a pair of 1,4-biradicals (**A** and **B**) which then collapse to the oxetanes (Scheme 2). The regiochemical outcome

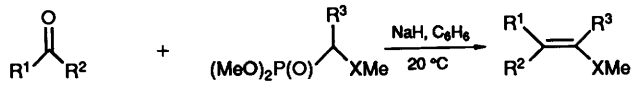


Scheme 2

of the triplet state reaction is then discussed in terms of the relative stabilities of **A** and **B** on the assumption that the transition state for the trapping steps resemble the biradical intermediates or that these steps are reversible.[1] Thus, regiochemical control in the triplet state reaction might result from the placing on the olefin of groups X,Y which stabilise a radical α to them. When the olefin is an enol ether (X = OR, Y = H) insufficient control accrues and the 2- and 3-alkoxyoxetanes are formed in a ratio varying from 16:84 to 30:70.[3] However, ketene diethyl acetal (X = Y = OEt) forms only the 3,3-diethoxyoxetane indicating that two oxy groups suffice to stabilise radical **A** over radical **B**.[3] Believing that a thioether would be better than an ether at stabilising a radical α to itself we decided to try alkenyl sulphides and ketene *S,S*-dithioacetals as the olefinic components in the Paterno–Büchi reaction in order to improve the regioselectivity.[4]

Results and Discussion

Synthesis of Alkenyl Sulphides and Ketene S,S-*Dithioacetals.*— The alkenyl sulphides **3a–f** and the alkenyl selenide **3g** were made by a Wadsworth–Emmons reaction following a literature procedure (Scheme 3).[5] The phosphonate precursor **1a**, pre-



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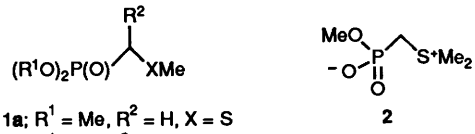
a; R^1 = Pr, R^2 = R^3 = H, X = S; 17.7%; *E* : *Z* = 6 : 1
b; R^1 = Pr^i, R^2 = R^3 = H, X = S; 40%; *E* : *Z* = 6 : 1
c; R^1 = Bu^t, R^2 = R^3 = H, X = S; 42%; *E* : *Z* = 97 : 3
d; R^1 = PhCHMe, R^2 = R^3 = H, X = S; 34%; *E* : *Z* = 7 : 1
e; R^1, R^2 = —$[CH_2]_5$— , R^3 = H, X = S; 30%
f; R^1 = Pr^i, R^2 = H, R^3 = Me, X = S; 60%; *E* : *Z* = 4 : 1
g; R^1 = Bu^t, R^2 = H, R^3 = Me, X = Se; 70%; *E* : *Z* = 1 : 1

Scheme 3



1a; R^1 = Me, R^2 = H, X = S
b; R^1 = Et, R^2 = Me, X = S
c; R^1 = Et, R^2 = Me, X = Se

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pared by heating chloromethyl methyl sulphide with trimethyl phosphite, proved to be rather unstable thermally. During distillation of this compound a solid, m.p. 155–157 °C, was deposited in the distillation pot. At room temperature reagent **1a** slowly decomposed to the same solid which appeared to be the betaine **2** by ^{1}H NMR spectroscopy and mass spectrometry and by its solubility in water. This problem could be alleviated to some extent by distilling **1a** as quickly, and at the lowest temperature, as possible when a 60% yield of **1a** could be realised. It is also advisable to use it within a short time to avoid prolonged storage. The homologous *O*-ethyl phosphonates **1b**[6] (50%) and **1c**[7] (70%) were much more stable than **1a** and were prepared by deprotonation of *O,O*-diethyl ethylphosphonate with BuLi at −78 °C followed by the addition of first elemental sulphur or selenium respectively and then methyl iodide. These homologues were also much better behaved in the subsequent Wadsworth–Emmons reaction; these facts together with the knowledge that the self-decomposition product **2** of phosphonate **1a** appears to derive from a methylation on sulphur by the phosphorus ester suggests that use of the diethyl ester corresponding to **1a** might be preferable in future studies.

The Wadsworth–Emmons reaction gave yields which were only moderate at best, but the method had the advantage of

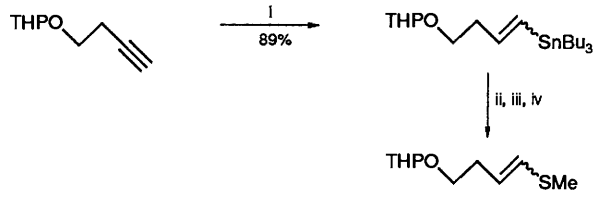
Table 1 Photochemical synthesis of the oxetanes **8** and **9** from the vinyl chalcogenides and benzophenone

Entry	Oxetane	R^1	R^2	R^3	X	Yield (%)	M.p. of **8** (*T*/°C)	Ratio **8**/**9**
1	**a**	Pr	H	H	S	59	29–31	13:1
2	**b**	Pr^i	H	H	S	79	54–8	**8** only
3	**c**	Bu^t	H	H	S	52	59–63	9:1
4	**d**	PhCHMe	H	H	S	36	60–68[a]	**8** only
5	**e**	$-[CH_2]_5-$		H	S	12	Gum	1:1.25
6	**f**	Pr^i	H	Me	S	60	59–67[b]	**8** only
7	**g**	Bu^t	H	Me	Se	45	58–60	**8** only
8	**h**	$THPO(CH_2)_2$	H	H	S	24	Gum[a]	**8** only

[a] Isolated as a 1:1 mixture of diastereoisomers. [b] *trans*-**8**:*cis*-**8** = 3:2.

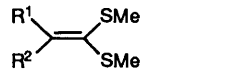
being short. The products **3a–d** showed a preference for the *E*-geometry by a factor of 6–9:1. This followed from the clearly larger coupling constant (J = 15–16 Hz) observed for the major isomer in the mixture. The same preference is believed to pertain for the methylated homologue **3f** (4:1), thereby placing the SMe substituent *cis* to the hydrogen rather than to the large Pr^i group, but the selenium analogue was obtained as a 1:1 mixture of geometrical isomers.

The alkenyl sulphide **3h**, as a mixture of *E*- and *Z*-isomers, was synthesized by the hydrostannylation of but-3-ynyl tetrahydropyranyl ether and tin–lithium exchange according to the procedure of Corey and co-workers,[8] followed by the trapping of the resultant vinyllithium with sulphur and methyl iodide (Scheme 4).

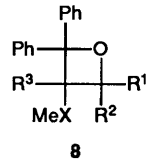


Scheme 4 *Reagents and conditions:* i, Bu_3SnH, azoisobutyronitrile (AIBN), *T* 95 °C; ii, BuLi, *T* −78 °C; iii, S_8; iv, MeI

The ketene *S*,*S*-dithioacetals **4**,[9] **5**,[9] **6**[10] and **7**[10] were made according to the literature.



4 $R^1 = R^2 = H$
5 $R^1 = H$, $R^2 = Me$
6 $R^1 = R^2 = Me$
7 $R^1, R^2 = —[CH_2]_5—$



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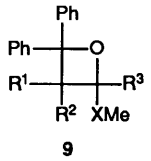

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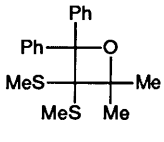

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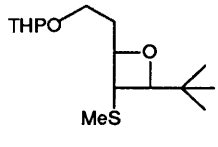

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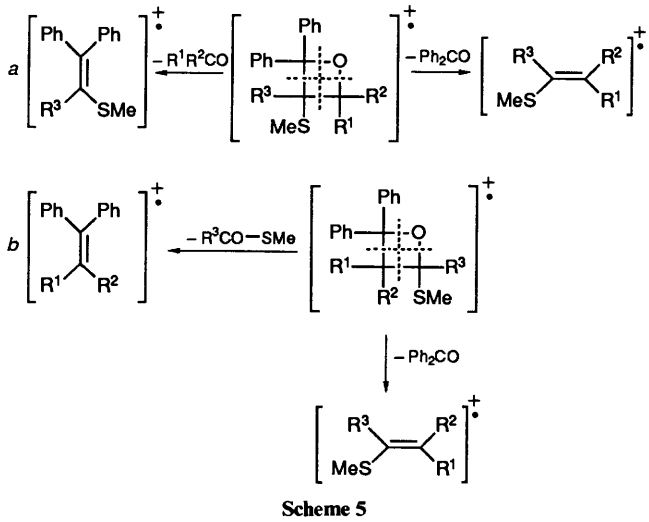
Photolyses.—In order to test the ability of alkenyl sulphides and ketene *S*,*S*-dithioacetals to act as the olefinic components in the Paterno–Büchi reaction benzophenone was chosen as the carbonyl partner since it is known to form oxetanes well with electron-rich alkenes and many of these are stable, crystalline solids. The results of the photolyses with alkenyl sulphides are shown in Table 1.

It is of synthetic interest that these reactions were much faster than those of the corresponding enol ethers, proceeding to fair yields with a much less powerful lamp (125 W instead of 400 W). Noteworthy also, was the high degree of regioselectivity observed for the formation of the 3-methylthiooxetanes **8**. In only three cases (Table 1, entries 1, 3 and 5) were the 2-methylthio regioisomers **9** detected in the ^1H NMR spectra of the crude photolysates. The subsequent isolation of these latter isomers by column chromatography on SiO_2 in quantities consistent with the ratio of regioisomers determined in the above ^1H NMR spectra indicated that they had not decomposed during purification to any significant extent. Therefore, the yields of the two isolated isomers genuinely reflect the partitioning of the photolysis reaction towards them. The assignment of the 3-methylthio structure to the major isomer in all cases (except for entry 5, Table 1) was made on the basis of ^1H NMR spectroscopy and mass spectrometry. Thus, the ring hydrogens for these oxetanes resonated in the δ 4.0–4.7 region which compares with the corresponding 3-alkoxyoxetanes which show peaks at δ *ca.* 4.6.[3] The mass spectra of the products do not exhibit a molecular ion but rather the alkenyl sulphide fragment ions derived by the two possible retrocycloadditions of the ring (Scheme 5*a*). In the case of the 4-isopropyl-3-methyl thiooxetane **8b** the matter of regiochemistry was put in no doubt by an X-ray crystallographic determination (Fig. 1).

Where they occurred, the 2-methylthiooxetanes were clearly distinguishable from the 3-methylthio isomers by peaks in the



Scheme 5

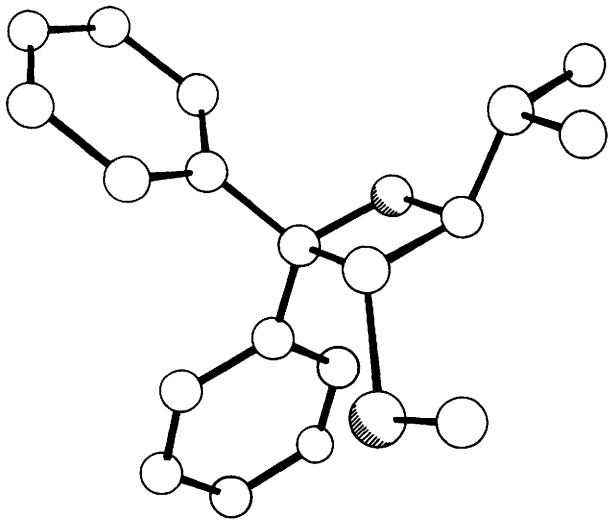


Fig. 1 *Crystal data:* $C_{19}H_{22}OS$, M = 298.4, monoclinic, a = 8.497(2), b = 19.151(4), c = 10.769(3) Å, β = 103.17(2)°, U = 1706 Å^3, space group $P2_1/a$, Z = 4, D_c = 1.16 g cm^{-3}, μ(Cu–Kα) = 16 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with Cu–Kα radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and refined anisotropically to give R = 0.044, R_w = 0.051 for 1981 independent observed reflections [$|F_o| \geqslant 3\sigma(|F_o|)$, $\theta \leqslant 58°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. [For details see ref. 4; also see 'Instructions for Authors (1991)', *J. Chem. Soc., Perkin Trans. 1*, 1991, Issue 1.]

^{1}H NMR spectra in the region δ 5.5–5.8 due to the thioacetal proton between the MeS group and the ring oxygen and by the retro-[2 + 2]cycloaddition fragment ion at $M^+ - 76$ due to loss of the HCO–SMe group in the mass spectra (Scheme 5*b*). The 2-methylthio isomer actually predominates when the alkenyl sulphide is disubstituted β to the MeS group **9e** (entry 5, Table 1).

Thus, the Paterno–Büchi reaction of alkenyl sulphides with benzophenone is highly regioselective when the double bond bears one β-alkyl group but is much less so when two alkyl groups are in this position. This can be rationalised on the basis of the stabilisation of the two biradicals **A** and **B** mentioned above in the sense that a radical centre adjacent to sulphur is more stable than a secondary alkyl radical but of a stability approximately equal to that of a tertiary alkyl radical.

The expectation that the presence of two sulphur atoms in ketene *S,S*-dithioacetals would redress the regiochemical imbalance observed for disubstituted alkenyl sulphides was sadly not realised. These alkenes showed a strong absorption in their UV spectra at a wavelength superimposable upon that of the n–π^* band of benzophenone and irradiation of mixtures containing the ketone and each of the dithioacetals all led to quantitative recovery of benzophenone and extensive polymerisation of the dithioacetal. Only in the case of dithioacetal **6** was a gum obtained whose ^{1}H NMR and mass spectral (retro-[2 + 2]cycloaddition fragments) data was consistent with its formulation as the 3,3-bis(methylthio)oxetane **10**. However, it was isolated in only very low yield (3%) and was insufficiently characterised to be certain of this assignment.

An alkenyl sulphide also proved capable of trapping a photoexcited carbonyl compound other than benzophenone. Thus, 3-tetrahydropyranyloxypropanal gave an oxetane with the alkenyl sulphide **3c** in a yield of 22% (for the aldehyde the use of a quartz apparatus with a copper sulphate filter together with acetonitrile as solvent was necessary because the n–π^* band was centred at λ = 293 nm). The product from the aldehyde was assumed to have the 3-methylthio structure **11** by the usual criteria above (δ 4.6 for the ring proton in the ^{1}H NMR spectrum and retro-[2 + 2] cleavage in the mass spectrum).

The X-ray crystal structure of the oxetane **8b** had also established the *trans*-relationship of the alkyl and SMe groups. The geometry had been strongly suggested for oxetanes **8a–d** by the observation of difference Nuclear Overhauser effects (DNOE) between the MeS–methyl and the hydrogen vicinal to the MeS group and the absence of such effects between the two ring hydrogens. Typical values for these small but positive effects

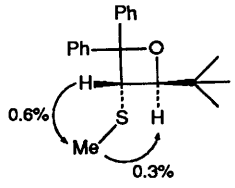
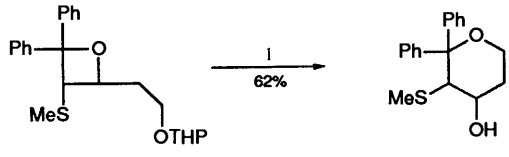


Fig. 2

are shown for the *tert*-butyl congener **8c** (Fig. 2). It is not sufficient to determine the ^{1}H–^{1}H NMR coupling constants between the two ring hydrogens for the assignment of geometry in oxetanes as the values for the *cis*- and *trans*-isomers are too close to be diagnostic; typically these are 6.6 Hz for the *trans*- and 7.3 Hz for the *cis*-isomer.[11] However, ^{1}H–^{13}C NMR coupling constants are known to be sensitive to stereochemistry in oxetanes[12] and this method and the DNOE method above complement one another. Despite this preference for one stereochemistry in the product oxetanes, the overall reaction is not stereospecific. This was shown by the isolation of the oxetane **8f** in the same ratio of stereoisomers irrespective of the isomer ratio of the starting alkenyl sulphide **3f** (4:1 or 1.8:1 *trans*:*cis*). Part of the explanation for this lack of stereospecificity is the equilibration of the alkenyl sulphide isomers under the irradiation conditions, a phenomenon seen with alkenyl sulphide **3f** during irradiation in the absence of benzophenone under conditions otherwise identical to those for oxetane synthesis.

The potential synthetic utility of these oxetanes is illustrated by the ring opening and reclosure of the congener **8h** in methanol in the presence of Amberlyst 15H (H^+ form) to give the pyran **12** (Scheme 6) as a white, crystalline solid in 62% yield.



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Scheme 6 *Reagents and conditions:* i, Amberlyst-15H, MeOH, rt, 3 h

Experimental

M.p.s are uncorrected and were determined using a Gallenkamp apparatus. Dry THF (tetrahydrofuran) was obtained by distillation from potassium diphenylketyl under argon. Benzene and light petroleum (b.p. range 40–60 °C) were dried over sodium. Light petroleum used for column chromatography was distilled. May and Baker Sorbsil C60 silica gel was used for gravity column chromatography. IR spectra were recorded for samples either neat (liquids) or as Nujol mulls (solids) using a Perkin-Elmer 881 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL FX90Q (90 MHz) or JEOL GSX270 (270 MHz) spectrometer for solutions in $CDCl_3$ using $SiMe_4$ as internal standard, J values are given in Hz. Mass spectra were recorded on an AEI MS9 or a VG Micromass 7070 instrument. UV spectra were recorded on a Shimadzu UV-160 or a Philips PU8740 spectrophotometer. Phosphonates **1b**[6] and **1c**[7] were made according to the literature.

O,O-*Dimethyl Methyl(methylthio)phosphonate* **1a**.—Chloromethyl methyl sulphide (15 g, 156 mmol) and trimethyl phosphite (23.25 g, 188 mmol) were mixed and heated at 130–140 °C. Initially the mixture boiled vigorously as methyl chloride was evolved but the vigour subsided and the liquid remained clear. Heating was stopped when the mixture started to become cloudy (3 h) and, on cooling, a white solid precipitated out. On distillation the product was obtained as a colourless liquid (13.27 g, 50%), b.p. 83–84 °C at 4 mmHg (lit.,[5] b.p. 138–140 °C at 30 mmHg); δ_H(60 MHz) 2.3 (3 H, s, SMe), 2.7 (2 H, d, *J* 13, CH_2), 3.8 (6 H, d, *J* 10, 2 × OMe). The product was stored in the freezer.

Betaine **2**.—In a separate experiment the solid formed in the preparation of phosphonate **1a** was filtered off and washed with diethyl ether to give the *betaine* as a white solid, m.p. 155–157 °C (Found: C, 27.6; H, 6.75; S, 21.4; P, 11.55. $C_4H_{11}O_3PS$ requires C, 28.23; H, 6.51; S, 18.84; P, 18.20%); *m/z* 170 (M^+).

Synthesis of Alkenyl Sulphides: General Procedure.—Sodium hydride (57% dispersion in oil; 3.52 g, 75 mmol) was washed with dry light petroleum (3 × 20 cm^3) under argon and then dried *in vacuo*. Dry benzene (120 cm^3) was added to the hydride and the suspension was stirred. A solution of the phosphonate (75 mmol) and freshly distilled aldehyde or ketone (75 mmol) in dry benzene (40 cm^3) was added dropwise with cooling, a temperature of *ca.* 20 °C being maintained. After the addition was complete the mixture was stirred for 0.5 h until evolution of hydrogen had ceased. Excess of sodium hydride was then destroyed by the slow addition of methanol (2 cm^3) to the reaction mixture. The resultant solution was poured into cold water (225 cm^3) and the benzene layer was separated. This layer was washed with water (3 × 20 cm^3) and dried ($MgSO_4$). After removal of the drying agent, the benzene was removed under reduced pressure and the residue was distilled to give the alkenyl sulphide. The following compounds were thus prepared.

1-*Methylthiopent*-1-*ene* **3a**. From butyraldehyde and **1a** as a *colourless oil* (17.7%), b.p. 36 °C at 11 mmHg (Found: C, 62.15; H, 10.55; S, 27.2. $C_6H_{12}S$ requires C, 62.01; H, 10.41; S, 27.59%); ν_{max}/cm^{-1} 1618; δ_H(90 MHz) 0.95 (3 H, t, *J* 7, terminal Me), 1.5 (2 H, m, CH_2), 2.1 (2 H, dt, *J* 7, *J'* 7, allylic CH_2), 2.3 (3 H, s, SMe), 5.4 (1 H, dt, *J* 7, *J'* 16, =C*H*CH_2) and 6.05 (1 H, d, *J* 16, MeSCH=).

3-*Methyl*-1-*methylthiobut*-1-*ene* **3b**.[5] From isobutyraldehyde and **1a** as a colourless, strong smelling liquid (40%), b.p. 60 °C at 40 mmHg (lit., b.p. 134–136 °C at 690 mmHg), ν_{max}/cm^{-1} 1600; δ_H(90 MHz) 1.0 (6 H, d, *J* 8, *Me*$_2$CH), 2.2 (3 H, s, SMe), 2.3 (1 H, d sept, *J* 6, *J'* 8, C*H*Me_2), 5.35 (1 H, dd, *J* 6, *J'* 15, =C*H*CH) and 5.95 (1 H, d, *J* 15, MeSC*H*=).

3,3-*Methyl*-1-*methylthiobut*-1-*ene* **3c**. From pivalaldehyde and **1a** as a *colourless oil* (42%), b.p. 64 °C at 30 mmHg (Found: C, 64.35; H, 11.05; S, 24.25. $C_7H_{14}S$ requires C, 64.55; H, 10.83; S, 24.62%); ν_{max}/cm^{-1} 1602; δ_H(90 MHz) 1.1 (9 H, s, Bu^t), 2.25 (3 H, s, MeS), 5.5 (1 H, d, *J* 15, =CH) and 5.95 (1 H, d, *J* 15, MeSC*H*=).

Methylthio-3-*phenylbut*-1-*ene* **3d**. From 2-phenylpropionaldehyde and **1a** as a *colourless oil* (34%), b.p. 78 °C at 2 mmHg (Found: C, 74.45; H, 8.05; S, 17.8. $C_{11}H_{14}S$ requires C, 74.10; H, 7.92; S, 17.98%); ν_{max}/cm^{-1} 1604; δ_H(90 MHz) 1.35 (3 H, d, *J* 7, *Me*CH), 2.25 (3 H, s, MeS), 3.50 (1 H, dq, *J* 7, *J'* 7, CH), 5.55 (1 H, dd, *J* 7, *J'* 15, CHCH=), 6.05 (1 H, d, *J* 15, MeSC*H*=) and 7.30 (5 H, br s, Ph).

Methylenethiomethylcyclohexane **3e**.[5] From cyclohexanone and **1a** as a colourless oil (30%), b.p. 79 °C at 11 mmHg (lit.,[5] b.p. 65–66 °C at 1.5 mmHg); ν_{max}/cm^{-1} 1630; δ_H(90 MHz) 1.5 [6 H, br m, $(CH_2)_3$], 2.1 (4 H, br m, allylic CH_2), 2.2 (3 H, s, MeS), 5.45 (1 H, s, MeSC*H*=).

4-*Methyl*-2-*methylthiopent*-2-*ene* **3f**. From isobutyraldehyde and **1b** as a *colourless oil* (60%) isolated from a SiO_2 column (ether–light petroleum 1:19) (Found: M^+, 130.0814. $C_7H_{14}S$ requires *M*, 130.0816); δ_H(90 MHz) major isomer: 1.0 (6 H, d, *J* 7, *Me*$_2$CH), 1.92 (3 H, d, *J* 1, allylic Me), 2.2 (3 H, s, MeS), 2.65 (1 H, dq, *J* 7, *J'* 7, Me_2CH) and 5.0 (1 H, dq, *J* 1, *J'* 7, CH=); minor isomer: 0.99 (6 H, d, *J* 7, *Me*$_2$CH), 1.98 (3 H, d, *J* 1, allylic Me), 2.22 (3 H, s, MeS), 2.55 (1 H, dq, *J* 7, *J'* 7, Me_2CH) and 5.25 (1 H, dq, *J* 1, *J'* 7, CH=).

4,4-*Dimethyl*-2-*methylselenopent*-2-*ene* **3g**. From pivalaldehyde and **1c**, purified by first SiO_2 column chromatography (ether–light petroleum 1:14) and then distillation, as a colourless, *foul smelling oil* (70%), b.p. 60 °C at 10 mmHg (Found: C, 49.9; H, 8.1. $C_8H_{16}Se$ requires C, 50.3; H, 8.44%); ν_{max}/cm^{-1} 1625; δ_H(270 MHz) 1.15 (9 H, s, Bu^t), 2.11 (3 H, s, allylic Me), 2.15 (3 H, s, MeSe) and 5.55 (1 H, s, CH=).

1-*Methylthio*-4-*tetrahydropyranyloxybut*-1-*ene* **3h**. To a stirred solution of 4-tetrahydropyranyloxybut-1-yne[14] (1.54 g, 10 mmol) and azobisisobutyronitrile (AIBN, 40 mg) under argon was added tributyltin hydride (3.64 g, 12 mmol) by syringe. The mixture was then heated to 95 °C for 3 h after which time more AIBN (16 mg) was added and heating continued for a further 2 h. After this time the crude reaction mixture was distilled in a Kugelrohr apparatus to give the *vinylstannane* as a colourless oil (4.45 g, 89%), ν_{max}/cm^{-1} 1600 and 1032; δ_H(90 MHz) 0.6–2.0 (33 H, m, 3 × Bu and 3 × ring CH_2), 2.35 (2 H, m, allylic CH_2), 3.2–4.0 (4 H, m, 2 × CH_2O), 4.55 (1 H, br s, OCHO) and 5.5–6.6 (2 H, m, vinylic CH). This somewhat unstable substance was used in the next stage as soon as possible. To a stirred solution of the vinylstannane (3.56 g, 8 mmol) in dry THF (tetrahydrofuran) under argon at −78 °C was added dropwise butyllithium (1.4 mol dm^{-3} solution in hexane; 5.6 cm^3, 8 mmol). The solution was then stirred at −78 °C for 2 h before it was warmed to −10 °C and stirred at this temperature for a further 1 h. The solution was cooled to −78 °C and powdered sulphur (0.256 g, 8 mmol) was added. The mixture was allowed to warm slowly to −20 °C at which point the sulphur had dissolved to give a deep orange solution. Iodomethane (1.36 g, 9 mmol) was added and the solution was allowed to warm to room temperature. Distilled water (50 cm^3) was added and the bulk of the THF was removed under reduced pressure. The aqueous residue was extracted with chloroform (3 × 25 cm^3) and the combined extracts were washed with water (3 × 15 cm^3) and dried ($MgSO_4$). After filtration the solvent was removed under reduced pressure and the residue was purified first by SiO_2 chromatography (ether–light petroleum 1:4) and then by Kugelrohr distillation to give the *product* as a colourless oil (0.65 g, 44%), b.p. 145 °C at 0.2 mmHg (Found: M^+, 202.1036. $C_{10}H_{18}O_2S$ requires *M*, 202.1028); ν_{max}/cm^{-1} 1610; δ_H(90 MHz) *trans*-isomer: 1.3–2.0 (6 H, m, 3 × ring CH_2), 2.23 (3 H, s, MeS), 2.43 (2 H, dt, *J* 2, *J'* 7, allylic CH_2), 3.2–4.0 (4 H, m, 2 × CH_2O), 4.58 (1 H, br s, OCHO), 5.44 (1 H, dt, *J* 7, *J'* 15, CH=) and 6.08 (1 H, d, *J* 15, MeSC*H*=); *cis*-isomer: 1.3–2.0 (6 H, m, 3 × ring CH_2), 2.27 (3 H, s, MeS), 2.43 (2 H, dt, *J* 2, *J'* 7, allylic CH_2), 3.2–4.0 (4 H, m, 2 × CH_2O), 4.58 (1 H, br s, OCHO), 5.52 (1 H, dt, *J* 7, *J'* 12, CH=) and 5.98 (1 H, d, *J* 12, MeSC*H*=); *m/z* 202 (M^+), 174, 129, 102, 101, 100, 87 and 85.

The Paterno–Büchi Reaction: General Procedure.—Equimolar quantities of the alkenyl sulphide (0.05–0.15 mol dm^{-3}) and benzophenone (0.05–0.15 mol dm^{-3}) were dissolved in dry benzene (50–80 cm^3) and the solutions were degassed in a standard photolysis apparatus by bubbling dry, deoxygenated nitrogen through them for 0.5 h prior to irradiation. Irradiations were carried out using a 125 W Hanovia medium pressure mercury arc lamp with agitation provided by a stream of dry nitrogen. The solutions were cooled externally by a refrigerated aqueous solution of copper sulphate so as to maintain an internal

temperature of approximately 10 °C. The copper sulphate solution acted as a light filter; for benzophenone a mixture of $CuSO_4 \cdot 5H_2O$ (35 g) and conc. H_2SO_4 (1 cm^3) in 1 dm^3 water in a Pyrex apparatus sufficed; for 3-tetrahydropyranyloxypropanal a mixture of $CuSO_4 \cdot 5H_2O$ (8.5 g) and conc. H_2SO_4 (1 cm^3) in water (1 dm^3) in a quartz apparatus was used. The cut-off points for these two solutions were λ 280 and 265 nm respectively. In this manner the following compounds were prepared.

4-*Butyl*-3-*methylthio*-2,2-*diphenyloxetane* **8a**. From benzophenone (0.05 mol) and alkenyl sulphide **3a** (0.05 mol dm^{-3}) under 6.5 h irradiation. The crude product was purified by alumina column chromatography (ether–light petroleum 1:14) to give the *oxetane* as a white solid (59%), m.p. 29–31 °C (Found: C, 76.2; H, 7.35; S, 10.75. $C_{19}H_{22}OS$ requires C, 76.47; H, 7.43; S, 10.74%); ν_{max}/cm^{-1} 980 (C–O stretch); δ_H(270 MHz) 0.95 (3 H, t, *J* 6, Me), 1.43 (2 H, m, CH_2), 1.75 (2 H, m, CH_2), 1.94 (3 H, s, MeS), 4.11 (1 H, d, *J* 7, MeSC*H*), 4.67 (1 H, dt, *J* 7, *J'* 7, CHO) and 7.2–7.52 (10 H, m, 2 × Ph); *m*/*z* 297 ($M^+ - 1$), 226 (retrocycloaddition), 211, 183, 116 (retrocycloaddition, 100%) and 87. Also isolated from the column was 3-*butyl*-4-*methylthio*-2,2-*diphenylthiooxetane* **9a** as a colourless gum (4.5%), δ_H(90 MHz) 0.84 (3 H, t, *J* 7, Me), 1.0–1.6 (4 H, m, 2 × CH_2), 2.04 (3 H, s, MeS), 3.64 (1 H, m, C*H*Bu), 5.50 (1 H, d, *J* 7, SCHO) and 7.1–7.6 (10 H, m, 2 × Ph).

4-*Isopropyl*-3-*methylthio*-2,2-*diphenyloxetane* **8b**. From benzophenone (0.15 mol dm^{-3}) and alkenyl sulphide (0.15 mol dm^{-3}) under 22 h irradiation. The crude product was purified by SiO_2 column chromatography (ether–light petroleum 1:4) to give the *oxetane* as a white solid (79%), m.p. 54–58 °C (Found: C, 76.4; H, 7.5; S, 10.7. $C_{19}H_{22}OS$ requires C, 76.47; H, 7.43; S, 10.74%); ν_{max}/cm^{-1} 980 (C–O stretch); δ_H(90 MHz) 0.86 (3 H, d, *J* 7, *Me*CH), 0.98 (3 H, d, *J* 7, *Me*CH), 1.84 (1 H, dq, *J* 7, *J'* 7, Me_2CH), 1.90 (3 H, s, MeS), 4.08 (1 H, d, *J* 7, MeSC*H*), 4.32 (1 H, dd, *J* 7, *J'* 12, CHO) and 7.1–7.6 (10 H, m, 2 × Ph); *m*/*z* 251 ($M^+ - 47$), 230, 226 (retrocycloaddition), 183, 116 (retrocycloaddition, 100%) and 101.

4-tert-*Butyl*-3-*methylthio*-2,2-*diphenyloxetane* **8c**. From benzophenone (0.1 mol dm^{-3}) and the alkenyl sulphide (0.1 mol dm^{-3}) under 10 h irradiation. The crude product was purified by SiO_2 column chromatography (ether–light petroleum 1:19) to give the *oxetane* as a white solid (52%), m.p. 59–63 °C (Found: C, 76.75; H, 7.85; S, 10.2. $C_{20}H_{24}OS$ requires C, 76.88; H, 7.74; S, 10.23%); ν_{max}/cm^{-1} 958 (C–O stretch); δ_H(270 MHz) 0.90 (9 H, s, Bu^t), 1.90 (3 H, s, MeS), 4.17 (1 H, d, *J* 7, MeSC*H*), 4.38 (1 H, d, *J* 7, CHO) and 7.1–7.5 (10 H, m, 2 × Ph); *m*/*z* 297 ($M^+ - 15$), 226 (retrocycloaddition), 182, 130 (retrocycloaddition, 100%), 115, 83 and 82. Also isolated from the column was 3-tert-*butyl*-4-*methylthio*-2,2-*diphenyloxetane* **9c** as a gum (6%), ν_{max}/cm^{-1} 960 (C–O stretch); δ_H(90 MHz) 0.78 (9 H, s, Bu^t), 1.96 (3 H, s, MeS), 3.59 (1 H, d, *J* 7, Bu^{t}C*H*), 5.80 (1 H, d, *J* 7, SCHO) and 7.1–7.6 (10 H, m, 2 × Ph); *m*/*z* 313 ($M^+ + 1$), 265, 236 (retrocycloaddition), 209, 130, 115 and 82.

3-*Methylthio*-2,2-*diphenyl*-4-(1'-*phenylethyl*)*oxetane* **8d**. From benzophenone (0.1 mol dm^{-3}) and the alkenyl sulphide (0.1 mol dm^{-3}) under 41 h irradiation. The crude product was purified by alumina column chromatography (ether–light petroleum 1:12) to give the *oxetane* as a white solid (36%), m.p. 60–68 °C (Found: C, 79.35; H, 6.8; S, 8.6. $C_{24}H_{24}OS$ requires C, 79.96; H, 6.71; S, 8.89%); ν_{max}/cm^{-1} 980 (C–O stretch); δ_H(270 MHz) one diastereoisomer: 1.20 (3 H, s, MeS), 1.40 (3 H, d, *J* 7, *Me*CH), 2.90 (1 H, dq, *J* 7, *J'* 9, C*H*Ph), 4.01 (1 H, d, *J* 7, MeSC*H*), 4.67 (1 H; dd, *J* 7, *J'* 9, CHO) and 7.1–7.55 (10 H, m, 2 × Ph); other diastereoisomer: 1.26 (3 H, d, *J* 7, *Me*CH), 1.80 (3 H, s, MeS), 3.03 (1 H, dq, *J* 7, *J'* 7, C*H*Ph), 4.11 (1 H, d, *J* 7, MeSC*H*), 4.70 (1 H, dd, *J* 7, *J'* 7, CHO) and 7.1–7.55 (10 H, m, 2 × Ph); *m*/*z* 226 (retrocycloaddition), 178 (retrocycloaddition), 163, 131, 130, 115, 105, 91 and 77.

3'-*Methylthio*-4',4'-*diphenylspiro*(*cyclohexane*-1,2'-*oxetane*) **8e**. From benzophenone (0.05 mol dm^{-3}) and the alkenyl sulphide (0.05 mol dm^{-3}) under 10.5 irradiation. The crude product was purified by SiO_2 column chromatography (ether–light petroleum 1:9) to give the *oxetane* as a gum which slowly crystallised to a white solid (12%), m.p. 57–59 °C (Found: M^+, 324.1540. $C_{21}H_{24}OS$ requires *M*, 324.1548); δ_H(270 MHz) 0.8–1.9 (10 H, m, 5 × CH_2), 2.08 (3 H, s, MeS), 4.10 (1 H, s, MeSC*H*) and 7.13–7.67 (10 H, m, 2 × Ph); *m*/*z* 324 (M^+), 277, 226 (retrocycloaddition), 178, 165, 142 (retrocycloaddition, 100%), 127, 116, 105 and 95. Also isolated from the column was the regioisomer, 2'-*methylthio*-4',4'-*diphenylspiro*(*cyclohexane*-1,3'-*oxetane*) **9e** as a colourless gum (15%) (Found: M^+, 324.1537. $C_{21}H_{24}OS$ requires *M*, 324.1548); δ_H(270 MHz) 0.8–1.9 (10 H, m, 5 × CH_2), 2.30 (3 H, s, MeS), 5.47 (1 H, s, SCHO), 7.13–7.67 (10 H, m, 2 × Ph); *m*/*z* 323 ($M^+ - 1$), 277, 259, 248 (retrocycloaddition).

4-*Isopropyl*-3-*methyl*-3-*methylthio*-2,2-*diphenyloxetane* **8f**. From benzophenone (0.05 mol dm^{-3}) and the alkenyl sulphide (0.05 mol dm^{-3}) under 3 h irradiation. The crude product was purified by SiO_2 column chromatography (ether–light petroleum 1:19) to give the *oxetane* as a white solid (60%), m.p. 59–67 °C (Found: C, 77.0; H, 7.8; S, 10.3. $C_{20}H_{24}OS$ requires C, 76.88; H, 7.74; S, 10.26%); δ_H(270 MHz) major stereoisomer: 0.85 (3 H, d, *J* 6, *Me*MeCH), 1.11 (3 H, d, *J* 6, Me*Me*CH), 1.39 (3 H, s, Me), 1.68 (3 H, s, MeS), 1.99 (1 H, m, Me_2CH), 4.21 (1 H, d, *J* 10, OCH), 7.1–7.82 (10 H, m, 2 × Ph); minor stereoisomer: 0.86 (3 H, d, *J* 6, *Me*MeCH), 1.13 (3 H, d, *J* 6, Me*Me*CH), 1.44 (3 H, s, Me), 1.86 (3 H, s, MeS), 2.27 (1 H, m, Me_2CH), 3.96 (1 H, d, *J* 10, OCH) and 7.1–7.82 (10 H, m, 2 × Ph); both stereoisomers: *m*/*z* 311 ($M^+ - 1$), 266, 240 (retrocycloaddition), 226, 221, 213, 183, 178, 167, 154, 143, 130 (retrocycloaddition, 100%), 115 and 99.

4-tert-*Butyl*-3-*methyl*-3-*methylseleno*-2,2-*diphenyloxetane* **8g**. From benzophenone (0.05 mol dm^{-3}) and the alkenyl selenide (0.05 mol dm^{-3}) under 12.5 h irradiation. The crude product was purified by SiO_2 column chromatography (ether–light petroleum 1:34) to give the *oxetane* as a white solid (45%), m.p. 58–60 °C (Found: M^+ – Bu^{t}CHO, 288.0420. $C_{21}H_{26}OSe$ – Bu^{t}CHO requires *M*, 288.0417); δ_H(90 MHz) 1.08 (9 H, s, Bu^t), 1.57 (3 H, s, Me), 1.58 (3 H, s, MeSe), 4.53 (1 H, s, CHO) and 7.1–7.9 (10 H, m, 2 × Ph); *m*/*z* 288 (retrocycloaddition), 258, 221, 192 (retrocycloaddition, 100%), 188, 177, 173, 115, 105 and 97.

3-*Methylthio*-2,2-*diphenyl*-4-(2'-*tetrahydropyranyloxyethyl*)-*oxetane* **8h**. From benzophenone (0.05 mol dm^{-3}) and the alkenyl sulphide (0.05 mol dm^{-3}) under 9 h irradiation. The crude product was purified by SiO_2 column chromatography (ether–light petroleum 1:4) to give the *oxetane* as a colourless gum (24%); ν_{max}/cm^{-1} 1035; δ_H(90 MHz) one diastereoisomer: 1.3–2.0 (6 H, m, 3 × CH_2), 1.93 (3 H, s, MeS), 2.0 (2 H, dt, *J* 7, *J'* 7, CH_2CHO), 3.3–4.0 (4 H, m, 2 × CH_2O), 4.30 (1 H, d, *J* 7, MeSC*H*), 4.60 (1 H, br s, OCHO), 4.83 (1 H, dt, *J* 7, *J'* 7, CHO) and 7.0–7.6 (10 H, m, 2 × Ph); other diastereoisomer: 1.3–2.0 (6 H, m, 3 × CH_2), 1.94 (3 H, s, MeS), 1.99 (2 H, dt, *J* 7, *J'* 7, CH_2CHO), 3.3–4.0 (4 H, m, 2 × CH_2O), 4.26 (1 H, d, *J* 7, MeSC*H*), 4.40 (1 H, br s, OCHO), 4.85 (1 H, dt, *J* 7, *J'* 7, CHO) and 7.0–7.6 (10 H, m, 2 × Ph).

4-*Hydroxy*-3-*methylthio*-2,2-*diphenylpyran* **12**.—To a solution of the oxetane **8h** (0.217 g, 0.6 mmol) in methanol was added Amberlyst-15H resin in the H^+-form (0.3 g) and the solution was stirred for 3 h at room temperature. The resin was then filtered off and the methanol removed under reduced pressure. The residue was chromatographed on SiO_2 (ether–light petroleum 1:1) to give the *pyran* as a white solid (62%), m.p. 163–166 °C (Found: C, 70.15; H, 6.6; S, 10.45; M^+, 300.1178. $C_{18}H_{20}O_2S$ requires C, 71.97; H, 6.71; S, 10.67%; *M*, 300.1184); ν_{max}/cm^{-1} 3358 (OH stretch); δ_H(90 MHz) 1.4–1.9 (2 H, m, CH_2), 1.64 (3 H, s, MeS), 2.93 (1 H, d, *J* 12,

MeSC*H*), 3.3–4.0 (4 H, m, CH_2O and C*HOH*) and 6.9–7.7 (10 H, m, 2 × Ph); *m/z* 300 (M^+), 183, 167, 152, 134, 118, 115, 105, 103 and 100.

2-tert-*Butyl*-3-*methylthio*-4-(2′-*tetrahydropyranyloxyethyl*)-*oxetane* **11**.—A solution of 3-tetrahydropyranyloxypropanal (0.395 g, 2.5 mmol) and 3,3-dimethyl-1-methylthiobut-1-ene (0.326 g, 2.5 mmol) in dry acetonitrile (50 cm^3) was irradiated in a quartz apparatus with an aqueous copper sulphate filter (see General Procedure) for 12 h. The solvent was evaporated under reduced pressure and the residue was chromatographed on SiO_2 (ether–light petroleum 1:2) to give the *oxetane* as a yellow oil (22%) (Found: M^+, 288.1750. $C_{15}H_{28}O_3S$ requires *M*, 288.1759); ν_{max}/cm^{-1} 978; δ_H(90 MHz) 0.93 (9 H, s, Bu^t), 1.3–2.0 (8 H, m, 4 × CH_2), 2.13 (3 H, s, MeS), 3.29 (1 H, dd, *J* 7, *J*′ 7, MeSC*H*), 3.3–4.05 (4 H, m, 2 × CH_2O), 4.21 (1 H, d, *J* 7, Bu^{t}C*HO*), 4.57 (1 H, br s, OCHO) and 4.60 (1 H, dt, *J* 7, *J*′ 7, CH_2C*HO*); *m/z* 287 ($M^+ - 1$), 241, 202 (retrocycloaddition), 158 (retrocycloaddition), 130 and 85.

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