Synthesis of Alkenyl Sulphoxides by Intramolecular and Intermolecular Addition of Sulphenic Acids to Alkynes

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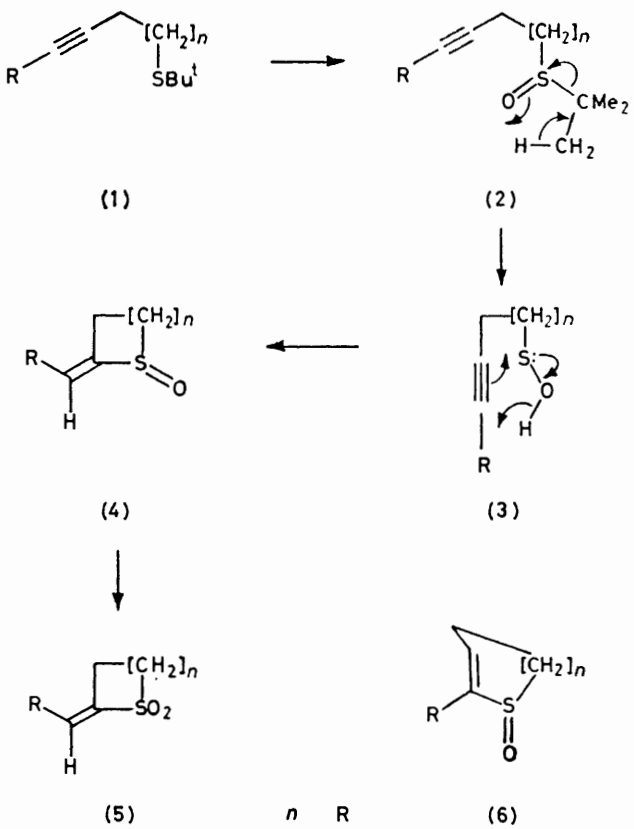
Alkyne-ω-sulphenic acids formed by thermolysis of ω-(t-butylsulphinyl)alkynes at 140 °C cyclized regiospecifically to 2-methylenethiacycloalkane 1-oxides; 2-methylenethietan 1-oxide was not formed in this way. 2-Methylpropane-2-sulphenic acid, obtained by heating di-t-butyl sulphoxide, added regioselectively to oct-1-yne to give predominantly 2-t-butylsulphinyloct-1-ene, which itself decomposed thermally to a mixture of dioctenyl sulphoxides by way of alkenesulphenic acid–dialkyl sulphine interconversions. Benzenesulphenic acid, methanesulphenic acid, and ethoxycarbonylmethanesulphenic acid, conveniently generated by thermolysis of 1-cyano-2-alkyl(or aryl)sulphinylethanes, underwent intermolecular addition to unactivated and activated alkynes regioselectively to give alkenyl sulphoxides in good yields.

ALKENYL sulphoxides are useful synthetic intermediates, particularly by virtue of their reactivity as dienophiles [1] and Michael acceptors.[2] They have also been converted into lithioalkenyl sulphoxides,[3] allylic sulphoxides,[4] alkenyl sulphides,[5] and chloroalkyl sulphides,[6] and into allenes [3,7] and enamines.[8] The methods usually employed for the preparation of alkenyl sulphoxides include the oxidation of alkenyl sulphides,[9] the elimination of a suitable group from β-substituted sulphoxides,[10] the reactions of anions of α-silyl and α-phosphoryl sulphoxides with aldehydes and ketones,[11] and the reaction of alkenyl Grignard reagents with sulphinate esters.[12] The limitations of these methods are related to their incompatibility with the presence of many common functional groups, and to their lack of stereospecificity and regiospecificity. In a quest for a more general and convenient method for the preparation of alkenyl sulphoxides we turned our attention to the addition of sulphenic acids to alkynes. When we started, it was known that sulphenic acids added efficiently to activated alkynes such as dimethyl but-2-yne-1,4-dioate,[13] methyl propiolate,[14-16] and ethynylbenzene.[15,16] Stereospecific *syn* addition was attributed to a concerted mechanism (Scheme 1) [15] and the observed regiospecificity was interpreted in terms of some charge separation in the cyclic transition state (*A*).† However, simple alkynes were considered to be unreactive,[15,16] despite a brief mention of the addition of ethanesulphenic acid to hept-1-yne in low yield.[16] After our work was completed another example appeared in penicillin chemistry.[17]



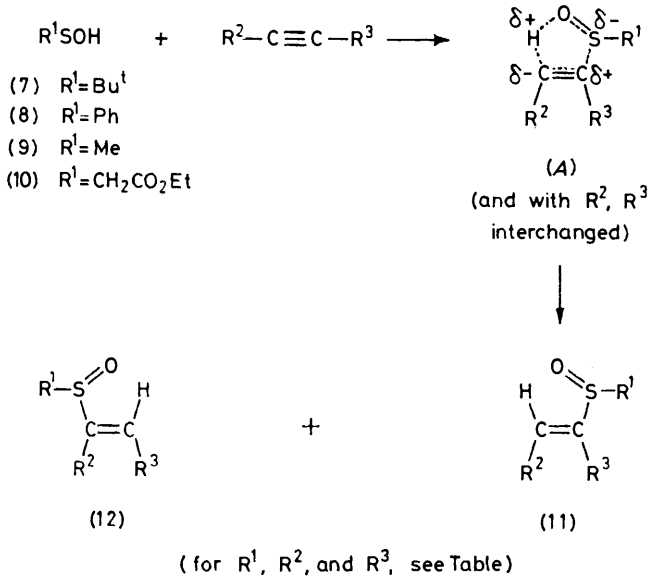
	n	R
a;	1	H
b;	2	H
c;	3	H
d;	4	H
e;	2	Me

As an initial test of the feasibility of the addition of sulphenic acids to unactivated alkynes we investigated the intramolecular additions of the sulphenic acids (3a—d) in the expectation that they would be facilitated by entropic factors. Analogous intramolecular additions of sulphenic acids to alkenes take place efficiently.[18] The sulphenic acids (3a—d) were generated by thermolysis of the ω-(t-butylsulphinyl)alkynes (2a—d) which were chosen because statistical and other factors, which have been discussed previously,[18] were expected to optimise β-elimination to give the required sulphenic acids and 2-methylpropene, and not 2-methylpropane-2-sulphenic acid and the associated enynes. Like most other sulphenic acids the compounds (3a—d) were too unstable to be isolated.[15,16,18] The sulphoxides (2a—d) were

† We accept this interpretation as no more than a working hypothesis since a rigorous investigation of the mechanism has not been performed. However, the stereospecificity and regioselectivity of all known additions of sulphenic acids to alkynes, including those in this work, are entirely in accord with the predictions of this hypothesis.

prepared by oxidation of the corresponding sulphides (1a—d) which were made by conventional methods (see Experimental section).

Thermolysis of 5-t-butylsulphinylpent-1-yne (2b), 6-t-butylsulphinylhex-1-yne (2c), and 7-t-butylsulphinylhept-1-yne (2d) separately in boiling xylene (140 °C) for 2.5 h gave respectively 2-methylenethiolan 1-oxide (4b)



SCHEME 1

(80%), 2-methylenethian 1-oxide (4c) (88%), and 2-methylenethiepan 1-oxide (4d) (53%). These were oxidised to the corresponding sulphones (5b—d) by peroxydodecanoic acid. The structures of the cyclic sulphoxides (4b—d) and sulphones (5b—d) were revealed by the n.m.r. characteristics of their vinyl protons, between which a geminal relationship was indicated by the absence of appreciable spin–spin coupling. The allocation of the signal at lower field in each compound to the vinyl proton *cis* to sulphoxide [19] or sulphone [20] was substantiated for the sulphoxides by ASIS experiments.[21] Models of the sulphoxide-deuteriobenzene complexes indicated that the *trans* protons should suffer the greater upfield shift. This accorded with experimental observation.

The regioselectivity of cyclization of the sulphenic acids (3b—d) is rational in terms of the concerted mechanism of addition of sulphenic acids to alkynes, since cyclic transition states connecting (3b—d) with (4b—d) respectively are relatively strain free according to models, whereas those leading to the highly strained endocyclic *trans*-alkenyl sulphoxides (6b—d) are clearly very unfavourable. These geometrical considerations are undoubtedly reinforced by the electronic factors which direct the addition of sulphenic acids to alk-1-ynes in a Markownikoff manner (see later). However, since thermolysis of 6-t-butylsulphinylhex-2-yne (2e) in boiling xylene gave only (*E*)-2-ethylidenethiolan 1-oxide (4e) (87%), in perfect accord with the requirements of a cyclic transition state for the intramolecular addition of the sulphenic acid (3e), it appears that a propensity for Markownikoff addition alone does not account for the observed stereoselectivity of cyclization of the sulphenic acids (3b—d).

The structures of (*E*)-2-ethylidenethiolan 1-oxide (4e) and the sulphone (5e) derived by peroxyacid oxidation were deduced from their n.m.r. spectra. These showed doublets for the methyl groups, and signals due to vinyl protons at δ 6.45 and 6.44 respectively in (4e) and

Alkenyl sulphoxides formed by addition of sulphenic acids to alkynes

				Products [a]		Reaction conditions	
	R¹	R²	R³	(11)	(12)	*T*/°C	*t*/h
a	Bu^t	H	$[CH_2]_5CH_3$	60 [b]	2	80	2.5
b	Ph	H	$[CH_2]_5CH_3$	94	0	126	0.5
c	Me	H	$[CH_2]_5CH_3$	86	3	126	9
d	CH_2CO_2Et	H	$[CH_2]_5CH_3$	83	0.5	126	1
e	Ph	H	CH_2OH	82	3	114	2
f	Me	H	CH_2OH	75	9	114	24
g	Ph	H	$CH(OH)CH_3$	85	0	107	3
h	Ph	H	$CH(OH)[CH_2]_4CH_3$	91	0	126	0.5
i	Me	H	$CH(OH)[CH_2]_4CH_3$	76	13	126	4
j	Ph	H	CH_2SCH_3	52	0	109	2
k	Me	H	CH_2SCH_3	50	0	109	4
l	Ph	H	$CH(OEt)_2$	81	0	110	2
m	Ph	H		91	0	126	0.5
n	Ph	H		94	0	126	0.5
o	Me	H		74	18	126	1.5
p	Ph	Br	$[CH_2]_3CH_3$	94	0	126	0.5
q	Ph	CO_2Me	$[CH_2]_3CH_3$	90	0	126	0.7
r	Me	CO_2Me	$[CH_2]_3CH_3$	81	0	126	1.5
s	Ph	CH_2OH	$[CH_2]_5CH_3$	53	8 [c]	120	3
t	Ph	$CH(OEt)_2$	$[CH_2]_5CH_3$	85	0	140	2.5
u	Ph	H	CH_2Br	36 [d]	0	90	12

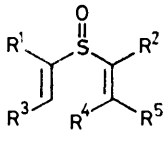
[a] Yield % of isolated products. [b] Together with (13) (10%) and recovered di-t-butyl sulphoxide (47%). [c] Not isolated pure. Yield estimated from n.m.r. data. [d] Together with (11e) (11%) and (22) (11%).

(5e) which were in better agreement with the calculated values for the (*E*)-isomers (δ 6.38 and 6.40) than for the (*Z*)-isomers (δ 6.22 and 6.23).[20,22] Corroborative evidence for the (*E*)-configuration was obtained by an ASIS experiment, in which the incremental shielding of the methyl group in the sulphoxide (4e) was greater than that for the vinyl proton.

Thermolysis of 4-t-butylsulphinylbut-1-yne (2a) in boiling xylene for 2.5 h gave an intractable tarry mixture of many products among which no 2-methylenethietan 1-oxide (4a) was detected. The use of shorter reaction times or lower temperatures failed to produce any cyclic sulphoxide (4a). Models indicate that considerable distortion of normal bond angles pertains in a cyclic transition state connecting but-1-yne-4-sulphenic acid (3a) with 2-methylenethietan 1-oxide (4a), so that if (3a) were formed this intramolecular process would be retarded, and the corresponding intermolecular process leading to polymeric alkenyl sulphoxides would become more important. Furthermore, other complex intermolecular reactions (typical of sulphenic acids)[16] of (3a) and 2-methylpropane-2-sulphenic acid[23] to give thiosulphinates, thiosulphonates, disulphides, and thiocarbonyl compounds would further contribute to the multiplicity of products. It is not unreasonable to expect 4-t-butylsulphinylbut-1-yne (2a) to decompose to a significant extent to 2-methylpropane-2-sulphenic acid and but-1-en-3-yne, since conjugation in the latter should provide a driving force which opposes the factors which usually favour the elimination of 2-methylpropene from alkyl t-butyl sulphoxides. It may be noted that 4-t-butylsulphinylbut-1-ene does cyclize, albeit in low yield, to *cis*-2-methylthietan 1-oxide.[18]

Having established that intramolecular additions of sulphenic acids to unactivated alkynes occurred readily, we next examined the scope of intermolecular reactions. Thermolysis of di-t-butyl sulphoxide in oct-1-yne at 80 °C for 2.5 h gave 2-t-butylsulphinyloct-1-ene (11a) (61%), 1-t-butylsulphinyloct-1-ene (12a) (4%), and a mixture of chromatographically identical dioctenyl sulphoxides (13) [mainly (13a), (13d), and (13e) (10% combined yield)], together with recovered di-t-butyl sulphoxide (47%). More di-t-butyl sulphoxide was consumed after longer reaction times, or when higher temperatures were employed, but these conditions led to lower yields of alkenyl sulphoxides (11a) and (12a), whilst the yield of dioctenyl sulphoxides (13) increased. The appearance of a pair of triplets at δ 5.63 (*J* 0.5 Hz) and δ 5.29 (*J* 1.5 Hz) in the n.m.r. spectrum of (11a) was consistent with the presence of the geminal protons respectively *cis* and *trans* to the sulphinyl group, both of which were subject to allylic ^4J coupling. In the n.m.r. spectrum of 1-t-butylsulphinyloct-1-ene (12a) the presence of a doublet of triplets at δ 6.46 (*J* 15 and 7 Hz) attributable to the vinyl proton at C-2, and a doublet of triplets at δ 5.84 (*J* 15 and 1.5 Hz) due to the vinyl proton at C-1 revealed the constitution and configuration of the compound. That a mixture of dioctenyl sulphoxides (13) was formed was indicated by a complex system of overlapping signals due to vinyl protons between δ 6.24 and 5.30, in which triplets at δ 6.09 (*J* 0.5 Hz), 5.95 (*J* 0.5 Hz), 5.41 (*J* 1.5 Hz), and 5.32 (*J* 1.5 Hz) were prominent, and by singlets attributable to alkenyl methyl groups at δ 1.74 and 1.57.

The formation of 2-t-butylsulphinyloct-1-ene (11a)

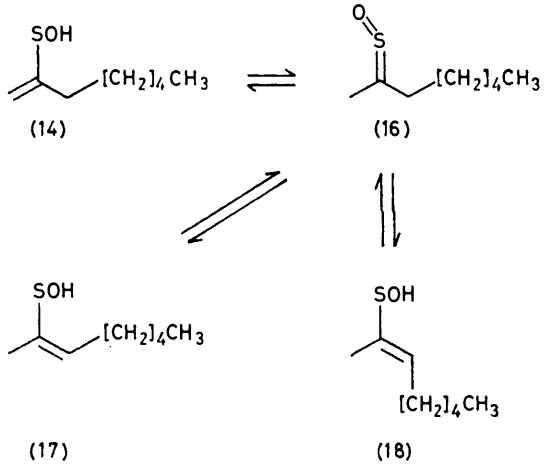


(13)

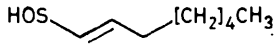
	R^1	R^2	R^3	R^4	R^5
a;	hex	hex	H	H	H
b;	hex	H	H	H	hex
c;	H	H	hex	H	hex
d;	hex	Me	H	H	pent
e;	hex	Me	H	pent	H
f;	H	Me	hex	H	pent
g;	H	Me	hex	pent	H

(hex = $[CH_2]_5CH_3$; pent = $[CH_2]_4CH_3$)

and its isomer (12a) was consistent with initial decomposition of di-t-butyl sulphoxide into 2-methylpropane-2-sulphenic acid (7)[15] which subsequently added to oct-1-yne. The regioselectivity of addition was that expected if the transition state were polarized in the manner proposed previously [(*A*) in Scheme 1].[15] The formation of a mixture of dioctenyl sulphoxides (13) may



(14) (16) (17) (18)

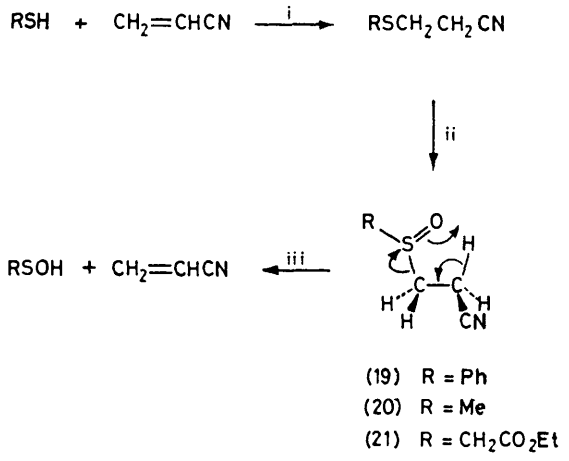


(15)

be rationalized in the following manner. Thermolytic decomposition of the t-butyl octenyl sulphoxides (11a) and (12a) furnished the unsaturated sulphenic acids (14) and (15), which added to oct-1-yne to give the dioctenyl sulphoxides (13a—c), among which (13a) predominated because of the initial predominance of (11a) and because of the propensity of sulphenic acids to add to alk-1-ynes in a Markownikoff manner. The

formation of the isomers (13d—g) was attributed to the rearrangement of oct-1-ene-2-sulphenic acid (14) by way of the sulphine (16) to the (*Z*)- and (*E*)-isomers of oct-2-ene-2-sulphenic acid (17) and (18), which subsequently added to oct-1-yne to give mainly (13d) and (13e) together with some (13f) and (13g). Interconversion of alkenylsulphenic acids and dialkyl sulphines has been demonstrated in other cases.[24] This interpretation was substantiated by the fact that heating 2-t-butylsulphinyloct-1-ene (11a) in oct-1-yne at 126 °C for 10 min gave a mixture of dioctenyl sulphoxides, considered to be (13a), (13d), and (13e) (67% combined yield), which was virtually identical spectroscopically (n.m.r., i.r.) with that obtained from heating di-t-butyl sulphoxide with oct-1-yne.

Benzenesulphenic acid (8), methanesulphenic acid (9), and ethoxycarbonylmethanesulphenic acid (10) were

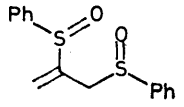


SCHEME 2 *Reagents:* i, NaOMe or NaOEt or $PhCH_2\overset{+}{N}Me_3HO^-$; ii, $NaIO_4$ or $C_{11}H_{23}CO_3H$; iii, heat

more suitable for the formation of stable alkenyl sulphoxides since they contained no β-hydrogens capable of participating in a further sulphoxide elimination.[25] They were generated by thermolysis of the appropriate 1-cyano-2-aryl(or alkyl)sulphinylethanes (19)—(21) (Scheme 2) which were chosen because thermolytic decomposition of sulphoxides is markedly facilitated by the activation of a β-hydrogen by an electron-withdrawing group.[15] The precursors (19)—(21) were readily prepared by base-catalysed addition of benzenethiol or the appropriate alkanethiol to acrylonitrile, followed by oxidation with sodium metaperiodate or peroxydodecanoic acid (Scheme 2). For ease of preparation, long shelf-life, rapid and clean thermal decomposition, and applicability to both aromatic and aliphatic sulphenic acids these precursors compare favourably with alkyl and aryl t-butyl sulphoxides,[15] alkyl thiosulphinates,[16] *N*-alkylidenearene-sulphinamides,[26] and 4-benzenesulphinyl-4-methylpentan-2-one,[27] thermolysis of which also gives sulphenic acids.

Heating the compounds (19)—(21) in various alkynes gave alkenyl sulphoxides (Table) generally in good yield except for 3-bromopropyne, which is discussed later. The efficiency of addition was reasonably insensitive to the presence of hydroxy, acetal, ester, and ethylenic groups in the alkyne. Yields were also satisfactory when a cyanosulphoxide [(19), (20), or (21)] and an alkyne in the molar ratio 1 : 2 were heated in an excess of toluene or xylene. The constitutions and configurations of the alkenyl sulphoxides were deduced from their n.m.r. spectra in a manner similar to that described earlier for alkenyl t-butyl sulphoxides. The regioselectivity of addition was rational in terms of the proposed polarization of the transition state and the relative inductive effects of the groups R^2 and R^3 [see (*A*) in Scheme 1]. Addition occurred predominantly in the Markownikoff manner with alk-1-ynes (Table), whilst bromo, ethoxycarbonyl, hydroxymethyl, and diethoxymethyl substituents at C-1 directed addition of the sulphinyl group towards C-2 (entries p—t; compare in particular entries e and s; and l and t) in accord with the greater electron withdrawal by these groups (σ* values) than alkyl groups.[28] The greater regioselectivity of addition of benzenesulphenic acid than methanesulphenic and 2-methylpropane-2-sulphenic acid to the alk-1-ynes may be due to greater stabilization by phenyl than alkyl groups of the polarized transition state (*A*), an interpretation which must be regarded with caution in view of the paucity of evidence concerning the detailed mechanism of the reaction. However, there is some analogy in the rationale offered for the faster thermal β-elimination of phenyl than methyl sulphoxides.[29]

The addition of benzenesulphenic acid to 3-bromopropyne was attended by hydrolysis and displacement to give the expected 3-bromo-2-phenylsulphinylprop-1-ene (11u) (36%), together with 3-hydroxy-2-phenylsulphinylprop-1-ene (11e) (11%), and 2,3-bis(phenylsulphinyl)prop-1-ene (22) (11%). The water for hydrolysis presumably arose from some intermolecular dehydration of benzenesulphenic acid to give phenylthiosulphinate.[15] In boiling wet acetone 3-bromo-2-phenylsulphinylprop-1-ene (11u) was hydrolysed quantitatively



(22)

to the hydroxy-compound (11e). The disulphoxide (22) probably arose by reaction of the bromide (11u) with benzenesulphenic acid, since thermolysis of 1-cyano-2-phenylsulphinylethane (19) in a boiling benzene solution of the bromide (11u) over molecular sieves gave the disulphoxide (22) (49%). The direct conversion of an allylic bromide into an allylic sulphoxide is unprecedented, and its mechanism remains to be established.

It is clear that, contrary to previous opinion,[15,16] alkynes need not be conjugated with activating groups in order to undergo efficient and regioselective addition to

sulphenic acids. The ready accessibility by this method of alkenyl sulphoxides bearing a variety of functional groups will hopefully facilitate the exploitation of these compounds for synthetic purposes.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were determined with either a Perkin-Elmer 457 or 180 spectrophotometer for chloroform solutions unless otherwise indicated, mass spectra with an A.E.I. MS902 or MS12 instrument, and n.m.r. spectra with a Varian HA-100 or a Perkin-Elmer R34 spectrometer for solutions in deuteriochloroform, unless otherwise indicated. Chromatography refers to separation on columns of alumina (Camag, neutral) or silica (Hopkin and Williams MFC) unless otherwise specified. Preparative t.l.c. was performed with silica gel G (Merck). Light petroleum refers to the fraction of b.p. 40—60 °C.

Poor combustion analytical data were obtained for some of the sulphoxides because they were very hygroscopic. Satisfactory data were obtained for sulphones derived by oxidation of the sulphoxides. Alkynes were prepared by established methods.[30]

Preparation of the Sulphides (1a—d).—(*a*) Methanesulphonyl chloride (22.5 ml, 0.29 mol) was added slowly to a stirred solution of but-3-yn-1-ol (10.0 g, 0.139 mol) in pyridine (90 ml) keeping the temperature below 10 °C. After 1 h at room temperature the solution was poured onto ice. An ethereal work-up gave the oily *but-3-ynyl methanesulphonate* (16.9 g, 80%), $\nu_{max.}$ 1 360 and 1 168 (SO_2O), 3 302 and 2 122 cm^{-1} (HC≡C), δ 4.28 (2 H, t, *J* 6.5 Hz, CH_2OSO_2), 3.03 (3 H, s, CH_3SO_2O), 2.65 (2 H, d of t, *J* 6.5 and 2.5 Hz, $CH_2C{\equiv}C$), and 2.07 (1 H, t, *J* 2.5 Hz, HC≡C) (Found: C, 40.4; H, 5.6; S, 21.8. $C_5H_3O_3S$ requires C, 40.5; H, 5.4; S, 21.6%). The methanesulphonate (22.0 g, 0.149 mol) was added to a solution of 2-methylpropane-2-thiol (25.1 ml, 0.218 mol) and sodium isopropoxide [from sodium (5.13 g, 0.223 mol)] in propan-2-ol (374 ml). After boiling for 10 min under nitrogen the solution was poured onto ice and extracted with ether (4 × 500 ml). The combined extract was washed with 5% aqueous KOH solution, then with water, and dried (Na_2SO_4). Evaporation of the ether and distillation of the residue afforded *4-t-butylthiobut-1-yne* (1a) (18.7 g, 88%), b.p. 162—168 °C at 756 mmHg, $\nu_{max.}$ (liquid film) 3 300 and 2 113 cm^{-1} (HC≡C), δ 2.30—2.85 (4 H, m, CH_2S and $CH_2C{\equiv}C$), 2.00 (1 H, t, *J* 2.5 Hz, HC≡C), and 1.33 (9 H, s, Me_3CS), *m/e* 142 (Found: C, 67.7; H, 9.9; S, 22.4. $C_8H_{14}S$ requires C, 67.5; H, 9.9; S, 22.5%).

(*b*) Treatment of pent-4-yn-1-ol in the above manner gave *pent-4-ynyl methanesulphonate* (77%) as an oil, $\nu_{max.}$ 1 358 and 1 163 (SO_2O), 3 300 and 2 212 cm^{-1} (HC≡C), δ 4.33 (2 H, t, *J* 5 Hz, CH_2OSO_2), 3.01 (3 H, s, CH_3SO_2O), 2.36 (2 H, m, $CH_2C{\equiv}C$), and 1.99 (3 H, m, HC≡C and 4-CH_2) (Found: C, 44.5; H, 6.2; S, 20.0. $C_6H_{10}O_3S$ requires C, 44.4; H, 6.2; S, 19.8%), and then *5-t-butylthiopent-1-yne* (1b) (82%), b.p. 84—86 °C at 18 mmHg, $\nu_{max.}$ 3 295 and 2 120 cm^{-1} (HC≡C), δ 2.64 (2 H, t, *J* 7.5 Hz, CH_2S), 2.31 (2 H, m, $CH_2C{\equiv}C$), 1.94 (1 H, t, *J* 2.5 Hz, HC≡C), 1.77 (2 H, t, *J* 6 Hz, 4-CH_2), and 1.32 (9 H, s, Me_3CS) (Found: C, 68.8; H, 10.1; S, 20.6. $C_9H_{16}S$ requires C, 69.2; H, 10.3; S, 20.5%).

(*c*) Hex-5-yn-1-ol (9.9 g) was converted into its oily *methanesulphonate* (17.3 g, 97%), $\nu_{max.}$ 1 355 and 1 167 (SO_2O), and 3 300 and 2 118 cm^{-1} (HC≡C), δ 4.25 (2 H, t, *J* 7.5 Hz, CH_2OSO_2), 2.99 (3 H, s, CH_3SO_2O), 2.66 (2 H, m, $CH_2C{\equiv}C$), 1.96 (1 H, t, *J* 2.5 Hz, HC≡C), and 1.92—1.53 (4 H, m, 4- and 5-CH_2) (Found: C, 48.0; H, 6.7; S, 18.2. $C_7H_{12}O_3S$ requires C, 47.7; H, 6.9; S, 18.2%), which was treated with 2-methylpropane-2-thiolate anions in the manner described above to give *6-t-butylthiohex-1-yne* (1c) (11.3 g, 76%), b.p. 206—209 °C at 752 mmHg, $\nu_{max.}$ 3 290 and 2 115 cm^{-1} (HC≡C), δ 2.54 (2 H, t, *J* 7.5 Hz, CH_2S), 2.21 (2 H, m, $CH_2C{\equiv}C$), 1.92 (1 H, t, *J* 2.5 Hz, HC≡C), 1.83—1.52 (4 H, m, 4- and 5-CH_2), and 1.32 (9 H, s, Me_3CS) (Found: C, 70.4; H, 10.5; S, 18.7. $C_{10}H_{18}S$ requires C, 70.5; H, 10.65; S, 18.8%).

(*d*) 2-Methylpropane-2-thiol (79 ml, 0.687 mol) and 7-chlorohept-1-yne (40.5 g, 0.31 mol) were added to a solution of sodium isopropoxide [from sodium (35 g, 1.52 mol)] in propan-2-ol (750 ml) and the mixture was boiled under nitrogen for 10 min. The usual work-up with ether gave *7-t-butylthiohept-1-yne* (1d) (53.3 g, 93%), b.p. 116—120 °C at 32 mmHg, $\nu_{max.}$ (liquid film) 3 302 and 2 110 cm^{-1} (HC≡C), δ 2.52 (2 H, t, *J* 7 Hz, CH_2S), 2.17 (2 H, m, $CH_2C{\equiv}C$), 1.89 (1 H, t, *J* 3 Hz, HC≡C), 1.53 (6 H, m, 4-, 5-, and 6-CH_2), and 1.31 (9 H, s, Me_3CS) (Found: C, 71.5; H, 11.1. $C_{11}H_{20}S$ requires C, 71.7; H, 10.9%).

(*e*) 6-Chlorohex-2-yne was similarly converted into *6-t-butylthiohex-2-yne* (1e) (70%), b.p. 100—104 °C at 10 mmHg, $\nu_{max.}$ 2 910, 1 455, 1 360, and 1 154 cm^{-1}, δ 2.61 (2 H, t, *J* 7.5 Hz, CH_2S), 2.22 (2 H, m, $CH_2C{\equiv}C$), 1.76 (3 H, t, *J* 2.5 Hz, $CH_3C{\equiv}C$), 1.86—1.62 (2 H, m, 5-CH_2), and 1.32 (9 H, s, Me_3CS) (Found: C, 70.4; H, 10.6; S, 19.05. $C_{10}H_{18}S$ requires C, 70.5; H, 10.65; S, 18.8%).

Preparation of the Sulphoxides (2a—e).—(*a*) Peroxydodecanoic acid (66% pure, 15.28 g, 0.047 mol) was added to a stirred solution of 4-t-butylthiobut-1-yne (6.86 g, 0.048 mol) in light petroleum (200 ml) at 0 °C. After 15 min, the solvent was evaporated off and the residue chromatographed on alumina (700 g). Elution with ether gave *4-t-butylsulphonylbut-1-yne* (76 mg, 0.9%), m.p. 56—58 °C, $\nu_{max.}$ 1 304 and 1 114 (SO_2), and 3 305 and 2 110 cm^{-1} (HC≡C), δ 3.14 (2 H, m, CH_2SO_2), 2.79 (2 H, m, $CH_2C{\equiv}C$), 2.06 (1 H, t, *J* 2.5 Hz, HC≡C), and 2.42 (9 H, s, Me_3CSO_2) *m/e* 174 (Found: C, 55.3; H, 8.3; S, 18.4. $C_8H_{14}O_2S$ requires C, 55.1; H, 8.1; S, 18.4%). Further elution with ether furnished the oily *4-t-butylsulphinylbut-1-yne* (2a) (6.17 g, 81%), $\nu_{max.}$ 1 034 (>SO), and 3 302 and 2 120 cm^{-1} (HC≡C), δ 3.67 (4 H, m, CH_2SO and $CH_2C{\equiv}C$), 2.06 (1 H, t, *J* 2 Hz, HC≡C), and 2.36 (9 H, s, Me_3CSO), δ(C_6D_6) 2.48 (2 H, m, $CH_2C{\equiv}C$), 2.10 (2 H, m, CH_2SO), 1.80 (1 H, t, *J* 2 Hz, HC≡C), and 0.84 (9 H, s, Me_3CSO) (Found: M^+, 158.0768. $C_8H_{14}OS$ requires *M*, 158.0765).

(*b*) Peroxydodecanoic acid oxidation of 5-t-butylthiopent-1-yne (18 g) in the above manner gave *5-t-butylsulphonylpent-1-yne* (0.28 g, 1.3%), m.p. 58—59 °C, $\nu_{max.}$ 1 296 and 1 116 (>SO_2). and 3 300 and 2 120 cm^{-1} (HC≡C), δ 3.06 (2 H, t, *J* 7.5 Hz, CH_2SO_2), 2.42 (2 H, m, $CH_2C{\equiv}C$), 2.16 (2 H, m, 4-CH_2), 2.03 (1 H, t, *J* 2.5 Hz, HC≡C), and 1.42 (9 H, s, Me_3CSO_2) (Found: C, 57.5; H, 8.6; S, 17.0. $C_9H_{16}O_2S$ requires C, 57.4; H, 8.6; S, 17.0%), and *5-t-butylsulphinylpent-1-yne* (2b) (19.8 g, 94%), m.p. 41—42 °C, $\nu_{max.}$ 1 035 (>SO), and 3 302 and 2 120 cm^{-1} (HC≡C), δ 2.57 (2 H, t, *J* 7 Hz, CH_2SO), 2.42 (2 H, m, $CH_2C{\equiv}C$), 2.10 (2 H, m, 4-CH_2), 1.98 (1 H, t, *J* 2.5 Hz, HC≡C), and 1.25 (9 H, s, Me_3CSO), δ(C_6D_6) 2.22 (2 H, t, *J* 7 Hz, CH_2SO), 2.07 (2 H, m, $CH_2C{\equiv}C$), 1.84 (2 H, m, 4-CH_2), 1.82 (1 H, t, *J* 2.5 Hz, HC≡C), and 1.19 (9 H, s, Me_3CSO), *m/e* 170 (Found: C,

62.6; H, 9.3; S, 18.7. $C_9H_{16}OS$ requires C, 62.7; H, 9.4; S, 18.6%).

(*c*) Oxidation of 6-t-butylthiohex-1-yne (21.5 g, 0.127 mol) with peroxydodecanoic acid (98% pure, 27.9 g, 0.127 mol) in the above manner gave 6-*t-butylsulphonylhex*-1-*yne* (0.75 g, 3%), m.p. 49—52 °C, $\nu_{max.}$ 1 284 and 1 112 (SO_2), and 3 302 and 2 118 cm^{-1} (HC≡C), δ 2.96 (2 H, t, *J* 7 Hz, CH_2SO_2), 2.28 (2 H, m, $CH_2C{\equiv}C$), 2.19—1.61 (4 H, m, 4- and 5-CH_2), 1.97 (1 H, t, *J* 2.5 Hz, HC≡C), and 1.42 (9 H, s, Me_3CSO_2) (Found: C, 59.3; H, 8.9; S, 16.1. $C_{10}H_{18}O_2S$ requires C, 59.4; H, 9.0; S, 15.85%), and 6-*t-butylsulphinylhex*-1-*yne* (2c) (19.8 g, 94%) as an oil, $\nu_{max.}$ 1 004 (>SO), and 3 300 and 2 116 cm^{-1} (HC≡C), δ 2.50 (2 H, t, *J* 8 Hz, CH_2SO), 2.26 (2 H, m, $CH_2C{\equiv}C$), 2.15—1.53 (4 H, m, 4- and 5-CH_2), 1.96 (1 H, t, *J* 3 Hz, HC≡C), and 1.25 (9 H, s, Me_3CSO) (Found: M^+, 186.1070. $C_{10}H_{18}OS$ requires *M* 186.1078).

(*d*) Treatment of 7-t-butylthiohept-1-yne as before with peroxydodecanoic acid gave 7-*t-butylsulphonylhept*-1-*yne* (3.7%), $\nu_{max.}$ 1 287 and 1 112 (>SO_2), and 3 305 and 2 115 cm^{-1} (HC≡C), δ 2.89 (2 H, t, *J* 8 Hz, CH_2SO_2), 2.21 (2 H, m, $CH_2C{\equiv}C$), 1.92 (1 H, t, *J* 3 Hz, HC≡C), 1.60 (6 H, m, 4-, 5-, and 6-CH_2), and 1.40 (9 H, s, Me_3CSO) (Found: C, 61.0; H, 9.4; S, 14.9. $C_{11}H_{20}O_2S$ requires C, 61.1; H, 9.3; S, 14.8%), and 7-*t-butylsulphinylhept*-1-*yne* (2d) (96%), $\nu_{max.}$ (liquid film) 1 020 (>SO), and 3 305 and 2 108 cm^{-1} (HC≡C), δ 2.53 (2 H, t, *J* 7 Hz, CH_2SO), 2.19 (2 H, m, $CH_2C{\equiv}C$), 1.96 (1 H, t, *J* 3 Hz, HC≡C), 1.92—1.37 (6 H, m, 4-, 5-, and 6-CH_2), and 1.24 (9 H, s, Me_3CSO), δ(C_6D_6) 2.33—1.88 (4 H, m, CH_2SO and $CH_2C{\equiv}C$), 2.02 (1 H, t, *J* 2 Hz, HC≡C), 1.79—1.17 (6 H, m, 4-, 5-, and 6-CH_2), and 1.00 (9 H, s, Me_3CSO) (Found: M^+, 200.1236. $C_{11}H_{20}OS$ requires *M*, 200.1235).

(*e*) 6-t-Butylthiohex-2-yne was oxidized in the above manner to furnish 6-*t-butylsulphonylhex*-2-*yne* (1.3%) as an oil, $\nu_{max.}$ 1 294 and 1 102 cm^{-1} (>SO_2), δ 3.14 (2 H, t, *J* 7.5 Hz, CH_2SO_2), 2.33 (2 H, m, $CH_2C{\equiv}C$), 2.09 (2 H, m, 5-CH_2), 1.77 (3 H, t, *J* 2 Hz, $CH_3C{\equiv}C$), and 1.42 (9 H, s, Me_3CSO_2) (Found: C, 59.1; H, 8.8; S, 15.7. $C_{10}H_{18}O_2S$ requires C, 59.4; H, 9.0; S, 15.85%), and the oily 6-*t-butylsulphinylhex*-2-*yne* (1e) (91%), $\nu_{max.}$ 1 022 cm^{-1} (>SO), δ 2.63 (2 H, m, CH_2SO), 2.35 (2 H, m, $CH_2C{\equiv}C$), 1.99 (2 H, m, 5-CH_2), 1.75 (3 H, t, *J* 2.5 Hz, $CH_3C{\equiv}C$), and 1.26 (9 H, s, Me_3CSO), δ(C_6D_6) 2.26 (2 H, m, CH_2SO), 2.17—1.68 (4 H, m, $CH_2C{\equiv}C$ and 5-CH_2), 1.52 (3 H, t, *J* 2.5 Hz, $CH_3C{\equiv}C$), and 0.94 (9 H, s, Me_3CSO) (Found: M^+, 186.1075. $C_{10}H_{18}OS$ requires *M*, 186.1078).

Oxidation of each of the sulphoxides (2a—e) with peroxydodecanoic acid in the manner described previously for the sulphides gave the corresponding sulphones (recorded above) in excellent yield.

Thermolysis of the Sulphoxides (2a—e).—The following procedure was typical. A solution of 5-t-butylsulphinylpent-1-yne (2b) (19.7 g, 0.11 mol) in degassed xylene (300 ml) was boiled for 2.5 h under nitrogen. The solution was poured onto a column of alumina (400 g), which was eluted first with light petroleum to remove the xylene and then with ether. Evaporation of the ether and distillation of the residue afforded 2-*methylenethiolan* 1-*oxide* (4b) (10.7 g, 80%), b.p. 130—132 °C at 13 mmHg, $\nu_{max.}$ 1 024 (>SO), and 1 632, 987, and 922 cm^{-1} ($H_2C{=}C$), δ 5.94 (1 H, s, CH=C< *cis* to >SO), 5.78 (1 H, s, CH=C< *trans* to >SO), and 3.11—2.37 (5 H, m, 3- and 5-CH_2, 4-CH), δ(C_6D_6) 5.62 (1 H, s, CH=C< *cis* to >SO), 5.25 (1 H, s, CH=C< *trans* to >SO), 2.63—1.65 (5 H, m, ring CH_2), and 1.56—1.08 (1 H, m, 4-CH) (Found: M^+, 116.0297. C_5H_8OS requires *M*, 116.0296).

Treatment of 6-t-butylsulphinylhex-1-yne (2c) (22.4 g) and 6-t-butylsulphinylhex-2-yne (2e) (5 g) in the same way gave respectively 2-*methylenethian* 1-*oxide* (4c) (13.8 g, 88%) as an oil, b.p. 131—132 °C at 14 mmHg, $\nu_{max.}$ 1 052 (>SO), and 1 630, 987, and 909 cm^{-1} ($H_2C{=}C$<), δ 5.67 (1 H, s, CH=C< *cis* to >SO), 5.50 (1 H, s, CH=C< *trans* to >SO), and 3.34—1.41 (8 H, m, ring $[CH_2]_4$), δ(C_6D_6) 5.69 (1 H, s, CH=C< *cis* to >SO), 5.11 (1 H, s, CH=C< *trans* to >SO), and 2.69—0.83 (8 H, m, ring $[CH_2]_4$) (Found: M^+, 130.0449. $C_6H_{10}OS$ requires *M*, 130.0452), and (E)-2-*ethylidenethiolan* 1-*oxide* (4e) (3.05 g, 87%), b.p. 146—148 °C at 15 mmHg, $\nu_{max.}$ 1 016 (>SO), and 1 630 and 915 cm^{-1} (CH=C<), δ 6.46 (1 H, q of t, *J* 7 and 2 Hz, CH=C<), 3.22—1.92 (6 H, m, ring $[CH_2]_3$), and 1.82 (3 H, d, *J* 7 Hz, $CH_3CH{=}C$<), δ(C_6D_6) 6.08 (1 H, m, CH=C<), 2.78—1.42 (6 H, m, ring $[CH_2]_3$), and 1.31 (3 H, d, *J* 7 Hz, $CH_3CH{=}C$<) (Found: M^+, 130.0456. $C_6H_{10}OS$ requires *M*, 30.0452).

7-t-Butylsulphinylhept-1-yne (2d) (25.0 g) was subjected to the same procedure, except that the product was purified by chromatography on silica (200 g, ether) and not by distillation, to furnish 2-*methylenethiepan* 1-*oxide* (4d) (9.77 g, 53%) as an oil, $\nu_{max.}$ 1 037 (>SO), and 1 620 and 910 ($H_2C{=}C$<) cm^{-1}, δ 5.80 (1 H, s, CH=C< *cis* to >SO), 5.57 (1 H, t, *J* 1 Hz, CH=C< *trans* to >SO), and 3.20—1.38 (10 H, m, ring $[CH_2]_5$), δ(C_6D_6) 5.84 (1 H, t, *J* 1 Hz, CH=C< *trans* to >SO), and 2.70—0.86 (10 H, m, ring $[CH_2]_5$), *m/e* 144 (Found: C, 58.2; H, 8.4; S, 22.0. $C_7H_{12}OS$ requires C, 58.3; H, 8.4; S, 22.2%).

Treatment of 4-t-butylsulphinylbut-1-yne (2a) for 2.5 h in the above manner gave an intractable tarry mixture. The sulphoxide (2a) (1.0 g) in degassed xylene (15 ml) was boiled for 10 min under nitrogen. The brown solution was cooled rapidly in ice and subjected to preparative t.l.c. on a 1 mm layer of silica gel G (Merck) eluted with ether. Extraction of a band at R_F 0.3 gave recovered 4-t-butylsulphinylbut-1-yne (2a) (386 mg). There were many other overlapping bands, none of which could be resolved chromatographically.

Oxidation of the Sulphoxides (4b—e) *to the Sulphones* (5b—e).—A solution of peroxydodecanoic acid (91% pure, 291 mg, 1.51 mmol) and 2-methylenethiolan 1-oxide (4b) (128 mg, 1.1 mmol) in a mixture of ether (6 ml) and light petroleum (1 ml) was kept at room temperature for 16 h. Chromatography on alumina (10 g) and elution with ether gave 2-*methylenethiolan* 1,1-*dioxide* (124 mg, 86%), m.p. 36—38 °C, $\nu_{max.}$ 1 300 and 1 114 (>SO_2) and 926 cm^{-1} ($H_2C{=}C$<), δ 5.96 (1 H, s, CH=C< *cis* to >SO_2), 5.79 (1 H, s, CH=C< *trans* to >SO_2), 3.03 (2 H, t, *J* 7 Hz, CH_2SO_2), 2.79 (2 H, m, 3-CH_2), and 2.19 (2 H, quint, *J* 7 Hz, 4-CH_2), *m/e* 132 (Found: C, 45.3; H, 6.2; S, 24.45. $C_5H_8O_2S$ requires C, 45.4; H, 6.1; S, 24.3%).

Oxidation of 2-methylenethian 1-oxide (4c) (131 mg), 2-methylenethiepan 1-oxide (4d) (105 mg), and (*E*)-2-ethylidenethiolan 1-oxide (4e) (200 mg) in the same way gave respectively 2-*methylenethian* 1,1-*dioxide* (5c) (121 mg, 83%), $\nu_{max.}$ 1 313 and 1 127 (>SO_2), 1 643, 948, and 908 cm^{-1} ($H_2C{=}C$<), δ 5.99 (1 H, s, CH=C< *cis* to >SO_2), 5.61 (1 H, t, *J* 1 Hz, CH=C< *trans* to >SO_2), 3.04 (2 H, t, *J* 6 Hz, CH_2SO_2), 2.74 (2 H, t, *J* 6 Hz, 3-CH_2), 2.18 (2 H, m, 5-CH_2), and 1.77 (2 H, m, 4-CH_2), *m/e* 146 (Found: C, 49.5; H, 7.0; S, 21.95. $C_6H_{10}O_2S$ requires C, 49.3; H, 6.9; S, 21.9%); 2-*methylenethiepan* 1,1-*dioxide* (5d) (109 mg, 93%), $\nu_{max.}$ 1 292 and 1 117 (>SO_2), and 949 cm^{-1}, δ 6.26

(1 H, s, CH=C< *cis* to >SO_2), 5.75 (1 H, t, *J* 1 Hz, CH=C< *trans* to >SO_2), 3.12 (2 H, t, *J* 6 Hz, CH_2SO_2), 2.64 (2 H, t, *J* 6 Hz, 3-CH_2), and 2.06—1.48 (6 H, m, 4-, 5-, and 6-CH_2), *m/e* 160 (Found: C, 52.8; H, 7.8; S, 20.1. $C_7H_{12}O_2S$ requires C, 52.5; H, 7.55; S, 20.0%); and (E)-2-*ethylidenethiolan* 1,1-*dioxide* (5e) (186 mg, 83%), $\nu_{max.}$ 1 293 and 1 137 (>SO_2), and 1 668 cm^{-1} (CH=C<), δ 6.44 (1 H, m, CH=C<), 3.01 (2 H, t, *J* 7 Hz, CH_2SO_2), 2.69 (2 H, m, 3-CH_2), 2.20 (2 H, quintet, *J* 7 Hz, 4-CH_2), and 1.81 (3 H, d of t, *J* 7 and 2 Hz, CH_3CH=C<), *m/e* 146 (Found: C, 49.2; H, 7.05; S, 22.0. $C_6H_{10}O_2S$ requires C, 49.3; H, 6.9; S, 21.9%) as oils.

1-*Cyano*-2-*phenylsulphinylethane* (19).—Acrylonitrile (60.3 g, 1.16 mol) was slowly added to a mixture of benzenethiol (41.7 g, 0.38 mol) and benzyltrimethylammonium hydroxide (40% in water; 1.5 ml) whilst the temperature was maintained below 45 °C. The mixture was stirred for 14 h at 20 °C, diluted with dichloromethane (500 ml), and washed with water. After drying over sodium sulphate and evaporation of the solvent, distillation of the residue afforded 1-cyano-2-phenylthioethane (54.8 g, 89%), b.p. 116—118 °C at 0.3 mmHg (lit.,[31] 154 °C at 8 mmHg). 1-Cyano-2-phenylthioethane (14.0 g, 86 mmol) in methanol (150 ml) was added quickly to a cooled, vigorously stirred solution of sodium metaperiodate (18.4 g, 86 mmol) in water (150 ml). The mixture was stirred at room temperature for 12 h, diluted with dichloromethane (500 ml) and water (200 ml), and filtered through glass wool. After separation of the non-aqueous layer, the aqueous phase was re-extracted with three 300 ml portions of dichloromethane, and the combined extract was washed with water and dried over sodium sulphate. Evaporation of the solvent gave 1-*cyano*-2-*phenylsulphinylethane* (19) (14.6 g, 95%), m.p. 57—59 °C (plates from dichloromethane–light petroleum), $\nu_{max.}$ 2 241 (C≡N), 1 038 cm^{-1} (>SO), δ 7.55 (5 H, m, C_6H_5) and 3.38—2.29 (4 H, m, $[CH_2]_2$), δ(C_6D_6) 7.39—7.01 (5 H, m, C_6H_5), and 2.56—1.59 (4 H, m, $[CH_2]_2$), *m/e* 179 (Found: C, 60.5; H, 5.2; N, 8.2; S, 18.1. C_9H_9NOS requires C, 60.3; H, 5.1; N, 7.8; S, 17.9%).

1-*Cyano*-2-*methylsulphinylethane* (20).—Acrylonitrile (88 ml, 1.66 mol) was added to stirred solution of methanethiol (25 ml, 0.466 mol) and sodium methoxide (0.19 g, 3.52 mmol) in benzene (75 ml) with intermittent cooling in a bath of acetone–carbon dioxide. The mixture was maintained at 0 °C for 2 h, and stirred at room temperature for 20 h, before removing the excess of acrylonitrile in a vacuum. Filtration of the residue and distillation gave 1-cyano-2-methylthioethane (44.0 g, 97%), b.p. 96—98 °C at 12 mmHg (lit.,[31] 97 °C at 15 mmHg), δ 2.71 (4 H, m, $[CH_2]_2$) and 2.18 (3 H, s, CH_3S). Peroxydodecanoic acid (97% pure; 22.3 g, 0.1 mol) was added to 1-cyano-2-methylthioethane (10.1 g, 0.1 mol) in dichloromethane (220 ml) with stirring at 0 °C. After 15 min, the solvent was evaporated off and the residue chromatographed on alumina (600 g). Elution with chloroform gave 1-*cyano*-2-*methylsulphinylethane* (20) (11.2 g, 96%) as an oil, $\nu_{max.}$ 1 031 (>SO), 2 245 cm^{-1} (C≡N), δ 3.22—2.81 (4 H, m, $[CH_2]_2$) and 2.66 (3 H, s, CH_3S) (Found: M^+, 117.0247. C_4H_7NOS requires *M*, 117.0248).

1-*Cyano*-2-*methylsulphonylethane*.—Treatment of 1-cyano-2-methylsulphinylethane (125 mg, 1.07 mmol) in dichloromethane (2 ml) with peroxydodecanoic acid (97% pure; 262 mg, 1.18 mmol) at 20 °C for 15 min gave, after evaporation of the solvent and chromatography of the residue on alumina (10 g) eluted with ether, 1-*cyano*-2-*methylsulphonylethane* (138 mg, 97%) as plates, m.p. 68 °C (from methanol), $\nu_{max.}$ 1 314 and 1 130 (>SO_2), 2 250 cm^{-1} (C≡N), δ 3.24 (2 H, t, *J* 7 Hz, CH_2SO_2), 2.97 (3 H, s, CH_3), and 2.85 (2 H, t, *J* 7 Hz, CH_2CN) (Found: M^+, 133.0197. $C_4H_7NO_2S$ requires *M*, 133.0197).

1-*Cyano*-2-(*ethoxycarbonylmethylsulphinyl*)*ethane* (21).—Acrylonitrile (26.5 g) was added slowly to a mixture of ethyl mercaptoacetate (20 g) and sodium ethoxide (0.57 g), keeping the temperature below 40 °C. After 14 h at room temperature the mixture was diluted with dichloromethane (200 ml), washed with water, and dried over sodium sulphate. Evaporation of the solvent and distillation of the residue afforded 1-cyano-2-(ethoxycarbonylmethylthio)-ethane (25.6 g, 90%), b.p. 151—154 °C at 0.65 mmHg, (lit.,[31] 169 °C at 16 mmHg), $\nu_{max.}$ 2 224 (C≡N) and 1 730 cm^{-1} (CO_2Et), δ 4.19 (2 H, q, *J* 7 Hz, OCH_2), 3.27 (2 H, s, SCH_2CO), 3.02—2.61 (4 H, m, $[CH_2]_2$), and 1.29 (3 H, t, *J* 7 Hz, CH_3), *m/e* 173. A solution of 1-cyano-2-(ethoxycarbonylmethylthio)ethane (14 g) in methanol (400 ml) was added quickly to a cooled, vigorously stirred solution of sodium metaperiodate (29.8 g) in water (400 ml). After stirring for 16 h at room temperature, the solution was poured into water (500 ml) and extracted with chloroform. The chloroform solution was washed with water, dried (Na_2SO_4), and evaporated to give 1-*cyano*-2-(*ethoxycarbonylmethylsulphinyl*)*ethane* (21) (24.5 g, 94%), as plates, m.p. 52 °C (from toluene), $\nu_{max.}$ 2 222 (C≡N), 1 730 (CO_2Et), and 1 040 cm^{-1} (>SO), δ 4.25 (2 H, q, *J* 7 Hz, OCH_2), 3.79 (2 H, s, SCH_2CO), 3.30—2.80 (4 H, m, $[CH_2]_2$), and 1.30 (3 H, t, *J* 7 Hz, CH_3), *m/e* 189 (Found: C, 44.7; H, 5.9; N, 7.5; S, 16.8. $C_7H_{11}O_3NS$ requires C, 44.45; H, 5.8; N, 7.4; S, 16.9%).

Thermolysis of Di-t-butyl Sulphoxide in Oct-1-yne.—A solution of di-t-butyl sulphoxide (4 g, 24.7 mmol) in oct-1-yne (27.1 g, 245.3 mmol) was kept at 80 °C under nitrogen for 2.5 h, cooled, and poured onto a column of alumina (100 g) prepared in light petroleum. Elution with light petroleum gave oct-1-yne, and elution with ether afforded an oil which was chromatographed on silica gel (160 g). Elution with ether–light petroleum (1 : 1 v/v) gave a mixture of isomeric dioctenyl sulphoxides (13) [mostly (13a), (13d), and (13e)] (0.34 g, 10%) as an oil, $\nu_{max.}$ (liquid film) 1 022 (>SO), and 1 628 and 915 cm^{-1} (C=C<), δ(C_6D_6) 6.24—5.30 (3—4 H, m, CH=C<), 2.56—1.78 (*ca.* 4 H, m, allylic CH_2), 1.74 and 1.57 (3—4 H, s, alkenyl CH_3), 1.52—0.99 (*ca.* 15 H, m, CH_2), and 0.85 (6 H, m, 2 × CH_3), *m/e* 270 (Found: C, 70.75; H, 11.3; S, 11.9. $C_{16}H_{30}OS$ requires C, 71.05; H, 11.2; S, 11.9%), followed by 2-*t-butylsulphinyloct-1-ene* (11a) (1.75 g, 60%), as an oil, $\nu_{max.}$ 1 010 (>SO), and 1 620 and 915 cm^{-1} (H_2C=C<), δ(C_6D_6) 5.63 (1 H, s, CH=C< *cis* to >SO), 5.29 (1 H, t, *J* 1.5 Hz, CH=C< *trans* to >SO), 2.03 (2 H, m, CH_2SO), 1.50—2.04 (8 H, m, $[CH_2]_4$), 0.98 (9 H, s, Me_3CSO), and 0.86 (3 H, m, CH_3), *m/e* 216 (Found: C, 66.5; H, 11.1; S, 15.0. $C_{12}H_{24}OS$ requires C, 66.6; H, 11.2; S, 14.8%). Further elution afforded 1-*t-butylsulphinyloct-1-ene* (12a) (0.11 g, 2%), $\nu_{max.}$ (liquid film) 1 022 (>SO), and 1 623 and 961 cm^{-1} (CH=CH), δ(C_6D_6) 6.46 (1 H, d of t, *J* 15 and 7 Hz, CH=C<), 5.84 (1 H, d of t, *J* 15 and 1 Hz, >C=CHSO), 1.90 (2 H, m, CH_3CH=C<), 1.38—1.05 (8 H, m, $[CH_2]_4$), 0.98 (9 H, s, Me_3CSO), and 0.84 (3 H, m, CH_3), *m/e* 216 (Found: C, 66.4; H, 11.0; S, 14.7. $C_{12}H_{24}OS$ requires C, 66.6; H, 11.2; S, 14.8%). Final elution with ether furnished recovered di-t-butyl sulphoxide (1.86 g, 47%).

Thermolysis of 2-t-Butylsulphinyloct-1-ene (11a) *in Oct-1-yne*.—A solution of 2-t-butylsulphinyloct-1-ene (11a) (200

mg, 0.93 mmol) in oct-1-yne (1.1 g, 0.01 mol) was boiled for 10 min under nitrogen. Chromatography on alumina (100 g) and elution with light petroleum gave oct-1-yne, whilst elution with ether afforded a mixture of isomeric dioctenyl sulphoxides (13) [mainly (13a), (13d), and (13e)] (168 mg, 67%), identical chromatographically and virtually identical spectroscopically (n.m.r., i.r.) with the sample obtained above.

2-*Phenylsulphinyloct*-1-*ene* (11b).—A solution of 1-cyano-2-phenylsulphinylethane (19) (1.6 g, 8.94 mmol) in oct-1-yne (9.8 g, 89.9 mmol) was boiled for 30 min under nitrogen, cooled, and chromatographed on alumina (100 g). Elution with light petroleum gave oct-1-yne, whilst elution with ether afforded *the product* (11b) (2.2 g, 94%) as an oil, $\nu_{max.}$ 1 034 (>SO), and 1 625 and 914 cm^{-1} (H_2C=C<), δ 7.71—7.39 (5 H, m, C_6H_5), 6.05 (1 H, s, CH=C< *cis* to >SO), 5.59 (1 H, t, *J* 1 Hz, CH=C< *trans* to >SO), 1.96 (2 H, m, allylic CH_2), 1.54—0.99 (8 H, m, $[CH_2]_4$), and 0.82 (3 H, t, *J* 6 Hz, CH_3), *m/e* 236 (Found: C, 70.7; H, 8.7; S, 13.4. $C_{14}H_{20}OS$ requires C, 71.1; H, 8.5; S, 13.6%).

2-*Methylsulphinyloct*-1-*ene* (11c) *and* 1-*Methylsulphinyloct*-1-*ene* (12c).—A rapidly stirred mixture of 1-cyano-2-methylsulphinylethane (20) (6.5 g, 0.056 mol) and oct-1-yne (65 g, 0.59 mol) was boiled for 9 h under nitrogen, cooled, and poured onto a column of alumina prepared in light petroleum. Elution with light petroleum gave oct-1-yne, and elution with ether afforded 2-*methylsulphinyloct*-1-*ene* (11c) (7.5 g), as an oil, $\nu_{max.}$ 1 029 (>SO), and 1 630, 951, and 920 cm^{-1} (H_2C=C<), δ 5.85 (1 H, s, CH=C< *cis* to >SO), 5.56 (1 H, t, *J* 2 Hz, CH=C< *trans* to >SO), 2.55 (3 H, s, CH_3SO), 2.22 (2 H, m, allylic CH_2), 1.78—1.12 (8 H, m, $[CH_2]_4$), and 0.88 (3 H, m, CH_3), δ(C_6D_6) 5.88 (1 H, s, CH=C< *cis* to >SO), 5.21 (1 H, t, *J* 2 Hz, CH=C< *trans* to >SO), 2.02 (3 H, s, CH_3SO), 1.83 (2 H, m, allylic CH_2), 1.45—0.97 (8 H, m, $[CH_2]_4$), and 0.85 (3 H, m, CH_3), *m/e* 174 (Found: C, 61.7; H, 10.4; S, 18.3. $C_9H_{18}OS$ requires C, 62.0; H, 10.4; S, 18.4%). Further elution with ether gave a mixture which was rechromatographed on silica (40 g). Elution with ether gave more 2-methylsulphinyloct-1-ene (0.8 g, total yield 86%), followed by 1-*methylsulphinyloct*-1-*ene* (12c) (0.25 g, 3%) as an oil, $\nu_{max.}$ 1 015 (>SO), and 1 628 and 953 cm^{-1} (CH=CH), δ 6.46 (1 H, d of t, *J* 15 and 7 Hz, CH_2CH=C<), 6.21 (1 H, d, *J* 15 Hz, >C=CHSO), 2.56 (3 H, s, CH_3SO), 2.21 (2 H, m, *J* 7 Hz, allylic CH_2), 1.59—1.11 (8 H, m, $[CH_2]_4$), and 0.86 (3 H, m, CH_3), δ(C_6D_6) 6.37 (1 H, d of t, *J* 15 and 7 Hz, CH_2CH=C<), 5.75 (1 H, d, *J* 15 Hz, >C=CHSO), 1.83 (2 H, m, allylic CH_2), 1.35—0.99 (8 H, m, $[CH_2]_4$), and 0.84 (3 H, m, CH_3) (Found: M^+, 174.1083. $C_9H_{18}OS$ requires *M*, 174.1078).

2-*Ethoxycarbonylmethylsulphinyloct*-1-*ene* (11d) *and* 1-*Ethoxycarbonylmethylsulphinyloct*-1-*ene* (12d).—A solution of 1-cyano-2-(ethoxycarbonylmethylsulphinyl)ethane (21) (0.5 g, 2.6 mmol) in oct-1-yne (5.5 g, 50 mmol) and bis-(2-methoxymethyl) ether (1 ml) was boiled under nitrogen for 1 h, cooled, dissolved in dichloromethane, and washed with water. After drying (Na_2SO_4) the solvent was removed under reduced pressure to leave an oil which was chromatographed (preparative t.l.c.) on silica eluted with ether–light petroleum (1 : 1 v/v). Extraction of the band at R_F 0.5 gave 2-*ethoxycarbonylmethylsulphinyloct*-1-*ene* (11d) (0.54 g, 83%) as an oil, $\nu_{max.}$ 1 726 (CO_2Et), 1 042 (>SO), and 1 626 and 917 cm^{-1} (H_2C=C<), δ 5.89 (1 H, s, CH=C< *cis* to >SO), 5.66 (1 H, s, CH=C< *trans* to >SO), 4.22 (2 H, q, *J* 7 Hz, CH_2OCO), 3.66 and 3.55 (2 H, q, J_{AB} 14 Hz, CH_2SO), 2.23 (2 H, m, CH_2CH=C<), 1.78—1.12 (8 H, m, $[CH_2]_4$), 1.28 (3 H, t, *J* 7 Hz, CH_3CH_2O), and 0.88 (3 H, m, CH_3), δ(C_6D_6) 5.87 (1 H, s, CH=C< *cis* to >SO), 5.25 (1 H, s, CH=C< *trans* to >SO), 3.92 (2 H, q, *J* 7 Hz, CH_2OCO), 3.23 (2 H, s, CH_2SO), 1.89 (2 H, m, CH_2CH=C<), 1.46—0.74 (11 H, m, $[CH_2]_4$ and CH_3), and 0.92 (3 H, t, *J* 7 Hz, CH_3CH_2O), *m/e* 246 (Found: C, 58.4; H, 9.15; S, 13.0. $C_{12}H_{22}O_3S$ requires C, 58.5; H, 9.0; S, 13.0%). Extraction of the band at R_F 0.4 gave 1-*ethoxycarbonylmethylsulphinyloct*-1-*ene* (12d) as an oil, $\nu_{max.}$ 1 725 (CO_2Et), 1 038 (>SO), and 1 622 and 950 cm^{-1} (CH=CH), δ 6.58 (1 H, d of t, *J* 16 and 6 Hz, CH_2CH=C<), 6.36 (1 H, d, *J* 16 Hz, >C=CHSO), 4.21 (2 H, q, *J* 7 Hz, CH_2OCO), 3.71 and 3.63 (2 H, q, J_{AB} 14 Hz, CH_2SO), 2.24 (2 H, m, CH_2CH=C<), 1.58—1.10 (8 H, m, $[CH_2]_4$), 1.27 (3 H, t, *J* 7 Hz, CH_3CH_2O), and 0.86 (3 H, m, CH_3), *m/e* 246 (Found: C, 58.3; H, 9.0; S, 13.0. $C_{12}H_{22}O_3S$ requires C, 58.3; H, 9.0; S, 13.0%).

Preparation of Alkenyl Sulphoxides (11e—q) *and* (12d, e, f, i, *and* o).—These compounds were prepared in the general manner described in the preceding three experiments from the appropriate alkyne and 1-cyano-2-aryl(or alkyl)-sulphinylethane. Reaction temperatures and times and percentage yields are recorded in the Table. Bis-(2-methoxyethyl) ether was added to aid solution in the preparation of (11m) and (11p). 3-*Hydroxy*-2-*phenylsulphinylprop*-1-*ene* (11e) had $\nu_{max.}$ 1 025 (>SO), and 1 679 and 931 cm^{-1} (H_2C=C<), δ 7.69—7.39 (5 H, m, C_6H_5), 6.03 (1 H, s, CH=C< *cis* to >SO), 5.86 (1 H, t, *J* 2 Hz, CH=C< *trans* to >SO), 4.26 and 3.90 (2 H, q, J_{AB} 16 Hz, CH_2OH), and 3.56br (1 H, s, OH), *m/e* 182 (Found: C, 59.0; H, 5.7; S, 17.35. $C_9H_{10}O_2S$ requires C, 59.3; H, 5.5; S, 17.6%). 3-*Hydroxy*-1-*phenylsulphinylprop*-1-*ene* (12e) had $\nu_{max.}$ 1 022 (>SO), and 1 622 and 928 cm^{-1} (CH=CH), δ 7.68—7.34 (5 H, m, C_6H_5), 6.70 (1 H, d of t, *J* 16 and 3 Hz, CH_2CH=C<), 6.47 (1 H, d, *J* 16 Hz, >C=CHSO), 4.31 (2 H, s, CH_2OH), and 2.56br (1 H, s, OH), *m/e* 182 (Found: C, 59.45; H, 5.7; S, 17.5). 3-*Hydroxy*-2-*methylsulphinylprop*-1-*ene* (11f) had $\nu_{max.}$ 3 340 (OH) and 1 010 cm^{-1} (>SO), δ 5.86 (1 H, s, CH=C< *cis* to >SO), 5.82 (1 H, s, CH=C< *trans* to >SO), 4.54—4.34 (3 H, m, CH_2 and OH), and 2.73 (3 H, s, CH_3SO), *m/e* 120 (Found: C, 39.6; H, 6.9; S, 26.65. $C_4H_8O_2S$ requires C, 40.0; H, 6.7; S, 26.7%). 3-*Hydroxy*-1-*methylsulphinylprop*-1-*ene* (12f) had $\nu_{max.}$ 3 350 (OH) and 1 015 cm^{-1} (>SO), δ 6.63—6.57 (2 H, m, CH=CH), 4.32br (2 H, s, CH_2), 4.27br (1 H, s, OH), and 2.62 (3 H, s, CH_3SO), *m/e* 120. 3-*Hydroxy*-2-*phenylsulphinylbut*-1-*ene* (11g) had $\nu_{max.}$ 3 360 (OH) and 1 010 cm^{-1} (>SO), δ 7.73—7.37 (5 H, m, C_6H_5), 6.01 (1 H, s, CH=C< *cis* to >SO), 5.85 (1 H, d, *J* 8 Hz, CH=C< *trans* to >SO), 4.38 and 4.17 (1 H, 2 m, >CHOH), 3.74br and 3.31br (1 H, 2 s, OH), and 1.29 and 1.13 (3 H, 2 d, *J* 6.5 Hz, CH_3), *m/e* 196 (Found: C, 60.9; H, 6.3; S, 16.45. $C_{10}H_{12}O_2S$ requires C, 61.2; H, 6.1; S, 16.3%). 3-*Hydroxy*-2-*phenylsulphinyloct*-1-*ene* (11h) had $\nu_{max.}$ 3 340 (OH) and 1 010 cm^{-1} (>SO), δ 7.70—7.38 (5 H, m, C_6H_5), 6.12 (1 H, s, CH=C< *cis* to >SO), 5.84 and 5.78 (1 H, 2 s, CH=C< *trans* to >SO), 4.06 (1 H, m, >CHOH), 3.30br (1 H, s, OH), 1.64—0.96 (8 H. m, $[CH_2]_4$), and 0.80 (3 H, t, *J* 6 Hz, CH_3), *m/e* 252 (Found: C, 66.8; H, 7.6; S, 12.8. $C_{14}H_{20}O_2S$ requires C, 66.7; H, 7.9; S, 12.7%). 3-*Hydroxy*-2-*methylsulphinyloct*-1-*ene* (11i) had $\nu_{max.}$ 3 360 (OH) and 1 010 cm^{-1} (>SO), δ 5.88 (1 H, s, CH=C< *cis* to >SO), 5.77 and 5.69 (1 H, 2 s, CH=C< *trans* to >SO), 4.42 (1 H, m, CHOH), 4.10br (1 H, s, OH), 2.75 (3 H, s, CH_3SO), 1.80—1.17 (8 H, m, $[CH_2]_4$), and 0.88 (3 H, t, *J* 7 Hz, CH_2CH_3), *m/e* 190 (Found: C, 56.55; H, 9.2; S, 16.8. $C_9H_{18}O_2S$ requires C, 56.85; H, 9.5; S, 16.85%). 3-*Hydroxy*-1-

methylsulphinyloct-1-ene (12i) had $\nu_{max.}$ 3 390 (OH) and 1 015 cm^{-1} (>SO), δ 6.53br (2 H, s, CH=CH), 4.33 (1 H, m, C*H*OH), 2.60 (3 H, s, CH_3SO), 2.58br (1 H, s, OH), 1.67—1.16 (8 H, m, $[CH_2]_4$), and 0.87 (3 H, m, CH_2-CH_3), *m/e* 190 (Found: C, 56.65; H, 9.5; S, 16.95). 3-*Methylthio-2-phenylsulphinylprop-1-ene* (11j) had $\nu_{max.}$ 1 025 cm^{-1} (>SO), δ 7.50 (5 H, m, C_6H_5), 6.18 (1 H, s, CH=C< *cis* to >SO), 5.87 (1 H, s, CH=C< *trans* to >SO), 3.22 and 2.86 (2 H, J_{AB} 16 Hz, CH_2), and 1.92 (3 H, s, CH_3S) (Found: M^+, 212.0328. $C_{10}H_{12}OS_2$ requires *M*, 212.0329). 3-*Methylthio-2-methylsulphinylprop-1-ene* (11k) had $\nu_{max.}$ 1 020 cm^{-1} (>SO), δ 5.97 (1 H, s, CH=C< *cis* to >SO), 5.77 (1 H, s, CH=C< *trans* to >SO), 3.39 (2 H, s, CH_2), 2.67 (3 H, s, CH_3SO), and 2.07 (3 H, s, CH_3S), *m/e* 150. It was further characterized by oxidation to the corresponding disulphone. A solution of (11k) (0.2 g) in dichloromethane (5 ml) was treated with peroxydodecanoic acid (91% pure, 0.195 g). After 1 h at room temperature, the solvent was evaporated off under reduced pressure and the residue chromatographed on alumina (20 g). Elution with ether gave 3-*methylsulphonyl-2-methylsulphonylprop-1-ene* (0.21 g, 92%), m.p. 88—89 °C (from benzene), $\nu_{max.}$ 1 320, 1 310, 1 136, and 1 127 cm^{-1} (>SO_2), δ 6.70 (1 H, s, CH=C< *cis* to >SO_2), 6.47 (1 H, s, CH=C< *trans* to >SO_2), 4.16 (2 H, s, CH_2), 3.04 (3 H, s, CH_3SO_2), and 3.01 (3 H, s, CH_3SO_2), *m/e* 198 (Found: C, 30.5; H, 5.15. $C_5H_{10}O_4S_2$ requires C, 30.3; H, 5.05%). 3,3-*Diethoxy-2-phenylsulphinylprop-1-ene* (11l) had $\nu_{max.}$ 1 040 cm^{-1} (>SO), δ 7.57 (5 H, m, C_6H_5), 6.28 (1 H, s, CH=C< *cis* to >SO), 6.03 (1 H, s, CH=C< *trans* to >SO), 4.71 [1 H, s, C*H*$(OEt)_2$], 3.35 (4 H, m, 2 × CH_2O), and 1.10 (6 H, m, 2 × CH_2CH_3), *m/e* 254 (Found: C, 61.2; H, 7.1; S, 12.4. $C_{13}H_{18}O_3S$ requires C, 61.4; H, 7.1; S, 12.6%). 1-(1-*Phenylsulphinylethenyl*)*cyclohex-1-ene* (11m) had $\nu_{max.}$ 1 019 (>SO), 1 630 and 909 (H_2C=C<), had 841 cm^{-1} (CH=C<), δ 7.44 (5 H, m, C_6H_5), 6.02 (1 H, s, CH=C< *cis* to >SO), 5.97 (1 H, t, *J* 4 Hz, CH_2CH=C<), 5.63 (1 H, s, CH=C< *trans* to >SO), 2.05 (4 H, m, 2 × allylic CH_2), and 1.84—1.33 (4 H, m, ring $[CH_2]_2$), *m/e* 232 (Found: C, 72.6; H, 7.2; S, 13.9. $C_{14}H_{16}OS$ requires C, 72.4; H, 6.9; S, 13.8%). 1-*Hydroxy*-1-(1-*phenylsulphinylethenyl*)*cyclohexane* (11n) had m.p. 115—117 °C (from toluene), $\nu_{max.}$ 1 010 cm^{-1} (>SO), δ 7.55 (5 H, m, C_6H_5), 6.03 (1 H, s, –CH=C< *cis* to >SO), 5.74 (1 H, s, CH=C< *trans* to >SO), 2.70br (1 H, s, OH), and 1.90—1.10 (10 H, m, ring $[CH_2]_5$), *m/e* 250 (Found: C, 67.1; H, 7.2; S, 12.8. $C_{14}H_{18}O_2S$ requires C, 67.2; H, 7.2; S, 12.8%). 1-*Hydroxy*-1-(1-*methylsulphinylethenyl*)-*cyclohexane* (11o) had m.p. 87—88 °C from toluene), $\nu_{max.}$ 3 360 (OH) and 1 010 cm^{-1} (>SO), δ 5.82 (1 H, d, *J* 1 Hz, CH=C< *cis* to >SO), 5.64 (1 H, d, *J* 1 Hz, CH=C< *trans* to >SO), 3.78br (1 H, s, OH), 2.77 (3 H, s, CH_3SO), and 1.82—1.50 (10 H, m, ring $[CH_2]_5$), *m/e* 188 (Found: C, 57.4; H, 8.65; S, 17.2. $C_9H_{16}O_2S$ requires C, 57.45; H, 8.5; S, 17.0%). 1-*Hydroxy*-1-(2-*methylsulphinylethenyl*)*cyclohexane* (12o) had $\nu_{max.}$ 3 360 (OH) and 1 025 cm^{-1} (>SO), δ 6.60 and 6.41 (2 H, J_{AB} 14 Hz, CH=CH), 3.60br (1 H, s, OH), 2.05 (3 H, s, CH_3SO), and 1.86—1.17 (10 H, m, ring $[CH_2]_5$), *m/e* 188 (Found: C, 57.15; H, 8.2; S, 17.0). (E)-1-*Bromo-2-phenylsulphinylhex-1-yne* (11p) had $\nu_{max.}$ 1 035 cm^{-1} (>SO), δ 7.56 (5 H, m, C_6H_5), 7.16 (1 H, s, C*H*Br=C<), 2.13 (2 H, m, allylic CH_2), 1.22 (4 H, m, $[CH_2]_2$), and 0.88 (3 H, t, *J* 7 Hz, CH_3) (Found: C, 50.0; H, 5 5; S, 11.4. $C_{12}H_{15}OSBr$ requires C, 50.2; H, 5.3; S, 11.2%). (E)-1-*Methoxycarbonyl-2-phenylsulphinylhex-1-ene* (11q) had m.p. 52 °C (from light petroleum), $\nu_{max.}$ 1 720 (CO_2Me) and 1 040 cm^{-1} (>SO), δ 7.57 (5 H, m, C_6H_5), 6.76 (1 H, s, CH=C<), 3.77 (3 H, s, OCH_3), 2.75 and 2.10 (2 H, 2 d of t, *J* 13 and 7 Hz, allylic CH_2), 1.50—1.05 (4 H, m, $[CH_2]_2$), and 0.81 (3 H, t, *J* 7 Hz, CH_3), *m/e* 266 (Found: C, 63.4; H, 6.9; S, 12.2. $C_{14}H_{18}O_3S$ requires C, 63.15; H, 6.8; S, 12.0%). (E)-1-*Methoxycarbonyl-2-methylsulphinylhex-1-ene* (11r) had $\nu_{max.}$ 1 720 (CO_2Me) and 1 056 cm^{-1} (>SO), δ 6.56 (1 H, s, CH=C<), 3.78 (3 H, s, OCH_3), 3.10 and 2.20 (2 H, 2 d of t, *J* 13 and 7 Hz, allylic CH_2), 2.65 (3 H, s, CH_3SO), 1.64—1.35 (4 H, m, $[CH_2]_2$), and 0.92 (3 H, t, *J* 7 Hz, CH_3), *m/e* 204 (Found: C, 52.65; H, 7.8; S, 15.8).

1-*Hydroxy-3-phenylsulphinylnon-2-ene* (11s).—1-Cyano-2-phenylsulphinylethane (19) (1 g, 5.6 mmol) in non-2-yn-1-ol (7.82 g, 56 mmol) was kept at 120 °C for 3 h under nitrogen, and the excess of alkynol was then removed by distillation under reduced pressure. Chromatography of the residue on silica (50 g) eluted with ether gave an oily mixture (300 mg) in equimolecular proportions (n.m.r.) of chromatographically identical 1-hydroxy-2-phenylsulphinylnon-2-ene (12s), $\nu_{max.}$ 1 030 cm^{-1} (>SO), δ 7.6 (5 H, m, C_6H_5), 6.52 (1 H, t, *J* 7 Hz, CH=C<), 4.18 (2 H, m, CH_2OH), 3.17 (1 H, s, OH), 2.29 (2 H, m, allylic CH_2), 1.27 (8 H, m, $[CH_2]_4$), and 0.82 (3 H, t, *J* 6 Hz, CH_3), and 1-cyano-2-phenylsulphonylethane, the spectral characteristics of which (see below) were superimposed upon those of (12s). Further elution with ether gave 1-*hydroxy-3-phenylsulphinylnon-2-ene* (11s) (1.0 g, 53%) as an oil, $\nu_{max.}$ 3 380 (OH), 1 030 cm^{-1} (>SO), δ(C_6D_6) 7.64 and 7.30 (2 H and 3 H, m, C_6H_5), 6.71 (1 H, t, *J* 6 Hz, >C=C*H*CH_2OH, collapsed to s on irradiation at δ 4.28), 4.79br (1 H, s, OH), 4.34 and 4.21 (2 H, J_{AB} 13 Hz, $J_{AX} = J_{BX}$ = 6 Hz, >C=CHCH_2OH), 2.05 (2 H, allylic CH_2), 1.07 (8 H, m, $[CH_2]_4$), and 0.82 (3 H, t, *J* 7 Hz, CH_3), *m/e* 266 (Found: C, 66.95; H, 8.75. $C_{15}H_{22}O_2S$ requires C, 67.6; H, 8.3%).

Oxidation of 1-cyano-2-phenylsulphinylethane (19) with peroxydodecanoic acid in dichloromethane in the usual manner (see preparation of 1-cyano-2-methylsulphonylethane above) gave 1-cyano-2-phenylsulphonylethane, m.p. 96—97 °C (from EtOH) (lit.,[32] 95 °C), $\nu_{max.}$ 2 240 (C≡N) and 1 142 cm^{-1} (>SO_2), δ 7.97 and 7.70 (2 H and 3 H, m, C_6H_5), 3.40 (2 H, t, *J* 7 Hz, CH_2SO_2), and 2.82 (2 H, t, *J* 7 Hz, CH_2CN), *m/e* 195 (Found: C, 55.35; H, 4.7; N, 7.0; S, 16.5. Calc. for $C_9H_9NO_2S$: C, 55.4; H, 4.65; N, 7.2; S, 16.4%), having chromatographic characteristics identical to that of the mixture with (12s) above.

(E)-1,1-*Diethoxy-3-phenylsulphinylnon-2-ene* (11t).—A mixture of 1-cyano-2-phenylsulphinylethane (19) (5.01 g, 29 mmol) and 1,1-diethoxynon-2-yne (31.8 g, 150 mmol) was kept at 140 °C for 2.5 h under nitrogen. The solvent was removed by vacuum distillation and the residue chromatographed on silica (70 g). Elution with ether–light petroleum (1 : 1 v/v) gave *the product* (11t) (8.17 g, 85%), as an oil, $\nu_{max.}$ 1 035 (>SO), δ 7.64 and 7.48 (2 H and 3 H, m, C_6H_5), 6.49 (1 H, d, *J* 6 Hz, >C=CH), 5.26 [1 H, d, *J* 6 Hz, C*H*$(OEt)_2$], 3.60 (4 H, m, 2 × CH_2O), 2.11 (2 H, m, allylic CH_2), and 0.81 (3 H, m, CH_3), *m/e* 338 (Found: C, 67.6; H, 8.9; S, 9.7. $C_{19}H_{30}O_3S$ requires C, 67.4; H, 8.9; S, 9.5%).

Thermolysis of 1-*Cyano-2-phenylsulphinylethane* (19) *in* 3-*Bromoprop-1-yne*.—A solution of 1-cyano-2-phenylsulphinylethane (19) (2.0 g, 11.2 mmol) in 3-bromoprop-1-yne (14.6 g, 123 mmol) was boiled for 12 h under nitrogen, then evaporated to dryness under reduced pressure, and the residue chromatographed on silica (100 g). Elution with ether gave 3-*bromo-2-phenylsulphinylprop-1-ene* (11u) (0.97 g, 36%), as an oil, $\nu_{max.}$ 1 031 (>SO), 3 050, 1 621, and 932

cm^{-1} ($H_2C{=}C<$), δ 7.58 (5 H, m, C_6H_5), 6.28 (1 H, s, $-CH{=}C<$ *cis* to >SO), 6.03 (1 H, s, $CH{=}C<$ *trans* to >SO), and 4.03 and 3.70 (2 H, J_{AB} 13 Hz, CH_2Br) (Found: M^+, 243.9558. $C_9H_9OS^{79}Br$ requires M, 243.9558). Further elution with ether furnished 3-hydroxy-2-phenylsulphinylprop-1-ene (11e) (0.22 g, 11%), followed by 2,3-*bis*(*phenylsulphinyl*)-*prop*-1-*ene* (22) (0.35 g, 11%), m.p. 90—91 °C, $\nu_{max.}$ 1 033 and 1 018 (>SO), 1 685, 1 616, and 932 cm^{-1} ($H_2C{=}C<$), δ 7.71—7.37 (10 H, m, 2 × C_6H_5), 6.23br and 6.17br (1 H, 2 s, $CH{=}C<$ *cis* to >SO in diastereoisomers), 5.90br and 5.83br (1 H, 2 s, $CH{=}C<$ *trans* to >SO in diastereoisomers), and 3.48 and 3.25 (2 H, J_{AB} 14 Hz, CH_2SO), *m/e* 290 (Found: C, 61.85; H, 4.95; S, 22.1. $C_{15}H_{14}O_2S_2$ requires C, 62.0; H, 4.9; S, 22.1%).

Reactions of 3-*Bromo*-2-*phenylsulphinylprop*-1-*ene* (11u) *with Water and Benzenesulphenic Acid.*—(*a*) A solution of 3-bromo-2-phenylsulphinylprop-1-ene (11u) in acetone (2 ml) and water (0.5 ml) was boiled for 48 h and worked up with ether in the usual way to give 2-hydroxy-2-phenylsulphinylprop-1-ene (11e) (0.09 g, 100%).

(*b*) A solution of 3-bromo-2-phenylsulphinylprop-1-ene (11u) (0.1 g) and 1-cyano-2-phenylsulphinylethane (19) (0.73 g) in benzene (30 ml) was boiled under a Soxhlet thimble containing molecular sieves (type 4A) for 12 h, and the solvent then removed under reduced pressure. Chromatography of the residue on silica (preparative t.l.c.) eluted with ether, and extraction of the band at R_F 0.3 gave 2,3-bis(phenylsulphinyl)prop-1-ene (22) (0.58 g, 49%) identical with the sample prepared previously.

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