Aust. J. Chem., 1995, **48**, 651–661

Preparation of Some Novel Butyl, Butenyl, Butadienyl and Butynyl Sulfone Electrophiles for Use in Enolate Trapping Studies

Wendy A. Loughlin[A,B] *and Richard K. Haynes*[A,C,D]

[A] Department of Organic Chemistry, University of Sydney, N.S.W. 2006.
[B] Present address: Faculty of Science and Technology, Griffith University, Nathan Campus, Kessels Road, Brisbane, Qld. 4111.
[C] Author to whom correspondence should be addressed.
[D] Present address: Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.

Abstract

The preparation of some novel four-carbon electrophiles and electrophile intermediates is described. Thus, the chlorobutenyl sulfone (5), the iodobutynyl sulfone (6) and the hitherto unreported chlorobutynyl sulfone (4) were prepared. The novel intermediates, containing a chelating imidazolyl functionality, the *N*-methylimidazolyl sulfides (13)–(15) were also prepared. However, they polmerized rapidly, thus preventing further synthetic manipulations. The preparation of the α-(trimethylsilyl)butadienyl sulfones (17) and (18) is described and the mode of formation of the intermediate α-trimethylsilyl sulfides (21) and (22) from the trimethylsilylbutenyl sulfide (27) is discussed.

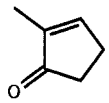
Introduction

A major difficulty in obtaining CD ring synthons is that in the traditional construction of the CD fragment, according to the Robinson annelation involving the enolate of 2-methylcyclopentenone (1) and a derivative or analogue of methyl vinyl ketone, a carbonyl group is introduced at C 9 (steroid numbering). This must subsequently be transposed to C 8 in order to provide the appropriate intermediate. Work in our group has already demonstrated that the enolate produced in the conjugate addition of the lithiated butenyldiphenylphosphine oxide (2) to 2-methylcyclopentenone (1) reacts efficiently with β-sulfonyl or β-chlorovinyl ketones to provide adducts that have been converted into hydrindanone precursors of vitamin D.[1,2] We now planned to overcome the drawback of this sequence, the

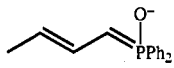
[1] Haynes, R. K., and Vonwiller, S. C., *J. Chem. Soc., Chem. Commun.*, 1987, 92; Haynes, R. K., Vonwiller, S. C., and Hambley, T. W., *J. Org. Chem.*, 1989, **54**, 5162.
[2] Vonwiller, S. C., Ph.D. Thesis, University of Sydney, 1987.

Manuscript received 20 September 1994 0004-9425/95/030651$05.00

transposal of oxygen from C9 to C8,[3–5] through use of novel, highly reactive electrophiles.



(1)



(2)

In choosing the electrophile, certain points must be borne in mind. Firstly, the electrophiles must react efficiently with the enolate. Secondly, manipulation of the adduct arising from the conjugate addition–enolate trapping reaction to generate a precursor suitable for cyclization must be straightforward and high yielding. Thirdly, the electrophile must bear functionality which is strategically placed to facilitate the subsequent annelation of the precursor, and which directly provides a product of annelation bearing an activating group at C8. That is, the electrophile must contain a group which not only promotes the cyclization step but also provides a synthetic 'handle' for use in the latter stages of the synthetic sequence. This is noteworthy as the correct relative configuration at C14 has to be introduced during the synthetic sequence. Fourthly, it is desirable that the electrophile be easily prepared from readily available starting materials.

As pointed out above, the electrophile must react efficiently with the enolate. This is by no means a trivial consideration. Ketone enolates are notoriously poor nucleophiles towards alkylating agents.[6] The reaction is characterized by the formation of a mixture of mono-, di- and poly-alkylated products even when equivalent quantities of reactants are used at the outset of the reaction.[7] One device that may be used to suppress enolate equilibration involves the exchange of the lithium counter ion with other counter ions or neutral reagents that tend to bind to the enolate through the oxygen atom,[6] so that either the basicity of the enolate is markedly reduced, or a neutral but reactive enol is produced. For example, it has been found in this laboratory that triphenyltin chloride efficiently suppresses polyalkylation during the reaction of the enolate arising from the conjugate addition of lithiated octenyl sulfide to 4-t-butoxycyclopent-2-ene.[8] Thus,

[3] Quinkert, G., Monforts, F.-P., Ockenfeld, M., and Rehm, D., *Synform*, 1985, **3**, 41, and references sited therein; Takahashi, T., Ueno, H., Miyazawa, M., and Tsuji, J., *Tetrahedron Lett.*, 1985, **26**, 4463; Suzuki, T., Sato, E., Unno, K., and Kametani, T., *J. Chem. Soc., Chem. Commun.*, 1988, 724.

[4] Baggiolini, E. G., Jacobelli, J. A., Hennessy, B. M., and Uskoković, M., *J. Am. Chem. Soc.*, 1982, **104**, 2945; Baggiolini, E. G., Jacobelli, J. A., Hennessy, B. M., Batcho, A. D., Sereno, J. F., and Uskoković, M., *J. Org. Chem.*, 1986, **51**, 3098; Daniewski, A. R., and Kiegiel, J., *J. Org. Chem.*, 1988, **53**, 5534.

[5] Kocienski, P. J., Lythgoe, B., and Ruston, S., *J. Chem. Soc., Perkin Trans. 1*, 1979, 1290; Nemoto, H., Kurobe, H., Fukumoto, K., and Kametani, T., *J. Org. Chem.*, 1986, **51**, 5311.

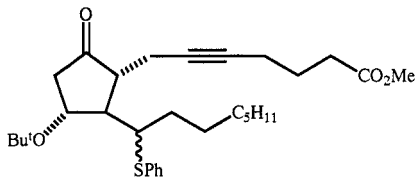
[6] House, H. O., 'Modern Synthetic Reactions' pp. 560, 565 (Benjamin: Menlo Park 1972); House, H. O., and Kramar, V., *J. Org. Chem.*, 1963, **28**, 3362; House, H. O., Gall, M., and Olmstead, H. D., *J. Org. Chem.*, 1971, **36**, 2361.

[7] d'Angelo, J., *Tetrahedron*, 1976, **32**, 2979.

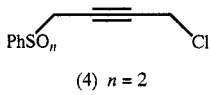
[8] Binns, M. R., Haynes, R. K., Lambert, D. E., and Schober, P. A., *Tetrahedron Lett.*, 1985, **26**, 3385; Haynes, R. K., Lambert, D. E., Schober, P. A., and Turner, S. G., *Aust. J. Chem.*, 1987, **40**, 1211.

treatment of this enolate with triphenyltin chloride and then with the alkylating agent, methyl 7-iodohept-5-ynoate, gave the alkylated product (3) in 70% yield.[8]

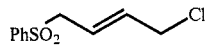
A four-carbon electrophile designed in cognizance of the results of foregoing work will thus incorporate a propargylic halide. The activating group required for the subsequent annelation cannot be a good leaving group, and for this purpose, the phenylsulfonyl group appears ideal. The electrophile must obviously contain a four-carbon chain which will form the part of the six-membered ring of the hydrindenone ring system. Thus the hitherto unreported chlorobutynyl sulfone (4) was selected initially. We now describe the preparation of some four-carbon electrophiles with varying degrees of saturation and bearing a terminal sulfonyl group.



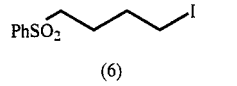
(3)



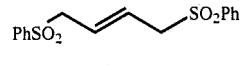
(4) $n = 2$
(9) $n = 0$



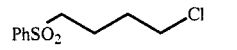
(5)



(6)



(7)



(8)

Discussion

Butyl, Butenyl and Butynyl Sulfone Electrophiles

For comparative purposes, the chlorobutenyl sulfone (5)[9,10] and the iodobutyl sulfone (6)[11] were also required, in addition to the chlorobutynyl sulfone (4). The chlorobutenyl sulfone (5) was directly prepared from 1,4-dichlorobut-2-ene and 0·5 equiv. of sodium benzenesulfinate in refluxing methanol in 87% yield, based on recovered dichlorobutene. Use of equimolar amounts of reactants gave the butenyl bissulfone (7) (40%).[12] Preparation of the iodobutyl sulfone (6) commenced with the reaction of 1,4-dichlorobutane with sodium benzenesulfinate in methanol. The chlorobutyl sulfone (8)[13] obtained in 38% yield based on recovery of dichlorobutane was submitted to halogen exchange with sodium iodide in acetone, to give the iodobutyl sulfone (6) (52%).

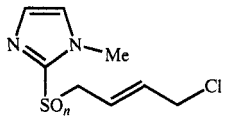
The synthesis of the chlorobutynyl sulfone (4) began with 1,4-dichlorobut-2-yne.[14] Nucleophilic displacement of chloride was achieved by overnight treatment of dichlorobutyne with 0·5 equiv. of thiophenol in the presence of triethylamine in dichloromethane. The chlorobutynyl sulfide (9) was produced in 45% yield or 93%

[9] Asscher, M., and Vofsi, D., *J. Chem. Soc.*, 1964, 4962.
[10] Tanaskov, M. M., Stadnichuk, M. D., and Kekisheva, L. V., *J. Gen. Chem. USSR*, 1980, 1411.
[11] Bordwell, F. G., and Brannen, Jr, W. T., *J. Am. Chem. Soc.*, 1964, **86**, 4645.
[12] Thyagarajan, B. S., Majumdar, K. C., and Bates, D. K., *Phosphorus Sulfur*, 1976, **1**, 67.
[13] Durst, T., Tin, K.-C., and Marcil, M. J. V., *Can. J. Chem.*, 1973, **51**, 1704; Truce, W. E., and Hoerger, F. D., *J. Am. Chem. Soc.*, 1955, **77**, 2496.
[14] Bailey, W. J., and Fujiwara, E., *J. Am. Chem. Soc.*, 1955, **77**, 165; Johnson, A. W., *J. Chem. Soc.*, 1946, 1009.

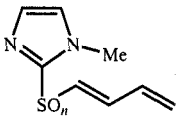
based on recovered dichlorobutyne.[15] Significant disubstitution was observed when 1 equiv. of thiophenol was used. Subsequent treatment of the chlorobutynyl sulfide (9) with *m*-chloroperbenzoic acid in dichloromethane at low temperature resulted in complete oxidation to the chlorobutynyl sulfone (4) in 75% yield and in an overall yield of 43% from butynediol. Attempts to prepare the chlorobutynyl sulfone (4) directly from dichlorobutyne and sodium benzenesulfinate were unsuccessful. The reactions of the electrophiles (4)–(6) with selected enolates are described elsewhere.[16]

N-*Methylimidazolyl Sulfone Electrophiles*

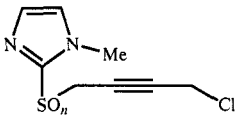
The novel *N*-methylimidazolyl sulfones (10)–(12) also were selected as targets. Both the presence of the chelating imidazolyl functionality and the varying degrees of saturation should provide a different kind of reactivity towards enolates.



(10) $n = 2$
(13) $n = 0$



(11) $n = 2$
(14) $n = 0$



(12) $n = 2$
(15) $n = 0$

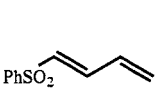
Treatment of dichlorobutene with 1-methylimidazole-2-thiol in the presence of triethylamine in dichloromethane gave the butenyl imidazolyl sulfide (13) (20%). Use of a stronger base, butyllithium, to deprotonate 1-methylimidazole-2-thiol followed by addition of dichlorobutene gave both the butenyl imidazolyl sulfide (13) (17%) and the product of elimination, the butadienyl imidazolyl sulfide (14) (21%). Attempts to obtain complete conversion into the butadienyl imidazolyl sulfide (14) by use of excess base gave no significant improvement in the ratio of the two compounds. Both products were difficult to handle as they polymerized rapidly on standing. The butynyl imidazolyl sulfide (15) was prepared in an analogous way from dichlorobutyne, 1-methylimidazole-2-thiol and triethylamine. The product, obtained in 64% yield, also polymerized on standing.

Attempts to oxidize the freshly prepared crude imidazolyl sulfides (13)–(15) to the corresponding sulfones (10)–(12) with an excess of *m*-chloroperbenzoic acid were unsuccessful, both because of the poor solubility of the freshly prepared imidazolyl sulfides (13)–(15) and their tendency to polymerize on contact with solvents. The butenyl imidazolyl sulfide (13) is evidently very prone to elimination. The elimination presumably is initiated by either inter- or intra-molecular deprotonation at C 1 of the butenyl system by the basic nitrogen atom at C 3. The resulting diene (14), in bearing a potent electron donor at C 1′, is obviously activated towards cationic, that is proton-initiated, polymerization. Thus, the target *N*-methylimidazolyl sulfone electrophiles could not be obtained.

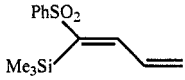
[15] Besace, Y., *Bull. Soc. Chim. Fr.*, 1971, **5**, 1793.
[16] Loughlin, W. A., and Haynes, R. K., *Aust. J. Chem.*, 1995, **48**, 663.

Butadienyl Sulfone Electrophiles

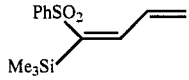
In turning to the preparation of electrophiles bearing a different type of substitution, the compound (16) was selected. The butadienyl sulfone (16) has been prepared previously,[10] but its reaction with an enolate has not been recorded. For the present work, the butadienyl sulfone (16) was very simply prepared in quantitative yield by treatment of the chlorobutenyl sulfone (5) with triethylamine in dichloromethane. However, reaction of the butadienyl sulfone (16) with either the lithium enolate or the titanium enol of cyclopentanone was unsuccessful, largely because of the tendency of the electrophile to polymerize under the reaction conditions. Generation of the electrophile *in situ* from chlorobutenyl sulfone (5) also resulted in polymerization. An anionic polymerization of this kind, triggered by addition of the enolate or other anionic species to the butadienyl sulfone (16), is not unexpected.



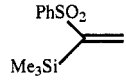
(16)



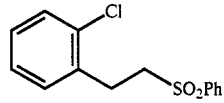
(17)



(18)



(19)

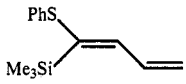


(20)

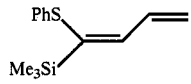
α-(Trimethylsilyl)butadienyl Sulfone Electrophiles

In order to prevent polymerization of the butadienyl sulfone, the α-trimethylsilyl derivatives (17) and (18) were selected. The use of methyl α-(trimethylsilyl)vinyl ketone in reaction with enolates under aprotic conditions succeeds for this reason; the use of this and related compounds to generate the diketone intermediates of the Robinson annelation sequence is well known.[17] It was also reported well after the inception of this work that α-(trimethylsilyl)vinyl sulfone (19) reacts cleanly and in high yield with aryllithium reagents to generate adducts which during workup were desilylated with fluoride ion to give sulfones such as compound (20).[18]

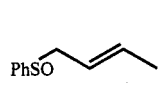
Although the α-(trimethylsilyl)butadienyl sulfones (17) and (18) are unknown compounds, the synthesis of the α-(trimethylsilyl)butadienyl sulfide derivatives (21) and (22) by two different approaches has been previously reported.[19,20] One method, reported by Miller, involved the treatment of the butenyl sulfoxide (23) with lithium diisopropylamine and then trimethylsilyl chloride to give the α-(trimethylsilyl)butadienyl sulfides (21) and (22) as a 3:2 mixture of isomers in 70% yield.[19]



(21)



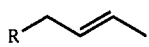
(22)



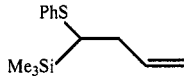
(23)

[17] Stork, G., and Jung, M. E., *J. Am. Chem. Soc.*, 1974, **96**, 3682. Stork, G., and Ganem, B., *J. Am. Chem. Soc.*, 1973, **95**, 6152; Boeckman, Jr, R. K., *Tetrahedron*, 1983, **39**, 925.
[18] Iwao, M., *J. Org. Chem.*, 1990, **55**, 3622.
[19] Miller, R. D., and Hässig, R., *Tetrahedron Lett.*, 1984, **25**, 5351.
[20] Han, D. I., and Oh, D. Y., *Synth. Commun.*, 1990, **20**, 267.

The butenyl sulfoxide (23)[21] was prepared in the following manner. Crotonaldehyde was reduced with lithium aluminium hydride ($LiAlH_4$) to give the butenol (24)[22] (63%) which was treated with phosphorus tribromide in ether to give the bromobutene (25)[23] (88%). Nucleophilic displacement of the bromide from bromobutene (25) with thiophenolate at 0° gave the butenyl phenyl sulfide (26)[24] (80%), which was oxidized to the butenyl sulfoxide (23) with *m*-chloroperbenzoic acid (87%).



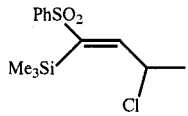
(24) R = OH
(25) R = Br
(26) R = SPh



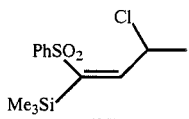
(27)

With the butenyl sulfoxide (23) in hand, preparation of the α-(trimethylsilyl)-butadienyl sulfides (21) and (22) was attempted according to the method of Miller.[19] However, in our hands, complex mixtures were obtained and attention was now turned to an alternative approach to the α-(trimethylsilyl)butadienyl sulfide (22). Oh reported that treatment of the α-(trimethylsilyl)butenyl sulfide (27)[25] with *N*-chlorosuccinimide in carbon tetrachloride directly gave the α-(trimethylsilyl)butadienyl sulfide (22).[20]

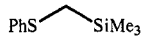
The synthesis of α-(trimethylsilyl)butenyl sulfide (27) was carried out as follows. Treatment of lithiated thioanisole with chlorotrimethylsilane gave phenylthiotrimethylsilylmethane (28) (96%).[26] The latter was deprotonated by butyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine at 0° and then treated with allyl bromide to give the α-(trimethylsilyl)butenyl sulfide (27) (85%). With α-(trimethylsilyl)butenyl sulfide (27) in hand, chlorination–elimination was attempted according to the method of Oh.[20]



(29)



(30)



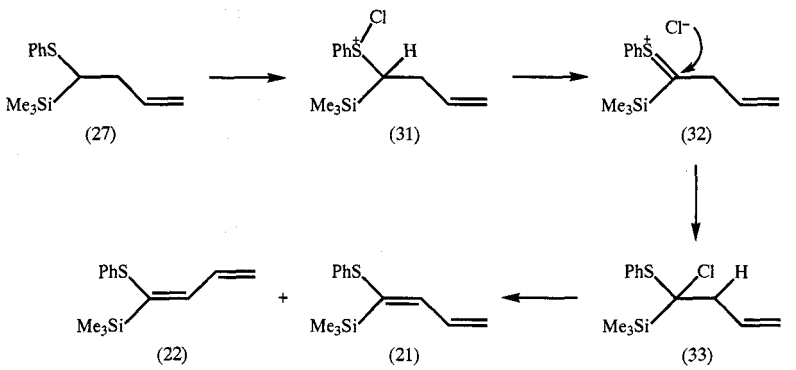
(28)

Treatment of the α-(trimethylsilyl)butenyl sulfide (27) with *N*-chlorosuccinimide in carbon tetrachloride gave a complex mixture of products which could not be satisfactorily purified. Analysis of the partially purified product mixture by 200 MHz ^1H n.m.r. spectroscopy indicated the presence of a compound with a conjugated diene system, and other major products. The mixture of sulfide products was oxidized with *m*-chloroperbenzoic acid and characterized as the sulfone derivatives. Separation of the mixture of sulfone products

[21] Antonjuk, D. J., Ridley, D. D., and Smal, M. A., *Aust. J. Chem.*, 1980, **33**, 2635.
[22] Hatch, L. F., and Nesbitt, S. S., *J. Am. Chem. Soc.*, 1950, **72**, 727.
[23] Young, W. G., Richards, L., and Azorlosa, J., *J. Am. Chem. Soc.*, 1939, **61**, 3070.
[24] Cope, A. C., Morrison, D. E., and Field, L., *J. Am. Chem. Soc.*, 1950, **72**, 59; Ridley, D. D., and Smal, M. A., *Aust. J. Chem.*, 1980, **33**, 1345.
[25] Ager D. J., and Cookson R. C., *Tetrahedron Lett.*, 1980, **21**, 1677; Ishibashi, H., Nakatani, H., Umei, Y., Yamamoto, W., and Ikeda, M., *J. Chem. Soc., Perkin Trans. 1*, 1987, 589.
[26] Cooper, G. D., *J. Am. Chem. Soc.*, 1954, **76**, 3713; Ager, D. J., *J. Chem. Soc., Perkin. Trans. 1*, 1983, 1131.

provided the (*E*)-α-(trimethylsilyl)butadienyl sulfone (17) (15%), the (*Z*)-α-(trimethylsilyl)butadienyl sulfone (18) (13%), the (*E*)-chlorobutenyl sulfone (29) (18%) and the (*Z*)-chlorobutenyl sulfone (30) (18%).

The geometry of the α-(trimethylsilyl)butadienyl sulfones (17) and (18) indicates that both isomers of the α-(trimethylsilyl)butadienyl sulfides (21) and (22) are formed in the chlorination–elimination sequence, which is contrary to the reported exclusive (*Z*)-selectivity in the overall process. The formation of both (*E*)- and (*Z*)-isomers can be explained by operation of the following mechanism. Chlorination will occur regioselectively at the carbon atom bearing the phenylthio group to give the α-(trimethylsilyl)-α-chlorobutenyl sulfide (33) (Scheme 1). This type of reaction has been thoroughly studied and proceeds via the chlorinated sulfonium ion (31).[27] The chloride ion is expelled through deprotonation at C α and formation of a sulfonium ion (32); chloride ion then attacks at C α to provide the α-(trimethylsilyl)-α-chlorobutenyl sulfide (33). Elimination of hydrogen chloride is likely to occur from the chloro sulfide by an antiperiplanar *E*2 mechanism to give both the (*E*)- and (*Z*)-α-(trimethylsilyl)butadienyl sulfides (21) and (22).



Scheme 1

The steric requirements of the trimethylsilyl and phenylthio groups must be very similar, and thus the conformers will differ little in energy. The literature report[20] of (*Z*)-selectivity in this reaction would require that formation of the α-(trimethylsilyl)-α-chlorobutenyl sulfide (33) does not take place, but that the formation of the diene proceeds directly by antiperiplanar proton loss from the allylic position of the sulfonium ion intermediate (32). In this case, each conformer will have identical steric interactions, but each will produce the (*Z*)-alkene.

The isolation of the (*E*)- and (*Z*)-chlorobutenyl sulfones (29) and (30) implies that the hydrogen chloride produced in the elimination adds to the terminal double bond of the α-(trimethylsilyl)butadienyl sulfides (21) and (22). The observation that the major adduct is the product arising from 1,2-addition indicates that addition occurs under conditions of kinetic control. In line with the kinetic effect, it is probable that there is a substantial steric restraint preventing attack of chloride ion at the alternative site. Attempts to reduce the loss of the α-(trimethylsilyl)butadienyl sulfides (21) and (22) by the addition of excess triethylamine to the product mixture to scavenge the hydrogen chloride resulted in

[27] Vilsmaier, E., and Sprügel, W., *Ann. Chem.*, 1971, **749**, 62; Vilsmaier, E., and Sprügel, W., *Ann. Chem.*, 1971, **747**, 151.

little improvement. After oxidation, the yield of the α-(trimethylsilyl)butadienyl sulfones (17) and (18) was only marginally increased and formation of the (*E*)- and (*Z*)-chlorobutenyl sulfones (29) and (30) was still observed. The questions of mechanism aside, the target α-(trimethylsilyl)butadienyl sulfones (17) and (18) were obtained in an overall mediocre, although workable, yield (28%).

The application of the target electrophiles (17) and (18) and that of the other successfully prepared electrophiles (4)–(6), as electrophiles in the attempted synthesis of a CD synthon is described elsewhere.[28]

Experimental

^{1}H n.m.r. spectra were recorded on Varian EM 390 and Bruker AC-200F spectrometers, with samples dissolved in $CDCl_3$ containing tetramethylsilane as an internal reference. ^{13}C n.m.r. spectra were recorded from $CDCl_3$ solutions on a Bruker AC-200F spectrometer. Infrared spectra were recorded on a Digilab FTS 20/80 Fourier transform spectrometer from the solutions in chloroform, as Nujol mulls or as otherwise indicated. Mass spectrometry was carried out on an AEI MS9 (e.i.) spectrometer equipped with a DS 90 data-handling system. Microanalyses were performed by the Chemical and Micro Analytical Services, Pty Ltd (CMAS) and the Australian Mineral Development Laboratories, Melbourne (AMDEL). Melting points were recorded on a Reichert melting point stage and are uncorrected.

All chromatographic separations were carried out by flash chromatography with Merck silica gel 60 (70-230 mesh ASTM). Merck silica gel (60 PF_{254}) was used for preparative centrifugal (radial) chromatography with a 7924T Chromatotron (Harrison Research U.S.A.). Analytical thin-layer chromatography (t.l.c.) was carried out with Merck precoated t.l.c. plastic sheets coated with silica gel 60 F_{254} (0·2 mm). Analytical high performance liquid chromatography (h.p.l.c.) and preparative h.p.l.c. were carried out on a system consisting of a Waters 6000A pump, a Waters 440 absorbance detector (λ 254 nm) or a Waters 510 EF pump, an Isco 226 absorbance detector (λ 254 nm), equipped with a Waters U6K injector, a Waters R-401 403 differential refractometer and a Goerz Metrawatt 120 dual-pen recorder. Solvents and commercially available reagents were purified in the standard manner.

Preparation of Electrophiles

The preparation of the compounds (5),[9,10] (6),[11] (7),[12] (8),[13] (9),[15] (16),[10] (23),[20] (24),[21] (25),[22] (26),[23] (27)[24] and (28)[25] has been described elsewhere. 1,4-Dichlorobut-2-yne is commercially available. The compounds (5) and (9) were also conveniently prepared as follows.

(E)-1-Chloro-4-(phenylsulfonyl)but-2-ene (5)

A solution of the sodium salt of benzenesulfinic acid (8·2 g, 0·05 mol, 0·5 equiv.) and (*E*)-1,4-dichlorobut-2-ene (12·5 g, 0·1 mol, 1·0 equiv.) in methanol (50 ml) was heated at reflux for 3 h, and the solvent was removed. The residue was dissolved in dichloromethane (200 ml), washed with water (2×100 ml) and brine (100 ml) and dried (Na_2SO_4). Removal of the solvent under reduced pressure left a pale yellow liquid. Distillation afforded firstly unreacted dichlorobutene as a colourless liquid (7·5 g, 60%), b.p. 80°/35 mm (Kugelrohr), and secondly (*E*)-1-chloro-4-(phenylsulfonyl)but-2-ene (5) as a colourless liquid (7·98 g, 35%; 86% based on reacted dichlorobutene), b.p. 180°/0·04 mm (Kugelrohr) (lit.[9] 120°/0·002 mm, lit.[10] 140–144°/0·01 mm). When 1·0 equiv. of the sodium salt of benzenesulfinic acid was used and the reaction mixture was heated at reflux for 16 h, (*E*)-1,4-bis(phenylsulfonyl)but-2-ene (7) was formed in 40% yield as white needles, m.p. 164–165° (lit.[12] 165–167°), from ethanol.

[28] Loughlin, W. A., Haynes, R. K., and Sitpaseuth S., *Aust. J. Chem.*, 1995, **48**, 491.

1-Chloro-4-(phenylthio)but-2-yne (9)

A solution of 1,4-dichlorobut-2-yne (14·76 g, 11·73 ml, 0·12 mol, 1·0 equiv.), thiophenol (6·17 ml, 0·06 mmol, 0·5 equiv.) and triethylamine (8·36 ml, 0·06 mmol, 0·5 equiv.) in dichloromethane (200 ml) was stirred overnight and then diluted with dichloromethane to a total volume of 500 ml. The dichloromethane layer was washed with water (2×200 ml), aqueous sodium carbonate (10%, 2×100 ml) and brine (2×200 ml) and dried (Na_2SO_4). Removal of the solvent under reduced pressure left the crude product as an orange liquid. Distillation afforded firstly unreacted 1,4-dichlorobut-2-yne (7·65 g, 52%), b.p. 85–87°/30 mm (Kugelrohr), and secondly, 1-chloro-4-(phenylthio)but-2-yne (9) as a pale yellow oil (10·65 g, 45%; 90% based on reacted dichlorobutyne), b.p. 125–130°/20 mm (Kugelrohr) (lit.[15] 111°/15 mm). When 1·0 equiv. of thiophenol (6·17 ml, 0·60 mol) and triethylamine (8·82 ml, 0·06 mol) were used in the above procedure, a viscous orange oil was obtained. Distillation afforded 1-chloro-4-(phenylthio)but-2-yne (9) as a pale yellow liquid (3·90 g, 33%), b.p. 155–160°/2 mm (Kugelrohr), and a solid residue. Recrystallization of the residue from ethanol gave (*E*)-1,4-bis(phenylthio)but-2-yne as white needles (4·71 g, 29%), m.p. 164–165° (lit.[29] 165–167°).

1-Chloro-4-(phenylsulfonyl)but-2-yne (4)

1-Chloro-4-(phenylthio)but-2-yne (9) (7·50 g, 38 mmol, 1·0 equiv.) was added slowly to a stirred solution of *m*-chloroperbenzoic acid (80%, 18·0 g, 2·2 equiv.) in dry ether (200 ml) at 0° under nitrogen. The reaction mixture was stirred for 1 h and the resulting precipitate of *m*-chlorobenzoic acid was removed by filtration. The filtrate was washed with aqueous sodium carbonate (10%, 3×100 ml), water (3×100 ml) and brine (3×100 ml) and dried (Na_2SO_4). Removal of the solvent under reduced pressure left a solid which was recrystallized from dichloromethane/light petroleum to afford *1-chloro-4-(phenylsulfonyl)but-2-yne* (4) as white prisms (6·52 g, 75%), m.p. 88–90° (Found: C, 52·2; H, 3·8. $C_{10}H_9ClO_2S$ requires C, 52·5; H, 4·0%). ν_{max} ($CHCl_3$) 2870m, 1575w, 1435m, 1380m, 1321s, 1155s, 1130s, 1075s, 860s cm^{-1}. ^1H n.m.r. (90 MHz) δ 3·91–4·14, 4H, m, $(H1')_2$, $(H4')_2$; 7·46–7·78, 3H, m, Ph *meta*, *para*; 7·88–8·10, 2H, m, Ph *ortho*. Mass spectrum *m/z* 228 (M, 0·5%), 193 (2), 141 (20), 125 (13), 77 (83), 52 (100).

N-Methylimidazolyl Sulfone Electrophiles

2-[(4'-Chlorobut-2'-enyl)thio]-1-methylimidazole (13)

A solution of triethylamine (2·44 ml, 17·5 mmol, 1·0 equiv.), (*E*)-1,4-dichlorobut-2-ene (2·2 g, 17·5 mmol, 1·0 equiv.) and 1-methylimidazole-2-thiol (2·0 g, 17·5 mmol, 1·0 equiv.) in dichloromethane (100 ml) were stirred for 22 h at room temperature. The pale yellow reaction mixture was diluted with dichloromethane (50 ml) and then washed with aqueous ammonium chloride (saturated, 100 ml), water (2×100 ml) and brine (100 ml) and dried (Na_2SO_4). Removal of the solvent under reduced pressure left a dark orange oil. Immediate purification by column chromatography with light petroleum/ethyl acetate (85:15), afforded *(2'E)-2-[(4'-chlorobut-2'-enyl)thio]-1-methylimidazole* (13) as a viscous orange oil (0·70 g, 20%) which polymerized upon standing (Found: $M^{+\bullet}$, 202·0310. $C_8H_{11}ClN_2S$ requires 202·0331). ν_{max} (Nujol) 3103w, 2951m, 1738w, 1668w, 1515w, 1460s, 1417m, 1375m, 1282s, 1255s, 1228m, 1125s, 1082m, 965s, 918m, 738s, 682s cm^{-1}. λ_{max} (ϵ) (ethanol) 268sh (3747), 230 nm (6476). ^1H n.m.r. (90 MHz) δ 3·59, 3H, s, 1-Me; 3·62, 2H, br d, $J_{1',2'}$ 6·0, $J_{1',3'} < 1·0$ Hz, $(H1')_2$; 3·90, 2H, br d, $J_{4',3'}$ 6·0, $J_{4',2'} < 1·0$ Hz, $(H4')_2$; 5·36–5·99, 2H, m, H2', H3'; 6·85, 1H, br s, H5; 6·98, 1H, br s, H4. Mass spectrum *m/z* 202 (M, 26%), 167 (100), 141 (19), 133 (16), 125 (12), 114 (34), 83 (14), 77 (24), 71 (24), 53 (16).

2-[(Buta-1,3-dienyl)thio]-1-methylimidazole (14)

Butyllithium (1·90 ml, 2·3 M, 1·0 equiv.) was added dropwise to a solution of 1-methylimidazole-2-thiol (0·5 g, 4·38 mmol) in tetrahydrofuran (20 ml) containing 2,2'-dipyridyl

[29] Porcelot, G., and Cadiot, P., *Bull. Soc. Chim. Fr.*, 1966, 3016.

as indicator, at −10° under nitrogen, until the first permanent orange colour appeared. The mixture was stirred for 5 min and then 1,4-dichlorobut-2-ene (0·55 g, 1·0 equiv.) in tetrahydrofuran (5 ml) was added. The reaction mixture was warmed to room temperature, stirred for 1 h and then quenched with aqueous ammonium chloride (20 ml). The mixture was extracted with ether (3×50 ml) and washed with aqueous sodium carbonate (saturated, 2×100 ml), water (100 ml) and brine (100 ml) and dried (Na_2SO_4). Removal of the solvent under reduced pressure left a dark orange oil. Immediate purification by chromatography with light petroleum/ethyl acetate (3:1) then ethyl acetate afforded firstly *2-[(buta-1,3-dienyl)thio]-1-methylimidazole* (14) as a mixture of (*E*)- and (*Z*)-isomers and as a dark yellow viscous oil (0·15 g, 21%) which polymerized on standing (Found: $M^{+\bullet}$, 166·0555. $C_8H_{11}ClN_2S$ requires 166·0565). ν_{max} (Nujol) 3111w, 2946m, 1669m, 1622m, 1558m, 1492m, 1460s, 1413s, 1279s, 1126m, 997m, 922m, 915m, 763m, 682m cm^{-1}. λ_{max} (ϵ) (ethanol) 262·8 (11452), 224·8 nm (10248). ^1H n.m.r. (90 MHz) δ 3·75, 3H, s, 1-Me; 4·73–5·38, 2H, m, $(H4')_2$; 6·18–6·66, 3H, m, H1′, H2′, H3′; 6·87–7·07, 2H, m, H4, H5. Mass spectrum *m/z* 166 (M, 44%), 165 (100), 139 (26), 133 (69), 114 (41), 81 (18), 72 (22), 55 (12), 53 (12).

The next fraction was 2-[(4′-chlorobut-2′-enyl)thio]-1-methylimidazole (13) as an orange viscous oil (0·15 g, 17%) which polymerized on standing.

When 1·0 equiv. of triethylamine was added to the reaction mixture after the addition of 1,4-dichlorobut-2-ene, the yield of the butadiene imidazole (14) did not significantly improve.

2-[(4′-Chlorobut-2′-ynyl)thio]-1-methylimidazole (15)

A solution of 1,4-dichlorobut-2-yne (1·28 ml, 1·62 g, 13·1 mmol, 1·0 equiv.), 1-methylimidazole-2-thiol (1·5 g, 13·1 mmol, 1·0 equiv.) and triethylamine (1·83 ml, 13·1 mmol, 1·0 equiv.) in dichloromethane (50 ml) was stirred overnight and then diluted with dichloromethane (50 ml). The organic layer was washed with aqueous sodium hydrogen carbonate (100 ml), water (2×100 ml) and brine (2×100 ml) and dried (Na_2SO_4). Removal of the solvent under reduced pressure left an orange oil which polymerized on standing. Immediate purification by chromatography with dichloromethane then ethyl acetate afforded *2-[(4′-chlorobut-2′-ynyl)thio]-1-methylimidazole* (15) as a yellow viscous oil (1·17 g, 45%) which polymerized rapidly upon standing (Found: $M^{+\bullet}$, 200·0176. $C_8H_9ClN_2S$ requires 200·0175). ν_{max} (Nujol) 3110s, 2960s, 2325w, 1738w, 1517s, 1418m, 1385m, 1285s, 1170m, 1132m, 1084m, 922m, 876w, 751m, 690s cm^{-1}. λ_{max} (ϵ) (ethanol) 238·4 nm (6476). ^1H n.m.r. (90 MHz) δ 3·68, 3H, s, 1-Me; 3·72, 2H, br s, $(H1')_2$; 4·03, 2H, br s, $(H4')_2$; 6·88, 1H, br s, H5; 7·00, 1H, br s, H4. Mass spectrum *m/z* 200 (M, 24%), 165 (100), 122 (26), 114 (19), 87 (71), 72 (31), 57 (15), 51 (40).

Butadienyl Sulfone Electrophiles

α-(Trimethylsilyl)butadienyl Sulfones (17) and (18)

A solution of 1-(phenylthio)(trimethylsilyl)but-3-ene (27)[24] (1·0 g, 4·2 mmol, 1·0 equiv.) in carbon tetrachloride (5 ml) was added to a stirred suspension of *N*-chlorosuccinimide (0·62 g, 1·1 equiv.) in carbon tetrachloride (20 ml). The suspension was stirred for 5 h and then filtered. The filtrate was concentrated, diluted with hexane and chilled. The precipitate was removed by filtration and the filtrate was concentrated under reduced pressure to give the crude product mixture as a yellow oil. Purification by radial chromatography with light petroleum/ethyl acetate (19:1) afforded a mixture of the (*E*)- and (*Z*)-isomers 1-(phenylthio)-1-(trimethylsilyl)buta-1,3-diene (21) and (22) and 3-chloro-1-(phenylthio)-1-(trimethylsilyl)but-1-ene as a yellow oil (0·38 g, *c.* 71%). The products could not be satisfactorily purified and were characterized as the corresponding sulfones which were prepared as follows.

The mixture of sulfides (0·38 g, *c.* 1·5 mmol) in dichloromethane (30 ml) at 0° under nitrogen were treated portionwise with *m*-chloroperbenzoic acid (0·91 g, 3·0 equiv.) over 30 min. The mixture was stirred for a further 4 h and then filtered. The solvent was removed from the filtrate under reduced pressure and the residue was dissolved in ether (100 ml). The ether layer was washed with aqueous sodium carbonate (2×100 ml), water (100 ml) and brine (100 ml) and dried (Na_2SO_4). Removal of the solvent under reduced pressure left a

viscous yellow oil. Purification by radial chromatography with light petroleum/ethyl acetate (19:1), afforded firstly a mixture of three compounds (0·272 g) as a viscous oil. Analysis of the mixture by analytical h.p.l.c. (light petroleum/ethyl acetate, 96:4; Whatman Partisil 5 column; 1·5 ml/min; 1200 p.s.i.) indicated that (*Z*)-1-(phenylsulfonyl)-1-(trimethylsilyl)buta-1,3-diene (18) (13%), (*E*)-3-chloro-1-(phenylsulfonyl)-1-(trimethylsilyl)but-3-ene (29) (18%) and (*E*)-1-(phenylsulfonyl)-1-(trimethylsilyl)buta-1,3-diene (17) (15%) were present. The second fraction obtained from radial chromatography was (*Z*)-3-chloro-1-(phenylsulfonyl)-1-(trimethylsilyl)but-3-ene (30), a white solid (0·114 g, 18%). Preparation of analytical samples was carried out as follows.

The first fraction was submitted to preparative h.p.l.c. with light petroleum/ethyl acetate (96:4) (Whatman Partisil 10 M20 column, 13·5 ml/min, 1100 p.s.i.) to give the following compounds in order of elution.

(Z)-*1-(Phenylsulfonyl)-1-(trimethylsilyl)buta-1,3-diene* (18) (R_t 57 min) was a viscous gum (Found: C, 58·8; H, 6·7. $C_{13}H_{18}O_2SSi$ requires C, 58·6; H, 6·8%). ν_{max} ($CHCl_3$) 3067m, 3015m, 2959m, 1595m, 1447m, 1301s, 1254s, 1143s, 1084s, 909s, 847s cm^{-1}. ^1H n.m.r. (200 MHz) δ 0·29, 9H, s, Me_3Si; 5·56, 1H, ddd, $J_{4,3}$ 12·0, $J_{4,4}$ 1·5, $J_{4,4} < 1·0$ Hz, H 4; 5·62, 1H, ddd, $J_{4,3}$ 6·0, $J_{4,4}$ 1·5, $J_{4,2} < 1·0$ Hz, H 4; 6·85, 1H, dd, $J_{2,3}$ 11·0, $J_{2,4} < 1·0$ Hz, H 2; 7·32–7·62, 4H, m, H 3, Ph *meta, para*; 7·83–7·91, 2H, m, Ph *ortho*. ^{13}C n.m.r. (50 MHz) δ −0·56, Me_3Si; 126·8, $PhSO_2$ *ortho*; 128·93, $PhSO_2$ *meta*; 128·96, C 4; 131·9, C 3; 132·7, $PhSO_2$ *para*; 143·4, C 1; 144·8, $PhSO_2$ *ipso*; 151·5, C 2. Mass spectrum *m/z* 266 (M, 14·5%), 251 (39), 180 (8), 135 (100), 106 (18), 92 (63), 77 (14), 73 (46), 59 (11), 51 (11).

The next fraction consisted of (E)-*3-chloro-1-(phenylsulfonyl)-1-(trimethylsilyl)but-3-ene* (29) (R_t 69 min) as a viscous gum (Found: $M^{+\bullet}$, 287·0340. $C_{12}H_{16}ClO_2SSi$ requires 287·0329). ν_{max} ($CHCl_3$) 3032m, 2965m, 1592m, 1447m, 1300s, 1257s, 1140s, 1086m, 870s, 850s cm^{-1}. ^1H n.m.r. (200 MHz) δ 0·21, 9H, s, Me_3Si; 1·66, 3H, d, $J_{4,3}$ 6·5 Hz, H 4; 4·83, 1H, dq, $J_{3,2}$ 10·5, $J_{3,4}$ 6·5 Hz, H 3; 7·24, 1H, d, $J_{2,3}$ 10·5 Hz, H 2; 7·48–7·66, 3H, m, Ph *meta, para*; 7·75–7·78, 2H, m, Ph *ortho*. ^{13}C n.m.r. (50 MHz) δ 0·5, Me_3Si; 24·5, C 4; 52·9, C 3; 127·5, Ph *ortho*; 129·0, Ph *meta*; 133·1, Ph *para*; 140·7, C 1; 144·1, Ph *ipso*; 154·4, C 2. Mass spectrum *m/z* 287 ($M - CH_3$, 59%), 267 (75), 135 (100), 125 (19), 93 (14), 77 (17), 73 (48), 53 (18).

The next fraction consisted of (E)-*[1-(trimethylsilyl)-1-(phenylsulfonyl)]buta-1,3-diene* (17) (R_t 77 min) as a viscous gum (Found: $M^{+\bullet}$, 266·0827. $C_{13}H_{18}O_2SSi$ requires 266·0797). ν_{max} ($CHCl_3$) 3069m, 3015m, 2960m, 1592m, 1447m, 1297s, 1255s, 1142s, 1085s, 850s cm^{-1}. ^1H n.m.r. (200 MHz) δ 0·19, 9H, s, Me_3Si; 5·70–5·84, 2H, m, $(H 4)_2$; 6·78, 1H, ddd, $J_{3,4}$ 16·5, $J_{3,2}$ 11·5, $J_{3,4}$ 9·5 Hz, H 3; 7·46–7·63, 3H, m, Ph *meta, para*; 7·74–7·84, 2H, m, H 2, Ph *ortho*. ^{13}C n.m.r. (50 MHz) δ 0·5, Me_3Si; 127·3, $PhSO_2$ *ortho*; 128·9, $PhSO_2$ *meta*; 128·9, C 4; 132·5, 132·7, C 3, $PhSO_2$ *para*; 141·7, C 1; 143·9, $PhSO_2$ *ipso*; 152·4, C 2. Mass spectrum *m/z* 266 (M, 14·5%), 251 (36), 180 (11), 135 (95), 106 (29), 92 (100), 77 (18), 73 (58), 66 (11), 59 (16), 51 (16).

Recrystallization from ether/light petroleum of the second fraction obtained by radial chromatography gave (Z)-*3-chloro-1-(phenylsulfonyl)-1-(trimethylsilyl)but-3-ene* (30) as white needles, m.p. 101–102° (Found: C, 51·8; H, 6·5%; $M^{+\bullet}$, 302·0545. $C_{13}H_{19}ClO_2SSi$ requires C, 51·6, H, 6·3%; $M^{+\bullet}$, 302·0563). ν_{max} ($CHCl_3$) 3030m, 2958m, 1594m, 1305s, 1252s, 1144s, 845s cm^{-1}. ^1H n.m.r. (200 MHz) δ 0·25, 9H, s, Me_3Si; 1·52, 3H, d, $J_{4,3}$ 6·5 Hz, H 4; 5·62, 1H, dq, $J_{3,2}$ 10·5, $J_{3,4}$ 6·5 Hz, H 3; 6·39, 1H, d, $J_{2,3}$ 10·5 Hz, H 2; 7·48–7·63, 3H, m, Ph *meta, para*; 7·82–7·92, 2H, m, Ph *ortho*. ^{13}C n.m.r. (50 MHz) δ −0·7, Me_3Si; 24·3, C 4; 51·7, C 3; 126·8, Ph *ortho*; 129·2, Ph *meta*; 133·2, Ph *para*; 142·5, C 1; 145·3, Ph *ipso*; 154·1, C 2. Mass spectrum *m/z* 302 (M, 0·2%), 287 (53), 267 (5), 135 (100), 125 (20), 93 (16), 77 (24), 73 (69), 53 (17).