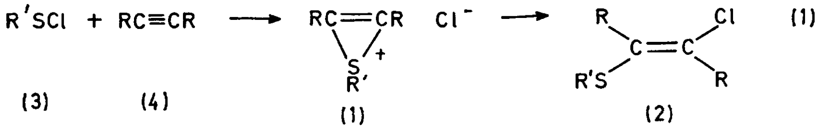
# Effect of Aryl Substitution at Ring Carbons on the Reactivity of Thiirenium Ions

By **Giuseppe Capozzi, Lino DaCol, Vittorio Lucchini,** and **Giorgio Modena,*** Centro Mecanism di Reazioni Organiche del CNR, Istituto di Chimica Organica, Università di Padova, 35100 Padova, Italy
**Giovanni Valle,** Centro di Studio sui Biopolimeri, Università di Padova, Padova, Italy

Methyl(bismethylthio)sulphonium (5) tetrafluoroborate or tetrachloroborate in liquid sulphur dioxide adds to 1-(4-methoxyphenyl)propyne to give methylthio-[*E*-1-(4-methoxyphenyl)-2-methylthioprop-1-enyl]methylsulphonium and methylthio-[*E*-1-(4-methoxyphenyl)-1-methylthioprop-2-enyl]methylsulphonium ions. The intermediacy of 1,2-dimethyl-3-(4-methoxyphenyl)thiirenium ion is postulated. The sulphonium salts react with pyridine or triethylamine to give *E*-1,2-bisalkylthio-1-(4-methoxyphenyl)propene, which interconverts partially to the *Z*-isomer. Similarly the addition of (5) to 1-phenylpropyne and to 1-phenylbutyne gives, after demethylthiolation, *E*- and *Z*-1,2-bismethylthio-1-phenylpropene and *E*- and *Z*-1,2-bismethylthio-1-phenylbut-1-ene.

SEVERAL recent reports[1-3] from this laboratory have shown that 2,3-dialkylthiirenium ions (1; R = alkyl) are fairly stable species in liquid sulphur dioxide at low temperature in the absence of strong nucleophiles. Under these conditions, even chloride ion reacts slowly with (1) to give the β-thiovinyl chloride (2). It was in fact shown[4] that the addition of sulphenyl chlorides (3) to dialkylacetylenes (4) occurs in two steps and that the formation of (1) is complete before (2) can be detected:



The reactivity of thiirenium ions (1) towards nucleophiles depends very much on the substitution pattern: *S*-aryl derivatives react faster than the *S*-alkyl analogues[4] and 1-methyl-2,3-di-t-butylthiirenium ion is so stable that can be isolated as tetrafluoroborate or hexachloroantimonate salt.[3] In contrast, the trimethyl derivative gives salts which decompose quickly above −40° to −30 °C.[5]

It might have been expected, as indeed has been found, that the substitution of one alkyl residue at a ring carbon with an aryl group would strongly modify the chemistry of this novel class of compounds. The results of our study in this area are reported here.

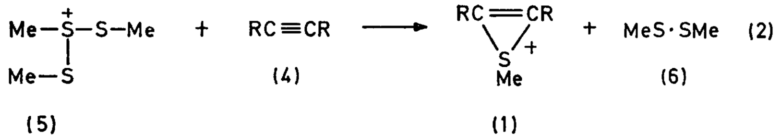
## RESULTS AND DISCUSSION

$^1$H *N.M.R. Investigation of the Addition in Liquid Sulphur Dioxide at* −60 °*C of Methyl*(*bismethylthio*)-*sulphonium Salts to* 1-*Arylalkynes*.—As reported in a previous paper,[2] the reaction of methyl(bismethylthio)-sulphonium (5) hexachloroantimonate[6] with dialkylacetylenes in liquid sulphur dioxide is both fast and quantitative and gives the corresponding thiirenium ions [see equation (2)]. The reaction may be easily monitored by $^1$H n.m.r. spectroscopy. For example in the reaction of (5) with but-2-yne (4; R = Me) the n.m.r. spectrum presents, within a few minutes, even at the lowest temperature, four peaks due to an excess of the butyne (δ 1.72), dimethyl disulphide (6) (δ 2.43), the ring methyls and the *S*-methyl of (1) (δ 2.51 and 2.77 respectively), the last three signals having the intensity ratio 2 : 2 : 1.

As models for arylalkylacetylenes, 1-(4-methoxyphenyl)propyne (7), 1-phenylpropyne (8), and 1-phenylbutyne (9) were chosen. When one of these compounds (7), (8), or (9) reacts with the sulphonium salt (5) in liquid sulphur dioxide at −60 °C, two major differences are observed with respect to the analogous reaction with dialkylacetylenes: (i) the reaction is much slower since several hours are necessary to reach the ' final ' n.m.r. spectrum of the solution; (ii) the spectrum presents a more complex signal system.

The first partial conclusion that can be drawn out of these results is that stable thiirenium ions are not formed in these reactions.

A more detailed study was carried out with 1-(4-methoxyphenyl)propyne (7) and the sulphonium (5) tetrafluoroborate in the ratio 2 : 1. The n.m.r. spectrum of the solution at the completion of the reaction is presented in Figure 1. Besides the absorption in the aromatic reaction and those of methoxy-hydrogens (δ 3.86 and 3.82), the spectrum presents eight singlets in the methyl region. One of them (δ 2.02) coincides with that expected for an excess of (7) and its relative intensity varies along with the excess of this reagent in the system. The other seven peaks may be interpreted as two sets of four non-equivalent methyl singlets, assuming



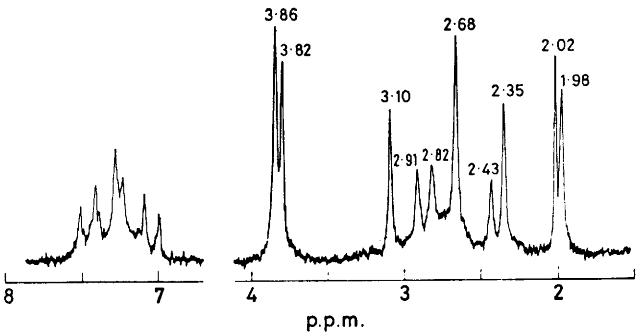
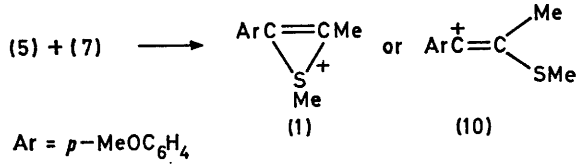


FIGURE 1 Addition of methyl(bismethylthio)sulphonium tetrafluoroborate to 1-(4-methoxyphenyl)propyne (molar ratio 1 : 2) in sulphur dioxide at −70 °C as monitored by n.m.r. spectroscopy at the completion of the reaction

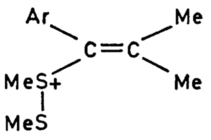
that two methyls have the same chemical shift. This interpretation is based on the relative intensity of the signals: three of them have higher intensity than the other three (intensity ratio *ca.* 3 : 1), whereas the seventh (δ 2.68) shows the intensity that may be expected from the contribution of two resonances, one from each set. It should be noticed that no absorption may be detected at the dimethyl disulphide frequency.

This spectrum would be consistent with the rapid reaction of the thiirenium ion (1) or the corresponding vinyl cation (10) with dimethyl disulphide (6) as nucleophile, in either a stereoselective but not regioselective reaction or in a regioselective but not stereoselective one:

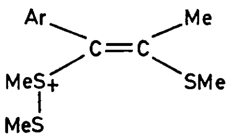


(1) (10) (3)

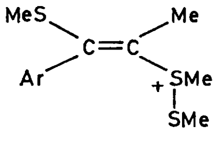
Indeed the n.m.r. spectrum accounts for the, at least predominant, formation of only two of the four possible isomeric sulphonium salts (11) and (12).



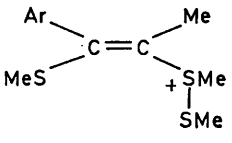
*E*-(11)



*Z*-(11)



*E*-(12)



*Z*-(12)

Assignment of structure to these two isomeric products solely on the basis of the chemical shifts or other magnetic resonance parameters would be both hard and open to doubt. A simplification of the system was therefore attempted.

It has been reported that alkylthiosulphonium salts [7] [*e.g.* (11) and (12)] as well as bisalkylthiosulphonium salts (5) [2,6,8] may easily transfer an alkylthio-moiety to appropriate nucleophiles. We therefore allowed the isomer mixture to react with a tertiary amine.

In Figure 2 the $^1$H n.m.r. spectrum of the solution after treatment with a slight excess of pyridine is shown. In the methyl region the signals of *N*-methylthiopyridinium ion (the expected reaction product), or dimethyl disulphide (a product of decomposition of the latter *), and those of an excess of 1-(4-methoxyphenyl)propyne are easily identified. Besides the methoxy-group peaks, only three other equally intense methyl signals are present. It follows that the two isomeric primary product give, as a consequence of the demethylthiolation process, the same compound, which must be either *E*-1,2-bismethylthio-1-(4-methoxyphenyl)propene *E*-(13) or its geometrical isomer *Z*-(13).

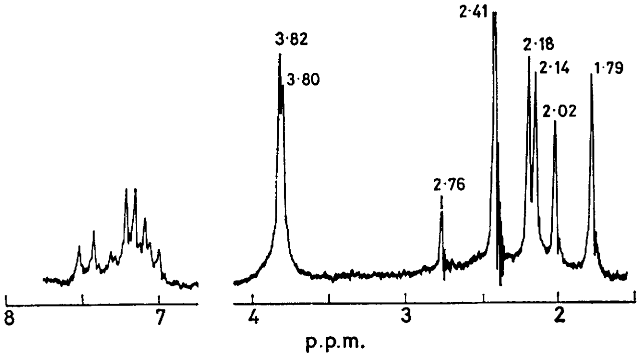
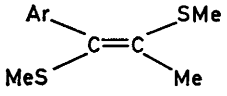
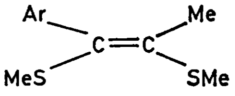


FIGURE 2 N.m.r. spectrum of the reaction mixture from the addition of methyl(bismethylthio)sulphonium tetrafluoroborate to 1-(4-methoxyphenyl)propyne after treatment with a slight excess of pyridine in sulphur dioxide at −70 °C



*E*-(13)



*Z*-(13)

Further evidence for the soundness of this interpretation stems from the $^1$H n.m.r. dynamic behaviour of the primary products (11) and (12).

The eight-band spectrum of Figure 1 undergoes at higher temperature a pairwise collapse of the signals of the two sub-systems to a system of four equally intense bands (Figure 3). This behaviour is not due to incipient

---

* *N*-Methylthiopyridinium ion, generated in liquid sulphur dioxide at −70 °C through the action of methyl(bismethylthio)sulphonium ion (5) on pyridine, is not stable. The methyl resonance of this ion at δ 2.76 slowly disappears with concurrent growth of the dimethyl-disulphide peak. A rationale for this behaviour could be the reduction, by the sulphur dioxide, of the *N*-methylthiopyridinium ion to pyridine and dimethyl disulphide.

decomposition since the original spectrum can be restored by lowering of the temperature. If, however, the temperature is too high and the experiment protracted, decomposition does occur.

The most probable process responsible for the dynamic behaviour observed is the equilibrium (11) $\rightleftharpoons$ (12) (both compounds either in the *E* or *Z* configuration) brought about by dimethyl disulphide (6) [equation (4)]: the latter may, in fact, accept a methylthio-group to give the sulphonium ion (5) which, in turn, gives it to a different sulphur atom in (13). In principle the transfer agent may also be either (11) or (12) acting through the two-co-ordinated sulphur atom to give the corresponding dication.[9] However it is quite probable that some disulphide is present in the system and, as a matter of fact, addition of this compound accelerates the exchange process. The absence of any signal at the dimethyl disulphide frequency may be justified by the already reported finding[6] that dimethyl disulphide (6) and methyl(bismethylthio)sulphonium ion (5) exchange rapidly in this solvent, giving rise to a single, broad band. This broad absorption might be responsible for the 'foot' which is evident in Figure 1.

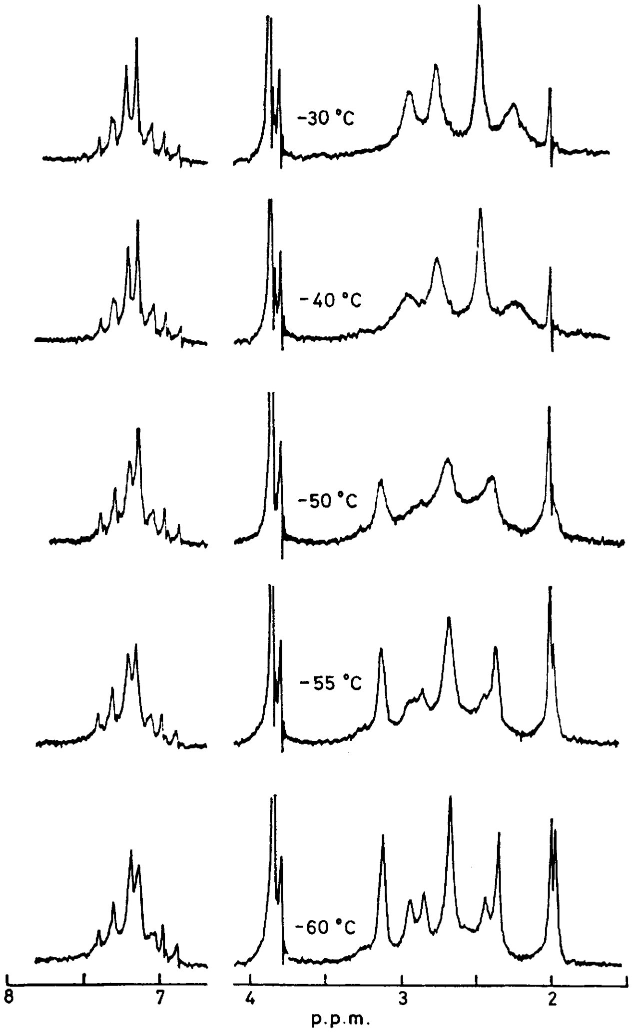
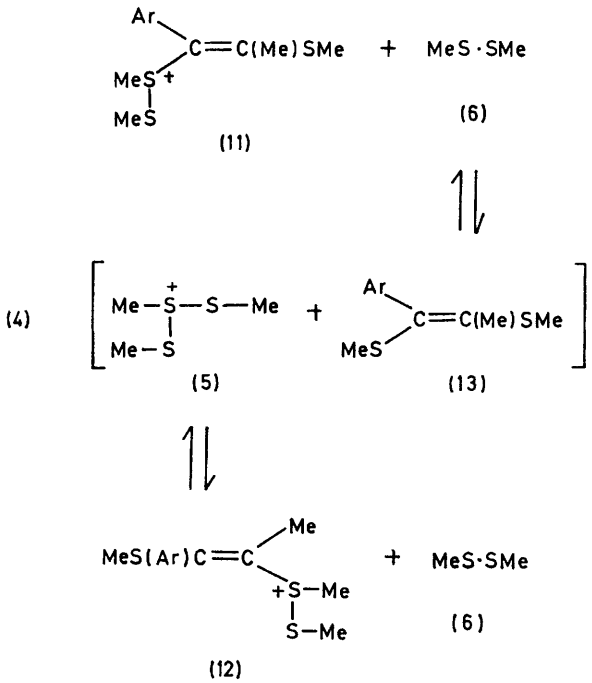


FIGURE 3 Dynamic n.m.r. spectra in sulphur dioxide of the reaction mixture from the addition of methyl(bismethylthio)-sulphonium tetrafluoroborate to 1-(4-methoxyphenyl)propyne



This interconversion process implies that the mixture of (11) and (12) (either *E* or *Z*) does not necessarily correspond to a kinetic system in the sense that both are primary products. In fact, the results presented do not give information on the regioselectivity of the addition of dimethyl disulphide to thiirenium ion; whereas they offer evidence in favour of a complete stereoselective addition (either *anti* or *syn*). On the other hand the *cis* $\rightleftharpoons$ *trans* interconversion of either (11) or (12) cannot be the cause of the dynamic process, because of the uniqueness of the demethylthiolated product (13).

The assignment of the *E*- or *Z*-configuration to this compound required a more extensive investigation which is reported in the following section.

*Product Study of the Addition of Methyl(bismethylthio)-sulphonium Tetrachloroborate to* 1-(4-*Methoxyphenyl*)-*propyne*, 1-*Phenylpropyne, and* 1-*Phenylbutyne*.—Methyl(bismethylthio)sulphonium (5) tetrachloroborate * was generated *in situ* by dissolving equimolar amounts of dimethyl disulphide (6), methanesulphenyl chloride (3; R' = Me), and boron trichloride in sulphur dioxide at —65 °C. To this solution the appropriate alkyne, 1-(4-methoxyphenyl)propyne (7), 1-phenylpropyne (8), or 1-phenylbutyne (9) was added and allowed to react for 3—6 h. The products were demethylthiolated without isolation with a slight excess of triethylamine. The

---

* We used the tetrachloroborate salt of the sulphonium ion (5) because of the difficulties encountered in the synthesis and isolation of the tetrafluoroborate salt, a very hygroscopic compound which decomposes easily. The hexachloroantimonate salt, a more stable derivative, cannot be used because of redox reactions of antimony(V) with the compounds in solution, leading to the formation of radical species. These species were detected through e.s.r. spectroscopy, but their nature was not further investigated.

solvent was then evaporated and the residue extracted with carbon tetrachloride.

The $^1$H n.m.r. spectra in chloroform of the extracts from each acetylenic precursor present two sets of absorptions which may be attributed to two isomeric products with structures corresponding to (13). The relative intensity of the two sets of absorptions varies from 9 : 1 to 7 : 3 depending on the individual reactions and the work-up procedure.

With time the set of lower intensity tends to increase at the expense of the intensity of the set initially present in greater amount. Quite clearly a process of equilibration is being observed, a phenomenon which has already been noted in the ready *cis,trans* isomerisation of vinyl sulphides in similar systems.[10]

The two isomeric compounds formed in each reaction were separated and purified by chromatography on silica gel; the two isomers isolated in this way show n.m.r. spectra corresponding to those of the initial mixture. The spectral parameters of the six $E$- and $Z$-vinyl bis-sulphides are reported in the Table.

It should also be noted that further isomerisation occurs on silica gel since the yield ratio of the isolated products is different from the ratio in the crude mixture as estimated from the integrated n.m.r. spectra. The acid-promoted isomerisation of these compounds was also checked by addition of gaseous hydrogen chloride to carbon tetrachloride solutions of the pure isomers: within minutes an almost equimolar mixture of $E$- and $Z$-isomers was obtained.

The structure of the six vinyl bis-sulphides was established by their oxidation to the corresponding vinyl bis-sulphones. Since it has been shown that isomerisation does not occur during the oxidation process,[11] the problem is reduced to the assignment of absolute configuration to the three sets of sulphones.

With this aim in mind the structure of the 1,2-bismethylsulphonyl-1-(4-methoxyphenyl)propene (16) (m.p. 155 °C and Me resonances at $\delta$ 2.57, 2.68, 2.72, and 3.86) was resolved by single-crystal $X$-ray diffractometry.[12] This investigation assigned unambiguously to this compound the $E$-configuration. Consequently the $Z$-configuration must be assigned to the isomer with methyl resonances at $\delta$ 2.08, 3.18, 3.39, and 3.85.

Inspection of the chemical shifts of this pair of isomers (see Table) reveals that the methylsulphonyl groups in (16) resonate at lower field ($\delta$ 3.18 and 3.39) in the $Z$-isomer than in the $E$-isomer ($\delta$ 2.58 and 2.68). This is not unexpected, since it is known [13] that a methyl group in ethylenic derivatives *cis* to electron-withdrawing residues (such as a sulphonyl group) is shifted to lower field than in the case of a *trans*-arrangement. Accordingly the chemical shifts of vinyl methyls also suffer the proximity effect of the sulphonyl groups: in the $E$-isomer the chemical shift ($\delta$ 2.72) is greater than in the $Z$-isomer ($\delta$ 2.08).

Because of the similarity of the magnetic parameters, the assignment of the $E$- or $Z$-configuration to the pairs of sulphones (17) and (18) is straightforward.

As already stated, the oxidation process is highly specific. Consequently, the absolute configurations of the three sets of vinyl bis-sulphides (13), (14), and (15) can be assigned as indicated in the Table.

The n.m.r. spectra of $E$- and $Z$-(13) have also been run in sulphur dioxide at −60 °C. The methyl resonances are reported in the Table in parentheses. The resonances of the $E$-isomer coincide exactly with those of the unique product formed from the demethylthiolation of (11) and (12) (see Figure 2) which, in turn, should also have the $E$-configuration. It follows that the addition, in sulphur dioxide, of the sulphonium salt (5) to 1-(4-methoxyphenyl)propyne (7) is stereospecifically *anti*. The same conclusion should apply to the addition of (5) to 1-phenylpropyne (8) and to 1-phenylbutyne (9), as suggested by the fact that the sulphides (14) and (15) in the $E$-configuration are initially formed in major amounts

The ready *cis,trans* isomerisation observed in these reactions is a general property of vinyl sulphides with a halogen atom or a further two-co-ordinate sulphur atom at the $\beta$ carbon.[10] The preference of the two sulphur atoms for a *cis*-arrangement has been object of some interest, although no definitive rationale for this fact has been so far suggested.[14]

## CONCLUSIONS

The most striking feature which emerges from these results is the different behaviour of dialkylacetylenes

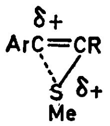
Chemical shifts ($\delta$) of the methyl resonances of 1,2-bismethylthio-1-arylalkenes and of their sulphonyl derivatives in chloroform at room temperature (values in parentheses: in sulphur dioxide at −60 °C)

| | | | SMe | Me | $CH_2$ | OMe | $^3J$(Hz) |
|---|---|---|---|---|---|---|---|
| $p$-$MeOC_6H_4(MeS)C{=}C(Me)SMe$ | (13) | $E$ | 1.84 and 2.15 | 2.33 | | 3.81 | |
| | | | (1.78 and 2.14) | (2.18) | | (3.82) | |
| | | $Z$ | 1.87 and 1.94 | 2.37 | | 3.81 | |
| | | | (1.80 and 1.90) | (2.32) | | (3.81) | |
| $Ph(MeS)C{=}C(Me)SMe$ | (14) | $E$ | 1.84 and 2.15 | 2.34 | | | |
| | | $Z$ | 1.87 and 1.94 | 2.38 | | | |
| $Ph(MeS)C{=}C(Et)SMe$ | (15) | $E$ | 1.80 and 2.32 | 0.97 | 2.21 | | 7.5 |
| | | $Z$ | 1.80 and 2.05 | 1.15 | 2.73 | | 7.5 |
| | | | $SO_2Me$ | Me | $CH_2$ | OMe | $^3J$(Hz) |
| $p$-$MeOC_6H_4(MeSO_2)C{=}C(Me)SO_2Me$ | (16) | $E$ | 2.57 and 2.68 | 2.72 | | 3.86 | |
| | | $Z$ | 3.18 and 3.39 | 2.08 | | 3.85 | |
| $Ph(MeSO_2)C{=}C(Me)SO_2Me$ | (17) | $E$ | 2.58 and 2.68 | 2.74 | | | |
| | | $Z$ | 3.21 and 3.39 | 2.03 | | | |
| $Ph(MeSO_2)C{=}C(Et)SO_2Me$ | (18) | $E$ | 2.51 and 2.66 | 1.41 | 3.27 | | 7.5 |
| | | $Z$ | 3.21 and 3.48 | 1.11 | 2.52 | | 7.5 |

and arylalkylacetylenes toward methyl(bismethylthio)-sulphonium salts (5). In liquid sulphur dioxide at low temperature dialkylacetylenes give 2,3-dialkylthiirenium ions which are almost unreactive towards a nucleophile such as dimethyl disulphide. In contrast arylalkylthiirenium ions, if they are assumed to be the intermediates in these addition reactions, are so readily attacked by dimethyl disulphide that their detection through n.m.r. spectroscopy is impossible.

In the latter case a different intermediate, the β-thiovinyl cation (10), may be suggested as an alternative. Theoretical investigations have demonstrated that the perhydrothiirenium ion is more stable than the corresponding β-thiovinyl cation,[15] and that methyl substitution at unsaturated carbons does not alter significantly this order of stability.[16] *Ab initio* calculations on (1) and (10) with aromatic substitution at the unsaturated carbons have not been undertaken, but elementary resonance theory suggests that the benzene ring should stabilize the open vinyl cation (10) more than the thiirenium ion (1). This is even more so in the case of substitution with a 4-methoxyphenyl group. On the other hand it is hard to expect a stereospecific *anti*-addition to the vinyl cation, as it is observed in the cases studied here. In fact recent reports [17] from this laboratory have shown that, when the intermediacy of the vinyl cation is very likely, as in the addition of alkyl halides to acetylenes, *syn*- and *anti*-products are both observed and a stereospecific course is confined to limiting cases.

Therefore the stereospecific *anti*-addition of sulphonium salts (5) seems to require the intermediacy of thiirenium ions, and the reactivity towards dimethyl disulphide may be ascribed to the enhanced electrophilicity of ring carbons because of aromatic substitution. In fact, if the aromatic substitution at the α carbon increases significantly the stability of the β-thiovinyl cation (10), it is expected that the cyclic ion 'mixes in' some character of the former, giving the asymmetric structure (19) with different C–S bond lengths and different SCC bond angles. More important, a significant positive charge is present at the ring carbon carrying the aromatic substituent, which should be accompanied by greater electrophilicity. With regard to this, the primary addition product of dimethyl disulphide to (19) should have the Markownikoff structure *E*-(11); the *anti*-Markownikoff isomer *E*-(12) may be thought to originate from the former *via* transfer of the methylthio-residue, as described by equation (4).



(19)

## EXPERIMENTAL

*Materials*.—Sulphur dioxide, silver tetrafluoroborate, boron trichloride, triethylamine, 3-chloroperbenzoic acid, 1-phenylpropyne (8), and 1-phenylbutyne (9) are commercially available products. Methanesulphenyl chloride,[18] methyl(bismethylthio)sulphonium (5) hexachloroantimonate,[6] and 1-(4-methoxyphenyl)propyne (7) [19] were prepared by literature methods.

*N.M.R. Experiments*.—$^1$H N.m.r. spectra were recorded on a Bruker HFX-10 90 MHz spectrometer equipped with a variable-temperature unit.

*Methyl(bismethylthio)sulphonium* (5) *Tetrafluoroborate*.—To a −78 °C (acetone–$CO_2$) solution of dimethyl disulphide (2.4 mmol) and methanesulphenyl chloride (2.4 mmol) in sulphur dioxide (3 ml), $AgBF_4$ (2.5 mmol) was added stepwise. The solution was stirred for 40 min, AgCl was filtered off, and the solvent evaporated at 0 °C under reduced pressure. A viscous oil was obtained, which failed to crystallize. The compound was very sensitive to moisture and it was not possible to obtain reproducible elemental analyses. However, the chemical behaviour towards alkenes [20] and alkynes [2] and the n.m.r. spectrum (in sulphur dioxide at −60 °C, single resonance at δ 3.09 because of rapid methyl rearrangement for the presence of dimethyl disulphide [6]) confirmed the structural assignment.

E- *and* Z-1,2-*Bismethylthio*-1-(4-*methoxyphenyl*)*propene* E- *and* Z-(13), E- *and* Z-1,2-*Bismethylthio*-1-*phenylpropene* E- *and* Z-(14), *and* E- *and* Z-1,2-*Bismethylthio*-1-*phenylbut*-1-*ene* E- *and* Z-(15).—To a −65 °C (chloroform–$CO_2$) solution of boron trichloride (30 mmol) in sulphur dioxide (6 ml), dimethyl disulphide (30 mmol) and freshly prepared methanesulphenyl chloride (30 mmol) were successively added with stirring. The vessel was then frozen in liquid air and the alkyne (7), (8), or (9) (36 mmol) were added. The vessel was slowly warmed to −65 °C while the alkyne was gently stirred with a glass rod. The solution reddened immediately. After 3—6 h triethylamine (120 mmol) was added dropwise with stirring. The reaction was rather exothermic. The solution was then poured into a beaker with carbon tetrachloride (200 ml) and solid sodium carbonate was added in portions until gas evolution stopped. The organic phase was washed with water to neutrality and dried ($Na_2SO_4$). The yellow oil obtained after evaporation of the solvent under reduced pressure was purified by chromatography on silica gel [eluants: for (7): 14% (v/v) ether–light petroleum; for (8): 40% (v/v) benzene–light petroleum; for (9): 10% (v/v) ether–light petroleum]. Total yields were *E*-, *Z*-(13): 53%; *E*-, *Z*-(14): 46%; *E*-, *Z*-(15): 86%. The individual compounds were purified by bulb-to-bulb distillation ($10^{-2}$—$10^{-3}$ mmHg). Elemental analyses (Found) were as follows: *E*-(13): C, 60.1; H, 6.75; S, 26.3. *Z*-(13): C, 60.1; H, 6.65; S, 27.0. ($C_{12}H_{16}S_2O$ requires C, 60.0; H, 6.66; S, 26.7%). *E*-(14): C, 62.8; H, 6.65; S, 30.3. *Z*-(14): C, 62.8; H, 6.60; S, 30.5 ($C_{11}H_{14}S_2$ requires C, 62.9; H, 6.66; S, 30.5%). *E*-(15): C, 64.6; H, 7.45; S, 28.5. *Z*-(15): C, 64.4; H, 7.05; S, 28.1 ($C_{12}H_{16}S_2$ requires C, 64.3; H, 7.14; S, 28.6%).

E- *and* Z-1,2-*Bismethylsulphonyl*-1-(4-*methoxyphenyl*)*propene* E- *and* Z-(16), E- *and* Z-1,2-*Bismethylsulphonyl*-*phenylpropene* E- *and* Z-(17), E- *and* Z-1,2-*Bismethylsulphonyl*-1-*phenylbut*-1-*ene* E- *and* Z-(18).—To an ice-cooled solution of the vinyl bis-sulphide [*E*- or *Z*-(13), (14), or (15)] in methylene chloride a 20% excess of 3-chloroperbenzoic acid in methylene chloride was added dropwise with stirring. The solution was kept for 2 days at room temperature. 3-Chlorobenzoic acid precipitated partially and was filtered off. The organic phase was washed with sodium carbonate in water and water to neutrality, dried ($Na_2SO_4$), and the solvent removed under reduced pressure. The white crystals (yield 75—85%) were recrystallized from methanol or ethanol; m.p. *E*-(16), 155 °C; *Z*-(16), 135 °C; *E*-(17), 171—172 °C; *Z*-(17), 148—149 °C; *E*-(18), 171—172 °C; *Z*-(18), 149—150 °C. Elemental analyses (Found) were as follows: *E*-(16): C, 47.2; H, 5.10; S, 21.1. *Z*-(16): C, 47.3; H, 5.30; S, 21.2 ($C_{12}H_{16}O_5S_2$ requires C, 47.4; H, 5.26; S, 21.1%). *E*(17): C, 48.1; H, 5.10; S, 23.3. *Z*-(17): C, 47.9; H, 5.30; S, 23.3 ($C_{11}H_{14}O_4S_2$ requires C, 48.2; H, 5.11; S, 23.4%). *E*-(18): C, 50.2; H, 5.40; S, 22.2 *Z*-(18): C, 49.6; H, 5.70; S, 21.6 ($C_{12}H_{16}O_4S_2$ requires C, 50.0; H, 5.55; S, 22.2%).

[9/304 *Received*, 26*th February*, 1979]

## REFERENCES

[1] G. Capozzi, V. Lucchini, and G. Modena, *Rev. Chem. Intermediates*, 1979, **2**, 347.

[2] G. Capozzi, O. DeLucchi, V. Lucchini, and G. Modena, *J.C.S. Chem. Comm.*, 1975, 248.

[3] G. Capozzi, V. Lucchini, G. Modena, and P. Scrimin, *Tetrahedron Letters*, 1977, 911.

[4] G. Capozzi, V. Lucchini, G. Modena, and P. Scrimin, *Nouveau J. Chim.*, 1978, **2**, 95.

[5] G. Capozzi, O. DeLucchi, V. Lucchini, and G. Modena, unpublished results.

[6] G. Capozzi, V. Lucchini, G. Modena, and F. Rivetti, *J.C.S. Perkin II*, 1975, 900.

[7] G. K. Helmkamp, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, 1965, **30**, 676; G. K. Helmkamp, B. A. Olsen, and J. R. Koskinen, *J. Org. Chem.*, 1965, **30**, 1623; J. L. Kice and N. A. Favstritsky, *J. Amer. Chem. Soc.*, 1969, **91**, 1751; S. H. Smallcombe and M. C Caserio, *J. Amer. Chem. Soc.*, 1971, **93**, 5826.

[8] G. Capozzi, O. DeLucchi, V. Lucchini, and G. Modena, *Synthesis*, 1976, 677.

[9] H. Braun and A. Amann, *Angew. Chem. Internat. Edn.*, 1975, **14**, 755.

[10] G. Modena and G. Scorrano, *Mechanisms of Reactions of Sulfur Compounds*, 1968, **3**, 115.

[11] L. Maioli, G. Modena, and F. Taddei, *Boll. Sci. Fac. Chim. ind. Bologna*, 1960, **18**, 58.

[12] G. Valle, G. Zanotti, and V. Busetti, *Cryst. Struct. Comm.*, 1977, **6**, 327.

[13] V. Calo', G. Modena, and G. Scorrano, *J. Chem. Soc.* (*C*), 1968, 1344; C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5856.

[14] M. Oky and K. Kobayashi, *Bull. Chem. Soc. Japan*, 1970, **43**, 1234.

[15] I. G. Csizmadia, F. Bernardi, V. Lucchini, and G. Modena, *J.C.S. Perkin II*, 1977, 542.

[16] I. G. Csizmadia, V. Lucchini, and G. Modena, *Gazzetta*, 1978, **108**, 543.

[17] F. Marcuzzi and G. Melloni, *J. Amer. Chem. Soc.*, 1976, **98**, 3295, and references cited therein.

[18] H. Britzinger, H. Koddesbuch, K. H. Kling, and G. Jung, *Chem. Ber.*, 1952, **85**, 455.

[19] N. Lozac'h, M. Denis, Y. Mollier, and J. Teste, *Bull. Soc. chim. France*, 1953, **20**, 1016.

[20] G. Capozzi, O. DeLucchi, V. Lucchini, and G. Modena, *Tetrahedron Letters*, 1975, 2603.