Elimination and Addition Reactions. Part 38.[1] Synthesis and Reactivity of Diene-bis-sulphonium Salts †

Peter J. Duggan and John L. Leng
I.C.I. Organics Division, Blackley, Manchester M9 3DA
Donald R. Marshall and Charles J. M. Stirling *
School of Physical and Molecular Sciences, University College of North Wales, Bangor LL57 2UW

Buta-1,3-diene-1,4-bis-sulphonium salts have been synthesised from buta-1,3-diyne. Reactions with oxygen, sulphur, nitrogen, and carbon nucleophiles have been examined. Except for primary amines and anions of enolisable carbon acids, 1,4-addition and subsequent elimination of the sulphonium group is observed in all cases. Subsequent addition occurs with alkoxide and thiolate ions, and is followed by de-alkylation of the remaining sulphonium group or its displacement by allylic substitution.

When hydroxy-thiols or dithiols are used, a second intramolecular addition at carbon 4 yields cyclic products. Such products are not formed from hydroxy-amines. The mono-adducts formed from alkenyl-thiols are potentially capable of, but do not undergo, intramolecular Diels–Alder reactions under a variety of conditions. Neither are intramolecular reactions found in the adduct with 2-methoxycarbonylethanethiol or in the bis-adduct formed by subsequent additions of azide ion and propene-3-thiolate ion.

The sulphonium group can legitimately be claimed to be the most versatile function in organic chemistry.[2] This versatility stems from the capability of the group to stabilise adjacent carbanion centres (ylide),[3] to render alkenes electrophilic and hence susceptible to nucleophilic addition,[4] and to act as a leaving group in displacement and elimination reactions comparable in behaviour with, for example, bromide.[5]

Additions to unsaturated sulphonium salts, both alkenyl [4] and alkynyl,[6,7] have been studied in considerable detail with particular emphasis on their synthetic application.[8] Some of these synthetic applications have depended upon addition followed by intramolecular attack by carbon of the resulting ylide upon an internal electrophile.[9]

In general, there has been rather little work on electrophilic polyenes with the exception of allenes and cumulenes.[7,10] The latter undergo predominantly 1,4-addition and, in this connection, Braun's [11] work on polyene monosulphonium salts is most relevant. Thus, reaction of the salt (1a) with base gave the cumulene (2) which is trappable as its Diels–Alder adduct with cyclopentadiene and which with nucleophiles gives products of type (1b). In even closer relationship to the present work, the bis-sulphonium salt (3a) [11] was reported to yield the diene-monosulphonium salt (4a) on treatment with base, and with methoxide to give a mixture of the conjugated compound (5a) and the non-conjugated mono-adducts (3b). Similar reaction with benzenethiolate gave 1,4-addition followed by allylic displacement of the sulphonium group to give (3c).[12] Carbon nucleophiles such as malononitrile gave either 1,4- or 1,2-addition with subsequent intramolecular displacement of the sulphonium group to give, for example, cyclopropanes.[13] By contrast, Garst [14] found that a simple carbonyl-stabilised carbanion such as that derived from butanone, adds with subsequent intramolecular addition of the derived sulphonium ylide to the carbonyl group, or by rearrangement of the ylide.

Against this background of considerable related work, we now report on the synthesis and reactivity of 1,3-diene-bis-sulphonium salts, having paid particular attention to the differing patterns of behaviour revealed by different types of nucleophile.

† Part of this work was presented at the 9th International Symposium on Organic Sulphur Chemistry, Riga, June 1980.

$RCH_2C{\equiv}CCH_2R'$

(1)

a; $R = R' = Me_2\overset{+}{S}\ \overset{-}{O}Ts$
b; $R = Me_2\overset{+}{S}$, $R' = Nu$
c; $R = R' = PhSO_2$
d; $R = R' = Me_2\overset{+}{S}\ \overset{-}{O}Ts$
e; $R = R' = OTs$
f; $R = R' = OMe$
g; $R = Me_2\overset{+}{S}$, $R' = OMe$
h; $R = OTs$, $R' = OMe$
i; $R = R' = PhCH_2SO$
j; $R = R' = PhCH_2S$
k; $R = R' = PhS$
l; $R = R' = Cl$
m; $R = R' = Me_2\overset{+}{S}\ \overset{-}{I}/HgI_2$
n; $R = R' = Et_2\overset{+}{S}\ \overset{-}{I}/HgI_2$
o; $R = Me_2\overset{+}{S}$, $R' = SPh$

$Me_2\overset{+}{S}CH{=}C{=}C{=}CH_2$

(2)

$RCH_2CH{=}CH{-}CHR'R''$

(3)

a; $R = R' = Me_2\overset{+}{S}$, $R'' = H$
b; $R = Me_2\overset{+}{S}$, $R' = OMe$, $R'' = H$
c; $R = R' = PhS$, $R'' = H$
d; $R = Et_2\overset{+}{S}$, $R' = Nu$, $R'' = Nu'$
e; $R = EtS$, $R' = Nu$, $R'' = Nu'$
f; $R = EtS$, $R' = R'' = OMe$
g; $R = Et_2\overset{+}{S}$, $R' = R'' = OMe$
h; $R = Et_2\overset{+}{S}$, $R', R'' = SCH_2CH_2O$
i; $R = EtS$, $R', R'' = SCH_2CH_2O$
j; $R = R' = EtS$, $R'' = SCH_2CH_2OH$
k; $R = Et_2\overset{+}{S}$, $R, R'' = SCH_2CH_2S$
l; $R = EtS$, $R, R' = SCH_2CH_2S$
m; $R = EtS$, $R' = EtS$, $R'' = SC_6H_4NH_2$-*o*
n; $R = Et_2\overset{+}{S}$, $R' = SCH_2CH{=}CH_2$, $R'' = N_3$
o; $R = R' = R'' = EtS$
p; $R = R' = EtS$, $R'' = OMe$
q; $R = EtS$, $R' = SCH_2CH{=}CH_2$, $R'' = N_3$
r; $R = R' = EtS$, $R'' = CH(SO_2Et)_2$

Synthesis.—1,3-Diene-1,4-bis-sulphonium salts were unknown prior to this work and a number of approaches to this type of structure were investigated.

(*a*) *Isomerisation of but-2-ynes.* In earlier work from this group [15] it has been shown that the bis-sulphone (1c) isomerises readily to compound (4b) when passed in chloroform solution through a column of basic activated alumina. The simplicity of this method recommended its application to sulphonium salts. Treatment of a chloroform solution of the salt (1d), readily obtained from the bistosylate, with alumina gave no isomerisation product. When methanol replaced chloroform as solvent, the bismethoxy-compound (1f) or monosulphonio-monomethoxy-derivative (1g) was obtained. These products could be formed either by solvolysis or, in the case of the monoether, by elimination–addition. Formation of the cumulene (2) in basic conditions was demonstrated by trapping with thiolate ion. The contrast in behaviour from the bis-sulphone (1b) is due to the different balance between elimination–addition from the α-carbanion and the reprotonation of the isomerised ion. For the sulphone, the nucleofugality of the sulphinate ion, which is substantially less than that of the sulphonium group,[5] allows prototropy to be more favourable than elimination.

The bistosylate (1e) was recovered from its methanol solution at 18 °C over long periods, and at 60 °C mixtures of the monomethoxy-monotosylate (1h) and bismethoxy-compounds (1f) were obtained.

The ready accessibility of compounds (1) prompted investigation of the bis-sulphoxide (1i). Treatment of the chloroform solution with alumina gave a mixture of the allene (6a) and the conjugated alkyne (7). The sulphides (1j) and (1k) were unaffected by alumina treatment of their solutions in chloroform, but in ethanolic 0.01M-sodium ethoxide at 80 °C slowly gave the allenes (6b) and (6c) together with conjugated alkyne as for the sulphoxide. In neither case was any 1,3-diene detected.

(b) *From butadiyne.* The failure of bis-sulphides,-sulphoxides, and -sulphonium salts (1) to isomerise to 1,3-dienes enforced the alternative involving bis-addition of thiols to buta-1,3-diyne. The alkyne was generated from the bischloride (1l) [16] and with methanolic solutions of sodium thiolates gave the bis-sulphides (4c).

The bisbenzyl sulphide (4d) did not react appreciably with benzyl chloride or benzyl tosylate at 18 °C, and at higher temperatures gave a mixture of several alkylation products consistent with reversion reactions.[17] Benzylation was preferred because diastereoisomer formation was avoided; its failure prompted an examination of alkylation with methyl iodide, dimethyl sulphate, and triethyloxonium fluoroborate. In each case, however, products consistent with alkylation–reversion reactions were obtained. With diethyl sulphate in dimethyl sulphoxide, only ethyldimethyloxosulphonium fluoroborate was formed.

The problem of reversion was circumvented, albeit unsatisfactorily, by carrying out alkylation with methyl iodide in the presence of mercuric iodide. The bis-sulphonium salt (4e) (2%) was obtained together with the mercuric iodide double salt with dimethylbenzylsulphonium iodide and trimethylsulphonium iodide. Variations in conditions gave no improvement in yield, evidently as a result of equilibration, and further attempts with benzyl sulphides were abandoned. The bis-sulphide (4f) with methyl iodide and mercuric iodide gave the double mercuric iodide salt (4g) quantitatively at 0 °C. At 18 °C, the salt was obtained in lower (50%) yield, the complementary product being the but-2-yne double salt (1m). Similarly, from the bisethyl sulphide (4h) the yield of bisdiethylsulphonium salt was 48% at 0 °C. This decreased at higher temperatures with competitive formation of the butyne salt (1n) occurring. It was not considered satisfactory to use the double mercuric iodide salts for other than preliminary experiments and most work was carried out with the bis-salt (4i) obtained in 68% yield by alkylation of the bis-sulphide (4h) with triethyloxonium fluoroborate. The bisethylsulphonium salt was preferred to the bismethyl salt because of the lower tendency of the former to dealkylation,[18] and fluoroborate to iodide as counter ion because of the much lower tendency to reversion.

Reactions of Diene-bis-sulphonium Salts.—Discussion of reactivity is best preceded by delineation of the possible reactions with nucleophiles and subsequent interpretation of the

$$RCH{=}CH{-}CH{=}CHR'$$

(4)

a; R = $Me_2\overset{+}{S}$, R′ = H
b; R = R′ = $PhSO_2$
c; R = R′ = RS
d; R = R′ = $PhCH_2S$
e; R = R′ = $MeS\overset{+}{C}H_2Ph\ \bar{I}/HgI_2$
f; R = R′ = MeS
g; R = R′ = $Me_2\overset{+}{S}\ \bar{I}/HgI_2$
h; R = R′ = EtS
i; R = R′ = $Et_2\overset{+}{S}\ \bar{B}F_4$
j; R = $Et_2\overset{+}{S}$, R′ = Nu
k; R = $Et_2\overset{+}{S}$, R′ = OMe
l; R = $Et_2\overset{+}{S}$, R′ = SPh
m; R = $Et_2\overset{+}{S}$, R′ = SEt
n; R = $Et_2\overset{+}{S}$, R′ = SCH_2CH_2OH
o; R = $Et_2\overset{+}{S}$, R′ = $SCH_2CH{=}CH_2$
p; R = $Et_2\overset{+}{S}$, R′ = $S(CH_2)_2CH{=}CH_2$
q; R = $Et_2\overset{+}{S}$, R′ = $SCH_2CH_2CO_2Me$
r; R = R′ = $S(CH_2)_2CH{=}CH_2$
s; R = $Et_2\overset{+}{S}$, R′ = N_3
t; R = $Et_2\overset{+}{S}$, R′ = $NHCH_2Ph$
u; R = $Et_2\overset{+}{S}$, R′ = $NH(CH_2)_2OH$
v; R = $Et_2\overset{+}{S}$, R′ = NC_5H_{10}
w; R = R′ = $Et_2\overset{+}{S}\ \bar{I}/HgI_2$
x; R = $Et_2\overset{+}{S}$, R′ = $CH(SO_2Et)_2$

$$RCH{=}CH{-}\underset{\displaystyle R'}{\underset{|}{CH}}{-}CH_2R''$$

(5)

a; R = $Me_2\overset{+}{S}$, R′ = R″ = OMe
b; R = EtS, R = R″ = OMe

$$RCH{=}C{=}CHCH_2R$$

(6)

a; R = $PhCH_2SO$
b; R = $PhCH_2S$
c; R = PhS

$$PhCH_2SOC{\equiv}CCH_2CH_2SOCH_2Ph$$

(7)

$$R_2\overset{+}{S}\bar{C}HCH{=}CHCH(Nu)\overset{+}{S}R_2$$

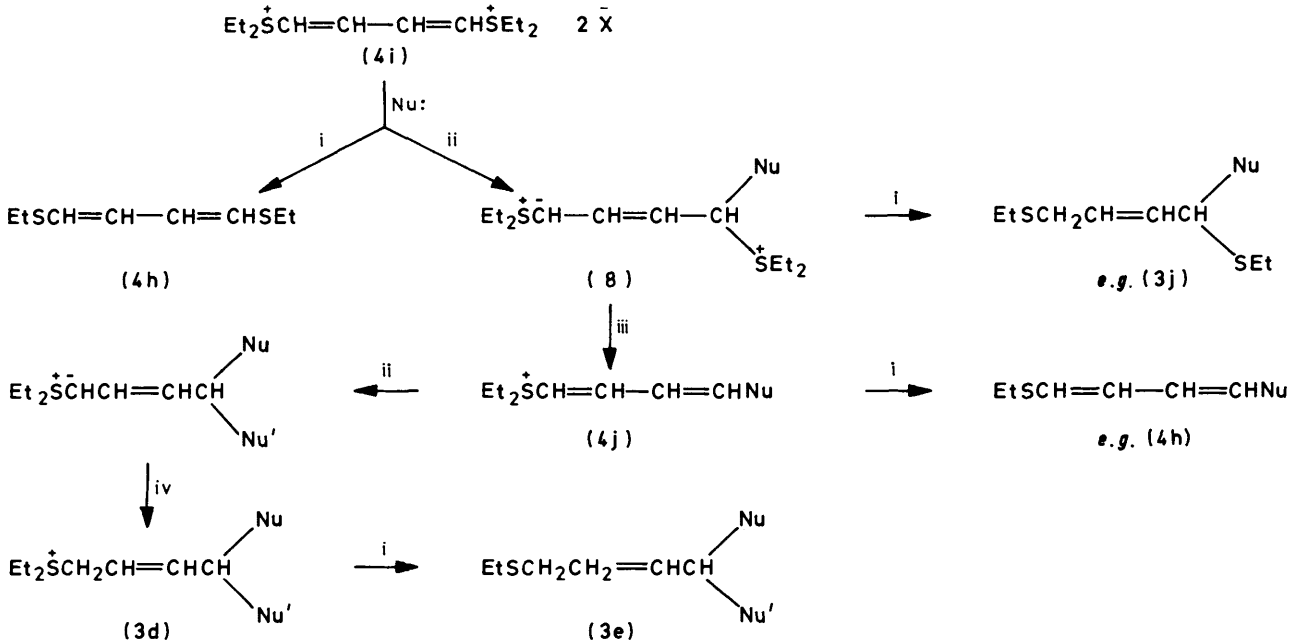
(8)

$$EtSCH_2CH(OMe)CH_2CH(OMe)_2$$

(9)

$$PhSCH_2CH{=}CHCH(SPh)_2$$

(10)



Scheme 1. i, Dealkylation; ii, Addition; iii, elimination; iv, protonation.

patterns of behaviour of the types of nucleophile studied. The course followed is, of course, dependent on the nucleophilicity of the nucleophile towards sp^3 (dealkylation) and sp^2 (addition) carbon. Simple dealkylation *e.g.* (4i) ⟶ (4h) competes at each stage of the addition–elimination–addition–dealkylation sequence (4i) ⟶ (8) ⟶ (4j) ⟶ (3d) ⟶ (3e) (Scheme 1). The final products are determined by the balance between the nucleophilicity of the nucleophile at sp^3 or sp^2 carbon and its basicity. The outline of the course of reaction for each type of nucleophile follows.

(*a*) *Oxygen nucleophiles.* The diene-bis-sulphonium salt (4i) showed negligible reaction with methanol or with a catalytic amount of sodium methoxide in methanol, which was rapidly consumed. Simple addition is not, therefore, involved, *i.e.* formation of the ion (8) and subsequent protonation. Elimination from the ion (8) with consumption of base is the most rapid process. With one equivalent of sodium methoxide in methanol, the hygroscopic product of 1,4-addition–elimination, (4k), is obtained. Under more forcing conditions (60 °C and two equivalents of methoxide per mole of bis-sulphonium salt), both sulphonium functions react and the product is a mixture of the sulphides (3f), (5b), and (9). The alkene (3f) is clearly the product of a second 1,4-addition [to (4k)] followed by dealkylation. It is notable that in these conditions, dealkylation occurs by attack at an ethyl group rather than at the allylic α-position, and one sulphur atom remains in the product. The olefin (5b) is produced from (4k) by 1,2-addition–dealkylation, and the butane (9), by prototropy and 1,2-addition–dealkylation in (3g). The putative intermediate (4k) in reactions with higher base : substrate ratios, on separate treatment with methanolic sodium methoxide at 18 °C, gave a mixture of bis- and tris-methoxysulphonium salts which were dealkylated by subsequent treatment under mildly basic conditions with sodium thioethoxide in methanol. P.l.c. gave diethyl sulphide and a 1 : 1 mixture of the bismethoxy-sulphides (3f) and (5b) (45%) together with the trimethoxy-compound (9).

The general pattern of products shows that in a strongly basic medium with an only moderately nucleophilic reagent,[19] addition to the terminus of the diene system is substantially preferred and subsequent prototropy of these labile unsaturated sulphonium salts occurs easily. The bis- and tris-methoxysulphonium salts are probably all in equilibrium.[20]

Treatment of the elimination–addition product (4k) with ethanethiolate gave the addition–dealkylation product (3p).

(*b*) *Sulphur nucleophiles, thiolate ions.* By comparison with alkoxide ions, thiolate ions are much less basic and much more nucleophilic.[21] Treatment of the diene-bis-sulphonium salt (4i) with one mole per mole of sodium benzenethiolate in methanol gave the addition–elimination product (4l) (96%). When an additional equivalent of benzenethiol was added, the tris-sulphide (10) (44%) was formed. Straightaway, the contrast with reactions with alkoxides is evident as the tris-sulphide must result from allylic dealkylation and displacement of the original dialkylsulphonium group intact. With ethanethiolate ion (1 mole per mole) the 1,4-addition–elimination sequence (4i) ⟶ (4m) is followed as for alkoxide ions.

We have used a number of polyfunctional thiolate ions with the intention of examining intramolecular reactions. 2-Hydroxyethanethiol gave the simple addition–elimination product (4n) (99%). When this adduct was treated with catalytic quantities of methanolic sodium methoxide, cyclisation by intramolecular addition occurred to give the alkene salt (3h). This was characterised by dealkylation with ethanethiolate ion to give the sulphide, (3i) (81%) which was separated by p.l.c. from the intermolecular competition product (3j) formed by addition of ethanethiolate. When ethane-1,2-dithiol was used, the cyclic derivative (3k) was obtained in quantitative yield and dealkylated with ethanethiolate to give the tris-sulphide (3l). Significantly, in this case there is no question of intermolecular addition; the internal nucleophile is as nucleophilic as the external one. By contrast, with 2-aminobenzenethiol, the simple addition–elimination product was formed and dealkylated without isolation to give the adduct (3m) (68%). No involvement of the poorly nucleophilic nuclear amino-group was detected.

Reactions with other functionalised thiols, propene-3-thiol, but-1-ene-4-thiol, and 2-methoxycarbonylethanethiol gave the usual addition–elimination products (4o) (88%), (4p) (92%)

and (4q) (77%), respectively. The salt (4p) was accompanied by a small amount (5%) of product (4r) in which both sulphonium groups have been replaced by the alkenylthio-group. In each case it was intended that subsequent cyclisation of the adduct should be explored. Treatment of compound (4o) with azide ion and buffering of the reaction mixture with acetic acid gave the azido-adduct (3n) also obtained in small quantities from the azide (4s) on treatment with propenethiol (below). In an attempt to produce the cyclic product (11), the adduct (3n) was kept at 50 °C but gave only dark viscous material. Infrared spectroscopic examination showed that the azido-group had reacted but there was no nitrogen present. No thiazoline (11) was detected.

The adduct (4p) and the bis-sulphide (4r) were kept at 60 °C in chloroform and at 150 °C, respectively. In neither case was the intramolecular Diels–Alder product *cf.* (12) observable in spite of ample literature precedent,[22] albeit in somewhat different systems. The conditions for reported examples are fairly severe and in our work decomposition products were obtained.

In reactions with 2-methoxycarbonylethanethiol, subsequent treatment of the initial adduct (4q) with methanolic sodium methoxide gave, after dealkylation, an unstable mixture of several components which decomposed on attempted low-pressure distillation. None of the product *cf.* (13) of intramolecular carbanion–ester reaction was found.

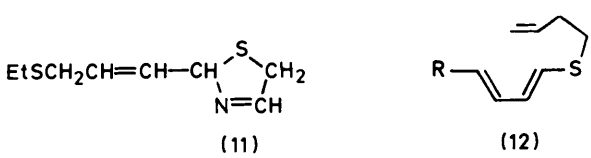
(*c*) *Nitrogen nucleophiles, amines.* Reactions with aromatic primary and aliphatic primary, secondary, and tertiary amines have been examined. *p*-Anisidine in acetonitrile in the presence of one equivalent of sodium methoxide gave a mixture of the addition–elimination product (4k) and recovered diene bis-sulphonium salt; *p*-anisidine was recovered in high yield. With benzylamine, the reaction occurred slowly in acetonitrile over a period of days; at 80 °C, reaction occurred and dealkylation ($Et\bar{S}$) of the predominantly ionic product, gave as the only identified product, the tris-sulphide (3o) (41%). When an equivalent amount of sodium methoxide was present, the dealkylation product was (3p) (40%). It seems probable that the initial reaction is addition–elimination as with oxygen and sulphur nucleophiles (above) but the unstable enamine (4t) whose formation requires two moles of amine per mole of diene-bis-sulphonium salt, subsequently decomposes. The dealkylation products isolated result from unchanged salt (*ca.* 50%). With ethanolamine, the dealkylation products similarly showed no incorporation of the nucleophile or product corresponding to (4u). Low yields of the bis- (4h) and tris- (3o) sulphide were obtained and the reaction was not pursued further. The bis-sulphide (4h) probably results from successive dealkylation by the amine and by ethanethiolate as it is not obtained from the diene-bis-sulphonium salt and ethanethiolate alone. Reaction with piperidine and one equivalent of sodium methoxide was straightforward. The salt (4v) (89%) was obtained by the addition–elimination route with methoxide serving to deprotonate the initial sulphonium-ammonium salt. Piperidine demonstrates its characteristically high nucleophilicity in this reaction by contrast to the other amines studied; triethylamine, however, fails to react even at 60 °C. This behaviour is in contrast to the previously reported reaction of triethylamine with the monoene-bis-sulphonium salt (14a) which readily gives the addition–elimination product (14b) [23] under the same conditions. The greater ground-state stabilisation of the diene may be partially responsible for this difference in reactivity which is, however, substantial.

With sodium azide in methanol, the simple addition–elimination product (4s) was obtained in 81% yield. Treatment of this adduct with propene-3-thiol gave the bis-addition product (3n), identical with that obtained from the allylthio-sulphonium salt (4o), and sodium azide in methanol buffered with acetic acid. No adduct was obtained in unbuffered conditions.

Intramolecular reaction between azido-groups and carbon–carbon double bonds are well known,[24] but the dealkylated azido-allylthio-adduct (3q) gave no cyclisation product on being kept in methanol for 1 h at 50 °C. Numerous unidentified products were formed and i.r. spectra showed the absence of an azido-group in the product mixture.

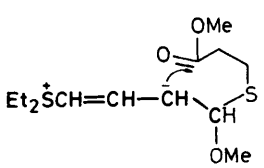
(*d*) *Carbon nucleophiles.* The nucleophiles were generated from both enolisable and non-enolisable carbon acids. With acetylacetone, in methanolic sodium methoxide, no incorporation of the derived anion could be detected, notwithstanding the ready incorporation of acetylacetone in classical Michael reactions, and its application in furan synthesis by addition to allenic sulphonium salts.[8] The methoxy-derivative (4k) was the sole (85%) identified product. By contrast, sodiodiethylsulphonylmethane in acetonitrile gave, after dealkylation of the initial product, the bis-adduct (3r) (33%). When the reaction was repeated with methanol as solvent, the same product (4k) (90%) as for acetylacetone was formed. Evidently the carbon nucleophiles fail to compete in addition with even small concentrations of methoxide ion, and there is no question of reversal of additions under these circumstances because of the very low nucleofugality of carbon leaving groups.[5]

It was considered possible that cyclisation of the initial

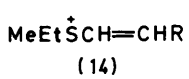


(11)

(12)



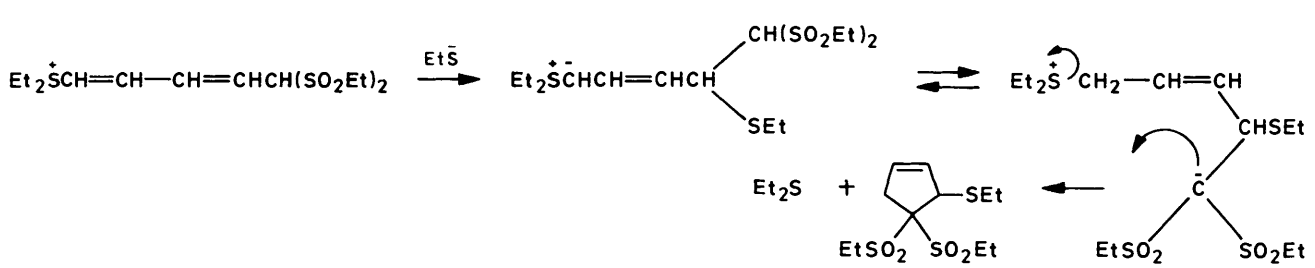
(13)



(14)

a ; R = $MeEt\overset{+}{S}$

b ; R = $\overset{+}{N}Et_3$



Scheme 2.

adduct might occur on further nucleophilic addition (Scheme 2), but no such products were obtained.

Conclusions

Buta-1,3-diene-bis-sulphonium salts have been shown to display patterns of reactivity towards nucleophiles which are strongly dependent upon the nucleophile. Reactions with poorly nucleophilic species, notably primary amines and highly stabilised carbanions, fail to show incorporation of the nucleophile and products from solvent incorporation dominate. With other nucleophiles, addition–elimination and subsequent addition of dealkylation reactions readily occur; intramolecular reactions with functionalised nucleophiles are variable in occurrence.

Experimental

All reactions were carried out under dry N_2. Extractions were performed with CH_2Cl_2. ^1H and ^{13}C N.m.r. spectra of all compounds were consistent with assigned structures and are given only when alternative structures may reasonably be considered. The rest of the n.m.r. data are available as a Supplementary Publication* (SUP No. 23591, 3 pages).

Some products were non-crystalline hygroscopic sulphonium salts which could not be purified without decomposition. In some of these cases, as well as for some unstable products, microanalytical data falls outside the usual limits for characterisation but spectroscopic data are then detailed. Some sulphonium salts were semi-solids with indefinite melting points.

1,4-*Bisbenzylthiobut*-2-*yne* (1j).—Sodium toluene-α-thiolate (34.6 mmol) in ethanol (20 ml) was added dropwise during 20 min to 1,4-bis(4-methylphenylsulphonyloxy)but-2-yne (17.3 mmol) in dichloromethane (10 ml) and ethanol (10 ml) at 40 °C. (*cf.* ref. 25) After 10 min, addition of water and extraction gave the bis-sulphide (96%), m.p. 41—42 °C (from methanol) (Found: C, 72.0; H, 6.0. $C_{18}H_{18}S_2$ requires C, 72.4; H, 6.0%).

1,4-*Bisbenzylsulphinylbut*-2-*yne* (1i).—The preceding sulphide (5 mmol) in methanol (5 ml) was treated with 30% aqueous hydrogen peroxide (1.13 g) and ammonium molybdate (0.5 g) in water (1.5 ml). After 12 h at 18 °C, the crude *sulphoxide* (79%) was filtered off, m.p. 151—152 °C (from methanol) (Found: C, 65.8; H, 5.5. $C_{18}H_{18}O_2S_2$ requires C, 65.5; H, 5.5%).

Attempted Conversions of But-2-*ynes into Buta*-1,3-*dienes.*—(*a*) 1,4-*Bisdimethylsulphoniobut*-2-*yne ditosylate* (1d). The salt [11] was kept at 18 °C in a 20% solution in methanol. No change occurred in 8 h (^1H n.m.r.) and, after 2 h at 60 °C, ^1H n.m.r. showed formation of the dimethylsulphonio(methoxy)but-2-yne (below). When the solution was stirred with basic alumina (Spence type H) for 3 days, ^1H n.m.r. showed that a mixture of mono- and bis-methoxybutynes had been formed.

Trapping of a cumulene intermediate (2). When sodium methoxide (1 equiv.) was added to a methanolic solution of the salt (1d) at −40 °C, subsequent addition of thiophenol (1.25 equiv.) and warming to 18 °C gave a mixture which on removal of the excess of thiophenol from the dichloromethane solution with aqueous sodium hydroxide, gave the 1-*dimethylsulphonio*-4-*phenylthiobut*-2-*yne tosylate* (1o) (52%); δ($CDCl_3$) 7.5 (m, 9 H), 4.4 (s, 2H), 4.3 (s, 2 H), 3.1 (s, 6 H), and 2.4 (s, 3 H) (Found: C, 57.8; H, 5.9. $C_{19}H_{22}O_3S_3$ requires C, 58.0; H, 5.8%).

(*b*) 1,4-*Bisphenylthiobut*-2-*yne* (1k). The bis-sulphide was unaffected (^1H n.m.r.) on treatment with alumina in chloroform and while it was recovered (93%) on treatment with triethylamine in dimethyl sulphoxide (DMSO) at 80 °C for 30 min, more prolonged treatment gave tars. Treatment with ethanolic 0.07M-sodium ethoxide at 78 °C or with potassium hydroxide in anhydrous tetrahydrofuran (THF) at 18 °C gave slow conversion into 1,4-*bisphenylthiobuta*-1,2-*diene* (6c) (*ca.* 50% in each case), b.p. 130—140 °C/0.7 mmHg; $\nu_{max.}$ 1 960 cm^{-1}; δ($CDCl_3$) 7.5 (m, 10 H), 5.5—6.0 (m, 2 H), 3.2 (d, 2 H) (Found: C, 76.2; H, 5.2. $C_{16}H_{14}S_2$ requires C, 76.7; H, 5.2%).

(*c*) 1,4-*Bisbenzylthiobut*-2-*yne* (1j). Treatment of the bis-sulphide with potassium hydroxide in THF as in (*b*) gave dark mixtures showing i.r. allene absorption from 1,4-bisbenzylthiobuta-1,2-diene (6b), but pure material could not be obtained.

(*d*) 1,4-*Bisbenzylsulphinylbut*-2-*yne* (1i). The sulphoxide (1 g) in chloroform (50 ml) was stirred with alumina (Carag 100—240 mesh neutral Brockman activated, 80 g) at 40 °C for 48 h. After filtration the product was concentrated to an oil (0.95 g). Its n.m.r. was very complex, $\nu_{max.}$ 1 960 (allene) and 2 220 cm^{-1} (unsymmetric acetylene).

1,4-*Bisalkylthiobuta*-1,3-*dienes.*—The following procedure is typical: 1,4-dichlorobut-2-yne was added (**caution**!) to potassium hydroxide (1.1 mol) in water (60 ml) and dioxan (6 ml) under N_2. The temperature of the mixture was slowly raised to 100 °C and the diacetylene evolved was carried in the nitrogen stream into toluene-α-thiol (2.2 mol) and potassium hydroxide (2.2 mol) in methanol (70 ml). When evolution of diacetylene was complete, the mixture was kept at 60 °C for 1 h; on cooling, 1,4-*bisbenzylthiobuta*-1,3-*diene* (4d) (42%) separated, m.p. 126—127 °C (from methanol) (Found: C, 72.3; H, 5.8. Calc. for $C_{18}H_{18}S_2$: C, 72.5; H, 6.0%) (lit.,[26] m.p. 129 °C for the *Z,Z*-isomer). The bismethylthio- (4f) [27] and bisethylthio-buta-1,3-dienes (4h) [28] were obtained similarly.

Alkylation of 1,4-*Bisethylthiobuta*-1,3-*diene.*—The sulphide (4h) (10 mmol), ethyl iodide (100 mmol), and mercuric iodide (2 mmol) were heated under reflux in acetone (5 ml). After 1 h, addition of ether precipitated 1,4-*bisdiethylsulphoniobuta*-1,3-*diene salt* (4w) (13%), m.p. >180 °C (decomp.) (Found: C, 10.5; H, 2.0. $C_{12}H_{24}Hg_2I_6S_2$ requires C, 10.4; H, 1.7%), δ($CDCl_3$) 7.94 (d, 2 H), 7.04 (d, 2 H), 3.65 (q, 8 H), and 1.41 (t, 12 H).

The bis-sulphide (10 mmol) in dichloromethane (10 ml) was added during 35 min to triethyloxonium fluoroborate (20 mmol) in dichloromethane (20 ml) under N_2. After 1 h, t.l.c. showed unchanged bis-sulphide, and further alkylating agent (30 mmol) was added. After a further 1 h, no bis-sulphide was present and evaporation gave a residue which, on addition of ether, gave 1,4-*bisdiethylsulphoniobuta*-1,3-*diene bistetrafluoroborate* (4i) (68%), m.p. 196—197 °C (from methanol) (Found: C, 35.5; H, 6.1. $C_{12}H_{24}B_2F_8S_2$ requires C, 35.5; H, 5.9%); δ[$(CD_3)_2SO$] 7.87 (d, 2 H), 6.91 (d, 2 H), 3.54 (q, 8 H), and 1.32 (t, 12 H); δ (^{13}C) 11.59, 39.97, 125.13 and 144.79 p.p.m.

Reactions of the Bis-sulphonium Salt (4i).—(*a*) *With sodium methoxide.* The salt (4i) (5 mmol) in methanol (20 ml) on treatment with methanolic 1M-sodium methoxide (5 ml, 5 mmol) gave a clear solution; after 4 h, evaporation gave a residue, extracted with dichloromethane (2 × 30 ml), which was found to be sodium tetrafluoroborate (94%). The extracts

* For details of the Supplementary Publications Scheme see 'Instructions to Authors (1983),' *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

were evaporated to give a residue of the hygroscopic 1-*diethylsulphonio*-4-*methoxybuta*-1,4-*diene salt* (4k) (69%) (Found: C, 36.0; H, 6.4. $C_9H_{17}BF_4OS\cdot H_2O$ requires C, 38.3; H, 6.8%) (C/H ratio: Found: 5.62; Calc. 5.7); δ[$(CD_3)_2SO$] 5.67—7.72 (m, 4 H), 3.85 (3 H), 3.43 (q, 4 H), 3.4 (s, 2 H, water), and 1.39 (t, 6 H).

Treatment of the salt (4k) (5 mmol) with ethanethiol (10 mmol) and sodium methoxide (5 mmol) in acetonitrile (10 ml) at 18 °C for 18 h gave the *methoxy-bis-sulphide* (85%) (4.5 min retention on a 5-ft SE 30 column under N_2 at 175 °C) (Found: C, 52.4; H, 8.7. $C_9H_{18}OS_2$ requires C, 52.4; H, 8.7%).

Repetition of this reaction with a 2 : 1 ratio of sodium methoxide and the sulphonium salt gave crude covalent material (460 mg) which on distillation gave first a fraction (100 mg), b.p. 108 °C/15 mmHg, whose ^1H n.m.r. spectrum [δ($CDCl_3$) 5.3 (d, 1 H), 4.7 (m, 1 H), 3.4 (d, 6 H), 2.65 (q, 4 H), and 1.3 (t, 3 H)] showed it to be a 1 : 1 mixture of bis-methoxysulphides (3f) and (5b) (Found: C, 54.6; H, 9.1%). The second fraction, b.p. 140 °C/15 mmHg (110 mg) was the 4-*ethylthio*-1,1,3-*trimethoxybutane* (9) (Found: C, 51.7; H, 9.9; $C_9H_{20}O_3S$ requires C, 51.9; H, 9.6%); δ($CDCl_3$) 4.7 (m, 2 H), 3.4 (d, 9 H), 2.6 (q, 4 H), 2.0 (m, 2 H), and 1.3 (t, 3 H).

(*b*) *With ethanethiolate ion.* The sulphonium salt (4i) (5 mmol) and ethanethiol (5 mmol) in methanol (20 ml) were treated with methanolic 1M-sodium methoxide (5 ml). After 16 h at 18 °C, removal of solvent and extraction of the residue with dichloromethane left sodium tetrafluoroborate (92%) and the hygroscopic semi-solid 1-*diethylsulphonio*-4-*ethylthiobuta*-1,3-*diene salt* (4m) (97%) (Found: C, 41.2; H, 6.3. $C_{10}H_{19}BF_4S_2$ requires C, 41.4; H, 6.6%); δ[$(CD_3)_2SO$] 6.0—7.8 (m, 4 H), 3.42 (q, 4 H), 2.9 (q, 2 H), and 1.41 (2 × s, 9 H).

(*c*) *With benzenethiolate ion.* In the same way the addition–elimination product 1-*diethylsulphonio*-4-*phenylthiobuta*-1,3-*diene* (4l) (95%) was obtained (Found: C, 50.0; H, 6.0. $C_{14}H_{19}BF_4S_2$ requires C, 49.7; H, 5.6%). Repetition with four moles of thiophenol and two moles of methoxide per mole of sulphonium salt gave a residue which on extraction with dichloromethane left sodium tetrafluoroborate (95%). The extracts were washed with aqueous sodium hydroxide which removed 86% of the thiophenol calculated to remain after consumption of three moles per mole of salt. Evaporation of the organic extracts and chromatography on alumina in Et_2O–CH_2Cl_2 (50 : 50 v/v) gave first a trace of diphenyl disulphide and then the 1,1,4-*trisphenylthiobut*-2-*ene* (10) (75%) as an oil (Found: C, 70.0; H, 5.3. $C_{22}H_{20}S_3$ requires C, 69.5; H, 5.3%); δ($CDCl_3$) 7.21 (m, 15 H), 5.7 (m, 1 H), 5.3 (m, 1 H), 4.5 (m, 1 H), and 3.3 (d, 2 H).

(*d*) *With* 2-*hydroxyethanethiol.* Reaction as before with 1 mole per mole of sulphonium salt (4i) gave the semi-crystalline 1-*diethylsulphonio*-4-(2-*hydroxyethylthio*)*buta*-1,3-*diene* (4n) (100%) (Found: C, 39.2; H, 6.3. $C_{10}H_{19}BF_4OS_2$ requires C, 39.2; H, 6.2%); δ (^{13}C) 8.71, 36.85, 36.9, 60.95, 108.25, 117.21, and 144.76 p.p.m.; $\nu_{max.}$ 3 520 cm^{-1}.

Conversion of the salt (4i) into the cyclic sulphide (3i) *via* the sulphonium salt (3 h) was accomplished by treatment of the salt (1.74 g) with ethanethiol (0.62 g, 0.01 mol) and 1M-methanolic sodium methoxide (10 ml). After 10 h, the usual work-up and p.l.c. gave first 3-*ethylthio*-1-(1,3-*oxathiolidin*-2-*yl*)*prop*-1-*ene* (3i) (81%) as an oil (Found: C, 50.3; H, 8.0. $C_8H_{14}O_2S$ requires C, 50.5; H, 7.5%); δ ($CDCl_3$) 5.7 (m, 2 H), 5.0 (m, 1 H), 3.7 (m, 2 H), 3.0—3.25 (2 H), 2.4—2.8 (m, 6 H), and 1.27 (t, 3 H). δ(^{13}C) 14.6, 24.7, 32.5, 38.3, 71.5, 85.4, 129.7, and 130.5 p.p.m. The middle fraction (0.01 g) was unidentified, and the final fraction (0.17 g, 16%) was 1,4-*bisethylthio*-1-(2-*hydroxyethylthio*)*but*-2-*ene* (3j) (Found: C, 47.5; H, 7.5. $C_{10}H_{20}OS_3$ requires C, 47.6; H, 7.9%); δ($CDCl_3$) 5.5—5.7 (2 H), 3.6—4.0 (3 H), 3.1—3.2 (2 H), 2.5—2.9 (m, 6 H), and 1.26 (t, 6 H); $\nu_{max.}$ 3 330 cm^{-1} (OH).

(*e*) *With ethane*-1,2-*dithiol.* Reaction was as before with the salt (4i) (5 mmol), sodium methoxide (5 mmol), and thiol (5 mmol). Dealkylation was by addition of ethanethiol (5 mmol) and sodium methoxide (5 mmol). Work-up gave the 3-*ethylthio*-1-(1,3-*oxathiolidin*-2-*yl*)*prop*-1-*ene* (3l) (91%), b.p. 120 °C/0.12 mmHg (Found: C, 46.3; H, 6.7. $C_8H_{14}S_3$ requires C, 46.4; H, 6.8%).

(*f*) *With propene*-3-*thiol.* Reaction of the salt (4i) (2.5 mmol) with the thiol (2.5 mmol) and sodium methoxide (2.5 mmol) in methanol at 18 °C for 16 h gave the semi-solid 1-*diethylsulphonio*-4-*prop*-2-*enylthiobuta*-1,3-*diene salt* (4o) (85%) (Found: C, 42.5; H, 6.5. $C_{11}H_{19}BF_4S_2\cdot\frac{1}{2}H_2O$ requires C, 42.8; H, 6.7%). The adduct (5 mmol), sodium azide (5 mmol), and acetic acid (4.5 mmol) were stirred in methanol for 16 h at 18 °C. Evaporation and extraction of the residue with dichloromethane gave the 1-*azido*-4-*diethylsulphonio*-1-*prop*-2-*enylthiobut*-2-*ene salt* (3n) (94%); $\nu_{max.}$ 2 170 cm^{-1} (s) (Found: C, 37.7; H, 6.0; N, 11.1. $C_{11}H_{20}BF_4N_3S_2$ requires C, 38.3, H, 5.8; N, 12.1%).

(*g*) *With but*-1-*ene*-4-*thiol.* The salt (4i) (10 mmol) was allowed to react with thiol (10 mmol), and sodium hydroxide (10 mmol) in methanol at 18 °C for 1 h. Evaporation to dryness and extraction of the residue with ether (2 × 50 ml) gave crude material (5%) whose spectral characteristics were consistent with the bis-sulphide (4r). The bis-sulphide decomposed on standing (100—170 °C) in $CDCl_3$. Extraction with dichloromethane gave the 1-*diethylsulphonio*-4-*but*-3-*enylthiobuta*-1,3-*diene salt* (4p) (92%) (Found: C, 42.8; H, 6.7. $C_{12}H_{21}BF_4S\cdot H_2O$ requires C, 43.1; H, 6.9%). The ^1H n.m.r. spectra [$(CD_3)_2SO$] at 50 °C showed slow decomposition of the salt.

(*h*) *With* 2-*methoxycarbonylethanethiol.* Reaction of the salt (4i) (2.5 mmol) with the thiol (2.5 mmol) and sodium methoxide (2.5 mmol) in methanol as before gave the 1-*diethylsulphonio*-4-(2-*methoxycarbonylethylthio*)*buta*-1,3-*diene salt* (4q) (77%) (Found: C, 39.4; H, 6.0. $C_{12}H_{21}BF_4O_2S_2\cdot H_2O$ requires C, 39.3; H, 6.3%).

Treatment of the adduct (4q) with methanolic 1M-sodium methoxide (1 equiv.) for 16 h at 18 °C followed by evaporation and extraction of the residue with dichloromethane gave a viscous residue which was dealkylated by treatment with ethanethiolate (1 equiv.) as before. Work-up and attempted distillation of the crude product gave tars.

(*i*) *With benzylamine and with ethanolamine.* The salt (4i) (2.5 mmol) and benzylamine (2.5 mmol) were stirred in acetonitrile (20 ml) for 3 days at 18 °C. T.l.c. showed unchanged benzylamine and the mixture was kept for 1 h at 80 °C and evaporated to a residue that t.l.c. showed to be largely ionic. Dealkylation with ethanethiol–sodium methoxide (1 equiv.) as before gave a liquid (440 mg) from which was separated by p.l.c. (Kieselgel 6F 254 and 50 : 50 ether–dichloromethane, the 1,1,4-*trisethylthiobut*-2-*ene* (3o); δ($CDCl_3$) 5.53—5.63 (m, 2 H), 4.28 (m, 1 H), 3.15 (d, 2 H), 2.56 (q, 6 H), and 1.25 (t, 9 H) (Found: C, 50.8; H, 8.5. $C_{10}H_{20}S_3$ requires C, 50.9; H, 8.5%).

Repetition of the experiment in the presence of sodium methoxide (2.5 mmol) gave 1,4-*bisethylthio*-1-*methoxybut*-2-*ene* (3p).

(*j*) *With piperidine.* The salt (4i) (2.5 mmol) and piperidine (2.5 mmol) in methanol were treated dropwise with methanolic sodium methoxide during 10 min. After 18 h at 18 °C, evaporation and extraction with dichloromethane left sodium tetrafluoroborate (97%). Evaporation of the extract gave the 1-*diethylsulphonio*-4-*piperidinobuta*-1,3-*diene salt* (4v) (89%), δ[$(CD_3)_2SO$] 6.8—7.4 (m, 2 H), 5.1—5.6 (2 H), 3.3 (m, 8 H), and 1.35—1.8 (m, 12 H) (Found, C, 47.9; H, 6.2; N, 4.6. $C_{13}H_{24}BF_4NS\cdot H_2O$ requires C, 47.1; H, 7.85; N, 4.2%).

(*k*) *With sodium azide.* The salt (4i) (1.25 mmol) was treated with sodium azide (1.25 mmol) in methanol (30 ml) for 10 h at

18 °C. Evaporation gave a residue which was extracted with dichloromethane to give the *4-azido-1-diethylsulphoniobuta-1,3-diene salt* (4s) (80%) as an oil, δ($CDCl_3$) 5.8—7.8 (m, 4 H), 3.5 (q, 4 H), and 1.5 (t, 6 H); δ (^{13}C) 143.98, 138.4, 109.42, 108.25, 37.94, and 9.23 p.p.m. (Found: C, 34.7; H, 5.1; N, 14.8. $C_8H_{14}BF_4N_3S$ requires C, 35.4; H, 5.2; N, 15.5); $\nu_{max.}$ 2 170 cm^{-1} (N_3 str.).

Treatment of the salt (4s) (1 mmol) in methanol with propene-3-thiol (1 mmol) and sodium methoxide (1 mmol) at 18 °C for 16 h was followed by addition of ethanethiol (2 mmol) and sodium methoxide (10 mmol). Usual work-up and p.l.c. on alumina type ' 0 ' in ether gave *1-azido-4-ethylthio-1-prop-2-enylthiobut-2-ene* (3q).

(*l*) *With diethylsulphonylmethane.* The salt (4i) (2.5 mmol) and sodiodiethylsulphonylmethane (2.5 mmol) were stirred in acetonitrile (10 ml) at 18 °C for 16 h. Evaporation and extraction of the residue with dichloromethane gave the crude adduct (4x) (76%) which was dealkylated with ethanethiolate ion as before to give *1-bis(ethylsulphonyl)methyl-1,4-bisethylthiobut-2-ene* (3r) (33%) after p.l.c. as an oil (Found: C, 41.3; H, 6.95. $C_{13}H_{26}O_4S_4$ requires C, 41.7; H, 6.95%); $\nu_{max.}$ 1 150 and 1 130 cm^{-1} (SO_2 str.). When methanol was used as solvent, the methoxy-salt (4k) was the sole product.

Acknowledgement

This work was carried out under the I.C.I. Joint Research Scheme which provided a studentship (to P. J. D.).

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Received 29th July 1982; *Paper* 2/1307