# Mass Spectral Rearrangements of 3-Arylsulphonyl-2-arylthiopropenes and *N*-(4′-Arylsulphonyl-2′-butynyl)-*N*-(4″-arylthio-2″-butynyl)anilines

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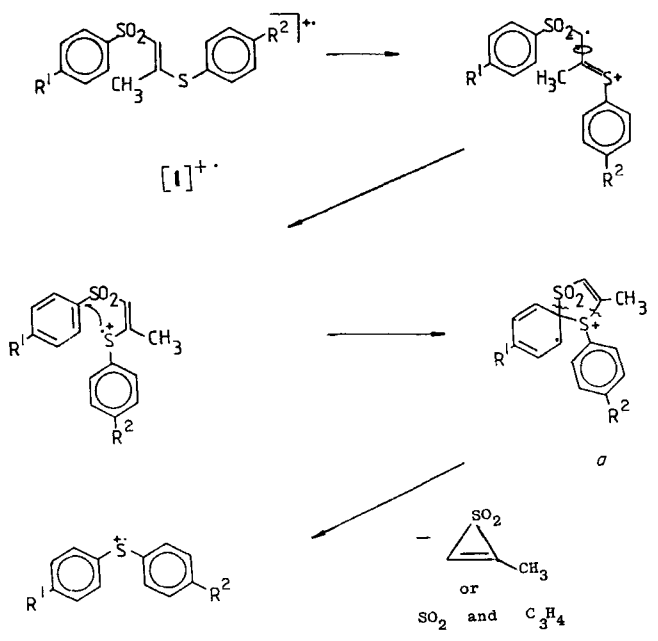
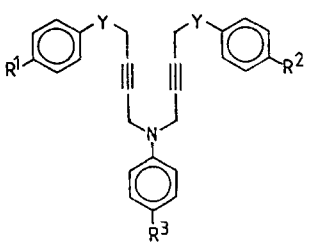
**Under electron impact the title compounds undergo skeletal rearrangement in addition to the anticipated modes of cleavage. The 3-arylsulphonyl-2-arylthiopropenes readily eliminate sulphur dioxide. Other modes of fragmentation include rearrangement to a bisaryl sulphide moiety and sulphone–sulphinate rearrangement. The formation of a bisaryl sulphide ion is analogous to the behaviour of the isomeric *trans*-1-arylsulphonyl-2-arylthiopropenes. *N*-(4′-Arylsulphonyl-2′-butynyl)-*N*-(4″-arylthio-2″-butynyl)anilines do not undergo any of the skeletal rearrangements mentioned above, but display the concerted loss of the arylsulphonyl and arylthio moieties. Similar eliminations have been observed from the analogous bis-sulphides and bis-sulphones.**

## INTRODUCTION

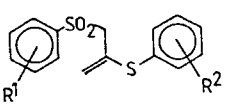
Organosulphur compounds undergo a large variety of electron impact induced skeletal rearrangements.[1] An unusual example is the formation of a bisaryl sulphide ion from *trans*-1-arylsulphonyl-2-arylthiopropene (**1**). This is postulated to occur via a five-membered cyclic intermediate *a*,[2] after rearrangement to the *cis* isomer, as shown in Scheme 1. The $C_3H_4SO_2$ portion may be lost either as 2-methylthiirene-1,1-dioxide or as sulphur dioxide and $C_3H_4$. Other unusual skeletal rearrangements include the elimination of $C_4H_4$ from 1,4-di(arylsulphonyl)-2-butynes,[3] the loss of a bisaryl disulphide moiety from *N*,*N*-bis(4′-arylthio-2′-butynyl)anilines (**2**)[4] and a concerted elimination of the arylsulphonyl groups from *N*,*N*-bis(4′-arylsulphonyl-2′-butynyl)anilines (**3**).[4]



Scheme 1.

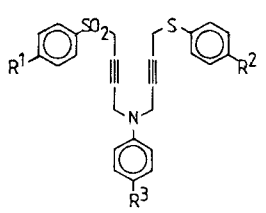


**2**: Y = S
**3**: Y = $SO_2$



**4**‡

**a**: $R^1 = R^2 = H$
**b**: $R^1 = H$, $R^2 = Cl$
**c**: $R^1 = H$, $R^2 = CH_3$
**d**: $R^1 = Cl$, $R^2 = H$
**e**: $R^1 = R^2 = Cl$
**f**: $R^1 = Cl$, $R^2 = CH_3$
**g**: $R^1 = CH_3$, $R^2 = H$
**h**: $R^1 = CH_3$, $R^2 = Cl$
**i**: $R^1 = R^2 = CH_3$
**j**: $R^1 = 2,3,5,6\text{-F}$, $R^2 = CH_3O$



**5**

**a**: $R^1 = Cl$, $R^2 = R^3 = H$
**b**: $R^1 = Cl$, $R^2 = CH_3$, $R^3 = H$
**c**: $R^1 = Cl$, $R^2 = H$, $R^3 = CH_3$
**d**: $R^1 = Cl$, $R^2 = R^3 = CH_3$
**e**: $R^1 = R^2 = Cl$, $R^3 = CH_3$
**f**: $R^1 = H$, $R^2 = Cl$, $R^3 = CH_3$
**g**: $R^1 = R^2 = Cl$, $R^3 = CH_3O$
**h**: $R^1 = H$, $R^2 = Cl$, $R^3 = CH_3O$

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‡ 4-$R^1$ and 4-$R^2$ unless stated.

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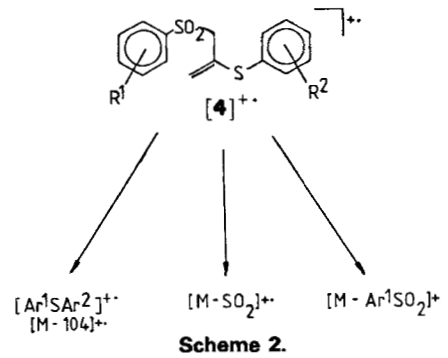



**Scheme 2.**

To investigate further the rearrangement of systems containing both arylthio and arylsulphonyl groups, we have examined 3-arylsulphonyl-2-arylthiopropenes(**4**) and *N*-(4′-arylsulphonyl-2′-butynyl)-*N*-(4″-arylthio-2″-butynyl)anilines(**5**) as extensions of the propene and aniline studies mentioned above.

## RESULTS AND DISCUSSION

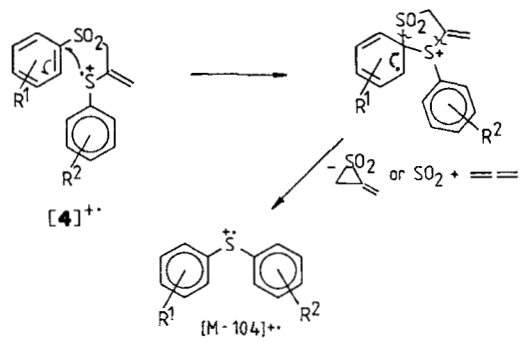
### Spectra of 3-arylsulphonyl-2-arylthiopropenes (4)

The preparation of 3-phenylsulphonyl-2-phenylthiopropene **4a** has been reported previously by Stirling[5] and 10 derivatives of **4** have been prepared employing his procedure. These compounds display the facile loss of the arylsulphonyl group, with the $[M-Ar^1SO_2]^+$ ion corresponding to the base peak in half of the cases. (The convention $Ar^1 = R^1C_6H_4$, $Ar^2 = R^2C_6H_4$, etc. is used.) The loss of sulphur dioxide is also a prominent fragmentation pathway, with the exception of **4j**. A striking feature is the appearance of an $[M-104]^{+\cdot}$ ion corresponding to the loss of $C_3H_4SO_2$. These fragmentations, summarized in Scheme 2, are substantiated by both metastable ion correlation and by *B*/*E* linked scanning studies (see Table 1). Exact mass analyses have confirmed the composition of the $[M-104]^{+\cdot}$ ion to be $[Ar^1SAr^2]^{+\cdot}$. Table 2 presents the relative abundances of significant ions in the mass spectra of **4a–j**.

**Table 1. Product ions identified by *B*/*E* linked scanning**

| Derivative | Molecular ion *m/z* | Neutral lost | Product ion *m/z* |
|---|---|---|---|
| **4a** | 290 | $SO_2$ | 226 |
| | | $C_3H_4SO_2$ | 186 |
| | | $Ar^1SO_2^{\cdot}$ | 149 |
| **4i** | 318 | $SO_2$ | 254 |
| | | $C_3H_4SO_2$ | 214 |
| | | $Ar^1SO_2^{\cdot}$ | 163 |
| **4j** | 392 | $SO_2$ | 328 |
| | | $C_3H_4SO_2$ | 288 |
| | | $Ar^1SO_2^{\cdot}$ | 179 |

The elimination of $C_4H_3SO_2$ from **4a–j** parallels the behaviour of the *trans*-1-arylsulphonyl-2-arylthiopropenes(**1**) and can thus be rationalized by a similar mechanism, illustrated in Scheme 3†. No prior rearrangement of **4** is required to facilitate formation of a five-membered intermediate similar to *a*. The eliminated portion may then leave as 2-methylenethiirane-1,1-dioxide or as sulphur dioxide and $C_3H_4$.




**Scheme 3.**

The relative abundance of the bisaryl sulphide ion is greatest in the spectrum of the 2,3,5,6-tetrafluoro derivative **4j**, which displays the smallest abundance of $[M-SO_2]^{+\cdot}$. The inhibiting effect of *ortho* groups upon the elimination of sulphur dioxide from propynylarylsulphones has been noted before and this observation is best accommodated by a [2+2]cycloaddition mechanism[6] leading to a benzocyclobutene-type intermediate. An analogous rearrangement pathway, but leading to a benzocyclobutane, is possible here for the elimination of sulphur dioxide. The observed increase in the abundance of $[Ar^1SAr^2]^{+\cdot}$ in the spectrum of **4j** is probably a result of the removal of the sulphur dioxide extrusion process as a competitive pathway. The presence of the *ortho* fluoro groups would not be expected to hinder the formation of a five-membered cyclic intermediate as postulated in Scheme 3.

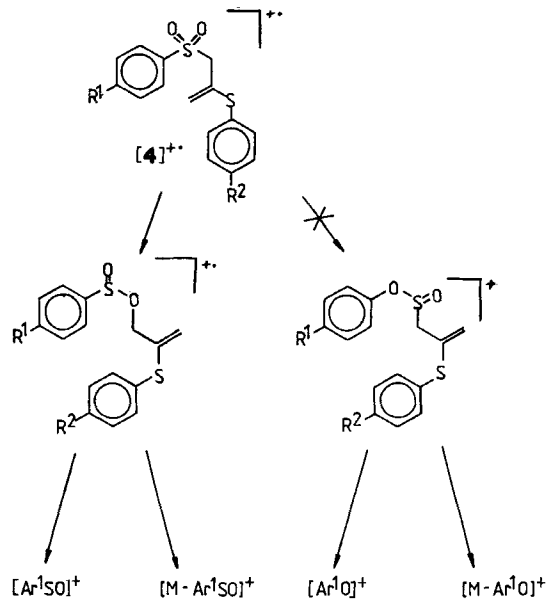
A sulphone–sulphinate rearrangement in **4** leading to $[M-Ar^1SO]^+$ and $[Ar^1SO]^+$ is evidenced by the presence of these ions in the mass spectra of **4a–j**. The absence of $[M-Ar^1O]^+$ and $[Ar^1O]^+$ indicates that alkyl migration to a sulphonyl oxygen predominates over aryl migration (see Scheme 4).

† The possibility of ion structures and neutral fragments other than those shown in Scheme 3 and those to follow is both present and implied.

**Table 2. Significant ions in the 70 eV mass spectra of 3-arylsulphonyl-2-arylthiopropenes(4); *m/z* (% rel. abund.)**

| Ion | 4a | 4b[a] | 4c[a] | 4d | 4e[a] | 4f | 4g | 4h[a] | 4i | 4j |
|---|---|---|---|---|---|---|---|---|---|---|
| $[M]^{+\cdot}$ | 290(35) | 324(19) | 304(65) | 324(16) | 358(13) | 338(30) | 304(22) | 338(17) | 318(42) | 392(64) |
| $[M-SO_2]^{+\cdot}$ | 226(35) | 260(14) | 240(20) | 260(23) | 294(15) | 274(15) | 240(70) | 274(33) | 254(46) | 328(1) |
| $[Ar^1SAr^2]^{+\cdot}$ | 186(7) | 220(3) | 200(7) | 220(3) | 254(3) | 234(7) | 200(6) | 234(3) | 214(8) | 288(12) |
| $[Ar^1SO]^+$ | 125(7) | 125(5) | 125(7) | 159(3) | 159(3) | 159(2) | 139(7) | 139(7) | 139(6) | 197(1) |
| $[M-Ar^1SO]^+$ | 165(1) | 199(1) | 179(1) | 165(1) | 199(1) | 179(1) | 165(2) | 199(1) | 179(1) | 195(1) |
| $[Ar^1SO_2]^+$ | 141(4) | 141(4) | 141(4) | 175(3) | 175(3) | 175(2) | 155(6) | 155(8) | 155(3) | 213(1) |
| $[M-Ar^1SO_2]^{+\cdot}$ | 149(100) | 183(30) | 163(83) | 149(100) | 183(26) | 163(100) | 149(100) | 183(23) | 163(100) | 179(32) |

[a] The base peak corresponds to *m/z* 148 and arises via the loss of $R^2$ from the $[M-Ar^1SO_2]^+$ ion.



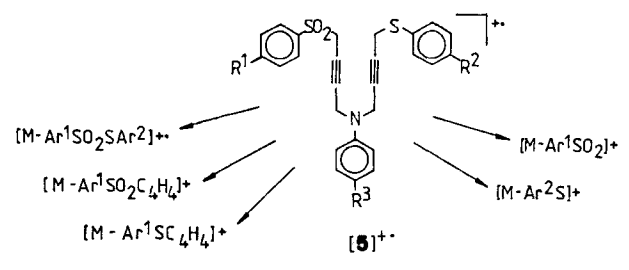

**Scheme 4.**

## Spectra of *N*-(4′-arylsulphonyl-2′-butynyl)-*N*-(4″-arylthio-2″-butynyl)anilines (5)

Eight derivatives of the title compounds **5**, previously unreported, have been prepared as described in the Experimental section.

Under electron impact, **5** undergoes the expected trivial cleavages, i.e. C—S and C—N bond fission, leading to $[M-Ar^1SO_2]^+$, $[M-Ar^2S]^+$, $[M-Ar^1SO_2C_4H_4]^+$ and $[M-Ar^2SC_4H_4]^{+\cdot}$. The more interesting aspect of the fragmentation of the molecular ions of **5a–h** is the concerted or rapid consecutive elimination of the arylthio and arylsulphonyl moieties, yielding the $[M-Ar^1SO_2SAr^2]^{+\cdot}$ ion in high abundance in all cases. These fragmentations summarized in Scheme 5 are substantiated by metastable peak correlation and by *B*/*E* linked scans (see Table 3). Table 4 contains the relative abundance of significant ions. Exact mass analyses have confirmed the composition of the $[M-Ar^1SO_2SAr^2]^{+\cdot}$ ion.

The elimination of $Ar^1SO_2SAr^2$ from **5** may be regarded as analogous to the concerted eliminations of the arylthio and arylsulphonyl groups from *N*,*N*-bis(4′-arylthio-2′-butynyl)-(**2**) and *N*,*N*-bis(4′-arylsulphonyl-2′-butynyl)-anilines(**3**), respectively.[4] Although [1,3]arylthio migrations, which are known under thermal conditions,[5] can occur in **2** prior to the elimination of the arylthio groups,[4] [1,3]arylsulphonyl migrations are not known and the elimination of $Ar^1SO_2SO_2Ar^2$ from **3** must occur from an unrearranged molecular ion. The possibility of [1,3]arylthio migration exists in **5** also, but such a migration increases the minimum possible distance between the sulphurs of the thio and sulphone functions. Thus, any elimination of $Ar^1SO_2SAr^2$ following an arylthio shift in **5** is less likely.

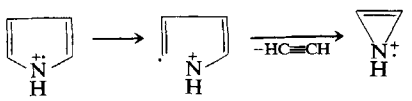



**Scheme 5.**

**Table 3. Product ions identified by *B*/*E* linked scanning**

| Derivative | Molecular ion *m/z* | Neutral lost | Product ion *m/z* |
|---|---|---|---|
| **5f** | 493 | $Ar^1SO^{\cdot}$ | 352 |
| | | $Ar^2S^{\cdot}$ | 350 |
| | | $Ar^1SO_2C_4H_4^{\cdot}$ | 300 |
| | | $Ar^1SO_2C_4H_5$ | 299 |
| | | $Ar^1SO_2SAr^2$ | 209 |
| **5h** | 509 | $Ar^1SO_2^{\cdot}$ | 368 |
| | | $Ar^2S^{\cdot}$ | 366 |
| | | $Ar^1SO_2C_4H_4^{\cdot}$ | 316 |
| | | $Ar^1SO_2C_4H_5$ | 315 |
| | | $Ar^2SC_4H_4^{\cdot}$ | 314 |
| | | $Ar^2SC_4H_5$ | 313 |
| | | $Ar^1SO_2SAr^2$ | 225 |

Metastable peak correlation and *B*/*E* scans have established that ions of the same nominal mass as $[M-Ar^1SO_2SAr^2]^{+\cdot}$ are formed by the losses of $Ar^2S$ from $[M-Ar^1SO_2]^+$ and $Ar^1SO_2$ from $[M-Ar^2S]^{+\cdot}$. The relative contributions of the stepwise and concerted eliminations cannot be ascertained. The presence of $[Ar^1SO_2SAr^2]^{+\cdot}$ ions in the spectra of **5a–h** provides evidence that interaction between the thio and sulphone functionalities is significant. Interestingly, this type of interaction predominates over the formation of a bisaryl sulphide ion, as observed in the spectra of **4a–j**. The extrusion of sulphur or sulphur dioxide also appears to be precluded by the elimination of $Ar^1SO_2SAr^2$. In the earlier study of **2** and **3**, the loss of a cumulene from $[M-Ar^1SSAr^2]^{+\cdot}$ and $[M-Ar^1SO_2SO_2Ar^2]^{+\cdot}$ was postulated to give an *N*-arylaziridine cation.[4] However, *B*/*E* linked scanning spectra of the $[M-Ar^1SO_2SAr^2]^{+\cdot}$ ions in the mass spectra of **5** indicate that this ion undergoes instead the losses of a hydrogen atom, $\dot{R}^3$, $C_2H_3^{\cdot}$ and $C_4H_4$, yielding $[Ar^3C_8H_7]^+$, $[C_6H_4NC_8H_8]^{+\cdot}$, $[Ar^3NC_6H_5]^+$ and $[Ar^3NC_4H_4]^{+\cdot}$, respectively. These fragmentations can be rationalized as shown in Scheme 6. The elimination of $C_4H_4$ is analogous to the loss of ethyne displayed by pyrrole:[7]

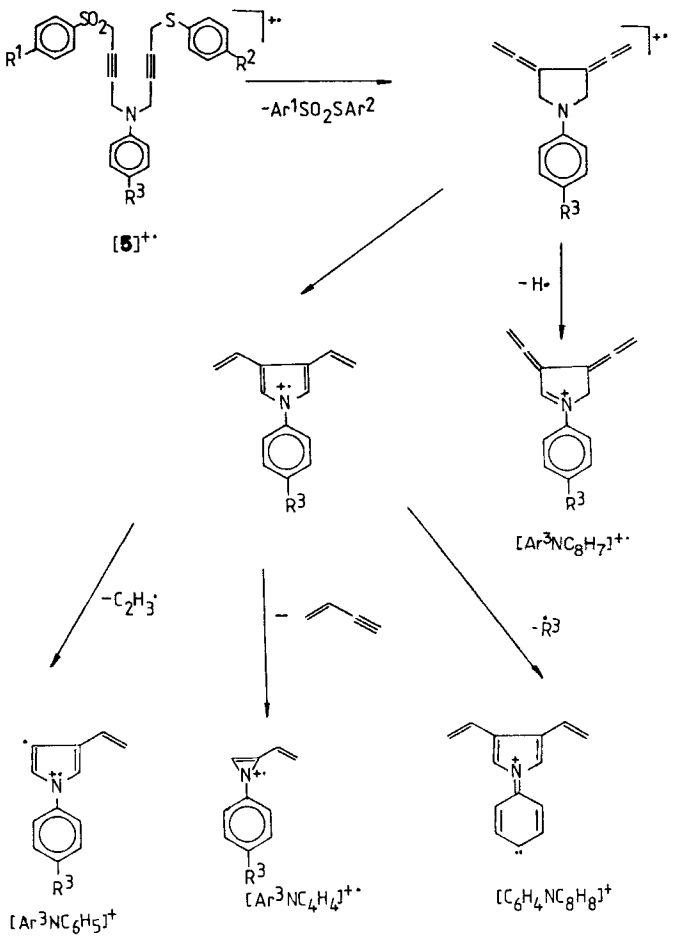



Base peaks in the spectra of **5a,b,c** and **f** correspond to $[Ar^3NC_8H_7]^+$, while $[Ar^3NC_4H_4]^{+\cdot}$ has the largest abundance in the spectrum of **5d** (*vide supra*). The most intense peak in the spectra of **5e** and **5g** corresponds to $[Ar^3C_4H_3]^+$ and is shown by *B*/*E* linked scans to arise from the losses of $Ar^1SO_2C_4H_5$ from $[M-Ar^2S]^+$ and $Ar^2SC_4H_5$ from $[M-Ar^1SO_2]^+$.

**Table 4. Significant ions in the 70 eV mass spectra of *N*-(4′-arylsulphonyl-2′-butynyl)-*N*-(4″-arylthio-2″-butynyl)anilines(5); *m/z* (% rel. abund.)**

| Ion | 5a | 5b | 5c | 5d | 5e | 5f | 5g | 5h |
|---|---|---|---|---|---|---|---|---|
| $[M]^{+\cdot}$ | 479(13) | 493(9) | 493(27) | 507(26) | 527(19) | 493(15) | 543(16) | 509(24) |
| $[M-Ar^1SO_2]^+$ | 304(12) | 318(8) | 318(13) | 332(11) | 352(13) | 352(14) | 368(8) | 368(9) |
| $[Ar^1SO_2]^+$ | 175(3) | 175(19) | 175(4) | 175(26) | 175(2) | 141(11) | 175(6) | 141(24) |
| $[M-Ar^2S]^+$ | 370(29) | 370(25) | 384(26) | 384(28) | 384(22) | 350(52) | 400(9) | 366(23) |
| $[Ar^2S]^+$ | 109(20) | 123(17) | 109(23) | 123(25) | 143(15) | 143(11) | 143(27) | 143(100) |
| $[M-Ar^2SSO_2Ar^1]^{+\cdot}$ | 195(72) | 195(75) | 209(86) | 209(99) | 209(56) | 209(93) | 225(48) | 225(56) |
| $[Ar^2SSO_2Ar^1]^{+\cdot}$ | [b] | [b] | 284(1) | 298(1) | 318(2) | 284(2) | 318(6)[a] | 284(9) |
| $[M-Ar^1SO_2C_4H_4]^+$ | 252(3) | 266(2) | 266(3) | 280(4) | 300(12) | 300(4) | 316(10) | 316(17) |
| $[M-Ar^2SC_4H_4]^+$ | [b] | 318(8) | [b] | 332(11) | 332(2) | 298(2) | 348(8) | 314(5) |
| $[Ar^2SC_4H_4]^+$ | 161(21) | 175(19) | 161(22) | 175(26) | 195(6) | 195(6) | 195(5) | 195(17) |
| Base peak | 194 | 194 | 208 | 157 | 156 | 208 | 172 | 143 |

[a] Approximately 50% contribution from $C_{17}H_{15}{}^{37}ClNOS$ ($[M-Ar^1SO_2C_4H_4]^{+\cdot}$).
[b] Present in less than 1% relative abundances.




**Scheme 6.**

## SUMMARY

The mass spectra of 3-arylsulphonyl-2-arylthiopropenes display *inter alia* prominent peaks arising from the loss of sulphur dioxide. Another skeletal rearrangement in which the elements of $SO_2C_3H_4$ are expelled, gives rise to bisaryl sulphide ions and parallels an analogous rearrangement of *trans*-1-arylsulphonyl-2-arylthiopropenes. A five-membered cyclic intermediate is implicated.

Contrary to the behaviour of the propenes, *N*-(4′-arylsulphonyl-2′-butynyl)-*N*-(4″-arylthio-2″-butynyl)-anilines do not extrude sulphur dioxide or rearrange to bisaryl sulphide ions. Instead, skeletal rearrangement leads to the consecutive if not concerted elimination of the arylthio and arylsulphonyl groups. This rearrangement is similar to the behaviour of the analogous bis-sulphones and bis-sulphides.[4]

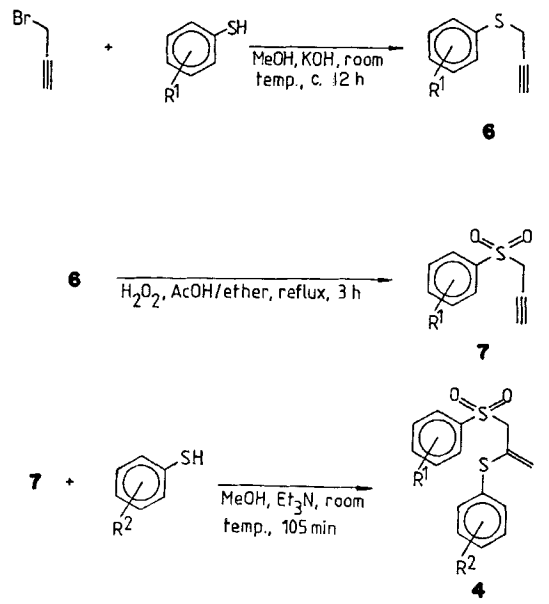
## EXPERIMENTAL

Melting points were obtained on a Thomas–Hoover Capillary melting point apparatus and are uncorrected. Mass spectra were obtained with a VG Micromass 12F single focusing mass spectrometer at 70 eV electron energy and an ion source temperature of *c.* 200 °C. Linked scanning *B/E* spectra and accurate mass measurements of selected samples were provided by Mr D. Carter (School of Pharmacy, University of London) using a VG ZAB double focusing mass spectrometer. NMR spectra were recorded using either a Varian EM 360, Varian A60 or a Hitachi Perkin–Elmer R24B spectrometer. Chemical shifts are reported in ppm from TMS (TMS = 0.0$\delta$, $CDCl_3$ solution, unless stated otherwise). Elemental analyses were provided by Galbraith Laboratories Inc., USA and Butterworth Laboratories Ltd, UK.

### Preparation of 3-arylsulphonyl-2-arylthiopropenes

Scheme 7 depicts the synthetic route employed for the preparation of the title compounds. General procedures for the preparations of **4**, **6** and **7** are given below.

**3-Arylthiopropynes (6).** A solution of the desired arenethiol (0.042 mol) and an equimolar amount of KOH (2.36 g) in methanol (50 $cm^3$) was added dropwise with stirring to a solution of propargyl bromide (5 g, 0.042 mol) in methanol (50 $cm^3$) under $N_2$ at ambient temperature. After stirring overnight, the precipitated KBr was filtered off and the solvent removed *in vacuo*. The crude product was dissolved in




**Scheme 7.**

chloroform (100 $cm^3$) and washed with 0.2N KOH (3 × 100 $cm^3$) and water (1 × 100 $cm^3$), dried ($MgSO_4$) and solvent removed *in vacuo* to give a pale yellow liquid which was distilled at reduced pressure to yield the pure product in *c.* 50% yield.

Physical and spectral data were as follows: 3-Phenylthiopropyne—b.p.: 54 °C (0.2 mm), lit.[8] 104–110 °C (10 mm); NMR: 2.3 (t, 1H), 3.65 (d, 2H), 7.2–7.8 (m, 5H). 3-*p*-tolylthiopropyne—b.p.: 64 °C (0.2 mm), lit.[8] 124 °C (15 mm); NMR: 2.3 (t, 1H), 3.65 (d, 2H), 7.42 (q, 4H).3-(4-Chlorophenyl)thiopropyne—b.p.: 76 °C (0.18 mm), lit.[9] 58 °C (0.1 mm); NMR: 2.3 (t, 1H), 3.65 (d, 2H), 7.5 (s, 4H). 3-(2,3,5,6-Tetrafluorophenyl)thiopropyne—b.p.: 44 °C (0.02 mm); NMR: 2.28 (t, 1H), 3.75 (d, 2H), 7.0–7.55 (m, 1H).

The tetrafluorophenyl derivative had not been previously reported.

**3-Arylsulphonylpropynes (7).** Oxidation of the 3-arylthiopropynes with 86% hydrogen peroxide in a mixture of glacial acetic acid and ether gave the corresponding sulphones in high yields. In a typical reaction, 0.0213 mol of the arylthiopropyne was dissolved in 1:1 glacial acetic acid and ether (100 $cm^3$). A 10-fold excess of hydrogen peroxide was added to the mixture and the reaction mixture refluxed for 3 h. The mixture was then poured into ice–water (500 $cm^3$) with stirring and the precipitated white solid was collected and washed with water. The product was then dried under vacuum. The products obtained in this manner were pure and usable without further purification.

Yields and melting points were as follows: 3-Phenylsulphonylpropyne—yield 99%; m.p.: 92–93 °C, lit.[10] 93 °C. 3-*p*-Tolylsulphonylpropyne—yield 90%; m.p.: 101–103 °C, lit.[11] 99–100 °C. 3-(4-Chlorophenyl)sulphonylpropyne—yield 85%; m.p.: 114–115 °C, lit.[12] 116–117 °C. 3-(2,3,5,6-Tetrafluorophenyl)sulphonylpropyne—yield 65%; m.p.: 69–71 °C; NMR: 2.57 (t, 1H), 4.39 (d, 2H), 7.38–7.97 (m, 1H).

The tetrafluorophenyl derivative had not been previously reported.

**3-Arylsulphonyl-2-arylthiopropenes (4).** The method of Stirling[5] was followed for the synthesis of the title compounds. He had only described the unsubstituted derivative. A general procedure is given below.

The sulphone (0.5 g) and an equimolar amount of the required arenethiol were dissolved in methanol (10 $cm^3$) and stirred for 105 min at ambient temperature in the presence of triethylamine (0.025 $cm^3$). Removal of the solvent *in vacuo* gave the products as solids in yields of 94–100% (with the exception of **4j** which was chromatographed on 30 g of silica gel (50% ether/pet. ether) to give 0.1 g of clear colourless oil which crystallized upon dissolution in ether/pet. ether and cooling. Analytical samples were prepared by recrystallization from ether/pet. ether ($R_f \simeq 0.45$, 50% ether/petroleum ether, silica gel). The unsubstituted compound was identical to that described by Stirling (m.p. 61–62 °C, lit.[5] 60–61 °C). Physical and analytical data are presented in Table 5. These compounds were characterized by NMR, mass spectrometry and elemental analysis.

## Preparation of *N*-(4′arylsulphonyl-2′-butynyl)-*N*-(4″-arylthio-2″-butynyl)anilines(5)

The syntheses of **5a–h** were achieved via the reactions of the known 4-arylsulphonyl-1-chloro-2-butynes[4] with *N*-(4′-arylthio-2′-butynyl)anilines(**8**) (see Scheme 8). The general procedures for the synthesis of **5** and **8** are described below.

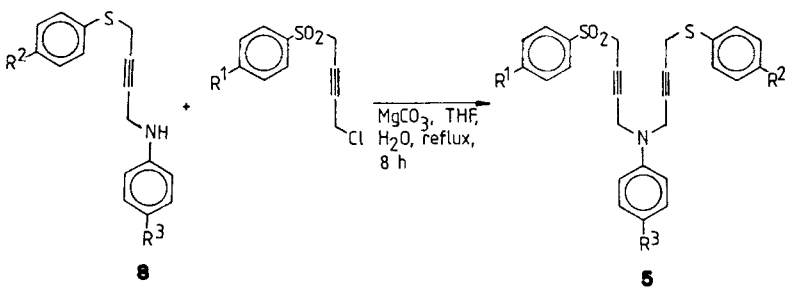
***N*-(4′-Arylthio-2′-butynyl)anilines(8).** The synthesis of some *N*-4′-arylthio-2′-butynyl)anilines had previously been reported[13] and a similar procedure was employed in this work. A solution of 4-arylthio-1-chloro-2-butyne[4] (0.0476 mol) and the desired arylamine (0.119 mol) in refluxing THF (200 $cm^3$) was stirred with a slurry of magnesium carbonate (0.0476 mol) in water (100 $cm^3$) for 3 days under an atmosphere of nitrogen. The organic layer was separated and the solvent removed *in vacuo* to give a brownish oil. The crude product was taken up in chloroform (100 $cm^3$) and washed with 1.0 N HCl (2 × 100 $cm^3$), 0.2 N KOH (1 × 100 $cm^3$) and water (1 × 100 $cm^3$). Drying the solution over sodium sulphate and removal of the solvent under vacuum gave a brown oil which solidified upon standing in some cases. The crude product was dissolved in refluxing petroleum spirit (b.p. 60–80 °C), filtered and cooled to give the pure products ($R_f \simeq 0.56$, 50% ether pet. ether, silica gel) as pale yellow crystals in moderate yields (35–70%). Recrystallization from petroleum spirit gave the analytical samples. The *N*-(4′-phenylthio-2′-butynyl)aniline and *N*-(4′-*p*-tolylthio-2′-butynyl)aniline were liquids and were purified by chromatography on silica gel, using toluene as the eluting solvent.

Physical and spectral data were as follows: *N*-(4′-*p*-Tolylthio-2′-butynyl)-*p*-toluidine—m.p.: 49–50 °C, lit.[13] 49°; NMR: 2.3 (s, 3H), 2.38 (s, 3H), 3.92 (t, 2H), 3.2–3.7 (m, 3H), 6.86 (q. 4H), 7.38 (q, 4H). *N*-(4′-Phenylthio-2′-butynyl)-*p*-toluidine—m.p.: 43–45 °C;

**Table 5. Spectral, physical and analytical data for 3-arylsulphonyl-2-arylthiopropenes (4)**

| Derivative | Mol. wt | M.p. (°C) | Yield (%) | Elemental analysis (%) $C_{calc.}$ | $H_{calc.}$ | $C_{found}$ | $H_{found}$ | NMR (δ, ppm) |
|---|---|---|---|---|---|---|---|---|
| **4a** | 290 | 61–62 | 94 | [a] | [a] | [a] | [a] | 3.99(s, 2H), 5.32(s, 1H), 5.55(s, 1H) 7.49(s, 5H), 7.70–8.30(m, 5H) |
| **4b** | 324 | 64–66 | 95 | 55.46 | 4.03 | 55.37 | 4.06 | 3.99(s, 2H), 5.32(s, 1H), 5.55(s, 1H) 7.45(q, 4H), 7.70–8.30(m, 5H) |
| **4c** | 304 | 81–83 | 95 | 63.12 | 5.30 | 63.06 | 5.34 | 2.35(s, 3H), 3.99(s, 2H), 5.20(s, 1H), 5.48(s, 1H), 7.33(s, 4H), 7.70–8.30(s, 5H) |
| **4d** | 324 | 49–50 | 100 | 55.46 | 4.03 | 55.35 | 4.04 | 3.99(s, 2H), 5.32(s, 1H), 5.55(s, 1H), 7.49(s, 5H), 7.90(q, 4H) |
| **4e** | 358 | 103–104 | 100 | 50.14 | 3.37 | 50.07 | 3.50 | 4.02(s, 2H), 5.35(s, 1H), 5.60(s, 1H), 7.52(q, 4H), 7.90(q, 4H) |
| **4f** | 338 | 94–96 | 99 | 56.71 | 4.46 | 56.44 | 4.47 | 2.37(s, 3H), 3.99(s, 2H), 5.25(s, 1H), 5.48(s, 1H), 7.33(s, 4H), 7.90(q, 4H) |
| **4g** | 304 | 84–86 | 96 | 63.13 | 5.30 | 63.04 | 5.15 | 2.52(s, 3H), 3.99(s, 2H), 5.30(s, 1H), 5.54(s, 1H), 7.50(s, 5H), 7.76(q, 4H) |
| **4h** | 338 | 85–86 | 95 | 56.71 | 4.46 | 56.68 | 4.48 | 2.52(s, 3H), 3.98(s, 2H), 5.30(s, 1H) 5.54(s, 1H), 7.45(s, 4H), 7.76(s, 4H) |
| **4i** | 318 | 76–77 | 100 | 64.12 | 5.70 | 63.66 | 5.40 | 2.38(s, 3H), 2.52(s, 3H), 3.95(s, 2H) 5.19(s, 1H), 5.42(s, 1H), 7.31(s, 4H), 7.75(q, 4H) |
| **4j** | 392 | 118–120 | 13 | 48.97 | 3.08 | 49.03 | 3.09 | 3.89(s, 3H), 4.25(s, 2H), 5.25(s, 1H), 5.61(s, 1H), 6.9–7.85(m, 5H) |

[a] Physical constants identical to those described by Stirling, Ref. 5.




**Scheme 8.**

**Table 6. Spectral, physical and analytical data for *N*-(4′-arylsulphonyl-2′-butynyl)-*N*-(4″-arylthio-2″-butynyl)anilines (5)**

| Derivative | Mol. wt | Yield (%) | M.p. (°C) | Elemental analysis (%) $C_{calc.}$ | $H_{calc.}$ | $C_{found}$ | $H_{found}$ | NMR (δ, ppm) |
|---|---|---|---|---|---|---|---|---|
| **5a** | 479 | 42 | 92–93 | 65.05 | 4.62 | 65.08 | 4.73 | 3.67(t, 2H), 4.08(m, 6H), 6.90–8.08(m, 14H) |
| **5b** | 493 | 85 | 95–96 | 65.64 | 4.90 | 65.70 | 4.86 | 2.43(s, 3H), 3.67(t, 2H), 4.1(m, 6H), 6.90–8.04(m, 13H) |
| **5c** | 493 | 48 | 99–100 | 65.64 | 4.90 | 65.61 | 4.99 | 2.33(s, 3H), 3.67(t, 2H), 4.1(m, 6H), 6.78–8.0(m, 13H) |
| **5d** | 507 | 39 | 118–119 | 66.19 | 5.16 | 66.03 | 5.19 | 2.33(s, 6H), 3.56(t, 2H), 3.99(m, 6H), 6.75–8.0(m, 12H) |
| **5e** | 527 | 27 | 126–128 | 61.36 | 4.37 | 61.65 | 4.59 | 2.34(s, 3H), 3.56(t, 2H), 3.93(m, 6H), 6.65–7.85(m, 12H) |
| **5f** | 493 | 40 | 101–103 | 65.64 | 4.90 | 65.80 | 4.97 | 2.36(s, 3H), 3.60(t, 3H), 3.98(m, 6H), 6.68–7.84(m, 13H) |
| **5g** | 543 | 41 | 111–112 | 59.55 | 4.26 | 59.45 | 4.37 | 3.55(t, 2H), 3.75(s, 3H), 3.89(m, 6H), 6.75(s, 4H), 7.20–7.80(m, 8H) |
| **5h** | 509 | 37 | 75–76 | 63.58 | 4.74 | 63.68 | 4.88 | 3.60(t, 2H), 3.81(s, 3H), 3.95(m, 6H), 6.82(s, 4H), 7.30–7.95(m, 9H) |

NMR: 2.3 (s, 3H), 3.43 (m, 3H), 3.93 (t, 2H), 6.9 (q, 4H), 7.5 (m, 5H). *N*-(4′-Phenylthio-2′-butynyl)aniline—NMR: 3.64 (m, 3H), 3.94 (t, 2H), 6.7–7.8 (m, 10H). *N*-(4′-*p*-Tolylthio-2′-butynyl)aniline—NMR: 2.34 (s, 3H), 3.58 (t, 2H), 3.9 (m, 3H), 6.68–7.58 (m, 9H). *N*-(4′-(4-Chlorophenyl)thio-2′-butynyl)-*p*-toluidine—m.p.: 61–62 °C, lit.[13] 61 °C; NMR: 2.26 (s, 3H), 3.4 (br.s, 1H) 3.57 (t, 2H), 3.85 (t, 2H), 6.78 (q, 4H), 7.21 (q, 4H). *N*-(4′-(4-Chlorophenyl)thio-2′-butynyl)-*p*-anisidine—m.p.: 52–53 °C; NMR: 3.68 (m, 3H), 3.9 (m, 5H), 6.75 (q, 4H), 7.3 (s, 4H).

**N-(4-Arylsulphonyl-2′-butynyl)-N-(4″-arylthio-2″-butynyl)-anilines (5).** The title compounds were synthesized by the following general procedure:

In THF (20 $cm^3$) were dissolved equimolar amounts of *N*-(4′-arylthio-2′-butynyl)aniline (1 g) and 4-arylsulphonyl-1-chloro-2-butyne. This solution was then added to a round-bottomed flask containing a slurry of water (20 $cm^3$) and an equimolar amount of magnesium carbonate. The mixture was then stirred at reflux, under an atmosphere of nitrogen, for 7.5 h. The organic layer was separated, dried over sodium sulphate and the solvent removed *in vacuo*. The product mixture was then triturated with hot petroleum spirit if a solid, or chromatographed on silica gel with toluene to give the desired product ($R_f \approx 0.39$). Analytical samples were obtained by recrystallization from $CH_2Cl_2$/petroleum spirit. The derivatives thus prepared are described in Table 6.

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