Mass Spectral Rearrangements of *N,N*-bis(4′-Arylthio-2′-butynyl)anilines and *N,N*-bis(4′-Arylsulfonyl-2′-butynyl)anilines

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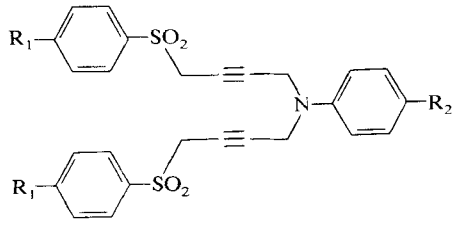
The title compounds display unusual modes of fragmentation under electron impact. One of the dominant modes is the concerted elimination of the two arylthio and arylsulfonyl moieties followed by further extrusion of the C_6H_4 unit as a cumulene. No elimination of SO_2 is observed from any of the sulfones nor an expulsion of the C_4H_4 fragment. Such behavior contrasts strikingly with that of 1,4-diarylsulfonyl-2-butynes and of the 1,6-diarylsulfonyl-2,4-hexadiynes.

In the course of our extensive studies on the electron impact (EI) induced fragmentation of aryl propynyl sulfones,[1] aryl propenyl sulfones,[2] 1,4-diarylsulfonyl-2-butynes[3] and 1,6-diarylsulfonyl-2,4-hexadiynes,[4] we have uncovered a variety of modes of fragmentation not widely encountered. Scheme 1 portrays several of these modes of cleavage.

Our earlier studies indicated clearly that separation of the SO_2 groups by more than one triple bond introduced a special constraint on the molecule such that the two sulfone groups could no longer interact directly across space. Consequently, the proposed 2+2 mode of interaction between the triple bond and the phenyl ring could be expected to accentuate the extrusion of one or both of the SO_2 units. Such extrusions were observed. The present study was undertaken with the following expectation: if the two sulfone functions could be brought closer together in a suitable molecule, then one ought to observe an enhanced interaction between them. Such a situation was easily created in the following system where the (4′-arylsulfonyl-2′-butynyl) moieties are attached to the same nitrogen of an aniline:



Free rotation around the N—CH_2 bonds makes it easy for the arylsulfonyl groups to swing close together for through-space interaction, even if the normal ground state configuration of the molecule may not be precisely that close in the situation of the triple bonds.

Synthesis of the *N,N*-bis(4′-arylthio-2′-butynyl)-anilines was attempted by two different approaches. Condensation of 1,4-dichloro-2-butyne with substituted anilines gave fair yields of the corresponding *N,N*-bis(4′-chloro-2′-butynyl)anilines. When the latter derivatives were reacted with the appropriate thiophenolate salts, only poor yields of the desired disulfides were obtained.

A second approach employed the condensation of 1-arylthio-4-chloro-2-butynes with less than one equivalent of the appropriate aniline in aqueous acetonitrile solution.[5] Commendable yields of the *N,N*-bis(4′-arylthio-2′-butynyl)anilines were secured. However, oxidation of these sulfides to the corresponding sulfones presented some difficulties. Mixtures of the disulfoxides and the sulfone sulfoxides were formed along with the desired disulfones. For the synthesis of the disulfones a further modification to the procedure was adopted. Oxidation of 1-arylthio-4-chloro-2-butynes with 30% hydrogen peroxide gave good yields of 1-arylsulfonyl-4-chloro-2-butynes. Condensation of the latter with anilines gave the desired sulfones in excellent yields. These reactions are summarized in Scheme 2.

Only two different anilines were employed for the present study (*para*-toluidine and *para*-anisidine); which made it easier to identify the ions from the sulfur-free fragments common to all of the sulfides and sulfones.

Spectra of *N,N*-bis(4′-arylthio-2′-butynyl)anilines

Electron impact on the sulfides produced some of the anticipated fragments such as $[ArS]^+$, $[ArSH]^{+\cdot}$, $[ArSC_4H_4]^+$ and $[ArNC_4H_4]^{+\cdot}$, along with some unusual ions as well. Some of these ions are shown in Scheme 3. The structures depicted for fragments are among several that can be envisaged. Therefore, alternative rationalizations are possible (and implied) for Schemes 3 and 4.

The more interesting aspect of the fragmentation process lies in the *simultaneous* expulsion of both ArS

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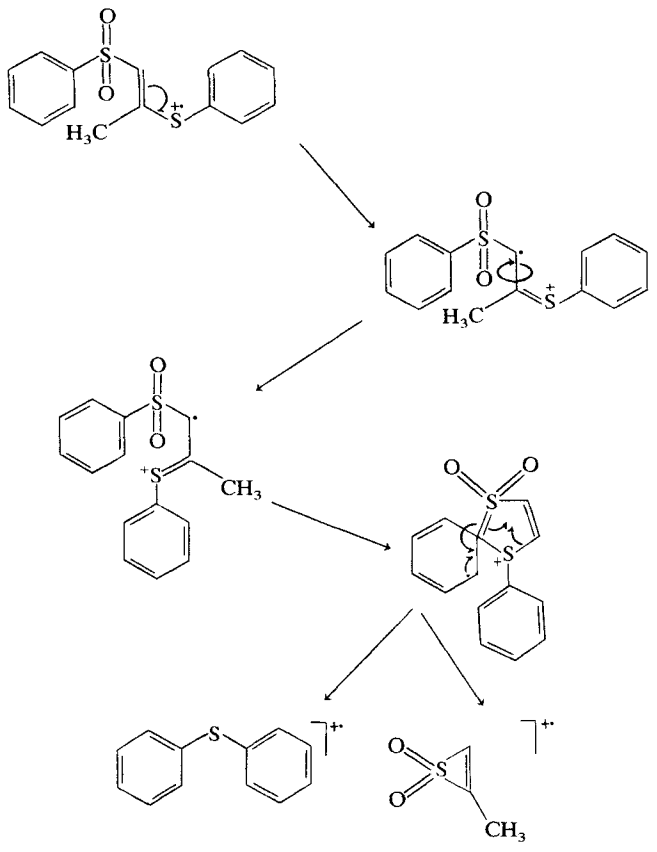
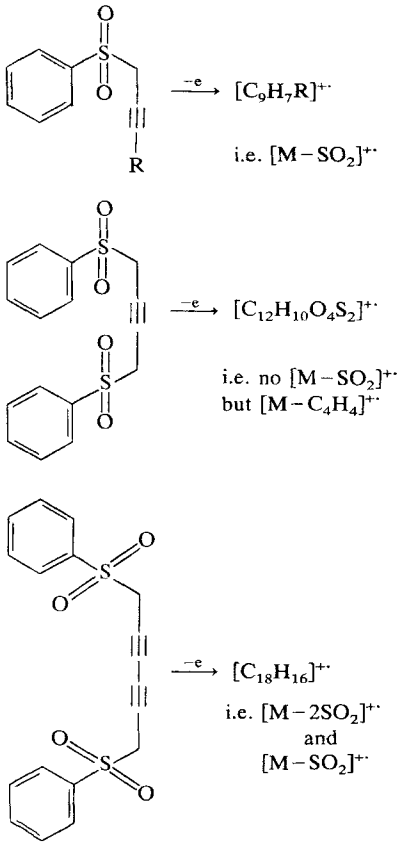
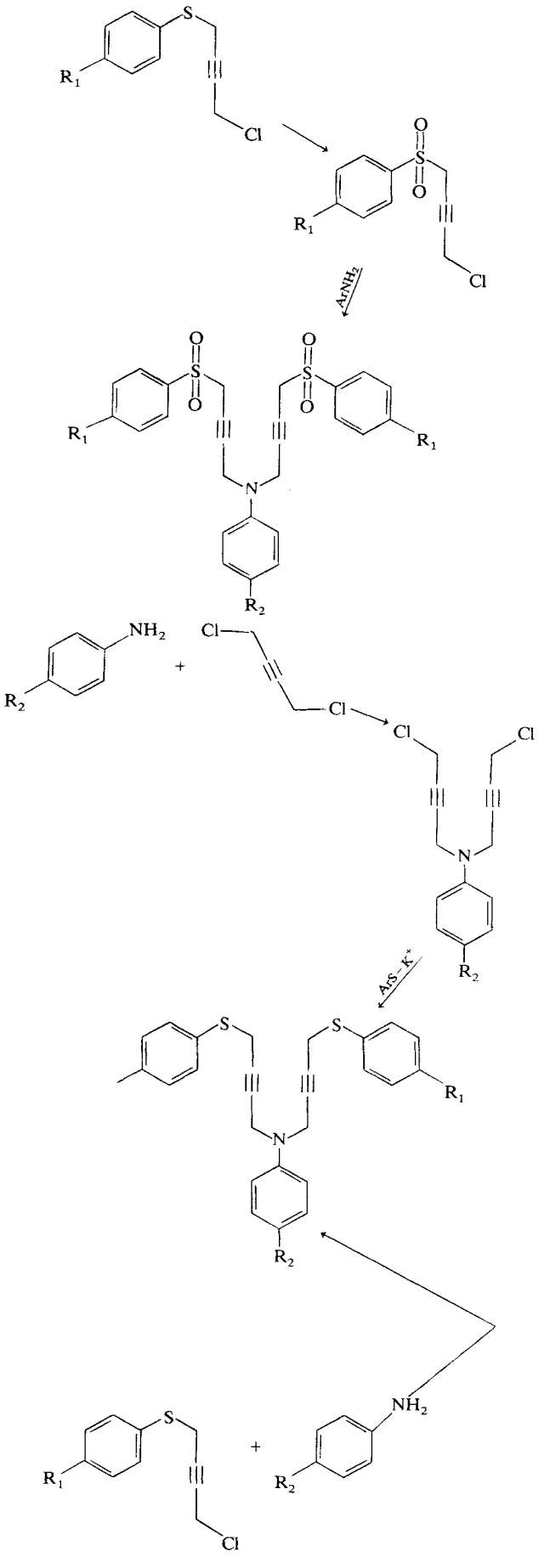
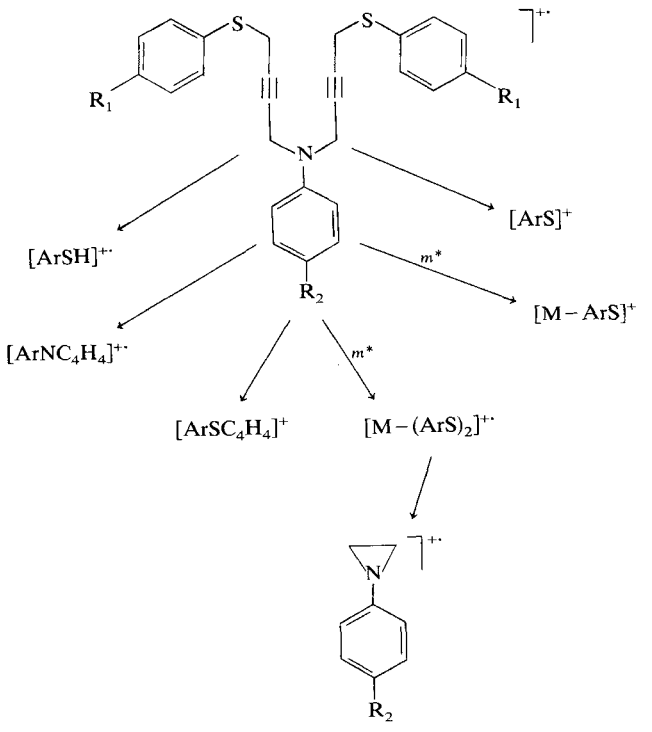




Scheme 1

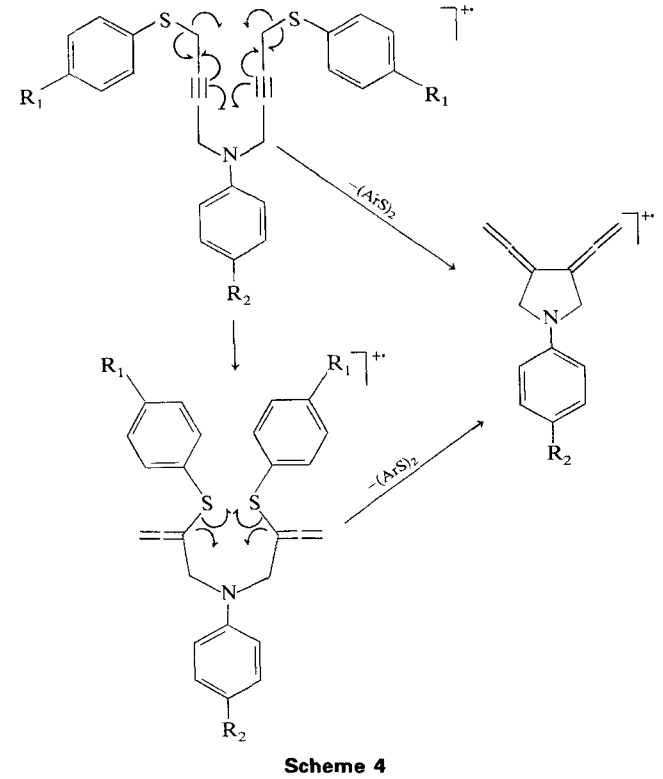


Scheme 2



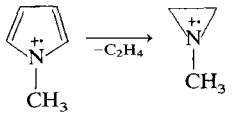
Scheme 3

functions from the molecular ion, giving [M−(ArSSAr)]+· as a prominent peak in *all* of the spectra. The *p*-toluidine carrying molecules gave *m/z* 209 in high percentage relative abundance (63%, 49%, 20% and 10%), while the *p*-anisidine carrying molecules gave *m/z* 225 corresponding to 34, 10 and 7% of the base peak. At the same time, the [ArSSAr]+· fragments were also formed to the extent of 7, 6, 5, 4 and 2% of the base peak, suggesting that the larger fraction of the charge was carried by the [M−(ArSSAr)]+· unit. Even though loss of ArS from the molecular ion was observed consistently for all of the sulfides, loss of the ArSSAr does not occur by *sequential* loss of one ArS after another. Metastable defocusing studies (see Experimental) clearly established that the expulsion of the two arylthio moieties occurs directly from the molecular ion. To account for this expulsion of ArSSAr, two different modes of interaction between the two ArS functions can be postulated. Both processes lead to the *same* ion. Scheme 4 illustrates these two pathways.



Scheme 4

It would be difficult to distinguish between the two pathways because the mass spectra of the molecular ion and the 1,3-rearrangement ion are indistinguishable. Further fragmentation of the [M−(ArSSAr)]+· ion then leads to the elimination of C_6H_4 and formation of an aziridine cation $[ArNC_2H_4]^{+\cdot}$. Such cleavages of pyrrolidine derivatives into aziridines are known in the literature,[6] e.g. as shown in the reaction below.



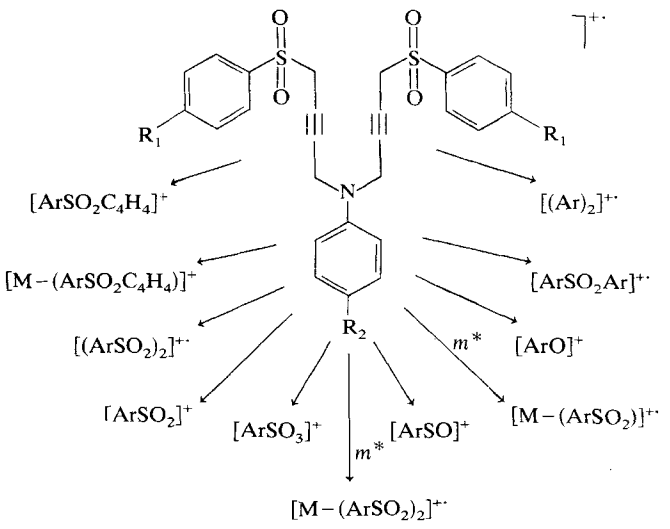
Thus, it is clear that the system *N,N*-bis(4′-arylthio-2′-butynyl)aniline is capable of direct interaction between the two ArS functions under electron impact, as is well substantiated by metastable defocusing experiments. Consequently, it gave further encouragement for similar possibilities in the corresponding sulfones. Results pertaining to the sulfones are discussed below.

Spectra of *N,N*-bis(4′-arylsulfonyl-2′-butynyl)anilines

As can be anticipated readily the mass spectra of the sulfones exhibited peaks from some of the well known fragmentation pathways such as $[ArSO_2]^+$, $[M-ArSO_2]^+$, $[ArSO_2C_4H_4]^+$, $[ArSO]^+$, $[ArO]^+$ and $[ArSO_2H]^{+\cdot}$ arising from the alkyl–sulfur bond cleavage, sulfone–sulfinate rearrangement and α-hydrogen abstraction. The more intriguing data, however, came from the loss of $ArSO_2SO_2Ar$ *directly from the molecular ion.* Simultaneous loss of the two arylsulfonyl functions was again confirmed emphatically by metastable correlations between the molecular ion and the $[M-(ArSO_2SO_2Ar)]^{+\cdot}$ ion. The resulting sulfur-free fragments are exactly the same as those obtained from the corresponding sulfides discussed earlier (*vide supra*). Consequently, they also showed a loss of the C_6H_4 unit leading to the aziridine ion $[ArNC_2H_4]^{+\cdot}$ which was encountered earlier.

Other fragment ions also reinforce the formation of the $[ArSO_2SO_2Ar]^{+\cdot}$ ion. Thus, *all* of the sulfones studied, show great abundance of the $[ArSO_2Ar]^{+\cdot}$ ion and the $[ArAr]^{+\cdot}$ ion. Indeed, in two of the examples studied, the $[ArSO_2Ar]^{+\cdot}$ ion forms the base peak. Scheme 5 illustrates unusual fragments discussed above.

Relative abundances of the important ions in both the sulfides and the sulfones are presented in Tables 1 and 2.



Scheme 5

Representative spectra of the sulfides and sulfones are presented in Figs. 1–4.

In summary, the aryl propynyl sulfones and the 1,6-diarylsulfonyl-2,4-hexadiynes show SO_2 expulsion as a dominant mode of cleavage under electron impact, whereas the 1,4-diarylsulfonyl-2-butynes and the *N,N*-bis(4'-arylsulfonyl-2'-butynyl)anilines show remote interaction between the sulfones forming $[ArSO_2SO_2Ar]^{+\cdot}$ as a prominent pathway for cleavage. No loss of SO_2 was observed in these instances.

EXPERIMENTAL

Melting points were obtained on a Buchi S.M.P.-20 capillary melting point apparatus and are not corrected. Nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ solution with TMS as internal standard (TMS = 0.00δ) on a Varian A-60 spectrometer. Mass spectra were obtained at Arizona State University, employing a Varian MAT 1125 double focusing reverse geometry mass spectrometer interfaced to a SS-200 mini-computer data system. Samples were run at an ion source temperature of 200 °C by direct probe (25–200 °C) at 70 and 20 eV. Metastable ion data were obtained by focusing on the molecular ion, then decreasing the electrostatic sector voltage in a continuous scan (direct analysis of daughter ion technique). All daughter ions generated from the

Table 1. Important ions in the mass spectra of *N,N*-bis(4'-arylthio-2'-butynyl)anilines

$(R_1—C_6H_4—S—CH_2—≡—CH_2—)_2N—C_6H_4—R_2$

R_1	4-Me	4-Me	H	H	4-Br	4-Br	4-Cl
R_2	4-Me	4-MeO	4-Me	4-MeO	4-Me	4-MeO	4-Me
Ion	(m/z)/% relative abundance						
$[M]^{+\cdot}$	455/20	471/15	427/30	443/5	585/8	601/13	495/9
Base peak	91	91	208	91	109	109	144
$[ArS]^+$	123/50	123/52	109/78	109/83	187/9	187/15	143/60
$[ArSH]^+$	124/42	124/70	110/76	110/57	188/52	188/42	144/100
$[ArNC_4H_4]^+$	157/37	173/30	157/44	173/–	157/26	173/22	157/35
$[ArSC_4H_4]^+$	175/34	175/15	161/18	161/32	239/2	239/–	194/20
$[M-ArS]^+$	332/10	348/8	318/15	334/1	398/5	414/5	352/10
$[M-(ArS)_2]^{+\cdot}$	209/49	225/34	209/63	224/7	209/50	225/35	209/50
$[ArNC_2H_4]^{+\cdot}$	133/4	149/13	133/3	149/5	133/3	149/3	133/3

Table 2. Important ions in the mass spectra of *N,N*-bis(4'-arylsulfonyl-2'-butynyl)anilines

$(R_1—C_6H_4—SO_2—CH_2—≡—CH_2—)_2N—C_6H_4—R_2$

R_1	Cl	Cl	Me	Me	Br	Br
R_2	MeO	Me	MeO	Me	MeO	Me
Ion	(m/z)/% relative abundance					
$[M]^{+\cdot}$	575/2	559/2	535/2	519/2	665/2	649/2
$[ArO]^+$	127/10	127/22	107/14	107/4	172/100	172/30
$[ArSO]^+$	159/100	159/100	139/52	139/53	204/15	204/24
$[ArSO_2]^+$	175/3	175/15	155/14	155/10	219/62	219/35
$[ArSO_3]^+$	—	191/2	171/100	—	235/2	—
$[(Ar)_2]^{+\cdot}$	222/5	222/2	182/2	182/2*	312/16	312/10
$[ArSO_2Ar]^{+\cdot}$	286/92*	286/20	246/2	246/5*	376/100	376/100
$[(ArSO_2)_2]^{+\cdot}$	350/12	350/5	—	—	440/20	—
$[ArSO_2C_4H_4]^+$	227/6	227/4	207/2	207/10	273/24	273/4
$[M-ArSO_2C_4H_4]^+$	348/9	332/20	328/32	312/5	393/45	—
$[M-ArSO_2]^+$	400/8[a]	384/8	380/3	364/5	446/12	430/7
$[M-(ArSO_2)_2]^{+\cdot}$	225/5	209/30	225/10	209/12	—	209/18

[a] Seen at 20 eV, but not at 70 eV.

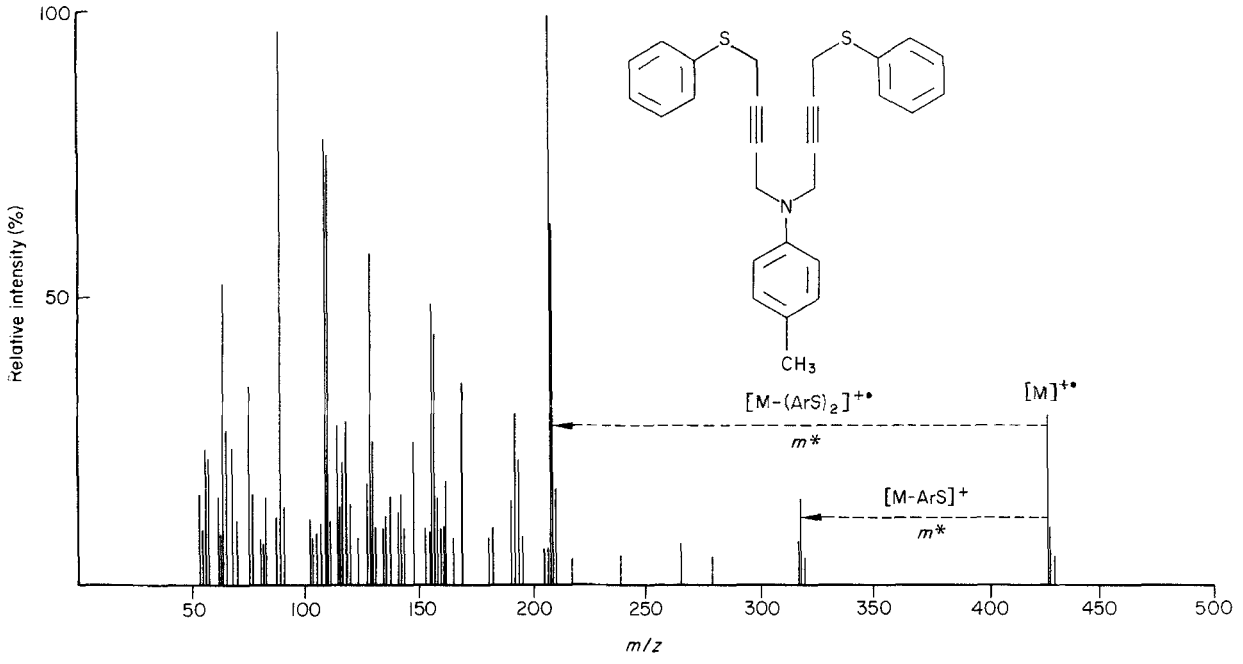


Figure 1. EI mass spectrum of *N*,-bis(4′-phenylthio-2′-butynyl)*p*-toluidine.

molecular ion in the second field free region between the magnet and the electrostatic sector were thus identified. Infrared (IR) spectra were taken on a Beckman 4210 spectrophotometer. Elemental analysis was provided by the Warner-Lambert Research Institute and by Galbraith Laboratories, Inc.

Preparation of *N,N* bis(4′-chloro-2′-butyl)anilines

To 0.4 mol of *p*-anisidine in 100 cm^3 of acetonitrile, a solution of 0.8 mol K_2CO_3 in 550 cm^3 of water and 1.6 mol of 1,4-dichloro-2-butyne were added. The resulting mixture was stirred vigorously under nitrogen at 45–50 °C for two days and at 25–30 °C for one day.

The organic and aqueous layers were then separated and the aqueous layer extracted with one 100 cm^3 portion of $CHCl_3$, the chloroform extract combined with the organic layer and the solvents removed *in vacuo* to give a brown oil. The unreacted 1,4-dichloro-2-butyne was removed under vacuum (*c.* 30 mmHg) and the residue chromatographed on a two phase column, composed of a 22 × 10 cm bed of acid washed alumina mixed with silica gel (1 : 1) topped by a 5 × 10 cm bed of granular charcoal, alumina and $CaCO_3$ in a ratio of 1 : 20 : 1.

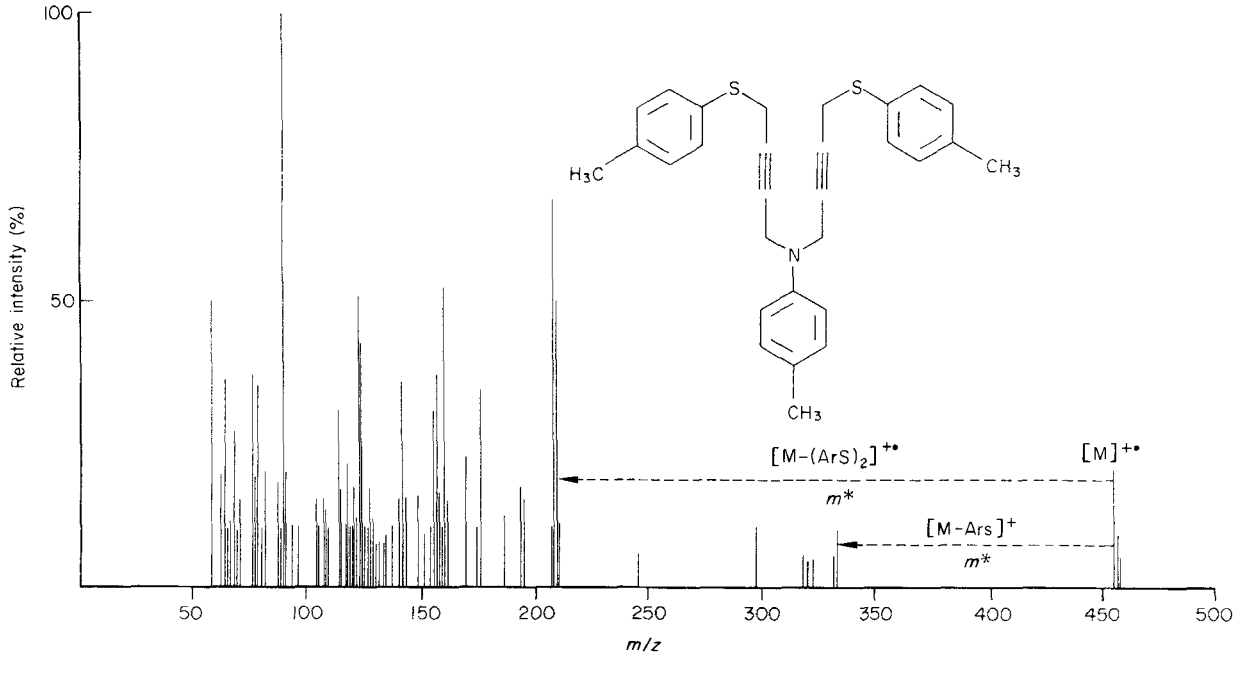


Figure 2. EI mass spectrum of *N,N*-bis(4′-*p*-tolylthio-2′-butynyl)*p*-toluidine

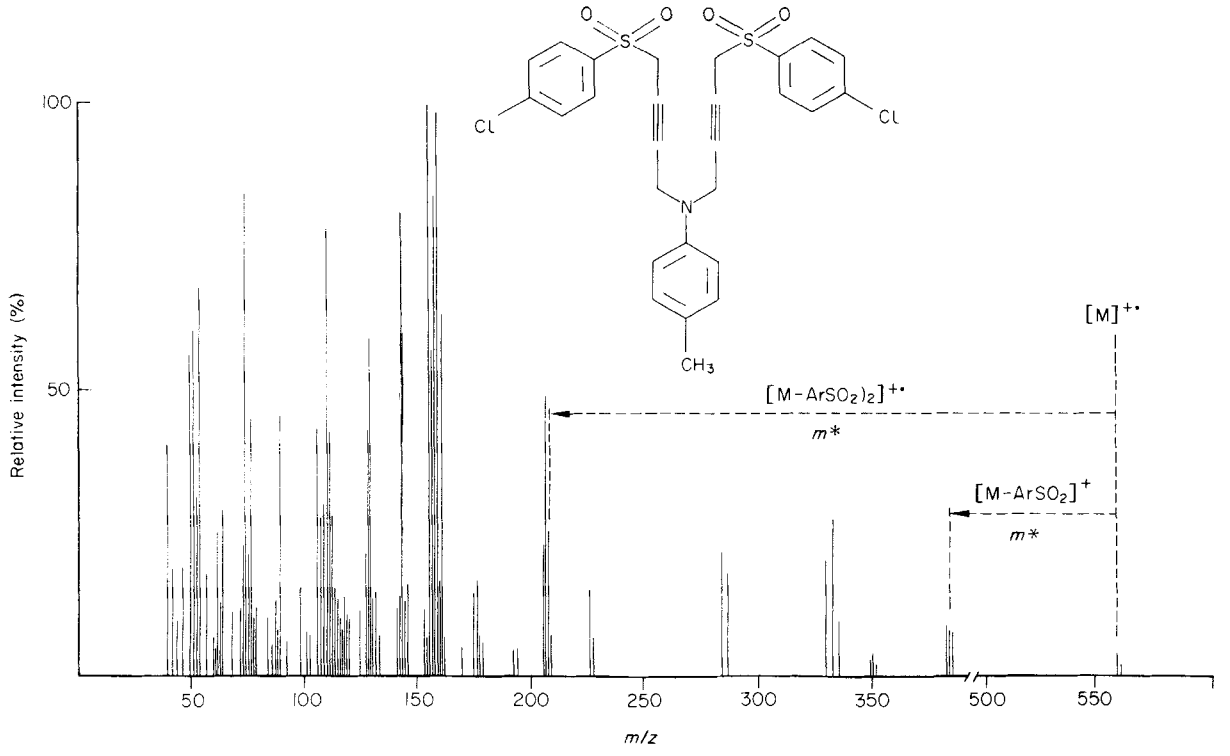


Figure 3. EI mass spectrum of *N,N*-bis(4'-*p*-chlorophenylsulfonyl-2'-butynyl)*p*-toluidine.

The column was developed with a mixture of 50% benzene and 50% hexane. *N,N*-bis(4'chloro-2'-butynyl)-*p*-anisidine was obtained in 33% yield and was identical to that reported in the literature: NMR 3.73 (s, 3H), 4.00–4.10 (m, 8H), 6.87–7.30 (m, 4H); mass spectrometry $[M]^{+\cdot}$ 295.

Condensation of *N,N*-bis(4'-chloro-2'-butynyl)-*p*-anisidine with *p*-chlorothiophenol

A solution of 0.67 g (0.0046 mol) of *p*-chlorothiophenol in 30 cm^3 of acetonitrile was added dropwise to a solution of 0.27 g (0.0048 mol) of KOH in

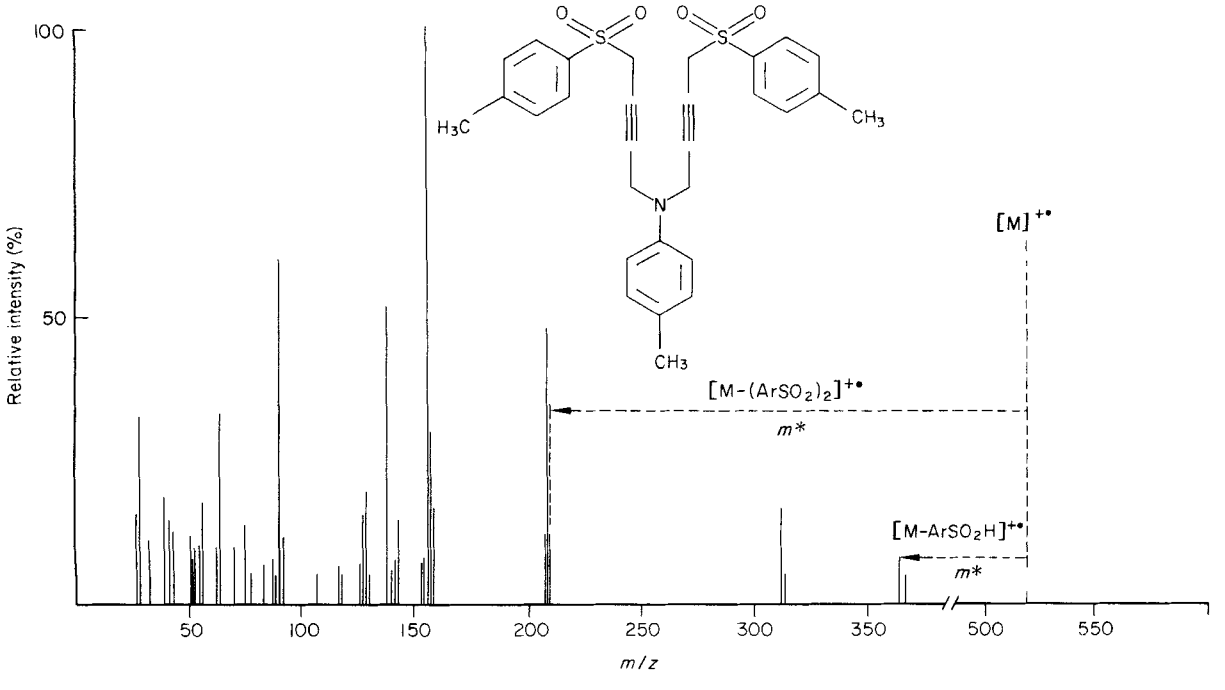


Figure 4. EI mass spectrum of *N,N*-bis(4'-*p*-tolylsulfonyl-2'-butynyl)*p*-toluidine.

50 cm^3 of 80% ethanol over 30 min at room temperature, with stirring, under a blanket of N_2. To the resulting mixture, a solution of 0.66 g (0.0022 mol) of the *N,N*-bis(4′-chloro-2′-butyl)-*p*-anisidine in 30 cm^3 of acetonitrile was added dropwise over 30 min, under slight positive pressure of N_2, with stirring at room temperature. The reaction mixture was stirred for an additional 5 h, after which 50 cm^3 of ether was added. The precipitated KCl was filtered, the filtrate dried over $MgSO_4$ and the solvents removed on a rotavapor. The residue was taken up in 100 cm^3 of $CHCl_3$, washed twice with 50 cm^3 of 0.2 KOH, three times with 100 cm^3 water, and dried over $MgSO_4$. Removal of solvent on a rotavapor yielded a clear yellow oil which was dissolved in $CHCl_3$ and diluted with pet. ether until turbid. Upon cooling in a refrigerator, 0.26 g (22% yield) of the *N,N*-bis(4′-*p*-chlorophenylthio-2′-butynyl)-*p*-anisidine was deposited as a white solid which was recrystallized from $CHCl_3$/pet. ether to give the analytical sample: m.p. 82–83 °C; NMR 3.55 (m, 4H), 3.76 (s, 3H), 3.86 (m, 4H), 7.23 (s, 8H); mass spectrometry $[M]^{+\cdot}$ 511.

Analysis calc. for $C_{27}H_{23}ONCl_2S_2$: C, 63.27; H 4.53. Found, C, 63.13; H, 4.67.

Synthesis of 1-arylthio-4-chloro-2-butynes

The procedure of Bates[7] was followed with some modifications. The following preparation of 1-*p*-bromophenylthio-4-chloro-2-butyne, which was not reported previously by Bates, provides an illustration. A methanolic solution of KOH (0.22 mol in 150 cm^3) was added dropwise to a solution of *p*-bromothiophenol (0.22 mol) in 150 cm^3 of methanol at room temperature over 30 min, with stirring and under a blanket of N_2. The resulting potassium thiophenolate solution was then added dropwise over 3 h to a solution of 0.33 mol of 1,4-dichloro-2-butyne in 600 cm^3 of methanol, with stirring at room temperature under a blanket of N_2. The reaction mixture was stirred overnight at room temperature. The mixture was filtered to remove KCl and the solvent removed on a rotavapor. The residue was dissolved in 300 cm^3 $CHCl_3$ and washed twice with 150 cm^3 of 0.2 M KOH and once with 150 cm^3 H_2O. The organic layer was dried over $MgSO_4$ and the solvent removed on a rotavapor to give a yellow oil. The crude product was distilled at high vacuum (0.05–0.15 mmHg). Unreacted 1,4-dichloro-2-butyne was collected first, distilling at *c.* 35 °C. The pure 1-*p*-bromophenylthio-4-chloro-2-butyne was collected in the second fraction, *c.* 50% yield: b.p. 130 °C per 0.1 mmHg; m.p. 43–44 °C; NMR 3.6(t, 2H), 4.1 (t, 2H), 7.18–7.31 (q, 4H).

Analysis calc. for $C_{10}H_8BrClS$: C, 43.58; H, 2.92. Found: C, 43.32; H, 2.85.

Condensation of 1-*p*-chlorophenylthio-4-chloro-2-butyne with *p*-anisidine

To 76 cm^3 of acetonitrile, 16 g (0.07 mol) of 1-*p*-chlorophenylthio-4-chloro-2-butyne and 5.77 g (0.047 mol) of *p*-anisidine were added and the resulting solution stirred with 15.51 g (0.094 mol) of K_2CO_3 in 140 cm^3 of H_2O at 45–55 °C (bath temp.) for two days under a blanket of N_2. At the end of two days, another 16 g of the 1-arylthio-4-chloro-2-butyne was added. A solution of 15.51 g of K_2CO_3 in 50 cm^3 H_2O was then added and the reaction mixture stirred for an additional two days at 45–55 °C, under N_2. The reaction mixture was extracted with 500 cm^3 $CHCl_3$ and the organic layer washed twice with 400 cm^3 H_2O, dried over Na_2SO_4 and the solvent removed on a rotavapor to give a brown oil which solidified upon standing. The crude product was chromatographed on a blended two-stage column, consisting of a 30×10 cm bed of 50% silica gel, 50% alumina topped by a 14×10 cm bed of 10% granular coconut charcoal, 90% alumina. Benzene was used to develop the column, yielding 18 g of the *N,N*-bis(4′-*p*-chlorothiophenyl-2′-butynyl)-*p*-anisidine (75% yield). Recrystallization from ether gave the pure product, whose physical and spectral properties were identical to those of the product obtained from the condensation of *p*-chlorothiophenol with *N,N*-bis(4′chloro-2′-butynyl)-*p*-anisidine described previously.

The physical and analytical data for the various *N,N*-bis(4′-arylthio-2′-butynyl)anilines obtained by this method are given in Table 3.

Attempted oxidation of *N,N*-bis(4′-*p*-chlorophenylthio-2′-butynyl)-*p*-anisidine

In a mixture of 10 cm^3 of glacial acetic acid and 10 cm^3 ether, 0.5 g (0.00097) mol of *N,N*-bis(4′-*p*-chlorophenylthio-2′-butyl)-*p*-anisidine was added, followed by 2.21 cm^3 of 30% H_2O_2 (0.0195 mol) added in one portion. One drop of concentrated H_2SO_4 was added and the reaction mixture was refluxed for 1 h. It was then diluted with 50 cm^3 of $CHCl_3$ and washed with 50 cm^3 H_2O, 50 cm^3 5% K_2CO_3 and 100 cm^3 of H_2O, respectively. Drying of the organic layer over Na_2SO_4 and removal of the solvents on a rotavapor yielded 0.5 g of a brown oil which was unresolved by thin-layer chromatography (TLC) (SiO_2; 40% benzene, 10% isopropanol, 50% hexanes). The NMR spectrum contained broad unresolved peaks from *c.* 3.5–4.1 and 6.8–8.0.

The oxidation was then attempted with 0.5 g of the *N,N*-bis(4′-*p*-chlorophenylthio-2′-butynyl)-*p*-anisidine in 40 cm^3 of glacial acetic acid and 20 cm^3 of ether to which 2.21 cm^3 of 30% H_2O_2 was added. The reaction mixture was refluxed for 1 h, diluted with 100 cm^3 $CHCl_3$ and then washed once with 100 cm^3 H_2O, twice with 100 cm^3 of 5% K_2CO_3, once again with 100 cm^3 of H_2O and dried over $Na_2SO_4/CaCO_3$. Removal of solvent on a rotavapor yielded 0.5 g of brown oil which was unresolved by TLC (same system described above). The NMR spectrum indicated decomposition of the starting material.

Preparation of 1-arylsulfonyl-4-chloro-2-butynes

The procedure described by Bates[7] for the oxidation of 1-arylthio-4-chloro-2-butynes to the corresponding sulfones was followed with some modifications. The preparation of 1-*p*-bromophenylsulfonyl-4-chloro-2-butyne, which was not reported previously, is representative and is described below.

Table 3. *N,N*-bis(4′-Arylthio-2′-butynyl)anilines

$(R_1—C_6H_4—S—CH_2—\equiv—CH_2—)_2N—C_6H_4—R_2$

R_1	R_2	$[M]^{+\cdot}$	m.p. (°C)	Analysis (%) Calc. C	Calc. H	Found C	Found H	NMR ($CDCl_3$) $H_a\delta$ (H_a)	NMR ($CDCl_3$) $H_b\delta$ (H_b)
4-Me	4-MeO	471	86–87	73.85	6.20	73.74	6.33	3.53 (m, 4H)	3.86 (m, 4H)
4-Br	4-MeO	601	76–77	53.91	3.86	53.80	3.99	3.55 (m, 4H)	3.86 (m, 4H)
4-Cl	4-MeO	511	82–83	63.27	4.53	63.13	4.67	3.55 (m, 4H)	3.86 (m, 4H)
H	4-MeO	443	48–49	73.09	5.69	73.06	5.64	3.58 (m, 4H)	3.85 (m, 4H)
4-Me	4-Me	455	70–71	76.42	6.42	76.32	6.33	3.53 (m, 4H)	3.91 (m, 4H)
4-Br	4-Me	585	104–105	55.40	3.96	55.61	3.92	3.55 (m, 4H)	3.92 (m, 4H)
4-Cl	4-Me	495	101–102	65.31	4.68	65.29	4.73	3.55 (m, 4H)	3.92 (m, 4H)
H	4-Me	427	54–55	75.84	5.89	76.01	5.85	3.58 (m, 4H)	3.94 (m, 4H)

To a mixture of 100 cm^3 of ether and 100 cm^3 of glacial acetic acid, 0.036 moles of 1-*p*-bromophenylthio-4-chloro-2-butyne and 41 cm^3 (0.36 mol) of 30% H_2O_2 was added. The reaction mixture was heated to reflux for 3 h. The reaction mixture was then poured over 500 cm^3 of crushed ice and stirred until the ice had melted. The mixture was filtered and the white solid thus obtained washed with H_2O. Drying the product in a vacuum desiccator containing an open beaker of KOH pellets yielded the pure 1-*p*-bromophenylsulfonyl-4-chloro-2-butyne in 80% yield: m.p. 112–114 °C; NMR 4.1 (m, 4H), 7.9 (m, 4H); IR λSO_2 at 1140 and 1320 cm^{-1} (paraffin mull).

Analysis calc. for $C_{10}H_8O_2BrCIS$: C, 39.05; H, 2.62. Found: C, 39.14; H, 2.53.

General procedure for the synthesis of *N,N*-bis(4′-arylsulfonyl-2′-butynyl)anilines

A solution of 0.013 mol of the 1-arylsulfonyl-4-chloro-2-butyne and 0.0058 mol of the aniline in 100 cm^3 of benzene was stirred with 3.59 g (0.026 mol) of K_2CO_3 in 50 cm^3 of H_2O at 55 °C, under a blanket of N_2, for 5.5 h. The organic layer was separated and washed once with 100 cm^3 H_2O, dried over Na_2SO_4 and placed in a freezer. After allowing the benzene solution to freeze, the mixture was thawed and filtered to give the *N,N*-bis(4′-arylsulfonyl-2-butynyl)anilines as white solids in *c.* 45% yield. Analytical samples were prepared by recrystallization from CH_2Cl_2/pet. ether, $CHCl_3$/pet. ether, or CH_2Cl_2. The *N,N*-bis(4′-arylsulfonyl-2′-butynyl)anilines thus prepared are described in Table 4.

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Table 4. *N,N*-bis(4′-arylsulfonyl-2′-butynyl)anilines

$(R_1—C_6H_4—SO_2—CH_2—\equiv—CH_2—)_2N—C_6H_4—R_2$

R_1	R_2	$[M]^{+\cdot}$	m.p. (°C)	Yield (%)	Analysis (%) Calc. C	Calc. H	Found C	Found H	NMR ($CDCl_3$) $H_{ab}\delta$
4-Me	4-MeO	535	136–137	41	65.01	5.47	65.29	5.27	3.91 (s, 8H)
4-Br	4-MeO	665	160–162	50	48.74	3.48	48.69	3.50	3.93 (s, 8H)
4-Cl	4-MeO	575	150–151	39	56.24	4.03	56.35	4.09	3.93 (s, 8H)
4-Me	4-Me	519	185–186	38	67.02	5.62	66.90	5.70	3.91 (s, 8H)
4-Br	4-Me	649	184–186	17	49.94	3.57	50.24	3.75	3.95 (s, 8H)
4-Cl	4-Me	559	172–174	48	57.86	4.14	57.74	4.21	3.95 (s, 8H)

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