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Synthetic Utility of 4'-Nitrobenzenesulfenanilide in the Functionalization of Carbon-Carbon Double and Triple Bonds : Its Use in the Bromosulfenylation of Alkenes and Alkynes

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Abstract. The reaction of 4'-nitrobenzenesulfenanilide (NBSA) with hydrobromic acid, suitably carried out at room temperature in the presence of cyclohexene, trans-hex-3-ene, hex-1-ene and 3,3-dimethylbut-1-ene, results in quantitative isolation of corresponding 2-bromoalkyl phenyl sulfides which occur with trans-stereospecificity and anti-Markovnikov regiospecificity through electrophilic addition of initially-formed benzenesulfenyl bromide to the alkene double bond. Similar reaction in the presence of mono- and di- substituted alkyl- and phenyl-acetylenes generally affords (E)-2-bromovinyl phenyl sulfides in good yields, which become lower with decreasing nucleophilic power of the alkyne employed. However, in the presence of parent acetylene, no virtual formation of the corresponding sulfide adduct occurs, but almost exclusive formation of diphenyl disulfide essentially ascribable to preferred decomposition of the highly unstable benzenesulfenyl bromide intermediate. The present additions of benzenesulfenyl bromide to alkenes and alkynes are believed to involve the initial intermediacy of thiiranium- and thiirenium-like ions, respectively, by analogy with related Ad_E reactions of sulfenyl chlorides.

It is well known that sulfenyl chlorides can smoothly undergo electrophilic addition to carbon-carbon double and triple bonds to give 1:1 adducts with trans-stereospecificity probably through the intermediacy of thiiranium and thiirenium ions respectively.[1]

Particularly in recent years these addition reactions have been extensively investigated and shown to be of remarkable interest for the preparation of a variety of useful synthetic intermediates.[1a] On the contrary, very little attention has been so far devoted to mechanistic aspects and/or synthetic applications of the corresponding additions of sulfenyl bromides, though the scant available data might suggest that these reactions should display a not dissimilar chemical trend. A limited number of sulfenyl bromides have been previously shown to add to alkenes in a trans-stereospecific fashion,[2] but the Ad_E reaction of sulfenyl

bromides with alkynes is virtually unexplored.[1a,d,e] A limiting factor for a parallel investigation of the Ad_E reactions of sulfenyl bromides is represented by the fact that such bromides (like especially the fluorides and iodides) are generally (very) unstable compounds which undergo easy decomposition to disulfide.[3] Consequently, they are normally prepared in situ by the usual reaction of disulfide (or thiol) with bromine, and the resulting sulfenyl bromide is then reacted with the appropriate π-nucleophile without isolation.[2] In principle, a sulfenyl bromide might be more easily prepared by the reaction of HBr with an appropriate sulfenamide, provided that the bromide ion might afford a sulfenyl bromide more stable than the protonated sulfenamide (Scheme 1).[1] Such method would have the advantage of permitting the "in situ" preparation of sulfenyl bromide in the presence of π-nucleophilic reactant.

We reasoned that the readily available (and quite stable) 4'-nitrobenzenesulfenanilides[4-7] should be regarded as ideal candidates for the production of arenesulfenyl bromides upon reaction with HBr. Earlier studies had revealed that the parent 4'-nitrobenzenesulfenanilide (NBSA), in the presence of a Lewis or Brönsted acid,[5] can very effectively perform phenylthio group transfer to various nucleophilic species,[4,5] including weak nucleophiles like alkenes[6] and alkynes.[7] We were therefore led to investigate the reaction of NBSA with hydrobromic acid, in the presence of various alkenes and alkynes, with the primary aim to uncover a novel one-pot procedure for the 1,2-bromosulfenylation of these unsaturated compounds. This study was especially encouraged by the recent interest in the preparation of (E)-1-bromo-2-(phenylthio)alkenes which have proved to be valuable intermediates for the synthesis of a variety of mono- and polyenes, inter-alia insect pheromones.[8,1]

$$RSNR_2 + HBr \rightleftharpoons RSNHR_2^{+}\,Br^{-} \rightleftharpoons RSBr + NHR_2$$

Scheme 1

RESULTS AND DISCUSSION

Addition of a slight excess (1.5 molar equiv.) of 48% hydrobromic acid to a solution of NBSA in acetonitrile or chloroform, at room temperature, brought about instantaneous decomposition of NBSA with concomitant formation of benzenesulfenyl bromide **1**. This was monitored by the immediate appearance of a yellow-orange colour, expected for arenesulfenyl halides,[3] as well as by TLC analysis which showed the total disappearance of starting NBSA and the parallel occurrence of 4-nitroaniline. When NBSA in chloroform containing cyclohexene (2 molar equiv.) was treated with ten-fold molar excess of hydrobromic acid, the yellow-orange colour caused by the initially formed sulfenyl bromide **1** almost immediately faded and concomitant precipitation of 4-nitroaniline hydrobromide occurred. After a few minutes the precipitated hydrobromide was filtered off and the excess hydrobromic acid was eliminated by decantation. Subsequent evaporation of the solvent and the excess alkene gave the trans-bromo sulfide adduct **2a** in quantitative yield. By a similar procedure the erythro-sulfide **3** was cleanly obtained, in virtually quantitative yield, from trans-hex-3-ene. Moreover, quantitative yields of the anti-Markovnikov (AM) adducts **4a, 5a** could be similarly obtained from unsymmetrical hex-1-ene and 3,3-dimethylbut-1-ene (Scheme 2).

In the above reactions the employment of a rather large excess of hydrobromic acid was generally preferred in order to favour total and rapid precipitation of the aniline hydrobromide and thence allow prompt isolation of the resulting sulfide products **2a, 3, 4a** and **5a**, which were found to be (highly) sensitive to hydrolytic and/or thermal conditions. In fact, the isolable yields of the adducts **2a** and **4a** were (very) strongly reduced when their preparation was alternatively attempted by using acetonitrile solvent and a slight excess of the acid and subjecting the crude reaction mixture to column chromatography after previous treatment with

aqueous potassium carbonate. By this procedure the compound **2a** could be isolated only in poor yield and the corresponding hydroxy sulfide **2b** and amino sulfide **2c** were instead obtained as the main products, whereas the bromo sulfide **4a** could be isolated in ca. 60% yield and was accompanied by a number of its decomposition products which were not investigated.

2a : X = Br; **2b** : X = OH

2c : X = $NHC_6H_4NO_2$-p

$PhSCHR^1— CHR^2Br$

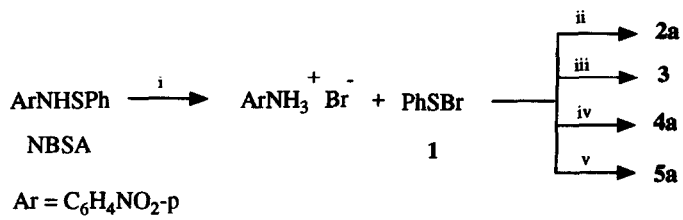
3 : $R^1 = R^2$ = Et (erythro)

4a : R^1 = Bu, R^2 = H; **4b** : R^1 = H, R^2 = Bu

5a : $R^1 = Bu^t$, R^2 = H; **5b** : R^1 = H, $R^2 = Bu^t$

However, the alternative employment of such procedure led to no virtual variation of the isolated yield of the sulfide **5a**. Moreover, the AM sulfide adducts **4a, 5a** were shown to undergo spontaneous isomerization to the Markovnikov (M) adducts **4b, 5b**. Upon standing in chloroform for ca. 24 h, the compounds **4a, 5a** in fact gave 85:15 mixtures of **4b, 5b** and **4a, 5a**, whose composition remained thereafter unchanged. Related spontaneous AM/M isomerizations of β-chloro sulfides have been previously uncovered[9].

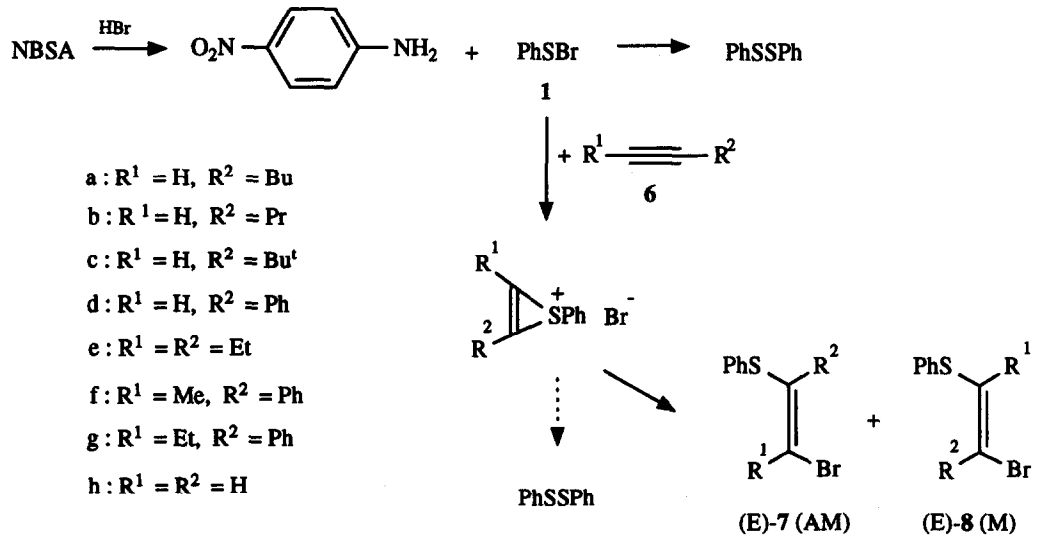
The trans sulfide **2a** had been previously reported[10]. Structural assignment of the new compounds **3, 4a,b** and **5a,b** was accomplished on the basis of ^1H NMR and MS spectral data. In particular, the regiochemistry of the AM-adducts **4a, 5a** and M-adducts **4b, 5b** was established by ^1H NMR analysis and was based on the fact that protons geminal to bromine are expected to occur at lower field relative to those geminal to the phenylthio group. Our above findings therefore showed that the reaction of NBSA with hydrobromic acid, suitably carried out in the presence of simple alkenes, can actually provide a quite simple and convenient procedure for the preparation of β-bromoalkyl phenyl sulfides.



Scheme 2. Reagents : i, 48% hydrobromic acid, chloroform; ii, cyclohexene; iii, trans-hex-3-ene; iv, hex-1-ene; v, 3,3-dimethylbut-1-ene

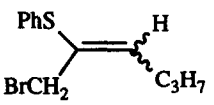
Additionally, the above findings supported previous chemical evidence[2] that the addition of sulfenyl bromides to alkenes, similarly to that of the chlorides, is likely to proceed through the initial occurrence of thiiranium -like intermediates and subsequent bromide attack at either "thiiranium" ring-carbon. The addition of sulfenyl chlorides to unsymmetrical alkyl olefins (including hex-1-ene) usually results in a non-regiospecific AM orientation, but with 3,3-dimethylbut-1-ene exclusive formation of AM adduct occurs[9, 1a,b]. The presently observed AM regiospecificity of the addition of benzenesulfenyl bromide **1** to hex-1-ene might conceivably reflect a greater reluctance of bulkier bromide relative to chloride to attack sterically hindered "thiiranium" carbons. The reaction of NBSA with 48% hydrobromic acid in the presence of the mono- and di-substituted acetylenes **6a-g** was generally carried out in acetonitrile by using a slight excess of

the acid (1.5 molar equiv.) and a five-fold excess of alkyne. With all alkynes **6a-g** complete reaction was found to occur within ca. 4-5 min.. After such time the resulting reaction mixture was neutralized with aqueous potassium carbonate and then chromatographed. Column chromatography led generally to isolation of the β-bromovinyl sulfides **7** and/or **8** and diphenyl disulfide in virtually quantitative overall yields in addition to 4-nitroaniline (ca. 100%) (Scheme 3 and Table).



Scheme 3

With hex-1-yne **6a**, pent-1-yne **6b**, and tert-butylacetylene **6c** the corresponding AM adducts **7a-c**, exclusive of their M regioisomers **8a-c**, were isolated in fairly satisfactory yields (Table, entries 1-3). The vinyl sulfide **7c** was obtained as the pure (E)-isomer, whereas the sulfides **7a,b** were obtained as inseparable 90:10 mixtures of the (E)- and (Z)-isomers. The (Z)-sulfides (Z)-**7a,b** most likely arose from some isomerization of the initially-formed (E)-sulfides (E)-**7a,b** under the acidic reaction conditions. This fact was supported by our observation that the above 90:10 mixture of (E)- and (Z)-**7a**, upon treatment with hydrobromic acid (10 equiv.) in acetonitrile for 10 min., was largely converted into a corresponding 25:75 mixture, which was however accompanied, to a minor extent, by the rearranged vinyl sulfides (E)- and (Z)-**9**.



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Further support came from our finding that the two geometrical isomers (E)- and (Z)-**7a** were produced to a comparable extent when we repeated our reaction in the presence of the alkyne **6a** by using a larger excess of hydrobromic acid (10 equiv.). However, only the (E)-sulfide (E)-**7a** was apparently formed, in a similar yield, when acetonitrile was replaced by chloroform (see Experimental section).

In acetonitrile phenylacetylene **6d** led to an inseparable mixture (55%) of the AM and M adducts (E)-**7d** and (E)-**8d** in ca. 55:45 ratio (Table, entry 4). In chloroform or dioxane these two adducts (E)-**7d** and (E)-**8d** occurred in a similar ratio (ca. 60:40), which was apparently unaffected by the amount of hydrobromic acid employed (1.5 or 10 molar equiv.). On the other hand, the proportion of the two isomers (E)-**7d** and (E)-**8d** was largely modified (their ratio was ca. 30:70) when the same reaction was repeated in acetonitrile by using a ten-fold molar excess of hydrobromic acid. Under these latter conditions the AM adduct (E)-**7d** was shown to undergo some isomerization to its geometrical isomer (Z)-**7d**. but not at all to its regioisomer (E)-**8d**. Curiously, the two adducts (E)-**7d** and (E)-**8d** were also found to occur in ca. 30:70 ratio under the usual less acidic conditions, but within the very early reaction time (≤ 30 sec) (see Experimental section). The observed dependence in acetonitrile of the proportion of the AM sulfide (E)-**7d** to the M sulfide (E)-**8d** upon hydrobromic acid concentration and reaction time remains unclear at this stage.

Table. Bromovinyl sulfides obtained from the reaction of NBSA with 48% hydrobromic acid (1.5 equiv.) in acetonitrile in the presence of the alkynes **6a-g** (5 equiv.)

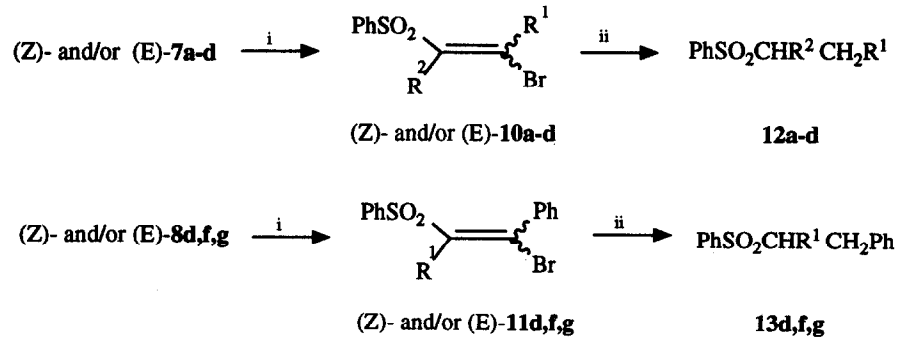
Entry	Alkyne	Bromovinyl sulfide	Yield, %[a]
1	Hex-1-yne **6a**	(E)- + (Z)-**7a**	50 [b]
2	Pent-1-yne **6b**	(E)- + (Z)-**7b**	50 [b]
3	tert-Butylacetylene **6c**	(E)-**7c**	60
4	Phenylacetylene **6d**	(E)-**7d** + (Z)-**8d**	55 [c]
5	Hex-3-yne **6e**	(E)-**7e**	86
6	1-Phenylpropyne **6f**	(E)- + (Z)-**8f**	84 [d]
7	1-Phenylbut-1-yne **6g**	(E)-**8g**	85

[a]Isolated yields based on starting NBSA. 4'-Nitroaniline (ca. 100%) and diphenyl disulfide(15-50%) were also generally isolated. The overall yield of diphenyl disulfide and bromovinyl sulfide product amounted in each case to ca. 100%. [b](E)/(Z) ratio of 90:10. [c](E)-**7d**/(E)-**8d** ratio of 55:45. [d](E)/(Z) ratio of 85:15.

Disubstituted acetylenes generally gave more satisfactory yields of bromovinyl sulfide products. The symmetrical dialkylacetylene **6e** afforded the exclusive (E)-sulfide (E)-**7e** in 86% yield (Table, entry 5). To a comparable extent, the alkylphenylacetylenes **6f,g** only gave the corresponding M adducts (E)-**8f**, which was mixed with some of its geometrical isomer, and (E)-**8g**, which was instead configurationally pure (Table, entries 6 and 7).

The regiochemistry of the bromo sulfides (Z)- and/or (E)-**7a-d, 8d,f,g** was determined through oxidation to the corresponding vinyl sulfones (Z)- and/or (E)-**10a-d, 11d,f,g** followed by reduction of these compounds to the alkyl sulfones **12a-d** and **13d,f,g**, which were readily identified on the basis of the alkyl NMR patterns. (Scheme 4). A similar method has been previously employed to establish the AM and M regiochemistry of chlorovinyl sulfide adducts.[11] The (E) configuration has been generally assigned to the primary addition products **7a-e** and **8d,f,g** on the assumption that the addition of benzenesulfenyl bromide **1** to acetylenes, analogously to that of sulfenyl chlorides, should involve initial formation of thiirenium-like intermediates and subsequent back-side attack of bromide at the thiirenium ring-carbons, which was actually substantiated by the generally observed stereospecificity. The (E)-configuration in the sulfides (E)-**7a,b,c,d** was also supported by our ^{1}H NMR spectral evidence that the chemical shift of their vinylic proton occurred

at remarkably higher field (ca. 1.4-1.7 ppm) than that of the vinylic proton in the corresponding (E)-sulfones (E)-**10a-d**. A similar vinylic shift, but comparatively much smaller (ca. 0.2 ppm), was observed on passing from the (Z)-sulfides (Z)-**7a,b,d** to the (Z)-sulfones (Z)-**10a,b,d**. Comparable spectral evidence has previously emerged from (E)- and (Z)-2-chloro-1-(4-chlorophenylthio)-1-phenylethene and their sulfonyl derivatives.[11]



Scheme 4. Reagents : i, m-chloroperbenzoic acid, chloroform ; ii, Et_3BHNa, THF.

The AM and M regiospecificity encountered in our additions of benzenesulfenyl bromide **1** to the alkylacetylenes **6a-c** and the alkylphenylacetylenes **6f,g** was consistent with the presumed involvement of thiirenium intermediates. Previous general evidence[1a,d,12]in fact suggests that steric rather than polar effects of thiirenium substituents should play a determining role in directing nucleophilic attack at either ring carbon atom, unless weak (and small) nucleophiles and/or polar (and protic) solvents are involved.[7] Accordingly, the reaction of sulfenyl chloride with terminal alkylacetylenes generally showed a marked tendency to afford AM adducts,[12] whereas with alkylphenylacetylenes it showed a gradual preference for M adducts with increasing size of the alkyl substituent.[13] Indeed, recent chemical evidence has been provided[14] that a phenyl substituent can make the adjacent thiirenium carbon less sterically hindered than an alkyl substituted one. Evidently, bromide bulkier than chloride could exhibit exclusive attack at the unsubstituted or phenyl-substituted thiirenium carbons at the expense of the alkyl-substituted ones.

This study therefore showed that the reaction of NBSA with hydrobromic acid can also be usefully employed for the trans-stereospecific and regiospecific synthesis of β-bromovinyl sulfides from simple alkynes. Our sulfenyl bromide **1** additions were shown to proceed satisfactorily with alkyl-, and particularly dialkyl- and alkylphenyl-acetylenes, but the concomitant occurrence of diphenyl disulfide was found to represent a general limitation, especially serious with the monosubstituted alkynes. On the other hand, diphenyl disulfide formation was never encountered in the corresponding additions to similarly substituted alkenes. Unfortunately, in the presence of more poorly nucleophilic alkynes, the unstable bromide **1** would generally suffer competing decomposition to diphenyl disulfide to an extent further increasing with further decreasing nucleophilic power of the alkyne itself. Indeed, we ascertained that, in the absence of any alkyne, the sulfenyl bromide **1** could undergo extensive decomposition to diphenyl disulfide under comparable conditions. This fact was clearly evidenced by the finding that the bromo sulfide adduct **5a** could be hardly produced in 5% yield (and diphenyl disulfide instead in ca. 95% yield) upon addition of excess 3,3-dimethylbut-1-ene to a mixture of NBSA and hydrobromic acid in acetonitrile which had previously been reacted for ca. 10 min. Nevertheless, it is possible that at least some of the generally observed diphenyl disulfide might have resulted from decomposition of the presumed 1-phenylthiirenium intermediates, which might have occurred to a certain degree in competition with nucleophilic trapping by bromide.

1-Phenylthiirenium ions have recently been shown[15] to exhibit a general tendency to suffer decomposition to diphenyl disulfide (and the appropriate alkyne) through a still unknown route whose feasibility appears to be strongly enhanced by a decrease in alkyl and/or phenyl substitution on the ring carbons. We could however obtain no conclusive evidence for possible involvement of a "thiirenium" route in the formation of diphenyl disulfide when we performed our usual reaction of NBSA with hydrobromic acid in acetonitrile in the presence of the parent alkyne **6h**. We expected that the possibly resulting parent 1-phenylthiirenium intermediate should be especially capable of affording diphenyl disulfide rather than being trapped by bromide. This reaction actually gave diphenyl disulfide as the almost exclusive product (96%) at the expense of the parent adduct **7h** (≤ 3%), but it concomitantly exhibited no appreciable enhancement of the rate of consumption of the intermediate bromide **1** with respect to the corresponding reaction carried out in the absence of any alkyne (vide supra), thereby suggesting that the bromide itself was probably almost incapable of adding to very poorly nucleophilic acetylene **6h**.

EXPERIMENTAL SECTION

4-Nitrobenzenesulfenanilide (NBSA) was prepared as previously reported[5]. Cyclohexene, trans-hex-3-ene, hex-1-ene, 3,3-dimethylbut-1-ene, the alkynes **1a-h**, 4-nitroaniline, and diphenyl disulfide were commercially available. Trans-2-(phenylthio)cyclohexanol **2b** and trans-1-(4-nitrophenylamino)-2-(phenylthio)cyclohexane **2c** were identified by spectral comparison with authentic specimens.[6] The known alkyl sulfones **12a**[16], **12b**[17], **12d**[18], **13d**[18], and **13g**[19] as well as the cyclohexyl sulfide **2a**[10] were identified by comparison of their physical and/or spectral data with those reported in the literature. Column chromatography was carried out on Merck silica gel (0.040--0.063 particle size) by gradual elution with light petroleum (b.p. 40-70 °C)-diethyl ether. ^{1}H NMR spectra were generally recorded at 200 MHz on a Varian Gemini 200 instrument for solutions in $CDCl_3$ with Me_4Si as internal standard. Mass spectra were determined by the electron impact method on a VG 7070 instrument. GC-MS analyses were performed on a C. Erba QMD 1000 instrument.

Reaction of NBSA with 48% Hydrobromic Acid in the Presence of Alkenes. (a) In chloroform. 48% Hydrobromic acid (1 cm^3, ca. 10 mmol) was added to a stirred to a solution of NBSA (246 mg, 1 mmol) and the appropriate alkene (cyclohexene, trans-hex-3-ene, hex-1-ene or 3,3-dimethylbut-1-ene)(2-5 mmol) in chloroform (10 cm^3) at room temperature. After ca. 3-4 min. the 4-nitroaniline hydrobromide which had precipitated was filtered off and the excess of hydrobromic acid was then separated from the filtrate by decantation. Subsequent evaporation of the excess of solvent and alkene gave the appropriate bromo sulfide adduct **2a**, **3**, **4a**, or **5a** in virtually quantitative yield. The following new sulfides were obtained as oily products : (i) *erythro-3-bromo-4-(phenylthio)hexane* **3**; δ_H(60 MHz) 0.95 (3H, t, J= 7 Hz), 1.1 (3H, t, J= 7 Hz), 1.5-2.3 (4H, m) 3.0-3.4 (1H, m), 3-9-4.3 (1H, m), 7.1-7.7 (5H, m) (Found: M$^+$, 272.0243. $C_{12}H_{17}BrS$ requires M, 272.0235); m/z 274, 272, 189, 188, 151, 123, 110, 109, and 83 (100); (ii) *1-bromo-2-(phenylthio)hexane* **4a**; δ_H 0.92 (3H, t, J= 7 Hz), 1.2-2.2 (6H, m), 3.2-3.35 (1H, m), 3.37 (1H, dd, J_1= J_2= 9.0 Hz), 3.62 (1H, dd, J_1= 9.0, J_2= 3.5 Hz), 7.1-7.5 (5H, m) (Found: M$^+$272.0240. $C_{12}H_{17}BrS$ requires M, 272.0235); m/z 274, 272, 193, 192, 149, 123, 110 (100) and 83; upon standing in chloroform at room temperature over ca. 24 h, this sulfide **4a** was converted into an inseparable mixture of **4a** and isomeric *2-bromo-1-(phenylthio)hexane* **4b** in ca. 15:85 ratio, as shown by ^{1}H NMR; δ_H 0.90 (3H, t, J= 7 Hz), 1.2-1.6 (4H, m) , 1.7.1.9 (1H, m), 2.0-2.2 (1H, m), 3.25 (1H, dd, J_1= 9, J_2= 13.5 Hz), 3.55 (1H, dd, J_1= 5, J_2= 13.5 Hz), 4.06 (1H, ten lines, dddd, J_1= J_2= 9, J_3= 5, J_4= 3.5 Hz), and 7.1-7.7 (5H, m); and (iii) *1-bromo-2-(phenylthio)-3,3-dimethylbutane* **5a**; δ_H 1.12 (9H, s), 3.22 (1H, dd, J_1= 4.8, J_2= 7.2 Hz), 3.51 (1H, dd, J_1= 7.2, J_2= 11 Hz), 3.83 (2H, dd, J_1= 4.8, J_2 = 11 Hz), 7.2-7.6 (5H, m) (Found: M$^+$ 272.0242. $C_{12}H_{17}BrS$ requires 272.0235); m/z 274, 272, 192, 177, 149, 135, 123 (100), 110, 109, and 83; upon standing in chloroform at room temperature over ca. 24 h, this sulfide **5a** was converted into an inseparable mixture of **5a** and isomeric *2-bromo-1-(phenylthio)-3,3-dimethylbutane* **5b** in ca. 15:85 ratio, as shown by ^{1}H NMR

spectroscopy; δ_H 0.97 (9H, s), 3.19 (1H, dd, J_1= 11, J_2= 14 Hz), 3.53 (1H, dd, J_1= 2.5, J_2= 14 Hz), 3.93 (1H, dd, J_1= 2.5, J_2= 11 Hz), 7.2-7.6 (5H, m).

(b) In acetonitrile. 48 % Hydrobromic acid (0.2 cm^3, ca. 2 mmol) was added to a solution of NBSA (246 mg, 1 mmol) and the appropriate alkene (cyclohexene, hex-1-ene or 3,3-dimethylbut-1-ene) (2-5 mmol) in acetonitrile (10 cm^3) at room temperature. The resulting mixture was stirred for ca. 4-5 min., after which was treated with 10% aqueous potassium carbonate. The organic layer was extracted with diethyl ether, the excess of solvent removed and the residue was chromatographed. In the case of cyclohexene chromatography gave (i) the sulfide adduct **2a** (10%); (ii) the cyclohexanol **2b** (30%); (iii) the amino sulfide **2c** (40%); and (iv) 4-nitroaniline (50%). In the case of hex-1-ene, chromatography gave (i) a mixture of the sulfide adducts **4a** and **4b** (60%); (ii) a rather complex mixture of unidentified products; and (iii) 4-nitroaniline. In the case of 3,3-dimethylbut-1-ene, chromatography gave (i) a mixture of the sulfide adducts **5a** and **5b** (95%) and (ii) 4-nitroaniline (90%).

In another experiment a stirred mixture of NBSA (1 mmol) and 48% hydrobromic acid (1.5 mmol) in acetonitrile (10 cm^3) was reacted for ca. 10 min. and then treated with excess 3,3-dimethylbut-1-ene (10 mmol). After usual work-up, the crude reaction mixture was directly subjected to GLC and GC-MS analyses to give the sulfide adduct **5a** (5%) and diphenyl disulfide (95%).

Reaction of NBSA with 48% Hydrobromic Acid in the Presence of Alkynes. General Procedure. 48% Hydrobromic acid (0.15 cm^3, 1.5 mmol) was added to a stirred solution of NBSA (246 mg, 1 mmol) and the appropriate alkyne **6a-h** (5 mmol; saturated solution in the case of acetylene **6h**) in acetonitrile (10 cm^3). The reaction mixture was stirred at room temperature for ca. 5 min (ca. 10 min in the case of acetylene **6h**) and then neutralized by treatment with 10% aqueous potassium carbonate. The organic layer was extracted with diethyl ether, the excess of solvent evaporated and the residue was chromatographed. Gradual elution with light petroleum-diethyl ether gave (i) variable amounts of diphenyl disulfide (15-50%); (ii) the appropriate (Z)- and/or (E)-bromovinyl sulfide(s) **7a-e** and **8d,f,g** (yields are given in the Table); and (iii) 4-nitroaniline (ca. 100%). In the case of acetylene **6h** the crude reaction mixture, after usual work-up, was directly analyzed by GLC and GC-MS to give (i) diphenyl disulfide (96%) and (ii) 1-bromo-2-(phenylthio)ethene **7h** (≤ 3%); m/z 214, 212 (M^+, 50), 135 (90), 134 (40), 109 (40), and 91 (100). Each reaction in the presence of alkyne **6a-g** furnished the appropriate new vinyl sulfide adducts **7** and/or **8** as follows:

(a) Reaction in the presence of Hex-1-yne 6a. Chromatography gave an inseparable mixture of (E)- and (Z)-*1-bromo-2-(phenylthio)hex-1-ene* **7a**, in ca. 90:10 ratio as shown by ^1H NMR spectroscopy; δ_H [(E)-isomer] 0.9 (3H, t, J = 7.5 Hz), 1.2-1.6 (4H, m), 2.35 (2H, t, J = 7.5 Hz), 6.25 (1H, s), and 7.2-7.5 (5H, m); m/z [(GC-MS); (E)-isomer] 272, 270 (M^+), 230, 228, 191, 149, 147, 135, 134, 110, and 109. δ_H [(Z)-isomer] 0.95 (3H, t, J = 7.5 Hz), 1.2-1.6 (4H, m), 2.65 (2H, t, J = 7.5 Hz). 6.53 (1H, s), and 7.2-7.4 (5H, m); m/z [(GC-MS); (Z)-isomer] 272, 270 (M^+), 229, 227, 190, 149, 148, 147, 110, 109, and 81. (Found: C, 53.55; H, 5.45; Br, 29.20; S, 12.00. $C_{12}H_{15}BrS$ requires C, 53.14; H, 5.57; Br, 29.46; and S, 11.82 %). Treatment of this mixture (1 mmol) with 48% hydrobromic acid (10 mmol) in acetonitrile (10 cm^3) at room temperature for 10 min and subsequent chromatographic separation gave (i) a mixture of the (E)- and (Z)-sulfide **7a** (65%) in ca. 25:75 ratio (^1H NMR); and (ii) an unresolved 60:40 mixture of two isomeric components (35%) which probably were the geometrical isomers of *1-bromo-2-(phenylthio)hex-2-ene* **9**, as suggested by ^1H NMR spectroscopy and GC-MS analysis; δ_H [(E)- or (Z)-isomer] 0.92 (3H, t, J = 7.5 Hz), 1.4-1.6 (2H, m), 2.35 (2h, dt, J_d=J_t= 7.5 Hz), 4.0 (2H, s), 5.7 (1H, t, J = 7.5 Hz) and 7.2-7.5 (5H, m); δ_H [(Z)- or (E)-isomer] 0.98 (3H, t, J 7.5 Hz), 1.4-1.6 (2H, m), 2.20 (2H, dt, J_d= J_t= 7.5 Hz), 4.0 (2H, s), 6.13 (1H, t, J = 7.5 Hz), and 7.2-7.5 (5H, m); the mass spectra of the two isomeric components were found to be virtually identical and showed peaks at m/z 272, 270 (M^+, 40), 242 (4), 191 (100), 162 (20), 161 (40), 149 (25), 135 (30), 110 (30), 109 (40), and 81 (100). When the title reaction was repeated in acetonitrile by using 1 cm^3 (ca. 10 mmol) of 48% hydrobromic acid, column chromatography, besides diphenyl disulfide and 4-nitroaniline, separated (i) a mixture of the (E)- and (Z)-sulfide **7a** (45%), in ca. 50:50 ratio (^1H NMR) and (ii) a 2:1 mixture of the likely geometrical isomers of the sulfide **9** (15%). When the title reaction was performed in

chloroform by using both 0.15 cm^3 (1.5 mmol) and 1 cm^3 (10 mmol) of 48% hydrobromic acid, direct GLC and GC-MS analyses of the ensuing reaction mixtures gave (i) diphenyl disulfide (55-57%) and (ii) the (E)-vinyl sulfide (E)-**7a** (40-42%).

(b) Reaction in the presence of Pent-1-yne 6b. Chromatography gave an inseparable mixture of (E)- and (Z)-*1-bromo-2-(phenylthio)pent-1-ene* **7b** in ca. 90:10 ratio, as shown by ^1H NMR spectroscopy; δ_H[(E)-isomer] 0.9 (3H, t, J = 7 Hz), 1.4-1.6 (2H, m), 2.35 (2H, t, J = 7.5 Hz), 6.25 (1H, s), and 7.1-7.4 (5H, m); m/z [(GC-MS); (E)-isomer] 258, 256 (M^+, 20), 177 (20), 147 (40), 135 (100),, and 109 (20). δ_H [(Z)-isomer] 0.9 (3H, t, J = 7 Hz), 1.4-1.6 (2H, m), 2.65 (2H, t, J = 7.5 Hz), 6.55 (1H, s), and 7.1-7.4 (5H, m); m/z [(GC-MS); (Z)-isomer] 258, 256 (M^+,50), 229, 227 (20), 177 (10), 148 (80), 147 (100), 135 (25), and 109 (50). (Found: C, 51.60; H, 5.15; Br, 30.65; S, 12.30. $C_{11}H_{13}BrS$ requires C, 51.37; H, 5.10; Br, 31.07; S, 12.46 %).

(c) Reaction in the presence of ter-Butylacetylene 6c. Chromatography gave *(E)-1-bromo-3,3-dimethyl-2-(phenylthio)but-1-ene* **7c**, m.p. 60-62 °C; δ_H 1.38 (9H, s), 6.40 (1H, s) and 7.30 (5H, m); m/z 272, 270, 175, 135, 134, 110, 109, 65, and 57. (Found: M^+ 270.0070. $C_{12}H_{15}BrS$ requires M, 270.0078).

(d) Reaction in the presence of Phenylacetylene 6d. Chromatography gave an inseparable mixture of (E)-β-*bromo*-α-*(phenylthio)styrene* (E)-**7d** and *(E)*-α-*bromo*-β-*(phenylthio)styrene* (E)-**8d**, in ratio of ca. 55:45 as shown by ^1H NMR spectroscopy; δ_H 6.60 [0.55 H, s, vinylic proton of (E)-**7d**], 6.90 [0.45 H, s, vinylic proton of (E)-**8d**], and 7.0-7.6 (10H, m); m/z [(GC-MS); (E)-**7d**] 292, 290 (M^+, 12), 212 (18), 211 (100), 210 (45), 178 (38), 109 (20), and 102 (60); m/z [(GC-MS); (E)-**8d**] 292, 290 (M^+, 60), 211 (70), 210 (30), 178 (100), 167 (20), 165 (25), 134 (30), 109 (60), and 102 (45). (Found: C, 57.40; H, 3.85; Br, 27.10; S, 11.15. $C_{14}H_{11}BrS$ requires C, 57.74; H, 3.81; Br, 27.44; S, 11.00 %). GLC analysis showed that the above ratio of the two isomeric adducts **7d** and **8d** remained virtually unchanged upon prolonging the reaction time for over 15 min. In such case, isomerization of (E)-**7d** to its geometrical isomer (Z)-**7d** (vide infra) was shown to occur, but to a very little extent (the observed (E)-**7d**/(Z)-**7d** ratio was 25:1). GLC analysis also revealed that the two isomeric sulfides (E)-**7d** and (E)-**8d** were produced in 30:70 ratio during the initial reaction stage (≤ 30 sec).

When the same reaction was carried out by using 1 cm^3 (ca. 10 mmol) of 48% hydrobromic acid, GLC analysis monitored the presence of (E)-**7d**, (Z)-**7d** and (E)-**8d** in 22:8:70 ratio and in 60% overall yield; the resulting (E)-**7d**/(Z)-**7d**/(E)-**8d** ratio was found to be essentially unaffected by the reaction time employed. Column chromatography of the reaction mixture allowed to isolate a fraction mainly constituted by the sulfide (Z)-**7d**; δ_H 6.70 (1H, s) and 7.0-7.6 (10H, m); m/z 292, 290 (M^+,), 211 (100), 178, 109, and 102.

When the reaction was carried out in chloroform or dioxane by using 0.15 cm^3 (ca. 0.15 mmol) and 1 cm^3 (ca. 10 mmol) of 48% hydrobromic acid, GLC analysis generally showed that the two sulfides (E)-**7d** and (E)-**8d**, exclusive of (Z)-**7d**, had occurred in ca. 60:40 ratio (in overall yields not determined).

(e) Reaction in the presence of Hex-3-yne 6e. Chromatography gave (E)-*3-bromo-4-(phenylthio)hex-3-ene* (E)-**7e** as an oily product; δ_H (60 MHz) 1.05 (3H, t, J = 7.3 Hz), 1.13 (3H, t, J = 7.3 Hz), 2.43 (2H, q, J = 7.3 Hz), 2.90 (2H, q, J = 7.3 Hz), and 7.3 (5H, m) (Found: M^+ 270.0085. $C_{12}H_{15}BrS$ requires M, 270.0078); m/z 272, 270, 191, 190, 175, 163, 149, 147, 135, 110, 109, 81, 79, 77, and 65.

(f) Reaction in the presence of 1-Phenylpropyne 6f. Chromatography gave an inseparable mixture of (E)- and (Z)-1-*bromo-1-phenyl-2-(phenylthio)propene* (E)- and (Z)-**8f**, in ratio 85:15, as shown by ^1H NMR spectroscopy; δ_H 1.68 [s, (Z)-isomer Me], 2.20 [s, (E)-isomer Me], and 7.0-7.5 (10H, m); these isomers could not be differentiated by GC-MS analysis, which monitored a sole peak showing ions at m/z 306, 304 (M^+, 40), 225 (50), 224 (20), 210 (100), 192 (20), 147 (30), 116 (20), and 115 (60). (Found: C, 59.30; H, 4.35; Br, 26.00; S, 10.40. $C_{15}H_{13}BrS$ requires C, 59.02; H, 4.29; Br, 26.18; S, 10.50 %).

(g) Reaction in the presence of 1-Phenylbut-1-yne 6g. Chromatography gave (E)-1-*bromo*-1-*phenyl*-2-*(phenylthio)but*-1-*ene* (E)-**8g**; m.p. 80-82 °C; δ_H(60 MHz) 1.33 (3H, t, J = 7 Hz), 2.92 (2H, q, J = 7 Hz), and 7.0-7.5 (10H, m) (Found: M^+ 318.0070; $C_{16}H_{15}BrS$ requires M, 318.0078); m/z 320, 318 (M^+, 25), 238 (15), 237 (15), 223 (40), 211 (100), 210 (40), 129 (80), 128 (60), and 115 (60).

Oxidation of the vinyl sulfides (Z)- and/or (E)-7a-d, 8d,f,g to the corresponding vinyl sulfones (Z)- and/or (E)-10a-d, 11d,f,g and their following reduction to the alkyl sulfones 12a-d, 13d,f,g. General Procedure. A solution of the appropriate title sulfide (either conformationally pure or as an isomeric mixture) (1 mmol) and m-chloroperbenzoic acid (2.2 mmol) in chloroform (20 cm^3) was allowed to stand at room temperature for 48 h. After such time, the reaction mixture was washed with 10% aqueous potassium carbonate, the organic layer separated and then evaporated. Flash chromatography of the resulting residue gave the corresponding (Z)- and/or (E)-vinyl sulfone in virtually quantitative yield. In each case a solution of the isolated (Z)- and/or (E)-vinyl sulfone (1 mmol) in anhydrous THF (10 cm^3) was treated with 1M solution of sodium triethylborohydride in THF (3 cm^3, 3 mmol) at room temperature. After ca. 5 min. the reaction mixture was washed with water, the organic layer separated and the solvent evaporated to give the appropriate alkyl sulfone **12a-d, 13d,f,g** in quantitative yield. All these eventual sulfones were directly analyzed by GC-MS and ^1H NMR without purification.

(a) Oxidation of the Vinyl Sulfides (E)- and (Z)-7a. The oxidation of a 90:10 mixture of the sulfides (E)- and (Z)-**7a** furnished (E)-*1-bromo-2-(benzenesulfonyl)hex-1-ene* (E)-**10a**, contaminated with some of its *geometrical isomer* (Z)-**10a**; δ_H 0.75 (3H, t, J = 7.5 Hz), 1.1-1.4 (4H, m), 2.3 (2H, t, J = 7.5 Hz), 7.4-7.6 (3H, m), 7.65 (1H, s), and 7.75-7.9 (2H, m); m/z 304, 302 (M^+, 4), 223 (30), 143 (100), 125 (45), and 77 (60). Oxidation of a corresponding 50:50 mixture gave an inseparable mixture of the isomeric sulfones (E)- and (Z)-**10a** in the same ratio, as shown by ^1H NMR spectroscopy; δ_H[(Z)-**10a**] 0.9 (3H, t, J = 7.5 Hz), 1.1-1.7 (4H, m), 3.0 (2H, t, J = 7.5 Hz), 6.72 (1H, s), 7.4-7.7 (3H, m), and 7.8-7.9 (2H, m); the mass spectrum of (Z)-**10a** was shown by GC-MS to be virtually identical to that of its isomer (E)-**10a**. (Found: C, 47.50; H, 4.95; Br, 26.10; S, 10.70. $C_{12}H_{15}BrO_2S$ requires C, 47.53; H, 4.98; Br, 26.35; S, 10.57 %). Reduction of this mixture gave phenyl 2-hexyl sulfone **12a**.

(b) Oxidation of the Vinyl Sulfides (E)- and (Z)-7b. The oxidation of a 70:30 mixture of the sulfides (E)- and (Z)-**7b** furnished an inseparable mixture of (E)-*1-bromo-2-(benzenesulfonyl)pent-1-ene* (E)-**10b** and its (Z)-*isomer* (Z)-**10b** in the same ratio, as shown by ^1H NMR spectroscopy; δ_H [(E)-**10b**] 0.85 (3H, t, J = 7 Hz), 1.2-1.7 (2H, m), 2.3 (2H, t, J = 7.5 Hz), 7.4-7.7 (3H, m), 7.70 (1H, s), and 7.8-7.9 (2H, m); m/z ((GC-MS); (E)-**10b**) 290, 288 (M^+, 2), 209 (6), 143 (100), 125 (70), 105 (80), and 77 (80). δ_H [(Z)-**10b**] 0.85 (3H, t, J = 7 Hz), 1.2-1.7 (2H, m), 3.0 (2H, t, J = 7,5 Hz), 6.75 (1H, s), 7.4-7.7 (3H, m), and 7.8-7.9 (2H. m); m/z [(GC-MS); (Z)-**10b**] 290, 288 (M^+, 1), 209 (10), 143 (90), 125 (50), and 77 (100) (Found: C, 45.85, H, 4.60; Br, 27.45; S, 11.09. $C_{11}H_{13}BrS$ requires C, 45.68, H, 4.53; Br, 27.63, S, 11.09 %). Reduction of this mixture gave phenyl 2-pentyl sulfone **12b**.

(c) Oxidation of the Vinyl Sulfide (E)-7c. The oxidation of the title sulfide gave (E)-*1-bromo-2-(benzenesulfonyl)- 3,3-dimethylbut-1-ene* (E)-**10c** as a thick oil; δ_H 1.32 (9H, s), 7.3-8.0 (5H, m), and 8.07 (1H, s); m/z 304, 302 (M^+, 3), 223 (10), 163 (100), 161 (100), 143 (30), and 125 (60) (Found: M^+ 301.9965. $C_{12}H_{15}BrO_2S$ requires M, 301.9976). Reduction of (E)-**10c** gave *phenyl 1,2,2-trymethylpropyl sulfone* **12c**; δ_H 1.15 (3H, d, J = 7 Hz), 1.22 (9H, s), 3.0 (1H, q, J = 7 Hz), 7.5-7.7 (3H, m), and 7.9 (2H, m) (Found: M^+ 226.1015. $C_{12}H_{18}O_2S$ requires M, 226.1027); m/z 226 (5), 170 (10), 143 (30), 85 (100), and 77 (30).

(d) Oxidation of the the Vinyl Sulfides (E)- and (Z)-7d, and (E)-8d. The oxidation of a 70:30 mixture of the sulfides (E)-**7d** and (E)-**8d** gave an unresolved mixture of (E)-β-*bromo*-α-*(benzenesulfonyl)styrene* (E)-**10d** and (E)-α-*bromo*-β-*(benzenesulfonyl)styrene* (E)-**11d** in the same ratio; δ_H 7.15 [0.3 H, s, vinylic proton of (E)-**11d**], 7.1-7.6 (10H, m), and 8.04 [0.7H, s, vinylic proton of (E)-**10d**]; m/z [(GC-MS), (E)-**10d**] 324, 322 (M^+, 4), 181 (45), 125 (25), 105 (35), 102 (100), and 77 (20); m/z [(GC-MS), (E)-**11d**] 324, 322 (M^+ 4), 197 (12), 179 (30), 178 (25), 169 (10), 141 (25), 125 (15), 118 (30), 105 (40), 102 (100), 89 (15), and 77 (80). (Found: C, 52.25; H, 3.50; Br, 24.80; S, 10.0. $C_{14}H_{11}BrO_2S$ requires C, 52.02; H, 3.43; Br, 24.72, S, 9.92 %). Reduction of this mixture furnished a ca. 70:30 mixture of phenyl 1-phenylethyl sulfone **12d** and phenyl 2-phenylethyl sulfone **13d**. The oxidation of a mixture of (E)-**8d**, (E)-**7d**, and (Z)-**7d** in ca. 10:10:80 ratio furnished a corresponding unresolved mixture of the sulfones (E)-**11d**, (E)-**10d**, and (Z)-**10d**. δ_H [(Z)-**10d**] 7.0 (1H, s) and 7.0-7.6 (10 H, m); m/z [(GC-MS), (Z)-**10d**] 324, 322 (M^+, 2), 243 (2), 182 (30), 181

(35), 125 (15), 105 (25), 102 (100), and 77 (25). Reduction of this mixture gave the sulfones **12d** and **13d** in about 90:10 ratio.

(e) Oxidation of the Vinyl Sulfides (E)- and (Z)-8f. The oxidation of a 85:15 mixture of the sulfides (E)- and (Z)-**8f** gave an unresolved mixture of (E)-1-*bromo-1-phenyl-2-(benzenesulfonyl)propene* (E)-**11f** and its (Z)-*isomer* (Z)-**11f** in about the same ratio; δ_H 2.10 [0.5 H, s, (z)-isomer Me], 2.45 [2.5H, s, (E)-isomer Me], and 7.0-8.3 (10H, m); GC-MS analysis revealed that the mass spectra of the two components were virtually identical and showed peaks at m/z 338, 336 (M^+, 5), 193 (30), 141 (10), 132 (15), 116 (40), 115 (100), 105 (40), and 77 (40) (Found: C, 53.20,; H 3.95; Br, 23.55; S, 9.60. $C_{15}H_{13}BrO_2S$ requires C, 53.42; H, 3.88; Br, 23.70; S, 9.50 %). Subsequent reduction furnished *phenyl 2-(1-phenylpropyl) sulfone* **13f**; δ_H 1.2 (3H, d, J = 7 Hz), 2.56 (1H, dd, J_1 = 13, J_2=10 Hz), 3.2-3.4 (1H, m), 3.46 (1H, dd, J_1= 13, J_2= 3 Hz), and 7.2-8.0 (10H, m); m/z (GC-MS) 260 (M^+, 1), 119 (15), 118 (90), 117 (20), 91 (100), and 77 (15).

(f) Oxidation of the Vinyl Sulfide (E)-8g. The oxidation of the title sulfide gave (E)-*1-bromo-1-phenyl-2-(benzenesulfonyl)- but-1-ene* (E)-**11g**, m.p. 80-82 °C; δ_H (60 MHz) 1.33 (3H, t, J = 7 Hz), 2.92 (2H, q, J = 7 Hz), and 7.0-7.7 (10H, m) (Found: M^+ 349.9970. $C_{16}H_{15}BrO_2S$ requires M, 349.9976); m/z 352, 350(10), 271 (10), 207 (30), 146 (20), 130 (40), 129 (100), 115 (80), 105 (40), and 77 (50). Subsequent reduction of this sulfone (E)-**11g** gave phenyl 2-(1-phenylbutyl) sulfone **13g**; δ_H 0.92 (3H, t, J = 7 Hz), 1.6-2.0 (2H, m), 2.76 (1H, dd, J_1= 12, J_2= 6 Hz), 3.18-3.30 (1H, m), 3.32 (1H, dd, J_1=12, J_2= 2 Hz), and 7.2-8.0 (10H, m).

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