Pergamon

Tetrahedron Vol. 50, No. 43, pp. 12395-12406, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00783-7

Reaction of 4'-Nitrobenzenesulfenanilide (NBSA) with Lewis acids. A Study of its Application in Sulfenocyclization of Alkenes and Alkynes

Luisa Benati, Laura Capella, Pier Carlo Montevecchi* and Piero Spagnolo

Dipartimento di Chimica Organica "A. Mangini", Viale Risorgimento 4, I-40136 Bologna, Italy

Abstract. Phenylsulfenocyclization of a number of alkenes and alkynes possessing internal hydroxyl, carboxyl or vinyl functionality has been investigated with NBSA. Thioetherification of 4-penten-1-ol **4** as well as thiolactonization of 4-penten-1-oic acid **7** and, to a modest extent, 4-pentyn-1-oic acid **8** can be successfully achieved with NBSA in the presence of boron trifluoride. On the other hand, under analogous conditions 3-buten-1-ol **3** and 3-buten-1-oic acid **6** fail to undergo thiocyclization and give instead oxa- and/or aza-sulfenylation 1,2-adducts. Similar failure is observed with 4-pentyn-1-ol **5**, in which case diphenyl disulfide and 4-nitroaniline are the exclusive products. Hexa-1,5-diene **9**, to some extent, affords a cyclized arylaminosulfide, i.e. **23**, ascribable to formal loss of a methylene unit from the initial (phenylthiomethyl)- cyclopentyl cation **24**. The reaction products are discussed in terms of intermediate thiiranium and thiirenium ions whose decomposition mode is strictly dependent upon their structural features. Novel evidence is also presented that aluminium chloride and bromide can promote reaction of NBSA with alkenes and alkynes to afford chloro- and bromo-sulfenylation adducts in varying yields.

In a number of previous papers we have shown that boron trifluoride transforms 4'-nitrobenzenesulfenanilide (NBSA), a readily available and quite stable compound, into a reactive electrophilic species capable of transferring the phenylthio moiety to various nucleophiles, including simple alkynes and alkenes.[1] Recent spectral and chemical evidence suggests that an anilide radical cation (NBSA$^{\cdot+}$), occurring through mono-electron transfer from NBSA to the Lewis acid, is the likely sulfenylating agent.[2] The BF_3-promoted reaction of NBSA with alkenes and alkynes results in the intermediacy of thiiranium and thiirenium ions, respectively. Thiiranium ions, in non nucleophilic solvents, can be efficiently trapped by the tetraborate counterion ($ArNHBF_3^-$) to give β-(4-nitrophenylamino)alkyl sulfides[1b], whereas in acetonitrile and benzonitrile they preferentially react with the poorly nucleophilic solvent to eventually afford β-amidino- and/or β-amido-akyl sulfides.[1c,d] Thiirenium ions generally failed to undergo counterion attack at the ring carbons, but reacted with smaller (though weaker) nucleophiles such as acetonitrile,[1f] acetic acid[1h] and a fluoroborate fluorine atom[1i] to give the corresponding vinyl sulfides with *trans*-stereospecificity and high regioselectivity (Markovnikov orientation). In all the investigated NBSA additions to alkenes and alkynes varying amounts of diphenyl disulfide **1** (and aniline **2**) were found. Their formation was initially claimed to result from self-reaction of NBSA. More recent studies have uncovered that 1-phenylthiirenium ions can also lead to the compound **1** (and the suitable alkyne) through a still unknown route, whose feasibility is strongly enhanced by a decrease in alkyl and phenyl substitution on the ring carbons.[1j]

However, despite numerous efforts to investigate mechanistic and synthetic aspects of the 1,2-difunctionalization of π-nucleophiles with NBSA, we made no attempts to exploit this reagent in cyclofunctionalization. In recent years sulfenium ion-induced cyclofunctionalization using various sulfenyl derivatives, especially sulfenyl chlorides and alkylthiosulfonium salts, has been shown to be an important synthetic method since the sulfenyl group introduced simultaneously with cyclization can be easily manipulated.[3] A large variety of alkenes, bearing internal nucleophilic centres such as oxygen, sulfur, nitrogen, and carbon, and a much lesser number of alkynes, mostly bearing a carboxyl or amido function, have been investigated for these thio-cyclizations.

On this basis we undertook a study of the BF_3/NBSA-mediated cyclofunctionalization of unsaturated substrates, including the alcohols **3-5** and carboxylic acids **6-8** as well as hexa-1,5-diene **9**. 3-Buten-1-ol **3** and 3-buten-1-oic acid **6** were chosen as models for alkene substrates which might undergo 5-*endo* cyclization; the *exo*-cyclization predicted by Baldwin's rules[4] should be discouraged by ring strain of the possible four-membered product. Phenylsulfenoetherification of alkenol **3**, previously investigated with N-(phenylthio)-morpholine in the presence of trimethylsilyl trifluoromethanesulfonate, had in fact been shown to occur only to a moderate extent in a 5-*endo* fashion exclusively.[5] The 4-penten-1-ol **4**, the 4-penten-1-oic acid **7** and the diene **9** were considered representative examples of alkenes which can favorably satisfy Baldwin's rules for 5-*exo* ring closure. Successful sulfenocyclization of the alkenoic acid **7**[6] and the alkenol **4**[5,6,7] had actually been achieved with various sulfenylating agents. Finally, 4-pentyn-1-ol **5** and 4-pentyn-1-oic acid **8** were chosen as alkyne substrates which might similarly undergo 5-*exo* cyclization. Phenylsulfeno-5-*exo*-lactonization of the alkynoic acid **8** had been accomplished, though in a modest yield, with benzenesulfenyl chloride in the presence of base,[8] whereas to our knowledge sulfenocyclization of the alkynol **5** (and, generally, of alkynols) is to date unexplored.

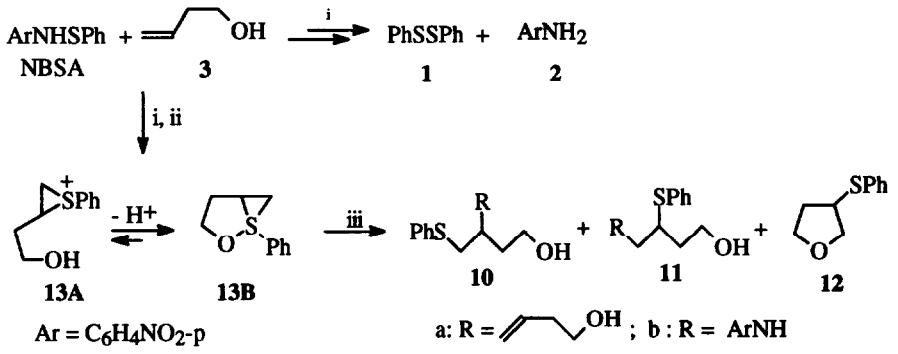
In this paper we report the results of this study as well as of a related study of NBSA reactions promoted by aluminium chloride and bromide. At the outset of this work the chemical reactivity of NBSA with Lewis acids other than boron trifluoride was pratically unexplored.[2]

RESULTS AND DISCUSSION

The BF_3-promoted reactions were carried out by reacting at room temperature NBSA (1 mmol) with boron trifluoride-diethyl ether (1.5 molar equiv) in benzene or acetonitrile (10 mL) containing a five-fold excess of the unsaturated substrate **3-9**. Complete reaction usually occurred within 30 min. The resulting reaction mixture was hydrolyzed with aqueous sodium carbonate and the products were isolated by column chromatography.

The reaction of NBSA with the butenol **3** in benzene mainly gave, in addition to the aniline **2** and small amounts of diphenyl disulfide **1**, an isomeric 1:1 mixture of the Markovnikov and anti-Markovnikov alkoxysulfides **10a** and **11a** (66%) together with minor amounts of the corresponding arylaminosulfides **10b** and **11b** (25%) (Scheme 1) The occurrence of the adducts **10a** and **11a** was totally suppressed when NBSA was reacted in the presence of equimolar amounts of the substrate **3**. Under these circumstances the aminosulfides **10b** and **11b** as well as the sulfenocyclization product **12**, but to a little extent, were the only identifiable products (Scheme 1). The isomeric sulfides **10b** and **11b**, accompanied by major amounts of the disulfide **1** and an unknown compound which had molecular formula $C_{20}H_{26}O_3S_2$, were the only identifiable products from the same reaction carried out in acetonitrile (Scheme 1). No evidence for any products

ascribable to trapping of a possible thiiranium ion **13A** by the acetonitrile solvent[1c,d] could be obtained, despite the fact that in such solvent NBSA and the butenol **3** were allowed to react at very low concentrations (see Experimental Section).



Scheme 1. *Reagents*: i, $BF_3.Et_2O$, benzene or acetonitrile; ii, - $ArNHBF_3^-$; iii, **3** and /or **2**

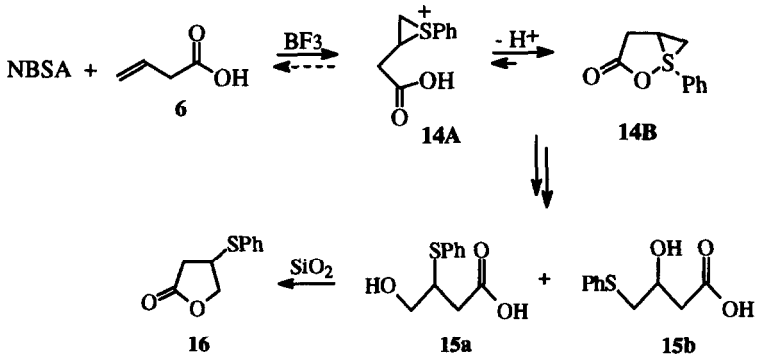
These findings are better explained by postulating that bicyclic sulfurane **13B**, rather than thiiranium ion **13A**, should be primarily involved in the reaction of NBSA with the alkenol **3**. The sulfurane **13B**, comparatively less electrophilic than the corresponding ion **13A**, would promptly react with the modest oxygen and nitrogen nucleophiles present, but would be totally unreactive towards poorly nucleophilic acetonitrile.

Related cyclic sulfuranes have often been invoked as the intermediates in the Ad_E reactions of sulfenyl halides with alkenes, though solid evidence for their possible involvement has never been offered.[3] In our case the intermediate **13B** might readily result from kinetically preferred attack of the internal nucleophile at the sulfonium sulfur of initially formed thiiranium ion **13A** (Scheme 1). Interestingly, the isolated 1:1 mixture of the aminosulfides **10b** and **11b**, upon brief heating in benzene at 100 °C in the presence of a slight excess of boron trifluoride, furnished the cyclized product **12** in high yield (90%). Under these conditions both sulphide adducts **10b** and **11b** could give back the thiiranium ion **13A**,[1d] which could then undergo smooth 5-*endo* cyclization to the thermodinamically stable product **12**.

With the butenoic acid **6** NBSA led in benzene to an inseparable 1:1 mixture of the regioisomeric hydroxysulfides **15a** and **15b** and provided no evidence for any sulfenocyclization product (Scheme 2). The mixture of the two isomers **15a,b** could be isolated by rapid flash chromatography. Usual silica gel chromatography gave instead the butyrolactone **16** (35%) and the isomers **15a** and **15b** in ca. 1:4 ratio (55%), thereby indicating that silica gel can promote intramolecular esterification of the hydroxy acid **15a** (Scheme 2). Comparable findings were provided by the corresponding reaction in acetonitrile, in which case no product arising from incorporation of the solvent could be observed. It is possible that also with the alkenoic acid **6** the total lack of any sulfenocyclization reaction and, especially, of any reaction with acetonitrile be a result of preferential occurrence of sulfurane **14B** rather than thiirenium **14A** intermediates (Scheme 2). The sulfides **15a,b** were presumably produced by hydrolysis of the sulfurane **14B** or its further reaction products (acyloxy- and/or amino- sulfides) during aqueous work-up.

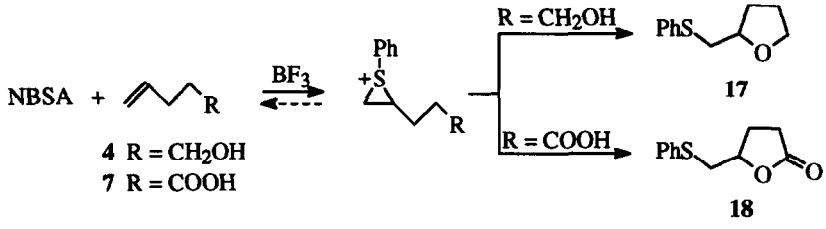
In contrast with the alkenes **3** and **6**, their homologous **4** and **7** gave the desired cyclization products **17** and **18** in high yield (85-90%) upon reaction with NBSA both in benzene and acetonitrile (Scheme 3). In such

cases the corresponding thiiranium ions would undergo smooth 5-*exo* cyclization, in agreement with similar earlier evidence.[5-7]



Scheme 2

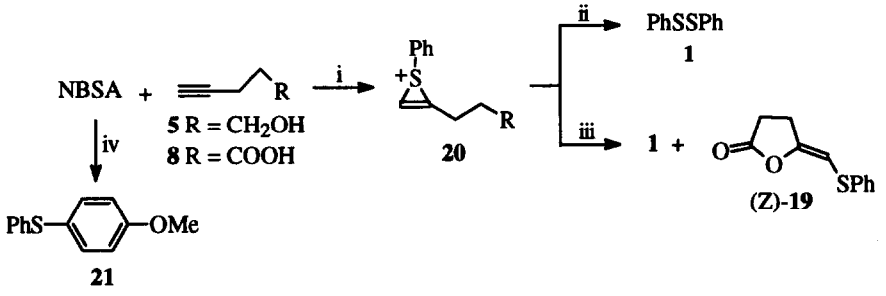
Similarly to its alkene counterpart, the pentynoic acid **8** reacted in benzene to give the (Z)-butyrolactone (Z)-**19**, though to a much lesser extent (Scheme 4). The (Z)-lactone (Z)-**19** presumably arose from isomerization of the initially formed (E)-isomer under the acid reaction conditions. The (E)-lactone (E)-**19** was exclusively produced by cyclization of alkyne **8** with PhSCl and base.[8] Compound **1** probably arose from decomposition[1J] of the intermediate 1-phenylthiirenium ion **20A** (R=COOH) occurring in competition with 5-*exo* cyclization to **19**.



Scheme 3

Frustrating results were obtained when NBSA was allowed to react in the presence of the pentynol **5** in benzene, 9:1 benzene/acetic acid or acetonitrile since these reactions exclusively led to the disulfide **1** (besides the amine **2**) (Scheme 4). The total lack of phenyl benzenethiosulfonate in benzene/acetic acid and acetonitrile clearly proved that the disulfide **1** had actually resulted from smooth reaction of NBSA with the alkynol **5**. In the absence of π-nucleophiles NBSA had been previously shown to react with these solvents to give anequimolar mixture of phenyl benzenethiosulfonate and the disulfide **1** in virtually quantitative yield.[1j] Further support came from the same reaction carried out in anisole. In such aromatic solvent also the disulfide **1** was largely produced, whereas the expected sulfide **21** only occurred to a modest extent (Scheme 4). In contrast, in neat anisole NBSA is known to lead almost exclusively to the aromatic sulfenylation product **21**.[1j]

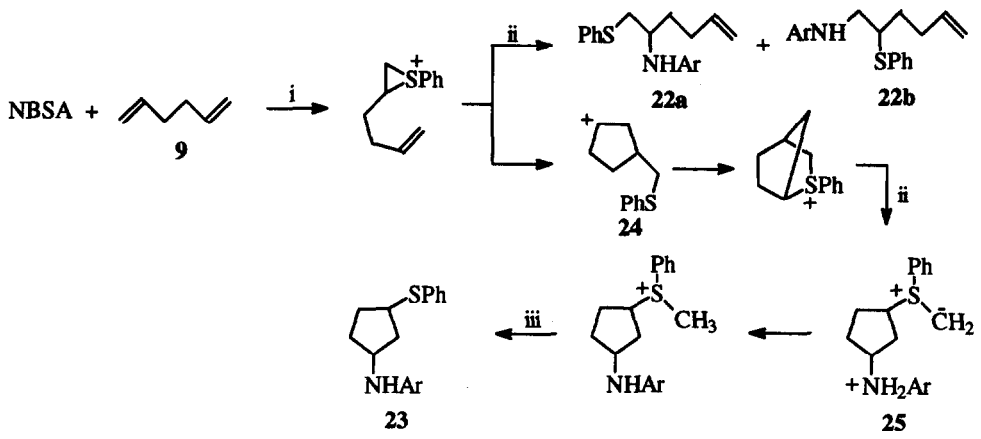
On the assumption that the reaction of NBSA with the alkyne **5** might result in the intermediacy of the thiirenium ion **20** (R=CH_2OH), it should be inferred that the hydroxyl substituent would strongly encourage decomposition to the disulfide **1** and, consequently, would totally discourage its capture by the internal nucleophile itself and/or by the acetonitrile[1f] and acetic acid[1h] solvents. However, a possible explanation of this fact would be only tentative at this stage, since no similar precedent seems to be available and, additionally, the route leading to the disulfide **1** from 1-phenylthiirenium ions is still unclear.[1j]



Scheme 4. *Reagents*: i, BF_3·Et_2O; ii, (**20** R = CH_2OH), benzene, acetonitrile, acetic acid or anisole; iii, (**20** R = COOH) benzene; iv, BF_3·Et_2O, anisole.

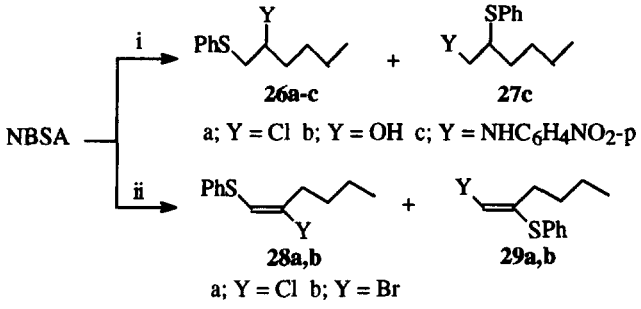
The reaction of hexa-1,5-diene **9** with NBSA in benzene provided only indirect evidence for some 5-*exo* cyclization of an intermediate thiiranium ion. This reaction gave, besides an isomeric mixture of the aminosulfides **22a** and **22b** (30%), minor amounts of the cyclized sulfide **23**, which probably arose from the initial cyclized cation **24** through the interesting sequence outlined in Scheme 5. This involves intramolecular trapping by the adjacent sulfur substituent and subsequent attack of anilino nucleophile which results in displacement of the internal ylide **25**. Protonation of ylide carbon followed by demethylation of ensuing sulfonium sulfur eventually affords the compound **23**.

In the light of our unsuccessful (and somewhat surprising) results obtained with the butenol **3**, butenoic acid **6** and especially pentynol **5**, we attempted their sulfenocyclization with NBSA by using aluminium halides in place of boron trifluoride. As mentioned above, the chemical reactivity of NBSA with Lewis acids other than boron trifluoride was virtually unknown, but there was some previous evidence indicating that aluminium chloride might behave similarly to boron trifluoride.[2] Initially we performed a brief investigation of the reaction of NBSA with aluminium chloride and bromide in benzene both in the absence and in the presence of hex-1-yne or hex-1-ene. Analogously to boron trifluoride, these halides were found to bring about rapid and virtually quantitative conversion of NBSA to the disulfide **1** and 4-nitroaniline **2**. Aluminium chloride reacted with NBSA in the presence of hex-1-ene to afford major amounts of the chlorosulfide (M)-adduct **26a** (43%) and its presumable hydrolytic product **26b** (19%) together with minor amounts (35%) of the aminosulfides **26c** and **27c** (in a ca. 1:1 ratio) (Scheme 6). Moreover, both aluminium chloride and bromide reacted with NBSA in the presence of hex-1-yne to give moderate yields of the (E)-chlorovinyl sulfides **28a** and **29a** (in 80:20 ratio) and (E)-bromovinyl sulfides **28b** and **29b** (in 1:1 ratio) (Scheme 7). In both cases no evidence for any aminovinyl sulfide adduct was provided. The above results clearly proved that $AlCl_3$ and $AlBr_3$ can behave similarly to BF_3 in promoting the addition of NBSA to alkenes and alkynes to afford thiiranium and thiirenium intermediates.



Scheme 5. *Reagents*: i, BF_3·Et_2O, benzene; ii, $ArNH_2$; iii, - Me.

The presumably resulting $ArNHAlX_3^-$ (X=Cl, Br) counterions, similarly to their $ArNHBF_3^-$ counterpart, appear to be capable of donating their bulky arylamino nitrogen to the thiiranium ring carbons, but not to the thiirenium ones. They can also transfer halide ion to both thiiranium and thiirenium rings; in contrast, $ArNHBF_3^-$ can only exhibit a similar behaviour towards thiirenium ions, but to a limited extent.[1g,i]



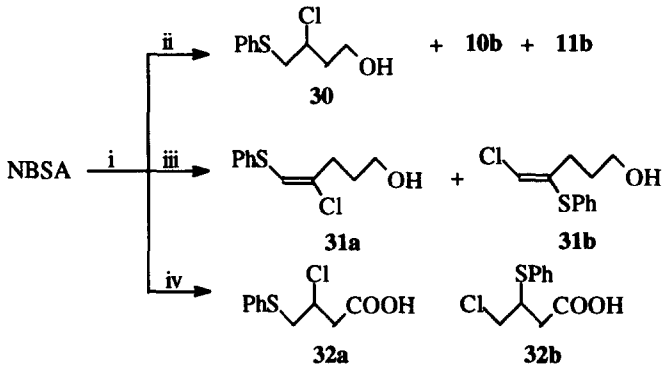
Scheme 6. *Reagents*: i, hex-1-ene, $AlCl_3$, benzene; ii, hex-1-yne, $AlCl_3$ or $AlBr_3$, benzene

The regiochemistry of the alkyl sulfides **26a,b** and of the vinyl sulfides **28a,b** was rather unusual for thiiranium and thiirenium ions. These ionic intermediates are known to react with bulky and (fairly) strong nucleophiles with preferential (or exclusive) anti-Markovnikov ring opening. However, the observed distribution of our adducts does not reflect the actual stereochemical outcome. In fact, control experiments clearly uncovered significant occurrence of AM ⟶ M isomerization under the experimental conditions.

Incidentally, NBSA also reacted in benzene with aluminium iodide to give cleanly the disulfide **1** (and the aniline **2**), but the same reaction in the presence of hex-1-yne failed to give any iodovinyl sulfide adduct. The compounds **1** and **2** were instead produced with concomitant formation of iodine. Under these circumstances,

the disulfide **1** and iodine were possibly formed through ready decomposition of benzenesulfenyl iodide[3,9] which might have resulted from iodide attack at the sulfonium sulfur of initially formed thiirenium ion.

Our subsequent efforts to achieve cyclization of the alkenes **3** and **6** and the alkyne **5** by using $AlBr_3$ and/or $AlCl_3$ as the acid promoter were unrewarding. In the presence of aluminium chloride the compounds **3**, **5** and **6** reacted with NBSA to give exclusively, besides the disulfide **1**, arylaminosulfide (**10b**, **11b**) and/or chlorosulfide adducts (**30**, **31a,b**, **32a,b**) in varying yields (Scheme 7). Similarly, the pentynol **5**, in the presence of $AlBr_3$, gave the disulfide **1** together with minor amounts of a bromovinyl sulfide product whose structure was not identified.



Scheme 7. *Reagents*: i, $AlCl_3$, benzene; ii, 3-buten-1-ol **3**; iii, 4-pentyn-1-ol **5**; iv, 3-buten-1-oic acid **6**.

In conclusion, the present work has shown that the BF_3-promoted reaction of NBSA with appropriate alkenes and alkynes can usefully result in sulfenocyclization, thus offering a new method alternative to those already available in the literature. We have also uncovered some interesting aspects with the alkenes **3** and **6**, the alkynol **5** and the diene **9**. The butenol **3** and the butenoic acid **6** essentially fail to undergo thiocyclization probably because their produced thiiranium ions prefer to be attacked by the internal nucleophile at the sulfonium sulfur rather than at either ring carbon. The pentynol **5** affords only diphenyl disulfide **1** as result of a peculiar reactivity of the corresponding thiirenium ion. The diene **9** gives the cyclized arylaminosulfide **23** formally ascribable to interesting extrusion of a methylene unit from initial 3-(phenylthiomethyl)ciclopentyl cation **24**. Finally, this work has additionally disclosed that the reaction of NBSA with aluminium chloride and bromide can be synthetically employed for halosulfenylation of alkenes and, especially, alkynes.

EXPERIMENTAL SECTION

All the alkenes and alkynes employed were commercially available. NBSA was prepared as previously reported.[1a] Separated reaction products such as the disulfide **1**, the aniline **2**, the cyclic ethers **12**[5] and **17**,[5] the sulfide **21**[10] and the adducts **26b**[1b], **26c**[1b], **27c**[1b] were identified by spectral comparison with authentic specimens. Structural assignment of hitherto unknown reaction products was made on the basis of spectral data; their homogeneity was ascertained by TLC and ^1H NMR.

^1H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) instrument and are for $CDCl_3$ solutions

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. 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.

Reactions of NBSA with Alkenes and Alkynes Promoted by Lewis Acids. General Procedure. To a stirred solution of NBSA (492 mg, 2 mmol) and the appropriate substrate (hex-1-ene, hex-1-yne, alcohols **3-5**, acids **6-8** or hexadiene **9**) (10 mmol) in benzene (unless otherwise stated) (20 mL) was added at room temperature the Lewis acid [boron trifluoride etherate containing ca. 47% BF_3 (0.37 mL, 3 mmol) or the appropriate aluminium halide (chloride, bromide or iodide) (ca. 0.5-0.7 g)]. The resulting mixture was stirred for ca. 30 min and then neutralized with 10% aqueous sodium carbonate. The organic layer was extracted with diethyl ether and the excess solvent evaporated. The residue was separated by column chromatography.

BF_3-Promoted Reaction with But-3-en-1-ol (3). Chromatography gave *3-(3-butenoxy)-4-(phenylthio)butanol* **10a** (33%) [oil; ^1H NMR δ_H 1.65-2.0 (2H, m), 2.28 (2H, dtt, $J_d = J_{t1} = 6.5$ Hz, $J_{t2} = 1.2$ Hz), 2.45 (1H, br s, OH), 2.96 (1H, A part of an ABX system, $J_{AB} = 13$ Hz, $J_{AX} = 7.5$ Hz), 3.18 (1H, B part of an ABX system, $J_{AB} = 13$ Hz, $J_{BX} = 4.7$ Hz), 3.41 (1H, dt, $J_d = 9$ Hz, $J_t = 6.7$ Hz), 3.6-3.8 (4H. m), 5.0-5.15 (2H, m), 5.76 (1H, ddt, $J_{d1} = 10$ Hz, $J_{d2} = 17$ Hz, $J_t = 6.5$ Hz, 7.1-7.4 (5H ,m); MS m/z 252 (M^+, 10), 198 (20), 55 (100); IR ν_{max} = 3510 (br.), 3414 (sh.). Found: M^+ 252.1178; $C_{14}H_{20}O_2S$ requires M, 252.1184], *4-(3-butenoxy)-3-(phenylthio)butan-1-ol* **11a** (33%) [oil; ^1H NMR δ_H 1.8-2.1 (2H, m), 2.30 (2H, ddt, $J_{d1} = J_t = 6.7$ Hz, $J_{d2} = 1.3$ Hz), 2.5 (1H, br s), 3.3-3.7 (5H, m), 3.75-3.85 (2H, m), 4.88-5.14 (2H, m), 5.77 (1H, ddt, $J_{d1} = 17$ Hz, $J_{d2} = 10$ Hz, $J_t = 6.7$ Hz), 7.2-7.5 (5H,m); MS m/z 252 (M^+, 10), 198 (50), 181 (20), 167 (40), 137 (70), 55 (100); IR ν_{max} 3425 (br). Found: M^+ 252.1190; $C_{14}H_{20}O_2S$ requires M, 252.1184], 4-nitroaniline **2** (28%), a 50:50 inseparable mixture of *3-(4-nitrophenylamino)-4-(phenylthio)-butan-1-ol* **10b** and *4-(4-nitrophenylamino)-3-(phenylthio)butan-1-ol* **11b** (25%) [^1H NMR δ_H (**10b**) 1.8-2.0 (2H, m), 3.15 (2H, ABX system, $J_{AB} = 13$Hz, $J_{AX} = 6$ Hz, $J_{BX} = 4.5$ Hz, $\delta_A = 3.12$, $\delta_B = 3.15$), 3.5-3.6 (1H, m), 3.83 (2H, br t), 4.9 (1H, br d, NH), 6.35 (2H, d, J = 9 Hz), 7.2-7.5 (5H, m), 8.0 (2H, d, J = 9 Hz); δ_H (**11b**) 1.8-2.0 (2H, m), 3.25-3.4 (1H, m), 3.4-3.5 (2H, m), 3.9 (2H,br t), 5.1 (1H, br s), 6.5 (2H, d, J = 8.5 Hz), 7.2-7.5 (5H, m), 8.05 (2H, d, J = 8.5 Hz); MS m/z 318 (M^+, 15), 195 (100), 168 (30), 151 (30); IR $\nu_{MA\Xi}$ 3615, 3410 (br). Found: M^+ 318.1030; $C_{16}H_{18}N_2O_3S$ requires M, 318.1038] and an unidentified product A (40 mg, 5%).

The same reaction carried out by using 1 molar equiv. of the butenol **3** gave the disulfide **1** (10%), 3-(phenylthio)tetrahydrofuran **12** (10%), the aniline **2** (60%) and a 50:50 mixture of the amino sulfides **10b** and **11b** (30%). A solution of this mixture (160 mg, 0.5 mmol) in benzene (5 mL) containing boron trifluoride etherate (0.12 mL, ca. 1 mmol) was heated in a sealed tube at 90 °C for 1h. The reaction mixture was neutralized with aqueous sodium carbonate and extracted with diethyl ether. Work-up and column chromatography of the residue gave 3-(phenylthio)tetrahydrofuran **12** (90%) besides the aniline **2** and an unidentified product [m/z 108 (M^+)].

The same reaction with butenol **3** was carried out in acetonitrile by adding with a syringe pump 5 mL of a 0.4 M solution of NBSA and 5 mL of a 2 M solution of **3** to a solution of $BF_3 \cdot Et_2O$ (0.37 mL, 3 mmol) in 20 mL of the solvent within 3 h. The mixture was stirred for further 30 min; subsequent work-up and chromatography gave the disulfide **1** (25%), the aniline **2** (70%), a mixture of the amino sulfides **10b** and **11b** (20%) and an unidentified product A (230 mg, 30%) [^1H NMR δ_H 1.6-1.9 (4H, m), 2.8-3.2 (6H, m), 3.5-4.0

(6H, m), 7.0-7.7 (10H, m); MS m/z 378 (M^+, 15) ($C_{20}H_{26}O_3S_2$ requires M, 378), 198 (10), 181 (100), 162 (15), 135 (15), 123 (30), 109 (20)]

BF_3-Promoted Reaction with Pent-4-en-1-ol (4). Chromatography gave 2-[(phenylthio)methyl]tetrahydrofuran **17** (85%) and aniline **2** (90%) as the only identifiable products. Same results were obtained from analogous reaction in acetonitrile.

BF_3-Promoted Reaction with Pent-4-yn-1-ol (5). Chromatography gave diphenyl disulfide **1** (90%) and 4-nitroaniline **2** (90%) as the only identifiable products. Same results were obtained when this reaction was performed in acetonitrile or in a 9:1 benzene/acetic acid mixture. This reaction, carried out in anisole, gave the disulfide **1** and 4-methoxyphenyl phenyl sulfide **21** in 70:30 ratio and 95% overall yield (GLC analysis) besides the aniline **2**.

BF_3-Promoted Reaction with But-3-en-1-oic acid (6). The reaction mixture was hydrolized with water and then subjected to usual work-up. Chromatography gave β-(phenylthio)butyrolactone **16** (35%), the aniline **2** (95%) and a ca. 4:1 mixture of *3-hydroxy-4-(phenylthio)butanoic acid* **15b** and *4-hydroxy-3-(phenylthio)-butanoic acid* **15a** (55% overall yield) [^1H NMR δ_H 2.5-2.8 (2.0H, m), 3.0-3.2 (1.6H, m), 3.5-3.75 (0.6H, m), 4.1-4.3 (0.8H, m), 6.1-6.6 (2.5H, br s), 7.2-7.6 (6H, m); MS m/z 212 (M^+, 60), 194 (30), 124 (100) 123 (80), 110 (30), 109 (25). Found: M^+ 212.0502. $C_{10}H_{12}O_3S_2$ requires M, 212.0507]. In a repeated experiment the reaction mixture was hydrolized with aqueous sodium carbonate. TLC of the organic layer showed exclusive presence of the aniline **2**, which was isolated in ca. 100% yield. The aqueous layer was neutralized with 1M HCl, extracted with ether and the excess solvent evaporated. The residue was subjected to rapid flash cromatography on a 15 cm column to give the lactone **16** in trace amounts (TLC) and a ca. 1:1 mixture of the butanoic acids **15a** and **15b** (85% overall yield).

BF_3-Promoted Reaction with Pent-4-en-1-oic acid (7). Chromatography gave γ *-[(phenylthio)methyl]-butyrolactone* **18** (92%) [^1H NMR δ_H 1.9-2.1 (1H, m), 2.2-2.45 (1H, m), 2.45-2.60 (2H, m), 3.03 (1H, A part of an ABX system, J_{AB} = 13.8 Hz, J_{AX} = 7.8, collapsing to A part of an AB system upon irradiation at δ 4.6), 3.34 (1H, B part of an ABX system, J_{AB} = 13.8 Hz, J_{BX} = 5.0 Hz, collapsing to B part of an ABX system upon irradiation at δ 4.6), 4.5-4.7 (1H, m), 7.2-7.5 (5H, m); MS m/z 208 (M^+, 80), 123 (100), 110 (20), 85 (90). Found: M^+ 208.0562; $C_{11}H_{12}O_2S$ requires M, 208.0558] and 4-nitroaniline **2** (90%). Same results were obtained from this reaction carried out in acetonitrile.

BF_3-Promoted Reaction with Pent-4-yn-1-oic acid (8). Chromatography gave diphenyl disulfide **1** (70%), (Z)-γ-[(phenylthio)methylidene]butyrolactone (Z)-**19** (25%), m. p. 50-52 °C [^1H NMR δ_H 2.72 (2H, m), 3.0 (1H, m) 6.0 (2H, t, J = .5 Hz), 6.9-7.3 (5H, m); MS m/z 206 (M^+, 80), 122 (100), 121 (70). Found: M^+206.0403; $C_{11}H_{10}O_2S$ requires M, 206.04015] and 4-nitroaniline **2** (95%).

BF_3-Promoted Reaction with Hexa-1,3-diene (9). Chromatography gave a mixture of unidentifiable products (200 mg), *6-(4-nitrophenylamino)5-(phenylthio)hex-1-ene* **22b** (15%) [thick pale yellow oil; ^1H NMR δ_H 1.6-1.8 (2H, m), 2.2-2.4 (2H, m), 3.2-3.4 (3H, m), 4.9-5.1 (3H, m, collapsing to 2H, m, upon shaking with D_2O), 5.77 (1H, ddt, J_{d1} = 17 Hz, J_{d2} = 10 Hz, J_t = 7 Hz), 6.42 (2H, d, J = 9 Hz), 7.2-7.5 (5H, m), 8.05 (2H, d, J = 9 Hz); MS m/z 328 (M^+, 40), 178 (70), 177 (60), 151 (100),123 (65), 105 (50), 67 (80). Found: M^+ 328.1242; $C_{18}H_{20}N_2O_2S_2$ requires M, 328.1245], *5-(4-nitrophenylamino)-6-(phenylthio)hex-1-ene* **22a** (15%) [thick pale yellow oil; ^1H NMR δ_H 1.55-1.75 (2H, m), 2.05-2.2 (2H, m), 3.05 (2H, d, J = 6.0 Hz, collapsing to singlet upon irradiation at δ 3.6), 3.55-3.75 (1H, m), 4.4 (NH, br d, J = 10 Hz, collapsing to singlet upon irradiation at δ 3.6), 4.9-5.05 (2H, m), 5.75 (1H, ddt, J_{d1} = 18 Hz, J_{d2} = 10.5 Hz, J_t = 7 Hz), 6.30

(2H, d, J = 9 Hz), 7.2-7.4 (5H, m), 8.0 (2H, d, J = 9 Hz); MS m/z 328 (M^+, 10), 205 (100), 124 (25). Found: M^+ 328.1250; $C_{18}H_{20}N_2O_2S_2$ requires M, 328.1245], *3-(4-nitrophenylamino)-1-(phenylthio)cyclopentane* **23** (17%) [thick pale yellow oil; ^1H NMR δ_H 1.6-2.0 (4H, m) 2.10-2.25 (1H, m), 2.25-2.35 (1H, m), 3.35 (1H, m), 3.70 (1H, m), 4.50 (1H, brd, collapsing upon shaking with D_2O), 6.30 (2H, d, J = 9 Hz), 7.2-7.5 (5H, m), 8.0 (2H, d, J = 9 Hz); MS m/z 314 (M^+, 80), 205 (80), 177 (70), 149 (70), 67 (100). Found: M^+ 314.1095; $C_{17}H_{18}N_2O_2S$ requires M, 314.1089] and 4-nitroanilne **2** (45%).

$AlCl_3$-Promoted Reaction with Hex-1-yne. This reaction was carried out for 10 min. Chromatography gave a 80:20 mixture of *(E)-2-chloro-1-(phenylthio)hex-1-ene* **28a** and *(E)-1-chloro-2-(phenylthio)hex-1-ene* **29a** (55% overall yield) [^1H NMR δ_H 0.8-0.95 (3H, m), 1.2-1.6 (4H, m), 2.35 (0.4H, t, J = 7 Hz), 2.60 (1.6H, t, J = 7Hz), 6.25 (0.2H, s), 6.30 (0.8H, s), 7.1-7.3 (5H, m); GC-MS, m/z **5a**: 226 (M^+,50), 147 (100) **5b**: 226 (M^+, 30), 135 (100). Found: M^+ 226.0589; $C_{12}H_{15}ClS$ requires M, 226.0583], diphenyl disulfide **1** (25%), and 4-nitroaniline **2** (yield not determined).

A 20:80 mixture of the sulfide adducts **28a** and **29a**, independently prepared by addition of benzenesulfenyl chloride to hex-1-yne according to a known procedure,[11] was treated in benzene solution at room temperature with excess $AlCl_3$ for 15 min. The reaction mixture was hydrolized with diluted hydrochloric acid, extracted with ether and the solvent evaporated. ^1H NMR analysis of the residue showed that the two isomers **28a** and **29a** occurred in 80:20 ratio.

$AlCl_3$-Promoted Reaction with Hex-1-ene. Chromatography gave *2-chloro-1-(phenylthio)hexane* **26a** [^1H NMR δ_H 0.9 (3H, t, J = 7 Hz), 1.2-1.6 (4H, m), 1.6-1.8 (1H, m), 1.9-2.1 (1H, m), 3.15 (1H, A part of an AB system, ABX, J_{AB} = 12 Hz, J_{AX} = 7.5 Hz), 3.35 (1H, B part of an AB system,, J_{AB} = 12 Hz, J_{BX} = 5 Hz), 3.9-4.05 (1H, m), 7.2-7.5 (5H, m); MS m/z 228 (M^+, 50), 123 (80), 110 (100). Found: M^+228.0734. $C_{12}H_{17}ClS$ requires M, 228.0739], 1-(phenylthio)hexan-2-ol **26b** (19%), a 1:1 mixture of 2-(4-nitrophenylamino)-1-(phenylthio)hexane **26c** and 1-(4-nitrophenylamino)-2-(phenylthio)hexane **27c** (35% overall yield), and 4-nitroaniline **2** (yield not determined).

A75:25 mixture of the sulfide **26a** and its regioisomer **27a** [^1H NMR δ_H 0.9 (3H,t), 1.2-1.8 (5H,m), 1.9-2.1 (1H,m), 3.25 (1H,m), 3.45 (1H, A part of an ABX system), 3.70 (1H, B part of an ABX system), and 7.2 - 7.5 (5H,m)], independently prepared from benzenesulfenyl chloride and hex-1-ene by a known procedure,[12] was treated in benzene solution at room temperature with excess $AlCl_3$ for 15 min. The reaction mixture was hydrolized with diluted hydrochloric acid and extracted with ether and the organic layer evaporated. ^1H NMR analysis of the residue showed the exclusive presence of the chloro adduct **26a**.

$AlCl_3$-Promoted Reaction with But-3-en-1-ol (3). Chromatography gave *3-chloro-4-(phenylthio)butan-1-ol* **30** [^1H NMR δ_H 1.85 (1H, m), 2.0 (1H, br s, OH), 2.3 (1H, m), 3.2 (1H, A part of an ABX system, J_{AB} = 14, J_{AX} = 8 Hz), 3.4 (1H, B part of an ABX system, J_{AB} = 14, J_{BX} = 5.7 Hz), 3.8 (2H, m), 4.15 (1H, m), 7.1-7.5 (5H, m); MS m/z 216 (M^+, 50), 180 (25), 123 (100), 110 (80). Found: 216.0372; $C_{10}H_{13}ClOS$ requires M, 216.0376], 4-nitroaniline **2** (80%) and a 1:1 mixture of the arylamino sulfides **10b** and **11b** (15%).

$AlCl_3$-Promoted Reaction with Pent-4-yn-1-ol (5). Chromatography gave diphenyl disulfide **1** (50%), a 25:75 mixture of *(E)-4-chloro-5-(phenylthio)pent-4-en-1-ol* **31a** and *(E)-5-chloro-4-(phenylthio)pent-4-en-1-ol* **31b** (40%) [^1H NMR δ_H 2.6-2.8 (2H, m), 2.42 (1.5H, t, J = 7.5 Hz), 2.67 (0.5H, t, J = 7.5 Hz), 3.58 (1.5H, t, J = 7 Hz), 3.68 (0.5H, t, J = 7 Hz), 6.26 (0.75H, s), 6.32 (0.25H, s), 7.2-7.4 (5H, m); MS m/z 228 (M^+, 60), 184 (40), 147 (50), 135 (70), 110 (100). Found: 228.0380; $C_{11}H_{13}ClOS$ requires M, 228.0376] and 4-nitroaniline **2** (97%).

$AlCl_3$-Promoted Reaction with But-3-en-1-oic acid (6). The reaction mixture was hydrolized with water and then subjected to the usual work-up. Chromatography gave a 1:1 mixture of the chlorosulfide adducts **32a** and **32b** (75% overall yield) [MS, m/z 230 (M+, 80), 194 (70), 149 (30), 135 (75), 134 (65), 123 (100), 110 (80), 109 (95). Found: 230.0165; $C_{10}H_{11}ClO_2S$ requires M, 230.0168] and 4-nitroaniline **2** (yield not determined). Repeated chromatography of the isolated mixture of the adducts **32a** and **32b** allowed partial separation of somewhat pure *3-chloro-4-(phenylthio)butanoic acid* **32a** [^{1}H NMR δ_H 2.74 (1H, dd, J_1 = 9 Hz, J_2 = 17 Hz), 3.16 (1H, dd, J_1 = 9 Hz, J_2 = 14 Hz), 3.25 (1H, dd, J_1 = 4 Hz, J_2 = 17 Hz), 3.43 (1H, dd, J_1 = 6 Hz, J_2 = 14 Hz), 4.2-4.36 (1H,m), 7.2-7.5 (5H,m)] and *4-chloro-3-(phenylthio)butanoic acid* **32b** [^{1}H NMR δ_H2.56 (1H, dd, J_1 = 17 Hz, J_2 = 8 Hz), 3.06 (1H, dd, J_1 = 17 Hz, J2 = 5 Hz), 3.53 (1H, dd, J_1 = J_2 = 9.5 Hz), 3.61-3.68 (1H, m), 3.80 (1H, dd, J_1 = 9.5 Hz, J_2 = 3 Hz), 7.2-7.6 (5H, m), 10.55 (1H,br s, OH)]. In a repeated experiment the reaction mixture was hydrolized with aqueous sodium carbonate; TLC analysis showed the presence of the hydroxy acids **15a** and **15b** and the absence of the chlorosulfides **32a** and **32b**.

$AlBr_3$-Promoted Reaction with Hex-1-yne. The reaction was carried out for 10 min. Chromatography gave a 1:1 mixture of the bromosulfide adducts **28b** and **29b**[1k] (33%), diphenyl disulfide **1** (55%) and 4-nitroaniline (80%). Repeated chromatography of the bromosulfide mixture separated pure *(E)-2-bromo-1-(phenylthio)hex-1-ene* **28b** [^{1}H NMR δ_H 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), 7.2-7.4 (5H, m); MS m/z 272, 270(M^+), 229, 227, 190, 149, 148, 147, 110, 109, 81. Found: 270.0083; $C_{12}H_{15}BrS$ requires M, 270.0078].

A solution of **28b** (270 mg, 1 mmol) and m-chloroperbenzoic acid (2 mmol) in chloroform (20 mL) was allowed to stand at room temperature for 48 h. The resulting mixture was washed with aqueous sodium carbonate and the solvent evaporated to give crude *1-(benzenesulfonyl)-2-bromohex-1-ene* in quantitative yield [oil; ^{1}H NMR δ_H 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), 7.8-7.9 (2H, m); MS m/z 304, 302 (M^+, 4), 223 (30), 143 (100), 125 (45), 77 (60). Found: 301.9980; $C_{12}H_{15}BrO_2S$ requires M, 301.9976]. This crude product was dissolved in THF (10 mL) and treated at room temperature with a 0.1 M THF solution of sodium triethylborohydride (30 mL). After 5 min the reaction mixture was washed with water, the organic layer extracted with ether and the solvent evaporated. The residue was chromatographed to give phenyl 1-hexyl sulfone[13] as the only isolable product (90%).

AlI_3-Promoted Reaction with Hex-1-yne. The reaction mixture immediately turned deep brown. After 10 min the mixture was neutralized with sodium carbonate and then washed with aqueous sodium sulfite to eliminate the produced iodine. Usual work-up and column chromatography gave 1,2-diiodohexene (yield not determined), diphenyl disulfide **1** (90%) and 4-nitroaniline **2** (95%).

Aluminium Halide-Promoted Decomposition of NBSA. NBSA (496 mg, 2 mmol) in benzene (20 mL) was allowed to react, at room temperature, with aluminium chloride, bromide or iodide (ca. 0.5-0.7 g) for 10 min. In each case TLC and GC-MS analysis of the reaction mixture showed the exclusive presence of diphenyl disulfide **1** and 4-nitroaniline **2**.

Acknowledgments. We thank the Ministero della Ricerca Scientica e Tecnologica (MURST) and CNR (Progetto Finalizzato Chimica Fine) for financial support. We also thank Mr. Luca Zuppiroli for performing NMR spectra.

REFERENCES

1. (a) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 2261-2266; (b) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *Tetrahedron*, **1986**, *42*, 1145-1155; (c) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *Tetrahedron Lett.*, **1986**, *27*, 1739-1742; (d) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1*,, **1987**, 2815-2818; (e) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *Tetrahedron Lett.*, **1988**, *29*, 2381-2384; (f) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1*, **1989**, 1105-1112; (g) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *Gazz. Chim. Ital.*, **1989**, *119*, 609-616; (h) Benati, L.; Casarini, D.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1*, **1989**, 1113-1116; (i) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1*, **1990**, 1691-1695; (j) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *Gazz. Chim. Ital.*, **1991**, *121*, 387-391; (k) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *Tetrahedron*, **1993**, *43*, 5365-5376
2. Grossi, L.; Montevecchi, P. C., *Tetrahedron Lett.*, **1991**, *32*, 5621-5624; Grossi, L.; Montevecchi, P. C., *Tetrahedron* , **1993**, *49*, 9095-9104
3. Capozzi, G.; Modena G.; Pasquato, L. "Chemistry of Sulphenyl Halides and Sulphenamides" in "The Chemistry of Sulphenic Acids and their derivatives", ed. S. Patai, Wiley, Chichester, 1990, ch. 10.
4. Baldwin, J. E. *J. Chem. Soc., Chem. Commun.*, **1976**, 734-736
5. Brownbridge, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1280-1281
6. O'Malley, G. J.; Cava, M. P. *Tetrahedron Lett.*, **1985**, *26*, 6159-6162
7. Brown, W. L.; Fallis, A. G. *Can. J. Chem.*, **1987**, *65*,1828-1832; Tuladhar, S. M.; Fallis, A. G.*Can. J. Chem*, **1987**, *65*, 1833-1837; Capozzi, G.; Menichetti, S.; Nicastro, M.; Taddei, M. *Heterocycles*, **1989**, *29*, 1703-1708.
8. Toru, T.; Fujita, S.; Maekawa, E. *J. Chem. Soc., Perkin Trans. 1*, **1986**, 1999-2004
9. Drabowicz, J.; Kielbasinski, P.; Micolajczyk, M. "Synthesis of Sulphenyl Halides and Sulphenamides" in ref. 3, ch. 6.
10. Gilbert, G. E.; Johnson, T. B. *J. Am. Chem. Soc.*, **1929**, *51*, 1526-1536.
11. Schmid, G. H.; Modro, A.; Lenz, F.; Garratt, D. G.; Yates, K. *J. Org. Chem.*, **1976**, *41*, 2331-2336.
12. Schmid, G. H.; Csizmadia, V. M.; Nowlan, V. J.; Garratt, D. G. *Can. J. Chem.* **1972**, *50*, 2457-2464.
13. Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1195-1200.

(*Received in UK* 8 *July* 1994; *revised* 2 *September* 1994; *accepted* 9 *September* 1994)