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LDA-Promoted Decomposition of Benzenesulfenamides. A Route to Aminyl Radicals by Dioxygen Oxidation of Lithium Amides.

Anna Barbieri, Pier Carlo Montevecchi,* Daniele Nanni and Maria Luisa Navacchia

Dipartimento di Chimica Organica "A. Mangini", Università di Bologna,
Viale Risorgimento 4, I40136 Bologna, Italy

Abstract. The LDA-promoted decomposition of N-monosubstituted sulfenamides **1a-d** occurs through the formation of thioaminyl anions, which undergo oxidation either at sulfur, with formation of sulfonamides, or at nitrogen, with formation of thioaminyl radicals, depending on the nature of the 4'-substituent. The reaction of N,N-disubstituted sulfenamides **1e-h** proceeds through the intermediacy of a lithium complex capable of generating aminyl radicals *via* sulfenyl group transfer to the di-*iso*-propylamido anion and subsequent aerial oxidation of the resulting lithium amides **3e-h**.

Benzenesulfenamides are useful synthetic intermediates. They can be a source of thioaminyl radicals[1] or undergo acid-promoted decomposition (with both protic and Lewis acids) by nucleophilic attack at the sulfur atom.[2] The boron trifluoride-promoted decomposition represents a good synthetic approach to 1,2-difunctionalization of both alkenes[3] and alkynes.[4]

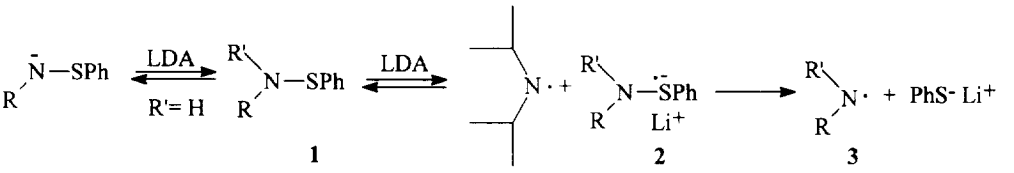
Benzenesulfenamides can afford aminyl radicals through homolysis of the (fairly) weak N-S bond. This process could occur by either radical-induced attack to the sulfur or thermal monomolecular fragmentation. Recently, it has been reported that stannyl radicals (thiophilic species) can readily promote the formation of aminyl radicals by S_H2 substitution at sulfur.[5] In contrast, thermal decomposition of benzenesulfenamides does not seem to be a good source of aminyl radicals, because thermal homolysis of the N-S bond occurs at rather high temperature; moreover, undesired and often predominant autoprotonation-induced side-reactions take place.[6]

In principle, benzenesulfenamides might be a source of aminyl radicals through initial electron transfer (SET) process followed by monomolecular (or electrophile-promoted) elimination of thiolate ion from the resulting radical anion intermediate. The reductive N-S bond scission could be achieved with metal reductants. For example, we have found that the samarium-diiodide-promoted reaction of N-arylsulfenamides smoothly leads to the corresponding aniline and thiophenol through a two-electron process. However, no evidence of any aminyl radical intermediates was obtained.[7]

Our interest in sulfenamides chemistry prompted us to study further the reductive N-S bond cleavage as a possible source of aminyl radicals and, with this aim, we have investigated the reaction of a series of sulfenamides **1** with LDA, which is known to be an efficient one-electron donor to molecules having favorable reduction potentials.[8] We reasoned that the weakly nucleophilic di-*iso*-propylamido anion might undergo a SET process with amides **1**, leading to the corresponding di-*iso*-propylaminyl radicals and amide radical anions **2**, that might eventually afford the desired aminyl radicals **3**. The driving force of the entire process would be the greater stability of the thiolate ion with respect to the di-*iso*-propylamido anion (Scheme 1). With N-mono-

substituted amides **1** (R'=H) competing proton transfer could be expected. However, the chemical behavior of benzenesulfenamido anions is still unexplored, and its investigation appeared worthy of interest.

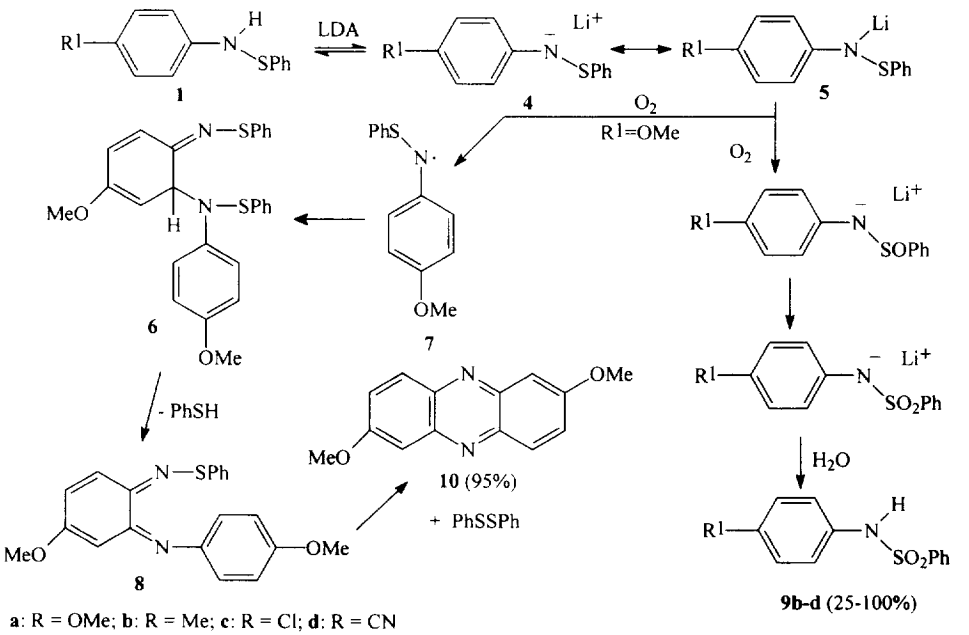
Scheme 1



RESULTS AND DISCUSSION

The reactions of sulfenamides **1a-i** were carried out at room temperature under a nitrogen atmosphere with 1.5 molar equiv of LDA for ca. 3-4 h. The reaction mixtures were then generally stirred in the presence of air for a further 20 h, and finally hydrolyzed. In some cases the reaction mixtures were hydrolyzed without exposure to air. The product patterns strongly depended on several factors, including the nature of R^1 substituents, the presence of an amidic proton (i.e., the nature of R^2), and the presence of oxygen.

Scheme 2

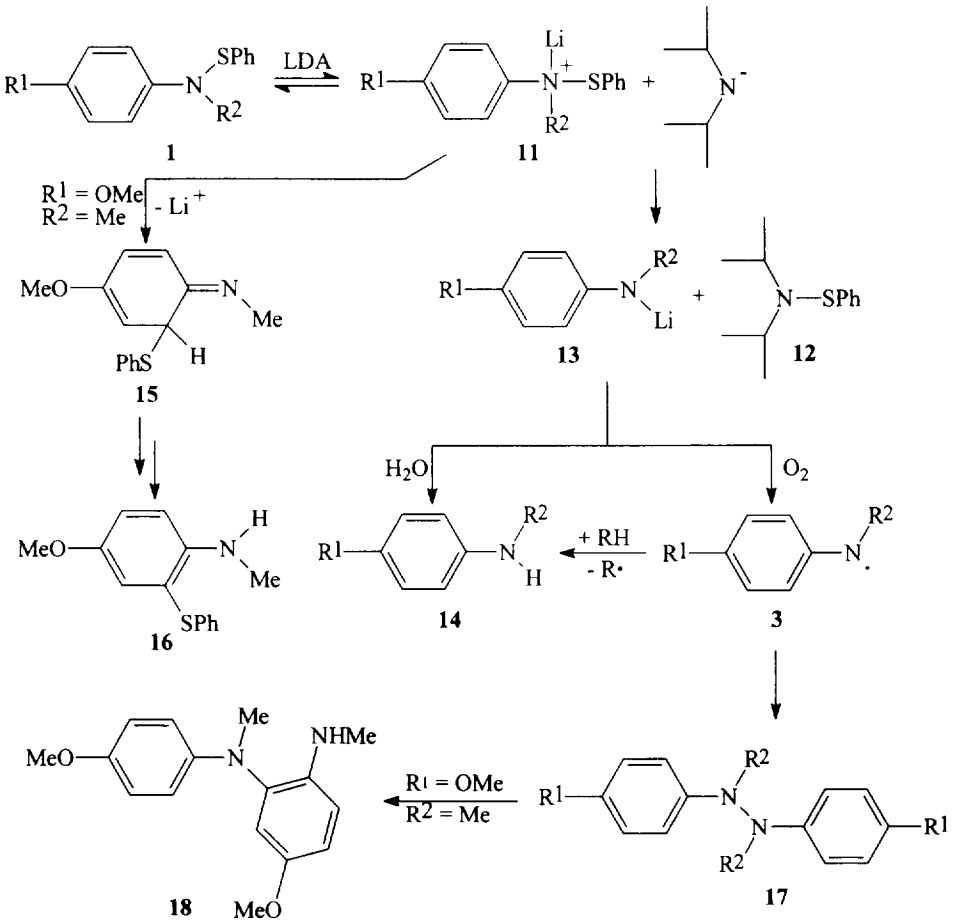


a: R = OMe; **b**: R = Me; **c**: R = Cl; **d**: R = CN

The chemical behavior of mono-substituted sulfenamides was studied with 4'-substituted amides **1a-d**. 4'-Cyano-substituted amide **1d** led to the formation of the corresponding sulfonamide **9d** in almost quantitative yield (Scheme 2). However, amide **1d** was recovered unchanged when the reaction mixture was hydrolyzed before exposure to air. Similar results were obtained with 4'-chloro- (**1c**) and 4'-methyl-substituted (**1b**) amides, although in these cases the corresponding sulfonamides **9c** and **9b** were obtained in lower yields (30 and 25%, respectively) together with unidentifiable tarry products. In the case of **1c**, significant amounts (23%) of the corresponding sulfinamide [4-ClC_6H_4NH-SOPh] were also found.

4'-Methoxy-substituted amide **1a** led to a completely different product pattern. The colorless reaction mixture turned deep red immediately upon exposure to air. Subsequent hydrolysis and column chromatography furnished 2,8-dimethoxyphenazine **10** in high yields (ca. 95%). The deep red color suggests the formation of o-quinonedi-imine **8**, which is known to cyclize to phenazine **10** under workup and chromatographic conditions.[1]

Scheme 3



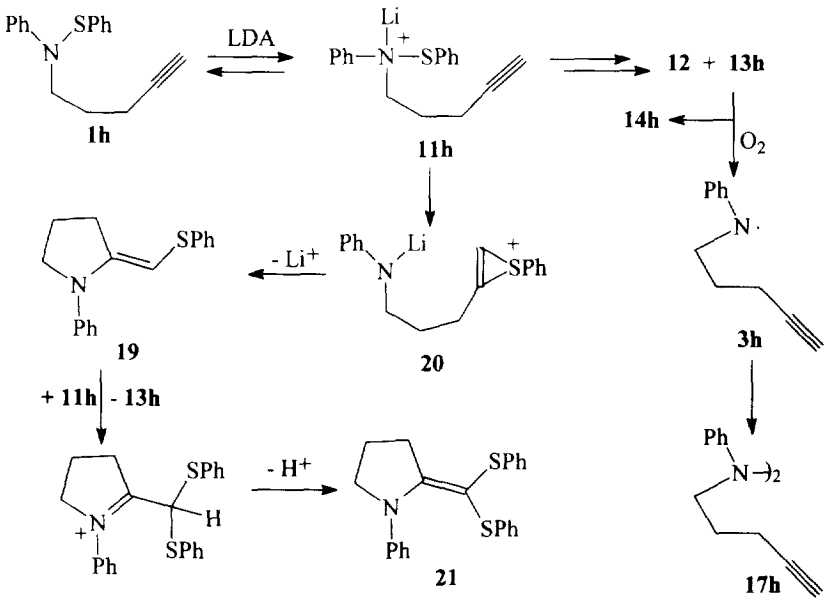
e: R^1= OMe, R^2=Me; **f**: R^1=H, R^2= Me; **g**: R^1=H, R^2=Ph

The reaction products obtained from the above reactions were accounted for as depicted in Scheme 2. Acid-base reaction between LDA and amides **1a-d** affords thioaminyl anions **4a-d** (or lithium thioamides **5a-d**). Anions **4b-d** undergo oxidation at sulfur giving, after hydrolysis, the corresponding sulfonamides **9b-d**.[9] In contrast, lithium amide **5a**, having a strong electron donor group in the 4'-position, undergoes rapid oxidation at nitrogen to the thioaminyl radical **7**, which is expected to afford the di-imine **8** by N-C_{ortho} dimerization to **6** and subsequent elimination of thiophenol (detected).[1]

The chemical behavior of N,N-disubstituted sulfenamides was explored through the reactions of amides **1e-g**. N,N-Diphenyl-substituted amide **1g** gave, according to the General Procedure (see Experimental Section), diphenylamine **14g** (14%), tetraphenylhydrazine **17g** (64%), and N,N-di-*iso*-propylbenzenesulfenamide **12** (70-80%) (Scheme 3). Decomposition of **1g** was complete after ca. 30 min. Hydrolysis without exposure to air furnished amine **14g** and di-*iso*-propylbenzenesulfenamide **12** almost exclusively (TLC analysis).

The reaction of N-methyl-N-p-anisylbenzenesulfenamide **1e**, carried out according to the General Procedure, gave, besides sulfenamide **12**, the semidine **18**, N-methyl-p-anisidine **14e**, and 2-phenylsulfanyl-N-methyl-p-anisidine **16** in a 57:37:6 ratio (85% overall yield).[10] This reaction, when repeated without exposure to air, gave the same mixture of **18**, **14e** and **16**, but in a 7:86:7 ratio. Small amounts of starting **1e** were also recovered in both cases. The semidine **18** is the formal N-C_{ortho} dimerization product of aminyl radical **3e**. However, this compound was not present in the reaction mixture before column chromatography. TLC and ^{1}H NMR analysis clearly showed the presence of another product **A** that showed two singlets at δ 2.85 (N-Methyl group) and 3.76 (methoxy group). In an independent experiment the reaction mixture was analyzed by ^{1}H NMR and then allowed to stand overnight in the presence of silica gel. Repeated ^{1}H NMR analysis showed disappearance of the above singlets and appearance of signals of equal overall intensity at δ 2.80 and 3.15 (N-methyl groups) and 3.70 and 3.75 (methoxy groups), due to the semidine **18**. We suggest that compound **A** is the hydrazine **17e**, which undergoes silica gel-catalyzed *ortho*-semidinic rearrangement to **18** under chromatographic conditions. Similar results were obtained from sulfenamide **1f**, which reacted with LDA according to the General Procedure to give, after column chromatography, N-methylaniline **14f** (55%) and dimethyldiphenylhydrazine **17f** (15%).

Scheme 4



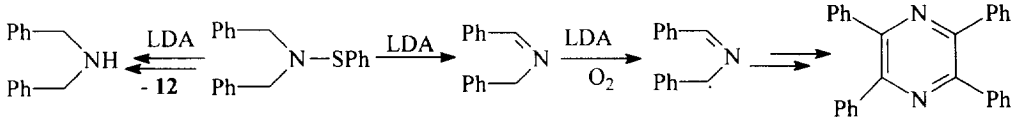
Hydrazine derivatives **17e-g**, obtained from the LDA-promoted decomposition of sulfenamides **1e-g**, could be accounted for through the intermediacy of aminyl radicals **3e-g**. We suggest a mechanism involving initial lithium transfer from LDA to the nitrogen atom of **1**; this behavior would parallel that observed in the protic acid catalyzed decomposition of sulfenamides.[2] The resulting complex **11** would undergo nucleophilic attack to the sulfur by the di-*iso*-propylamido anion leading to sulfenamide **12** and lithium amide **13**, from which aniline **14** and aminyl radicals **3** can be formed by hydrolysis and aerial oxidation, respectively. Radicals **3** can lead to amines **14** by hydrogen abstraction or to hydrazines **17** by N,N-dimerization. The small amounts of the rearranged product **16** were formed in competition with lithium amide **13e**, as indicated by the fact that the (**14e+18**)/**16** ratio is independent of the presence of air. We suggest that compound **16** arises from complex **11e** through N-C_{ortho} cationic migration of the sulfenyl group.

The determining role played by the lithium cation in the LDA-promoted decomposition of sulfenamides **1e-g** is strongly supported by the fact that the presence of Crown-12 (2 molar equiv) inhibits the decomposition of **1e** (TLC after 8h).

To obtain further evidence of the intermediacy of aminyl radicals **3e-g** in the LDA-promoted decomposition of sulfenamides **1e-g** we reacted the pentynyl-substituted sulfenamide **1h** with the aim of trapping aminyl radical **3h** by intramolecular addition to the carbon-carbon triple bond (5-*exo* cyclization). Although such cyclization was not observed, the results were interesting all the same. In fact, besides amide **12** and amine **14h**, we separated small amounts of hydrazine **17h** (ascribable to N,N-dimerization of radicals **3h**) and 2-bis(phenylsulfanyl)methylidenepyrrolidine **21** (13%). According to a previous report[3d] on the sulfenocyclization of alkenes and alkynes, pyrrolidine **21** probably resulted from lithium complex **11h** through an ionic mechanism. Initial intramolecular sulfenyl group transfer to the alkyne triple bond would lead to the thiirenium ion **20**, which could reasonably undergo nucleophilic attack by the nitrogen atom with formation of pyrrolidine **19**. The enaminic exocyclic double bond of **19** is very electron rich and could easily afford pyrrolidine **21** by an intermolecular sulfenyl group addition/deprotonation process (Scheme 4).

In contrast with the above results, the LDA-promoted decomposition of the N,N-dialkyl sulfenamide **1i** did not lead to any hydrazine derivative. Dibenzylamine **14i** (77%) and sulfenamide **12** were the main reaction products, besides small amounts of tetraphenylpyrazine **24** (7%) and an unidentified product (M^+ 296) (6%). The mechanism of formation of pyrazine **24** is still unclear. Probably, it derives from **1i** by initial E_1cB elimination of thiophenol (Scheme 5) through the intermediacy of imine **22**. Studies on the LDA-promoted reactions of imines are in progress to investigate if radicals **23** are involved as intermediates.

Scheme 5



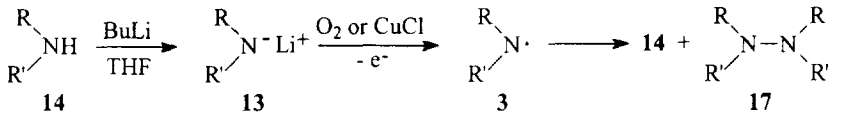
14i **1i** **22** **23** **24**

The overall results indicate that sulfenamides **1** generally undergo LDA-promoted decomposition. The LDA-promoted decomposition of N-monosubstituted sulfenanilides **1a-d** occurs through the formation of thioaminyl anions, which undergo oxidation either at sulfur, with formation of sulfonamides, or at nitrogen, with formation of thioaminyls radicals, depending on the nature of the 4'-substituent.

The reaction of N,N-disubstituted sulfenamides proceeds through the intermediacy of a lithium complex capable of generating aminyl radicals *via* sulfenyl group transfer to the di-*iso*-propylamido anion and subsequent aerial oxidation of the resulting lithium amides. When a nucleophilic group is linked to the nitrogen atom (i.e., 4-methoxyphenyl in amide **1e** or pent-4-yn-1-yl in amide **1h**) intramolecular sulfenyl transfer occurs in competition with the formation of lithium amides.

Our results suggest that lithium amides might be a source of aminyl radicals under mild conditions.[11] Taking this into account, we have briefly studied the oxidation of lithium amides **13e-g, j-l** promoted by either dioxygen or copper(I) chloride. Amides **13e-g, j-l** were readily generated from the corresponding amines **14e-g, j-l** with butyl lithium and they were allowed to react at room temperature for several hours, as described in Experimental Section (Scheme 6) . Workup and column chromatography of the reaction mixtures generally gave the corresponding amines **14** and hydrazines **17** in a ratio strongly dependent on the nature of the amino substituents (see Table).

Scheme 6



14 **13** **3** **17**

e: R=Me, R'=4-MeOC$_6$H$_5$; **f**: R=Me, R'=C$_6$H$_5$; **g**: R=R'=Ph; **j**: R=H, R'=o-Ph-C$_6$H$_5$; **k**: R=C$_{12}$H$_{25}$, R'=  ; **l**: R=Ph, R'= 

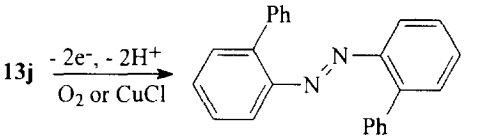
Table. Yields (%) of products obtained from amides **13e-g, j-l** by dioxygen oxidation and copper(I) chloride oxidation (in brackets)

Amide	**13e**[a]	**13f**	**13g**	**13j**[b]	**13k**	**13l**[c]
Amine **14**, %	33 (20)	66 (58)	41 (35)	48 (30)	n.d.[d]	13
Hydrazine **17** %	0 (0)	2 (2)	31 (53)	16 (3)	0	17

[a]Semidine **18** was obtained in 31% (20%) yield. [b]Azo derivative **25** was separated in 31% (20%) yield. [c]Complex reaction mixture; column chromatography gave a lot of unidentifiable products in very low yield. [d]Yield not determined. GC-MS analysis showed the aniline **14m** as the only reaction product.

With 4-methoxy-N-methylaniline **1e**, the hydrazine derivative **17e** underwent rearrangement to semidine **18** under chromatographic conditions. The reaction of amide **13j** led to the formation of the azo-compound **25**, which was probably formed by further oxidation of the corresponding hydrazine **17j** (Scheme 7).

Scheme 7



25

Amides **13k** and **13l** did not afford any cyclization product onto the CC double bond. Moreover, amide **13k** did not give hydrazine **17k** (see Table). It is known that N-alkyl-N-pentenylaminyl radicals can cyclize onto the CC double bond, although in a reversivble manner.[12] The failure to obtain any hydrazine derivative **17k**

and/or cyclization products from anilide **13k** suggests that aminyl radical **3k** is not formed with oxygen or copper(I) chloride. This finding is consistent with the the reported evidence that N,N-dialkyl amides can be oxidized only with strong one-electron oxidants.[12] Probably, the presence of the aryl group linked to the nitrogen atom lowers the reduction potential of amides **1e-g, j, l** and makes them more readily oxidizable under our mild conditions.

EXPERIMENTAL SECTION

Benzenesulfenamides **1a-d**,[1b] **1e,f**,[13] **1g**,[2] **1h** and **1i**,[14] were prepared in 60-70% yield according to the sulfenyl chloride method. Thiophenol (5 mmol) was slowly added at 0 °C to sulforyl chloride (5 mmol) under stirring, and the resulting red oil was stirred under reduced pressure (15 mm Hg) for 2-3 min. The obtained sulfenyl chloride was dissolved in dichloromethane (5 mL) and was added dropwise to a stirred solution of the appropriate amine **14a-i** (5 mmol) and triethylamine (5 mmol) in dichloromethane (50 mL) at 0 °C (15 °C in the case of **1d**, - 10 °C in the case of **1h**). The resulting mixture was stirred for further 3 h, and then the solvent was removed. The residue was dissolved in diethyl ether, triethylammonium chloride was filtered off, the solvent removed, and the residue chromatographed on a silica gel column. [**1h**: ^{1}H NMR δ (200 MHz) 1.9-2.1 (3H, m, collapsing, upon irradiation at δ 3.85, to a doublet, J=2.3 Hz, superimposed on a triplet, J=7 Hz), 2.2-2.35 (2H, dt, J_d=2.3 Hz, J_t=7 Hz), 3.85 (2H, t, J=7 Hz), 6.8-7.3 (10H, m); MS m/z (rel intensity) 267 (M^+, 90), 214 (65), 158 (30) , 106 (100), 105 (60), 104 (60), 77 (70). HRMS calcd for $C_{17}H_{17}NS$ 267.1082, found 267.1083]

Reaction products such as amines **14a-i**, diphenyl disulfide, phenyl benzenethiosulfonate, phenazine **10**[1b] and sulfonamides **9b,c,d**[15] were identified by comparison with authentic specimens. Hydrazines **17f,g**,[16] pyrazine **24**,[17] 2-phenylsulfanyl-4-methoxy-N-methylaniline **16**, and semidine **18**[18] were identified by spectral analyses (^{1}H NMR and MS)

Reaction of Sulfenamides 1a-i with Lithium Di-*iso*-propylamide (LDA). General Procedure. To a solution of di-*iso*-propylamine (3 mmol) in anhydrous THF (10 mL) at - 20 °C a commercially available 0.1 M THF solution of butyl lithium (30 mL) was added under a nitrogen atmosphere. The resulting solution was stirred for ca. 30 min and then a solution of the appropriate sulfenamide **1a-i** (2 mmol) in THF (5 mL) was added with a syringe. The reaction mixture was generally stirred at room temperature for 4 h (unless otherwise stated) under a nitrogen atmosphere and for further 20 h under an air atmosphere, afterwards it was washed with brine and extracted with diethyl ether. The organic layer was separated, the solvent removed and the residue chromatographed on a silica gel column (and/or analyzed by GC-MS and ^{1}H NMR).

From 4'-Methoxybenzenesulfenanilide 1a. The colorless reaction mixture was stirred overnight under a nitrogen atmosphere and then exposed to air. The solution immediately turned deep red. After 2 h it was subjected to workup and chromatography. Elution with light petroleum gave diphenyl disulfide (120 mg, 55%); elution with light petroleum/diethyl ether 90:10 gave 2,7-dimethoxyphenazine **10** (230 mg, 95%).

From 4'-Methylbenzenesulfenanilide 1b. Elution with light petroleum/diethyl ether 85:15 gave 4'-methylbenzenesulfonanilide **9b** (120 mg, 25%); further elution afforded complex mixtures of inseparable and unidentifiable products.

From 4'-Chlorobenzenesulfenanilide 1c. Elution with light petroleum/diethyl ether 85:15 gave 4'-chlorobenzenesulfonanilide **9c** (160 mg, 30%) and 4'-chlorobenzenesulfinanilide[19] [4-ClC_6H_4NH-$S(O)C_6H_5$] (115 mg, 23%); further elution afforded complex mixtures of inseparable and unidentifiable products.

From 4'-Cyanobenzenesulfenanilide 1d. Workup of the reaction mixture gave, after solvent removal, pure 4'-cyanobenzenesulfonanilide **9d**. In a repeated experiment the reaction mixture was stirred overnight

under a nitrogen atmosphere and then hydrolyzed. TLC analysis showed the presence of unreacted **1d** exclusively.

From N-Methyl-4'-methoxybenzenesulfenanilide 1e. Chromatography gave N,N-di-*iso*-propylbenzenesulfenamide **12** (165 mg, 40%) [^{1}H NMR (200 MHz) δ 1.1 (12H, d, J=7 Hz; collapsing to singlet upon irradiation at δ 3.3), 3.3 (2H, seven lines, J=7 Hz), 7.0-7.3 (5H, m); M/S m/z (rel intensity) 209 (M^+, 80), 194 (100), 152 (95), 109 (70). HRMS calcd for $C_{12}H_{19}NS$ 209.1238, found 209.1235], phenyl benzenethiosulfonate (50 mg, 20%), a mixture of N-methyl-p-anisidine **14e**, 2-phenylsulfanyl-N-methyl-p-anisidine **16**, and 4,4'-dimethoxy-2-(N-methylamino)-N-methyldiphenylamine **18** [in a 37:6:57 ratio, as determined by ^{1}H NMR analysis (370 mg, 85% overall yield). Further column chromatography gave a fraction consisting mainly of 2-phenylsulfanyl-N-methyl-p-anisidine **16** contaminated by anisidine **14e** [**16**: ^{1}H NMR δ (200 MHz) 2.70 (3H, s), 3.80 (3H, s), 6.40 (1H, d, J=2.8 Hz), 6.58 (1H, dd, J_1=8.6 Hz, J_2=2.8 Hz; collapsing to doublet, J=2.8 Hz, upon irradiation at δ 6.8), 6.80 (1H, d, J=8.6 Hz), 7.2-7.4 (5H, m); MS m/z (rel intensity) 245 (M^+, 100), 230 (80). HRMS calcd for $C_{14}H_{15}NOS$ 245.0874, found 245.0876], and the semidine **18** [^{1}H NMR δ (200 MHz) 2.80 (3H, s), 3.15 (3H, s), 3.70 (3H, s), 3.75 (3H, s), 3.9 (1H, br s), 6.6-6.9 (7H, m); MS m/z (rel intensity) 272 (M^+, 100), 257 (50). HRMS calcd for $C_{16}H_{20}N_2O_4$ 272.1525, found 272.1522. IR ν_{max}/cm^{-1} 3400]. In a repeated experiment the residue was analyzed by ^{1}H NMR before column chromatography. Signals were present in the aromatic region in addition to singlets ascribable to N-methyl and methoxy groups of compounds **14e** and **16** and singlets at δ 2.85 and 3.76, ascribable to hydrazine **17e**. The reaction mixture was allowed to stand overnight in the presence of silica gel, and then was dissolved in diethyl ether; the silica gel was filtered, the solvent evaporated, and the residue analyzed by ^{1}H NMR. Signals of hydrazine **17e** were absent, whilst signals due to compounds **14e**, **16**, **and 18** were present in a 37:57:6 ratio.

In a repeated experiment the reaction mixture was stirred overnight under a nitrogen atmosphere and then hydrolyzed. After the usual workup the residue was cromatographed. The fraction containing compounds **14e**, **16**, and **18** (ca. 70% overall yield) was analyzed by ^{1}H NMR (85:7:7 ratio).

From N-Methylbenzenesulfenanilide 1f. Column chromatography gave sulfenamide **12** (290 mg, 70%), N,N'-dimethyl-N,N'-diphenylhydrazine **17f** (30 mg, 15%), and N-methylaniline **14f** (55%; determined by ^{1}H NMR analysis of the reaction mixture before column chromatography).

From N-Phenylbenzenesulfenanilide 1g. Column chromatography gave sulfenamide **12** (310 mg, 75%), diphenylamine **14g** (47 mg, 14%), and tetraphenylhydrazine **17g** (215 mg, 64%). In a repeated experiment the reacion mixture was hydrolyzed after 30 min. TLC analysis showed the almost exclusive presence of amide **12** and diphenylamine **14g**.

From N-Pent-4-yn-1-ylbenzenesulfenanilide 1h. Chromatography gave amide **12** (traces), diphenyl disulfide (12 mg, 5%), hydrazine **17h** (11 mg, 3.5 %) [^{1} H NMR δ (200 MHz) 1.85-2.0 (3H, m; collapsing to a triplet at δ 1.87, J=7.5 Hz, and a triplet at δ 1.95, J=2.2 Hz, upon irradiation at δ 3.58), 2.24 (2H, dt, J_d=2.2 Hz, J_t=7 Hz), 3.58 (2H, br t, J ca. 7 Hz), 6.75, (2H, d, J=8 Hz), 7.1-7.3 (3H, m); MS m/z (rel intensity) 316 (M^+, 100), 249 (45), 158 (25), 106 (30), 77 (45). HRMS calcd for $C_{22}H_{24}N_2$ 316.1940, found 316.1936], N-phenyl-2-bis-(phenylsulfanyl)methylidenepyrrolidine **21** (50 mg, 13%) [^{1}H NMR δ (200 MHz) 2.05 (2H, quintuplet, J=6.8 Hz), 3.15 (2H, t, J=6.8 Hz; collapsing to singlet upon irradiation at δ 2.05), 3.80 (2H, t, J=6.8 Hz; collapsing to a singlet upon irradiation at δ 2.05), 6.8-7.3 (15H, m); MS m/z (rel intensity) 375 (M^+, 50), 266 (35), 157 (100). HRMS calcd for $C_{23}H_{21}NS_2$ 375.1115, found 375.1118], and amine **14h** (80 mg, 25%) [^{1}H NMR δ (200 MHz) 1.80 (2H, quintuplet, J=6.8 Hz), 1.98 (1H, t, J=3 Hz), 2.28 (2H, dt, J_d=3 Hz, J_t=6.8 Hz), 3.22 (2H, t, J=6.8 Hz), 3.5 (1H, br s), 6.5-6.7 (3H, m), 7.1-7.2 (2H, m); MS m/z (rel intensity) 159 (M^+, 30), 106 (100). HRMS calcd for $C_{11}H_{13}N$ 159.1048, found 159.1046].

From N,N-Dibenzylbenzenesulfenamide 1i. Chromatography gave, besides amide **12** (yield not determined), dibenzylamine **14i** (300 mg, 77%), an unidentified product [M^+ 296] (30 mg), and tetraphenyl-1,4-pyrazine **24** (25 mg, 7%).

Copper(I) and Dioxygen-promoted oxidation of Lithium Amides 13e-g, j-l. A THF solution (30 mL) of the appropriate amine **14e-g, j-l** (3 mmol) was treated at room temperature under a nitrogen atmosphere with butyl lithium (1.6 M pentane solution, 2 mL) to give the amide **13**. The resulting solution was allowed to react for ca. 30 min, then copper(I) chloride was added. The mixture was stirred overnight and then filtered to eliminate the copper salt. The filtrate was evaporated and the residue chromatographed on silica gel column. In a similar procedure, the THF solution of the lithium amide was allowed to react overnight under stirring in the presence of air. The colorless solutions immediately turned green-blue, and then green-yellow, when exposed to the air.

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REFERENCES AND NOTES

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