carbanionic center would stabilize the negative charge.[14]

We sought to explain the discrepancy in the configuration of **2-*d***, oxidizing the deuteriated sulfoxide (Figure 2c) ($[\alpha]^{24}_D$ +131.35°) to the corresponding sulfone. The deuteriated sulfone thus obtained showed a negative rotation (−0.273°) in contrast to the positive rotation (+0.6°) reported by Durst and his co-workers.[3] Since the starting S_R-**2** has a large positive rotation (+167°),[3] it seems possible that the contamination of the product sulfone with this sulfoxide led Durst and his co-workers to misassign the steric course of the reaction.

Experimental Section

Melting points were not corrected. ^{1}H NMR spectra were recorded at 400 MHz on a JEOL GX-400 Fourier transform NMR spectrometer. The optical activity was measured on a Perkin-Elmer 241 polarimeter. Elemental analyses were performed with a Yanako MT-3 elemental analyzer.

Materials. S_S-Methyl phenylmethyl sulfoxide (S_S-**1**) and S_R-*tert*-butyl phenylmethyl sulfoxide (S_R-**2**) were prepared by Drs. Nishio and Nishioka of Meiji Seika Kaisha, Ltd., according to literature procedures.[7,15] (*S*)-(+)-α-Deuteriobenzyl alcohol obtained as described in a previous paper[5,6] was converted into C_R,S_{rac}-**1-*d*** and C_R,S_{rac}-**2-*d*** according to the literature procedure.[1]

Deuteriation of Sulfoxide. Into a 200-mL flask were placed 3.1 g (20.1 mmol) of S_S-**1** [$[\alpha]^{24}_D$ +100° (*c* 1.30, EtOH); mp 56–58 °C] and 70 mL of THF under an argon atmosphere. The mixture was cooled to −78 °C and stirred. A solution of *n*-butyllithium in hexane (13 mL, 20.3 mmol) was added to this mixture through a syringe. The mixture was kept at −78 °C for an additional 1 h and quenched with 4 mL of deuterium oxide. The reaction mixture was further stirred without cooling. Then, 20 mL of 2 N HCl was added, and the solvent was evaporated under reduced pressure. The residue was extracted with dichloromethane, and the organic layer was washed with water and dried over sodium sulfate. After evaporation of the solvent under reduced pressure, the residue was chromatographed on a column of silica gel with EtOAc/EtOH (9/1) as eluent to afford 1.4 g (45.2%) of S_S-**1-*d*** (mp 56–58 °C).

Oxidation of Sulfoxide. C_R,S_{rac}-**1-*d*** (mp 59–60 °C) was oxidized with *m*-chloroperbenzoic acid in dichloromethane into the corresponding sulfone [$[\alpha]^{24}_D$ +0.885° (*c* 0.565, $CHCl_3$); mp 123–125 °C], and the sign of optical rotation was compared with that of sulfone obtained from sulfoxide S_S-**1-*d*** [$[\alpha]^{24}_D$ −0.561° (*c* 0.535, $CHCl_3$); mp 123–124 °C].

S_R-**2** [$[\alpha]^{24}_D$ +140° (*c* 1.10, EtOH); mp 72–73 °C] was deuteriated similarly to give S_R-**2-*d***, which was further oxidized into *tert*-butyl phenylmethylsulfone [$[\alpha]^{24}_D$ −0.273° (*c* 2.56, EtOH); mp 122–123 °C] by *m*-chloroperbenzoic acid in dichloromethane at 0 °C, and the sign of optical rotation of this sulfone was compared with that of the sulfone obtained from C_R,S_{rac}-**2-*d*** [$[\alpha]^{24}_D$ +0.419 (*c* 4.53, EtOH); mp 124–125 °C].

Thus, it was confirmed, from the viewpoint of optical rotation, that the configurations at the benzylic carbons of both **1** and **2** are *S*, in agreement with the results from ^{1}H NMR spectroscopy.

Measurement of Nuclear Overhauser Effect. A sulfoxide, **1** or **2** (10 mg), was dissolved in 500 μL of $CDCl_3$, and the solution was subjected to ^{1}H NMR spectroscopy at room temperature or at −50 °C with tetramethylsilane as an internal standard.

The irradiation of the signal from the methyl group caused no appreciable difference in the increase in the intensity of the signal between the benzylic *pro-R* and *pro-S* protons in **1** and **2**.

(14) Lett, R.; Chassaing, G.; Marquet, A. *J. Organomet. Chem.* **1976**, *111*, C17–C20.

(15) We thank them for the gift.

Dipolar Cycloaddition Reactions of (Phenylsulfonyl)alkynes and (Phenylsulfonyl)propadiene with *C*,*N*-Diphenylnitrone

Patrizia Parpani and Gaetano Zecchi*

Dipartimento di Chimica Organica e Industriale dell'Università, 20133 Milano, Italy

Received July 30, 1986

The reaction of the title nitrone with (phenylsulfonyl)alkynes **1a,b** results in 3-acylindoles **6a,b** via unstable 4-isoxazoline cycloadducts which evolve by fission of the N–O bond and subsequent reclosure onto the ortho position of the *N*-phenyl substituent. Under the same conditions, the title nitrone reacts with (phenylsulfonyl)propadiene (**10**) to give the isomeric benzazepinone **12** and pyrrolidone **11**, both of which are presumably formed from a common, transient cycloadduct. Compound **12** changes readily through a novel pathway leading to the indole derivative **14**.

Extensive interest has been shown in Diels–Alder[1,2] and 1,3-dipolar[3] cycloadditions to ethylenic sulfones in view of the activating and (potentially) regiocontrolling effect of the sulfonyl group as well as of the synthetic usefulness of the resulting adducts through alkylation and/or desulfonylation. However, minor investigation has been done on the dienophilic[1,4] and dipolarophilic[5–8] reactivity of allenic and acetylenic sulfones. In previous papers,[6] we reported the reactions of (phenylsulfonyl)alkynes (**1a,b**) and (phenylsulfonyl)propadiene (**10**) with nitrile oxides and imines. In continuation of this line of research, we

(1) De Lucchi, O.; Modena, G. *Tetrahedron* **1984**, *40*, 2585 and references therein.

(2) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976. Kinney, W. A.; Crouse, G. D.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4986.

(3) For recent examples, see: De Benedetti, P. G.; Quartieri, S.; Rastelli, A.; De Amici, M.; De Micheli, C.; Gandolfi, R.; Gariboldi, P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 95. Caramella, P.; Albini, E.; Bandiera, T.; Corsico Coda, A.; Grünanger, P.; Marinone Albini, F. *Tetrahedron* **1983**, *39*, 689. Barzaghi, M.; Beltrame, P. L.; Dalla Croce, P.; Del Buttero, P.; Licandro, E.; Maiorana, S.; Zecchi, G. *J. Org. Chem.* **1983**, *48*, 3807. Bened, A.; Durand, R.; Pioch, D.; Geneste, P.; Guimon, C.; Guillouzo, G. P.; Declercq, J. P.; Germain, G.; Briard, P.; Rambaud, J.; Roques, R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1. Komatsu, M.; Yoshida, Y.; Uesaka, M.; Ohshiro, Y.; Agawa, T. *J. Org. Chem.* **1984**, *49*, 1300.

(4) Veniard, L.; Benaim, J.; Pourcelot, G.; Normant, M.-H. *C. R. Seances Acad. Sci., Ser. C* **1968**, 1092. Barbarella, C.; Cinquini, M.; Colonna, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1646. Guildford, A. J.; Turner, R. W. *J. Chem. Soc., Chem. Commun.* **1983**, 466. Hayakawa, K.; Nishiyama, H.; Kanematsu, K. *J. Org. Chem.* **1985**, *50*, 512.

(5) Guillerm, G.; L'Honoré, A.; Veniard, L.; Pourcelot, G.; Benaim, J. *Bull. Soc. Chim. Fr.* **1973**, 2739.

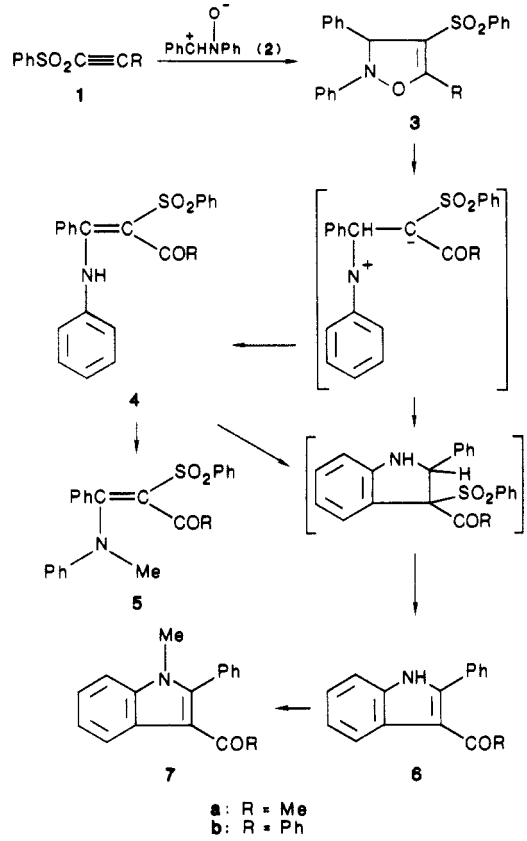
(6) (a) Bruché, L.; Gelmi, M. L.; Zecchi, G. *J. Org. Chem.* **1985**, *50*, 3206. (b) Dalla Croce, P.; La Rosa, C.; Zecchi, G. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2621.

(7) Blechert, S. *Justus Liebigs Ann. Chem.* **1985**, 673.

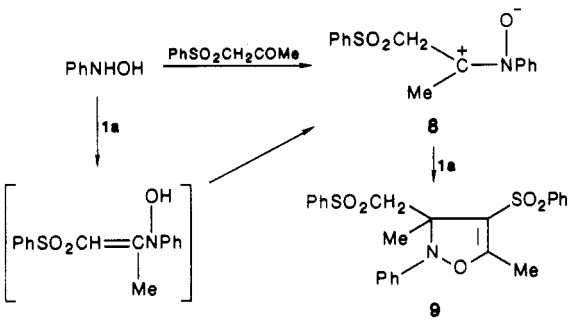
(8) Padwa, A.; Carter, S. P.; Chiacchio, U.; Kline, D. N. *Tetrahedron Lett.* **1986**, *27*, 2683.

0022-3263/87/1952-1417$01.50/0

Scheme I



Scheme II



have explored the behavior of the same dipolarophiles toward *C,N*-diphenylnitrone (**2**).

Results and Discussion

Compound **1** was treated with an equimolar amount of nitrone **2** in chloroform solution at room temperature. After 20 h, the chromatography of the product mixture gave compounds **3a**, **6a**, and **9** in 21%, 43%, and 7% yields, respectively. While the indole derivative **6a** was recognized upon comparison with an authentic sample,[9] the 4-isoxazoline structures **3a** and **9** were assigned on the basis of analytical and spectral data. Both IR and ^1H and ^{13}C NMR spectra compare well with the literature data for 4-isoxazolines.[10,11] The cycloadduct **3a** was found to decompose upon standing at room temperature (e.g., 30 h in chloroform) to afford the indole derivative **6a** in high yield; accordingly, compound **6a** was shown to be absent at an early stage of the reaction between **1a** and **2**.

When nitrone **2** was treated with alkyne **1b** under the same conditions, the 3-acylindole **6b** was again obtained as the major product along with its precursor, to which however was assigned the open-chain structure **4b** on the basis of analytical and spectral evidence. Treatment of **4b** with methyl iodide in the presence of sodium hydride led to the stable derivative **5b**, indeed accompanied by a sizable amount of **7b** due to the concomitant transformation of **4b** into **6b**.

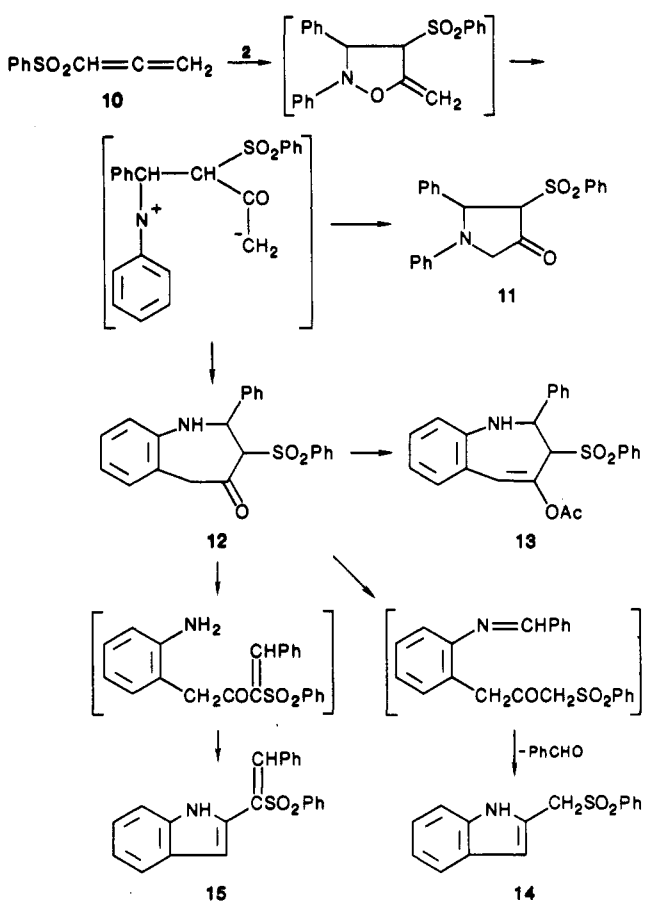
To accommodate the above results, we suggest a common multistep pathway in which the relative stability of the intermediates is strongly dependent on the substituents. As depicted in Scheme I, the proposed sequence involves (i) regiospecific 1,3-dipolar cycloaddition, (ii) ring cleavage of the cycloadduct through fission of the N–O bond, eventually followed by hydrogen shift, (iii) 1,5-cyclization onto the ortho position of the *N*-phenyl group, and (iv) aromatization of the so-formed dihydroindole by elimination of benzenesulfinic acid. Although 4-isoxazolines are known to undergo a wide variety of rearrangement and fragmentation reactions,[10] there is only a recent example of conversion to 3-acyl-2,3-dihydroindoles which has been interpreted in terms of a radical mechanism.[12] In the present case, an ionic pathway would seem more consistent with the obtainment of **4b** as well as with the observed acceleration on going from chloroform to ethanol as solvent. In spite of the presumable difficulty to generate nitrenium ions, the heterolysis of the N–O linkage in isoxazolines **3** may be facilitated by the stabilizing effect of the substituents at the incipient carbanionic center and/or by some degree of concertedness with the removal of the 3-hydrogen.

As to the side formation of **9**, Scheme II illustrates a plausible rationale in line with the following findings: (a) nitrone **2** slowly decomposes originating phenylhydroxylamine;[13] (b) treatment of **1a** with PhNHOH in a 2:1 molar ratio affords **9** in high yield; (c) nitrone **8**, prepared by treating (phenylsulfonyl)acetone with PhNHOH, reacts with **1a** to give **9** as the only product. The proposed formation of **8** from **1a** parallels the reported reaction of monosubstituted hydroxylamines with electron-poor acetylenes.[12,14]

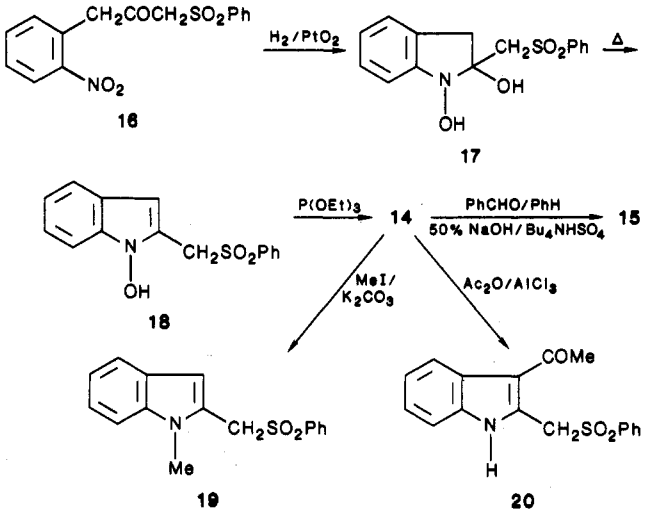
Let us consider now the reaction of allene **10** with nitrone **2** in chloroform solution at room temperature. After 16 h, the chromatography of the product mixture gave, in addition to some quantity of benzaldehyde, the pyrrolidone **11** (15%) and the indole **14** (47%) (Scheme III). However, both TLC and NMR analyses of the crude product mixture showed that another compound was present as the main component, which could be isolated in 36% yield upon fractional crystallization and identified as the benzazepinone **12**.[15] It was then ascertained that **12** originates a mixture of benzaldehyde and indole **14** on column chromatography as well as on prolonged standing in solution. When compound **12** was decomposed under heating, the new indole derivative **15** was obtained in a small quantity near to the largely predominant product **14**. The structures **11**, **12**, **14**, and **15** rely upon elemental analyses, molecular weights, and IR and NMR spectra. Chemical support is also available. In fact, the benzazepinone **12** was converted to the stable enol acetate **13** on treatment with acetic anhydride in the presence of triethylamine, while an independent synthesis and some

(9) Buchmann, G.; Rossner, D. *J. Prakt. Chem.* **1964**, *25*, 117.
(10) Freeman, J. P. *Chem. Rev.* **1983**, *83*, 241.
(11) For ^{13}C NMR of 4-isoxazolines, see: Pennings, M. L. M.; Okay, G.; Reinhoudt, D. N.; Harkema, S.; van Hummel, G. J. *J. Org. Chem.* **1982**, *47*, 4413. Khan, N.; Wilson, D. A. *J. Chem. Res.* **1984**, 150. Ashburn, S. P.; Coates, R. M. *J. Org. Chem.* **1984**, *49*, 3127.
(12) Padwa, A.; Wong, G. S. K. *J. Org. Chem.* **1986**, *51*, 3125.
(13) Hamer, J.; Macaluso, A. *Chem. Rev.* **1964**, *64*, 473.
(14) Aurich, H. G.; Hahn, K. *Chem. Ber.* **1979**, *112*, 2769.
(15) The isolation of compound **12** was facilitated (43%) when the reaction between **2** and **10** was carried out in ethanol (6 h).

Scheme III



Scheme IV



chemical transformations of indole **14** were performed as outlined in Scheme IV.

The mechanistic picture given in Scheme III deserves comment. The proposed intermediacy of a common, unstable cycloadduct in the formation of **11** and **12** is in line with previous findings.[16] On the other hand, while the rearrangement of 1-benzazepin-4-ones to 2-vinylindoles is already documented in the literature,[7] the conversion of **12** to **14** is novel and can be interpreted as proceeding through a retroaldol-type cleavage.

In conclusion, the reactions of **1a,b** and **10** with nitrone **2** exhibit two interesting, common features: (i) regiospecific 1,3-dipolar cycloaddition and (ii) ring opening of the cycloadduct followed by 1,5- or 1,7-cyclization onto the ortho position of the *N*-phenyl substituent. Within the frontier orbital model, the exclusive bond formation between the oxygen of the nitrone and the β-carbon of the sulfone is in harmony with the presence of a strongly electron-attracting group which determines a low-energy LUMO with the larger coefficient at the β-carbon. The poorer regioselectivity previously observed in the reaction of **10** with nitrile oxides[6a] reflects the increasing importance of the HOMO(dipole)–LUMO(dipolarophile) interaction on going from nitrile oxides to nitrones.[17] The site specificity observed in the case of **10** remains to be noted as a consequence of the pronounced activating effect of the sulfonyl group.

Experimental Section

Melting points were taken on a Büchi apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer 377 spectrophotometer. NMR spectra were recorded on Varian EM-390 (^{1}H) and Bruker WP80SY (^{13}C) instruments; chemical shifts are given in ppm from internal standard Me_4Si.

Compounds **1a**,[18] **1b**,[19] **2**,[20] and **10**[18] were prepared according to the literature methods.

Reaction of Nitrone 2 with Alkyne 1a. A solution of **2** (3.3 g) and **1a** (3.0 g) in chloroform (130 mL) was left at room temperature for 20 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column by using a diethyl ether–light petroleum (1:1) mixture as the eluent. First fractions gave 2,3-diphenyl-5-methyl-4-(phenylsulfonyl)-2,3-dihydroisoxazole (**3a**) (1.3 g, 21%): mp 82–83 °C (from hexane–benzene); IR (Nujol) 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.52 (d, 3 H, J = 1.2 Hz), 5.61 (q, 1 H, J = 1.2 Hz), 6.8–7.5 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 11.6 (q), 77.1 (d), 111.2 (s), 115.5 (d), 124.2 (d), 126.6 (d), 128.0 (d), 128.4 (d), 128.5 (d), 128.6 (d), 129.1 (d), 132.4 (d), 138.7 (d), 142.0 (s), 150.8 (s), 161.8 (s); MS, m/e 377 (M^+). Anal. Calcd for $C_{22}H_{19}NO_3S$: C, 70.01; H, 5.06; N, 3.71. Found: C, 69.96; H, 5.18; N, 3.52.

Subsequent fractions contained indole **6a**[9] (1.7 g, 43%). Further elution gave 3,5-dimethyl-2-phenyl-4-(phenylsulfonyl)-3-[(phenylsulfonyl)methyl]-2,3-dihydroisoxazole (**9**) (0.27 g, 7%): mp 126–127 °C dec (from diisopropyl ether); IR (Nujol) 1625 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 1.10 (s, 3 H), 2.57 (s, 3 H), 3.67, 3.93 (AB, 2 H, J = 15 Hz), 6.9–8.1 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 12.0 (q), 20.6 (q), 64.6 (t), 73.1 (s), 111.4 (s), 122.5 (d), 126.7 (d), 127.0 (d), 127.9 (d), 128.7 (d), 129.1 (d), 129.2 (d), 133.3 (d), 133.4 (d), 141.9 (s), 142.8 (s), 145.0 (s), 167.7 (s); MS, m/e 469 (M^+). Anal. Calcd for $C_{24}H_{23}NO_5S_2$: C, 61.39; H, 4.95; N, 2.99. Found: C, 61.38; H, 5.03; N, 3.00.

Conversion of Cycloadduct 3a to Indole 6a. A solution of **3a** (0.19 g) in chloroform (2 mL) was left at room temperature for 30 h. Evaporation of the solvent followed by recrystallization from acetone gave indole **6a** (0.10 g, 85%). When carried out in ethanol, the reaction was complete after 12 h.

***C*-Methyl-*N*-phenyl-*C*-[(phenylsulfonyl)methyl]nitrone (8).** A solution of phenylhydroxylamine (0.27 g) and (phenylsulfonyl)acetone[21] (0.50 g) in chloroform (20 mL) was treated with anhydrous sodium sulfate (2.0 g) and stirred at room temperature for 24 h. After filtration, the solvent was removed under reduced pressure, and the residue was taken up with diisopropyl ether to afford nitrone **8** (0.17 g, 24%): mp 108–112 °C (from diisopropyl ether); NMR ($CDCl_3$) δ 2.18 (s, 3 H), 4.78 (s, 2 H), 6.85–7.05 (m, 2 H), 7.25–7.45 (m, 3 H), 7.55–7.75 (m, 3 H), 8.0–8.15 (m, 2 H); MS, m/e 289 (M^+). Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.45; H, 5.35; N, 4.63.

Reaction of Nitrone 8 with Alkyne 1a. A solution of **8** (0.87 g) and **1a** (0.54 g) in chloroform (30 mL) was left at room tem-

(16) Tufariello, J. J. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Chapter 9; p 127.

(17) Houk, K. N.; Chang, Y.-M.; Strozier, R. W.; Caramella, P. *Heterocycles* **1977**, *7*, 793.

(18) Stirling, C. J. M. *J. Chem. Soc.* **1964**, *5856*.

(19) Beccalli, E. M.; Manfredi, A.; Marchesini, A. *J. Org. Chem.* **1985**, *50*, 2372.

(20) Wheeler, O. H.; Gore, D. H. *J. Am. Chem. Soc.* **1956**, *78*, 3363.

(21) Otto, R.; Otto, W. *J. Prakt. Chem.* **1887**, 403.

perature for 3 h. The solvent was evaporated, and the residue was treated with little diisopropyl ether to give adduct **9** (1.2 g, 85%).

Reaction of Alkyne 1a with Phenylhydroxylamine. A solution of **1a** (0.54 g) in chloroform (30 mL) was treated with phenylhydroxylamine (0.16 g) and left at room temperature for 25 h. Evaporation of the solvent gave practically pure **9** (0.63 g, 89%).

Reaction of Nitrone 2 with Alkyne 1b. A solution of **2** (1.7 g) and **1b** (2.1 g) in chloroform (70 mL) was left at room temperature for 22 h. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column with light petroleum–dichloromethane–diethyl ether (3:2:1) as the eluent. First fractions contained benzaldehyde (0.35 g). Subsequent fractions gave 1,3-diphenyl-3-(phenylamino)-2-(phenylsulfonyl)-2-propen-1-one (**4b**) (0.53 g, 14%): mp 155–156 °C (from diisopropyl ether–ethanol); IR (Nujol)[22] 1595 cm^{-1}; NMR (CD_3SOCD_3) δ 6.6–8.1 (m, 20 H), 10.2 (br s, 1 H, exchangeable); MS, m/e 439 (M^+). Anal. Calcd for $C_{27}H_{21}NO_3S$: C, 73.79; H, 4.82; N, 3.19. Found: C, 73.59; H, 4.86; N, 3.11.

Further elution provided 3-benzoyl-2-phenylindole (**6b**) (0.78 g, 30%): mp 218 °C (from hexane–benzene); IR (Nujol) 3180, 1590 cm^{-1}; NMR (CD_3SOCD_3) δ 7.0–7.9 (m, 14 H), 12.2 (br s, 1 H); MS, m/e 297 (M^+). Anal. Calcd for $C_{21}H_{15}NO$: C, 84.82; H, 5.09; N, 4.71. Found: C, 84.87; H, 5.22; N, 4.80.

Conversion of Adduct 4b to Indole 6b. A solution of **4b** (013 g) in chloroform (2 mL) was left at room temperature for 24 h. Evaporation of the solvent followed by recrystallization from acetone gave indole **6b** (65 mg, 72%).

Methylation of Adduct 4b. To a solution of **4b** (0.30 g) in dry benzene (15 mL) were added sodium hydride (70 mg) and methyl iodide (2.8 g). After 48 h of being stirred at room temperature, the mixture was poured into ice. The organic layer was separated, dried over sodium sulfate, and evaporated. The residue was chromatographed on a silica gel column with diethyl ether–light petroleum (1:1) as the eluent. The first product was indole **7b**[23] (80 mg). Subsequent fractions gave 1,3-diphenyl-3-(methylphenylamino)-2-(phenylsulfonyl)-2-propen-1-one (**5b**) (0.11 g): mp 153–155 °C (from pentane–chloroform); IR (Nujol) 1630 cm^{-1}; NMR ($CDCl_3$) δ 3.10 (s, 3 H), 6.3–8.0 (m, 20 H); MS, m/e 453 (M^+). Anal. Calcd for $C_{28}H_{23}NO_3S$: C, 74.14; H, 5.11; N, 3.08. Found: C, 73.89; H, 5.03; N, 2.86.

Reaction of Nitrone 2 with Allene 10. (A) A solution of **2** (2.24 g) and **10** (2.04 g) in chloroform (100 mL) was left at room temperature for 16 h. A part of the solvent was removed under reduced pressure, and the remaining solution was cooled at 0 °C. The separated crystals were collected by filtration to provide 4-oxo-2-phenyl-3-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepine (**12**) (1.5 g, 36%): mp 121 °C dec (from hexane–benzene); IR (Nujol) 3385, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.55 (br s, 1 H), 3.73 (d, 1 H, J = 13 Hz), 4.67 (d, 1 H, J = 10 Hz), 4.95 (d, 1 H, J = 13 Hz), 5.31 (dd, 1 H, J = 10 and 2 Hz), 6.4–7.7 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 47.6 (t), 59.4 (d), 82.8 (d), 118.2–145.5, 198.0 (s); MS, m/e 377 (M^+). Anal. Calcd for $C_{22}H_{19}NO_3S$: C, 70.01; H, 5.06; N, 3.71. Found: C, 70.19; H, 4.93; N, 3.88.

The mother liquor was evaporated, and the residue was subjected to chromatography on a silica gel column using a mixture of light petroleum–dichloromethane–diethyl ester (3:2:1) as the eluent. First fractions contained benzaldehyde (0.20 g). Subsequent fractions gave 1,5-diphenyl-3-oxo-4-(phenylsulfonyl)-2,3,4,5-tetrahydropyrrole (**11**) (0.63 g, 15%): mp 110–115 °C (from diisopropyl ether); IR (Nujol) 1765 cm^{-1}; ^1H NMR (C_6D_6) δ 3.43 (br s, 2 H), 3.62 (d, 1 H, J = 2.5 Hz), 5.70 (d, 1 H, J = 2.5 Hz), 6.0–6.15 (m, 2 H), 6.3–6.9 (m, 9 H), 7.3–7.7 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 55.4 (t), 60.9 (d), 78.6 (d), 112.5 (d), 118.4 (d), 125.5–144.7, 200.1 (s); MS, m/e 377 (M^+). Anal. Calcd for $C_{22}H_{19}NO_3S$: C, 70.01; H, 5.06; N, 3.71. Found: C, 69.98; H, 5.35; N, 3.66.

Further elution afforded 2-[(phenylsulfonyl)methyl]indole (**14**) (0.41 g, 14%): mp 190 °C dec (from hexane–benzene); IR (Nujol) 3320 cm^{-1}; NMR (CD_3COCD_3) δ 4.75 (s, 2 H), 6.20 (d, 1 H, J = 1.5 Hz; s after deuteriation of NH), 6.8–7.8 (m, 9 H), 10.2 (br s, 1 H); MS, m/e 271 (M^+). Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.84; N, 5.16. Found: C, 66.61; H, 4.57; N, 4.99.

(B) A solution of **2** (2.1 g) and **10** (1.9 g) in absolute ethanol (100 mL) was stirred at room temperature for 6 h. The precipitate was collected by filtration and washed with little ethanol to afford pure **12** (1.8 g, 43%).

Decomposition of Benzazepinone 12. (A) A solution of **12** (0.10 g) in chloroform (2 mL) was left at room temperature for 96 h. Evaporation of the solvent followed by washing with diisopropyl ether gave indole **14** (0.060 g). Benzaldehyde was detected in the mother liquor.

(B) A solution of **12** (1.8 g) in chloroform (40 mL) was refluxed for 65 h. The solvent was removed and the residue was chromatographed on a silica gel column. Elution with light petroleum–dichloromethane–diethyl ether (3:2:1) afforded benzaldehyde (0.40 g) followed by 2-[2-phenyl-1-(phenylsulfonyl)ethenyl]indole (**15**) (0.10 g, 6%): mp 210 °C dec (from hexane–benzene); IR (Nujol) 3410 cm^{-1}; NMR (CD_3SOCD_3) δ 6.10 (d, 1 H, J = 1.5 Hz; s after deuteriation of NH), 6.8–7.8 (m, 14 H), 8.05 (s, 1 H), 11.2 (br s, 1 H); MS, m/e 359 (M^+). Anal. Calcd for $C_{22}H_{17}NO_2S$: C, 73.54; H, 4.78; N, 3.90. Found: C, 73.74; H, 4.81; N, 3.79.

Subsequent fractions contained indole **14** (1.0 g, 77%).

4-Acetoxy-2-phenyl-2-(phenylsulfonyl)-2,3-dihydro-1*H*-1-benzazepine (13). Compound **12** (0.20 g) was treated with acetic anhydride (9 mL) and triethylamine (3 mL) and left at room temperature for 18 h. The mixture was poured into water and extracted with dichloromethane. The organic solution was dried over sodium sulfate and evaporated under reduced pressure. After addition of diisopropyl ether, filtration gave compound **13** (0.11 g): mp 180–182 °C dec (from hexane–benzene); IR (Nujol) 3360, 1755 cm^{-1}; NMR ($CDCl_3$) δ 2.03 (s, 3 H), 4.91 (d, 1 H, J = 4.0 Hz), 5.00 (d, 1 H, J = 8.0 Hz, exchangeable), 5.52 (dd, 1 H, J = 8.0 and 4.0 Hz, d after deuteriation of NH), 6.31 (s, 1 H), 6.35–7.45 (m, 12 H), 7.9–8.1 (m, 2 H); MS, m/e 419 (M^+). Anal. Calcd for $C_{24}H_{21}NO_4S$: C, 68.73; H, 5.05; N, 3.34. Found: C, 68.55; H, 5.22; N, 3.17.

1-(2-Nitrophenyl)-3-(phenylsulfonyl)-2-propanone (16). A solution of 1-bromo-3-(2-nitrophenyl)-2-propanone[24] (5.85 g) in DMF (25 mL) was treated with sodium benzenesulfinate (4.6 g). The mixture was stirred at room temperature for 40 min and then poured into cold water (80 mL). The precipitate was collected by filtration and recrystallized from ethanol to afford compound **16** (4.6 g): mp 112 °C; IR (Nujol) 1710 cm^{-1}; NMR ($CDCl_3$) δ 4.40 (s, 2 H), 4.44 (s, 2 H), 7.2–8.2 (m, 9 H); MS, m/e 319 (M^+). Anal. Calcd for $C_{15}H_{13}NO_5S$: C, 56.42; H, 4.10, N, 4.38. Found: C, 5.26; H, 4.07; N, 4.18.

1,2-Dihydroxy-2-[(phenylsulfonyl)methyl]-2,3-dihydroindole (17). A solution of **16** (0.60 g) in ethyl acetate (40 mL) was treated with 80% PtO_2 (30 mg) and stirred under hydrogen. When no more hydrogen was consumed, ethyl acetate was added (40 mL), the catalyst was filtered off, and the solvent was evaporated under reduced pressure. The residue was taken up with diisopropyl ether and filtered to afford **17** (0.33 g): mp 149–151 °C dec (from acetone); IR (Nujol) 3400, 3350 cm^{-1}; NMR (CD_3SOCD_3) δ 2.95, 3.38 (AB, 2 H, J = 16 Hz), 3.53, 3.93 (AB, 2 H, J = 14 Hz), 6.04 (s, 1 H, exchangeable), 6.5–7.2 (m, 4 H), 7.5–8.0 (m, 5 H), 8.85 (s, 1 H, exchangeable); MS, m/e 287 ($M^+ - 18$). Anal. Calcd for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.49; N, 4.59. Found: C, 58.78; H, 4.93; N, 4.72.

1-Hydroxy-2-[(phenylsulfonyl)methyl]indole (18). A solution of **17** (1.0 g) in toluene (50 mL) was refluxed for 1 h. After removal of the solvent, the residue was chromatographed on silica gel column with dichloromethane–diethyl ether (1:1) as the eluent to give **18** (0.81 g): mp 152–153 °C dec (from hexane–benzene); IR (Nujol) 3420 cm^{-1}; NMR ($CDCl_3$) δ 4.67 (s, 2 H), 5.95 (s, 1 H), 6.9–7.8 (m, 9 H), 8.0 (br s, 1 H, exchangeable); MS, m/e 287 (M^+). Anal. Calcd for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.55; N, 4.88. Found: C, 62.95; H, 4.49; N, 4.87.

Independent Synthesis of Indole 14. Compound **18** (0.56 g) was treated with triethyl phosphite (3 mL) and heated at 160 °C for 4 h. The mixture was taken up with ether and washed with an aqueous sodium chloride solution. The organic layer was

(22) No NH band was detectable, as amply precedented for β-amino α,β-unsaturated ketones: Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Methuen: London, 1958; p 254.

(23) Szmuszkovicz, J. *J. Org. Chem.* **1962**, *27*, 511.

(24) Schumack, W. *Arch. Pharmaz.* **1975**, 755.

dried over sodium sulfate and evaporated. Recrystallization of the residue from hexane–benzene gave indole **14** (0.25 g).

3-Acetyl-2-[(phenylsulfonyl)methyl]indole (20). A solution of **14** (0.16 g) in acetic anhydride (8 mL) was treated with anhydrous aluminum chloride and stirred at 100 °C for 72 h. The mixture was poured into ice and extracted with chloroform. The organic layer was washed with aqueous sodium hydrogen carbonate and dried over sodium sulfate. The solvent was removed, and the residue was taken up with diisopropyl ether to afford **20** (0.12 g): mp 175–177 °C (from hexane–benzene); IR (Nujol) 3320, 1665 cm^{-1}; NMR (CD_3SOCD_3) δ 2.40 (s, 3 H), 5.27 (s, 2 H), 7.1–8.0 (m, 9 H), 12.2 (br s, 1 H); MS, *m/e* 313 (M^+). Anal. Calcd for $C_{17}H_{15}NO_3S$: C, 65.16; H, 4.81; N, 4.47. Found: C, 65.23; H, 4.97; N, 4.59.

1-Methyl-2-[(phenylsulfonyl)methyl]indole (19). To a solution of **14** (0.15 g) in dry acetone (20 mL) were added potassium carbonate (4.0 g) a methyl iodide (4 mL). The mixture was stirred at room temperature for 5 days. The undissolved material was filtered off, the solvent was evaporated under reduced pressure, and the residue was recrystallized from hexane–benzene to give **19** (85 mg): mp 177 °C; NMR (CD_3COCD_3) δ 3.80 (s, 3 H), 4.89 (s, 2 H), 6.22 (s, 1 H), 6.8–7.9 (m, 9 H); MS, *m/e* 285 (M^+). Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.35; H, 5.29; N, 4.91. Found: C, 67.13; H, 5.31; N, 5.01.

Conversion of 14 into 15. To a solution of **14** (0.30 g) in benzene (30 mL) were added 50% sodium hydroxide (15 mL), tetrabutylammonium hydrogen sulfate (0.15 g), and benzaldehyde (0.30 g). The mixture was stirred at room temperature for 2 h. The organic layer was separated, washed with water, dried over sodium sulfate, and evaporated. The residue was chromatographed on a silica gel column with light petroleum–dichloromethane–diethyl ether (3:2:1) as the eluent to afford **15** (0.12 g).

Acknowledgment. We are indebted to M.P.I. (Rome) for financial support.

Registry No. **1a**, 2525-41-9; **1b**, 5324-64-1; **2**, 1137-96-8; **3**, 107081-84-5; **4b**, 107081-87-8; **5b**, 107081-88-9; **6a**, 17375-64-3; **6b**, 26862-65-7; **7b**, 26821-93-2; **8**, 107081-86-7; **9**, 107081-85-6; **10**, 2525-42-0; **11**, 107081-90-3; **12**, 107081-89-0; **13**, 107081-93-6; **14**, 107081-91-4; **15**, 107081-92-5; **16**, 107081-94-7; **17**, 107081-95-8; **18**, 107081-96-9; **19**, 107081-98-1; **20**, 107081-97-0; PhNHOH, 100-65-2; $PhSO_2CH_2COMe$, 5000-44-2; PhCHO, 100-52-7; 2-$O_2NC_6H_4CH_2COCH_2Br$, 57662-22-3; $PhSO_2Na$, 873-55-2.

Synthesis of 2-, 3- and 4-(Phenylseleno)benzonitrile by Electrochemically Induced Aromatic Nucleophilic Substitution in Acetonitrile

Chantal Degrand

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (UA 33), Faculté des Sciences Gabriel, 21000 Dijon, France

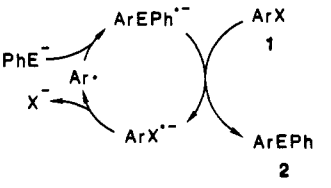
Received September 9, 1986

2-, 3- and 4-bromobenzonitrile have been electrolyzed in acetonitrile with sonication in the presence of an equivalent amount of benzeneselenate initially prepared by electrochemical reduction of diphenyl diselenide. Thus 2-, 3-, and 4-(phenylseleno)benzonitrile have been isolated in 36%, 42%, and 59% yields, respectively. The electrochemically generated aryl radical $NCC_6H_4^{\cdot}$ which is involved in the $S_{RN}1$ mechanism is deactivated partially by its further reduction to the corresponding anion and so the yields remain moderate. These yields can be improved by electrolysis of chlorobenzonitrile. A yield of 70% has been thus achieved in the case of 4-(phenylseleno)-benzonitrile. The two-electron cathodic reduction of the seleno derivatives is accompanied by the formation of cyanobenzeneselenate. Electrochemical reduction of 4-(phenylseleno)benzonitrile followed by chemical oxidation by air has given a mixture of 4,4'-dicyanodiphenyl diselenide and diphenyl diselenide, which have been isolated in 76% and 24% relative yields, respectively.

Benzenechalcogenates PhE^- (E = S, Se, Te) react with aromatic halides ArX under light stimulation by the $S_{RN}1$ aromatic nucleophilic substitution[1] (Scheme I) to give a large variety of unsymmetrical diaryl chalcogenides PhEAr.[1-6]

Liquid ammonia, which is a poor H atom donor, has mainly been used as solvent (SH) since the competitive reaction (1) is prevented.[1,3,7] However, satisfactory results

Scheme I[a]



[a] E = S, Se, Te.

can be also obtained in solvents such as dimethyl sulfoxide (Me_2SO).[3]

$$Ar^{\cdot} + SH \rightarrow ArH + S^{\cdot} \quad (1)$$

Saveant et al. have shown that electrons supplied from a cathode can initiate $S_{RN}1$ reactions with benzenethiolate

(1) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.
(2) (a) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173. (b) Galli, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 7140.
(3) Bunnett, J. F.; Scamehorn, R. G.; Traber, R. P. *J. Org. Chem.* **1976**, *41*, 3677.
(4) (a) Pierini, A. B.; Rossi, R. A. *J. Organomet. Chem.* **1978**, *144*, C12; (b) **1979**, *168*, 163. (c) Pierini, A. B.; Penenory, A. B.; Rossi, R. A. *J. Org. Chem.* **1984**, *49*, 486. (d) Penenory, A. B.; Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1984**, *49*, 3834.
(5) (a) Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1979**, *44*, 4667. (b) Rossi, R. A.; Palacios, S. M. *J. Org. Chem.* **1981**, *46*, 5300. (c) Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164.
(6) Palacios, S. M.; Alonso, R. A.; Rossi, R. A. *Tetrahedron* **1985**, *41*, 4147.
(7) (a) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120. (b) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. (c) Andrieux, C. P.; Savéant, J. M.; Zann, D. *Nouv. J. Chim.* **1984**, *8*, 107.

0022-3263/87/1952-1421$01.50/0