Cycloadducts of Phenylsulfonyl Cyanide *N*-Oxide and N-Substituted 1,2-Dihydropyridines. Regio- and Stereospecificity

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The regiospecific 1,3-dipolar cycloaddition reaction of phenylsulfonyl cyanide *N*-oxide with N-substituted 1,2-dihydropyridines (**1**) affords 3-(phenylsulfonyl)-3a,4,5,7a-tetrahydropyrido[3,4-*d*]isoxazoles (**2**). The stereochemical features of the cycloadducts **2** are described.

1,3-Dipolar cycloaddition reactions are valuable methods for the synthesis of a variety of five-membered heterocycles.[1] The reaction of simple olefins with phenylsulfonyl cyanide *N*-oxide,[2] cyanogen *N*-oxide, and carbethoxyformonitrile oxide[3] is a useful procedure for the preparation of cis vicinal cyano hydroxy compounds. The reaction of activated nitrile oxides with heterocyclic dienamines is an attractive route applicable to the synthesis of novel bicyclo heterocycles with potentially useful pharmacological activities. In our studies of various addition reactions[4] to *N*-substituted 1,2-dihydropyridines, we now describe the reaction of phenylsulfonyl cyanide *N*-oxide with **1** and the stereochemistry of the cycloadducts obtained.

Chemistry

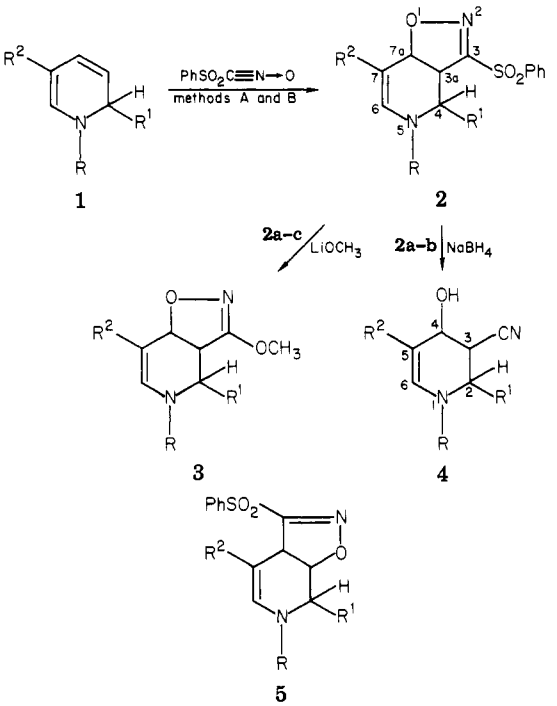
The reaction of *N*-(methoxycarbonyl)-2-phenyl-1,2-dihydropyridine (**1a**) with phenylsulfonyl cyanide *N*-oxide using methods A[2a] and B[2b] (Scheme I) afforded only one regioisomer, viz., 3-(phenylsulfonyl)-5-(methoxycarbonyl)-4-phenyl-3a,4,5,7a-tetrahydropyrido[3,4-*d*]isoxazole (**2a**), in 38% and 40% yield, respectively. Similarly reactions of **1b–e** with phenylsulfonyl cyanide *N*-oxide using methods A and B gave **2b–e** in comparable yield (Table I).[5] Treatment of **2a–c** with lithium methoxide in methanol yielded the 3-methoxy derivatives **3a–c**. The sodium borohydride reduction of **2a–b** at 0 °C in methanol gave the cis cyano alcohols **4a–b**.

Discussion

The assignment of the regio- and the stereochemistry of products **2–4** was based on their ^{1}H NMR spectral data and the single crystal X-ray analysis of **2a**. Proton resonance assignments rest largely on decoupling experiments. The ^{1}H NMR spectra of **2a–d**, **3a–c**, and **4a–b** were not well-resolved at 25 °C due to the presence of rotational conformers which differ in configuration at the carbonyl to nitrogen bond (amide bond) of the tetrahydropyridine ring system.[4a,6] The ^{1}H NMR spectra of these compounds were well-resolved at temperatures of +60–110 °C (Table I) which is sufficient to induce coalescence of the rotamers. On the other hand, product **2e**, in which hindered internal rotation about N-5 is not possible, exhibited a well-resolved ^{1}H NMR spectrum at 25 °C. The ^{1}H NMR spectra for compounds **2a–e** indicate that addition of phenylsulfonyl cyanide *N*-oxide occurred at the C_3–C_4 olefinic bond of dihydropyridines **1**. A comparison of the ^{1}H NMR spectral data for products **2**, **3**, and **4** indicates that regioisomer **2**, rather than **5**, was obtained. Thus, substitution of the phenylsulfonyl moiety by a methoxyl substituent resulted in an upfield shift of δ 0.5 for H4 of **2**. This indicates that the shielded proton must have been located in the deshielding cone of the sulfonyl group thereby precluding regioisomer **5**. The chemical shift positions for H6 and H7 for compounds **2** and **3** were very similar providing further evidence for regioisomer **2**. Finally, irradiation studies for **4a–b** showed that the hydroxyl substituent was located at the C-4 position[7] which confirms the cycloadduct as regioisomer **2**.

A single crystal X-ray diffraction analysis for **2a** was obtained to study the stereochemical aspects of the cy-

Scheme I[a]



a, R = COOMe; R^1 = Ph; R^2 = H; **b**, R = COOMe, R^1 = R^2 = H; **c**, R = COMe; R^1 = Ph; R^2 = H; **d**, R = COMe; R^1 = *n*-Bu; R^2 = H; **e**, R = Me; R^1 = *t*Bu; R^2 = CN

[a] Method A: $PhSO_2(Br)C{=}NOH$/TEA. Method B: $PhSO_2CH_2NO_2/CH_2N_2$/sodium metasilicate.

(1) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565 and 633.
(2) (a) Wade, P. A.; Hinney, H. R. *J. Am. Chem. Soc.* **1979**, *101*, 1319. (b) Wade, P. A.; Pillay, M. K. *J. Org. Chem.* **1981**, *46*, 5425.
(3) Kozikowski, A. P.; Adamczyk, M. *J. Org. Chem.* **1983**, *48*, 366.
(4) (a) Knaus, E. E.; Avasthi, K.; Giam, C. S. *Can. J. Chem.* **1980**, *58*, 2447. (b) Ondrus, T. A.; Knaus, E. E.; Giam, C. S. *Can. J. Chem.* **1978**, *56*, 1026. (c) Dubey, S. K.; Knaus, E. E. *Ibid.* **1983**, *61*, 565.
(5) The chemical yields were calculated from the amount of 1,2-dihydropyridine **1** employed in the reaction. The unreacted **1** present in the reaction product was recovered after TLC or column separation thereby providing a near quantitative material balance for the 1,2-dihydropyridines **1**.
(6) Szarek, W. A.; Wolfe, S.; Jones, J. K. N. *Tetrahedron Lett.* **1964**, 2743. (b) Yamamoto, G.; Raban, M. *J. Org. Chem.* **1976**, *41*, 3788.
(7) For compound **4b**, irradiation at δ 6.8 (H6) causes coalescence of the dd at δ 4.94 to a doublet which identified the position of H5. Irradiation at δ 4.94 identified H4 at δ 4.3 while irradiation of H4 caused coalescence of the doublet at δ 5.54 to a singlet. Irradiation at δ 5.54 reduced only the quartet at δ 4.3 to a triplet. Addition of deuterium oxide confirmed the position of the hydroxyl at δ 5.54. Furthermore, irradiation of H3 at δ 3.24–3.88 has no effect on the hydroxyl resonance at δ 5.54 thereby establishing the position of the hydroxyl at C4. A similar study for **4a** also showed the hydroxyl was located at C4.

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Table I. ^{1}H NMR Data for 3a,4,5,7a-Tetrahydropyrido[3,4-*d*]isoxazoles (2 and 3) and *cis*-1-(Methoxycarbonyl)-3-cyano-4-hydroxy-1,2,3,4-tetrahydropyridines (4a,b)

compd	% yield, method A	% yield, method B	mp, °C	chemical shifts[a] and coupling constants, Hz	formula[b]
2a	38.4	41.9	115.5–116.5	(Me_2SO-d_6, +50 °C): 7.68–8.06 (m, 5 H, SO_2Ph), 7.18–7.46 (m, 5 H, Ph), 7.12 (d, $J_{6,7}$ = 8.5 Hz, 1 H, H_6), 5.94 (br s, 1 H, H_4), 5.29 (d, $J_{3a,7a}$ = 10 Hz, of d, $J_{7a,7}$ = 3 Hz, 1 H, H_{7a}), 4.9 (br dd, 1 H, H_7), 4.76 (d, $J_{3a,7a}$ = 10 Hz, of d, $J_{3a,4}$ = 2 Hz, 1 H, H_{3a}), 3.66 (s, 3 H, OMe)	$C_{20}H_{18}N_2O_5S$
2b	33	35	viscous oil	(Me_2SO-d_6, +60 °C): 7.66–8.04 (m, 5 H, Ph), 7.05 (d, $J_{6,7}$ = 8 Hz, 1 H, H_6), 5.2 (d, $J_{3a,7a}$ = 8 Hz, of d, $J_{7a,7}$ = 4 Hz, 1 H, H_{7a}), 5.13 (dd, 1 H, H_7), 3.88–4.07 (m, 2 H, H_{3a}, H_{4eq}), 3.72 (s, 3 H, OMe), 3.43 (q, $J_{4ax,4eq}$ = 14.5 Hz, $J_{4ax,3a}$ = 9.5 Hz, 1 H, H_{4ax})	$C_{14}H_{14}N_2O_5S$
2c	37	41	162–162.5	(Me_2SO-d_6, +100 °C): 7.66–8.06 (m, 5 H, SO_2Ph), 7.28–7.44 (m, 5 H, Ph), 7.23 (d, $J_{6,7}$ = 7.5 Hz, 1 H, H_6), 6.16 (br s, 1 H, H_4), 5.26 (d, $J_{3a,7a}$ = 10 Hz, of d, $J_{7a,7}$ = 3 Hz, 1 H, H_{7a}), 4.9 (dd, 1 H, H_7), 4.72 (dd, $J_{3a,4}$ = 2 Hz, 1 H, H_{3a}), 2.08 (s, 3 H, COMe)	$C_{20}H_{18}N_2O_4S$
2d	55	29	121–122	(Me_2SO-d_6, +100 °C): 7.6–8.0 (m, 5 H, Ph), 6.7–7.3 (br s, 1 H, H_6), 5.49 (d, $J_{3a,7a}$ = 10 Hz, of d, $J_{7a,7}$ = 3 Hz, 1 H, H_{7a}), 4.7–5.2 (m, 2 H, H_4, H_7), 4.3 (dd, $J_{3a,4}$ = 1.5 Hz, 1 H, H_{3a}), 3.0 (s, 3 H, COMe), 1.86–2.3 (m, 2 H, C_4-CH_2CH_2), 1.1–1.75 (m, 4 H, $-CH_2CH_2CH_3$), 0.88 (t, 3 H, $-CH_2CH_3$)	$C_{18}H_{22}N_2O_4S$
2e	14		216	($CDCl_3$): 7.64–7.98 (m, 5 H, Ph), 7.08 (s, 1 H, H_6), 5.29 (d, $J_{3a,7a}$ = 10 Hz, 1 H, H_{7a}), 4.29 (dd, $J_{3a,4}$ = 1 Hz, 1 H, H_{3a}), 3.88 (br d, 1 H, H_4), 3.2 (s, 3 H, N-*Me*), 1.08 (s, 9 H, *t*-C_4H_9)	$C_{18}H_{21}N_3O_3S$
3a	59		130–131	(Me_2SO-d_6, +60 °C): 7.2–7.42 (m, 5 H, Ph), 7.10 (d, $J_{6,7}$ = 7.25 Hz, 1 H, H_6), 5.45 (br s, 1 H, H_4), 4.9 (d, 2 H, H_7, H_{7a}), 4.24 (d, $J_{3a,7a}$ = 8.5 Hz, of d, $J_{3a,4}$ = 2 Hz, 1 H, H_{3a}), 3.84 (s, 3 H, OMe), 3.68 (s, 3 H, CO_2Me)	$C_{15}H_{16}N_2O_4$
3b	86		viscous oil	(Me_2SO-d_6, +60 °C): 6.99 (d, $J_{6,7}$ = 8.25 Hz, 1 H, H_6), 5.02 (d, $J_{7,7a}$ = 4.5 Hz, 1 H, H_7), 4.9 (dd, $J_{3a,7a}$ = 7.5 Hz, 1 H, H_{7a}), 3.8 (s, 3 H, OMe), 3.66–3.78 (m, 4 H, H_{4eq}, CO_2Me), 3.4–3.56 (m, 2 H, H_{3a}, H_{4ax})	$C_9H_{12}N_2O_4$
3c	61		75.5–77	(Me_2SO-d_6, +110 °C): 7.22–7.44 (m, 5 H, Ph), 7.18 (br d, $J_{6,7}$ = 7.5 Hz, 1 H, H_6), 5.68 (br s, 1 H, H_4), 4.84–4.96 (m, 2 H, H_{7a}, H_7), 4.25 (d, $J_{3a,7a}$ = 9 Hz, of d, $J_{3a,4}$ = 2.25 Hz, 1 H, H_{3a}), 3.84 (s, 3 H, OMe), 2.15 (s, 3 H, COMe)	$C_{15}H_{15}N_2O_3$
4a	17.4		viscous oil	(Me_2SO-d_6, +50 °C): 7.2–7.46 (m, 5 H, Ph), 7.06 (d, $J_{5,6}$ = 8.5 Hz, of d, $J_{4,6}$ = 2 Hz, of d, $J_{2,6}$ = 1.0 Hz, 1 H, H_6), 5.65 (br d, $J_{2,3}$ = 2.5 Hz, 1 H, H_2), 5.52 (d, $J_{4,OH}$ = 4.5 Hz, 1 H, OH, exchanges with D_2O), 4.9 (d, $J_{5,6}$ = 8.5 Hz, of d, $J_{4,5}$ = 2 Hz, of d, $J_{3,5}$ = 1.5 Hz, 1 H, H_5), 3.64–3.84 (m, 5 H, H_3, H_4, OMe)	$C_{14}H_{14}N_2O_3$
4b	18		viscous oil	(Me_2SO-d_6, +60 °C): 6.8 (d, $J_{5,6}$ = 9 Hz, of d, $J_{4,6}$ = 1.5 Hz, 1 H, H_6), 5.54 (d, $J_{4,OH}$ = 5.25 Hz, 1 H, OH, exchanges with D_2O), 4.94 (dd, $J_{4,5}$ = 3.75 Hz, 1 H, H_5), 4.3 (d, $J_{4,OH}$ = 5.25 Hz, of d, $J_{3,4}$ = 3.75 Hz, 1 H, H_4), 3.6–3.9 (m, 5 H, OMe, H_{2ax}, H_{2eq}), 3.24–3.38 (m, $J_{2ax,3}$ = 7.1 Hz, $J_{2eq,3}$ = 3.4 Hz, 1 H, H_3)	$C_8H_{10}N_2O_3$

[a] Chemical shifts in ppm relative to Me_4Si (δ 0). [b] All the compounds gave analyses for C, H and N within ±0.4% of theoretical values and/or exact mass high-resolution mass measurements.

cloadducts. (See the paragraph at the end of the paper about supplementary material). The projection illustrated in Figure 1 clearly defines the stereochemistry at C4, C3a, and C7a. The torsional angle between C3–C3a–C4–CPh is 164.5° indicating for **2a** that the phenyl substituent at C4 and the 3a–3 carbon–carbon bond are in axial conformations while the two hydrogen atoms at C4 and C3a are equatorial since the H3a–C3a–C4–H4 torsional angle is −70.5°. The small torsional angle H3a–C3a–C7a–H7a of −26.5° between H3a and H7a indicates the ring junction is cis. The orientation of the R^1 substituent for **2c–e** at C4, by analogy to **2a**, was assigned an axial conformation since the $J_{3a,4}$ coupling constant was in the range of 1–3 Hz in all compounds. Wenkert et al.[8] have shown that a methyl or 3-pyridyl substituent at C2 in *N*-benzoylpiperidines exists in the axial conformation.

A comparative ^{1}H NMR study revealed that the adducts obtained from the reaction of phenylsulfonyl cyanide *N*-oxide with 2-substituted (**1a**, **1c–e**) and 2-unsubstituted (**1b**) 1,2-dihydropyridines have different conformations.

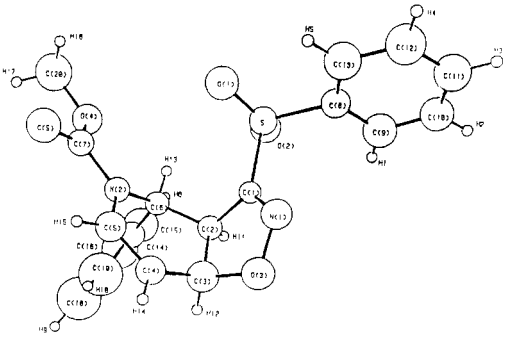
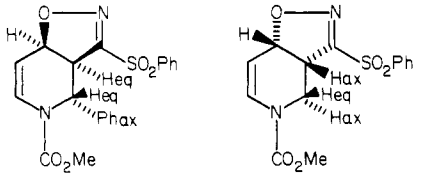


Figure 1. Perspective view of the molecule **2a** showing the atom numbering scheme. Atoms are represented as 50% thermal ellipsoids except for the H atoms which are drawn arbitrarily small for clarity.

The coupling constant $J_{4ax,3a}$ for **2b** was 9.5 Hz thereby fixing the proton at C3a as axial. On the other hand, the $J_{3a,4}$ coupling constant for **2a** and **2c–e** was always in the range of 1–3 Hz thereby suggesting that the proton at C3a is in the equatorial orientation. The X-ray diffraction data for **2a** show the protons at C4 and C3a as being equatorial. The different orientations of the protons at C3a for **2a,c–e**

(8) Wenkert, E.; Bindra, J. S.; Chang, C. J.; Cochran, D. W.; Schell, F. M.; *Acc. Chem. Res.* **1974**, *7*, 46.

and **2b** clearly indicate that the most stable conformation



2a **2b**

for compound **2b** is opposite to that for compounds **2a,c–e**. The N5 atom of **2b** is directed away from the five-membered ring whereas for compounds **2a,c–e** the N5 atom is directed toward the five-membered ring. However, in case of 2-substituted 1,2-dihydropyridines **2a,c–e** addition of the 1,3-dipole is from the least-hindered face opposite to the R^1 substituent.

Experimental Section

Melting points were determined with a Büchi capillary apparatus and are uncorrected. Nuclear magnetic resonance spectra were determined for solutions of deuteriodimethyl sulfoxide or deuteriochloroform with a Bruker WH-200 spectrometer. Double resonance studies were used to confirm assignments. Infrared spectra (potassium bromide unless otherwise noted) were recorded on a Unicam SP-1000 spectrometer. Mass spectra were measured on an AEI MS-50 mass spectrometer. N-Substituted 1,2-dihydropyridines (1) were prepared by literature procedures.[9]

3-(Phenylsulfonyl)-4-phenyl-5-(methoxycarbonyl)-3a,4,5,7a-tetrahydropyrido[3,4-*d*]isoxazole (2a). Method A. A solution of the bromo oxime[2a] (0.264 g, 1 mmol) in tetrahydrofuran (10 mL) was added dropwise to a mixture of **1a** (0.235 g, 1.1 mmol) and triethylamine (0.144 mL, 1 mmol) in tetrahydrofuran (40 mL) at 0 °C during 30 min with stirring. The reaction was allowed to proceed at 25 °C with stirring for 24 h. Water (10 mL) was added and the reaction mixture was extracted with chloroform (4 × 20 mL). The combined extracts were dried (Na_2SO_4) and the solvent was removed in vacuo. The product was purified on silica gel G plates (20 × 20 cm, 0.75 mm in thickness) using chloroform as development solvent to yield **2a** (0.153 g, 38.4%): mp 115.5–116.5 °C (MeOH); IR 1730 (CO) and 1655 cm^{-1} (C=N, C=C). Anal. Calcd for $C_{20}H_{18}N_2O_5S$: C, 60.30; H, 4.52; N, 7.03. Found: C, 60.25; H, 4.54; N, 7.06.

Crystals for X-ray analysis were obtained by slow growth in a sealed chamber saturated with hexane with **2a** dissolved in methanol in a small vial inside the chamber.

Method B. A solution of diazomethane, prepared from *N*-methyl-*N*-nitrosourea (1.5 g) and potassium hydroxide (2.2 g), in ether was added during 10 min to an ice-cold solution of (phenylsulfonyl)nitromethane (1.0 g, 5 mmol) in methylene chloride (20 mL) with stirring until the yellow color persisted. The ice-cooled reaction mixture was allowed to stir for 30 min and the excess diazomethane was removed at 0–5 °C under vacuum. A solution of **1a** (1.07 g, 5 mmol) in methylene chloride (100 mL) and aqueous sodium metasilicate (1.0 M, 15 mL) were added and the reaction mixture was heated at reflux with stirring for 12 h. The organic layer was separated and the aqueous layer extracted with methylene chloride (2 × 10 mL). The combined extracts were washed with water (5 mL) and dried (Na_2SO_4) and the solvent was removed in vacuo to yield crude **2a**. The pure sample was obtained by elution from a short neutral alumina oxide column using chloroform which afforded pure **2a** (0.625 g, 41.9%).

Compounds **2b–e** were also prepared by methods A and B as described above.

3-Methoxy-4-phenyl-5-(methoxycarbonyl)-3a,4,5,7a-tetrahydropyrido[3,4-*d*]isoxazole (3a). A solution of **2a** (0.398 g, 1 mmol) and lithium methoxide (0.038 g, 1 mmol) in dry methanol (40 mL) was heated at reflux for 4 h with stirring. The solvent was removed in vacuo and water (10 mL) was added. Extraction with chloroform (5 × 10 mL), drying (Na_2SO_4), and removal of the solvent in vacuo gave crude **3a**. Purification on silica gel G plates (20 × 20 cm, 0.75 mm thickness) with chloroform as development solvent yielded **3a** (0.17 g, 59%): mp 130–131 °C; IR 1730 (CO), 1650 (C=C), and 1625 cm^{-1} (C=N). Anal. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.5; H, 5.55; N, 9.72. Found: C, 62.51; H, 5.59; N, 9.71.

Compounds **3b–c** were similarly prepared from **2b–c**.

***cis*-1-(Methoxycarbonyl)-2-phenyl-3-cyano-4-hydroxy-1,2,3,4-tetrahydropyridine (4a).** Sodium borohydride (0.228 g, 6 mmol) was added in small aliquots during 15 min to a solution of **2a** (0.796 g, 2 mmol) in dry methanol (50 mL) at 0 °C with stirring. The reaction was allowed to proceed at 0 °C until the starting material was consumed as indicated by micro TLC with chloroform as development solvent. The reaction mixture was poured onto ice (50 g). Extraction with chloroform (5 × 15 mL), drying (Na_2SO_4), and removal of the solvent in vacuo gave impure **4a**. Purification on silica gel G plates (20 × 20 cm, 0.75 mm thickness) with chloroform–ether (2:3 v/v) as development solvent afforded **4a** (0.09 g, 17.44%); IR 3480–3500 (OH), 2260 (CN), 1725 (CO), and 1655 cm^{-1} (C=C); exact mass calcd for $C_{14}H_{14}N_2O_3$, 258.1005; found (high-resolution ms), 258.1003.

Compound **4b** was similarly prepared from **2b**.

Crystallographic Experimental Data. Crystals of 3-(phenylsulfonyl)-4-phenyl-5-(methoxycarboxyl)-3a,4,5,7a-tetrahydropyrido[3,4-*d*]isoxazole (**2a**) were obtained from methanol/hexane as triclinic, space group *P*-1 with a = 7.830 (1), b = 16.636 (3), c = 7.596 (2) Å, α = 90.77 (2), β = 104.07 (1), γ = 81.69 (1)°, v = 949.44 Å^3, Z = 2, D_c = 1.394 g/cm^3 and μ = 1.95 cm^{-1} ($C_{20}H_{18}N_2O_5S$ = 398.44). A small crystal fragment, of approximate dimensions 0.15 × 0.04 × 0.21 mm, was mounted in a nonspecific orientation on an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed using Mo Kα radiation (γ = 0.71073 Å) with a graphite crystal, incident beam monochromator. The intensity data were collected at room temperature using an ω–2θ scan ranging in speed from 10.1 to 1.1 deg/min (in ω). A total of 2719 reflections were collected, to a maximum 2θ limit of 45°, and after correction for Lorentz, polarization, and background effects, there were 697 reflections ($I \geq 3\sigma(I)$) which were considered observed. The structure was solved by direct methods. Refinement of atomic parameters was carried out by using full-matrix least-squares techniques on F_o, giving final agreement factors of R_1 = 0.091 and R_2 = 0.112. The final model had all non-hydrogen atoms refined as isotropic atoms and included the contributions for the hydrogen atoms in their calculated positions.

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Registry No. **1a**, 54732-59-1; **1b**, 33707-36-7; **1c**, 35022-78-7; **1d**, 61340-79-2; **1e**, 87843-05-8; **2a**, 87843-06-9; **2b**, 87843-07-0; **2c**, 87843-08-1; **2d**, 87843-09-2; **2e**, 87843-10-5; **3a**, 87843-11-6; **3b**, 87843-12-7; **3c**, 87843-13-8; **4a**, 87843-14-9; **4b**, 87843-15-0; $PhSO_2C(Br)$=NOH, 70367-23-6; (phenylsulfonyl)nitromethane, 21272-85-5; phenylsulfonyl cyanide *N*-oxide, 70367-24-7.

Supplementary Material Available: X-ray data tables for compound **2a**, positional and thermal parameters and their estimated standard deviations, derived positional and thermal parameters for hydrogen atoms, bond distances (Å), bond angles (deg), torsional angles (deg), and observed and calculated structure factors for observed data (11 pages). Ordering information is given on any current masthead page.

(9) (a) Giam, C. S.; Knaus, E. E.; Pasutto, F. M. *J. Org. Chem.* **1974**, *39*, 3565. (b) Fowler, F. W. *Ibid.* **1972**, *37*, 1321. (c) El Din, M. G.; Knaus, E. E.; Giam, C. S. *Can. J. Chem.* **1982**, *60*, 821.

(10) (a) This X-ray crystallographic study was carried out by Dr. R. G. Ball at the Structure Determination Laboratory, Department of Chemistry, University of Alberta. Inquiries regarding the crystallographic results should be directed to the above address quoting report number SR: 242004-01-82. (b) The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD4F diffractometer with some local modifications and additions. (c) The computer programs used in this analysis include the Enraf-Nonius Structure Determination Package by Fenz (Fenz, B. A. "Computing in Crystallography"; Delft University Press: Delft, Holland; 1978, pp 64–71) and several locally written or modified programs. (d) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. "MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data".