Table I. Arylsulfonamides and Arylsulfonates

substrate	mol % imidazolium reagent 2[a]	coupling time[b] (h)	yield (%)	product
1. diisopropylamine	120	21	71	*N*-(benzenesulfonyl)diisopropylamine (**3a**)
2. proline	400	10	80	*N*-(benzenesulfonyl)proline (**3b**)
3. 1,3,5-trihydroxybenzene	350	15	100	1,3,5-tris(TsO)benzene (**4a**)
4. 1,3,5-trihydroxybenzene	350	5	100	1,3,5-tris(BsO)benzene (**4b**)
5. catechol	240	1.5	100	1,2-bis(BsO)benzene (**4c**)
6. 2,6-dimethylphenol	125	1.5	76	[(benzenesulfonyl)oxy]-2,6-dimethylbenzene (**4d**)
7. (−)-menthol	125	24	95	(−)-menthyl benzenesulfonate (**4a**)
8. methyl α-D-glucoside	800	21	100	methyl *O*-tetrakis(benzenesulfonyl)-α-D-glucoside (**4f**)

[a] Formation of the imidazolium reagent proceeded for 30–35 min; for entries 3–8, 100 mol % of *N*-methylimidazole was then added. [b] All couplings began at 0 °C and were then allowed to reach rt.

mixture was stirred at 0 °C for 2 h and rt for 21 h. Isolation as for **4a** followed by passage through a short silica column (20% EtOAc/hexanes) afforded 170 mg, 71% yield, of **3a**: mp 88–89 °C; ^{1}H NMR δ 7.87 (d, 1 H, *J* = 6.0, *p*-ArH), 7.48 (m, 4 H, *o*-, *m*-ArH), 3.71 (septet, 2 H, *J* = 6.8, isopropyl-H), 1.25 (d, 12 H, *J* = 6.8, isopropyl-CH_3); ^{13}C NMR δ 142.5, 131.8, 128.7, 127.1, 48.6, 21.9; R_f 0.36 (20% EtOAc/hexanes). Anal. Calcd for $C_{12}H_{19}NO_2S$: C, 59.7; H, 7.9; N, 5.8. Found: C, 59.6; H, 8.0; N, 5.6.

***N*-(Benzenesulfonyl)proline (3b).** To a slurry of *S*-proline (230 mg, 2.0 mmol) in THF (12 mL) was added the 1-(benzenesulfonyl)-3-methylimidazolium triflate reagent (**2b**, 8.6 mmol). Following stirring at 0 °C for 1 h and rt for 10 h, the reaction mixture was diluted with half-saturated Na_2CO_3 (40 mL) and extracted with ethyl acetate (2 × 30 mL). The aqueous phase was adjusted to pH 2 with 85% H_3PO_4 and extracted with 2-propanol/$CHCl_3$ (1/4, 3 × 30 mL). The resulting combined organic phase was washed with brine (25 mL), dried over $MgSO_4$, filtered, and evaporated, affording 400 mg, 80% yield, of crystalline *N*-(benzenesulfonyl)proline, mp 83–85 °C (lit.[3b] mp 84–86 °C).

1,3,5-Tris[(*p*-toluenesulfonyl)oxy]benzene (4a). To a solution of 1,3,5-trihydroxybenzene (126 mg, 1.0 mmol) in THF (20 mL) containing *N*-methylimidazole (42 mg, 0.5 mmol) was added the 1-tosyl-3-methylimidazolium triflate reagent (**2a**, 3.55 mmol). Following stirring at 0 °C for 1 and 10 h at rt, the now homogenous solution was subjected to the isolation procedure used for **4a**. Chromatography (20% EtOAc/hexanes) afforded 590 mg, 100% yield, of **4a**: mp 84–86 °C (lit.[11] mp 82–83 °C); R_f 0.53 (50/50 EtOAc/Hex).

1,3,5-Tris[(benzenesulfonyl)oxy]benzene (4b). To a solution of 1,3,5-trihydroxybenzene (151 mg, 1.2 mmol) in THF (25 mL) containing *N*-methylimidazole (82 mg, 1.0 mmol) was added the 1-(benzenesulfonyl)-3-methylimidazolium triflate reagent (**2b**, 3.6 mmol). Following stirring at 0 °C for 30 min and rt for 6 h and isolation as for **4a**, LPC (40% EtOAc/hexanes) afforded 655 mg, 100% yield, of **4b**: mp 108–110 °C; TLC (20% EtOAc/hexanes) R_f 0.36. Anal. Calcd for $C_{24}H_{18}O_9S_3$: C, 52.7; H, 3.3. Found: C, 53.4; H, 3.2.

1,2-Bis[(benzenesulfonyl)oxy]benzene (4c). Following the procedure for preparation of **4b**, from the 1-(benzenesulfonyl)-3-methylimidazolium triflate reagent (**2b**, 2.4 mmol) and a solution of 1,2-dihydroxybenzene (110 mg, 1.0 mmol) and *N*-methylimidazole (82 mg, 1.0 mmol) in THF (10 mL), was obtained 1,2-bis[(benzenesulfonyl)oxy]benzene (**4c**) in 100% yield, 390 g, after LPC (30% EtOAc/hexanes): mp 153–155 °C; ^{1}H NMR δ 7.74 (m, 6 H), 7.67 (m, 2 H), 7.49 (m, 6 H); ^{13}C NMR δ 141.1, 135.1, 134.5, 129.1, 128.6, 128.4, 124.5. Anal. Calcd for $C_{18}H_{14}O_6S_2$: C, 55.4; H, 3.6. Found: C, 55.6; H, 3.6.

1-[(Benzenesulfonyl)oxy]-2,6-dimethylbenzene (4d). A solution of 2,6-dimethylphenol (122 mg, 1.0 mmol) and *N*-methylimidazole (82 mg, 1.0 mmol) in THF (5 mL) and 1-(benzenesulfonyl)-3-methylimidazolium triflate reagent (**2b**, 1.25 mmol) were treated as in the preparation of **4b**. LPC (20% EtOAc/hexanes) and sublimation (80 °C/0.05 Torr) afforded 190 mg, 76% yield, of the benzenesulfonate **4d**: mp 79–80 °C. Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.1; H, 5.4. Found: C, 64.2; H, 5.3.

Methyl *O*-Tetrakis(benzenesulfonyl)-α-D-glucoside (4f). A slurry of methyl α-D-glucoside (195 mg, 1.0 mmol) and *N*-methylimidazole (330 mg, 4.0 mmol) in THF (10 mL) and the 1-(benzenesulfonyl)-3-methylimidazolium triflate reagent (**2b**, 8 mmol) were treated by the procedure for preparation of **4b**. LPC (EtOAc/hexanes (1/1)) afforded 755 mg, 100% yield, of the tetrabenzenesulfonate **4f**: mp 69–71 °C; $[\alpha]^{20}_D$ +38.1 (*c* 0.5, $CHCl_3$). Anal. Calcd for $C_{31}H_{30}O_{14}S_4$: C, 49.3; H, 4.0. Found: C, 49.4; H, 3.9.

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(11) Kampouris, E. M. *J. Chem. Soc.* **1968**, 2125.

A Convenient and General Preparation of *N*-Sulfonylimines

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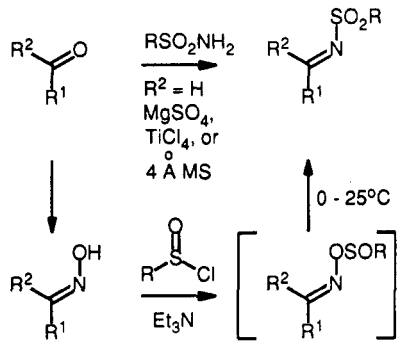
In recent studies we have detailed the effective 4π participation of α,β-unsaturated *N*-sulfonylimines in diastereoselective inverse electron demand Diels–Alder reactions (≥20:1 endo:exo)[2-7] which has proven to be a productive addition to the limited number of useful 1-aza-1,3-butadienes.[8-15] In these studies, the *N*-sulfonylimines have been shown to constitute stable, nonbasic electron-deficient imine derivatives capable of simple isolation and purification. In our initial studies, the *N*-sulfonylimines were prepared through the clean, homolytic rearrangement of in situ generated *O*-sulfinyl derivatives of aldehyde or ketone oximes[16-18] or through the direct

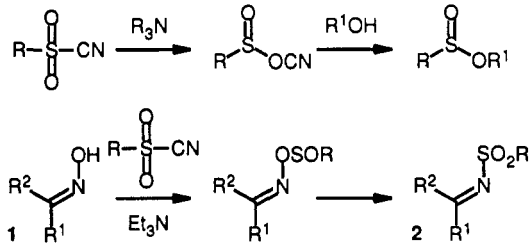
(1) ICI Americas Inc. ACS Organic Division Fellowship Recipient, 1990–1991.
(2) Boger, D. L.; Corbett, W. L.; Curran, T. T.; Kasper, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 1713.
(3) Boger, D. L.; Nakahara, S. *J. Org. Chem.* **1991**, *56*, 880.
(4) Boger, D. L.; Curran, T. T. *J. Org. Chem.* **1990**, *55*, 5439.
(5) Boger, D. L.; Corbett, W. L.; Wiggins, J. M. *J. Org. Chem.* **1990**, *55*, 2999.
(6) Boger, D. L.; Kasper, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 1517.
(7) Boger, D. L.; Zhang, M. *J. Org. Chem.*, in press.
(8) Boger, D. L.; Weinreb, S. M. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: San Diego, 1987. Boger, D. L. *Tetrahedron* **1983**, *39*, 2869.
(9) Teng, M.; Fowler, F. W. *J. Org. Chem.* **1990**, *55*, 5646.
(10) Hwang, Y. C.; Fowler, F. W. *J. Org. Chem.* **1985**, *50*, 2719.
(11) Ito, Y.; Nakajo, E.; Saegusa, T. *Synth. Commun.* **1986**, *16*, 1073.
(12) Poncin, B. S-.; Frisque, A.-M. H-.; Ghosez, L. *Tetrahedron Lett.* **1982**, *23*, 3261.
(13) Dolle, R. E.; Armstrong, W. P.; Shaw, A. N.; Novelli, R. *Tetrahedron Lett.* **1988**, *29*, 6349.
(14) Ihara, M.; Kirihara, T.; Kawaguchi, A.; Fukumoto, K.; Kametani, T. *Tetrahedron Lett.* **1984**, *25*, 4541.
(15) Boger, D. L.; Zhu, Y. *Tetrahedron Lett.* **1991**, *32*, 7643.
(16) Brown, C.; Hudson, R. F.; Record, K. A. F. *J. Chem. Soc., Perkin Trans. 2* **1978**, 822.
(17) Brown, C.; Hudson, R. F.; Record, K. A. F. *J. Chem. Soc., Chem. Commun.* **1977**, 540.
(18) Hudson, R. F.; Record, K. A. F. *J. Chem. Soc., Chem. Commun.* **1976**, 831.

0022-3263/92/1957-4777$03.00/0

Scheme I



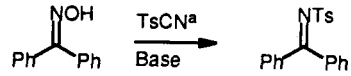
Scheme II



condensation of primary sulfonamides with selected aldehydes,[19-25] Scheme I. Although the direct condensation of primary sulfonamides with aldehydes has been conducted successfully with a variety of dehydrating agents ($TiCl_4$, 4-Å molecular sieves, $MgSO_4$),[2,19-24] this approach has proven to be of limited value for nonenolizable ketones (0–30%) and not applicable to enolizable or hindered ketones.[19] In contrast, the homolytic rearrangement (0–25 °C) of in situ generated aldehyde or ketone oxime *O*-sulfinates has proven general and applicable to the preparation of a wide range of *N*-sulfonylimines including tautomerizable α,β-unsaturated *N*-sulfonylimines. However, the use of the unstable and reactive sulfinyl chloride reagents detracts from the technical convenience of this preferred procedure.

Herein, we detail a convenient preparation of *N*-sulfonylimines based on the preparation and in situ rearrangement of oxime *O*-sulfinates employing readily available and stable sulfonyl cyanides as reagents. Barton and co-workers[26,27] have recently described the preparation of sulfinates from alcohols upon treatment with methanesulfonyl cyanide or *p*-toluenesulfonyl cyanide (TsCN)

Table I



base (equiv)	solvent	temp[b] (°C)	% yield
PPh_3 (1.5)	CH_2Cl_2	0	0
DBU (4.5)	CCl_4	0	19
DBU (4.5)	Et_2O	−78	25
DBN (1.5)	CH_2Cl_2	0	0
DABCO (4.5)	Et_2O	−78	0
DABCO (4.5)	CCl_4	0	41
iPr_2NEt (2.0)	CCl_4	0	42
Et_3N (4.5)	CH_2Cl_2	0	61
Et_3N (4.5)	CCl_4	0	69
Et_3N (2.0)	CCl_4	−23	62
Et_3N (2.0)	Et_2O	−78	63

[a] 1.5–2.5 equiv of TsCN. [b] Initial reaction temperature, reaction allowed to warm to 25 °C (6–12 h).

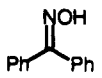
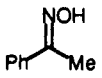
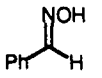
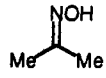
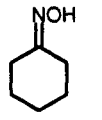
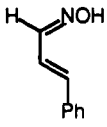
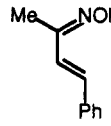
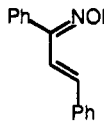
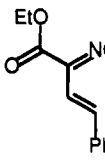
in the presence of DBU or DABCO through a process that proceeds by base-catalyzed rearrangement of the sulfonyl cyanide to the corresponding sulfinyl cyanate,[26] Scheme II. On the basis of these observations, we have examined the applicability of these and related reagent combinations for the in situ generation of oxime *O*-sulfinyl derivatives and their subsequent homolytic rearrangement to *N*-sulfonylimines.

A range of reaction conditions was examined for effecting the in situ isomerization of *p*-toluenesulfonyl cyanide to *p*-toluenesulfinyl cyanate and its subsequent reaction with the oxime of benzophenone. Representative results of this study are summarized in Table I. The desired reaction was not observed in the presence of secondary imines (Et_2NH, iPr_2NH) or nonamine bases (NaH, K_2CO_3) and was found to require the use of a tertiary amine base. Of those examined, Et_3N was found to be superior to iPr_2NEt which in turn proved more effective than DABCO or DBU in reactions conducted initially at −20 to 0 °C with gradual warming to 25 °C. A range of solvents was examined and CCl_4 generally proved superior (cleaner reaction) to CH_2Cl_2 or Et_2O which in turn proved substantially more effective than THF, C_6H_6, or toluene. This same preference for the solvent is observed employing sulfinyl chloride reagents and may be attributed to the solvent effects on the efficiency of the homolytic (free radical) rearrangement of the oxime *O*-sulfinate to the *N*-sulfonylimine. Thus, in instances when the solubility properties of the substrate preclude the use of CCl_4 as solvent, CH_2Cl_2 or Et_2O are the preferred alternatives.

More difficult to assess was the effect of the reaction temperature on the overall reaction cascade. The tertiary amine catalyzed in situ generation of sulfinyl cyanates from sulfonyl cyanides proceeds at temperatures as low as −60 to −50 °C in CH_2Cl_2.[26] Although the sulfinyl cyanates have proven unstable in solution at temperatures above ca. −20 °C, they have been successfully generated and trapped in situ in reactions conducted at 0–5 °C.[26,27] The oxime *O*-sulfinates may be generated cleanly at low temperature (−20 °C) and rearrange to the corresponding *N*-sulfonylimines at temperatures of ca. 0–25 °C.[2] In the examination of conditions for effecting the direct conversions of oximes to the *N*-sulfonylimines, efficient conversions were observed in reactions conveniently conducted initially at −20 or 0 °C (sulfinyl cyanate and subsequent oxime *O*-sulfinate generation) and allowed to warm to room temperature (oxime *O*-sulfinate → *N*-sulfonylimine rearrangement) if excess sulfonyl cyanide reagent (1.5–2.5 equiv) was employed. Lower initial reaction temperatures (−78 °C, Et_2O or CH_2Cl_2; or −20 °C, CCl_4) may be employed but do not

(19) Jennings, W. B.; Lovely, C. J. *Tetrahedron* **1991**, *47*, 5561.
(20) Jennings, W. B.; Lovely, C. J. *Tetrahedron Lett.* **1988**, *29*, 3725.
(21) Davis, F. A.; Zhou, P.; Lal, G. S. *Tetrahedron Lett.* **1990**, *31*, 1653.
(22) Davis, F. A.; Reddy, R. T.; Weismiller, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 5964.
(23) Davis, F. A.; Lamendola, J., Jr.; Nadir, U.; Kluger, E. W.; Sedergran, T. C.; Panunto, T. W.; Billmers, R.; Jenkins, R., Jr.; Turchi, I. J.; Watson, W. H.; Chen, J. S.; Kimura, M. *J. Am. Chem. Soc.* **1980**, *102*, 2000.
(24) Vishwakarma, L. C.; Stringer, O. D.; Davis, F. A. *Org. Synth.* **1988**, *66*, 203.
(25) For alternatives, see: (a) Albrecht, R.; Kresze, G.; Mlakar, B. *Chem. Ber.* **1964**, *97*, 483. (b) Albrecht, R.; Kresze, G. *Chem. Ber.* **1965**, *98*, 1431. (c) Melnick, M. J.; Freyer, A. J.; Weinreb, S. M. *Tetrahedron Lett.* **1988**, *29*, 3891. (d) Sisko, J.; Weinreb, S. M. *Tetrahedron Lett.* **1989**, *30*, 3037. (e) Trost, B. M.; Marrs, C. *J. Org. Chem.* **1991**, *56*, 6468.
(26) Barton, D. H. R.; Jaszberenyi, J. Cs.; Theodorakis, E. A. *Tetrahedron* **1991**, *47*, 9167.
(27) Barton, D. H. R.; Jaszberenyi, J. Cs.; Theodorakis, E. A. *Tetrahedron Lett.* **1991**, *32*, 2585.
(28) In the case of **1f–1h**, the starting oxime was a mixture of *E*:*Z* isomers and the yield of **2f–2h** is that of the pure anti *N*-sulfonylimine. Although it was not investigated in the present work, in related studies[3] we have observed that the anti oxime (anti to olefin) participates cleanly in the *O*-sulfinyl homolytic rearrangement while the syn oxime (syn to olefin) fails to provide the *N*-sulfonylimine.

Table II. Preparation of *N*-Sulfonylimines

	substrate	cond: equiv of Et_3N, TsCN,[a] temp (°C), solvent	product (% yield)
1a		4.5, 0, CH_2Cl_2	2a (61)
		4.5, 0, CCl_4	2a (69)
		2.0, -23, CCl_4	2a (62)
		2.0, -78, Et_2O	2a (63)
1b		4.0, 0, CH_2Cl_2	2b (49)
		4.5, 0, CCl_4	2b (61)
1c		2.0, 0, CCl_4	2c (59)
1d		4.0, 0, CH_2Cl_2	2d (47)
		4.5, 0, CCl_4	2d (63)
1e		2.0, -23, CCl_4	2e (62)
1f		2.0, 0, CCl_4	2f (59)
1g		2.0, 0, CCl_4	2g (63)
1h		2.0, 0, CH_2Cl_2	2h (67)
1i		2.0, 0, CCl_4	2i (65)

[a] 1.5–2.0 equiv of TsCN.

appear to improve the observed efficiency of the reaction.

The generality of the scope of the reaction was investigated and the results of the study are summarized in Table II. Ketone as well as aldehyde oximes were converted to the corresponding *N*-sulfonylimines in good yields, including those which provide tautomerizable products. Notably, the sulfonate derivatives of the oximes and their potential Beckmann rearrangement products (ketone or aldehyde oximes) or simple dehydration products (nitriles from aldehyde oximes) were not detected in the reaction mixtures. The yields of the conversions of the oximes to the *N*-sulfonylimines correspond to or exceed those obtained employing sulfinyl chlorides as the reagents, suggesting that the conversions reported in Table II reflect the inherent yield of the homolytic rearrangement of the oxime *O*-sulfinate and the sensitivity of *N*-sulfonylimines to purification rather than the efficiency of the intermediate sulfinyl cyanate or oxime *O*-sulfinate generation. CCl_4 proved to be the optimal solvent for the reaction consistent with the observation that it is the solvent of choice for the homolytic rearrangement of oxime *O*-sulfinates. Thus, the effective use of the stable sulfonyl cyanides as reagents for the direct preparation of *N*-sulfonylimines from oximes provides a convenient procedure for the general preparation of *N*-sulfonylimines derived from ketones *or* aldehydes.

Experimental Section[29]

General Procedure for the Preparation of *N*-Tosylimines from Oximes Using *p*-Toluenesulfonyl Cyanide: *N*-(Diphenylmethylene)-4-methylbenzenesulfonamide (2a). A solution of benzophenone oxime (1.00 g, 5.07 mmol, 1.0 equiv) in anhydrous CCl_4 (50 mL, 0.10 M) was cooled to 0 °C and treated with Et_3N (2.31 g, 3.20 mL, 22.8 mmol, 4.5 equiv). The solution was stirred under Ar for 5 min at 0 °C before a suspension of *p*-toluenesulfonyl chloride[30] (2.30 g, 12.7 mmol, 2.5 equiv) in 1 mL of CCl_4 was added. The resulting reaction mixture was stirred at 0 °C for 1 h, allowed to warm to 23 °C over 30 min, and further stirred at 23 °C (9 h). Filtration of the mixture and concentration of the filtrate afforded a gold oil. Flash chromatography (SiO_2, 4 × 20 cm, 60% Et_2O–hexane eluant) afforded **2a** (1.17 g, 1.70 g theoretical, 69%) as a white powder: mp 101–102 °C (Et_2O–hexane) (lit.[31] mp 103–104 °C); ^1H NMR ($CDCl_3$, 400 MHz, ppm) 7.82 (2 H, d, J = 8.2 Hz, *o*-SO_2ArH), 7.52 (6 H, app t, J = 7.3 Hz, ArH), 7.40 (4 H, br s, ArH), 7.26 (2 H, d, J = 8.2 Hz, *m*-SO_2ArH), 2.41 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm), 178.7 (e, C=N), 143.3 (e), 138.4 (e), 130.6 (e), 129.3 (o), 128.1 (o), 127.3 (o), 21.5 (o, CH_3); FABHRMS (NBA-CsI) m/e 468.0043 ($M + Cs^+$, $C_{20}H_{17}NO_2S$ requires 468.0034).

Anal. Calcd for $C_{20}H_{17}NO_2S$: C, 71.62; H, 5.11; N, 4.18; S, 9.56. Found: C, 71.36; H, 4.98; N, 4.45; S, 9.95.

4-Methyl-*N*-(1-phenylethylidene)benzenesulfonamide (2b). Tan solid: mp 88–89 °C (Et_2O–hexane) (lit.[32] mp 71.5–73.5 °C (Et_2O)); ^1H NMR ($CDCl_3$, 400 MHz, ppm) 7.93 (2 H, d, J = 8.3 Hz, *o*-ArH), 7.90 (2 H, d, J = 8.0 Hz, *o*-SO_2ArH), 7.54 (1 H, t, J = 7.5 Hz, *p*-ArH), 7.41 (2 H, t, J = 7.5 Hz, *m*-ArH), 7.34 (2 H, d, J = 8.0 Hz, *m*-SO_2ArH), 2.99 (3 H, s, CH_3), 2.45 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) 179.8 (e, C=N), 143.5 (e), 138.6 (e), 137.5 (e), 133.1 (o), 129.4 (o), 128.6 (o), 128.2 (o), 127.0 (o), 21.6 (o, CH_3), 21.1 (o, CH_3).

***N*-Benzylidene-4-methylbenzenesulfonamide (2c).** White solid: mp 108–109 °C (EtOAc–hexane) (lit.[25a] mp 107 °C (benzene)); ^1H NMR ($CDCl_3$, 400 MHz, ppm) 9.03 (1 H, s, HC=N), 7.92 (2 H, d, J = 7.9 Hz, *o*-ArH), 7.89 (2 H, d, J = 8.0 Hz, *o*-SO_2ArH), 7.62 (1 H, t, J = 7.3 Hz, *p*-ArH), 7.48 (2 H, t, J = 7.7 Hz, *m*-ArH), 7.34 (2 H, d, J = 8.0 Hz, *m*-SO_2ArH), 2.43 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz ppm) 170.1 (o, HC=N), 144.6 (e), 135.0 (e), 134.9 (o), 132.3 (e), 131.3 (o), 129.8 (o), 129.1 (o), 128.0 (o), 21.6 (o, CH_3).

4-Methyl-*N*-(1-methylethylidene)benzenesulfonamide (2d). Clear yellow viscous oil:[16] ^1H NMR ($CDCl_3$, 400 MHz, ppm) 7.85 (2 H, d, J = 8.2 Hz, *o*-SO_2ArH), 7.32 (2 H, d, J = 8.2 Hz, *m*-SO_2ArH), 2.47 (3 H, s, CH_3), 2.43 (3 H, s, CH_3), 2.18 (3 H, s, CH_3).

***N*-Cyclohexylidene-4-methylbenzenesulfonamide (2e).** Clear viscous oil:[33] ^1H NMR ($CDCl_3$, 400 MHz, ppm) 7.75 (2 H, d, J = 8.2 Hz, *o*-SO_2ArH), 7.27 (2 H, d, J = 8.2 Hz, *m*-SO_2ArH),

(29) For DEPT ^{13}C NMR, e = even and o = odd number of attached protons. Ether (Et_2O) was distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from phosphorus pentoxide. Carbon tetrachloride (CCl_4) and triethylamine (Et_3N) were distilled from CaH_2. All chromatographic solvents, ethyl ether (Et_2O), ethyl acetate (EtOAc), and hexane were distilled prior to use. All reactions requiring anhydrous conditions and/or an inert atmosphere were performed under a positive pressure of Ar or N_2.

(30) Commercially available from Aldrich Chemical Co.

(31) Dubina, V. L.; Burmistrov, S. I. *Zh. Org. Khim.* **1967**, *3*, 424.

(32) Kobayashi, T.; Kakiuchi, H.; Kato, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 392.

(33) Abramovitch, R. A.; Knaus, G. N.; Pavlin, M.; Holcomb, W. D. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2169.

2.43 (3 H, s, CH_3), 1.95 (2 H, m), 1.84 (3 H, m), 1.54 (2 H, m), 1.40 (3 H, m).

(*E*)-1-[[(4-Methylphenyl)sulfonyl]imino]-3-phenyl-2-propene (2f). Pale yellow solid: mp 109–110 °C (EtOAc–hexane); R_f 0.28 (25% EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) 8.78 (1 H, d, J = 9.4 Hz, HC=N), 7.86 (2 H, d, J = 8.2 Hz, *o*-SO_2ArH), 7.55 (2 H, m, ArH), 7.49 (1 H, d, J = 15.9 Hz, PhCH=), 7.43 (3 H, m, ArH), 7.34 (2 H, d, J = 8.2 Hz, *m*-SO_2ArH), 6.99 (1 H, dd, J = 15.8, 9.4 Hz, *H*C=CHN), 2.44 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) 170.9 (o, HC=N), 153.8 (o, Ph*C*H=CH), 144.5 (e), 135.3 (e), 134.1 (e), 131.6 (o), 129.8 (o), 129.2 (o), 128.6 (o), 127.9 (o), 124.7 (o, PhCH=*C*H), 21.6 (o, CH_3); IR (KBr) ν_{max} 3049, 2908, 2862, 1620, 1573, 1444, 1308, 1285, 1173, 1150, 1085, 1010, 963, 860, 777, 755 cm^{-1}; FABHRMS (NBA-CsI) *m/e* 417.9899 (M + Cs$^+$, $C_{16}H_{15}NO_2S$ requires 417.9878).

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.35; H, 5.30; N, 4.91; S, 11.23. Found: C, 67.01; H, 5.55; N, 4.63; S, 11.39.

(*E*)-2-[[(4′-Methylphenyl)sulfonyl]imino]-4-phenyl-3-butene (2g). Oil: R_f 0.38 (25% EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) 7.90 (2 H, d, J = 8.2 Hz, *o*-SO_2ArH), 7.52 (2 H, m, ArH), 7.50 (1 H, d, J = 16.4 Hz, PhCH=), 7.40 (3 H, m, ArH), 7.33 (2 H, d, J = 8.2 Hz, *m*-SO_2ArH), 6.78 (1 H, d, J = 16.3 Hz, PhCH=C*H*), 2.77 (3 H, s, CH_3), 2.44 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) 179.2 (e, C=N), 144.0 (o, PhCH=), 143.5 (e), 131.2 (e), 130.8 (o), 129.4 (o), 129.0 (o), 128.3 (o), 127.1 (o), 122.6 (o, PhCH=*C*H), 21.6 (Ar*C*H$_3$), 20.0 (*C*H$_3$CH=); IR (neat) ν_{max} 3061, 2920, 1622, 1556, 1495, 1449, 1372, 1301, 1210, 1150, 1089, 1029, 971, 880, 814, 725 cm^{-1}; FABHRMS (NBA-CsI) *m/e* 432.0034 (M + Cs$^+$, $C_{17}H_{17}NO_2S$ requires 432.0034).

Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68; S, 10.71. Found: C, 68.20; H, 5.71; N, 4.79; S, 10.65.

(*E*)-1,3-Diphenyl-1-[[(4′-methylphenyl)sulfonyl]imino]-2-propene (2h). Pale yellow solid: mp 152–153 °C (Et_2O–hexane); R_f 0.41 (25% EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) 7.92 (2 H, d, J = 8.0 Hz, *o*-SO_2ArH), 7.6–7.7 (6 H, m, ArH, PhC*H*=), 7.41–7.46 (5 H, m, ArH), 7.31 (2 H, d, J = 8.0 Hz, *m*-SO_2ArH), 7.07 (2 H, d, J = 16 Hz, PhCH=C*H*), 2.43 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) 177.6 (e, C=N), 148.9 (o, PhCH=), 143.4 (e), 134.5 (e), 131.9 (e), 131.1 (o), 130.2 (e), 129.4 (o), 129.0 (o), 128.7 (o), 128.3 (o), 127.2 (o), 122.7 (o, PhCH=*C*H), 21.6 (o, CH_3); IR (KBr) ν_{max} 3056, 3016, 2908, 1612, 1578, 1522, 1445, 1298, 1210, 1147, 1083, 976, 862, 823, 756 cm^{-1}; FABHRMS (NBA-CsI) *m/e* 494.0186 (M + Cs$^+$, $C_{22}H_{19}NO_2S$ requires 494.0191).

Anal. Calcd for $C_{22}H_{19}NO_2S$: C, 73.10; H, 5.30; N, 3.88; S, 8.87. Found: C, 73.10; H, 5.40; N, 3.83; S, 8.80.

Ethyl (*E*)-2-[[(4′-Methylphenyl)sulfonyl]imino]-4-phenyl-3-butenoate (2i). Oil: R_f 0.33 (25% EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) 7.90 (2 H, d, J = 8.1 Hz, *o*-SO_2ArH), 7.41–7.51 (6 H, m, ArH, PhCH=), 7.34 (2 H, d, J = 8.1 Hz, *m*-SO_2ArH), 6.82 (1 H, d, J = 16.4 Hz, PhCH=C*H*), 4.55 (2 H, q, J = 7.0 Hz, $CO_2CH_2CH_3$), 2.43 (3 H, s, C*H*$_3$), 1.49 (3 H, t, J = 7.0 Hz, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) 167.6 (e, C=N), 164.4 (e, C=O), 149.4 (o, PhCH=), 144.7 (e), 135.7 (e), 133.9 (e), 131.7 (o), 129.7 (o), 129.1 (o), 128.7 (o), 128.0 (o), 123.5 (o, PhCH=CH), 63.15 (e, CH_2), 21.6 (o, ArCH_3), 13.9 ($CO_2CH_2CH_3$); IR (neat) ν_{max} 3056, 2986, 2925, 1732, 1614, 1574, 1556, 1450, 1369, 1327, 1266, 1214, 1159, 1089, 1016, 970, 868, 768 cm^{-1}; FABHRMS (NBA-CsI) *m/e* 490.0094 (M + Cs$^+$, $C_{19}H_{19}NO_4S$ requires 490.0089).

Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.85; H, 5.36; N, 3.92; S, 8.97. Found: C, 63.54; H, 5.06; N, 3.73; S, 9.13.

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