Et_2O (10 mL) were added, and the vigorously stirred mixture was exposed to air until the aqueous phase was deep blue (~15 min). The phases were separated, and the aqueous phase was extracted with Et_2O (4 × 10 mL). The combined organic extracts were washed with saturated aqueous $CuSO_4$ (3 × 10 mL) and brine (2 × 10 mL) and then were dried ($MgSO_4$) and concentrated. Flash chromatography[8] (3:97 Et_2O–petroleum ether) of the crude product and distillation (~130 °C/2.0 Torr) of the oil thus obtained gave 91 mg (65%) of the ester **31**: IR (neat) 1702, 1599, 1176, 1274, 838, 776 cm^{-1}; ^1H NMR (300 MHz) δ 0.04 (s, 6 H), 0.11 (s, 9 H, $^2J_{Sn-H}$ = 55 Hz), 0.87 (s, 9 H), 1.28 (t, 3 H, J = 7 Hz), 1.93 (s, 3 H, $^4J_{Sn-H}$ = 7.1 Hz), 4.17 (q, 2 H, J = 7 Hz), 4.40 (s, 2 H, $^3J_{Sn-H}$ = 48 Hz); exact mass calcd for $C_{15}H_{31}O_3SiSn$ (M^+ – Me) 407.1072, found 407.1064.

Ethyl (*Z*)-4-(*tert*-Butyldimethylsiloxy)-2-(2-propenyl)-3-(trimethylstannyl)-2-butenoate (32). This material was prepared via a procedure very similar to that described above, except that 5.5 mmol of alkylating agent (3-iodopropene) was used and the reaction was carried out at –20 °C for 30 min. Distillation (115 °C/2.0 Torr) of the final product gave 91 mg (60%) of pure **32**: IR (neat) 3080, 1703, 1639, 1154, 1073, 776 cm^{-1}; ^1H NMR (300 MHz) δ 0.03 (s, 6 H), 0.13 (s, 9 H, $^2J_{Sn-H}$ = 54 Hz), 0.86 (s, 9 H), 1.26 (t, 3 H, J = 8 Hz), 3.14 (m, 2 H), 4.16 (q, 2 H, J = 8 Hz), 4.39 (s, 2 H, $^3J_{Sn-H}$ = 49 Hz), 4.93 (m, 1 H), 4.98 (m, 1 H), 4.77 (m, 1 H); exact mass calcd for $C_{17}H_{33}O_3SiSn$ (M^+ – Me) 433.1221, found 433.1216.

Ethyl (*Z*)-4-(*tert*-Butyldimethylsiloxy)-2-(2-propynyl)-3-(trimethylstannyl)-2-butenoate (33). A procedure similar to that outlined above was employed, except that 1.67 mmol of alkylating agent (3-bromopropyne) was used and the reaction was carried out at –78 °C for 1 h and at –20 °C for 1 h. The crude product consisted of a 3:1 mixture of **33** and the corresponding protonation products **27** and **29**. Distillation (140 °C/2.0 Torr) of the appropriate oil derived from chromatography afforded 59 mg (40%) of pure **33**: IR (neat) 3312, 2121, 1704, 1599, 1206, 1043, 839, 779 cm^{-1}; ^1H NMR (300 MHz) δ 0.06 (s, 6 H), 0.15 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.87 (s, 9 H), 1.30 (t, 3 H, J = 7 Hz), 1.94 (t, 1 H, J = 2.8 Hz), 3.31 (d, 2 H, J = 2.8 Hz), 4.22 (q, 2 H, J = 7 Hz), 4.49 (s, 2 H, $^3J_{Sn-H}$ = 44 Hz); exact mass calcd for $C_{17}H_{31}O_3SiSn$ (M^+ – Me) 431.1064, found 431.1059.

Ethyl 6-Iodo-2-hexynoate (35). To a cold (–78 °C) stirred solution of 5-chloro-1-pentyne (2 g, 19.5 mmol) in 100 mL of dry THF (argon atmosphere) was added a solution of MeLi (19.5 mmol) in Et_2O. After the mixture had been stirred at –78 °C for 10 min and at –20 °C for 45 min, EtO_2CCl (2.8 mL, 29 mmol) was added, and stirring was continued at –20 °C for 1 h and at room temperature for 1 h. Saturated aqueous $NaHCO_3$ (30 mL) and Et_2O (50 mL) were added, and the phases were separated. The aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. Distillation (85–90 °C/2.0 Torr) of the residual oil gave 3.0 g (88%) of ethyl 6-chloro-2-hexynoate (**34**).

To a soluton of NaI (17.2 g, 115 mmol) in dry acetone (150 mL) (argon atmosphere) was added a solution of the chloro ester **34** (2 g, 11.5 mmol) in 10 mL of dry acetone, and the mixture was refluxed overnight. Most of the solvent was removed, and water (50 mL) and Et_2O (50 mL) were added to the residue. The phases were separated, and the aqueous phase was washed with Et_2O (2 × 20 mL). The combined extracts were dried ($MgSO_4$) and concentrated. Distillation (100–110 °C/2.0 Torr) of the remaining oil gave 2.62 g (86%) of the iodo ester **35**: IR (neat) 2237, 1703, 1273, 1078 cm^{-1}; ^1H NMR (300 MHz) δ 1.26 (t, 3 H, J = 8 Hz), 2.02 (m, 2 H), 2.45 (t, 2 H, J = 8 Hz), 3.24 (t, 2 H, J = 8 Hz), 4.17 (q, 2 H, J = 8 Hz); exact mass calcd for $C_8H_{11}IO_2$ 265.9804, found 265.9815.

Ethyl 2-(Trimethylstannyl)-1-cyclopentenecarboxylate (36). To a cold (–78 °C), stirred solution of the cuprate reagent **10** (0.5 mmol) in 10 mL of dry THF (argon atmosphere) was added a solution of the iodo ester **35** (102 mg, 0.38 mmol) in 0.5 mL of dry THF, and the mixture was stirred at –78 °C for 2 h and at –48 °C for 1 h. The workup procedure was identical with that described previously (see preparation of **18**). Flash chromatography (3:97 Et_2O–petroleum ether) of the crude product and distillation (110 °C/2.0 Torr) of the oil thus obtained produced 73 mg (62%) of the pure ester **36**: IR (film) 1699, 1592, 1187, 768 cm^{-1}; ^1H NMR (400 MHz) δ 0.17 (s, 9 H, $^2J_{Sn-H}$ = 50 Hz), 1.27 (t, 3 H, J = 6 Hz), 1.90 (m, 2 H), 2.49 (br t, 4 H), 4.18 (q, 2 H, J = 6 Hz); exact mass calcd for $C_{10}H_{17}O_2Sn$ (M^+ – Me) 289.0250, found 289.0252.

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Generation and Cycloaddition Reactions of Phenylthio Nitrile Oxide. A Preparation of 3-(Phenylthio)- and 3-(Phenylsulfonyl)-Δ^2-isoxazolines

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The research of Wade and co-workers[2] has established that 3-(phenylsulfonyl)-Δ^2-isoxazolines are versatile synthetic intermediates (Scheme I). These isoxazolines are usually prepared by 1,3-dipolar cycloaddition reactions of phenylsulfonyl nitrile oxide. For example, the treatment of oxime bromide **1** with aqueous sodium carbonate in the presence of an alkene gives 3-(phenylsulfonyl)-Δ^2-isoxazolines **2**.[2c] The phenylsulfonyl group of **2** can be displaced by a variety of nucleophiles[2c] to provide substituted isoxazolines **3**, some of which are not directly available by nitrile oxide cycloaddition reactions. Subsequent hydrogenolytic cleavage of **3** gives β-hydroxy ketones or esters **4**.[3] β-Hydroxy nitriles are directly available by reduction of **2** with 2% sodium amalgam.[2e]

Oxime bromide **1** is an excellent precursor for small-scale preparations of **2**. However, practical problems arise on a preparative scale: several steps are needed to prepare **1** from phenylsulfonylnitromethane, a relatively low overall yield is obtained, and a large quantity of diazomethane is required at one stage. The cycloaddition procedure often uses a large excess of olefin, perhaps due to the tendency of the highly reactive phenylsulfonyl nitrile oxide to dimerize. To circumvent these problems, other useful methods to generate phenylsulfonyl nitrile oxide have been developed.[2,4] We now report a practical, two-step method for the preparation of 3-(phenylsulfonyl)-Δ^2-isoxazolines **2**. Phenylthioisoxazolines **6**[5] are readily available from dipolar cycloaddition reactions of phenylthio nitrile oxide with alkenes, and they are rapidly oxidized to 3-(phenylsulfonyl)-Δ^2-isoxazolines by *m*-chloroperoxybenzoic acid.

(1) Recipient of a Sloan Foundation Fellowship, 1985–87. Dreyfus Teacher–Scholar, 1985–89. Eli Lilly Grantee, 1985–87. Merck Faculty Development Awardee, 1986–87. NIH Research Career Development Awardee, 1987–92.

(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. (c) Wade, P. A.; Yen, H.-K.; Hardinger, S. A.; Pillay, M. K.; Amin, N. V.; Vail, P. D.; Morrow, S. D. *J. Org. Chem.* **1983**, *46*, 1796. (d) Wade, P. A.; Amin, N. V.; Yen, H.-K.; Price, D. T.; Huhn, G. F. *J.Org. Chem.* **1984**, *49*, 4595. (e) Wade, P. A.; Bereznak, J. F. *J. Org. Chem.* **1987**, *52*, 2973.

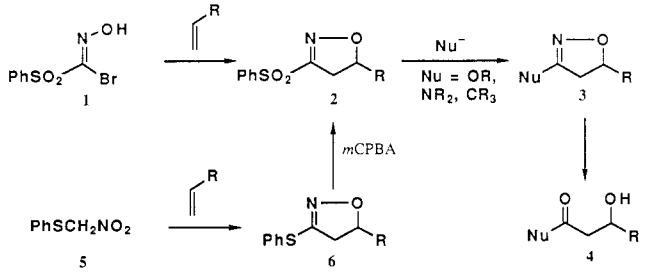
(3) Curran, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 5826. Curran, D. P.; Scanga, S. A.; Fenk, C. J. *J. Org. Chem.* **1984**, *49*, 3474. Curran, D. P. In *Advances in Cycloaddition*; Curran, D. P., Ed.; JAI: Greenwich, CT, 1988; p 137.

(4) Whitney, R. A.; Nicholas, R. S *Tetrahedron Lett.* **1981**, *22*, 3371.

(5) Four (phenylthio)isoxazolines are described in the literature. One is prepared from an oxime bromide (a), two from phenylthionitromethane (b), and one from displacement of a 3-nitro-Δ^2-isoxazoline (c). (a) Rieber, N.; Böhm, H. *J. Heterocycl. Chem.* **1981**, *18*, 1. (b) Harada, K.; Kaji, E.; Zen, S. *Nippon Kagaku Kaishi* **1981**, *1197*; *Chem. Abstr.* **1981**, *95*, 150508*x*. (c) Wade, P. A. *J. Org. Chem.* **1978**, *43*, 2020.

0022-3263/88/1953-5369$01.50/0

Scheme I



Following the usual Mukaiyama procedure,[6] phenylisocyanate and triethylamine were added to a solution of (phenylthio)nitromethane (**5**)[7] and 1-hexene (1.25 equiv) in dry benzene at 25 °C. The reaction mixture was heated at 45 °C for 12 h. After standard workup and purification by flash chromatography, 5-butyl-3-(phenylthio)-Δ^2-isoxazoline (**6a**) was isolated in 80% yield (Table I). This product must result from the dipolar cycloaddition of in situ generated phenylthio nitrile oxide with 1-hexene. An inherent advantage of the Mukaiyama method is that slow generation of the nitrile oxide maximizes the yield of isoxazoline by discouraging nitrile oxide dimerization.

A survey of examples revealed that the reaction was general and followed the expected trends for a nitrile oxide cycloaddition: reactive alkenes (entries a–f) gave good yields of products while less reactive (more substituted) alkenes (entries g, h) gave modest yields. In all cases, only 1–1.25 equiv of the alkene was used. (It is common practice to use a large excess of a less reactive alkene.) The cycloaddition reaction with 2-[(*tert*-butyldimethylsilyl)oxy]-3-butene gave a 40/60 mixture of syn and anti diastereomers (entry b). The degree of asymmetric induction is somewhat lower than that observed in the reaction of this alkene with other nitrile oxides.[8]

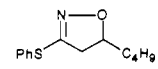
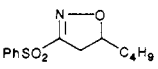
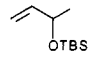
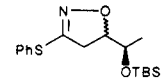
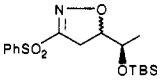
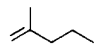
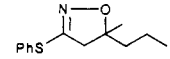
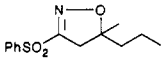
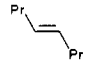
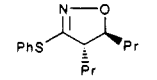
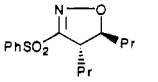
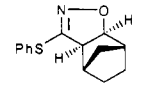
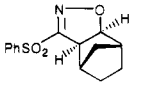
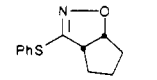
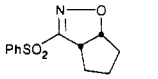
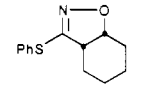
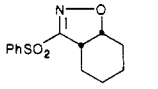
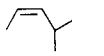
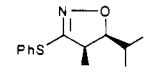
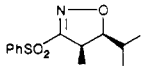
Treatment of (phenylthio)-Δ^2-isoxazolines **6a–h** with 2 equiv of *m*-CPBA in methylene chloride (0 to 25 °C)[5c] rapidly and cleanly formed the corresponding (phenylsulfonyl)-Δ^2-isoxazolines **2a-h**. The structures and isolated yields of these products are also shown in Table I. Spectroscopic data for three of the (phenylsulfonyl)isoxazolines (**2a,e,g**) were identical with the data reported by Wade.[2c]

This work provides a direct two-step route to 3-(phenylsulfonyl)-Δ^2-isoxazolines. In addition, the intermediate 3-(phenylthio)-Δ^2-isoxazolines may be of interest in their own right.

Experimental Section

General Procedures. Reactions were conducted under an atmosphere of dry nitrogen. Benzene was freshly distilled from sodium benzophenone. Triethylamine was distilled from calcium hydride and stored over potassium hydroxide pellets. Phenylisocyanate and *m*-CPBA were used as purchased from Aldrich. All compounds were purified by flash chromatography. The eluting solvent was hexane/EtOAc (8/1) for all (phenylthio)-isoxazolines and hexane/EtOAc (6/1) for all (phenylsulfonyl)-isoxazolines.

Table I. The Preparation of (Phenylthio)- and (Phenylsulfonyl)isoxazolines

entry	dipolarophile[a]	cycloadduct (yield, %)[b] **6**	sulfonylisoxazoline (yield, %)[b] **2**
a	1-hexene	 (80)	 (97)
b		 (69[c])	 (77[c])
c		 (75)	 (73)
d		 (46)	 (89)
e	norbornene	 (94)	 (78)
f	cyclopentene	 (79)	 (71)
g	cyclohexene	 (36)	 (77)
h		 (24)	 (51)

[a] One equivalent of dipolarophile was used in all cases. [b] All yields refer to isolated yields. [c] The syn/anti ratio was 40/60. The stereochemistry of the major diastereomer was assigned by analogy with past results (ref 8).

General Procedure for the Preparation of (Phenylthio)-isoxazolines: 5-Butyl-4,5-dihydro-3-(phenylthio)isoxazole (6a). To a solution of (phenylthio)nitromethane[7] (1.01 g, 6.0 mmol), 1-hexene (0.9 mL, 7.2 mmol), and phenylisocyanate (1.57 mL, 14.4 mmol), in dry benzene (50 mL), was added triethylamine (0.1 mL, 0.7 mmol). The solution was stirred for 30 min at 25 °C and then heated to 45 °C for 12 h. During this time, a white precipitate (diphenylurea) formed. The reaction was cooled to 25 °C, and water (0.2 mL) was added. After being stirred for 1 h to destroy excess isocyanate, the resulting mixture was passed through a short column of Florisil (ether), and the filtrate was concentrated. Flash chromatography of the crude product gave **6a** (1.128 g, 80% yield) as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (2 H, m), 7.38 (3 H, m), 4.59 (1 H, m), 3.00 (1 H, dd, J = 10.0, 16.5 Hz), 2.60 (1 H, dd, J = 8.4, 16.5 Hz), 1.73 (1 H, m), 1.59 (1 H, m), 1.32 (4 H, m), 0.89 (3 H, t); IR (thin film) 3050, 2955, 2932, 2861, 1478, 1441, 1277, 1117, 747 cm^{-1}; MS, m/e calcd for $C_{13}H_{17}NOS$ 235.1031, obsd 235.1032. Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.35; H, 7.28. Found: C, 66.30; H, 6.72.

4,5-Dihydro-5-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-ethyl]-3-(phenylthio)isoxazole (6b): ^{1}H NMR (300 MHz, $CDCl_3$) major (anti) isomer δ 7.55 (3 H, m), 7.37 (2 H, m), 4.45 (1 H, m), 3.94 (1 H, m), 3.03 (1 H, dd, J = 7.6, 16.8 Hz), 2.84 (1 H, dd, J = 10.0, 16.8 Hz), 1.07 (3 H, d, J = 6.5 Hz), 0.86 (9 H, s), 0.06 (3 H, s), 0.04 (3 H, s); minor (syn) isomer δ 4.53 (1 H, m), 1.09 (3 H, d, J = 6.5 Hz); IR (thin film) 3050, 2955, 2928, 2855, 1254, 837, 774 cm^{-1}; MS, m/e calcd for $C_{13}H_{18}NO_2SSi$ ($M^+ - C_4H_9$) 289.0828, obsd 289.0828.

4,5-Dihydro-5-methyl-3-(phenylthio)-5-propylisoxazole (6c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (2 H, m), 7.37 (3 H, m), 2.76 (1 H, d, J = 6.6 Hz), 2.61 (1 H, d, J = 6.6 Hz), 1.62 (2 H, m), 1.33 (5 H, m), 0.92 (3 H, t); ^{13}C NMR δ 154.8 (s), 133.4 (d), 129.3 (d), 128.9 (d), 87.2 (s), 48.4 (t), 42.2 (t), 25.3 (q), 14.3 (t), 11.9 (q); IR (thin film) 3050, 2961, 2932, 2872, 1477, 1441, 1302,

(6) The Mukaiyama method is generally used only for the preparation of alkyl-substituted nitrile oxides from nitroalkanes. Most previously known heteroatom-substituted nitrile oxides have been prepared by the Huisgen method (dehydrohalogenation of an oxime halide). One attempt to prepare a 3-alkoxyisoxazoline by the reaction of phenoxynitromethane with 1-hexene under the Mukaiyama conditions was not successful.

(7) Two methods are available for the preparation of (phenylthio)-nitromethane: nitration of the dianion derived from (phenylthio)acetic acid with propyl nitrate (Miyashita, M.; Kumazowa, T.; Yoshikoshi, A. *J. Org. Chem.* **1980**, *45*, 2945), and sulfenylation of nitromethane (Seebach, D.; Lehr, F. *Helv. Chim. Acta.* **1979**, *62*, 2239). We used the former procedure and obtained about one-third of the reported yield of 53% on a 0.125-mol scale. Although we have not tried the Seebach procedure, Barrett recommends that it is more convenient for the large-scale preparation of (phenylthio)nitromethane. See: Barrett, A. G. M.; Graboski, G. G.; Sabat, M.; Taylor, S. J. *J. Org. Chem.* **1987**, *52*, 4693.

(8) Houk, K. N.; Moses, S. R.; Wu, Y.-D.; Rondan, N. G.; Jäger, V.; Schohe, R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1984**, *106*, 3880.

904, 747 cm^{-1}; MS, m/e calcd for $C_{13}H_{17}NOS$ (M^+) 235.1031, obsd 235.1032.

***trans*-4,5-Dihydro-3-(phenylthio)-4,5-dipropylisoxazole (6d)**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (2 H, m), 7.35 (3 H, m), 4.29 (1 H, m), 2.80 (1 H, m), 1.7–1.2 (8 H, m), 0.90 (6 H, m); ^{13}C NMR δ 158.4 (s), 133.9 (d), 129.2 (d), 128.7 (d), 85.8 (d), 55.2 (d), 37.3 (t), 33.2 (t), 19.7 (t), 18.5 (t), 13.9 (q), 13.8 (q); IR (thin film) 3050, 2959, 2932, 2872, 1477, 1441, 876, 747 cm^{-1}; MS, m/e calcd for $C_{15}H_{21}NOS$ (M^+) 263.1345, obsd 263.1344.

(3aα,4β,7β,7aα)-3a,4,5,6,7,7a-Hexahydro-4,7-methano-3-(phenylthio)-1,2-benzisoxazole (6e): ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (2 H, m), 7.36 (3 H, m), 4.51 (1 H, d, J = 8.3 Hz), 3.04 (1 H, d, J = 8.3 Hz), 2.53 (1 H, br s), 2.40 (1 H, br s), 1.6–0.9 (6 H, m); IR (thin film) 3050, 2963, 1476, 1441, 1219, 864, 748 cm^{-1}; MS, m/e calcd for $C_{14}H_{15}NOS$ (M^+) 245.0876, obsd 245.0876. Anal. Calcd for ($C_{14}H_{15}NOS$): C, 68.54; H, 6.16. Found: C, 68.60; H, 6.30.

3a,5,6,6a-Tetrahydro-3-(phenylthio)-4*H*-cyclopent[*d*]isoxazole (6f): ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (2 H, m), 7.35 (3 H, m), 5.09 (1 H, m), 3.58 (1 H, br t), 2.06 (2 H, m), 1.66 (4 H, m); ^{13}C NMR δ 157.6 (s), 133.6 (d), 129.4 (d), 128.9 (d), 87.1 (d), 55.2 (d), 36.0 (t), 31.2 (t), 23.2 (t); IR (thin film) 3050, 2959, 1441, 1476, 884, 746, 691 cm^{-1}; MS, m/e calcd for $C_{12}H_{13}NOS$ (M^+) 219.0718, obsd 219.0719.

3a,4,5,6,7,7a-Hexahydro-3-(phenylthio)-1,2-benzisoxazole (6g): ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 (2 H, m), 7.35 (3 H, m), 4.45 (1 H, m), 2.91 (1 H, q), 2.02 (1 H, m), 1.9–1.6 (6 H, m), 1.21 (1 H, m); ^{13}C NMR δ 162.8 (s), 136.7 (d), 129.3 (d), 128.8 (d), 79.6 (d), 47.8 (d), 25.4 (t), 21.8 (t), 20.2 (t); IR (thin film) 3050, 2936, 2861, 1476, 1441, 862, 747 cm^{-1}; MS m/e calcd for $C_{13}H_{15}NOS$ (M^+) 233.0874, obsd 233.0874.

***cis*-4,5-Dihydro-5-isopropyl-4-methyl-3-(phenylthio)isoxazole (6h)**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.6–7.3 (5 H, m), 3.93 (1 H, m), 2.94 (1 H, m), 2.02 (1 H, m), 1.08 (6 H, two overlapping doublets), 0.90 (3 H, d, J = 6.6 Hz); ^{13}C NMR δ 157.9 (s), 133.3 (d), 129.4 (d), 128.9 (d), 90.1 (d), 46.4 (d), 27.3 (d), 19.8 (q), 11.1 (q); MS, m/e calcd for $C_{13}H_{17}NOS$ (M^+) 235.1031, obsd 235.1032.

General Procedure for the Preparation of (Phenylsulfonyl)isoxazolines: 5-Butyl-4,5-dihydro-3-(phenylsulfonyl)isoxazole (2a). *m*-CPBA (176 mg, 1.02 mmol) was added in one portion to a solution of 3-(phenylthio)-5-butyl-Δ^2-isoxazoline **6a** (100 mg, 0.43 mmol) in methylene chloride (5 mL) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was diluted with water and poured into a separatory funnel. After extraction with Et_2O (×3) and washing with brine, the mixture was dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography to give 111 mg (97%) of **2a**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (2 H, d), 7.72 (1 H, t), 7.61 (2 H, t), 4.84 (1 H, m), 3.36 (1 H, dd, J = 10.7, 17.0 Hz), 2.96 (1 H, dd, J = 8.5, 17.0 Hz), 1.9–1.2 (6 H, m), 0.88 (3 H, t, J = 6.6 Hz); ^{13}C NMR δ 160.0 (s), 137.0 (s), 134.8 (d), 129.5 (d), 128.8 (d), 85.3 (d), 37.4 (t), 34.5 (t), 27.0 (t), 22.3 (t), 13.9 (q); IR (thin film) 3050, 2957, 2934, 1448, 1332, 1167, 1128, 923, 723 cm^{-1}; MS, m/e calcd for $C_9H_8NO_3S$ ($M^+ - C_4H_9$) 210.0225, obsd 210.0224.

4,5-Dihydro-5-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]ethyl]-3-(phenylsulfonyl)isoxazole (2b): ^1H NMR (300 MHz, $CDCl_3$) major (anti) isomer δ 8.0–7.5 (5 H, m), 4.72 (1 H, m), 4.03 (1 H, m), 3.40 (1 H, dd, J = 8.6, 17.0 Hz), 3.24 (1 H, dd, J = 11.4, 17.0 Hz), 1.07 (3 H, d, J = 6.2 Hz), 0.78 (9 H, s), 0.04 (3 H, s), 0.01 (3 H, s); minor (syn) isomer δ 3.91 (1 H, m), 0.84 (9 H, s), –0.07 (6 H, s); IR (thin film) 3050, 2955, 2930, 1335, 1169, 837, 611 cm^{-1}; MS, m/e calcd for $C_{13}H_{18}NO_3SSi$ ($M^+ - C_4H_9$) 312.0721, obsd 312.0722.

4,5-Dihydro-5-methyl-3-(phenylsulfonyl)-5-propylisoxazole (2c): ^1H NMR (300 MHz, $CDCl_3$) δ 8.0–7.55 (5 H, m), 3.16 (1 H, d, J = 17.2 Hz), 2.97 (1 H, d, J = 17.2 Hz), 1.65 (2 H, m), 1.39 (3 H, s), 1.31 (2 H, m), 0.93 (3 H, t); ^{13}C NMR δ 159.0 (s), 137.4 (s), 134.6 (d), 129.4 (d), 128.6 (d), 92.5 (s), 42.1 (t), 25.3 (q), 17.0 (t), 14.0 (q); IR (thin film) 3050, 2963, 2934, 1449, 1330, 1169, 723 cm^{-1}; MS, m/e calcd for $C_{13}H_{17}NO_3S$ (M^+) 267.0929, obsd 267.0929.

***trans*-4,5-Dihydro-3-(phenylsulfonyl)-4,5-dipropylisoxazole (2d)**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.00–7.55 (5 H, m), 4.52 (1 H, m), 3.31 (1 H, m), 2.0–1.2 (8 H, m), 0.94 (3 H, t, J = 7.2 Hz), 0.91 (3 H, t, J = 7.1 Hz); IR (thin film) 3050, 2961, 2934, 2874, 1448, 1327, 1166, 725 cm^{-1}; MS, m/e calcd for $C_{15}H_{21}NO_3S$ (M^+) 295.1242, obsd 295.1242.

(3aα,4β,7β,7aα)-3a,4,5,6,7,7a-Hexahydro-4,7-methano-3-(phenylsulfonyl)-1,2-benzisoxazole (2e): mp 86–87 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00–7.55 (5 H, m), 4.70 (1 H, d, J = 8.5 Hz), 3.44 (1 H, d, J = 8.5 Hz), 2.77 (1 H, br s), 2.59 (1 H, br s), 1.7–1.0 (6 H, m); IR (thin film) 2966, 1448, 1332, 1166, 1131, 722 cm^{-1}; MS, m/e calcd for $C_{14}H_{15}NO_3S$ (M^+) 277.0772, obsd 277.0772. Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45. Found: C, 60.71; H, 5.51.

3a,5,6,6a-Tetrahydro-3-(phenylsulfonyl)-4*H*-cyclopent[*d*]isoxazole (2f): ^1H NMR (300 MHz, $CDCl_3$) δ 8.0–7.5 (5 H, m), 5.28 (1 H, m), 4.02 (1 H, br t), 2.33 (1 H, m), 2.16 (1 H, m), 1.76 (3 H, m), 1.47 (1 H, m); IR (thin film) 3050, 2965, 1447, 1327, 1161, 725, 639 cm^{-1}; MS, m/e calcd for $C_{12}H_{13}NO_3S$ (M^+) 251.0616, obsd 251.0615.

3a,4,5,6,7,7a-Hexahydro-3-(phenylsulfonyl)-1,2-benzisoxazole (2g): ^1H NMR (300 MHz, $CDCl_3$) δ 8.05–7.55 (5 H, m), 4.62 (1 H, m), 3.43 (1 H, br q), 2.06 (2 H, m), 1.8–1.2 (6 H, m); IR (thin film) 3050, 2940, 2865, 1447, 1310, 1163, 725 cm^{-1}; MS, m/e calcd for $C_{13}H_{15}NO_3S$ (M^+) 265.0773, obsd 265.0772. Anal. Calcd for $C_{13}H_{15}NO_3S$: C, 58.85; H, 5.70. Found: C, 58.52; H, 5.97.

***cis*-4,5-Dihydro-5-isopropyl-4-methyl-3-(phenylsulfonyl)isoxazole (2h)**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.01–7.55 (5 H, m), 4.10 (1 H, dd, J = 8.5, 9.8 Hz), 3.52 (1 H, m), 2.04 (1 H, m), 1.25 (3 H, d, J = 7.2 Hz), 1.06 (3 H, d, J = 6.4 Hz), 0.95 (3 H, d, J = 6.6 Hz); IR (thin film) 1447, 1329, 1211, 1165, 723 cm^{-1}; MS, m/e calcd for $C_{13}H_{17}NO_3S$ (M^+) 267.0929, obsd 267.0929.

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Registry No. 2a, 70367-25-8; **2b** (isomer 1), 116503-05-0; **2b** (isomer 2), 116503-10-7; **2c**, 116503-06-1; **2d**, 116503-07-2; **2e**, 70367-26-9; **2f**, 108470-81-1; **2g**, 108470-80-0; **2h**, 116503-08-3; **6a**, 116502-97-7; **6b** (isomer 1), 116502-98-8; **6b** (isomer 2), 116503-09-4; **6c**, 116502-99-9; **6d**, 116503-00-5; **6e**, 116503-01-6; **6f**, 116503-02-7; **6g**, 116503-03-8; **6h**, 116503-04-9; H_2C=CHCH(OTBS)CH_3, 90270-45-4; H_2C=C(CH_3)$(CH_2)_2CH_3$, 763-29-1; (*E*)-PrCH=CHPr, 14850-23-8; (*Z*)-H_3CCH=CHCH$(CH_3)_2$, 691-38-3; phenylthionitrile oxide, 77721-72-3; phenylthionitromethane, 60595-16-6; 1-hexene, 592-41-6; norbornene, 498-66-8; cyclopentene, 142-29-0; cyclohexene, 110-83-8.

Tetrazolo[1,5-*b*][1,2,4]triazines: An Alternate Synthesis and Chemistry

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We recently reported on the synthesis and chemistry of some furazano- and furoxano[3,4-*b*]piperazines (**1** and **2**).[1] This paper summarizes some similar work on the related 5,6,7,8-tetrahydrotetrazolo[1,5-*b*][1,2,4]triazines (**3**) in which a tetrazole ring has replaced the furazan or furoxan ring in **1** and **2**. These compounds were of interest be-

(1) Willer, R. L.; Moore, D. W. *J. Org. Chem.* **1985**, *50*, 5123.

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