3200, 1720 cm^{-1}; NMR δ 1.08 (s, 3), 2.00 (s, 3), 2.2–2.6 (br m, ~6), ~3.7 (m, 1), 3.75 (~t, 4). Anal. Calcd for $C_{19}H_{33}NO_4$: C, 67.22; H, 9.80; N, 4.13. Found: C, 67.07; H, 9.82; N, 3.97.

8β-[2-(*N*-Morpholino)ethyl]-9α-acetoxy-10β-methyldecal-2-one (27). To a solution of 75 mg (0.221 mmol) of **36**, mp 118–119.5 °C, in 12 mL of acetone was added 0.1 mL of Jones reagent[19] with stirring at room temperature. After 10.0 min, 40 mL of ice-cold 5% $NaHCO_3$ was added quickly, and the mixture was extracted quickly with 200 mL of ether which had been cooled to −10 °C. The organic layer was washed with brine (2 × 75 mL) at −10 °C, dried over $MgSO_4$, and concentrated under reduced pressure without heating to afford a solid residue which was quickly recrystallized from 4 mL of ether to afford 55.5 mg (74%) of **27**, mp 123–125 °C. An analytical sample was obtained from ether: mp 120–121 °C; IR 1725, 1710 cm^{-1}; NMR δ 1.28 (s, 3), 1.93 (s, 3), 2.25–2.5 (m, ~6), 2.75 (d, 1, J = 15 Hz), 3.37 (d, 1, J = 15 Hz), 3.7 (~t, 4). Anal. Calcd for $C_{19}H_{31}NO_4$: C, 67.63; H, 9.26; N, 4.15. Found: C, 67.69; H, 9.20; N, 4.11.

8β-[2-(*N*-Morpholino)ethyl]-10β-methyl-Δ^{1,9}-octal-2-one (37). A rapidly prepared solution of 24 mg (0.071 mmol) of **27**, mp 123–125 °C, in 250 μL of CD_3OD was monitored by NMR. Over a period of 55 min, a singlet developed at δ 5.77, and the initial singlet for the CH_3COO function of **27** at δ 1.92 was replaced by a singlet at δ 1.95, indicating conversion of **27** to **37** plus CH_3COOH. No further change in the NMR spectrum occurred over 24 h. The mixture was diluted with ether, washed twice with 5% $NaHCO_3$, and once with brine, dried over $MgSO_4$, and evaporated to give essentially pure **37**: NMR δ 1.30 (s, 3), 2.5 (~t, 6), 3.7 (~t, 4), 5.72 (s, 1). An analytical sample of **37** was prepared by two distillations of material formed by dehydration of **26** and had the following: bp 140–145 °C (0.05 mm); UV λ_{max} (99:1 H_2O–CH_3OH) 247 nm (ε 11 000);[21] IR 1740, 1610 cm^{-1}; NMR same as above. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.57; H, 9.72; N, 4.78.

8α-[2-(*N*-Morpholino)ethyl]-10β-methyl-Δ^{1,9}-octal-2-one (38). A sample of **37** was prepared from the reaction of 25 mg (0.085 mmol) of **26** in a mixture of 9 mL of CH_3OH and 1 mL of 5% K_2CO_3 solution at room temperature. The progress of the reaction was monitored by UV spectroscopy, and it was complete after 2 h. The mixture was concentrated under reduced pressure and partitioned between ether and water. The ether layer was dried over $MgSO_4$ and evaporated to afford 26 mg of oil which had an IR spectrum identical with that of **37** prepared above and had NMR (C_6D_6) peaks at δ 0.95 (s, 3), 2.15 (~t, 6), 3.6 (~t, 4), and 5.84 (s, 1), plus a trace of the peaks characteristic of **38** described below. To the C_6D_6 solution of this 26 mg of crude **37** was added 30 μL of a solution of 20 mg of sodium in 250 μL of CD_3OH, and the mixture was monitored by NMR. Over a period of about 40 h the peaks at δ 0.95 and 5.84 diminished and were replaced by peaks at δ 0.85 and 5.93, indicating conversion of **37** to **38**. After 4 days there still appeared to be a trace of **37**, but the mixture was partitioned between ether and water, and the ether layer was dried over $MgSO_4$ and evaporated to afford 22 mg of crude **38** which was distilled to give 12 mg of **38**, bp 150–160 °C (0.1 mm), still contaminated with a trace of **37**. This sample of **38** had an IR spectrum slightly different in the fingerprint region from that of **37** and had the following: UV λ_{max} (99:1 H_2O–CH_3OH) 247 nm (ε 11 000);[21] NMR (C_6D_6) δ 0.85 (s, 3), 2.15 (~t, 6), 3.6 (~t, 4), 5.93 (br s, 1); mass spectrum, m/e 277.2056 (M^+) (calcd for $C_{17}H_{27}NO_2$, 277.2042).

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Registry No. 3a, 4087-39-2; **6**, isomer 1, 18676-25-0; **6**, isomer 2, 72938-77-3; **7**, 72938-40-0; **8**, 72938-41-1; **9**, 72938-42-2; **10**, 72938-43-3; **11**, 72938-44-4; **12**, 72938-45-5; **13**, 72938-46-6; **14**, 72984-22-6; **15**, 72938-47-7; **16**, 72938-48-8; **17**, 72938-49-9; **18**, 72938-50-2; **19**, 72938-51-3; **20**, 72938-52-4; **21**, 72968-12-8; **22**, 72938-53-5; **23**, 72938-54-6; **24**, 72938-55-7; **25**, 72938-86-8; **26**, 72938-57-9; **27**, 72938-58-0; **28**, 72938-59-1; **29**, 72938-60-4; **30**, 72938-61-5; **31**, 72968-06-0; **32**, 72938-33-1; **33**, 72938-34-2; **34**, 72938-35-3; **35**, 72938-36-4; **36**, 72938-37-5; **37**, 72938-38-6; **38**, 72938-39-7.

Chemistry of Sulfenic Acids. 1. Synthesis of Trimethylsilyl Arenesulfenates (Arenesulfenic Acids)

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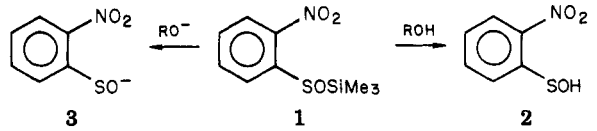
Trimethylsilyl arenesulfenates (**5**), masked sulfenic acids, are prepared in low yield by trapping the intermediate arenesulfenic acid generated by thermolysis of the corresponding *N*-benzylidenearenesulfinamide (**4**) with chlorotrimethylsilane–hexamethyldisilazane. Attempts to prepare **5** by oxidation of trialkyl(phenylthio)silanes (**8**) with 2-(benzenesulfonyl)-3-phenyloxaziridine (**11**), an aprotic oxidizing reagent, gave instead the previously unknown trialkylsilyl benzenesulfinates (**12**). These results are attributed to the enhanced nucleophilicity (α effect) of the intermediate trialkylsilyl arenesulfenate ester.

The importance of sulfenic acids (RSOH) as key intermediates in a wide variety of chemical transformations including biological ones is well recognized.[1] However, the difficulty in studying these species stems not only from their high reactivity but also from the lack of mild methods to generate them. Recently we reported that trimethylsilyl 2-nitrobenzenesulfenate (**1**) was a convenient, high-yield source of 2-nitrobenzenesulfenic acid (**2**) and 2-nitrobenzenesulfenate ion (**3**) when treated with alcohols and alkoxides, respectively.[2] The success of this approach in generating these species under comparatively mild,



3 **1** **2**

(1) For reviews of sulfenic acids see (a) F. A. Davis, A. J. Friedman, and U. K. Nadir, *J. Am. Chem. Soc.*, **100**, 2844 (1978); (b) D. R. Hogg in *Compr. Org. Chem.*, **4**, 261 (1979).

(2) F. A. Davis and A. J. Friedman, *J. Org. Chem.*, **41**, 897 (1976).

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nonaqueous conditions encouraged us to pursue the synthesis of other examples of trimethylsilyl arenesulfenates ($ArSOSiMe_3$), and we report the results of that study here.

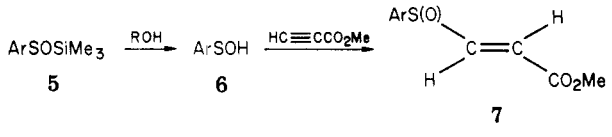
Trimethylsilyl arenesulfenates (**5**) are prepared in low

$$\underset{\mathbf{4}}{ArS(O)N{=}CHPh} \xrightarrow[(Me_3Si)_2NH,\ 83\ ^\circ C]{Me_3SiCl} \underset{\mathbf{5}}{ArSOSiMe_3} + PhCN$$

a, Ar = phenyl; **b**, Ar = 4-chlorophenyl; **c**, Ar = 3-nitrophenyl; **d**, Ar = 4-nitrophenyl

to poor yields by trapping the arenesulfenic acids generated by thermolysis of the corresponding *N*-benzylidenearenesulfinamides (**4**)[2] with chlorotrimethylsilane–hexamethyldisilazane. Silyl esters **5a–d** were isolated as oils by vacuum distillation but were contaminated with small amounts of benzonitrile (~2–3% by GC analysis) and unidentified silylated compounds. All attempts to modify the conditions, such as increasing the temperature to 110 °C (toluene solvent), resulted in lower yields. By contrast **1** could be prepared and isolated in a similar manner in greater than 85% yield.[2]

Proof of structure for **5a–d** is based upon the similarity of IR and NMR spectra to **1** as well as chemical properties. These compounds display NMR absorption in the region 0.13–0.32 ppm, attributed to the trimethylsilyl group. These silyl esters are rapidly hydrolyzed by protic reagents to the corresponding sulfenic acids **6** which are trapped



5 **6** **7**

in the presence of methyl propiolate to afford vinyl sulfoxides **7** in 24–40% yield.[2]

A number of factors may be responsible for the low yields of **5a–d** isolated in the thermolysis of **4a–d**. First, the rate of rearrangement of **4a–d** to the sulfenic acids is quite slow, requiring 36–96 h for complete reaction.[1a] We have previously shown that heating **1** for 15 h at 83 °C results in approximately 30% loss of product.[3] Thus the thermal lability of **5** is probably another factor which contributes to the lower isolated yields of these compounds.

Another reason for the low yields of **5a–d** may be related to the reactivity of the sulfenic acid. Presumably, a less reactive or more stable sulfenic acid would be more efficiently trapped by the chlorotrimethylsilane–hexamethyldisilazane reagent. While factors responsible for sulfenic acid reactivity are currently unclear, steric hindrance to dimerization or thiolsulfinate formation has been suggested as one factor stabilizing 2-methyl-2-propanesulfenic acid.[4] Thus, one effect of the *o*-nitro group in **2** may be steric inhibition of thiolsulfinate formation, stabilizing this sulfenic acid relative to **6**.[1,5]

The greater reactivity of sulfenic acids **6** compared to **2** may also be responsible for the lower yields of **7** obtained on reaction with methyl propiolate. Under similar conditions **2** gave a greater than 82% yield of this sulfoxide (**7**, Ar = 2-nitrophenyl).[2]

The difficulties encountered in the preparation and isolation of **5** via the thermal rearrangement of sulfinimines **4** prompted an investigation of alternative sources of these compounds.

The preparation of alkyl arenesulfenates (ArSOR) by reaction of sulfenyl chlorides (ArSCl) with metal alkoxides is well documented[6] and suggests that a similar reaction between the sulfenyl chloride and potassium trimethylsilanolate might be a useful source of **5**. Addition of 2-nitrobenzenesulfenyl chloride to 1 equiv of a THF solution of potassium trimethylsilanolate gave a blue colored solution which faded within minutes to a pale yellow. TLC (silica gel) indicated only the presence of bis(2-nitrophenyl) disulfide (ArSSR) and 2-nitrophenyl 2-nitrobenzenethiolsulfonate ($ArSO_2SAr$). The silyl ester **1** could not be detected by NMR spectroscopy.

A rationalization of these results is presented in Scheme I. All of the reactions proposed have ample precedent in

Scheme I

$$ArSCl + Me_3SiO^- \rightarrow \underset{\mathbf{1}}{ArSOSiMe_3}$$

$$ArSOSiMe_3 + Me_3SiO^- \rightarrow \underset{\mathbf{3}}{ArSO^-} + (Me_3Si)_2O$$

$$ArSO^- + ArSCl \rightarrow ArS(O)SAr$$

$$2ArS(O)SAr \rightarrow ArSSAr + ArSO_2SAr$$

Ar = 2-nitrophenyl

the literature.[1,7] In Scheme I we propose that as **1** is formed it immediately reacts with the nucleophilic trimethylsilanolate anion to afford the blue 2-nitrobenzenesulfenate ion (**3**)[2] which reacts further as shown. Inverse addition, the addition of sodium trimethylsilanolate to the sulfenyl chloride, gave similar results.

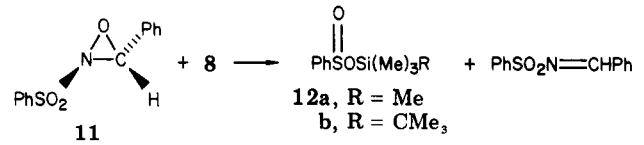
Another approach to trimethylsilyl arenesulfenate **5** would be via the oxidation of the readily available trialkyl(phenylthio)silanes (**8**).[8] We reasoned that the silyl

$$\underset{\mathbf{8}}{PhSSi(Me)_2R} \rightarrow \underset{\mathbf{9}}{PhS(O)Si(Me)_2R} \rightarrow \underset{\mathbf{10}}{PhSOSi(Me)_2R}$$

a, R = Me; **b**, R = CMe_3

sulfoxide **9**, if formed, would rearrange to the thermodynamically more stable silyl ester **10**. Attempts to carry out this transformation using protic oxidizing agents were unsuccessful. **8a** and *m*-chloroperbenzoic acid gave, as the only isolated product, approximately 30% yield of a moisture-sensitive oil believed to be trimethylsilyl *m*-chlorobenzoate as indicated by its facile hydrolysis to *m*-chlorobenzoic acid. Even if **10** were formed, its high reactivity toward nucleophilics and protic reagents would probably preclude its isolation under these conditions (Scheme I).

Recently we reported a new class of oxidizing reagents, 2-(benzenesulfonyl)-3-phenyloxaziridines (**11**), which se-



11 **12a**, R = Me; **b**, R = CMe_3

lectively oxidizes sulfides to sulfoxides and disulfides to thiosulfinates.[9] The aprotic nature of this reagent appears

(3) A. J. Friedman, unpublished results.
(4) F. A. Davis, S. G. Yocklovich, and G. S. Baker, *Tetrahedron Lett.*, 97 (1978).
(5) Other factors which may contribute to the relative stability of **2** are the electronegativity of the adjacent nitro group and interaction between sulfur and an oxygen of this nitro group. See W. C. Hamilton and S. J. LaPlaca, *J. Am. Chem. Soc.*, **86**, 2289 (1964); E. N. Givens and H. Kwart, *ibid.*, **90**, 378 (1968).
(6) E. Kuhle, *Synthesis*, 617 (1971).
(7) D. R. Hogg and P. W. Vipond, *J. Chem. Soc. B*, 1242 (1970); P. Koch, E. Ciuffarin, and A. Fava, *J. Am. Chem. Soc.*, **92**, 5671 (1970); D. R. Hogg and A. Robertson, *J. Chem. Soc., Perkin Trans. 1*, 1125 (1979).
(8) R. S. Glass, *J. Organomet. Chem.*, **61**, 83 (1973).

to be well-suited to the oxidation of 8 to 10. Reaction of 1 equiv of 11 with 8a and 8b affords, virtually instantaneously, a 50% yield of the trialkylsilyl benzenesulfinates (12). Even in the presence of a large excess of 8b this same stoichiometry is observed; i.e., 1 equiv of 11 gives 0.5 equiv of the silyl sulfinic ester 12b and unreacted 8b. Quantitative yields of 12a and 12b are obtained when the oxidation of 8a and 8b is carried out with 2 equiv of the oxidizing reagent. Yields are determined by integration of NMR peaks.

The previously unknown silyl esters of sulfinic acids (12) were isolated in 70–80% yield as clear liquids by distillation of the reaction mixture. The extreme lability of these compounds toward moisture precluded satisfactory elemental analyses, and identification was based upon spectral properties, chemical properties, and independent synthesis.

The trimethylsilyl group in 12a appears as a singlet at δ 0.25 whereas the diastereotopic methyl groups in 12b absorb at δ 0.2 and 0.28. Strong IR absorption in the region 1260 and 1140 cm^{-1} is attributed to the sulfinate ester acid functional group. Both 11a and 11b were prepared independently by reaction of the chlorosilane with benzenesulfinic acid and triethylamine. Interestingly, hydrolysis of 12a and 12b with a few drops of ethanol in chloroform affords diphenyl disulfide (10–30%), benzene phenylthiosulfonate (45–53%), and ethyl benzenesulfinate (25–40%).[10] A similar product distribution is obtained when benzenesulfinic acid is treated in a comparable manner.

The mechanism for oxidation of organosulfur compounds by 11 is believed to be related to that proposed for the oxidation of sulfides by peroxy acids, namely, a nucleophilic attack by the sulfur atom on the oxaziridine oxygen atom.[9] We propose that the formation of 12 in the oxidation of 8 involves oxidation of the intermediate trialkylsilyl sulfenate ester 10 by the oxaziridine. The preferential oxidation of 10 even in the presence of a large excess of 8 probably results from a combination of steric and electronic factors.

Greater steric hindrance in the starting material 8 is anticipated to slow the rate of oxidation as compared to the less hindered sulfenate ester 10. Oxidation of sulfides by 11 has been shown to be sensitive to steric factors.[9] However, steric effects should be of much less importance in silyl sulfides such as 8 than in the corresponding sulfides since an S–Si bond is considerably longer than a C–S bond (2.13 vs. 1.76 Å, respectively).[11]

Sulfenic acids (RSOH) have been considered to be examples of "α-effect" nucleophiles in that the nucleophilic sulfur atom is adjacent to a heteroatom containing lone pairs of electrons.[12] Such nucleophiles often display much greater nucleophilicity than the parent nucleophile. Trialkylsilyl arenesulfenate esters 1 and 10 are "masked" sulfenic acids, and the sulfur atom in these compounds will be much more nucleophilic than in the corresponding silyl sulfides 8. Thus, the preferential oxidation of 8 to 12 provides additional evidence for the enhanced nucleophilicity of sulfenic acids.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^1H NMR spectra were measured on a Varian A-60A spectrometer and IR spectra on a Perkin-Elmer 457 spectrometer. Gas chromatographic analyses were performed on a Perkin-Elmer 900 gas chromatograph with a 6 ft × $^1/_8$ in. 3% OV-17 on Anakorm Q 90/100-mesh column. The analyses were determined by comparison of peak areas with standard solutions of the reaction products. Analyses were performed at least twice and the results averaged. Elemental analyses were obtained from Micro-Analyses Inc., Wilmington, DE. Solvents were purified by standard methods.

Trimethylsilyl Arenesulfenates 5a–d. A mixture of 0.03 mol of the appropriate *N*-benzylidenearenesulfinamide (4),[1] 10.0 g (0.084 mol) of 1,1,1,3,3,3-hexamethyldisilazane, and 13.8 g (0.087 mol) of chlorotrimethylsilane (Aldrich) were dissolved in 50 mL of benzene distilled from CaH_2. The reaction mixture was placed in a Carius combustion tube, 0.5 mL of distilled triethylamine was added, and the tube was sealed under nitrogen. The reaction mixture was thermostated in an oil bath heated to 83 °C for 96 h in the case of 4a and 4b and 36 h for 4c and 4d. The precipitated solids were filtered under nitrogen and the solvent was removed under vacuum to afford a semisolid mixture which was distilled under high vacuum. At 0.05 torr the first fraction distilled at 35–50 °C and proved to be benzonitrile as identified by IR spectroscopy.

Trimethylsilyl Benzenesulfenate (5a): 1.4 g (24%) of a clear liquid; bp 60–65 °C (0.05 torr); IR (film) 1250 cm^{-1} (SOSi); NMR ($CDCl_3$) δ 0.133 (s, 9 H, $SiMe_3$) and 7.23 (s, 5 H).

Trimethylsilyl 4-Chlorobenzenesulfenate (5b): 2.3 g (33%) of a clear liquid; bp 75 °C (0.05 torr); IR (film) 1260 cm^{-1} (SiOS); NMR ($CDCl_3$) δ 0.38 (s, 9 H, $SiMe_3$) and 7.5 (m, 4 H).

Trimethylsilyl 3-Nitrobenzenesulfenate (5c): bp 135–140 °C (0.025 torr); 2.6 g (35%) of a yellow oil; IR (film) 1247 cm^{-1} (SiOS); NMR ($CDCl_3$) δ 0.38 (s, 9 H, $SiMe_3$) and 7.5–8.6 (m, 4 H).

Trimethylsilyl 4-Nitrobenzenesulfenate (5d): bp 130–140 °C (0.08 torr); 2.9 g (40%) of a yellow oil; sublimed at 130–135 °C (0.05 torr) to give a yellow solid; IR (film) 1247 cm^{-1} (SiOS); NMR ($CDCl_3$) δ 0.35 (s, 9 H, $SiMe_3$), 7.5–8.13 (AB q, J = 9 Hz, 4 H).

Methyl *trans*-(Arenesulfinyl)acrylate (7). In a dry 25-mL single-necked flask equipped with a magnetic stirring bar, reflux condenser, and nitrogen inlet was placed 2.0 mmol of the appropriate trimethylsilyl arenesulfenate (5a–d) in 10 mL of dry toluene and 1.0 mL of methyl propiolate (Chemical Samples Co.). Ethanol, approximately 5 drops, was added and the reaction mixture thermostated in an oil bath at 55–60 °C for 8 h. After removal of the solvent under vacuum, products were isolated by preparative TLC (silica gel G) (7a (23%), 7b (35%), 7c (38%), and 7d (40%)) and identified by comparison with authentic samples of 7a–d.[1]

Attempted Synthesis of Trimethylsilyl 2-Nitrobenzenesulfenate (1) from Potassium Trimethylsilanolate. In an oven-dried 50-mL 3-necked flask equipped with a dropping funnel, syringe cap, magnetic stirring bar, and nitrogen inlet was placed 0.93 g (5 mmol) of 2-nitrobenzenesulfenyl chloride (Aldrich) in 20 mL of dry THF. The reaction mixture was stirred and 0.56 g (5 mmol) of potassium trimethylsilanolate (Petrarch Systems Inc.) in 20 mL of THF added dropwise over 0.5 h. On addition of the first drop a blue color was observed which had turned to a pale yellow by the time all of the silanolate had been added. TLC of the reaction mixture indicated only the presence of bis(2-nitrophenyl) disulfide and 2-nitrophenyl 2-nitrobenzenethiolsulfonate. An NMR of the reaction mixture after removal of solvent under vacuum indicated the absence of any absorptions attributable to trimethylsilyl 2-nitrobenzenesulfenate (1).

Phenyl Trialkylsilyl Sulfides (8a and 8b). In a dry 100-mL single-necked flask equipped with a magnetic stirring bar, syringe cap, and nitrogen inlet was placed 5.5 g (0.05 mol) of thiophenol and 0.055 mol of chlorotrimethylsilane or chlorodimethyl-*tert*-

(9) F. A. Davis, R. Jenkins, Jr., and S. G. Yocklovich, *Tetrahedron Lett.*, 5171 (1978).

(10) Free sulfinic acids ($ArSO_2H$) disproportionate to thiolsulfonate ($ArSO_2SAr$) and sulfonic acid ($ArSO_3H$) via a sulfinyl sulfone intermediate ($ArS(O)SO_2Ar$). Attack of ethanol on this intermediate may afford the ethyl sulfinate esters observed in the hydrolysis of 12a and 12b. See J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, 84, 605 (1962); *J. Org. Chem.*, 28, 1162 (1963).

(11) H. A. Bent in "Organic Chemistry of Sulfur", S. Oae, Ed., Plenum Press, New York, 1977, Chapter 1.

(12) For discussions of the "α effect" as related to sulfenic acids see E. Ciuffarin, S. Gambaratta, M. Isola, and L. Senatore, *J. Chem. Soc., Perkin Trans. 2*, 554 (1978); F. A. Davis, A. J. Friedman, E. W. Kluger, E. B. Skibo, E. R. Fretz, A. P. Milicia, W. C. LeMasters, M. D. Bentley, J. A. Lacadie, and I. B. Douglass, *J. Org. Chem.*, 42, 967 (1977); J. L. Kice and J. P. Cleveland, *J. Am. Chem. Soc.*, 95, 104 (1973).

butylsilane in 25 mL of dry ether. The reaction mixture was stirred and triethylamine (6.0 g, 0.059 mol) in 25 mL of dry ether added slowly via syringe. After the mixture was allowed to stir for 12 h under nitrogen, the precipitated triethylamine hydrochloride was filtered and the solvent removed under vacuum to afford a clear oil which was distilled.

Phenyl Trimethylsilyl Sulfide (8a): 7.7 g (85%); bp 73–75 °C (3.0 torr) [lit.[8] 72–74 °C (3.0 torr)].

Phenyl Dimethyl-*tert*-butylsilyl Sulfide (8b): 9.5 g (85%); bp 78–83 °C (4–5 torr); NMR ($CDCl_3$) δ 0.13 (s, 6 H, Me), 0.96 (s, 9 H, CMe_3), and 7.02 (m, 5 H). Anal. Calcd for $C_{12}H_{20}SiS$: C, 64.26; H, 8.92; S, 14.29. Found: C, 64.39; H, 8.74; S, 14.47.

Trialkylsilyl Benzenesulfinates (12a and 12b): Oxidation of 8a and 8b. NMR-Scale Reaction. In a dry 5-mm NMR tube was placed 0.31 mmol of the appropriate silyl sulfide (**8a** or **8b**) in 1 mL of $CDCl_3$ or CCl_4 followed by 0.082 g (0.31 mmol) of 2-(benzenesulfonyl)-3-phenyloxaziridine (**11**).[7] After the reaction was complete (immediately in the case of **8a** and approximately 10 min for **8b**), the NMR spectra of the reaction mixture indicated the presence of **8a** and **8b**, **12a** and **12b**, and benzenesulfonimine ($PhSO_2N{=}CHPh$) in the ratio of 1:1:1 as determined by the integrated peak areas.

Preparative-Scale Reaction. In a dry 50-mL single-necked flask equipped with a magnetic stirring bar, syringe cap, and nitrogen inlet was placed 10.0 mmol of the appropriate silyl sulfide (**8a** and **8b**) in 10 mL of dry CH_2Cl_2. Via syringe was added dropwise with stirring 5.34 g (20.4 mmol) of **11** in 10 mL of CH_2Cl_2. After 1 h the solvent was evaporated with a stream of dry nitrogen, affording an oily semisolid which was distilled under vacuum.

Trimethylsilyl Benzenesulfinate (12a): 1.5 g (70%) of a clear oil, extremely moisture sensitive; bp 55–60 °C (0.25 torr); IR (film) 1250 (s) and 1140 (s) cm^{-1} (S=O); NMR ($CDCl_3$) δ 0.38 (s, 9 H, $SiMe_3$) and 7.4–7.8 (m, 5 H).

Phenyl Dimethyl-*tert*-butylsilyl Sulfide (12b): 2.0 g (80%) of a clear moisture-sensitive oil; bp 98–104 °C (0.25 torr); IR (film) 1265 (s) and 1140 (s) cm^{-1} (S(O)O); NMR (CCl_4) δ 0.2 (s, 3 H, Me), 0.28 (s, 3 H, Me), 0.92 (s, 9 H, Me_3C), and 7.62 (m, 5 H).

Synthesis of 12a and 12b from Benzenesulfinic Acid. Benzenesulfinic acid was prepared by addition of 4.0 g of sodium benzenesulfinate (Aldrich) to 40 mL of a 7% H_2SO_4 solution cooled to 0 °C in an ice bath. The reaction mixture was stirred for 0.5 h and extracted with ether (3 × 50 mL) followed by water (2 × 15 mL). The ether extracts were dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum to afford the solid benzenesulfinic acid (~70%) which was used without further purification.

In a dry 100-mL single-necked flask equipped with a magnetic stirring bar, nitrogen inlet, and syringe cap was placed 2.35 g (16.5 mmol) of benzenesulfinic acid and 17.0 mmol of the appropriate chlorosilane in 25 mL of dry CH_2Cl_2. The reaction mixture was cooled to 0 °C in an ice bath and 1.98 g (19.6 mmol) of triethylamine in 10 mL of CH_2Cl_2 added dropwise via syringe. The reaction mixture was stirred for 0.5 h at room temperature, the precipitated triethylamine hydrochloride filtered under nitrogen, and the solvent removed under vacuum to afford an oil. Distillation of the oil under vacuum afforded **12a** and **12b** (50–60%) whose IR and NMR spectra were identical with those of **12a** and **12b** prepared as described above.

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Registry No. **4a**, 52778-10-6; **4b**, 53075-89-1; **4c**, 53075-91-5; **4d**, 66883-59-8; **5a**, 73116-69-5; **5b**, 73116-70-8; **5c**, 73116-71-9; **5d**, 73116-72-0; **7a**, 49833-30-9; **7b**, 73116-73-1; **7c**, 66883-79-2; **7d**, 66883-80-5; **8a**, 4551-15-9; **8b**, 73116-74-2; **11**, 69849-45-2; **12a**, 73116-75-3; **12b**, 73116-76-4; methyl propiolate, 922-67-8; thiophenol, 108-98-5; benzenesulfinic acid, 618-41-7.

Furazans and Furazan Oxides. 8.[1] Preparation of 2-Oxy- and 2-Aminoindazoles by Rearrangement of Benzofurazan Oxide Derivatives

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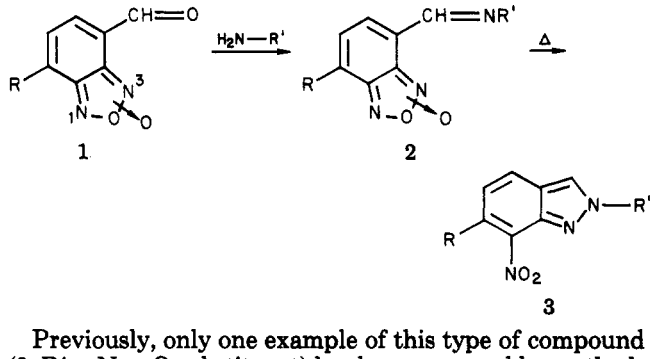
Oximes and hydrazones of 4-formylbenzofurazan oxides rearrange on heating to 2-oxy- and 2-amino-substituted indazoles. ^1H NMR spectral studies on the benzofurazan oxide derivatives are reported.

In an earlier paper in this series,[1] the preparation of a variety of 2-alkyl- and 2-aryl-7-nitroindazoles (**3**; R′ = alkyl, Ph) by condensation of 4-formylbenzofurazan oxides (**1**) with primary amines and rearrangement of the intermediate imines **2**, which could not be isolated, was reported. Oximes and hydrazones of the aldehydes **1** have obvious potential for conversion into 2-hydroxy-, 2-alkoxy-, 2-amino-, and 2-(substituted amino)indazoles, which are very little investigated classes of compound. We now report on the realization of this objective. At the outset, it was not obvious whether these compounds (**3**; R′ = OH, OR″, NH_2, NR''_2 etc.) would be thermodynamically more, or less, stable than the aldehyde derivatives **2**, and since our early experiments gave ambiguous results, their publication has been deferred until now, when further work has clarified the position.



Previously, only one example of this type of compound (**3**; R′ = N or O substituent) has been prepared by methods analogous to those described here; the 2-anilinoindazole

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