Chemistry of Oxaziridines. 1. Synthesis and Structure of 2-Arenesulfonyl-3-aryloxaziridines. A New Class of Oxaziridines

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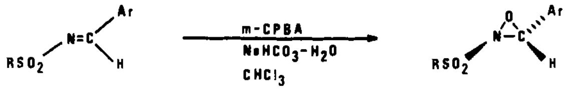
Abstract: A new class of oxaziridine derivatives, 2-arenesulfonyl-3-aryloxaziridines (**2**), is prepared by *m*-CPBA oxidation of sulfonimines ($RSO_2N{=}CHAr$). These compounds are the first stable examples of this ring system to have a substituent other than carbon attached to nitrogen and are characterized by a highly electrophilic oxaziridine oxygen atom. These oxaziridines have the *E* configuration as determined by X-ray crystallography. The presence of the powerful electron-attracting sulfonyl group attached to nitrogen apparently has little effect on the structure of the oxaziridine three-membered ring. Of more significance are the observations that the nitrogen lone pair in **2** is opposite to one of the sulfonyl oxygens and that the long S-N bond length implies little if any conjugative interaction between sulfur and nitrogen. Attempts to prepare oxaziridines via oxidation of sulfonimines, **5**, derived from acetophenone gave imidoyl ether **14**, a novel Baeyer-Villiger oxidation product of a C-N double bond.

Three-membered heterocyclic compounds are important synthetic reagents and have played key roles in elucidating the fundamental properties of organic molecules. Unique members of this class of heterocycles are the oxaziridines, compounds containing O, N, and C atoms in a three-membered ring. Oxaziridines, in general, are highly reactive molecules that display novel and unusual chemistry.[2] At present an understanding of the reactions and properties of these compounds, particularly from a mechanistic standpoint, remains undefined.[3] Furthermore, the synthetic potential of oxaziridines has yet to be realized.

2-Arenesulfonly-3-aryloxaziridines (**2**) are a new class of oxaziridines prepared by oxidation of the corresponding sulfonimine, **1**, according to eq 1.[4] These compounds are the first stable examples of this ring system to have an atom other than carbon attached to nitrogen and are characterized by a highly electrophilic oxaziridine oxygen atom. Synthetically these compounds are a new class of aprotic oxidizing agents capable of selectively oxidizing sulfides and disulfides to sulfoxides and thiolsulfinates without overoxidation.[5a] An optically active example of these compounds, 2-(*d*-camphor-10-sulfonyl)-3-aryloxaziridine, is an important new reagent for chiral oxidations.[5b] Organometallic reagents (R′M) are hydroxylated (R′OH) in good yield on treatment with **2**.[6] Photolysis of these oxaziridines affords the isomeric amides ($RSO_2NHC(O)Ar$),[7] while thermolysis provides synthetic entry into *C*-aryl-*N*-arenesulfonylnitrones ($RSO_2N(O){=}CHAr$), a new class of nitrones.[4]



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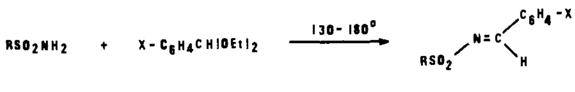
1 2

In this paper we report on the synthesis and structure of this new class of oxaziridines, 2-arenesulfonyl-3-aryloxaziridines (**2**).

Results and Discussion

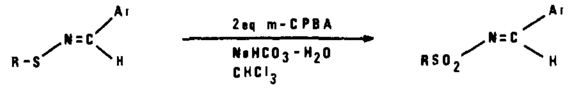
Synthesis of Sulfonimines (1). Sulfonimines (**1**) of aromatic aldehydes are conveniently prepared by heating an aliphatic or aromatic sulfonamide with an equivalent amount of the diethyl acetal of the aldehyde at 130–180 °C (eq 2).[8] Yields are in the range of 70–90%. Alternatively **1** may be prepared by the oxidation of the corresponding sulfenimine **3** (eq 3).[4]



(2)

1

a, R=p-tolyl, X=4-MeO
b, " X=4-Me
c, " X=2-Me
d, " X=H
e, " X=4-Cl
f, " X=3-NO2
g, " X=4-NO2
h, R=p-methoxyphenyl, X=4-MeO
i, R=p-methoxyphenyl, X=H
j, R=phenyl, X=H
k, R=4-chlorophenyl, X=H
l, R=3-nitrophenyl, X=H
m, R=4-nitrophenyl, X=H
n, R=methyl, X=H
o, R=benzyl, X=H



(3)

3 1

A special two-phase oxidation procedure is necessary for the high-yield oxidation of **3** to **2**, and involves the dropwise addition of 2 equiv of *m*-chloroperbenzoic acid (*m*-CPBA) in $CHCl_3$ to a rapidly stirring solution of **3** in $CHCl_3$-10% $NaHCO_3$. Although single-phase oxidation of **3** will also afford **2**, yields were lower and the product was more difficult to purify. Sulfenimines, **3**, are prepared via the metal-assisted procedure previously described.[9]

Sulfonimines, **1**, are crystalline solids giving satisfactory elemental analyses. The imino proton appears in the ^1H NMR at δ 8.9-9.1, and IR absorption at 1620 cm^{-1} is attributed to the C-N double bond stretching vibration. Sulfonimines are resistant to hydrolysis and may be stored indefinitely.

Attempts to prepare sulfonimines, **5**, derived from acetophenone using the diethyl acetal (eq 2) failed. Although ethanol was evolved on heating the sulfonamide with the acetophenone diethyl acetal, the residue polymerized. Perhaps a styrene derivative ($ArC(OEt){=}CH_2$) is formed which polymerizes.

Sulfonimines such as **5** may be prepared in 70-80% yield by oxidation of the corresponding sulfenimines, **4**, with 2 equiv

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Table I. Properties of 2-Sulfonyl-3-aryloxaziridines (**9–11**)

oxaziridine	yield, %	mp, °C dec	anal. calcd C	anal. calcd H	anal. found C	anal. found H	NMR ($CDCl_3$), δ
9b[a]	50	97–98					2.45 (d, 6 H, Me), 5.4 (s, 1 H, 3-H), 7.2–8.0 (s, 8 H)
9c	65	83–40	62.28	5.19	62.09	5.33	2.45 (s, 6 H, Me), 5.6 (s, 1 H, 3-H), 7.3–8.0 (m, 8 H)
9d	65	87–88	59.77	4.21	59.62	4.26	2.5 (s, 3 H, Me), 5.4 (s, 1 H, 3-H), 7.2–8.0 (m, 8 H)
9e	70	97–98	54.36	3.88	54.25	3.99	2.5 (s, 3 H, Me), 5.45 (s, 1 H, 3-H), 7.3–8.1 (m, 8 H)
9f	40	124–126	52.52	3.74	52.44	3.78	2.5 (s, 3 H, Me), 5.6 (s, 1 H, 3-H), 7.4–8.4 (m, 8 H)
9g	61	146–147	52.50	3.75	52.53	4.04	2.5 (s, 3 H, Me), 5.6 (s, 1 H, 3-H), 7.2–8.2 (m, 8 H)
10a	54	103	57.73	4.46	57.88	4.52	3.8 (s, 3 H, OMe), 5.35 (s, 1 H, 3-H), 7.0 (d, J = 9 Hz, 2 H) 7.3 (s, 5 H, Me), 7.9 (d, J = 9 Hz, 2 H)
10b	65	87–89	61.09	4.72	61.09	4.85	2.5 (s, 3 H, Me), 5.45 (s, 1 H, 3-H), 7.4 (s, 7 H), 7.9 (d, 2 H)
10d	61	97	59.77	4.21	59.62	4.26	5.6 (s, 1 H, 3-H), 7.5 (s, 5 H), 7.6–8.2 (m, 5 H)
10e	45	92	52.79	3.38	52.89	3.46	5.4 (s, 1 H, 3-H), 7.2–7.85 (m, 9 H)
10f	45	97	50.98	3.26	50.69	3.49	5.6 (s, 1 H, 3-H), 7.3–8.0 (m, 9 H)
10g	43	96	50.98	3.26	51.09	3.36	5.65 (s, 1 H, 3-H), 7.5 (s, 5 H)
11a	64	59–61	48.22	4.56	48.45	4.64	3.2 (s, 3 H, Me), 5.35 (s, 1 H, 3-H), 7.35 (s, 5 H)
11b	50	118	61.10	4.72	61.30	4.48	4.55 (s, 2 H, CH_2), 5.4 (s, 1 H, 3-H), 7.5 (s, 10 H)

[a] A satisfactory elemental analysis could not be obtained.

of *m*-CPBA (eq 3). In contrast to **1**, which was resistant to hydrolysis, **5** slowly formed the sulfonamide and acetophenone on long standing.

4 **5**

a, X=H
b, X=4-Cl

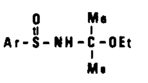
Although sulfenimines ($ArSN{=}CR_2$) derived from aliphatic aldehydes and ketones can be oxidized to sulfinimines ($ArS(O)N{=}CR_2$) in excellent yield,[10] they cannot be oxidized further to sulfonimines. The C–N double bond in sulfenimines, **3**, becomes increasingly susceptible to Michael-type additions as the electronegativity of sulfur increases (increasing oxidation state).[10a,11] Attempted oxidation of aliphatic sulfenimines to sulfonimines invariably resulted in complex reaction mixtures. For example, oxidation of *N*-isopropylidine-3-nitrobenzenesulfenamide (**6a**) according to eq 3 gave ethyl 3-nitrobenzenesulfonate (**7**) in 40% yield. Apparently ethanol present in the chloroform adds across the C–N bond in the sulfinimine (**6b**) to give the adduct **8**.[10a] Attack of ethanol at the S–N bond in **8**, which appears to be acid catalyzed,[12] would afford the ethyl sulfinate ester (ArS(O)OEt) and further oxidation yields the sulfonate ester, **7**. Supportive of this scheme is the isolation of adduct **8** (OEt = OMe) in good yield on treatment of **6b** with chloroform-methanol.[10a,c] The sulfonamide ($ArSO_2NH_2$) was the only identifiable product when the oxidation of **6a,b** was carried out in ethanol-free chloroform or methylene chloride.

$ArS(O)_n{-}N{=}CMe_2$

6a, n=0
b, n=1

$ArS(O)_2OEt$

7



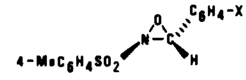
$Ar{-}\overset{O}{\overset{\|}{S}}{-}NH{-}\underset{Me}{\underset{|}{\overset{Me}{\overset{|}{C}}}}{-}OEt$

8

Ar=3-nitrophenyl

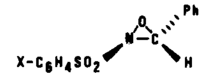
Synthesis of Oxaziridines. 2-Arenesulfonyl-3-aryloxaziridines (**2**) are prepared by dropwise addition of 2-5 equiv of *m*-CPBA in $CHCl_3$ to a rapidly stirring solution of **1** or **3**, respectively, in $CHCl_3$-H_2O-10% $NaHCO_3$ at 0 °C (eq 1). The properties of oxaziridines **9–11** prepared in this way are summarized in Table I.

Compounds **9–11** are relatively stable crystalline solids giving satisfactory elemental analyses and melting with decomposition (Table I). The ^1H NMR spectra of these compounds are characterized by a sharp singlet appearing in the region δ 5.4–5.6 and these are attributed to the 3-H proton. Further verification of the oxaziridine structure is seen in reactions with HI and with triphenylphosphine (Scheme I). When **2** is stirred in benzene with an equivalent amount of triphenylphosphine for 8 h, triphenylphosphine oxide and the sulfonimine, **1**, are obtained in good yield. With aqueous potassium iodide in acetic acid, **2** liberated iodine (97–100%). Both reactions (Scheme I) are characteristic of oxaziridines.[13]



9

a, X=4-MeO
b, X=4-Me
c, X=2-Me
d, X=H
e, X=4-Cl
f, X=3-NO2
g, X=4-NO2



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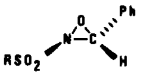
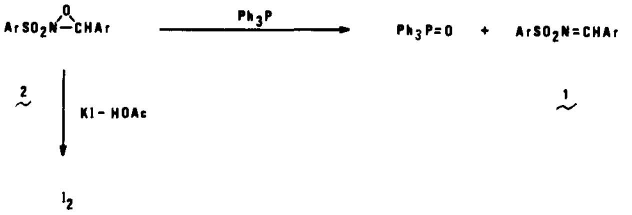


11a, R=Me
b, R=PhCH2

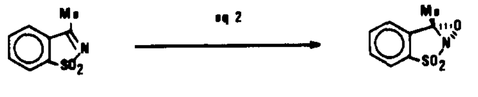
Not every oxidation of a sulfonimine, **1**, resulted in the corresponding oxaziridine. Attempts to prepare 2-(*p*-methoxybenzenesulfonyl)-3-(*p*-methoxyphenyl)oxaziridine from **1h** failed. Oxidation of **1h** according to eq 1 gave a dark oil which did exhibit the characteristic absorption at δ 5.6 ppm due to the oxaziridine 3-H proton, but attempts to isolate the oxaziridine failed. The thermal stability of **9–11**, as suggested by their storage lifetimes, parallels this result. Electron-donating groups attached to the sulfonyl group appear to increase the stability of the oxaziridine, while these same groups have the opposite effect when attached to the iminoaryl group (Ar in **2**).

Oxidation of 3-methyl-1,2-benzisothiazole 1,1-dioxide

Scheme I



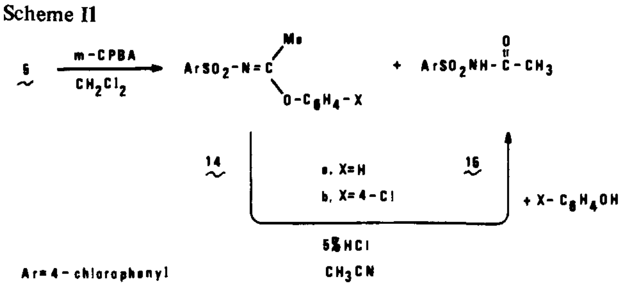
(**12**)[14] gave **13** in greater than 90% yield. The elemental analysis of **13**, the fact that this compound affords iodine (93%) when treated with KI-HOAc-H_2O solution, and the upfield shift of the methyl protons in **13** to δ 2.1 ppm (δ 2.7 in **12**) all support the proposed structure.



12 **13**

In contrast to the high-yield oxidation of **12 to 13**, oxidation of sulfonimine **5** under similar conditions failed. Starting material was recovered in high yield in addition to a small amount (ca. 10%) of the sulfonamide ($ArSO_2NH_2$). Refluxing **5** in methylene chloride with 1.1 equiv of *m*-CPBA for 24 h gave a 40-50% yield of aryl imidoyl ether **14** and a 13% yield of *N*-(*p*-chlorophenylsulfonyl)acetamide (**15**); see Scheme II.

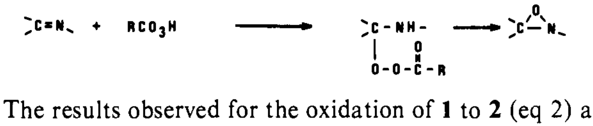
Scheme II



Proof of structure for **14** rests with the elemental analysis, the lack of reaction with triphenylphosphine and KI-HOAc, and the C-O stretching absorption appearing at 1250 cm^{-1}. Additional support for the proposed structures is derived from the hydrolysis of **14** to **15** and the corresponding phenol in good yield (Scheme II).

The isolation of products attributed to the Baeyer-Villiger oxidation of a C-N double bond of an imine is rare. The only other example is the formation of oxazolines in the *m*-CPBA oxidation of 2-methoxyazetines.[15] However, formation of dibenzamide and phenol in the oxidation of *N*-diphenylmethylenebenzamide, reported by Padwa, is consistent with the hydrolysis of a Baeyer-Villiger oxidation intermediate similar to **14**.[16] Two mechanisms have been proposed for peracid oxidation of imines to oxaziridines: a one-step epoxidation-type mechanism where the π system of the C-N double bond attacks the peroxy acid (eq 4)[13b,17] and a two-step Baeyer-Villiger-type oxidation occurring by addition of the peracid to the C-N double bond followed by elimination of 1 mol of acid used as the peroxy acid (eq 5),[18] the first step in both reactions being rate determining.[17,18] A recent ab initio MO study of the mechanism finds support for the two-step process, i.e., eq 5.[18c]

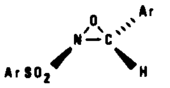
(4)



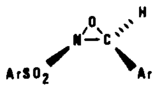
(5)

The results observed for the oxidation of **1** to **2** (eq 2) are consistent with a Baeyer-Villiger-type oxidation mechanism (eq 5). First, the C-N double bond in sulfonimines, **1**, is an electron-deficient double bond and such compounds are good Michael acceptors. The necessity for carrying out the oxidation of **1** to **2** in a two-phase system suggests that the peroxy acid anion (RCO_3^-) is adding to the C-N double bond of **1**. This is reminiscent of the epoxidation of α,β-unsaturated carbonyl compounds using alkaline peroxide. Finally, the isolation of **14**, a Baeyer-Villiger-type oxidation product, further supports this mechanism (eq 5).

Structure of 2-Arenesulfonyl-3-aryloxaziridines (2). The barriers for syn-anti isomerization in sulfonimines are on the order of 12-13 kcal/mol.[19] Thus oxidation of **1** (eq 1) would be anticipated to afford both *E* and *Z* oxaziridines **2**. Furthermore, depending on the barrier to nitrogen inversion in **2**, interconversion between the *E* and *Z* forms of **2** is possible.



2E



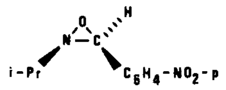
2Z

The barriers to nitrogen inversion for *N*-alkyloxaziridines have been estimated to be in the range of 30-35 kcal/mol,[20] and the isolation of enantiomeric and diastereomeric oxaziridines[21] further establishes the noninverting nature of the nitrogen in these compounds. On the other hand, the attachment of a sulfonyl group to nitrogen in aziridines lowers the barrier to nitrogen inversion by about 8 kcal/mol as compared to *N*-alkylaziridines.[22] This effect has been attributed to a p-d π conjugative action between the sulfonyl group and nitrogen.[22]

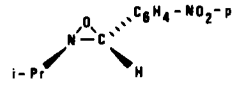
The 2-arenesulfonyl group in **2** apparently does not significantly lower the nitrogen inversion barrier in these oxaziridines. The 3-H proton in **9b** and **9c** remains a sharp singlet on cooling to −80 °C. If there had been rapid interconversion between the *E* and *Z* forms of **2**, broadening of the proton would have been anticipated. We conclude, therefore, that oxidation of the sulfonimines **1** affords a single oxaziridine isomer.

The dependence of proton chemical shifts on the orientation of an adjacent lone pair of electrons is well known. The proton cis to the lone pair absorbs at lower field than those that are trans.[23] Several explanations have been proposed to account for this phenomenon and include transfer of electron density via the back lobe of the lone pair,[29] by steric factors and the anisotropic character of this lone pair of electrons.[25]

Oxaziridines are examples of compounds which illustrate this dependence of chemical shift on the orientation of the nitrogen lone pair of electrons, and this effect has been used to assign the oxaziridine structure.[26-28] For example, the chemical shift of the 3-H proton in (*Z*)-2-isopropyl-3-(*p*-nitrophenyl)oxaziridine (**16a**), whose structure was rigorously determined by X-ray crystallography, appears at δ 5.36 ppm.[27,28] In the *E* oxaziridine, **16b**, this proton appears almost 1 ppm upfield at 4.61 ppm (Table II). A similar structural dependence for the 3-^{13}C-H coupling constant in oxaziridines has been observed.[27] Thus, the ^{13}C-H coupling constant in **16a** is larger (185.6 Hz) than in **16b** (179.0 Hz).[26] A positive contribution to the coupling constant via a direct through-space orbital overlap of the cis lone pair has been proposed to explain these results.[27]



Z-16a



E-16b

In an effort to assign the configuration of 2-arenesulfonyl-3-aryloxaziridines (**2**) we measured the chemical shifts of the 3-H proton as well as the ^{13}C-H coupling constants (Table II). As noted in Table II, the chemical shifts for the 3-H proton in these oxaziridines fall in the narrow range of δ 5.36-5.55 ppm and the 3-^{13}C-H coupling constants lie in the range of 186-189

Table II. ^{1}H and ^{13}C NMR Data for Oxaziridines

oxaziridine	3-H, ppm[a]	3-^{13}C, ppm[a]	3-H-^{13}CH, Hz
16a (*E*)	4.61		179.0
16b(*Z*)	5.63		185.6
9b	5.45	77.4	186.4
9d	5.4	76.3	185.6
9e	5.45	75.6	186.5
9f	5.55	74.8	188.3
10d	5.60	76.4	187.8
10e	5.40	76.5	188.8
10g	5.65	76.7	

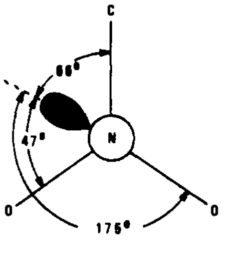
[a] Me_4Si reference.

Hz. Both these results suggest, when compared with those for *N*-alkyloxaziridines, that **2** has the *Z* configuration. However, without the other isomer of **2** the structure of these oxaziridines could not be assigned with confidence.

The X-ray crystal structures of 2-(*p*-toluenesulfonyl)-3-(*m*-nitrophenyl)oxaziridine (**9f**)[29a] and 2-(*p*-toluenesulfonyl)-3-(*p*-chlorophenyl)oxaziridine (**9e**)[29b] reveal that these oxaziridines have the *E* configuration in the solid state. Thus, based on the NMR data (Table II), all known examples of this class of compounds have the same relative configuration (*E* configuration). The ^{1}H and ^{13}C NMR data, suggesting that **1** had the *Z* configuration, must be a consequence of the powerful electron-attracting sulfonyl group. This group apparently reduces the electron density in the nitrogen lone pair and is responsible for the shift to lower field of the 3-H proton as well as the increase in the ^{13}C-H coupling constants (Table II).

As illustrated in Figure 1, the bond angles and bond length of **2** are not significantly different than those reported for **16a**[28] and (*RS*)-(*E*)-2-methyl-3-(2,6-dimethyl-4-chlorophenyl)-oxaziridine.[30] Apparently, the presence of the powerful electron-attracting sulfonyl group attached to the oxaziridine nitrogen has little effect on the structural parameters of the oxaziridine three-membered ring.

In contrast to sulfonamides[31,32] and α-sulfonyl carbanions[33,34] the nitrogen lone pair in **2** is located anti to one of the sulfonyl oxygens (structure I) and the nitrogen is pyramidal.[29] The S–N bond length of 1.734 Å is considerably longer than in the aforementioned sulfonamides. Evidently the ring structure in **2** makes it energetically unfavorable for the nitrogen atom to adopt a pseudoplanar configuration where the bond angles approach 120°. We interpret this to mean that there is little, if any, conjugative interaction between the sulfonyl group in **2** and the nitrogen lone pair of electrons.



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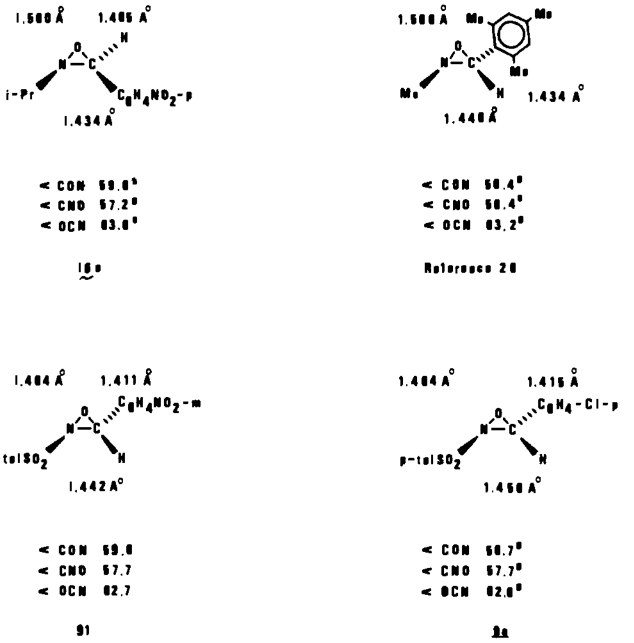

Figure 1.

Conclusions

The reactivity of oxaziridines is determined by the substituents attached to carbon and nitrogen, with substituents attached to nitrogen apparently having the greatest influence.[1-3] *N*-Alkyl substituents confer thermal stability on oxaziridines with the stability increasing in the order N-Me < N-*i*-Pr < N-*t*-Bu.[2,3] On the other hand, *N*-aryl stubstituents increase the reactivity of oxaziridines to such an extent that most *N*-aryloxaziridines can only be detected in solution.[3,35] The conclusion by a number of authors is that electron-attracting groups attached to nitrogen decrease the thermal stability of oxaziridines while electron-donating groups attached to nitrogen have the opposite effect.[3,35] This account of oxaziridine reactivity is almost certainly oversimplified in light of the stability of 2-arenesulfonyl-3-aryloxaziridines (**2**), which have the powerful electron-attracting sulfonyl group attached to nitrogen. While explanations for oxaziridine substituent reactivity are currently lacking, the answer probably involves some combination of steric and electronic factors which control the ring-opening reactions. The dominant factor determining ring-opening reactions in cyclopropenes[36] and oxadiaziridines[37] appears to be steric and not electronic.

The ease of preparation and stability of 2-arenesulfonyl-3-aryloxaziridines (**2**) coupled with the fact that these compounds are characterized by a highly electrophilic oxaziridine oxygen atom suggests that these oxaziridines will be useful synthetic reagents.[4-6] Furthermore, studies of the reactions and properties of this new class of oxaziridines, which are more easily manipulated than other oxaziridines, will provide further insight into the factors responsible for the unique reactivity of this class of heterocyclic compounds.

Experimental Section

Melting points were obtained on a Mel-Temp apparatus and are uncorrected. IR spectra were measured on a Perkin-Elmer Model 457 IR spectrometer and NMR spectra were obtained on a Varian A-60A or Perkin-Elmer R24B spectrometer. ^{13}C NMR spectra were measured on a Varian CFT-20 pulse Fourier transform NMR spectrometer. Chemical shifts are referenced against internal Me_4Si. Solvents were purified by literature methods.

General Synthesis of Sulfonimines (1).[8] In a 100-mL single-necked flask equipped with magnetic stirring bar and short-path distilling head were placed equivalent amounts (typically 50 mmol) of the appropriate sulfonamide and aldehyde diethyl acetal. The reaction mixture was heated at 150–180 °C in an oil bath until all the ethanol had ceased distilling over (about 0.5 h), at which time the solution was placed under high vacuum (0.1 mm) and allowed to cool to room temperature. The solid sulfonimine, **1**, was dissolved in a small amount of CH_2Cl_2 and precipitated by slow addition of *n*-pentane with stirring. Analytical samples were crystallized from 4:1 v/v petroleum ether (30–60 °C)-benzene. Sulfonimines, **1**, have the following properties (% yield, mp).

1c, 70, 91–92 °C. NMR ($CDCl_3$): 2.4 (s, 3 H, *p*-Me), 2.6 (s, 3 H, Me), 7.2 (m, 5 H), 7.9 (m, 3 H), and 9.2 ppm (s, 1 H).

Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.93; H, 5.49. Found: C, 65.83; H, 5.65.

1f, 60, 139–140 °C. NMR ($CDCl_3$): 2.4 (s, 3 H, Me), 7.2–7.8 (m, 8 H), and 9.0 ppm (s, 1 H).

Anal. Calcd for $C_{14}H_{12}N_2O_4S$: C, 55.26; H, 3.95. Found: C, 55.50; H, 3.75.

1h, 80, 93–94 °C. NMR ($CDCl_3$): δ 3.7 (s, 6 H, MeO), 6.8 (m, 4 H), 7.7 (m, 4 H), and 8.8 ppm (s, 1 H)

Anal. Calcd for $C_{15}H_{15}NO_4S$: C, 59.09; H, 4.90. Found: C, 58.72; H, 5.04.

1l, 75, 121–123 °C. NMR ($CDCl_3$): 7.4–9 (m, 9 H) and 9.1 ppm (s, 1 H).

Anal. Calcd for $C_{13}H_{10}NO_4S$: C, 53.79; H, 3.45. Found: C, 54.03; H, 3.40.

1n, 80, 90–92 °C. NMR ($CDCl_3$): δ 3.0 (s, 3 H, Me), 7.4 (m, 3 H), 7.7 (m, 2 H), and 8.85 ppm (s, 1 H).

A satisfactory elemental analysis could not be obtained.

1o, 75, 92 °C. NMR ($CDCl_3$): 4.65 (s, 2 H, Me), 7.68 (m, 10 H), and 8.85 ppm (s, 1 H).

Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.86; H, 5.02. Found: C, 64.65; H, 5.04.

Synthesis of Acetophenone and 4-Chloroacetophenone Sulfenimines 4a,b. Sulfenimines **4a,b** were prepared from 19.0 g (66.4 mmol) of 4-chlorophenyl disulfide and a threefold excess of acetophenone or 4-chloroacetophenone using the metal-assisted sulfenimine synthesis previously described.[9] The excess ketone was removed by vacuum distillation using a bath temperature below 50 °C. The residue was washed with *n*-pentane and the sulfenimines were crystallized from absolute ethanol.

4a: 70% yield; mp 71–73 °C; NMR ($CDCl_3$) δ 2.45 (s, 3 H, Me) and 7.2–7.8 (m, 9 H).

Anal. Calcd for $C_{14}H_{14}ClNS$: C, 64.36; H, 4.59. Found: C, 64.74; H, 4.79.

4b: 49% yield; mp 69–70 °C; NMR ($CDCl_3$) δ 2.45 (s, 3 H, Me) and 7.2–7.9 (m, 8 H).

Anal. Calcd for $C_{14}H_{11}Cl_2NS$: C, 56.95; H, 3.73; N, 4.75. Found: C, 56.73; H, 3.84; N, 4.92.

Oxidation of Sulfenimines 4a,b to Sulfonimines 5a,b. In a 250-mL three-necked flask equipped with mechanical stirrer and dropping funnel were placed 7.0 mmol of **4a** or **4b** in 60 mL of $CHCl_3$, 2.5 g of $NaHCO_3$, and 20 mL of H_2O. The reaction mixture was cooled to 0 °C in an ice bath and 3.25 g (16.1 mmol) of 85% *m*-chloroperbenzoic acid (*m*-CPBA) (Aldrich Chemical Co.) in 60 mL of $CHCl_3$ added dropwise over 0.5 h. After the addition was complete the reaction mixture was stirred for an additional 4 h and the $CHCl_3$ solution washed with 10% Na_2SO_3 (3 × 50 mL) and 10% $NaHCO_3$ (3 × 50 mL) and dried over anhydrous $MgSO_4$. Sulfonimines were crystallized from ether–pentane and had the following properties.

5a: 48% yield; mp 59–60 °C; NMR ($CDCl_3$) δ 3.9 (s, 3 H, Me) and 7.3–8.0 (m, 9 H); IR (KBr) 1615 (s, C=N), 1230, 1170 (SO) cm^{-1}.

Anal. Calcd for $C_{14}H_{12}ClNO_2S$: C, 57.26; H, 4.07. Found: C, 57.41; H, 3.95.

5b: 79% yield; mp 78–80 °C; NMR ($CDCl_3$) δ 2.8 (s, 3 H, Me) and 7.1–7.9 (m, 8 H); IR (KBr) 1610 (s, C=N), 1315, 1170 (SO) cm^{-1}. A satisfactory elemental analysis could not be obtained.

Oxidation of *N*-Isopropylidene-3-nitrobenzenesulfenamide (6a). *N*-Isopropylidine-3-nitrobenzenesulfenamide (**6a**,[9] 1.64 g, 7.8 mmol) was oxidized as described above with 3.5 g (17.2 mmol) of *m*-CPBA. However, the solution was not washed with aqueous Na_2SO_3. Workup gave an oily, brown solid which was chromatographed on Florisil. Elution with ether gave 0.72 g (40%) of an oil (lit.[37] mp 37 °C) identified as ethyl 3-nitrobenzenesulfonate (**7**) by comparison with an authentic sample.

General Synthesis of Oxaziridines (2). In a 250-mL three-necked flask equipped with mechanical stirrer and dropping funnel were placed 25 mmol of the appropriate sulfonimine, **1**, in 80 mL of $CHCl_3$, 5.25 g (65 mmol) of $NaHCO_3$, and 60 mL of H_2O. The solution was cooled to 0 °C in an ice bath and rapidly stirred and 11.0 g (54 mmol) of *m*-CPBA in 150 mL of $CHCl_3$ added dropwise over 45 min. After the addition was complete the solution was stirred for an additional 4 h and the $CHCl_3$ solution washed with 10% Na_2SO_3 (3 × 50 mL) and 10% $NaHCO_3$ (3 × 50 mL). After the solution was dried over anhydrous K_2CO_3 (0.5–1.0 h at 0 °C) the solvent was removed on the rotatory evaporator keeping the bath temperature below 35 °C. If the oxaziridine was a solid it was washed once with a small amount of *n*-pentane. If the oxaziridine was an oil it was washed several times with a small amount of *n*-pentane until it was transformed into a solid. The solid oxaziridine was dissolved in a small amount of ethyl acetate (5–10 mL) and precipitated by slow addition of *n*-pentane with stirring. The properties of 2-arenesulfonyl-3-aryloxaziridines prepared in this way are summarized in Table I.

Reactions of 2-Arenesulfonyl-3-aryloxaziridines (2) with Triphenylphosphine. Into a 25-mL single-necked flask equipped with magnetic stir bar and reflux condenser with nitrogen inlet were placed 0.8 mmol of the appropriate oxaziridine, **2**, and 0.21 g (0.8 mmol) of triphenylphosphine in 10 mL of benzene. After the solution was stirred for 30 h under nitrogen the precipitated sulfonimine, **1**, was removed by filtration (yield 30–40%) and the solvent removed under vacuum. The oily residue was subjected to preparative TLC (silica gel) using benzene–ether. The sulfonamide corresponding to the sulfonimine **1** (50–60% yield) and triphenylphosphine oxide (80–85% yield) were identified by comparison of their properties with those of authentic samples. On a silica gel TLC plate sulfonimines, **1**, are hydrolyzed to the corresponding sulfonamide and aldehyde.

Reactions of 2-Arenesulfonyl-3-aryloxaziridines (2) with Hydrogen Iodide. In a 50-mL Erlenmeyer flask equipped with magnetic stir bar was dissolved 0.4 mmol of the appropriate oxaziridine **2** in 10 mL of glacial acetic acid. Approximately 2.0 mL of a 5% potassium iodide solution was added and the resulting iodine titrated with standard 0.1 N sodium thiosulfate solution until clear.

3-Methyl-1,2-benzothiazole 1,1-Dioxide Oxide (13). 3-Methyl-1,2-benzothiazole 1,1-dioxide (**12**,[14] 0.75 g, 4.14 mmol) was dissolved in 40 mL of $CHCl_3$ and oxidized with 0.9 g (4.55 mmol) of *m*-CPBA as described above. The reaction mixture was worked up as described above to afford 0.75 g (92%) of a white solid which, when crystallized by precipitation from ether with *n*-pentane, had mp 91–92 °C. Oxaziridine **13** gave 93% I_2 when treated with HI and had the following properties: NMR ($CDCl_3$) δ 2.15 (s, 3 H, Me) and 7.6 (s, 4 H); IR (KBr) 1360 and 1180 cm^{-1} (SO_2).

Anal. Calcd for $C_8H_7NO_3S$: C, 48.73; H, 3.55; N, 7.11. Found: C, 48.83; H, 3.73; N, 6.83.

Oxidation of Sulfonimines 5a,b. In a 50-mL single-necked flask equipped with magnetic stir bar, reflux condenser, and drying tube was placed 4.0 mmol of **5a** or **5b** in 20 mL of CH_2Cl_2. After addition of 0.9 g (4.44 mmol) of *m*-CPBA the reaction mixture was refluxed for 12 h and cooled to −78 °C and the precipitated *m*-chlorobenzoic acid filtered under an atmosphere of nitrogen. Removal of solvent gave an oily solid, which when washed with *n*-pentane gave the crystalline imidoyl ethers **14a,b**. The imidoyl ethers were crystallized from methanol and had the following properties.

14a: 43% yield; mp 86–88 °C; NMR ($CDCl_3$) δ 2.75 (s, 3 H, Me) and 7.0–7.7 (m, 9 H); IR (KBr) 1615 (C=N), 1320 (SO_2), 1260 (C–OAr), and 1150 cm^{-1} (SO_2).

Anal. Calcd for $C_{14}H_{12}ClNO_3S$: C, 54.36; H, 3.88. Found: C, 54.33; H, 4.02.

14b: 50% yield; mp 144–146 °C; NMR ($CDCl_3$) δ 2.75 (s, 3 H, Me) and 6.8–7.7 (m, 8 H); IR (KBr) 1610 (s, C=N), 1315 (s, SO_2), 1255 (s, C–O–Ar), and 1160 cm^{-1} (s, SO_2).

Anal. Calcd for $C_{14}H_{11}Cl_2NO_3S$: C, 48.99; H, 3.21; N, 4.08; S, 9.33. Found: C, 48.89; H, 3.18; N, 3.98; S, 9.58.

Hydrolysis of Imidoyl Ethers 14a,b. Into a 25-mL single-necked flask equipped with magnetic stirring bar and reflux condenser were placed 0.87 mmol of **14a** or **14b** in 10 mL of acetonitrile, 1 mL of water, and 2 drops of concentrated HCl. After the solution was refluxed for 12 h the solvent was removed under vacuum to afford an oil. The oil was washed several times with *n*-pentane (5-mL portions) to yield 0.18–0.19 g of a white solid which was crystallized from aqueous ethanol, mp 192 °C (lit.[38] mp 192.5 °C), and identified as *N*-(*p*-chlorophenylsulfonyl)acetamide (**15**): NMR (Me_2SO-d_6) δ 2.0 (s, 3 H, Me), 3.5 (bs, 1 H, exchange with D_2O), and 7.8 (AB quartet, 4 H, J = 10 Hz). Evaporation of the *n*-pentane washings afforded 70–80% yields of the appropriate phenols, identified by comparison with authentic samples.

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Reduction of *cis*-Bicyclo[4.3.0]non-3-ene and Its 8-Substituted Heterocyclic Analogues

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Abstract: The preparation and competitive catalytic hydrogenation of members of the 8-heterobicyclo[4.3.0]non-3-ene series are discussed. The heteroatom's specific coordination with the catalyst is rationalized as the origin of the observed heteroatom effects.

During the past several years, we have been interested in the ways a heteroatom influences the structure and reactivity of nonaromatic heterocyclic molecules.[1] As part of this continuing study, we embarked on an analysis of the catalytic reduction of various members of the *cis*-8-heterobicyclo[4.3.0]non-3-ene series. Of particular interest in this series is the skeletal similarity, which enables us to examine how the heteroatom expresses its effects throughout the molecule. The preparations of these compounds are outlined in Scheme I.

The commercially available anhydride **1** was reduced with lithium aluminum hydride to **2**.[2] Treatment of **2** with *p*-toluenesulfonyl chloride in refluxing pyridine resulted in a high-yield conversion to *cis*-8-oxabicyclo[4.3.0]non-3-ene (**3**).[3] Tosylation of **2** at 0 °C yielded **5**. Refluxing an ethanolic solution of **5** with sodium sulfide[4] produced *cis*-8-thiabicyclo[4.3.0]non-3-ene (**4**). Cyanide displacement of the tosylate groups on **5** gave the dinitrile **6**,[5] which was immediately converted to **7**[5] by hydrolysis. Ruzicka cyclization of **7** produced **8**, which after Wolff–Kishner reduction gave *cis*-bicyclo[4.3.0]non-3-ene (**9**).[5] *cis*-8-Azabicyclo[4.3.0]non-3-ene (**11**) was prepared by the lithium aluminum hydride reduction of **10**.[1b]

Although we were aware of the possibility of ring-juncture epimerization by palladium catalysts, the short reaction times anticipated for our studies suggested that we examine this metal, particularly with the potential for catalyst-heteroatom studies. Because of the simplicity of preparation, the test compounds used were **3** and *trans*-8-oxabicyclo[4.3.0]non-3-ene (**16**).[15] The preparation of **16** is presented in Scheme II. Diethyl fulmarate and butadiene were allowed to undergo a Diels–Alder reaction to yield **14**. Reduction of the diester with lithium aluminum hydride gave the trans diol **15**, which was converted to **16** by the action of *p*-toluenesulfonyl chloride in hot pyridine.

Hydrogenation of **3** with 10% Pd–C at 20 psi hydrogen pressure in a Parr hydrogenation apparatus for 30 min resulted in a complex reaction mixture, as judged by examination of the GLC chromatogram. By comparing aliquots with authentic samples of the reduction products, **17** and **18**, through the reaction conditions, we were able to determine that simple product epimerization was not occurring.

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