Synthesis of a New Class of Sulfone Linked Bisheterocycles

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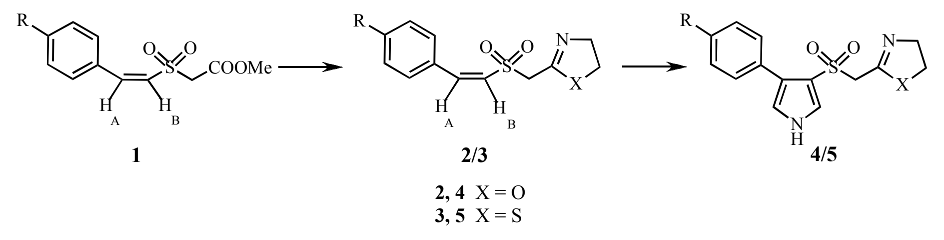

2, 4 X = O
3, 5 X = S

Some bisheterocycles having pyrrole and oxazoline/thiazoline units were synthesized from *Z*–styrylsulfonylacetic acid methyl esters using samarium chloride.

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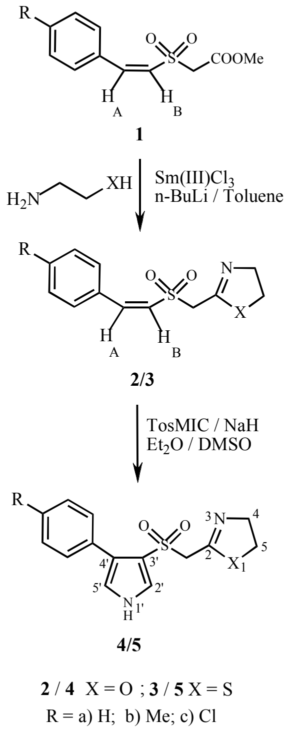
INTRODUCTION

The development of simple, facile and efficient synthetic methods for the construction of five membered heterocycles is one of the major challenges in organic synthesis. Amongst these five membered heterocycles pyrroles, oxazoles and thiazoles have gained importance because of their varied physiological activities. 4-Aminopyrrole-2-carboxylates exhibit antibiotic, antiviral and oncolytic properties [1]. Several 2-oxazolines have been used as therapeutic agents. Because of their structural relationship to procaine, 2-oxazoline derivatives might be expected to have local anaesthetic properties [2]. Hence, it is thought that a worthwhile program would be to prepare molecules having both pyrrole and oxazole/thiazole rings. In the literature, multistep synthetic routes of 3,4-disubstituted pyrroles have been reported either by coupling of imines and nitroalkanes or using Friedel-Crafts acylation with an electron withdrawing group on the pyrrole nitrogen or 3,4-silylated precursors [3]. However, these synthetic routes are often complicated and limited to only some substituents. 3,4-Disubstituted pyrroles have also been synthesized from Michael acceptors with tosylmethyl isocyanide (TOSMIC) [4,5]. A variety of methods have been reported for the synthesis of oxazolines *viz.*, cyclodehydration of amido alcohols, condensation of imidate hydrochlorides [6], carboxylic acids [7], ortho esters [8], iminoether hydrochlorides [9] and nitriles [10] with aminoalcohols. Similarly, thiazolines are prepared by the coupling of imidates and esters with aminothiols [11], cyclodehydration of hydroxy thioamides [12] and heterocyclic interconversions from oxazoline [13] or oxazolidines [14]. Earlier we have reported the synthesis of oxazolines by the traditional four-step three intermediate route, starting from sulfonylacetic acid methyl ester *via* hydroxyethylacetamide followed by treatment with thionyl chloride and cyclocondensation in the presence of base [15]. However, the use of lanthanide (III) compounds as catalyst or promoters in organic synthesis is of recent origin. Although lanthanide triflates, alkoxides and amides have been extensively used, lanthanide amino alkoxide complexes as reagents for similar purposes are sparsely reported [16]. The present communication deals with the synthesis of hitherto unknown sulfone linked bisheterocycles having a pyrrole in combination with an oxazole or a thiazole unit.

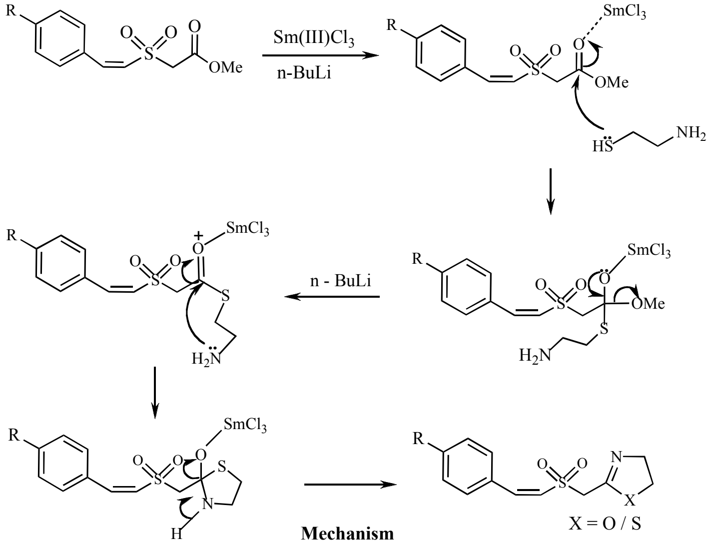
Scheme



2 / **4** X = O ; **3** / **5** X = S
R = a) H; b) Me; c) Cl

The synthetic scheme is based on the reactivity of *Z*-styrylsulfonylacetic acid methyl ester (**1**) towards the development of pyrrole and oxazole/thiazole units by exploiting olefinic and ester functionalities, respectively. The reaction of **1** with 2-aminoethanol and *n*-butyllithium complexed with a 5-10 % molar equivalent of anhydrous samarium chloride suspension in toluene gave 2-(2-aryl-ethenesulfonylmethyl)-4,5-dihydrooxazole (**2**). Adopting similar methodology, **1** is condensed with 2-aminoethanethiol and the compound obtained is found to be 2-(2-aryl-ethenesulfonylmethyl)-4,5-dihydrothiazole (**3**). The reaction proceeds by the nucleophile attack of aminoethanol/aminoethanethiol on the carbonyl carbon of an ester in the presence of samarium chloride and *n*-butyllithium followed by the displacement of alcohol (mechanism).

The IR spectra of **2a** and **3a** showed absorption bands in the regions 1331, 1320 and 1129, 1144 (SO_2), 1561, 1559 (C=N) and 1650, 1642 cm^{-1} (C=C) respectively (Scheme and Table 1). The ^{1}H NMR spectra of **2a** and **3a** showed two triplets for C_4-H and C_5-H of 2-oxazoline and 2-thiazoline rings at δ 4.06, 4.44 and 4.41, 3.32. Apart from this, two doublets and a singlet are observed at 7.58, 6.65 and 3.78 in **2a** and at 7.61, 6.63 and 3.65 in **3a** which



Mechanism

Table 1

Physical properties and IR data of Compounds **2**-**5**

Compd.	m.p.	Yield	Mol. formula	Calcd. (Found) %			IR (cm^{-1})			
	(°C)	(%)	(Mol. Wt.)	C	H	N	SO_2	C=N	C=C	NH
2a	82-84	80	$C_{12}H_{13}NO_3S$ (251.30)	57.35 (57.45)	5.21 (5.28)	5.57 (5.68)	1129 1331	1561	1650	-
2b	122-123	85	$C_{13}H_{15}NO_3S$ (265.33)	58.85 (58.92)	5.70 (5.64)	5.28 (5.36)	1134 1328	1558	1649	-
2c	134-135	86	$C_{12}H_{12}ClNO_3S$ (285.75)	50.44 (50.38)	4.23 (4.28)	4.90 (4.81)	1124 1334	1556	1652	-
3a	78-80	90	$C_{12}H_{13}NO_2S_2$ (267.37)	53.91 (53.99)	4.90 (4.97)	5.24 (5.32)	1144 1320	1559	1642	-
3b	110-112	82	$C_{13}H_{15}NO_2S_2$ (281.40)	55.49 (55.60)	5.37 (5.40)	4.98 (5.03)	1147 1322	1562	1647	-
3c	128-129	86	$C_{12}H_{12}ClNO_2S_2$ (301.81)	47.75 (47.62)	4.01 (3.96)	4.64 (4.57)	1124 1326	1560	1643	-
4a	185-187	86	$C_{14}H_{14}N_2O_3S$ (290.34)	57.92 (58.04)	4.86 (4.32)	9.65 (9.78)	1132 1329	1558	-	3340
4b	205-207	75	$C_{15}H_{16}N_2O_3S$ (304.37)	59.19 (59.29)	5.30 (5.36)	9.20 (9.29)	1137 1332	1554	-	3352
4c	228-230	78	$C_{14}H_{13}ClN_2O_3S$ (324.78)	51.77 (51.68)	4.03 (4.00)	8.63 (8.70)	1122 1330	1557	-	3360
5a	165-167	72	$C_{14}H_{14}N_2O_2S_2$ (306.41)	54.88 (54.92)	4.61 (4.68)	9.14 (9.04)	1144 1330	1552	-	3358
5b	180-182	76	$C_{15}H_{16}N_2O_2S_2$ (320.43)	56.22 (56.33)	5.03 (5.00)	8.74 (8.80)	1139 1335	1554	-	3354
5c	198-200	81	$C_{14}H_{13}ClN_2O_2S_2$ (340.85)	49.33 (49.25)	3.84 (4.90)	8.22 (8.33)	1130 1332	1561	-	3362

Table 2

^{1}H and ^{13}C NMR data of Compounds **2-5**

Compd.	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
2a	3.78 (s, 2H, SO_2-CH_2), 4.06 (t, 2H, C_4-H, *J*= 5.9 Hz), 4.44 (t, 2H, C_5-H, *J* = 5.9 Hz), 6.65 (d, 1H , $H_{B,}$ *J* = 9.7 Hz), 7.34 -7.76 (m, 5H, Ar-H), 7.58 (1H, d, $H_{A,}$ *J* = 9.7 Hz)	52.1 (C-4), 54.3 (SO_2-CH_2), 55.1 (C-5), 126.4 ($CHSO_2$), 145.2 (CH-Ar), 161.4 (C-2), 128.2, 128.6, 130.6, 132.1 (aromatic carbons)
2b	2.20 (s, 3H, Ar-CH_3), 3.72 (s, 2H, SO_2-CH_2), 4.05 (t, 2H, C_4-H, *J* = 5.6 Hz), 4.46 (t, 2H, C_5-H, *J* = 5.6 Hz), 6.61 (d, 1H, $H_{B,}$ *J* = 9.9 Hz), 7.18 -7.74 (m, 4H, Ar-H), 7.59 (1H, d, $H_{A,}$ *J* = 9.9 Hz)	21.2 (Ar-CH_3), 52.4 (C-4), 54.6 (SO_2-CH_2), 55.6 (C-5), 125.7 ($CHSO_2$), 144.8 (CH-Ar), 158.2 (C-2), 128.4, 128.6, 129.1, 134.4 (aromatic carbons)
2c	3.79 (s, 2H, SO_2-CH_2), 4.06 (t, 2H, C_4-H, *J* = 5.7 Hz), 4.48 (t, 2H, C_5-H, *J* = 5.7 Hz), 6.66 (d, 1H, $H_{B,}$ *J* =10.1 Hz), 7.26 -7.65 (m, 4H, Ar-H), 7.57 (1H, d, $H_{A,}$ *J* = 10.1 Hz)	52.8 (C-4), 54.2 (SO_2-CH_2), 55.9 (C-5), 124.8 ($CHSO_2$), 145.3 (CH-Ar), 157.9 (C-2), 127.2, 128.8, 130.0, 134.5 (aromatic carbons)
3a	3.32 (t, 2H, C_5-H, *J* = 8.0 Hz), 3.65 (s, 2H, SO_2-CH_2), 4.41 (t, 2H, C_4-H, *J* = 8.0 Hz), 6.63 (d, 1H, $H_{B,}$ *J* = 9.8 Hz), 7.35 -7.75 (m, 5H, Ar-H), 7.61 (1H, d, $H_{A,}$ *J* = 9.8 Hz)	35.8 (C-5), 56.8 (SO_2-CH_2), 63.5 (C-4), 125.8 ($CHSO_2$), 146.3 (CH-Ar), 161.2 (C-2), 128.4, 128.9, 132.5, 137.6 (aromatic carbons)
3b	2.37 (s, 3H, Ar-CH_3), 3.34 (t, 2H, C_5-H, *J* = 8.0 Hz), 3.62 (s, 2H, SO_2-CH_2), 4.40 (t, 2H, C_4-H, *J* = 8.0 Hz), 6.64 (d, 1H, $H_{B,}$ *J* = 10.1 Hz), 7.17 -7.74 (m, 4H, Ar-H), 7.57 (1H, d, $H_{A,}$ *J* = 10.1 Hz)	21.4 (Ar-CH_3), 34.7 (C-5), 57.1 (SO_2-CH_2), 64.7 (C-4), 127.3 ($CHSO_2$), 144.8 (CH-Ar), 162.4 (C-2), 128.6, 129.3, 135.2, 137.9 (aromatic carbons)
3c	3.34 (t, 2H, C_5-H, *J* = 8.4 Hz), 3.59 (s, 2H, SO_2-CH_2), 4.46 (t,2H, C_4-H, *J* = 8.4 Hz), 6.63 (d, 1H, $H_{B,}$ *J* = 10.5 Hz), 7.30-7.42 (m, 4H, Ar-H), 7.58 (1H, d, $H_{A,}$ *J* = 10.5Hz)	34.9 (C-5), 56.6 (SO_2-CH_2), 68.4 (C-4), 126.9 ($CHSO_2$), 145.7 (CH-Ar), 163.8 (C-2), 128.5, 129.1, 135.7, 138.4 (aromatic carbons)
4a	3.72 (s, 2H, SO_2-CH_2), 4.04 (t, 2H, C_4-H, *J* = 5.9 Hz), 4.46 (t, 2H, C_5-H, *J* = 5.9 Hz), 6.84 (s,1H, C_2'-H), 7.04 (s,1H, C_5'-H), 7.34 -7.76 (m, 5H, Ar-H), 9.27 (bs, 1H, NH)	52.3 (C-4), 54.5 (SO_2-CH_2), 54.9 (C-5), 103.6 (C-4'), 106.5 (C-3'), 116.6 (C-5'), 121.8 (C-2'), 160.4 (C-2), 128.3, 128.7, 130.2, 132.4 (aromatic carbons)
4b	2.20 (s, 3H, Ar-CH_3), 3.74 (s, 2H, SO_2-CH_2), 4.02 (t, 2H, C_4-H, *J* = 5.6 Hz), 4.42 (t, 2H, C_5-H, *J* = 5.6 Hz), 6.78 (s,1H, C_2'-H), 7.02 (s,1H, C_5'-H), 7.32 -7.69 (m, 4H, Ar-H), 9.37 (bs, 1H, NH)	21.5 (Ar-CH_3), 51.9 (C-4), 54.6 (SO_2-CH_2), 55.4 (C-5), 104.2 (C-4'), 106.9 (C-3'), 117.3 (C-5'), 120.6 (C-2'), 157.8 (C-2), 128.2, 128.6, 129.2, 134.6 (aromatic carbons)
4c	3.78 (s, 2H, SO_2-CH_2), 4.09 (t, 2H, C_4-H, *J* = 5.8 Hz), 4.46 (t, 2H, C_5-H, *J* = 5.8 Hz), 6.79 (s,1H, C_2'-H), 7.05 (s,1H, C_5'-H), 7.34 -7.72 (m, 4H, Ar-H), 9.34 (bs, 1H, NH)	52.4 (C-4), 54.8 (SO_2-CH_2), 55.9 (C-5), 104.5 (C-4'), 106.7 (C-3'), 117.8 (C-5'), 120.8 (C-2'), 158.1 (C-2), 128.2, 128.6, 129.2, 134.6 (aromatic carbons)
5a	3.34 (t, 2H, C_5-H, *J* = 8.1 Hz), 3.64 (s, 2H, SO_2-CH_2), 4.42 (t,2H, C_4-H, *J* = 8.1 Hz), 6.81 (s, 1H, C_2'-H), 7.09 (s, 1H, C_5'-H), 7.42 -7.74 (m, 5H, Ar-H), 9.12 (bs, 1H, NH)	35.8 (C-5), 56.8 (SO_2-CH_2), 63.7 (C-4), 103.9 (C-4'), 105.8 (C-3'), 116.8 (C-5'), 120.3 (C-2'), 160.2 (C-2), 128.3, 128.5, 132.6, 132.4 (aromatic carbons)
5b	2.24 (s, 3H, Ar-CH_3), 3.36 (t, 2H, C_5-H, *J* = 7.8 Hz), 3.69 (s, 2H, SO_2-CH_2), 4.04 (t, 2H, C_4-H, *J* = 7.8 Hz), 6.83 (s, 1H, C_2'-H), 7.02 (s, 1H, C_5'-H), 7.37 -7.82 (m, 4H, Ar-H), 9.16 (bs, 1H, NH)	21.2 (Ar-CH_3), 34.7 (C-5), 57.2 (SO_2-CH_2), 64.5 (C-4), 102.9 (C-4'), 104.7 (C-3'), 115.5 (C-5'), 120.6 (C-2'), 162.2 (C-2), 128.4, 129.1, 134.4, 135.2 (aromatic carbons)
5c	3.37 (t, 2H, C_5-H, *J* = 8.0 Hz), 3.65 (s, 2H, SO_2-CH_2), 4.08 (t, 2H, C_4-H, *J* = 8.0 Hz), 6.81 (s, 1H, C_2'-H), 7.06 (s, 1H, C_5'-H), 7.34 -7.89 (m, 4H, Ar-H), 9.15 (bs, 1H, NH)	35.2 (C-5), 56.8 (SO_2-CH_2), 68.2 (C-4), 103.6 (C-4'), 104.5 (C-3'), 116.8 (C-5'), 121.3 (C-2'), 161.7 (C-2), 129.1, 130.2, 134.8, 135.2 (aromatic carbons)

are assigned to olefinic protons H_A, H_B and methylene protons, respectively. The *J* value (*J* = 9.7, 9.8 Hz) indicates that H_A and H_B possess *cis* geometry. The ^{13}C NMR spectra of **2a** and **3a** displayed signals at 161.4, 161.2 (C-2), 52.1, 63.5 (C-4), 54.3, 56.8 (SO_2-CH_2), 55.1, 35.8 (C-5), 126.4, 125.8 ($CHSO_2$), 145.2, 146.3 (CHPh) apart from signals due to aromatic carbons. (Table 2).

The olefin functionality in **2** and **3** is utilized for the development of pyrrole ring. When **2** is subjected with tosylmethyl isocyanide in the presence of sodium hydride in a mixture of ether and dimethyl sulfoxide, a solid is obtained which is identified as 2-(4'-aryl-1'*H*-pyrrole-3'-sulfonylmethyl)-4,5-dihydro-oxazole (**4**). Similarly, the reaction of **3** with tosylmethyl isocyanide in the presence of sodium hydride gave 2-(4'-aryl-1'*H*-pyrrole-3'-sulfonylmethyl)-4,5-dihydro-thiazole (**5**). In the IR spectra of **4a** and **5a** the absence of bands due to C=C and the presence of absorption bands at 3340, 3358 cm^{-1} for NH apart from bands due to SO_2 and C=N indicates their formation (Scheme and Table 1). The ^{1}H NMR spectra of **4a** and **5a** exhibited two singlets at δ 6.84, 7.04 and 6.81, 7.09 which are accounted for $C_{2'}$-H and $C_{5'}$-H of the pyrrole ring, apart from signals due to methylene and oxazoline/thiazoline protons. A broad singlet is observed at 9.21 (**4a**) and 9.12 (**5a**) for N*H*, which disappeared on deuteration. The ^{13}C NMR spectra of **4a** and **5a** displayed signals at δ 160.4, 160.2 (C-2), 52.3, 63.7 (C-4), 54.9, 35.8 (C-5), 116.6, 116.8 (C-5'), 103.6, 103.9 (C-4'), 106.5, 105.8 (C-3'), 121.8, 120.3 (C-2') and 54.5, 56.8 (SO_2CH_2), respectively (Table 2).

CONCLUSION

The use of lanthanide complexes provides a direct and an efficient synthetic pathway to construct 2-oxazolines and 2-thiazolines. Further, tosylmethyl isocyanide to olefinic moiety provides a simple, elegant and well-versed methodology to develop pyrroles. Thus, bisheterocycles having pyrrole and oxazoline/thiazoline linked by sulfone moiety are developed.

EXPERIMENTAL

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. The purity of the compounds was checked by TLC (Silica gel H, BDH, ethyl acetate-hexane, 1:3). The IR spectra were recorded on a Thermo Nicolet IR 200 FT-IR spectrometer as KBr pellets and the wave numbers are given in cm^{-1}. The ^{1}H NMR spectra were recorded in $CDCl_3$/DMSO- d_6 on a Varian EM-360 spectrometer. The ^{13}C NMR spectra were run on a Varian VXR spectrometer operating at 75.5 MHz with $CDCl_3$ as solvent. All chemical shifts are reported in ppm from TMS as an internal standard. Elemental analyses were performed using Perkin-Elmer 240C elemental analyzer. The starting substrates *Z*-styrylsulfonylacetic acid methyl esters (**1**) were prepared by standard procedure [17].

2-(2-Arylethenesulfonylmethyl)-4,5-dihydrooxazole (2) and 2-(2-Arylethenesulfonylmethyl)-4,5-dihydrothiazole (3). To a flask charged with 0.1 mmoles of anhydrous samarium chloride, 10 ml of dry toluene and 2 mmoles of aminoalcohol/aminothiol were added followed by 2.2 mmoles of *n*-butyllithium at 0°C. The reaction mixture was stirred at 0°C for 15 minutes. Then the flask was warmed to reflux at 100°C and 1 mmoles of *Z*-styrylsulfonylacetic acid methyl ester (**1**) was added and refluxing was continued for an additional 10-12 hours. The suspension was cooled to room temperature and filtered. The filtrate was extracted with chloroform, washed with water and the solvent was removed *in vacuo*. The product was purified by column chromatography (Silica gel, ethyl acetate: hexane, 1:3).

2-(4'-Aryl-1'*H*-pyrrole-3'-sulfonylmethyl)-4,5-dihydrooxazole (4) and 2-(4'-Aryl-1'*H*-pyrrole-3'-sulfonylmethyl)-4,5-dihydrothiazole (5). A mixture of 1 mmoles of TosMIC and 1 mmoles of 2-(2-arylethenesulfonyl- methyl)-4,5-dihydrooxazole (2) or 2-(2-arylethenesulfonylmethyl)-4,5-dihydrothiazole (3) in Et_2O/DMSO (2:1) was added dropwise to a stirred mixture of NaH (50 mg) in dry Et_2O (10 ml) at lab temperature. Stirring was continued for 8-10 hours at which time the mixture was diluted with water and extracted with ether. The ethereal layer was dried over anhydrous Na_2SO_4. Concentration of the solvent gave crude product, which was purified by filtration through a column of silica gel, BDH (60-120 mesh) with hexane/ethyl acetate, 4:1 as eluent.

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