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11. Compound **3**, a mixture of two diastereomers : TLC(SiO_2, 9 : 1 ethyl acetate/methanol) R_f=0.57; IR 1208 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.38 (d), 4.48 (dd), 4.9 (dd), 5.58 (s), 5.69 (dd), 5.92 (dd), 6.12 (d), 6.28 (d), 6.13 (d), 6.44 (d), 7.21-7.41 (m), 7.88 (s), 7.98 (s), 8.10 (s), 8.16 (s).
12. Compound **4** : TLC(SiO_2, 9 : 1 ethyl acetate/methanol) R_f=0.64; IR 1212, 1400 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.38 (d, 2H), 4.65 (dd, 1H), 5.61 (brs, 2H), 5.81 (dd, 1H), 6.23 (d, 1H), 6.37 (dd, 1H), 7.22-7.38 (m, 15H), 7.86 (s, 1H), 8.11 (s, 1H).
13. Compound **5**, a mixture of two diastereomers : TLC(SiO_2, 9 : 1 ethyl acetate/methanol) R_f=0.80; IR 1210 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 3.40-3.52 (m), 3.97-4.25 (m), 5.42-5.64 (m), 5.81-6.00 (m), 7.10-7.35 (m), 7.70-7.88 (m), 9.73 (brs).
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15. Compound **6** : TLC(SiO_2, 9 : 1 ethyl acetate/methanol) R_f=0.60; mp. 216-218℃ (Ref.[3], mp. 217-219℃); ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 3.15 (d, 1H), 3.52 (d, 2H), 4.08-4.39 (m, 3H), 5.37 (d, 1H), 5.86 (d, 1H), 7.22-7.46 (m, 15H), 7.94 (d, 1H).
16. Compound **7** : mp. 209-211℃ (Ref.[2], mp. 208.5-215℃); $[\alpha]^{25}_D$ +126.5 (c 0.5, H_2O) (Ref.[2], +126); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.90-4.04 (m, 2H), 4.05-4.15 (m, 1H), 4.23 (dd, 1H), 4.52 (dd, 1H), 5.97 (d, 1H), 6.29 (d, 1H), 7.96 (d, 1H).

Synthesis of 4-Carbethoxy-5-aryl-5,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-Dioxides

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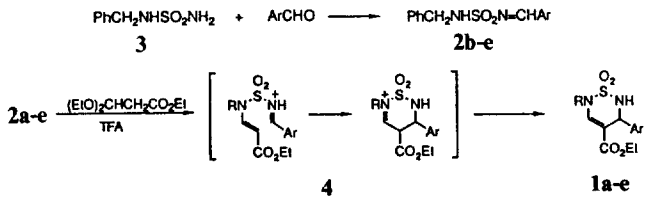
In recent years an increasing number of articles describing the synthesis, properties and biological activities of various heterocycles containing sulfamide unit have appeared,[1] and we have demonstrated that the intramolecular α-sulfamidoalkylation transformations of N-alkylsulfamides could provide those kinds of heterocycles, such as 5,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide derivatives.[2] Two general, acid-mediated procedures have been reported for the preparation of such 1,2,6-thiadiazine 1,1-dioxides.[3] The first entails the reaction of sulfamides with an equimolar amounts of 1,3-difunctionalized compounds and the second process entails the treatment of sulfamides with two equivalents of a carbonyl compound containing an acidic alpha hydrogen.

Table 1. Synthesis of N-Arylidenesulfamides **2** and 1,2,6-Thiadiazine 1,1-Dioxides **1**

Compound	mp. (℃)	yield (%)	Compound	mp (℃)	yield (%)
2a[2b]	105-106	65	**1a**	oil	42
2b	106-108	75	**1b**	122-124	50
2c	81-83	68	**1c**	oil	43
2d	118-120	81	**1d**	116-118	53
2e	130-133	73	**1e**	oil	40

We now wish to report on the use of the above α-sulfamidoalkylation process for the preparation of 4-carbethoxy-5-aryl-5,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxides **1** from N-arylidenesulfamides **2** and ethyl 3,3-diethoxypropionate in trifluoroacetic acid.



a R=H, Ar=phenyl. **b** R=benzyl, Ar=phenyl. **c** R=benzyl, Ar=1-naphthyl. **d** R=benzyl, Ar=4-methoxyphenyl. **e** R=benzyl, Ar=4-bromophenyl

N-Benzylidenesulfamide (**2a**) and N-benzylsulfamide (**3**) were prepared following the known procedures[2b,4,5] and the N-arylidene-N′-benzylsulfamides **2b-e** were prepared by condensing aromatic aldehydes with N-benzylsulfamide (**3**) in the presence of *p*-toluenesulfonic acid (see Table 1). Reaction of these N-arylidenesulfamides **2** with ethyl 3,3-diethoxypropionate in trifluoroacetic acid then afforded the 4-carbethoxy-5-aryl-5,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxides **1** (see Table 1) by undergoing intramolecular α-sulfamidoalkylation process through iminium ion **4**.

The typical procedure for the synthesis of **1** is as follows: A solution of **2d** (305 mg, 1 mmol) and ethyl 3,3-diethoxypropionate (190 mg, 1 mmol) in trifluoroacetic acid (10 m*l*) was stirred at rt for 48 hr and then concentrated in vacuo. Column chromatography (chloroform) of the residue afforded 220 mg (53% yield) of **1d**: IR (KBr) 3350, 1705, 1355, 1125 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.97 (t, 3H, *J*=7.0, $-CH_3$), 3.77 (s, 3H, $-OCH_3$), 3.92-3.97 (m, 2H, $-OCH_2-$), 4.63 (d, 1H, *J*=15.2 Hz, CH_2Ph), 4.68 (d, 1H, *J*=8.2 Hz, CHAr), 4.75 (d, 1H, *J*=15.2 Hz, CH_2Ph), 5.50 (d, 1H, *J*=8.2 Hz, NH), 6.83 (d, 2H, *J*=11.6 Hz), 7.20 (d, 2H, *J*=11.6 Hz), 7.35-7.45 (m, 5H), 7.38 (s, 1H, =CH-) ppm; ^{13}C-NMR ($CDCl_3$) δ 13.88, 52.37, 55.21, 59.14, 60.33, 108.00, 114.02, 128.34, 128.49, 128.92, 129.00, 129.48, 130.16, 134.85, 140.77, 159.58 ppm.

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Heteroleptic Crown Thioether Chemistry. Synthesis and Characterization of the Group 9 Metal Complexes of 1,4,7-Trithiacyclononane

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Owing to the unique electronic and structural properties, 1,4,7-trithiacyclononane(9S3), a nine-membered crown thioether, has been successfully employed in the development of crown thioether chemistry.[1-3] Particularly, 9S3 derives its strong chelating ability from the retention of endodentate conformation on binding to a trigonal face of a metal, leading to an observation of large set of homoleptic complexes of lower oxidation state transition metal ions[3] as well as *p*-block metal ion.[4] On the other hand, heteroleptic 9S3 complexes, which appear in the form of metal carbonyls,[5] metal halides,[6] metal hydride,[7] metal oxides[8] or organometallic compounds,[9] constitute a newly emerging class. Described herein are brief accounts of synthesis and structural characterization of the type $[L_nM(9S3)]^{c+}$, a set of novel heteroleptic crown thioether complexes with varying L, c and the Group 9 metal M.

Dicationic $[Cp^*M(9S3)]^{2+}$(**1**: M=Co; **2**: M=Rh; **3**: M=Ir) and monocationic $[M(CO)(PPh_3)(9S3)]^+$(**4**: M=Rh; **5**: M=Ir) were prepared as perchlorate salts according to the reaction Scheme I and II, respectively.[10] In the Scheme I, acetonitrile solutions of $[Cp^*M(CH_3CN)_3](ClO_4)_2$ (M=Co, deep purple; Rh, yellow; Ir, orange) were generated *in situ* by stirring the slurry of $Cp^*Co(CO)I_2$[11] or $[Cp^*MCl_2]_2$(M=Rh, Ir) with stoichiometric amount of $AgClO_4$ in acetonitrile for 1.5-2 h followed by filtration. Addition of 9S3 to the filtrate, stirring the resulting solutions for a period of 12-18 h at r.t., and filtration resulted in orange-red, pale green and pale yellow solution for M=Co, Rh, and Ir, respectively. Recrystallization (CH_3CN/Et_2O) of the solids obtained by treating the foregoing solutions with large amount of Et_2O afforded analytically pure crystalline $(ClO_4)_2 \cdot$ **1**$\cdot(CH_3CN)$ (orange-red; 35%; Anal. Found (Calc.) C, 35.2 (35.2); H, 4.85 (4.92); N, 2.05 (2.28)), $(ClO_4)_2 \cdot$ **2** $\cdot (CH_3CN)$ (green; 80%; Anal. Found (Calc.): C, 32.3 (32.8); H, 4.59 (4.59); N, 1.85 (2.12)) and $(ClO_4)_2$ $\cdot$ **3** $\cdot (CH_3CN)$ (pale-yellow; 70%; Anal. Found (Calc.): C, 29.2 (28.9); H, 3.98 (4.04); N, 1.69 (1.87)). In the Scheme II, analogous work-up yielded spectroscopically pure

$$\text{I}: [Cp^*M(CH_3CN)_3](ClO_3)_2 \xrightarrow[CH_3CN]{9S3} [Cp^*M(9S3)_3](ClO_3)_2$$

$$\text{II}: \textit{trans}\text{-}[M(CO)Cl(PPh_3)_2] \xrightarrow[CH_3CN]{AgClO_4} \xrightarrow{9S3} [M(CO)(PPh_3)(9S3)](ClO_4)$$

crystalline orange-red **4** $\cdot (ClO_4)$ and yellow **5** $\cdot (ClO_4)$.

Solid infrared spectra of $[Cp^*M(9S3)](ClO_4)_2(CH_3CN)$ are all similar and contain the features of Cp^*, 9S3, ClO_4 and CH_3CN, which and other spectroscopic data listed in Table 1 indicate that the three complexes have the same structural core whose nature for M=Rh was determined by single crystal X-ray analysis.[12] The structure of cationic species **2**, displayed in Figure 1, reveals endo-tridentate ligating nature

Table 1. Spectroscopic Data for 9S3 Complexes of Group 9 Metals.

$[Cp^*M(9S3)](ClO_4)_2(CH_3CN)$

M	NMR	Cp*	9S3
Co	^1H (CD_3CN)[a]	1.70 (s, 15H)	2.91-3.16 (m, 12H)
	^{13}C (CD_3CN)[a]	10.2 (C_5Me_5)	38.9
		104 (C_5Me_5)	
Rh	^1H (d_6-DMSO)	1.94 (s, 15H)	3.18-3.27 (m, 12H)
	^{13}C (d_6-DMSO)	9.04 (C_5Me_5)	36.7
		106 (C_5Me_5, $^1J_{Rh\text{-}C}$=6.3 Hz)	
Ir	^1H (CD_3CN)	2.04 (s, 15H)	2.84-2.96 (m, 12H)
	^{13}C (CD_3CN)	9.27 (C_5Me_5)	38.5
		102 (C_5Me_5)	

$[M(CO)(PPh_3)(9S3)](ClO_4)$

M	ν_{CO}[b], cm^{-1}	^1H-NMR (d_6-DMSO)	$^{31}P\{^1H\}$-NMR[c] (d_6-DMSO)
Rh	1950	2.41-2.73 (m, 12H, 9S3) 7.53-7.72 (m, 15H, PPh_3)	42.4 (d, $J_{Rh\text{-}P}$=128 Hz)
Ir	1932	2.33-2.73 (m, 12H, 9S3) 7.50-7.69 (m, 15H, PPh_3)	12.4

[a] Referenced to TMS. [b] KBr. [c] Referenced to 85% aq H_3PO_4.