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THE FIRST 1,4,2-OXATHIAZOLIUM SALTS: REMARKABLE SIMILARITIES TO THEIR 1,3,4-ISOMERS

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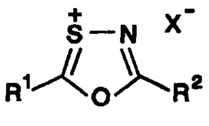
Key Words: *1,4,2-Oxathiazolium; 1,3,4-Oxathiazolium; 1,4,2-Oxathiazole; 1,3-Dipolar Cycloaddition; ^{13}C NMR spectra.*

Abstract: *5-Methylmercapto-1,4,2-oxathiazoles, formed by 1,3-dipolar cyclo-addition between nitrile oxides and methyl dithiocarboxylates, are readily solvolysed with strong acid and an acyl anhydride to give in high yields the first examples of 1,4,2-oxathiazolium salts. Remarkable similarities between the ^{13}C NMR spectra of these and identically-substituted 1,3,4-oxathiazolium salts suggest that electronically the structures of the isomeric cations are very close.*

We recently reported the preparation of 1,3,4-oxathiazolium salts **1**, which were the first representatives of the then-unknown six possible classes of aromatic oxathiazolium cations.[1] We now report a simple, high-yielding synthesis of the first examples of 1,4,2-oxathiazolium salts **2**. Our interest in the compounds **1** and **2** lies in establishing the extent of charge delocalisation and hence of aromaticity in the cations in comparison with the 1,4,2-dithiazolium salt analogs **3**.[2,3] The unique canonical structures **4** of **1** and **5** of **2**, in addition to the alternative arrangements of heteroatoms, suggested that electronically the cations **1** and **2** should be significantly different. We report here some surprising preliminary findings.



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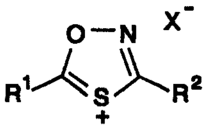

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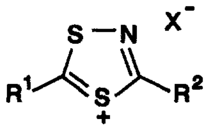

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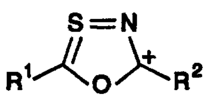

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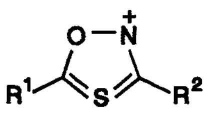

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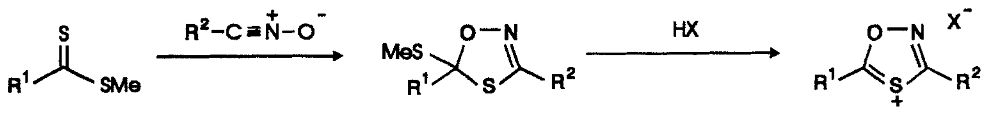
Huisgen[4] and other workers[5] have shown that nitrile oxides add to thiocarbonyl compounds by 1,3-dipolar cyclo-addition yielding 1,4,2-oxathiazoles. It seemed likely that such adducts from dithiocarboxylate esters would solvolyse in strong acid to give the target salts **2**.[6]

Dropwise addition of a solution of triethylamine (5 mmol) in ether (10 mL) to a mixture of methyl 4-methoxydithiobenzoate **6** (5 mmol) and benzhydroxamyl chloride (5 mmol) also in ether (60 mL), with stirring at 25 °C until the orange colour was discharged, followed by washing with water, evaporation of the ether (< 40 °C) and chromatography of the residue (SiO_2; eluant CH_2Cl_2-light petroleum, 1:1) gave the oxathiazole **9b** (82%).[7] Other adducts **9-11** having R^2 = aryl were prepared similarly; for those having R^2 = Me, the nitrile oxide was generated from nitroethane.[8] Yields were 40-94%.



6: R^1 = 4-$MeOC_6H_4$
7: R^1 = Ph
8: R^1 = MeS

9: R^1 = 4-$MeOC_6H_4$
10: R^1 = Ph
11: R^1 = MeS

12: R^1 = 4-$MeOC_6H_4$
13: R^1 = Ph
14: R^1 = MeS

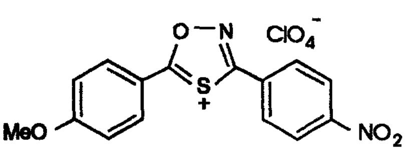
a: R^2 = Me; **b**: R^2 = Ph; **c**: R^2 = 4-$MeOC_6H_4$;
d: R^2 = 4-ClC_6H_4; **e**: R^2 = 4-$NO_2C_6H_4$.

X = ClO_4; BF_4

Treatment of the adducts **9-11** (0.1 g) in acetic anhydride (5 mL) with 70% $HClO_4$ (5 drops) followed by stirring at 25 °C (0.25-2.0 h), gave after addition of anhydrous ether (15 mL) the 1,4,2-oxathiazolium salts **12-14** as perchlorates (81-99%).[9] CAUTION - Samples of **13a** and **13c** exploded during isolation; the corresponding fluoroborates were prepared from the precursor oxathiazoles using 54% HBF_4 and trifluoroacetic anhydride.

As is the case with their isomers **1**, the salts **2** are extremely electrophilic, being attacked by solvents more nucleophilic than CF_3CO_2H and $MeNO_2$. They also decompose within a few days in the solid state, even when stored over P_4O_{10}.

A comparison of the ^{13}C NMR data (22.53 MHz) for the isomers **12e** and **15**[1] (Table 1) shows them to be remarkably similar, chemical shifts for analogous sites differing, with one exception, by less than 0.4 ppm. The differences increase slightly as R^2 becomes more electron-releasing, being largest (<0.7 ppm at all but three sites) for R^2 = 4-$MeOC_6H_4$ or Me.



12e

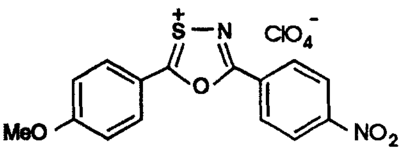


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Table 1. NMR Data (CF_3CO_2D/CD_3NO_2) for the Salts **12e** and **15**.

Salt	4-$MeOC_6H_4$		4-$NO_2C_6H_4$		Heterocycle	
	δ_H	δ_C	δ_H	δ_C	$\delta_{C\text{-}N}$	$\delta_{C\text{-}S}$
12e		116.53(C-*i*)		129.61(C-*i*)	167.88	205.34
	8.51(*o*-H)	138.60(C-*o*)	8.32(*o*-H)	132.10(C-*o*)		
	7.40(*m*-H)	119.05(C-*m*)	8.53(*m*-H)	126.49(C-*m*)		
		174.87(C-*p*)		152.99(C-*p*)		
	4.19(Me)	58.56(Me)				
15		116.66(C-*i*)		129.89(C-*i*)	167.87	205.65
	8.50(*o*-H)	137.40(C-*o*)	8.59(*o*-H)	132.33(C-*o*)		
	7.38(*m*-H)	119.03(C-*m*)	8.59(*m*-H)	126.48(C-*m*)		
		174.63(C-*p*)		153.30(C-*p*)		
	4.17(Me)	58.46(Me)				

It appears not only that analogous carbon atoms within the two isomeric heterocyclic cations are experiencing the same environment, but also that the aryl groups are "seeing" essentially the same substituent cation. Since aryl carbon chemical shifts are influenced by a number of factors, these differing in weighting for atoms in the *ipso*, *ortho*, *meta* or *para* positions,[10] the observation of closely similar δ_C values at all sites in the two series suggests that contrary to expectations the 1,4,2- and 1,3,4-oxathiazolium cations are closely similar electronically. Total charge-densities as determined by MO calculations should be informative.

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6. For analogous solvolyses, see ref 3.

7. Fully characterized by microanalysis, ^{1}H and ^{13}C NMR spectroscopy. *E.g.* **9b** δ_H ($CDCl_3$) 2.24(3 H, s), 3.80(3 H, s), 6.92(2 H, m), 7.39(3 H, m) and 7.66(4 H, m); δ_C 14.92(q), 55.34(q), 113.87(2 C, d), 113.98(s, C-5), 127.33(2 C, d), 127.74(2 C, d), 127.88(s), 128.80(2 C, d), 131.15(d), 131.99(s), 157.45(s, C-3) and 160.19(s); **10a** δ_H ($CDCl_3$) 2.16(3 H, s), 2.17(3 H, s), 7.37(3 H, m) and 7.63(2 H, m); δ_C 13.65(q), 14.63(q), 113.82(s, C-5), 125.63(2 C, d), 128.42(2 C, d), 128.93(d), 140.23(s) and 154.07(s, C-3); and **11a** δ_H ($CDCl_3$) 2.20(3 H, s) and 2.34(6 H, s); δ_C 13.84(q), 15.28(2 C, q), 116.91(s, C-5) and 155.40(s, C-3).
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9. Characterized by IR, ^{1}H and ^{13}C NMR spectroscopy. *E.g.* **12b** as perchlorate salt υ_{max} (Nujol) 1595, 1390 and 1070 cm^{-1}; δ_H (CF_3CO_2D/CD_3NO_2) 4.15(3 H, s), 7.36(2 H, m), 7.76(3 H, m), 8.02(2 H, m) and 8.44(2 H, m); δ_C 58.43(q), 116.74(s), 118.96(2 C, d), 123.84(s), 130.56(2 C, d), 131.83(2 C, d), 136.84(d), 138.28(2 C, d), 169.62(s, C-3), 174.55(s) and 205.51(s, C-5); **13a** as fluoroborate salt δ_H (CF_3CO_2D/CD_3NO_2) 3.03(3 H, s), 7.84(2 H, m), 8.11(1 H, m) and 8.41 (2 H, m); δ_C 13.79(q), 124.33(s), 132.67(2 C, d), 134.16(2 C, d), 143.86(d), 170.02(s, C-3) and 211.93(s, C-5); and **14a** as perchlorate salt υ_{max} (Nujol) 1440, 1270, 1230 and 1070 cm^{-1}; δ_H (CF_3CO_2D/CD_3NO_2) 2.91(3 H, s) and 3.27(3 H, s); δ_C 13.59(q), 20.45(q), 169.72(s, C-3) and 218.82(s, C-5).
10. See *e.g.* Nelson, G.L.; Levy, G.C.; Cargioli, J.D. *J. Am. Chem. Soc.* **1972**, *94*, 3089; Schulman, E.M.; Christensen, K.A.; Grant, D.M.; Walling, C. *J. Org. Chem.* **1974**, *39*, 2686; Membrey, F.; Duvernoy, J. *Spectrochim. Acta* **1985**, *41A*, 765; Hutton, H.M.; Kunz, K.R.; Bozek, J.D.; Blackburn, B.J. *Can. J. Chem.* **1987**, *65*, 1316.

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