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THE FIRST OXATHIAZOLIUM CATIONS - A SIMPLE SYNTHESIS OF 1,3,4-OXATHIAZOLIUM SALTS

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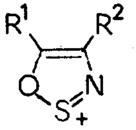
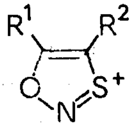
ABSTRACT: The 1,3,4-oxathiazolium salts (11,12), which are the first representatives of the six possible classes of aromatic oxathiazolium cations, are readily prepared by *N*-acylation of the *S*-acylthiohydroxylamines (7, 8) followed by cyclization with a strong acid and an acyl anhydride. The positive charge appears to be delocalized to a smaller extent than in analogous dithiazolium salts.

As an extension of our studies into 1,4,2-dithiazolium salts[1] we wished to prepare 1,3,4- and 1,4,2-oxathiazolium salt analogues in order to compare properties such as aromaticity and reactivity towards nucleophiles. However, we found to our surprise that none of the six possible heteroaromatic oxathiazolium cations (1)-(6) has been reported, although mesoions derived from structure (2) have been studied.[2] We describe here a simple synthesis of the first representatives of this family of cations, the 1,3,4-oxathiazolium salts (6), and compare the extent of charge delocalization in the ring with that in analogous 1,4,2-dithiazolium salts.



(1)



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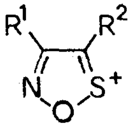

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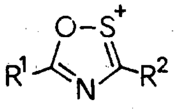

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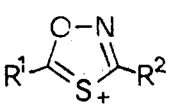

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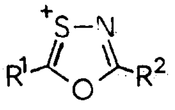
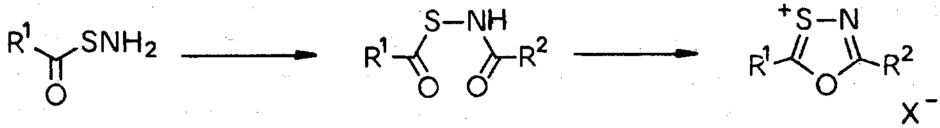


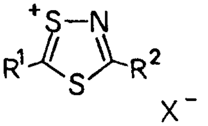
(6)

The synthetic route adopted uses a strategy analogous to that described by Shibuya and co-workers[3] for the preparation of 5-amino-1,4,2-dithiazolium salts, but uses different reaction conditions. Addition of a dichloromethane solution of the thiohydroxylamine (7)[4] to a mixture containing equimolar amounts of an acid chloride R^2COCl and pyridine at 0°C, followed by stirring at room temperature for 15 h and work-up with 2 M HCl, yielded the novel *N*-acyl derivatives (9) (73-96%).[5] The *N*-formyl derivative (9f) was prepared (67%) using formic acetic anhydride.[6] Subsequent treatment of intermediates (9) (0.1 g) with acetic anhydride (5 mL) and 70% $HClO_4$ (5 drops) at 40-45°C, and stirring at this temperature for 4 h, gave after cooling and dropwise addition of anhydrous ether the oxathiazolium salts (11a-e) (19-30%),[7] while (9f) gave an unidentifiable mixture of products. Similar acylation of the thiohydroxylamine (8),[4] (only 3 h for MeCOCl), led to the *N*-acyl compounds (10) (49-91%);[5] however, attempts to cyclise these as above, and using various temperatures, times and concentrations, yielded in all cases the salt (12a)[7], (>90%) *via* acyl exchange. The salts (12b) and (12c) (60-70%), (12f) (17%), and (9f) (38%) were isolated successfully using trifluoroacetic anhydride and 54% HBF_4 at 40°C for 3 h,[7] a method which preliminary results indicate has wider applicability than the alternative described above.



(7): R^1 = 4-$MeOC_6H_4$
(8): R^1 = Piperidino
(9): R^1 = 4-$MeOC_6H_4$
(10): R^1 = Piperidino
(11): R^1 = 4-$MeOC_6H_4$
(12): R^1 = Piperidino
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-$NO_2C_6H_4$; f: R^2 = H
X = ClO_4 or BF_4

The salts (11), in which the charge is expected to reside predominantly inside the heterocyclic ring, are extremely electrophilic, being attacked by solvents more nucleophilic than CF_3CO_2H or $MeNO_2$. NMR signals for the oxathiazolium ring carbon atoms C-2 and C-5 in the salts (11a-f) were in the ranges δ_C 205.4-206.1 and 158.9-172.2 respectively, the lowest field signals in both cases being for the 5-methyl compound (11a). Analogous ring carbon signals in six identically-substituted 1,4,2-dithiazolium salts (13a-f) were observed in the ranges δ_C 210.6-213.0 and 168.2-182.1.[6] While it is not possible to draw conclusions regarding charge density, and aromaticity from these data,[8] the positions of the ring methyl signals for (11a) (δ_H 2.98; δ_C 15.82) and for its analog (13a) (δ_H 3.13; δ_C 22.04), and for the ring protons in (11f) and (13f) (δ_H 9.08 and 9.98 respectively), suggest that there is significantly less positive charge density and/or ring current effect at C-5 in the salts (11), and hence less charge delocalization than in the analogues (13).



(13) R^1 = 4-MeOC$_6$H$_4$
(14) R^1 = Piperidino

In contrast with compounds (11) the positive charge in the salts (12) appears to reside predominantly on the exocyclic nitrogen atom as evidenced by restricted rotation of the piperidino moiety,[9] and the reduced charge density at C-5 [δ_C 163.7 for (12a) as compared with δ_C 172.2 for (11a)]. Compounds (12) are also less electrophilic, being stable in a wider range of solvents than are the salts (11). These properties parallel those of the piperidinodithiazolium salts (14).[1a]

This method promises to make available a range of novel 1,3,4-oxathiazolium salts for further studies in aromaticity and reactivity.

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REFERENCES AND NOTES

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2. H. Gotthardt, F. Reiter, and C. Kromer, Liebigs Ann. Chem., 1025(1981); and references cited.
3. I. Shibuya and K. Yonemoto, Bull. Chem. Soc. Jpn., **59**, 2017(1986).
4. M.S. Raasch, J. Org. Chem., **37**, 3820(1972).
5. Fully characterized by microanalysis, IR, ^{1}H and ^{13}C NMR spectroscopy. E.g. (9d) $\nu_{max.}$ (Nujol) 3 230(NH), 1 680, and 1 660 (C=O) cm^{-1}; δ_H (CDCl$_3$) 3.86(3 H, s), 6.91(2 H, m), 7.32(2 H, m), 7.73(1 H, s, br), 7.81(2 H, m), 7.84(2 H, m); δ_C 55.60(q), 114.25(2 C, d), 126.77(s), 128.89(4C, d), 129.24(2C, d), 131.32(s), 138.74(s), 164.55(s), 167.68(s, C=O), and 189.36(s, C=O); (9f) $\nu_{max.}$ (Nujol) 3 220(NH), 1 690, and 1 660 (C=O) cm^{-1}; δ_H (CDCl$_3$) (mixed rotational isomers) 3.89(3 H, s), 6.54 and 6.73 (total 1 H, NH), 6.97(2 H, m, br), 7.86(2 H, m), and 8.00 and 8.64 (total 1 H, CHO); δ_H 55.65(q), 114.38 and 114.46 (total 2 C), 126.24 and 126.56 (total 1 C), 129.46(2 C, s), 161.86 and 161.88 (total 1 C), 164.67 and 164.85 (total 1 C), and 169.28 (1 C); (10a) $\nu_{max.}$ (Nujol) 3 205(NH),

1 705, and 1 650 (C=O) cm^{-1}; δ_H ($CDCl_3$) 1.63(6 H, s, br), 2.21(3 H, s), 3.40(4 H, s, br), and 7.58(1 H, s, br); δ_C 24.30(q), 25.60(3 C, t), 45.59(2 C, t), 165.96(s), and 172.65(s).

6. S.K. Xie, S.Y. Fan, X.Y. Wang, and M.P. Sammes, *J. Chem. Soc., Perkin Trans. 1*, in the press (paper 0/00765J).

7. Characterized by IR, ^{1}H and ^{13}C NMR spectroscopy. *E.g.* (11d) as perchlorate salt $\nu_{max.}$ (Nujol) 1 595, 1 395, and 1 095 cm^{-1}; δ_H (CF_3CO_2H/CD_3NO_2) 4.16(3 H, s), 7.37(2 H, m), 7.73(2 H, m), 8.33(2 H, m), and 8.47(2 H, m); δ_C 58.36(q), 116.73(s), 118.74(2 C, d), 123.07(s), 131.48(2 C, d), 132.27(2 C, d), 136.92(2 C, d), 143.65(s), 169.24(s, C-5), 173.89(s), and 205.59(s, C-2); (11f) as fluoroborate salt $\nu_{max.}$ (Nujol) 1 597, 1 406, 1 310, 1 115, and 1 078 cm^{-1}, δ_H (CF_3CO_2H/CD_3NO_2) 4.14(3 H, s), 7.35(2 H, m), 8.40(2 H, m), and 9.08(1 H, s); δ_C 58.34(q), 116.53(s), 118.83(2 C, d), 137.30(2 C, d), 158.86(d, C-5), 174.19(s), and 205.59(s, C-2); (12a) as perchlorate salt $\nu_{max.}$ (Nujol) 1 670, 1 635, and 1 130 cm^{-1}; δ_H (CF_3CO_2H/CD_3NO_2) 1.90(6 H, m), 2.61(3 H, s), 3.70(2 H, m), and 4.10(2 H, m); δ_C 15.66(q), 23.40(t), 26.06(2C, t), 53.44(t), 57.10(t), 163.74(s, C-5), and 181.91(s, C-2).

8. ^{13}C Chemical shifts for unsaturated carbon atoms adjacent to oxygen in five membered ring aromatic heterocycles may lie to higher or lower field than signals in their sulphur analogues, depending on the number, location and nature of other heteroatoms.

9. See NMR data for salt (12a), ref. 7 above.

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