

Studies of Heterocyclic Compounds. Part XVIII.¹ Protonation of 1,6-Dioxa-6a-thia- and 1,6-Dioxa-6a-selena-pentalenes: Formation of 1,2-Oxathiolium and 1,2-Oxaselenolium Cations

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A ¹H n.m.r. spectroscopic study of the protonation of 1,6-dioxa-6a-thia- and 1,6-dioxa-6a-selena-pentalenes shows that *O*- and *C*(3)-protonation occurs. Equilibrium mixtures are formed which contain the unprotonated heterocycle and the *O*- and the *C*(3)-protonated species in varying relative amounts, depending on the nature of the heterocycle and the acid medium. 1,6-Dioxa-6a-thia- and 1,6-dioxa-6a-selena-pentalene remained largely unprotonated in trifluoroacetic acid, but the occurrence of H-D exchange at C-3 and C-4 in trifluoroacetic [²H]acid revealed the presence of the 3-formylmethyl-1,2-oxathiolium and -1,2-oxaselenolium cations. The major species in a solution of 2,5-dimethyl-1,6-dioxa-6a-thiapentalene in trifluoroacetic acid were the unprotonated heterocycle and two isomeric 3-(2-hydroxypropenyl)-5-methyl-1,2-oxathiolium cations in a 4 : 6 : 1 ratio. 2,5-Dimethyl-1,6-dioxa-6a-selenapentalene was largely unprotonated in trifluoroacetic acid. In trifluoroacetic acid containing 5% (v/v) perchloric acid 2,5-dimethyl-1,6-dioxa-6a-thia- and 2,5-dimethyl-1,6-dioxa-6a-selena-pentalene gave the 3-acetonyl-5-methyl-1,2-oxathiolium and -1,2-oxaselenolium cations, respectively, as the only observable species. The *O*- and *C*(3)-protonated 1,6-dioxa-6a-thia- and 1,6-dioxa-6a-selena-pentalenes are the first members of the 1,2-oxathiolium and the 1,2-oxaselenolium systems to be identified. The structure of the *C*(3)-protonated 1,6-dioxa-6a-thia- and 1,6-dioxa-6a-selena-pentalenes is discussed in relation to the mechanism of electrophilic substitution of 1,6-dioxa-6a-thiapentalenes and related hypervalent heterocyclic compounds.

We have recently described¹ a convenient two-step synthesis of 1,6-dioxa-6a-thia- and 1,6-dioxa-6a-selena-pentalenes from 4-pyrones. We now report a study of the protonation of these compounds.

Protonation of 1,6-Dioxa-6a-thiapentalenes.—The ¹H n.m.r. spectrum of 1,6-dioxa-6a-thiapentalene (1) in trifluoroacetic acid showed two doublets (*J* 2.7 Hz) at δ 7.02 and 8.66. These chemical shifts are similar in magnitude to those of 3(4)-H (δ 6.90) and 2(5)-H (δ 8.64) (*J* 2.8 Hz) in 1,6-dioxa-6a-thiapentalene in CDCl₃.¹ The spectrum of 1,6-dioxa-6a-thiapentalene in trifluoroacetic [²H]acid consisted simply of a singlet at δ 8.66. In a preparative-scale experiment, a solution of compound (1) in trifluoroacetic [²H]acid was quenched with deuterium oxide containing an excess of sodium carbonate. This gave 3,4-dideuterio-1,6-dioxa-6a-thiapentalene (2) quantitatively, the spectrum of which in CDCl₃ showed a singlet at δ 8.63 (2- and 5-H). These results indicated that the major species in trifluoroacetic acid is unprotonated 1,6-dioxa-6a-thiapentalene, but that a protonated species which we formulate as (5) is also present. This species is formed rapidly and reversibly at concentrations below the limit of detection by ¹H n.m.r. spectroscopy. The dideuterio-derivative (2) results from an H-D exchange involving *C*(1')-deuteriated derivatives of the intermediate (5).

The ¹H n.m.r. spectrum of 2,5-dimethyl-1,6-dioxa-6a-thiapentalene (3) in trifluoroacetic acid revealed the presence of unprotonated solute and two protonated species in a 4 : 6 : 1 ratio [Figure (a)]. The dimethyl-dioxathiapentalene (3) gives rise to two singlets at δ 2.43 (2- and 5-Me) and 6.84 (3- and 4-H). (In CDCl₃ the corresponding signals occur at δ 2.32 and 6.49.¹) The spectral patterns of the protonation products indicate that

† Restricted rotation about the C-3,C-1' bond would double the number of possible isomeric 3-(2-hydroxypropenyl)-1,2-oxathiolium cations.

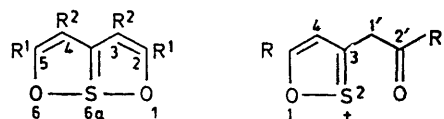
‡ The assignments of structures (8a and b) to the major and minor protonated species, respectively, are tentative and may require to be interchanged.

they are the 3-(2-hydroxypropenyl)-1,2-oxathiolium cations (8a and b)† resulting from *O*-protonation. The major species (8a) shows two methyl singlets at δ 1.71 (2'-Me) and 2.69 (5-Me) and two one-proton singlets at δ 4.43 (1'-H) and 6.55 (4-H). The corresponding signals of the minor species (8b) occur at δ 1.82, 2.75, 4.29, and 6.64, respectively.‡

In trifluoroacetic [²H]acid 2,5-dimethyl-1,6-dioxa 6a-thiapentalene underwent rapid H-D exchange at positions 3 and 4, shown by the absence of all low-field signals from its ¹H n.m.r. spectrum in this solvent. 3,4-Dideuterio-2,5-dimethyl-1,6-dioxa-6a-thiapentalene (4) was subsequently isolated; its spectrum in CDCl₃ consisted of a singlet at δ 2.31 (2- and 5-Me). These results showed that a solution of compound (3) in trifluoroacetic acid contains the *C*(3)-protonated species (6), in addition to the unprotonated solute and the *O*-protonation products (8a and b). Unexpectedly, the cation (6) was the only directly observable species in a solution of 2,5-dimethyl-1,6-dioxa-6a-thiapentalene in trifluoroacetic acid containing 5% (v/v) perchloric acid. The ¹H n.m.r. spectrum of this solution [Figure (b)] showed two three-proton singlets at δ 2.68 (2'-Me) and 2.90 (5-Me), a two-proton singlet at δ 5.08 [C(1')H₂], and a low-field singlet at δ 7.64 (4-H). Spin-decoupling experiments showed that the 2'-Me protons are weakly coupled to the methylene protons. The signals of 5-Me and 4-H in the cation (6) occur much further downfield than the corresponding signals of the cations (8a and b) (5-Me: Δδ 0.21 and 0.15; 4-H: Δδ 1.09 and 1.00, respectively), because delocalisation of the positive charge is confined to the ring in the cation (6) but extends into the 3-(2-hydroxypropenyl) substituent in the cations (8a and b). We conclude that solutions of the dioxathiapentalenes (1) and (3) in trifluoroacetic acid or in trifluoroacetic acid containing perchloric acid consist of equilibrium mixtures of the unprotonated bases [(1) or (3)], the *O*-protonated species

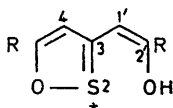
¹ Part XVII, D. H. Reid and R. G. Webster, (a) *J.C.S. Chem. Comm.*, 1972, 1283; (b) *J.C.S. Perkin I*, 1975, 775.

[(7) or (8)], and the C(3)-protonated species [(5) or (6)], whose relative amounts vary with the base and the nature

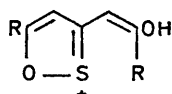


- (1) R¹ H R² H
 (2) R¹ H R² D
 (3) R¹ Me R² H
 (4) R¹ Me R² D

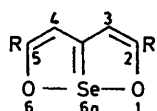
- (5) R = H
 (6) R = Me



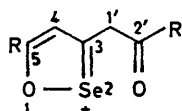
- (7a) R = H
 (8a) R = Me



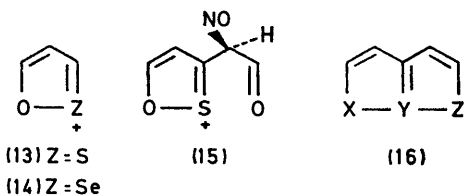
- (7b) R = H
 (8b) R = Me



- (9) R = H
 (10) R = Me



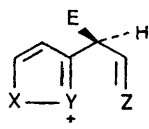
- (11) R = H
 (12) R = Me



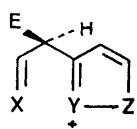
- (13) Z = S
 (14) Z = Se

(15)

(16)



(17)



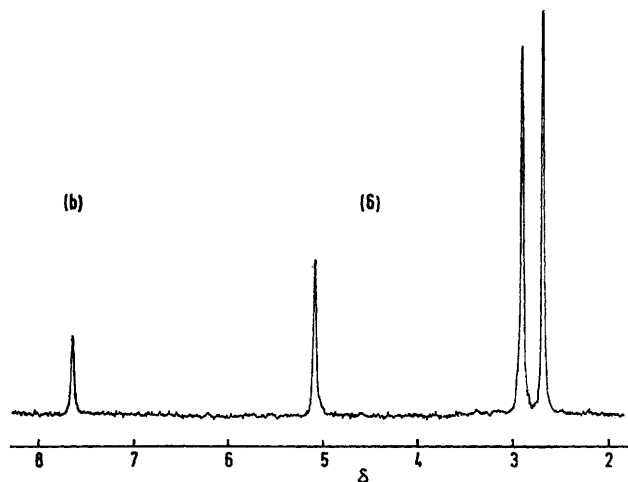
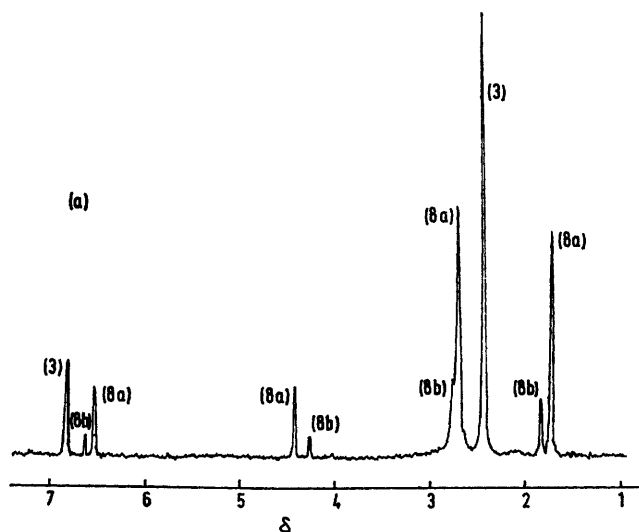
(18)

of the acid medium. Interconversion of the protonated species takes place through the unprotonated base, which acts as a 'turntable'.

1,6-Dioxo-6a-thiapentalenes decompose upon prolonged exposure to acids. The ¹H n.m.r. spectrum of 1,6-dioxo-6a-thiapentalene in trifluoroacetic acid showed additional signals of progressively increasing intensity after *ca.* 1 h. A solution in trifluoroacetic acid containing 5% (v/v) perchloric acid showed numerous broad signals immediately after preparation and rapidly became blue. 2,5-Dimethyl-1,6-dioxo-6a-thiapentalene, although more stable to acid than compound (1), also showed evidence of some decomposition in trifluoroacetic acid after several hours.

Protonation of 1,6-Dioxo-6a-selenapentalenes.—The ¹H n.m.r. spectrum of 1,6-dioxo-6a-selenapentalene (9) in trifluoroacetic acid showed two broad signals at δ 7.21 (3- and 4-H) and 8.91 (2- and 5-H) (*J ca.* 2.7 Hz) arising

from the unprotonated base. The spectrum of 2,5-dimethyl-1,6-dioxo-6a-selenapentalene (10) also showed exchange-broadened signals at δ 2.51 (2- and 5-Me) and 6.92 (*W*_{1/2} *ca.* 60 Hz) (3- and 4-H) arising from the unprotonated heterocycle. The signals from 3- and 4-H in the spectra of compounds (9) and (10) in trifluoroacetic acid were absent from the spectra of these compounds in trifluoroacetic [²H]acid, and in the case of compound (9) the signal from 2- and 5-H had collapsed to a singlet. The occurrence of H-D exchange at positions 3 and 4 indicated that in trifluoroacetic acid compounds (9) and (10) are in equilibrium with small amounts of the C(3)-protonated species (11) and (12), respectively. In trifluoroacetic acid containing 5% (v/v) perchloric acid, compound (9) was rapidly destroyed, but 2,5-dimethyl-1,6-dioxo-6a-selenapentalene (10) underwent C(3)-protonation cleanly to



100 MHz ¹H N.m.r. spectrum of 2,5-dimethyl-1,6-dioxo-6a-thiapentalene; (a) in trifluoroacetic acid, (b) in trifluoroacetic acid containing 5% (v/v) perchloric acid

give the cation (12) as the only observable species, the spectrum of which showed two methyl signals at δ 2.77 [2'-Me, weakly coupled to C(1')H₂] and 2.81 (5-Me), a two

proton singlet at δ 5.10 [$C(1')H_2$], and a singlet at δ 7.81 (4-H). Although *O*-protonated dioxaselenapentalenes were not detected in the acid solutions, it is likely that they too exist in equilibrium with the corresponding unprotonated bases and the *C*(3)-protonated species, in view of the behaviour of 2,5-dimethyl-1,6-dioxa-6a-thiapentalene (3) in trifluoroacetic acid.

Discussion.—The cations (6), (8a and b), and (12) are the first reported derivatives of the hitherto unknown 1,2-oxathiolium (13) and 1,2-oxaselenolium (14) systems. We have previously suggested² that the derivative (15) of the oxathiolium cation is an intermediate in the nitrosation of 1,6-dioxa-6a-thiapentalene (1). The spectroscopic identification of the cations (6) and (12) lends experimental support to this suggestion and to the more general proposal² that the electrophilic substitution of hypervalent heterocyclic systems of the type (16), where X, Y, and Z are heteroatoms of Groups V and VI and Y is a second- or lower-row element, proceeds by way of intermediate 6π -electron monocyclic cations (17) and/or (18).

EXPERIMENTAL

M.p.s. were determined with a Kofler hot-stage apparatus. For 1H n.m.r. measurements tetramethylsilane was used as internal reference. Mass spectra were obtained with an

² R. M. Christie, A. S. Ingram, D. H. Reid, and R. G. Webster, *J.C.S. Perkin I*, 1974, 722.

A.E.I. MS902 spectrometer. Petroleum was of boiling range 40–50°. Perchloric acid refers to 70–72% (w/w) perchloric acid.

Preparation of Deuteriated 1,6-Dioxa-6a-thiapentalenes.—3,4-Dideuterio-1,6-dioxa-6a-thiapentalene (2). 1,6-Dioxa-6a-thiapentalene (1)¹ (256 mg, 2 mmol) was dissolved in trifluoroacetic [2H]acid (7.7 ml, 100 mmol; isotopic purity 99.8%). After 3 min sodium carbonate (6 g, 56.6 mmol) in deuterium oxide (20 ml; isotopic purity 99.7%) was added and the resulting mixture was extracted with dichloromethane (\times 3). The extracts were dried (Na_2SO_4) and evaporated, and the residue (255 mg, 98%) was recrystallised from petroleum to give *needles*, m.p. 61–63°, δ ($CDCl_3$; 100 MHz) 8.63 (2- and 5-H), M^+ 130.0048 (Found: C, 46.2. $C_5H_2D_2OS$ requires C, 46.1%).

3,4-Dideuterio-2,5-dimethyl-1,6-dioxa-6a-thiapentalene (4). The procedure was identical with that of the preceding experiment, with 2,5-dimethyl-1,6-dioxa-6a-thiapentalene (3)¹ (312 mg, 2 mmol) in place of 1,6-dioxa-6a-thiapentalene. The residue from the extracts was chromatographed [alumina (5×1.9 cm)] with benzene. The eluates afforded *spars* (119 mg, 38%), m.p. 70–71° (from petroleum), δ ($CDCl_3$; 100 MHz) 2.31 (2- and 5-Me), M^+ 158.0380 (Found: C, 53.2. $C_7H_6D_2O_2S$ requires C, 53.1%).

The isotopic purity of compounds (2) and (4) was > 95%.

We thank the Carnegie Trust for the Universities of Scotland for financial assistance.

[5/910 Received, 13th May, 1975]