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CYCLIC SULPHONES. PART XII.[1] THIIN-YL-S,S-DIOXIDE ANIONS.

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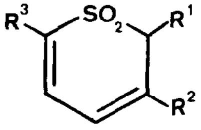
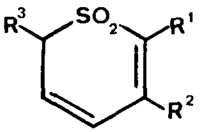
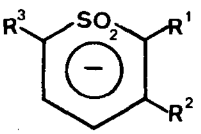
Cyclic delocalisation of the π electron sextet present in thiin-yl-S,S-dioxide anions was invoked to account for their considerable conjugative stabilisation[2] as inferred from the remarkable acidity of the neutral precursors. The intermediacy of thiin-yl-S,S-dioxide anion species was thought to be responsible for: (i) deuterium exchange in 3-phenyl-2H-thiin-1,1-dioxide,[3] (ii) crotonic dehydration of 5-hydroxy-3-phenyl-5,6-dihydro-2H-thiin-1,1-dioxide by strong alkalies,[4] (iii) lack of addition of strongly basic nucleophiles, in contrast with the addition of mildly basic nucleophiles[4] or dipolarophiles.[5] We now report the facile formation of some substituted thiin-yl-S,S-dioxide anions; also, the direct observation of these anionic species substantiates the occurrence of an extensive π electron delocalisation within the heterocycle.



(I)



(II)



(III)

a : $R^1 = R^3 = H$; $R^2 = C_6H_5$
b : $R^1 = CH_3$; $R^2 = C_6H_5$; $R^3 = H$
c : $R^3 = CH_3$; $R^2 = C_6H_5$; $R^1 = H$
d : $R^1 = R^3 = H$; $R^2 = CH_3$

Previously reported synthetic methods[4,6] generally afforded mixtures of the 2H- and 6H-thiin-1,1-dioxide isomers (I) and (II). 3-Phenyl-2H-thiin-1,1-dioxide (Ia) was obtained isomerically pure from the mixture (Ia-IIa) by repeated treatment

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with ethyl ether; 3-phenyl-6-methyl-2H-thiin-1,1-dioxide (Ic) was instead the only detectable isomer. Usual chromatografic techniques failed in the separation of the mixtures (Ib-IIb) and (Id-IId) and no particular effort was taken in the isolation of the pure isomers. Isomer ratios, ^{1}H n.m.r. data of the pure compounds and of the isomeric mixtures are reported in the Table.

Thiin-yl-S,S-dioxide anions (III) were obtained upon treatment of the precursors (I)-(II) with sodium dimsyl in DMSO: in the case of the anion (IIIa) the same species was obviously obtained starting from the pure isomer (Ia) and from the isomer mixture (Ia-IIa). ^{1}H n.m.r. data of anions (III) are collected in the Table. The following features of the thiin-yl-S,S-dioxide anions appear to be relevant: (i) a low field shift is experienced by the protons bonded to the carbanion carbon, in relation to the methylene of the precursors, both in the case of deprotonation in position 2 and 6. Also, methyl groups bonded to a saturated carbon in the pre-

TABLE

^{1}H n.m.r. data[a] of thiin-yl-S,S-dioxide anions[b] and their precursors.[c]

Compd.	2	4	5	6	R^1	R^2	R^3	|J| (Hz)
Ia[d]	5.41s	← 2.8-3.6m →			-	2.3-2.8m	-	
IIa[e]				5.81m	-		-	
Ib[e]	5.48q	← 3.22m →			8.65d	2.60m	-	J_{CH-CH_3}=7.5
IIb[d]	-	← 3.80m →		5.82m	8.00s	2.60m	-	
Ic[d]	5.46s	← 3.35m →		-	-	2.3-2.8m	7.92s	
Id[e]	5.96bs	← 3.2-3.8m →			-	8.02d	-	J_{4-CH_3}=1.5
IId[e]		3.9-4.7m		5.98bd	-	8.05d	-	
IIIa	4.81m	4.81m	3.50t	4.94bt	-	2.70m	-	J_{26}=4.2; J_{45}=8.1; J_{46}=0.7; J_{56}=8.5.
IIIb	-	5.28dd	3.67dd	5.20dd	8.11s	2.73m	-	J_{45}=8.2; J_{46}=0.7; J_{56}=9.2.
IIIc	5.07bs	4.93bd	3.68bd[f]	-	-	2.70m	g	J_{24}=0.6; J_{45}=8.2;
IIId	5.18d	5.26dd	3.77m	5.08m	-	8.14bs	-	J_{26}=4.2; J_{45}=8.2; J_{46}=0.7; J_{56}=9.2; J_{5-CH_3}=0.5.

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[a] τ scale using TMS as internal reference. [b] in DMSO ca. 1M. [c] in [$^2H_6$]DMSO. [d] Pure isomer. [e] determined in isomer mixtures whose isomer ratio was: Ia,d:IIa,d=80:20 and Ib:IIb=20:80. Unreported figures refer to peaks covered by (or common with) those of the predominant isomer. [f] in methanol-sodium methoxide solution 3.38dq (J_{5-CH_3} = ca. 1 Hz.). [g] covered by the solvent peak at 100 Mc.

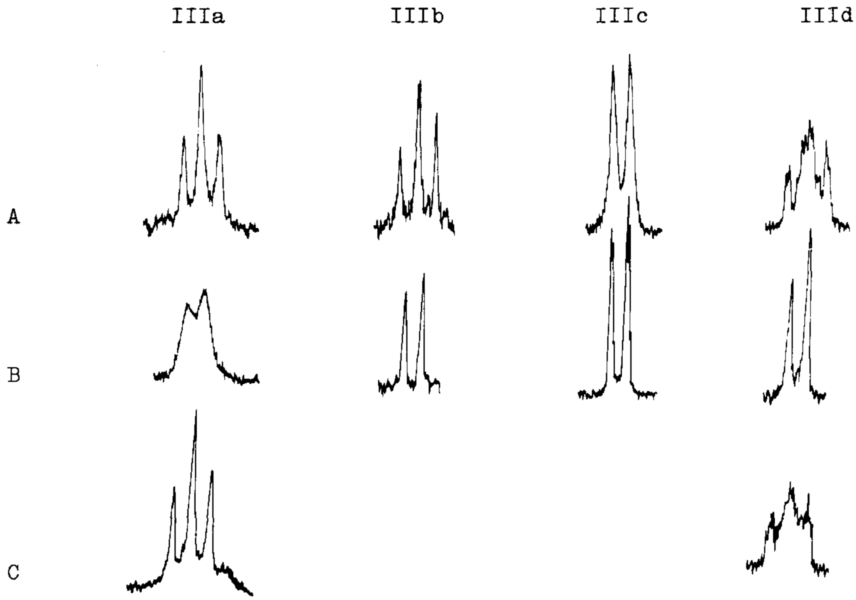

Figure. ^{1}H n.m.r. pattern of proton at C_5 in thiin-yl-S,S-dioxide anions (III). A: in DMSO. B: in CH_3OH at 38°C. C: in CH_3OH at -40° or -30°C.

cursor appear lowfield in the corresponding anion. These behaviours are analogous to those found[1] for benzo- and dibenzothiin-yl-S,S-dioxide anions and can analogously be ascribed to the effect of trigonalisation of the carbanion carbon, which overtakes the shielding effect due to the negative charge. (ii) Line positions of protons at C_2 and C_4 are present at similar magnetic field: the highfield displacement of proton at C_4 finds analogy with similar shifts in allylic anions[7] and aromatic anions.[8] In this respect the spectrum of (IIId) is strongly reminiscent of that of m.cresoate in DMSO.[9] (iii) A large value of ^4J is found between protons 2 and 6; this finds analogy with the spectrum of thiin-yl-S,S-dioxide anion[10] and with that of benzo[c]thiin-yl-S,S-dioxide anion[1] and appears to be due to a considerable contribution of the π coupling mechanism between the protons. ^3J between protons 2 and 3, and 3 and 4 are analogous to those found for the benzo-derivatives.[1]

Thiin-yl-S,S-dioxide anions (III) were also obtained upon treatment of their precursors with ca. 1.5M sodium methoxide in methanol. In such conditions spectra of (IIIc) at room temperature and of (III a,d) at low temperature were nearly superimposable with those of the corresponding anions in DMSO, apart from some displacements due to the different solvents. At higher temperatures however a considerable simplification of the spectra was obtained as a result of the fast (on n.m.r. time scale) chemical exchange at positions 2 and 6 in anions (III a,b, and d). To show this, resonances of the proton at C_5 in (III a-d) are reported in the Figure: under exchange conditions, in methanol, the triplet, or double doublet or multiplet in (III a,b, and d) is reduced to a doublet. In all cases, in anions (III a-d) no fast chemical exchange occurs at C_4. Low temperature spectra of (IIIb) could not be recorded owing to the low solubility of the product.

Results obtained from the direct observation of thiin-yl-S,S-dioxide anions are consistent with an extensive charge delocalisation within the heterocyclic ring. To determine exact pK_a values, titrimetric methods cannot be used for thiins--S,S-dioxide.[4] However, the formation of thiin-yl-S,S-dioxide anions in methanol using sodium methoxide as a base indicates that pK_a values of the thiin-S,S-dioxide derivatives (I)-(II) must be lower than ca. 16, as deduced from the value of H_-[11] in such solutions, and in the assumption that metallation has proceeded at least for 95%. These low pK_a values (cyclopentadiene $pK_a = 15$) substantiate the kinetic acidity enhancement found[2] for the benzo- and dibenzothiins-S,S-dioxide, relative to their corresponding open chain analogs.

The nature of the S-O bond in related anionic substrates is being investigated and results will be reported elsewhere.

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