Chemical Reactivity and Charge Densities in Certain 6a-Thiathiophthens

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THE formation of monosubstitution products by the action of bromine on 2,5-diphenyl- and 2,5-dimethyl-6a-thiathiophthen has been reported.[1] We have examined the reactivity of some unsymmetrically substituted thiathiophthens and compared their observed behaviour with that predicted by molecular orbital theory.

Bromination of 2-methyl-5-phenyl-6a-thiathiophthen (I; R = H) gives a monobromo-derivative, believed to be 3-bromo-2-methyl-5-phenyl-6a-thiathiophthen (I; R = Br) m.p. 113°; λ_{max} 251, 273, 334, and 504 mμ (log ϵ 4·68, 4·51, 4·04, and 4·03); τ 7·27 (3H, s), τ 2·14—2·68 (5H, m), τ 1·51 (1H, s). The position of bromination is inferred from a comparison of n.m.r. data in the series (see Table).

TABLE

Substituents	Chemical shifts in CDCl$_3$ (τ) 3-position	Chemical shifts in CDCl$_3$ (τ) 4-position
2,5-Diphenyl	1·82	1·82
3-Bromo-2,5-diphenyl ..	—	1·26
2,5-Dimethyl	2·43	2·43
3-Bromo-2,5-dimethyl ..	—	2·06
2-Methyl-5-phenyl ..	2·31	1·97
3-Bromo-2-methyl-5-phenyl	—	1·51

2-Methylthio-5-phenyl-6a-thiathiophthen[1,2] (II; R = H) also brominates smoothly, but its nitration (with concentrated nitric acid in hot acetic acid) is of greater interest, since the structure of the product (II; R = NO$_2$) has been confirmed by an unambiguous synthesis from 3-methylthio-5-phenyl-1,2-dithiolium methosulphate (III) and methyl nitrodithioacetate (IV). The nitro-compound, m.p. 158—159°, has the characteristic[3] thiathiophthen absorption spectrum; λ_{max} 254, 322, and 480 mμ (log ϵ 4·53, 4·26, and 4·04).

The 3-position is also attacked on nitrosation of 2-methylthio-5-phenyl-6a-thiathiophthen with nitrous acid in acetic acid at 5°, but the product, m.p. 138—139° (λ_{max} 324 and 422 mμ; log ϵ 4·28 and 4·04), probably exists in the isomeric form V; R = CS$_2$Me).

The methylthio-group in 2-methylthio-5-phenyl-6a-thiathiophthen is slowly replaceable by nucleophiles. Thus prolonged reaction with sodium ethoxide in ethanol under reflux gave 2-ethoxy-5-phenyl-6a-thiathiophthen, (70%) m.p. 90—91°; λ_{max} 258, [280—290], and 478 mμ (log ϵ 4·48, [4·28], and 4·02). Primary aliphatic amines reacted similarly with 2-methylthio-5-phenyl-6a-thiathiophthen, giving 2-alkylamino-derivatives.

Attempted nitration and nitrosation of 2,5-diphenyl-6a-thiathiophthen yielded the same nitroso-compound (VI; R = NO) or (V; R = COPh), m.p. 172—173°; λ_{max} 252, 298, [330], and 416 mμ (log ϵ 4·30, 4·01, [3·94], and 4·01). This product, also obtained by nitrosation of 5-phenyl-1,2-dithiol-3-ylidene-acetophenone, is not intensely coloured, as one might expect for structure (VI; R = NO) and its i.r. spectrum contains a carbonyl-stretching band at 1640 cm.$^{-1}$. Dithiolylidene ketones in which the carbonyl group is adjacent to, and interacts with, the disulphide linkage do not show normal C=O stretching bands.[4] We suggest that the nitroso-compound exists in the form (V; R = COPh), with some interaction between the oxygen atom of the nitroso-group and the adjacent sulphur atom.

The nitroso-derivative obtained from 2-methylthio-5-phenyl-6a-thiathiophthen, in contrast to the nitro-derivative (II; R = NO$_2$), does not have the electronic absorption spectrum of a thiathiophthen, but resembles the nitroso-ketone (V; R = COPh) and thus should probably be formulated as (V; R = CS$_2$Me). Conversion to the simpler nitroso-compound (V; R = H), m.p. 131—132° (λ_{max} 327 and 420 mμ; log ϵ 4·00 and 4·04) was achieved by the action of mercuric acetate.†

Whatever the precise structure of the nitroso-compounds, it is clear that 2-methylthio-5-phenyl-6a-thiathiophthen is attacked at the 3-position by electrophiles and at the 2-position by nucleophiles (with displacement of the methylthio-group). Charge densities for the non-alternant 6a-thiathiophthen system have been calculated both by the Wheland–Mann ω-technique[5] and by a PPP-SCF method,[6] using the Maeda model[7] in which the three sulphur atoms are bonded through $3p$–$3d_{xz}$ hybridisation of the central sulphur atom. Values of the calculated[8] charge densities and localisation energies for 2-methyl-5-phenyl-6a-thiathiophthen and charge densities for 2-methylthio-5-phenyl-6a-thiathiophthen, obtained by the ω-method, are

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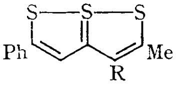
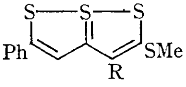
† For similar desulphurisation reactions with mercuric acetate, see ref. 2.



(I)



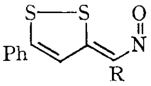
(II)

$MeSO_4^-$

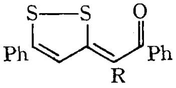
(III)

$O_2N\cdot CH_2\cdot CS_2Me$

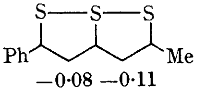
(IV)



(V)

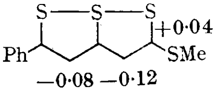


(VI)



$L_3^+ = 1{\cdot}43\beta$ (VII)

$L_4^+ = 1{\cdot}38\beta$



(VIII)

shown in diagrams (VII) and (VIII). On the basis of the charge-density values, the 3-position in both molecules should be the position of attack by electrophiles, in agreement with our observed results. Consideration of localisation energies, on the other hand, suggests that the 4-position should be the more reactive (the non-crossing rule[9] is broken), but it has been noted[10] that charge densities in sulphur-containing non-alternants usually give a better correlation with reactivity than do localisation energies.

The positive charge density at the 2-position in 2-methylthio-5-phenyl-6a-thiathiophthen (VIII) is in accordance with the susceptibility of this compound to attack by nucleophiles. Much other evidence could be adduced to support the view that the 2-position in 6a-thiathiophthens is electron-deficient.

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