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SOME ASPECTS OF THE CHEMISTRY OF 6a-THIATHIOPHTHENS

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The appearance of two publications[1,2] dealing with the chemistry of 6a-thiathiophthens prompts us to report related work carried out in our laboratory.

Halogenation of 6a-thiathiophthens. Current interest[3] in 6a-thiathiophthens [e.g. (I)] stems partly from the possibility that these compounds may be aromatic in character, as represented by structures (II) and (III). In this connexion, the recently reported[1] failure of attempts to chlorinate certain thiathiophthens (with sulphuryl chloride) is of interest.

We have successfully brominated two thiathiophthens in high yield under normal conditions (i.e. with bromine in inert solvents at room temperature). 2,5-Dimethyl-6a-thiathiophthen (I; R=Me, R'=H) gave 3-bromo-2,5-dimethyl-6a-thiathiophthen (I; R=Me, R'=Br); orange needles, m.p. 95-6°, from light petroleum; $\lambda_{max.}$ 263, 481 mμ (ε 50,300, 7,050); N.M.R. spectrum[*] τ 7.37 (3H, singlet), τ 7.28 (3H, singlet), τ 2.06 (1H, singlet). The structure of this product is established by the N.M.R. spectrum and by the similarity of its electronic absorption spectrum to that of 2,5-dimethyl-6a-thiathiophthen, which has $\lambda_{max.}$ 261, 474 mμ (ε 54,400, 7,020).

Bromination of 2,5-diphenyl-6a-thiathiophthen yielded the 3-bromo-derivative (I; R=Ph, R'=Br); purple needles, m.p. 135-6°, from light petroleum; $\lambda_{max.}$ 254, 293, 510 mμ (ε 52,200, 23,200, 13,050); N.M.R. spectrum τ 2.0-2.7 (10H, multiplet), τ 1.26 (1H, singlet). For comparison, the N.M.R. spectrum of 2,5-diphenyl-6a-thiathiophthen has signals at τ 2.0-2.7 (10H, multiplet) and τ 1.82 (2H, singlet).

The structures assigned to the two bromo-compounds are supported by their mass spectra which will be discussed in detail elsewhere.

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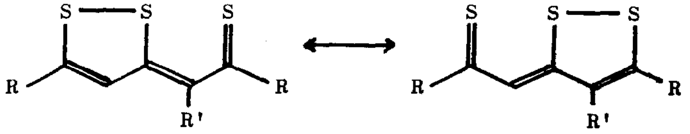
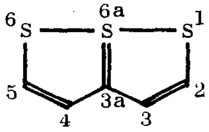
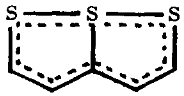
[*] The N.M.R. spectra recorded in this communication were measured in $CDCl_3$ solution.


S
S
S
R
R
R'
S
S
S
R
R
R'

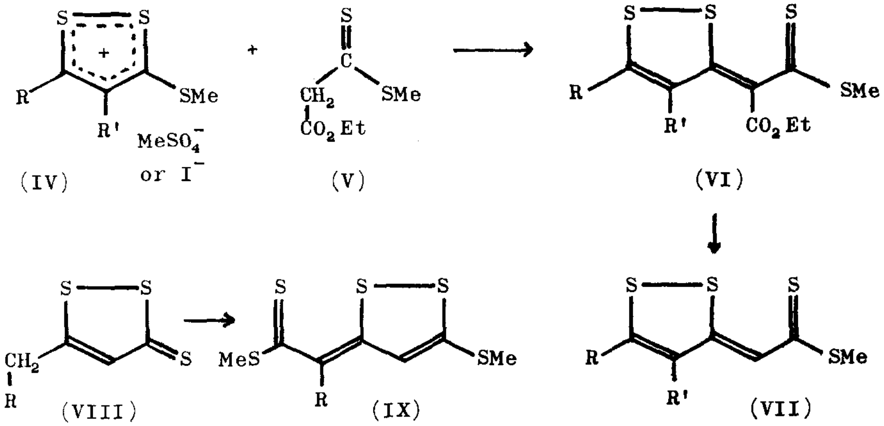
(I)

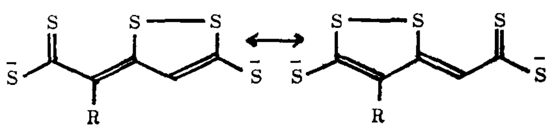

6
6a
1
S
S
S
5
3a
2
4
3

(II)

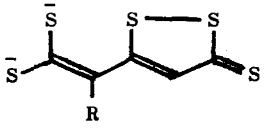

S
S
S

(III)


S
S
+
R
SMe
R'
MeSO$_4^-$
or I$^-$
(IV)
S
C
CH$_2$
SMe
CO$_2$Et
(V)
S
S
S
R
SMe
R'
CO$_2$Et
(VI)
S
S
CH$_2$
R
S
(VIII)
S
S
S
MeS
SMe
R
(IX)
S
S
S
R
SMe
R'
(VII)


S
S
S
$\bar{S}$
R
$\bar{S}$
S
S
S
$\bar{S}$
R
$\bar{S}$

(X)


$\bar{S}$
S
S
$\bar{S}$
R
S

(XI)

2-*Methylthio*- *and* 2,5-*bismethylthio*-6a-*thiathiophthens*. The facile condensation of 3-methylthio-5-phenyl-1,2-dithiolium methosulphate (IV; R=Ph, R'=H) with methyl benzoyldithioacetate, giving 3-benzoyl-2-methylthio-5--phenyl-6a-thiathiophthen, has been described previously.[4] In an extension of this synthesis, methyl ethoxycarbonyldithioacetate (V) was condensed with dithiolium methosulphate (IV; R=Ph, R'=H) at room temperature in methanol containing a catalytic amount of pyridine, giving *almost quantitatively* 3-ethoxycarbonyl-2-methylthio-5-phenyl-6a-thiathiophthen (VI; R=Ph, R'=H);[5] red needles, m.p. 112-3°, from ethanol; $\lambda_{max.}$ 260, 315, 357, 492 mμ (ε 49,400, 24,000, 5,300, 14,400); N.M.R. spectrum τ 8.45-8.69 (3H, triplet), τ 7.46 (3H, singlet), τ 5.40-5.75 (2H, quadruplet), τ 2.2-2.9 (5H, multiplet) and τ 1.70 (1H, singlet). Prolonged heating with concentrated hydrobromic acid in acetic acid gave 2-methylthio-5-phenyl-6a-thiathiophthen (VII; R=Ph, R'=H); red needles, m.p. 125-6°, from cyclohexane; $\lambda_{max.}$ 261, 313, 354, 514 mμ (ε 48,800, 21,700, 5,510, 15,500); N.M.R. spectrum τ 7.38 (3H, singlet), τ 2.3-2.7 (5H, multiplet), τ 2.32 (1H?, singlet) τ 2.28 (1H, singlet).

Similarly, using 3,5-bismethylthio-4-phenyl-1,2-dithiolium methiodide[6] (IV; R=MeS, R'=Ph) as starting material, we have prepared the 2,5-bismethylthio--6a-thiathiophthen (VI; R=MeS, R'=Ph), m.p. 150-2°, and converted it, by the action of hydrochloric acid in acetic acid, to (VII; R=MeS, R'=Ph), m.p. 139-140°. The latter compound was also obtained (in 65% yield) by condensation of carbon disulphide with 5-benzyl-1,2-dithiole-3-thione (VIII; R=Ph) using sodium hydride in tetrahydrofuran, and subsequent methylation of the resulting dianion [(X) rather than (XI)], thus providing further evidence for "no-bond resonance" in the 6a-thiathiophthen system.[7,8,9] The recent paper of Portail and Vialle[2] describes two further methods for the preparation of the bismethylthio-compound (VII; R=MeS, R'=Ph), one by condensation of 5-methyl-4-phenyl--1,2-dithiole-3-thione with carbon disulphide, and the other involving an interesting addition reaction of methylthioacetylene and 5-methylthio-4-phenyl--1,2-dithiole-3-thione.

2,5-Bismethylthio-3-phenyl-6a-thiathiophthen has, in fact, now been prepared by five methods, the fifth being the base-catalysed condensation of 3,5-bismethylthio-4-phenyl-1,2-dithiolium methiodide (IV; R=MeS, R'=Ph) with methyl benzoyldithioacetate; the extrusion of the benzoyl group, although not anticipated, is understandable in retrospect and can be rationalised.

Like Portail and Vialle,[2] we have condensed 5-methyl-1,2-dithiole-3-thione (VIII; R=H) with carbon disulphide and methylated the dianion produced (X; R=H) to give, in poor yield, 2,5-bismethylthio-6a-thiathiophthen[5] (IX; R=H) or (VII; R=MeS, R'=H); orange plates, m.p. 97°, from light petroleum; $\lambda_{max.}$ 251, 321, 354, 500 mµ (ε 46,700, 12,100, 6,420, 16,600).

References

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