The Rearrangement of 6a-Thiathiophthenes by Nucleophiles

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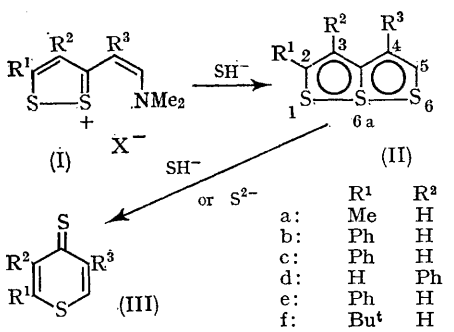
WE recently reported[1] that the Vilsmeier salts (I), prepared by the condensation of 3-methyl(ene)-1,2-dithiolium salts with *NN*-dimethylthioformamide in acetic anhydride, are converted into 6a-thiathiophthenes (II) by sodium hydrogen sulphide in aqueous dimethylformamide at room temperature. It was noted that the salt (I;R^1 = Me, R^2 = R^3 = H; X = Br) gave, in addition to 2-methyl-6a-thiathiophthene (IIa) (29%), a substantial quantity (31%) of 2-methyl-4*H*-thiapyran-4-thione (IIIa). We have now established that 6a-thiathiophthenes react with sodium hydrogen sulphide in aqueous dimethylformamide to give 4*H*-thiapyran-4-thiones (III), provided at least one of the positions 2 and 5 is unsubstituted. The difference between the rates of formation and decomposition of 6a-thiathiophthenes at room temperature is sufficiently large in most cases to allow the 6a-thiathiophthene to be isolated in high yield. Results of comparative studies illustrating substituent effects on the rate of rearrangement are summarised in Table 1.



	R^1	R^2	R^3
a:	Me	H	H
b:	Ph	H	Ph
c:	Ph	H	Me
d:	H	Ph	Ph
e:	Ph	H	H
f:	Bu^t	H	H

6a-Thiathiophthenes rearrange more rapidly and completely to 4*H*-thiapyran-4-thiones when

TABLE 1

Reaction of 6a-thiathiophthenes (1 mmole) with sodium hydrogen sulphide (10 mmoles) in dimethylformamide (20 ml.) and water (5 ml.) at 70° for 30 min.

6a-Thiathiophthene	4*H*-Thiapyran-4-thione	Products: Yield	Yield of recovered starting material (%)
2-Methyl-(IIa)[a]	2-Methyl-(IIIa)[b]	42	27
2,4-Diphenyl-(IIb)	2,5-Diphenyl-(IIIb)[b]	44	40
2-Phenyl-4-methyl-(IIc)	2-Phenyl-5-methyl-(IIIc)[b]	29	65
3,4-Diphenyl-(IId)[b,c]	3,5-Diphenyl-(IIId)[b]	99	—
2-Phenyl-(IIe)	2-Phenyl-(IIIe)	65	3
2-t-Butyl-(IIf)[b]	2-t-Butyl-(IIIf)[b]	59	34

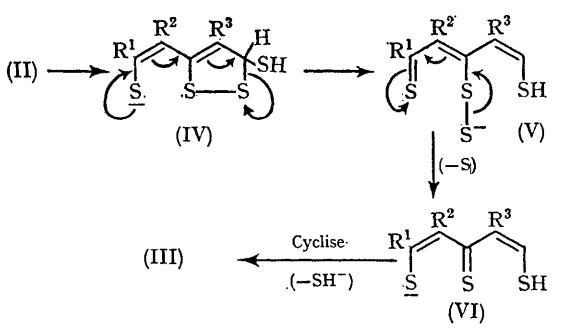
[a] Heated 15 min. at 50°. [b] New compounds.
[c] Stood 5 min. at room temperature.

treated with sodium sulphide in aqueous dimethylformamide (Table 2). For preparative purposes the corresponding Vilsmeier salt precursors may be employed in place of the 6a-thiathiophthenes to give the 4*H*-thiapyran-4-thiones directly, in comparable yields. The sequence 1,2-dithiolium salt → Vilsmeier salt → 4*H*-thiapyran-4-thione thus constitutes a novel flexible synthesis of 4*H*-thiapyran-4-thiones.

TABLE 2

Rearrangement of 6a-thiathiophthenes (1 mmole) into 4H-thiapyran-4-thiones by sodium sulphide (10 mmoles) in dimethylformamide (20 ml.) and water (5 ml.) at 60°. Reaction time 5 min.

6a-Thiathiophthene	4*H*-Thiapyran-4-thione	Yield (%)
2,4-Diphenyl-(IIb)	2,5-Diphenyl-(IIIb)	80
2-Phenyl-4-methyl-(IIc)	2-Phenyl-5-methyl-(IIIc)	77
2-Phenyl-(IIe)	2-Phenyl-(IIIe)	69
2-t-Butyl-(IIf)	2-t-Butyl-(IIIf)	76



A probable precursor of the 4*H*-thiapyran-4-thiones is the anion (VI) (or tautomer) formed according to the sequence (II) → (IV) → (V) → (VI) → (III). We envisage the anion (VI) arising by disproportionation of the intermediate (V), rather than by reductive cleavage of an S–S bond in the 6a-thiathiophthenes by hydrosulphide or sulphide. It is significant in this connection that the 6a-thiathiophthenes (IIb) and (IIe) also react with sodium hydroxide in aqueous dimethylformamide to form the 4*H*-thiapyran-4-thiones (IIIb) and (IIIe), respectively, as the major reaction products. We defer further discussion of the mechanism until further studies of 6a-thiathiophthenes with nucleophiles are complete.

Satisfactory elemental analyses and n.m.r. spectral data were obtained for all new compounds.

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[1] J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc.* (*C*), 1968, in the press.