Synthesis of Condensed Thiophens *via* [2,3] and [3,3] Sigmatropic Rearrangements of Aryl Prop-2-ynyl Sulphoxides

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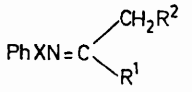
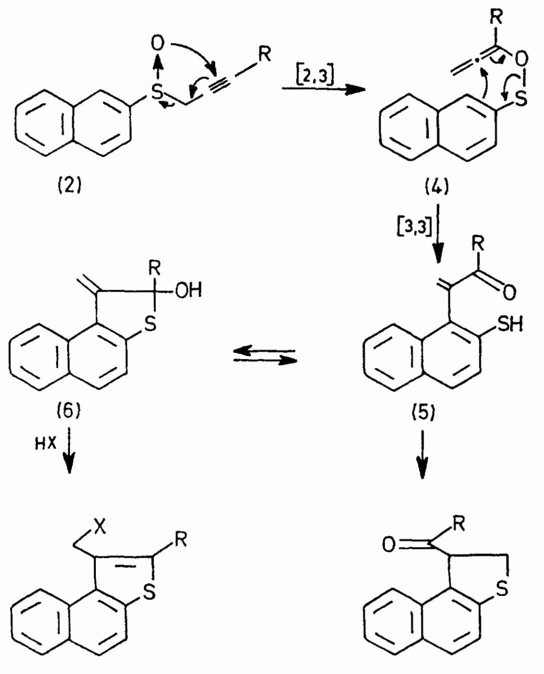
Summary Condensed thiophens are obtained by heating aryl prop-2-ynyl sulphoxides in a suitable protic solvent *via* consecutive [2,3] and [3,3] sigmatropic rearrangements, ketolization, and S_N2' attack of the solvent molecule.

[3,3] SIGMATROPIC rearrangements have been frequently employed in syntheses *e.g.* the Fischer indole synthesis[1] using the phenylhydrazones (**1**; X = NH). Benzo[*b*]furans have been prepared analogously from the *O*-phenyloxime ethers[2] (**1**; X = O), but attempts to extend these reactions to the preparation of benzo[*b*]thiophens from the aryl sulphenamides (**1**; X = S) have failed.[2c,3] We now report a convenient synthesis of condensed thiophens by the thermal reaction of aryl prop-2-ynyl sulphoxides in a suitable protic solvent.

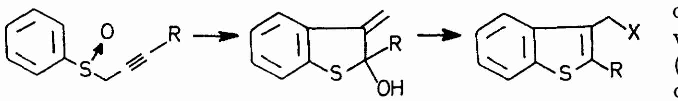


$PhXN{=}C(CH_2R^2)R^1$

(1) X = NH, O, or S



a; R = H
b; R = Me



a; R = H
b; R = Me

TABLE

Conversion of prop-2-ynyl sulphides into thiophens by the one-flask procedure (yield %)

X	(**3a**)[a]	(**3b**)[a]	(**10a**)[b]	(**10b**)[b]
PhS	93	87	67	81
EtO	76	78	58	85
HO	76	83	67	72
AcO	54	56	—	—

[a] From (**2**). [b] From (**8**).

The sulphoxides (**2**)† were prepared from the corresponding sulphides by periodate oxidation. When the sulphoxide (**2a**) was heated at 80° for 5 h in benzenethiol, the naphthothiophen (**3a**; X = PhS) was obtained in 60% yield. Thermal reaction of (**2a**) in ethanol or acetic acid also afforded the naphthothiophens (**3a**; X = EtO or AcO) as major products. But-2-ynyl 2-naphthyl sulphoxide (**2b**) was also transformed into the naphthothiophens (**3b**; X = PhS, EtO, and AcO) in 60—80% yield. These reactions are considered to involve : (i) [2,3] sigmatropic rearrangement of (**2**) to the allenyl sulphenates (**4**), (ii) [3,3] sigmatropic rearrangement of (**4**) to the $\alpha\beta$-unsaturated carbonyl compounds (**5**), and (iii) ketolization to the hemithioacetal intermediates (**6**),[4] which undergo S_N2' attack by the solvent to the allyl alcohol (Scheme).

Heating the sulphoxides (**2a,b**) in dioxan at 100° for 2 h quantitatively afforded the hemithioacetals (**6a,b**) which were transformed into the naphthothiophens (**3a,b**) by treatment with protic solvents. Conversion of (**6**) into (**3**) is catalysed by a small amount of acid (*e.g.*, TsOH). Synthesis of the naphthothiophens (**3**) from the sulphoxides (**2**) could thus be an efficient 'one-flask' procedure, in which a dioxan solution of (**6**) obtained by heating (**2**) in dioxan, was warmed with a suitable protic solvent and a catalyst (TsOH). By this method the phenyl prop-2-ynyl sulphoxides (**8**) afforded the corresponding benzo[*b*]thiophens (**10**) *via* the intermediates (**9**). The products are shown in the Table.

Conversely, thermal reaction of (**2a,b**) in basic media (*e.g.* dimethylaniline) at 80 °C for 2 h afforded the 1-formyl- and 1-acetyl-naphthothiophens (**7a,b**) in 72 and 83% yield, respectively, which could also be prepared by treatment of the intermediates (**6a,b**) with aqueous KOH.[4]

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† The n.m.r. and i.r. spectra and elemental analyses of all new compounds were consistent with the structures assigned.

[1] For reviews on the Fischer indole synthesis, see B. Robinson, *Chem. Rev.*, 1963, **63**, 373; 1969, **69**, 227.

[2] (a) T. Sheradsky, *Tetrahedron Letters*, 1966, 5225; (b) A. Mooradian, *ibid.*, 1967, 407; (c) D. Kaminsky, J. Shavel, Jr., and R. I. Meltzer, *ibid.*, p. 859; (d) A. Mooradian and P. E. Dupont, *ibid.*, p. 2867.

[3] F. A. Davis and E. B. Skibo, *J. Org. Chem.*, 1974, **39**, 807.

[4] *Cf.* K. C. Majumdar and B. S. Thyagarajan, *J.C.S. Chem. Comm.*, 1972, 83.