The Direct Bradsher Reaction: Synthesis of Benzodithiophens and Related Systems

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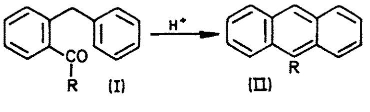
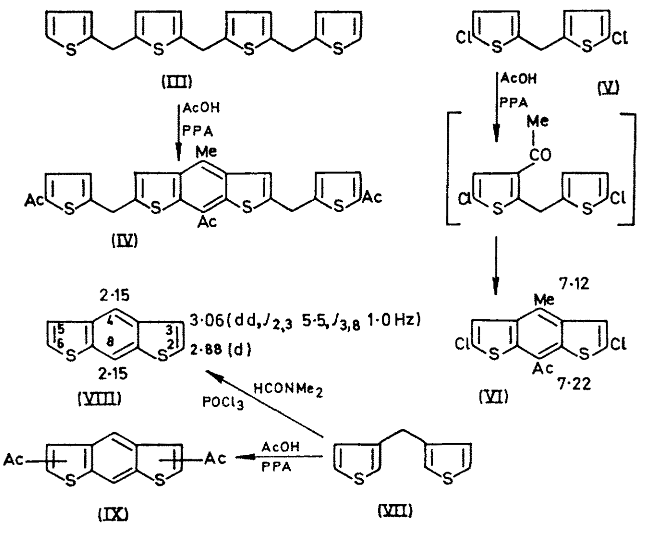
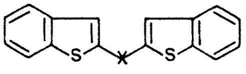
Summary The acylation of dithienylmethanes, a bis(benzothienyl)methane, and a bis(benzothienyl) sulphide gives, respectively, benzodithiophenes, a condensed analogue, and a thiapyrylium salt, by a direct Bradsher reaction.

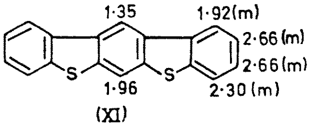
THE Bradsher reaction, involving the acid-catalysed cyclodehydration of *o*-acyldiaryl-alkanes (*e.g.* I → II) offers a useful alternative to the Elbs reaction as a primary synthetic route to specifically substituted anthracenes. However, the preparation of the starting materials frequently presents difficulty. We now report the synthesis of the little known thiophen isosteres of anthracene and some condensed analogues by a direct Bradsher reaction, which incorporates acylation of a hydrocarbon followed by cyclisation in one step and in good yield.†



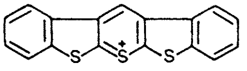




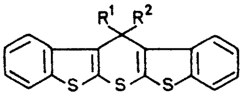
(X) X = CH_2
(XII) X = S



(XI)



(XIII) Cl^-



(XIV) $R^1 = H, R^2 = OH$
(XV) $R^1 = R^2 = H$
(XVI) $R^1, R^2 = O$

During attempts to acetylate the tetrathiophen (III) we recently reported that the only product obtained was the tetra-acetylated derivative (IV) in which cyclodehydration in a Bradsher manner had occurred after introduction of the third acetyl group.[1] In order to establish this mechanism we have now similarly acetylated the dithienylmethane (V) and isolated the benzodithiophen (IV) (16%, m.p. 240°). This reaction has been further extended to the synthesis of several other related systems. Thus 3,3′-dithienylmethane gave under Vilsmeier–Haack conditions the parent benzodithiophen (33%, m.p. 184°) which requires several steps in the conventional syntheses.[2] The use of acetic acid and polyphosphoric acid gave a mixture of diacetylated compounds (IX) as indicated by analysis, n.m.r., and mass spectral data. The bis(benzothienyl)methane (X) was unaffected by Vilsmeier–Haack reagents ($HCONMe_2$–$POCl_3$ or *N*-methylformanilide–$POCl_3$) but gave the required pentacyclic product (XI) with the Rieche reagent,[3] dichloromethyl butyl ether–$SnCl_4$ at 0° (96%, m.p. 216—218°). Formylation of the sulphide (XII) with $HCONMe_2$–$POCl_3$ gave the required thiapyrylium chloride

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† All new compounds gave satisfactory elemental analyses, i.r., mass, and n.m.r. spectra.

(XIII) [37% m.p. 310° (d)], while use of the Rieche reagent gave the corresponding compound as its stannic chloride complex [100%, m.p. 350° (d)]. The former compound, obtained as red-brown needles from the reaction mixture slowly became colourless on repeated crystallisation from dimethyl sulphoxide. It would appear that a mixture of the thiapyran (XV) and the thiapyrone (XVI) is formed by way of the hydrated product (XIV). The mass spectrum, empirical analysis, and t.l.c. of the mixture suggest the proportion of (XV) to (XVI) is 30 : 70.

The starting compounds were prepared by application of standard literature procedures and will be reported fully later.

The chemistry of benzo[1,2-*b* : 5,4-*b*′]dithiophen (VIII) has not been reported. Metallation with butyl-lithium in ether followed by addition of dimethylformamide gave the 2-aldehyde (35%), m.p. 171—173°, n.m.r. (τ, $CDCl_3$) 0·43 (CHO), 1·35, 1·60, and 1·95 (3-,4-,8-H, s),2·12 (5-H dd, $J_{5,6}$ 6, $J_{5,6}$ 1 Hz), and 1·21 (6-H, d). The 2-aldehyde gave the 2-methyl derivative under Huang-Minlon conditions (80%), m.p. 170—171°, n.m.r. (τ, $CDCl_3$) 2·25 and 2·27 (4-,8-H, s), 2·87 (5-H, dd, $J_{5,6}$ 5·5, $J_{5,8}$ 1·5 Hz), 3·09 (6-H, d), 3·34 (3-H, s), and 7·87 (Me, s).

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