THIOPHENES AND THIAPYRANS

Part XI. A New Route to Polycyclic Thiophenes

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The synthesis of dibenzothiophene, 1:2-benzo-9-thiafluorene and 3:4-benzo-9-thiafluorene (IV) starting from 2-bromocyclohexanone and thiophenol, \( \alpha \)-thionaphthol and \( \beta \)-thionaphthol has been described in the previous communications.\(^1\), \(^2\) The synthesis of polycyclic thiophenes starting from aryl thiols and 2-bromo-1-tetralone (I) is now described.

\[
\text{PhSH} + \overset{\text{Br}}{\text{Br}} \rightarrow \overset{\text{O}}{\text{O}} \quad \overset{\text{H}}{\text{H}}
\]

(II)

Condensation of thiophenol with (I) gave 2-phenylmercapto-1-tetralone (II) which failed to cyclize when treated with phosphorus pentoxide in boiling benzene, but underwent cyclization on heating with phosphorus pentoxide-phosphoric acid mixture under reduced pressure to give 1:2-dihydro-3:4-benzo-9-thiafluorene (III). Dehydrogenation of (III) with N-bromosuccinimide gave 3:4-benzo-9-thiafluorene (IV) which proved to be identical with the product prepared by us earlier by an alternative route.\(^2\) Davies et al.\(^3\) have recently described the synthesis of (IV) by the pyrolysis of thionaphthene-1:1-dioxide and by the hydrolytic decarboxylation of 3:4-benzo-9-thiafluorene-1:2-dicarboxylic anhydride.

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Among the different dibenzo-9-thiafluorenes only 3:4:5:6-dibenzo-9-thiafluorene (V) is known. It was prepared by Barber and Smiles\(^4\) from 1-naphthylamine-2-sulphonic acid in five steps. The yield of the product is, however, not quoted. The synthesis of (V) starting from β-naphthol through β-dinaphthol in two steps has also been described by us earlier, but the yield was low.\(^5\) Compound (V) has now been synthesised by an alternative route. In addition, the synthesis of 1:2:5:6-dibenzo-9-thiafluorene (VI) is also described.

Condensation of β-thionaphthol with (I) gave 2-(2'-naphthylmercapto)-1-tetralone (VII), which on cyclization with phosphorus pentoxide-phosphoric acid gave 1:2-dihydro-3:4:5:6-dibenzo-9-thiafluorene (VIII). The latter, on dehydrogenation with selenium, gave (V) (overall yield, 78%). Neither (V) nor (VIII) gave a picrate or a \textit{sym}-trinitrobenzene derivative.

Starting from α-thionaphthol and (I), 1:2:5:6-dibenzo-9-thiafluorene (VI) was similarly prepared (overall yield, 76%) through 2-(1'-naphthylmercapto)-1-tetralone (IX) and 1:2-dihydro-3:4:7:8-dibenzo-9-thiafluorene (X). In contrast to (V) and (VIII), (VI) and (X) gave picrates. The cyclization of (IX) may occur in the \textit{peri}-position but this appears unlikely in view of the β-cyclization of 2-(1'-naphthylmercapto)cyclohexanone.\(^2\) Raney nickel desulphurization of (VI) will be studied to confirm its structure.