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PHOTOCYCLISATION OF THIOPHEN ANALOGUES OF STILBENE

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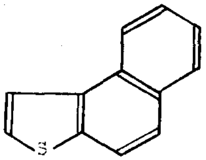
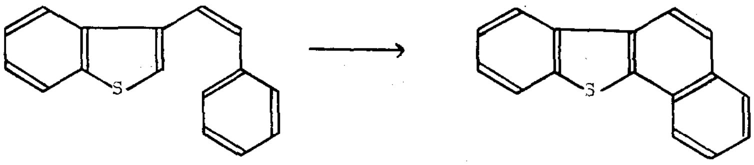
Irradiation of solutions of cis or trans stilbenes with ultraviolet light in presence of a suitable oxidant leads to formation of phenanthrenes in good yield.[1] Similarly, azo compounds,[2] when irradiated under strongly acidic conditions give rise to benzo[c]cinnolines, as well as benzidine-rearrangement products, and Schiff bases are converted into phenanthridines.[3] All of these reactions result in coupling of two benzene rings. We have found that photocatalysed cyclisation of diarylethylenes takes place with equal facility on to the thiophen nucleus.

$C_4H_3SCH=CHC_6H_5 \longrightarrow$

I



II



III IV

Thus, irradiation of a solution in hexane of 2-β-styrylthiophen (I) and 5 mol. per cent of iodine[1] with a 125 W mercury vapour lamp in a quartz reaction vessel gave naphtho[2,1-b] thiophen (II) in almost quantitative yield after 2 hr. With molecular oxygen as oxidant instead of iodine reaction was much slower, and was only 25% complete after 24 hr. Both the *cis* and the *trans* isomer of the styrylthiophen could be used, but as in other cases[4,5] cyclisation with the *trans* isomer appears to be preceded by its isomerisation to the *cis*.

The reaction has been extended to 3-α-styrylbenzo[b]thiophen (III), which was smoothly converted into 11-thiabenz[a]fluorene (IV), and to a number of methyl homologues of (I) and (III) from which methyl derivatives of the two parent condensed systems (II) and (IV) were readily obtained. The *m*-tolyl compounds (I and III, *m*-C_6H_4- for C_6H_5-) gave a mixture of the two possible cyclisation products. With the *o*-tolyl derivatives (I and III, *o*-C_6H_4- for C_6H_5-) cyclisation took place mainly at the available unsubstituted position, but small amounts of the parent compounds (II) and (IV) were also produced by displacement of the methyl group.

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