Reaction of 1,2,3-Benzothiadiazole with Aryl Radicals

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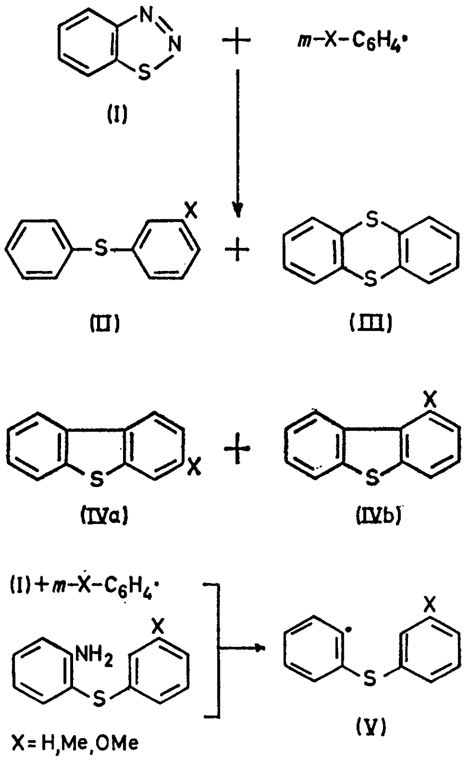
Summary The reaction of 1,2,3-benzothiadiazole with aryl radicals affords diarylsulphides, dibenzothiophens, and thianthrene; a reaction mechanism for the formation of these products is proposed.

Homolytic substitutions at the sulphur atom take place with disulphides and thiolsulphonates[1] and less easily with diaryl sulphides.[2] No examples of attack of a radical on a heteroaromatic sulphur atom seem to be reported; in the phenylation of several sulphur containing heterocyclic compounds, like thiophen,[3] benzo[*b*]thiophen,[4] thiazole,[5] dibenzothiophen,[6] and two isomeric thienothiophenes,[7] products derived from the attack on the sulphur atom were never reported. The present results represent the first example of such a process.

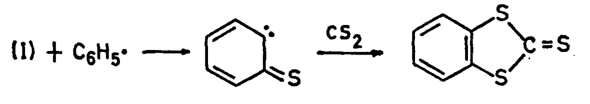
Phenyl radicals, generated from *N*-nitrosoacetanilide, react at room temperature with 1,2,3-benzothiadiazole (I) in ethyl acetate to give diphenyl sulphide (II), thianthrene (III), and dibenzothiophen (IV); *m*-substituted phenyl radicals afford *m*-X-phenyl, phenyl sulphide, thianthrene (III), and a mixture of 2- (IVa) and 4-X-dibenzothiophen (IVb) (X = H, Me, or OMe). The formation of products (II) and (IV) can be explained assuming the intermediate existence of the radical (V), generated by attack of the aryl radical on (I) followed by loss of nitrogen. Radical (V) can give (II) by hydrogen abstraction and (IV) by an intramolecular homolytic aromatic substitution; this seems to be confirmed by the fact that the ratio in which (IVa) and (IVb) are formed is identical to that obtained on generation of radical (V) by the aprotic diazotization of 2-aminophenyl-3′-X-phenyl sulphide (Scheme 1).

Thianthrene presumably forms by dimerization of (VI); its formation is suppressed by carbon disulphide which traps[8] (VI) to give the dibenzodithiol-2-thione (VII) (Scheme 2). In this reaction the dibenzothiophen is still present, as expected, and trace of diphenyl sulphide are also formed.



Scheme 1

The stability of (I) under the experimental conditions employed indicates that the thioketocarbene (VI) forms through the interaction of (I) with a radical generated from *N*-nitrosoacetanilide; a reasonable process could be the attack of the phenyl radical on the heterocyclic nitrogen atoms.



(VI) (VIII)

Scheme 2

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