Mononuclear Heterocyclic Rearrangements involving a Sulphur atom: Conversion of 1,2,4-Oxadiazoles into 1,2,4-Thiadiazoles

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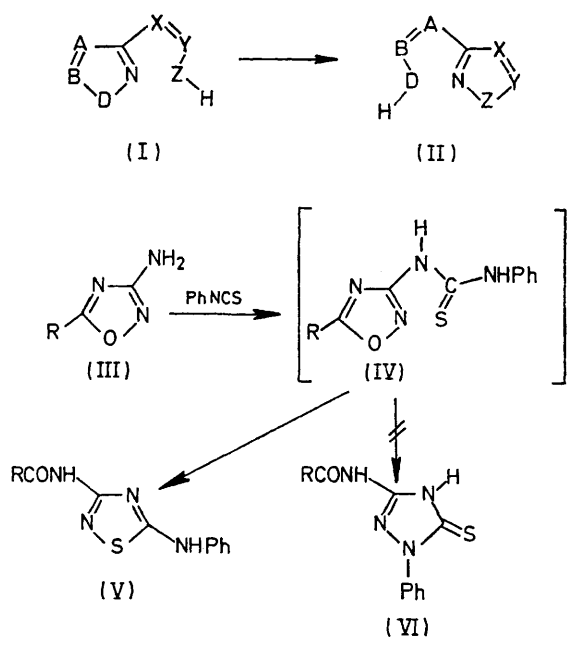
Summary 3-Amino-5*R*-1,2,4-oxadiazoles (IIIa—b) react at 120—130 °C with phenyl isothiocyanate to give 3-acylamino-5-anilino-1,2,4-thiadiazoles (Va—b) presumably through a thermally induced rearrangement of the intermediates, *N*-(5*R*-1,2,4-oxadiazol-3-yl)-*N'*-phenylthioureas (IVa—b).

MONONUCLEAR heterocyclic rearrangements generalised as (I) → (II),[1] have been related to an XYZ side-chain with Z an oxygen, nitrogen[1-3] or a carbon atom.[4] No rearrangement involving a sulphur atom in an XYZ sequence has previously been reported.

In connection with previous research in the field[2b,3,4] and with the aim of elucidating the influence of the Z atom in this type of reaction we have looked at compounds of Type (IV). The reaction of compounds [(IIIa—b) 0·005M] with phenyl isothiocyanate (0·008M) at 120—130°C gave compounds (Va), m.p. 214 °C; (lit.[5] m.p. 212—213 °C) and (Vb), m.p. 278 °C (decomp) (dioxan) (yield 80%). Compound (Vb), with acetic anhydride in pyridine, gave a diacetyl [m.p. 270 °C (decomp) (lit.[5]: m.p. 272 °C)] and a triacetyl derivative [m.p. 165—167 °C (lit.[5]: m.p. 165—167 °C)].

The reaction probably proceeds as in the scheme. Formation of 1,2,4-thiadiazole derivatives (Va—b) from (IIIa—b) and phenyl isothiocyanate can be explained by a thermally induced rearrangement of intermediates (IVa—b).

This rearrangement is of interest in view of the report that *N*-(5*R*-1,2,4-oxadiazol-3-yl)-*N'*-phenylureas, containing both NCO and NCN sequences, undergo a base-induced rearrangement giving only the ring closure compound with a NCN sequence.[3]



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