# A New Rearrangement in the 1,2,4-Oxadiazole Series

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*Summary* The base-induced rearrangement of *N*-(5-R-1,2,4-oxadiazol-3-yl)-*N'*-phenylureas (R = Me or Ph) into 4-acylamino-1-phenyl-1,2,4-triazolin-5-one (acyl= acetyl or benzoyl, respectively) is described.

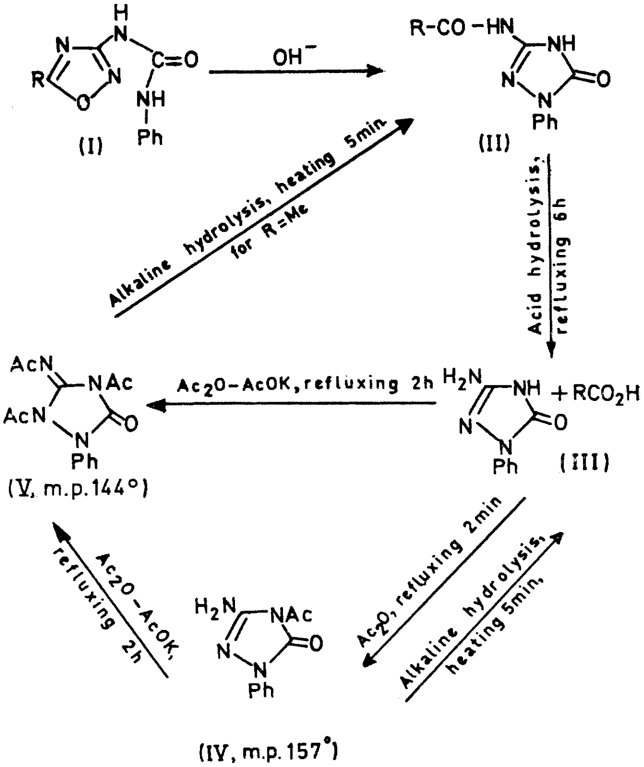
IT is well known that isoxazoles and oxadiazoles[1] containing a suitable side-chain at position 3 make available a large number of heterocyclic compounds by a monocyclic rearrangement.

Attempts to obtain 1,2,4-triazolin-5-one derivatives from isoxazoles and 1,2,4-oxadiazoles have so far failed. In fact, it has been reported by A. R. Katritzky and his co-workers[1] that *N*-(5-methylisoxazol-3-yl)-*N'*-phenylurea does not undergo rearrangement on heating at 195° or on refluxing with potassium hydroxide in methanol. It has also been reported[2] that 5-phenyl-3-ureido-1,2,4-oxadiazole gives 3-amino-5-phenyl-1,2,4-oxadiazole on hydrolysis in aqueous 2N-sodium hydroxide in ethanol under reflux, and on further degradation yields benzoic acid.

In our opinion the lack of success may be related to the structure of the compounds considered. Therefore, in connection with previous work concerning rearrangements of 3-substituted-1,2,4-oxadiazoles,[3,4] we have examined the behaviour of *N*-(5-methyl-1,2,4-oxadiazol-**3**-yl)-*N'*-phenylurea (Ia, m.p. 190°) and *N*-(5-phenyl-1,2,4-oxadiazol-3-yl)-*N'*-phenylurea (Ib, m.p. 198°).†

On being heated (30 min) at their melting points, the ureas (Ia and b) were recovered unchanged. However, refluxing (90 min) 3·5 mM of (Ia and b) with potassium hydroxide (7 mM) in 30 ml of 80% aqueous ethanol, gave 4-acetamido- and 4-benzamido-1-phenyl-1,2,4-triazolin-5-one (IIa, m.p. 245° and IIb, m.p. 250°, respectively) in nearly quantitative yield. Acid hydrolysis of (IIa and b) gave acetic or benzoic acid, respectively and 3-amino-1-phenyl-1,2,4-triazolin-5-one (III),[5] thus supporting the assigned structures. The behaviour of the amino-derivative (III) with acetic anhydride is shown in the Scheme.

The compounds (IIa and b), (III), and (IV) give rise to a complicated case of tautomerism. Tentatively, on the basis of spectroscopic data (u.v., i.r., and n.m.r.), we assign the structures shown in the Scheme.



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† (Ia) and (Ib) were prepared from 3-amino-1,2,4-oxadiazole derivatives by the action of phenyl isocyanate.

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