Ring Expansion of 1-Azirine-3-carboxamides by Hydrazine. Novel Synthesis of 1,2,4-Triazin-6-ones

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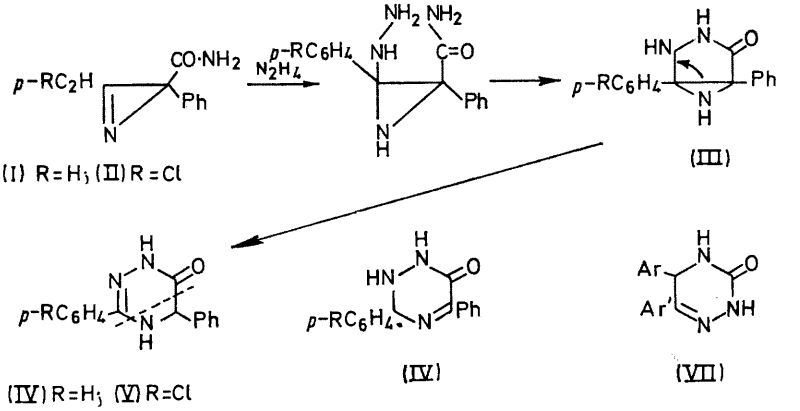
Summary The reaction of 2,3-diaryl-1-azirine-3-carboxamides with hydrazine produces 1,2,4-triazin-6-one derivatives in moderate yield.

NUCLEOPHILIC reaction of 1-azirine-3-carboxamides with arylamines was reported by us to yield *NN'*-diarylureas.[1] We report here the formation of 1,2,4-triazin-6-one derivatives (IV) and (V) in moderate yield from the reaction of 2,3-diaryl-1-azirine-3-carboxamides (I) and (II) with hydrazine.



The reaction is quite rapid: on mixing the methanolic solution of the azirine (I) (m.p. 181—182°) with hydrazine hydrate (80%) at room temperature, a u.v. maximum at 304 nm developed within a few min. Silica gel chromatography (ether) of the mixture gave a compound (m.p. 203—204°, from ethyl acetate–n-hexane) in 38% yield, the analyses and mass spectrum established this to be $C_{15}H_{13}N_3O$ (M^+, 251). Reaction of the azirine (II) (m.p. 119—121°) with hydrazine proceeds analogously, giving the compound $C_{15}H_{12}ClN_3O$ (M^+, 285/287), m.p. 231—233° (from benzene) (36% yield).

On the basis of u.v., i.r., n.m.r., and mass-spectral data, we assign the 1,2,4-triazin-6-one structures (IV), (V) to the products, rather than the isomeric structure (VI) (R = H and Cl). Mass-spectral fragmentation is satisfactorily explained in terms of the structures (IV) and (V). The compound (IV) has ions at *m/e* 105 (R.I. 26%) and *m/e* 146 (R.I. 100%), while the compound (V) has ions at *m/e* 105 (R.I. 31%) and 180/182 (R.I. 100/33%). They must be generated by scission at the dotted line. Another isomer

(VII), which also satisfies the n.m.r. spectral data, is ruled out by reference to the literature.[2]

We postulate a bicyclic intermediate (III) for the reaction. Ring opening accompanied by hydrogen shift produces the hitherto little studied[3] 1,2,4-triazin-6-one ring system, thus providing an interesting case where the ring expansion of 1-azirine with a nucleophile affords a six-membered ring. However, this ring expansion is only feasible when there is another substituent at C-3 in addition to a carboxamido-group. Otherwise, the reaction gives only a highly coloured rubazonic acid[4]-like substance *via* 4-aminopyrazol-5-one, as expected from the reaction of 3-benzoyl-2-phenyl-1-azirine with hydrazine.[5]

As the azirines (I) and (II) were prepared by the thermally induced valence bond isomerization[6] of 5-amino-3,4-diarylisoxazoles, the present report again attests to the usefulness[7] of isoxazoles in the syntheses of heterocyclic compounds.

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