

MECHANISM OF BASE CATALYSED CYCLIZATION
OF SUBSTITUTED GLYOXAL ALDOXIME SEMICARBAZONES

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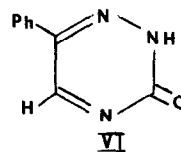
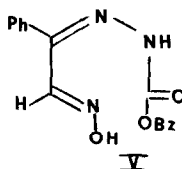
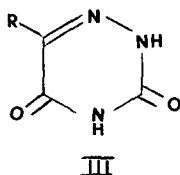
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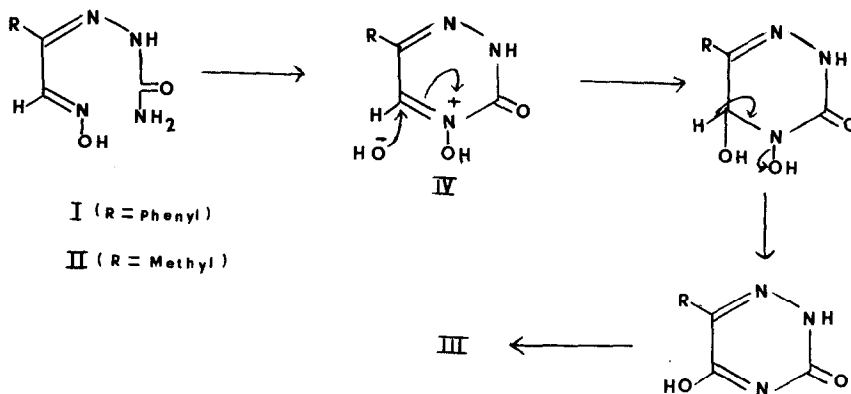
Earlier work on the cyclization of arylglyoxal aldoxime semicarbazone (I) and pyruvaldehyde aldoxime semicarbazone (II) in aqueous potassium carbonate to *as*-triazine-3,5(2H,4H)-diones (III)¹ appeared to have as an intermediate the *N*-oxide (IV) which on rearrangement of the oxygen atom would give (III). Examples of this type of rearrangement of *N*-oxides have been recorded². In this communication we describe experiments which indicate that the reaction follows a different path.

Refluxing phenylglyoxal aldoxime-(carboxylic acid benzyl ester)-hydrazone (V) (obtained as a viscous oil from heating aminocarbonic acid benzyl ester with phenylglyoxal aldoxime in absolute alcohol³) with a 10% solution of aqueous potassium carbonate led to the formation of (III, R=phenyl) in 50% yield. This indicates that it is the oxime nitrogen atom which is retained while the $C_6H_5CH_2O^-$ ion in this and NH_2^- ion in the case of the cyclization of (I) are the groups that are lost.

When (I) was refluxed in dry pyridine instead of aqueous potassium carbonate, the product isolated after acidification with dilute hydrochloric acid was 6-phenyl-*as*-triazine-3(2H)-one (VI). It appeared therefore that the formation of (III) required hydroxyl ion from the solvent and that with pyridine as a base no *N*-oxide intermediate of the type of (IV) is formed.



To further clarify the extent of hydroxyl ion involvement in the formation of (III) cyclization of (I) was carried out in aqueous potassium carbonate using a 30% ^{18}O enriched water, the *as*-triazine-3,5(2H,4H)-dione (III) obtained in this way was analysed by mass spectroscopy. It showed an $\frac{m+2}{m}$ ratio of 1:3 corresponding to a 100% incorporation of ^{18}O in the molecule from the medium. On the basis of these results we propose that hydroxyl ion attack rather than N-oxide rearrangement is involved in the formation of (III) from (I) (see scheme).



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- 3) Gave correct NMR and IR analysis.
- 4) I. Lalezari, N. Sharghi, A. Shafiee and M. Yalpani, *J. Heterocyclic Chem.*, in press.