

A NOVEL SYNTHESIS OF SELENIUM HETEROCYCLES:

SUBSTITUTED 1,2,3-SELENADIAZOLES

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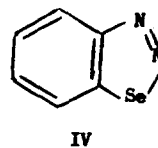
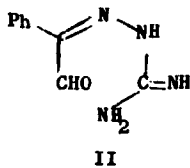
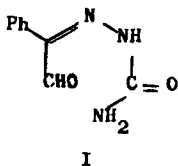
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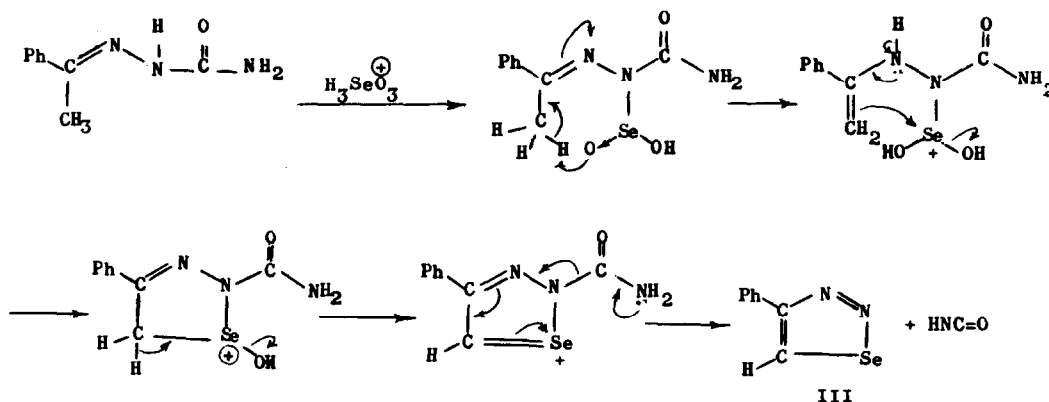
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As a part of our current research program on the chemistry of *as*-triazines¹⁻³, we required phenylglyoxal-keto-semicarbazone (I) which we proceeded to prepare through the selenium dioxide oxidation of acetophenone semicarbazone in a similar way as we had previously prepared phenylglyoxal-keto-guanylhydrazone (II)². However, in this case the reaction took an unusual path. When acetic acid was used as solvent, a solid separated which after recrystallization from diluted acetone gave 66% of light colored flakes mp 76°, u.v. $\lambda_{\max}^{\text{EtOH}}$ 316 nm ($\epsilon = 2400$) 245 nm ($\epsilon = 14000$). Its i.r. spectrum showed no carbonyl or N-H absorption. The n.m.r. consisted of a singlet, τ : 0.70(1H), and a multiplet, τ : 1.8-2.7(5H). Its mass spectrum showed a molecular ion peak at 210 m/e with the characteristic isotopic abundance pattern for a selenium containing substance. Elemental analysis of this compound showed: C: 45.58, H: 2.90, N: 13.06%. Calculated for $\text{C}_8\text{H}_6\text{N}_2\text{Se}$: C: 45.71, H: 3.14, N: 13.31%.



The above data can only correspond to structure (III) which represents a new class of heterocyclic ring system. To our best knowledge the only other 1,2,3-selenadiazole reported is the 1,2,3-benzoselenadiazole (VI) prepared from *o*-aminobenzeneselenol⁴. While this latter reaction appears to be limited to the formation of benzoselenadiazole the selenium dioxide oxidation of arylketone semicarbazones appears to be quite general⁵. We propose the following scheme for the formation of this compound.



Some confirmation of this mechanism is indicated by the formation of ammonium bicarbonate in the reflux condenser during the reaction when dioxan was used as solvent. This is possibly formed from the decomposition of isocyanic acid⁶. When acetophenone-4-phenylsemicarbazone was used sym-diphenylurea was isolated instead of ammonium bicarbonate. This is probably formed from phenylisocyanate. This mechanism is in good agreement with that proposed for the selenium dioxide oxidation of ketones⁷.

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