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THERMOLYSIS OF 3-HYDROXY-1,2,3-BENZOTRIAZIN-4-ONE

Pat Ahern, Tom Navratil and Keith Vaughan*
Department of Chemistry, St. Mary's University
Halifax, Nova Scotia, CANADA

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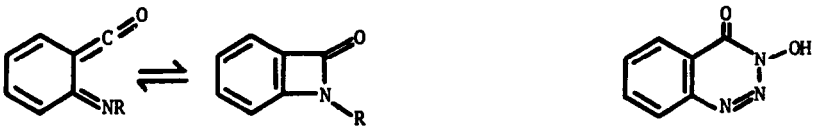
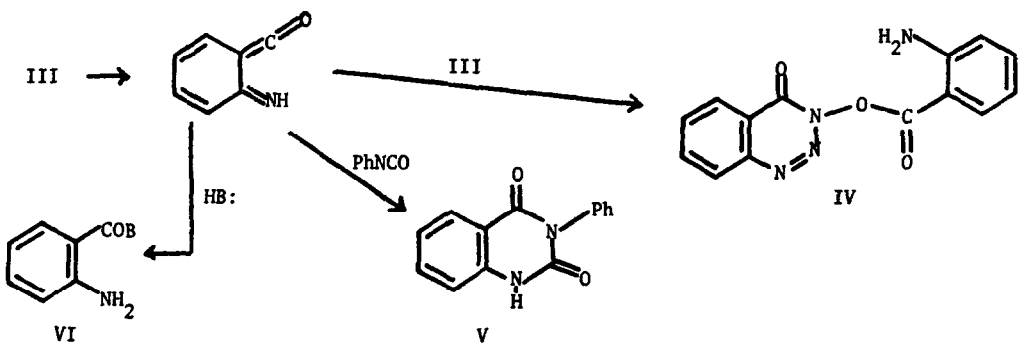
Ketenimines (I), valence tautomers of benzazetidones (II), have been postulated as intermediates in the thermolysis of 1,2,3-benzotriazin-4(3H)-one[1], isatoic anhydride[1b], saccharin[2] and 3-phenyl-1,2,3-benzotriazin-4-one[3]. We wish to report evidence for the intermediacy of the ketenimine (I, R=H) in the thermolysis of 3-hydroxy-1,2,3-benzotriazin-4-one (III).



I II III

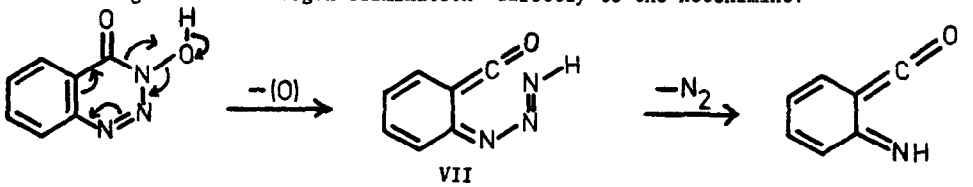
The N-hydroxytriazinone (III) was obtained by diazotisation of *o*-aminobenzohydroxamic acid[4]. Thermolysis of III in refluxing benzene (6 days), toluene (20 h), *p*-xylene (2.5 h) or diglyme (1.5 h) afforded excellent yields (70-95%) of 3-(*o*-aminobenzoyloxy-)1,2,3-benzotriazin-4-one (IV), m.p. 202-4° (benzene). Structure assignment of IV is based on the following spectral data: M^+ 282.0743 ($C_{14}H_{10}N_4O_3$ requires 282.0753) ; ν_{max}(nujol) 3480 and 3365 (NH_2), 1740(C=O) and 1713 (C=O) $cm.^{-1}$; λ_{max}(EtOH) 226,253,276,310 and 350 nm. In addition, the mass spectrum of IV displayed peaks at *m/e* 163(M - NHC_6H_4CO), 147(M - $NHC_6H_4CO_2$), 137($C_7H_7NO_2$) and 120($NH_2C_6H_4CO$, base peak). In contrast to the general lability of the N-benzoyloxy-function in heterocycles to hydrolysis, IV was stable in concentrated acid at room temperature and resisted methylation by Me_2SO_4 in the presence of strong base. However, attempted acetylation of IV with Ac_2O or AcCl resulted in cleavage of the N-benzoyloxy-group, affording the N-acetoxytriazinone (III, Ac for H) and N-acetylanthranilic acid in approximately equimolar amounts; similar cleavage was apparent when IV was diazotised in acid media at 0-5°, affording the N-hydroxytriazinone (III)(yield 82%).

The isolation of IV from the thermolysis of III is most readily explained by the initial formation of the ketenimine (I, R=H), followed by nucleophilic addition to the ketene by the hydroxylic function of a second molecule of III (see below). Further evidence for the intermed-



-iacy of the ketenimine is provided by the formation of (i) the Diels-Alder adduct, 3-phenylquinazolin-2,4(1H)-dione (V), in the reaction of III with phenyl isocyanate in refluxing *p*-xylene; (ii) the anthranilate ester (VI, B=OAm) by refluxing III in n-amyl alcohol; and (iii) N-phenylanthranilamide (VI, B=NHPh) by refluxing III in aniline.

A likely mode of formation of the ketenimine from III is a concerted deoxidative ring-cleavage mechanism, giving rise to the open-chain triazene intermediate (VII), which would be expected to undergo facile nitrogen elimination[5] directly to the ketenimine:



An analogous mechanism, also involving a triazene intermediate, has been postulated to account for the formation of acridone in the photolysis of 3-phenyl-1,2,3-benzotriazin-4-one[6]. Thermal deoxygenation of cyclic hydroxamic acids has been reported previously in only a few cases.[7]

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