A New Heteroaromatic Ring System derived from 3,4-Dihydro-4-oxo-1,2,3-benzotriazine

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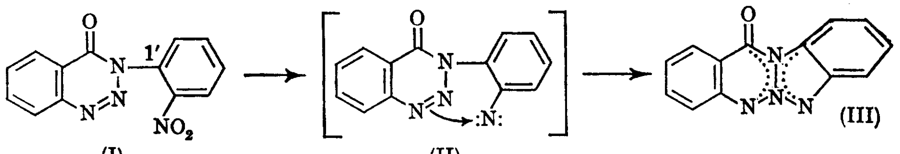
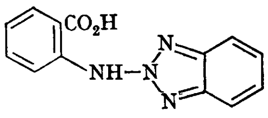
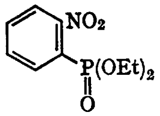
A RECENT paper[1] on the synthesis of benzotriazolo-[2,1-*a*]naphtho[1,8-*de*]triazine prompts us to report our observations on the reaction of 3,4-dihydro-2-(*o*-nitrophenyl)-4-oxo-1,2,3-benzotriazine (I)[2] under reflux with triethyl phosphite. The product of the reaction, a yellow crystalline solid, $C_{13}H_8N_4O$, m.p. 261—262° (55% yield), displayed absorption at 1715 cm.$^{-1}$ (C=O) in the infrared but showed no bands characteristic of nitro-group absorption while it exhibited three main regions of absorption in the ultraviolet region,[3] λ_{max} 228 (ϵ 17,600), 240 (ϵ 18,900), 267 (ϵ 10,900), 295 (ϵ 3,290), 304 (ϵ 3,080), 358 (ϵ 17,200), 369 (ϵ 17,600), and 404 mμ (ϵ 17,000). On alkaline hydrolysis it afforded 2-(*o*-carboxyphenylamino)benzotriazole (IV) which was identified by elemental analysis, infrared,



(I) (II) (III)



(IV)



(V)

ultraviolet, and mass spectra. On these grounds $C_{13}H_8N_4O$ is assigned the 13-oxobenzotriazolo[2,1-*b*]benzo[1,2-*e*]triazine structure (III). This structure is supported by the mass spectrum which shows the molecular ion peak at *m/e* 236 and a fragmentation pattern compatible with structure (III).

Treatment of (III) with bromine in glacial acetic acid and nitration at 5° with 75% nitric acid gives dibromo- and dinitro-derivatives, respectively.

The formation of (III) may be explained in terms of a nitrene intermediate (II) since the generation of nitrene-like intermediates in the phosphite deoxygenation of nitro-compounds is well known.[4] Thus interaction of the π-electrons of the triazine ring with the developing nitrene would yield 13-oxobenzotriazolo[2,1-*b*]benzo[1,2-*e*]-triazine (III).

The only other product obtained, in very small yield, from the reaction, was *o*-nitrophenylphosphoric acid diethyl ester (V). The only reasonable interpretation for the formation of this ester is to postulate a competing Michaelis–Arbusov reaction[5,6] in which nucleophilic attack by phosphorus at the 1′-position of the nitro-substituted aryl group displaces the triazine residue.

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