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THERMOLYSIS OF ISATOIC ANHYDRIDE AND BENZOTRIAZINONE

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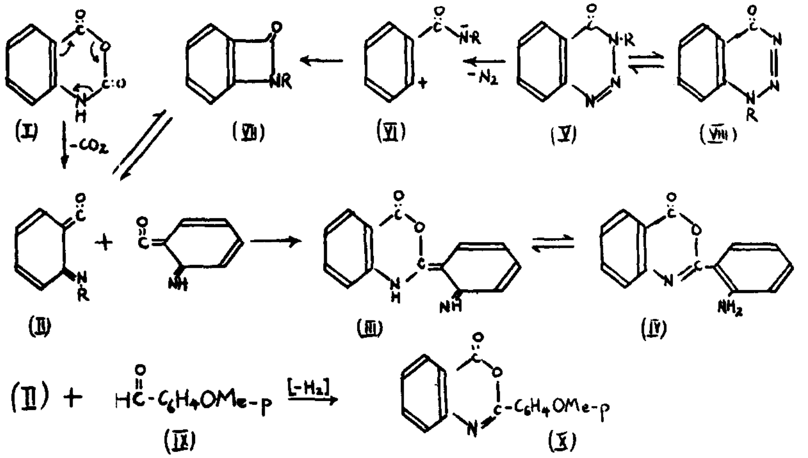
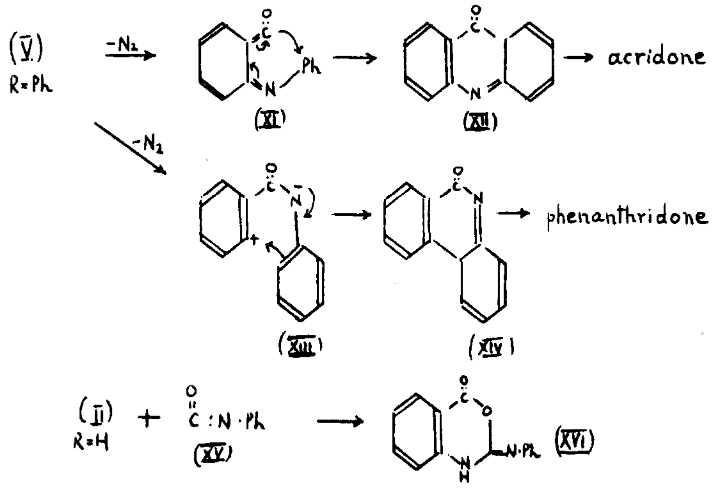
Recent reports (1,2) of the intermediacy of the keten-imine (II; R = Ph) or its valence tautomer (VII; R = Ph) in the photolysis of the benzotriazinone (V; R = Ph) induce us to record our results obtained from the thermolysis of isatoic anhydride (I) and benzotriazinone (V; R = H). Heating the anhydride (I) in a high boiling, inert solvent (e.g. 1-methylnaphthalene b.p. 243-245°) gave the benzoxazinone (III or IV) m.p. 170-172° in 20% yield with slow liberation of CO_2. Constitution of this heterocycle followed from analysis, its infrared and mass spectrum and finally from an unambiguous synthesis by the method of Schroeter and Eisleb (3) and also by catalytic reduction of the o-nitro-compound (4) (IV; NH_2 replaced by NO_2).

Formation of the oxazinone (IV) is rationally explained by intermediacy of the keten-imine (II; R = H) which arises from the anhydride (I) by loss of CO_2. Dimerization of this intermediate which can be regarded as a diene, with another molecule functioning as a dienophile leads to the observed product (IV) as set out (I ⟶ III). By analogy we expected the triazinone (V; R = H) in which the O - C : O group of the anhydride (I) is replaced by - N_2 - to give the



same keten-imine (II; R = H) on pyrolysis. This was confirmed when the benzotriazinone (V; R = H) on being heated dry or in a solvent (e.g. 1-methyl-naphthalene) gave the benzoxazinone (IV) in 45% yield with brisk evolution of nitrogen. Formation of the heterodiene intermediate (II; R = H) occurs feasibly by the steps (V ⟶ VII) i.e. via the valence tautomer (VII; R = H) as postulated in the photolysis (1,2) of the phenyl derivative

(V; R = Ph). This is then followed by a Diels-Alder reaction as before (II→ IV). Alternatively loss of nitrogen from the tautomeric form (VIII; R = H) would give the intermediate (II; R = H) directly. Its existence was further demonstrated by decomposition of the benzotriazinone (V; R = H) in refluxing anisaldehyde (IX) in a nitrogen atmosphere. Removal of the solvent followed by chromatography of the remaining oil over alumina with chloroform as the eluant gave 2-(p-methoxyphenyl) benzoxazine (X) (5). A Diels-Alder addition of the carbonyl group (IX) across the diene (II) accompanied by spontaneous dehydrogenation plausibly accounts for the product (X). Its structure was confirmed by mixed m.p. and comparison of its infrared spectrum with an authentic sample prepared by acylation of anthranilic acid in pyridine solution (6).



Previous observations (7) on the thermal decomposition of the 3-phenylbenzotriazinone (V; R = Ph) can also be accommodated within a similar reaction scheme. Thus heating the compound (V; R = Ph) is reported to give a mixture of acridone and phenanthridone a result for which the authors suggested a radical mechanism. By analogy with our intermediates (II or VI) these heterocycles (XII and XIV) could feasibly originate from analogous intermediates (XI and XIII) respectively as set out. Also, the recently described (8) reaction of benzotriazinone (V; R = H) with phenylisocyanate to give the iminobenzoxazine (XVI) provides additional evidence for the participation of the heterodiene intermediate (II) which is trapped as in the previous case (II → IV or II + IX → X) by a cycloaddition (II + XV → XVI).

We were not able to decide definitely whether the oxazinone is best represented by structure (III) or (IV). On the available evidence we favour the ortho-quinonoid form (III) because a dilute solution of the compound in carbon tetrachloride showed bands in the infrared at 3483 and 3310 cm^{-1} when measured under high resolution. This indicates two NH-groups as in (III) particularly since the frequencies of the two bands do not satisfy the diagnostic relationship (9) for free NH_2-frequencies. A possible deviation from the expected figures for a NH_2-group cannot be accounted for by hydrogen bonding since this is not indicated by dilution experiments. Moreover, the substance is bright-yellow and diazotises and couples only with great difficulty in contrast to the *p*-aminoisomer. The methylene-quinone structure (III) has previously been proposed (3) on the grounds that the compound polymerises readily on heating.

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