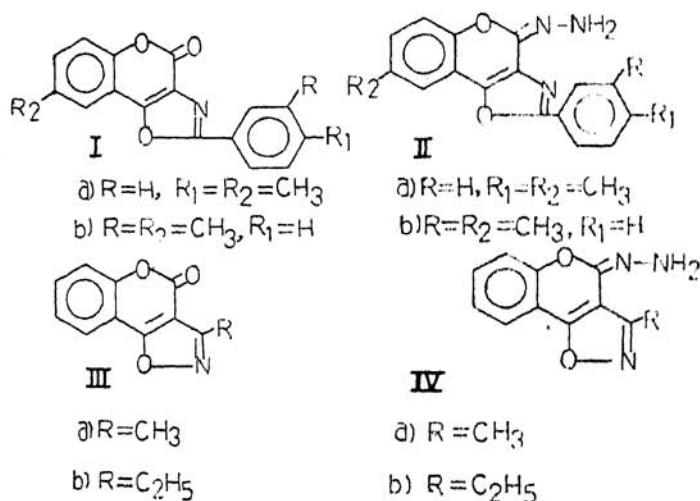


**AN INTERESTING REACTION OF  
4H-1-BENZOPYRANO (3, 4-d)-OXAZOL- AND  
ISO-OXAZOL-4-ONES**

IN a previous communication<sup>1</sup>, we have reported the synthesis of 4H-1-benzopyrano(3, 4-d) oxazol-4-one derivatives. With a view to studying some of the reactions of these compounds such as the replacement of the heterocyclic oxygen by nitrogen, we investigated the reaction of (Ia) with hydrazine hydrate. It is pertinent to mention that Baddar *et al.*<sup>2</sup> have reported the replacement of heterocyclic O by N with hydrazine hydrate in some  $\alpha$ -pyrones to form 1-amino-2-pyridones.



The reaction was carried out by refluxing equimolecular quantities of the reactants, *e.g.*, (Ia) and hydrazine hydrate in alcohol solution for 5 hr. Dilution with water afforded a colourless crystalline compound (IIa), m.p. 147–49°. Its molecular weight (mass spectrum) was found to be 323 and the elemental analysis corresponded with the molecular formula C<sub>18</sub>H<sub>15</sub>O<sub>2</sub>N<sub>3</sub>.H<sub>2</sub>O. It u.v. had  $\lambda_{\text{max}}^{\text{MeOH}}$  215 nm (log  $\epsilon$  4.39), 290 nm (log  $\epsilon$  4.37) 320nm (log  $\epsilon$  4.21). In the i.r. spectrum the lactone band, which in the original compound appeared at 1765 cm<sup>-1</sup>, was completely absent. Further, the spectrum showed a NH<sub>2</sub> band at 3400 cm<sup>-1</sup>, whereas the >C=N band appeared at 1610 cm<sup>-1</sup>. The n.m.r. spectrum (CDCl<sub>3</sub>  $\delta$ ) of the compound

integrated for fifteen protons and showed the following signals: 2.4 (s, 6H, Ar-CH<sub>3</sub>), 4.3 (b, s, 2H, -NH<sub>2</sub>), 7.0~8.0 (m, 7H, aromatic).

From the above evidence the compound was assigned the structure (IIa). The latter is consistent with the observation that on boiling it with either acetic anhydride or with dilute hydrochloric acid the original compound (Ia) was obtained in almost quantitative yield.

The formation of IIa may be due to the opening of the coumarin ring in (Ia) by a strong base like hydraline hydrate giving the hydroxy hydrazide as an intermediate which recycles to give back the resulting compound.

The reaction also succeeds with other 4H-1-benzopyrano (3, 4-d) oxazole-4-one derivatives. The compound (IIb) had m.p. 158-60°. However, a similar hydrazide formation is not observed with 4H-1-benzothiopyrano (3, 4-d) oxazol-4-ones.

The same reaction occurs also in the case of the known<sup>3</sup> 3-methyl- and 3-ethyl-4H-1-benzopyrano (3, 4-d)-isooxazol-4-ones giving the corresponding hydrazones IVa, m.p. 148-50°, IVb, m.p. 114-16°.

In our procedure for the preparation of the two isooxazol-4-ones, which is somewhat different from that reported,<sup>3</sup> the oximes of 4-hydroxy-acetyl- and 4-hydroxy-3-propionyl coumarins were acetylated to yield the corresponding unknown acetates of the oximes, m.p. 183-84° and 128-30° respectively. The oxime acetates on boiling with pyridine afforded the required isooxazole-4-ones in 50-60% yields.

With a view to study the general applicability of the reaction we studied the reaction of hydrazine hydrate with 7-hydroxy-3-ethyl-4-methylcoumarin. In this case the reaction failed and the original coumarin was obtained back. The reaction was unsuccessful with 7-hydroxy-6-ethyl-3, 4-cyclopenteno- and 7-hydroxy-6-ethyl-3, 4-cyclohexenocoumarins. The reactions also failed to give a pure product with 4-methoxy-6-methylcoumarin. It, therefore, seems that the presence of an oxazole or an isooxazole ring in 3, 4 positions is very necessary for the reaction to occur.

All compounds gave satisfactory C, H and N analyses.

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