

RING TRANSFORMATION REACTION OF 1,3-OXAZINES TO PYRIMIDINES

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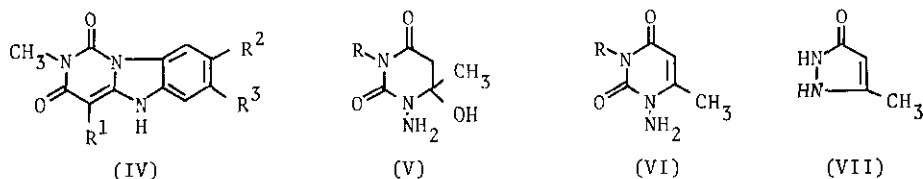
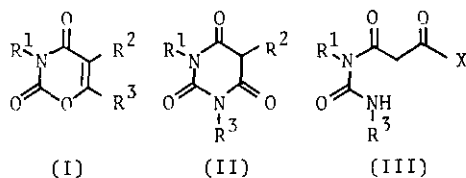
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Reactions of 1,3-oxazine-2,4-dione derivatives with nucleophiles such as amines and hydrazine have been investigated.

Treatment of the 6-chloroxazines (Ia: $R^1=CH_3$, $R^2=H, CH_3$, $R^3=Cl$; Ib: $R^1=C_2H_5$, $R^2=CH_3$, $R^3=Cl$) with an aqueous solution of ammonia, methylamine, or ethylamine in THF at 0-5°C caused a ring transformation to pyrimidine ring system giving the corresponding barbituric acids (II: $R^1=CH_3$, $R^2=H$, $R^3=H, CH_3, C_2H_5$; $R^1=CH_3, C_2H_5$, $R^2=R^3=CH_3$) along with the open-chain urea (III: $X=NHR^3$). Further examination of the ring transformation showed that it proceeded *via* formation and recyclization of an intermediate (III: $X=Cl$). Reaction of Ia with *o*-phenylenediamines also gave the ring transformation products, pyrimido[1,6-*a*]-benzimidazole-1,3(2H,5H)-diones (IV: $R^1=H, CH_3$, $R^2, R^3=H, CH_3, Cl$).

The 6-methyloxazines (Ic: $R^1=H, CH_3$, $R^2=H$, $R^3=CH_3$) were treated with hydrazine hydrate in ethanol at room temperature giving the compounds (V: $R=H, CH_3$) which were considered to be intermediates in the ring transformation* of Ic into the 1-aminouracils (VI: $R=H, CH_3$) or 5-methylpyrazol-3-one (VII). The best evidence for the structure of V has come from ^{15}N -NMR Fourier transform spectra. Further examination of the ring transformation suggested that dehydration of V affords VI and, on the other hand, VII is formed by the reaction of V with an additional molecule of hydrazine hydrate.



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