4-Pyrones from Enamines

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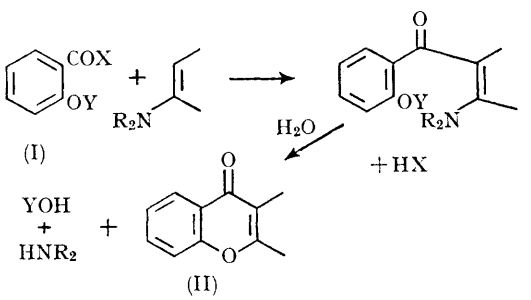
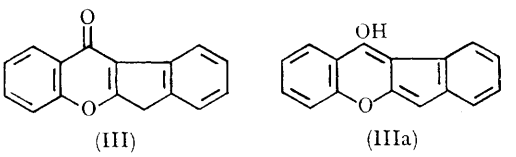
4-PYRONES have been obtained from the reaction of enamines with diketen,[1,2] while chromones are formed by oxidation of the adducts of enamines and *o*-hydroxyaraldehydes.[3] We report two further methods of forming the 4-pyrone ring employing enamines; the methods appear to be quite general.

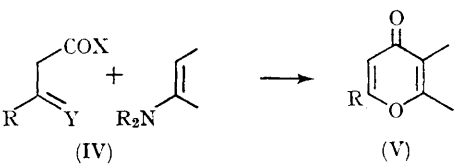
Chromones (II) are obtained in yields of up to 45% from an enamine and a suitably protected and activated salicylic acid (I):



For example, on stirring a mixture of piperidinocyclopentene with the mixed anhydride of acetylsalicylic acid and ethyl hydrogen carbonate (I, X = OCO_2Et, Y = Ac) at 0° for 4 hrs., followed by vigorous acid hydrolysis, 2,3-cyclopentenochromone[4] was formed, while a similar reaction between *o*-methoxycarbonylbenzoyl chloride (I, X = Cl, Y = CO_2Me) and piperidinocyclohexene gave 1,2,3,4-tetrahydroxanthone.[5] The mixed-anhydride method, when applied to 2-piperidinoindene, yielded the colourless indenochromone (III), m.p. 176—177°, ν_{CO} 1650 cm.$^{-1}$, which showed no evidence of existing in the tautomeric pseudoazulene[6] form (IIIa).



4-Pyrones (V) can be prepared by a similar method from enamines and derivatives of β-ketonic acids (IV):



Thus, piperidinocyclopentene was condensed with the hemithioketal of acetoacetic acid by the mixed-anhydride method (IV, R = Me, X = OCO_2Me, Y = $-O[CH_2]_2\cdot S-$) and the product was hydrolysed with ethanolic hydrochloric acid to give 2,3-cyclopenteno-6-methyl-4-pyrone.[1]

Further work on the synthetic possibilities of these methods and their extension to nitrogen and sulphur heterocycles is in progress.

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