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# OXIDATION OF AMINES TO CARBONYL COMPOUNDS BY PYRIMIDO[4,5-b]QUINOLINE-2,4(3H,10H)-DIONE (5-DEAZAFLAVIN)

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Pyrimido[4,5-b]quinoline-2,4(3H,10H)-dione (5-deazaflavin) oxidized amines under aqueous conditions to give the corresponding carbonyl compounds. This 5-deazaflavin-dependent oxidation of amines was automatically recycled and gave more than 100% of carbonyl compounds based on the 5-deazaflavin.

The oxidation of various biological amines to imines, followed usually by hydrolysis to carbonyl compounds, is catalyzed by a group of enzymes that contain either $NAD(P)^+$, flavin, or copper as a cofactor.[1] However biomimetic conversion of amines to carbonyl compounds with a $NAD(P)^+$-model or a flavin has apparently never been described.[2]

Recently we reported that 5-deazaflavins are considered as "flavin shaped nicotinamide analogs" and do, in fact, oxidize alcohols under alkaline conditions to the corresponding carbonyl compounds.[3] This communication describes the first example of the practical oxidation of amines to carbonyl compounds *via* imines by a 5-deazaflavin.

A mixture of 10-ethyl-3-methyl-5-deazaflavin (I)[4] (0.5 g, 0.002 mol), benzylamine (5 g, 0.047 mol) and water (5 ml) was heated at 100 °C for 10 h under stirring. After the reaction mixture was allowed to stand overnight at room temperature, the separated 5-deazaflavin (I) was recovered by filtration. The filtrate was treated with a saturated solution of 2,4-dinitrophenylhydrazine in 2N hydrochloric acid to cause the separation of benzaldehyde 2,4-dinitrophenylhydrazone, mp 237 °C, in 203% yield based on the 5-deazaflavin. Similarly, other amines gave the corresponding carbonyl compounds under the same conditions in the yields indicated in Table.

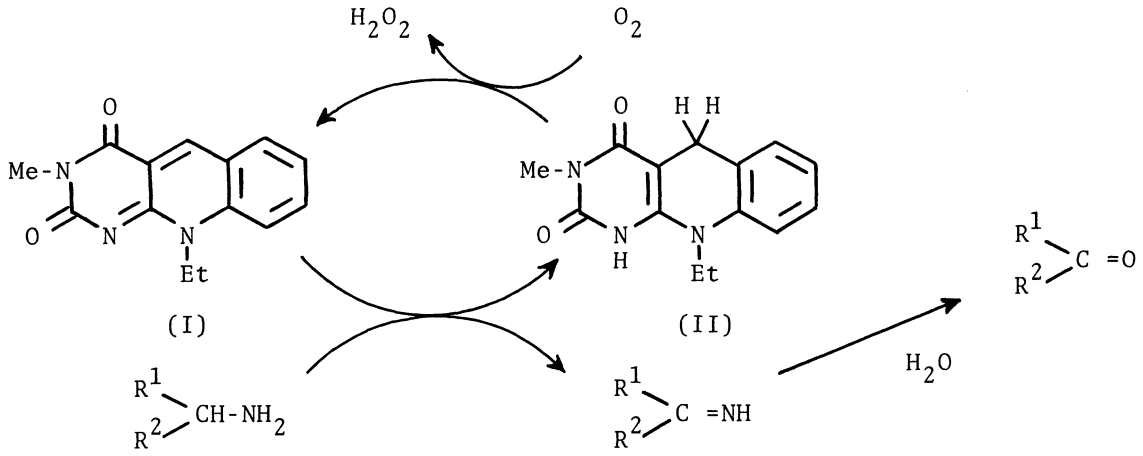
It is interesting to note that this 5-deazaflavin-dependent oxidation of amines to carbonyl compounds is automatically recycled; under those conditions, the 1,5-dihydro-5-deazaflavin (II) initially formed is reoxidized to the original 5-deazaflavin (I) by adventitious air (see Scheme). In fact, compound II can be isolated from the initial reaction mixture.

The scope and limitation of this reaction are currently under investigation.

TABLE Oxidation of Amines to Carbonyl Compounds by 5-Deazaflavin (I)

| Amine | Solvent | Product | Yiled (%)[a] | Mp (°C)[b] |
|---|---|---|---|---|
| Benzylamine | $H_2O$ | Benzaldehyde | 203 | 237 |
| Cyclohexylamine | $H_2O$ | Cyclohexanone | 110 | 161 |
| dl-α-Methylbenzylamine | $H_2O$ | Acetophenone | 212 | 252 |
| Benzhydrylamine | $H_2O$ + DMF[c] | Benzophenone | 180 | 231 |

a) Based on the 5-deazaflavin. b) 2,4-Dinitrophenylhydrazone. c) $H_2O$:DMF=1:1

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