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PREPARATION OF POLYSTYRENE-BOUND 5-DEAZAFLAVINS AND THEIR USE IN OXIDATION OF ALCOHOL

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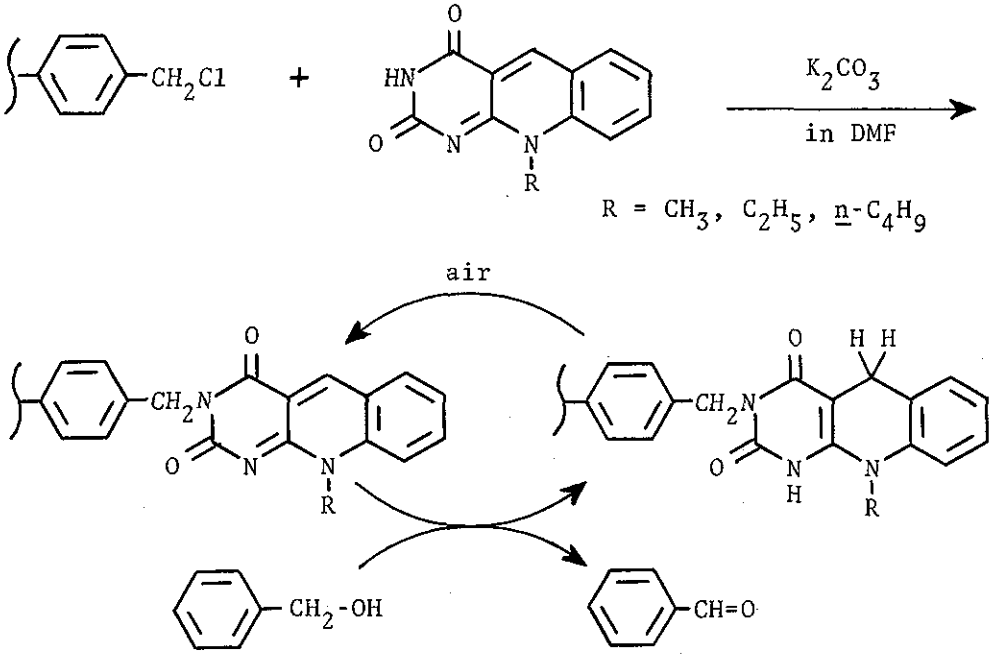
The resins with 5-deazaflavin group attached to polystyrene *via* methylene linkage were prepared by condensation of the corresponding 10-alkyl-5-deazaflavins with chloromethylpolystyrene. These resins oxidized benzyl alcohol under alkaline conditions to yield benzaldehyde in the same way as 5-deazaflavins themselves.

Recently we have reported that 5-deazaflavin (pyrimido[4,5-*b*]quinoline-2,4(3*H*,10*H*)-dione), where N-5 of the flavin is replaced by CH, oxidized simple alcohols under alkaline conditions to yield the corresponding carbonyl compounds in high yields, while it is itself hydrogenated to 1,5-dihydro-5-deazaflavin.[1] On the basis of the above observation, we have designed to prepare several polymers containing 5-deazaflavin molecule as the functional group in order to examine their oxidative ability from the viewpoint of organic synthesis.

First, the preparation of 5-deazaflavin resins whose 5-deazaflavin group is bound to polystyrene *via* a methylene linkage at the 3-position was carried out. A mixture of 10-*n*-butylpyrimido-[4,5-*b*]quinoline-2,4(3*H*,10*H*)-dione (10-*n*-butyl-5-deazaflavin)[2] (0.3 g) and chloromethylpolystyrene (Cl; 0.95 mmol/g)[3] (1 g) in dimethylformamide (10 ml) was refluxed in the presence of potassium carbonate (0.23 g) for 3 hr with stirring. The resulting precipitates were filtered off, washed with methanol and dried at room temperature in a vacuum desiccator to give a pale brown resin. From the analytical value, the portion of the 5-deazaflavin group introduced on the resin is presumed to be 66% of chlorine on the starting resin. Similarly, the resins with 10-methyl- and 10-ethyl-5-deazaflavin were prepared,



in which 55 and 57% of chlorine on the starting resin were substituted by the 5-deazaflavin group respectively.

A mixture of 10-n-butyl-5-deazaflavin resin (50 mg) which includes 8.4 mg (0.031 mmol) of the 5-deazaflavin, benzyl alcohol (100 mg, 0.93 mmol) and potassium hydroxide (20 mg, 0.34 mmol) was stirred at 90° for 1 hr under aerobic conditions. The reaction

TABLE Oxidation of Benzyl Alcohol to Benzaldehyde by 5-Deazaflavin Resins

Starting material	Reaction conditions		Yield (%)[a]
	Temp (°C)	Time (hr)	
10-n-butyl-5-deazaflavin resin, 50 mg (8.4 mg of the 5-deazaflavin) benzyl alcohol, 100 mg potassium hydroxide, 20 mg	90	1	88
10-n-butyl-5-deazaflavin resin, 100 mg (16,8 mg of the 5-deazaflavin) benzyl alcohol, 200 mg potassium carbonate, 100 mg	170	1	347
10-ethyl-5-deazaflavin resin, 100 mg (12.6 mg of the 5-deazaflavin) benzyl alcohol, 200 mg potassium carbonate, 100 mg	90	3	147
10-ethyl-5-deazaflavin resin, 100 mg (12.6 mg of the 5-deazaflavin) benzyl alcohol, 200 mg potassium carbonate, 100 mg	170	3	258

a) % yield per 5-deazaflavin included in the resin.

mixture was analyzed by gas chromatography to detect benzaldehyde (2.9 mg, 88% per 5-deazaflavin included in the resin). The results obtained from the experiments under different conditions were summarized in Table.

The same reactions as above in the absence of the resin led to complete recovery of benzyl alcohol. As shown in the Table, some recycling of 5-deazaflavin resin was observed in this 5-deazaflavin-dependent oxidation of benzyl alcohol.

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3 Chloromethylpolystyrene (Cl; 0.95 mmol/g) was purchased from the Protein Research Foundation, Osaka, Japan.

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