OXIDATION WITH FUSED HETEROAROMATIC o-QUINONES

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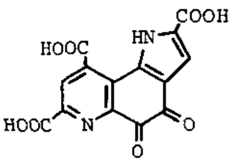
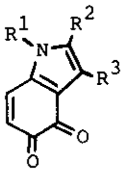
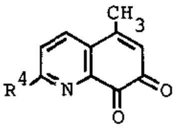
Oxidation of amines with coenzyme PQQ was investigated. Under aerobic conditions, benzylamine was oxidized catalytically by PQQ in the presence of CTAB-micelle to benzaldehyde and benzoic acid (3690 % and 1750 %, respectively, based on PQQ). Kinetic studies under anaerobic conditions indicated that the reaction was first-order in PQQ and benzylamine concentration, respectively, and the free amine was active species. The large isotope effect (k_H/k_D = 7.24) in the oxidation of α,α-dideuteriobenzylamine suggests that the oxidation proceeds via covalent addition and rate-limiting base catalyzed elimination mechanisms through carbinolamine and imine intermediates.



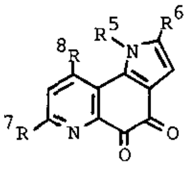
PQQ



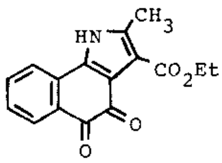
Indole-
4,5-Quinone



Quinoline-
7,8-Quinone



Pyrrolo[2,3-f]-
quinoline-4,5-
quinone



Benzo[g]indole-
4,5-quinone

Some of fused heteroaromatic o-quinones such as indole-4,5-quinone, quinoline-7,8-quinone, benzo[g]indole-4,5-quinone, and pyrrolo[2,3-f]quinoline-4,5-quinone derivatives were synthesized as PQQ-models, and their catalytic activities on the aerobic oxidation of benzylamine were compared to that of PQQ. The catalytic activities of the indole-4,5-quinone and quinoline-7,8-quinone derivatives were not so high because of their instability under these conditions. On the contrary, the pyrrolo[2,3-f]quinoline-4,5-quinones were evaluated to be effective catalysts for the present oxidation.