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Photochemical Oxidative C_{α} - C_{β} Bond Cleavage of Tryptophan Side-Chain by Pyrimido (5,4-g) pteridine N-oxide.

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Tryptophan derivatives undergo with ease the oxidative C_{α} - C_{β} bond cleavage by pyrimido (5,4-g) pteridine N-oxide under irradiation with UV-visible light in the presence of acid-catalyst to give 3-indolecarboxaldehydes and the corresponding glycine derivatives. The product, 3-indolecarboxaldehyde, has been observed in human adrenal tumour tissue as well as in normal pancreas and spleens and as one of the metabolites of tryptophan in rats, cabbage plants, tomato plants, holoparasitic dicotyledonus plants, Ceratocystis fagacearum, Endomycopsis vernalis, and Cordyceps militalis. The present reaction has interesting mechanistic implication and is also intriguing in connection with the metabolism of tryptophan in animals, plants, and microorganisms.

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Photochemical Oxygen Atom Transfer Reaction by Heterocycle N-Oxides Involving a Single-Electron-Transfer Process: Oxidative Demethylation of N, N-Dimethylaniline.

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N,N-Dimethylaniline (DMA) undergoes the oxidative demethylation by heterocycle N-oxides, e. g., pyrimido (5,4-g) pteridine N-oxide, isoalloxazine N-oxide, pyridine N-oxide, quinoline N-oxide, 4-nitropyridine N-oxide, and 4-nitroquinoline N-oxide, under irradiation with UV-visible light. The reaction can be explained in terms of the formation of the N-oxide/DMA CT-complex in a ground state followed by a single-electron transfer from DMA to the N-oxides in the excited complex. The present result formally parallels the mechanism proposed for the cytochrome P-450 catalyzed N-dealkylation.

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Photochemical Intramolecular Cyclisation of Purine and Pyrimidine Nucleosides Induced by an Electron Acceptor.

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Irradiation of appropriately protected purine nucleosides (guanosine and adenosine) and cytidine in the presence of pyrimido (5,4-g) pteridine N-oxide, which is a good electron acceptor, with UV-visible light results in the exclusive formation of the corresponding 5'-O,8-cyclopurine nucleosides and 5'-O,6-cyclocytidine. The present reaction provides the first example of photoinduced intramolecular cyclisation of purine and pyrimidine nucleosides proceeding through charge-transfer complex formation and also is of interest in connection with reactions involving electron donor-acceptor interaction in biological substances.