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Efficient Oxygen-atom Transfer Agent: Photochemical Hydroxylation of Benzene Derivatives by Pyrimido (5, 4-g) pteridine N-oxide.

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Pyrimido (5, 4-g) pteridine N-oxide (1) oxidizes efficiently benzene, toluene, and anisole under UV irradiation to give the corresponding phenol derivatives, though the easiness of the reaction significantly depends upon the nature of the substituents on the benzene ring. The present result indicates that the N-oxide 1 is an efficient oxygen-atom transfer agent and serves as a tool in the elucidation of the mechanism, remaining equivocal as yet, on the photochemical oxygen-atom transfer reaction by the heterocyclic N-oxides.

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Reactions of 6-(N-Methylanilino)-5-(N-Phenylimino) pyrimidine-2, 4 (3H, 5H)-dione with Benzyl Hydrosulfide and Benzylamine.

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Treatment of 6-(N-methylanilino)-5-(N-phenylimino) pyrimidine-2,4(3H, 5H)-dione (2a) with benzyl hydrosulfide or benzylamine under mild conditions without any catalyst resulted in the concurrent occurrence of a redox reaction and nucleophilic substitution at the C(6)-position of 2a to give 5-anilino-6-(N-methylanilino) uracil (1a), 6-substituted 5-(N-phenylimino) pyrimidine-2, 4 (3H, 5H)-diones (2b, c), and the oxidation product (dibenzyl disulfide or N-benzylidenebenzylamine). The substitution products 2b, c also oxidized benzyl hydrosulfide and benzylamine under the same conditions. The present results suggest that the conjugated diimine bond of 2a is susceptible to nucleophilic addition and also possesses the capacity to oxidize thiol and amino compounds without any base catalyst.

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Regio- and Stereoselective Terminal Allylic Carboxymethylation of gem-Dimethyl Olefins. Synthesis of Biologically Important Linear Degraded Terpenoids.

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gem-Dimethyl olefins (III) were transformed regiospecifically to the terminal β -methallyl sulfides (IV) bearing the methoxycarbonylmethyl substituent on the sulfur atom via (A) CIS-CH₂CO₂Me addition followed by dehydrochlorination or (B) allylic chlorination with SO₂Cl₂ followed by sulfenylation with HSCH₂CO₂Me. Treatment of IV with tert-BuOK or NaH in DMF or DMSO at r. t. gave stereoselectively the sulfur-free esters (V) through a novel one-pot desulfurizative (2,3)-sigmatropic rearran gement. By utilizing this method, biologically and pharmacologically important linear degraded terpenoids, a diol component (1) of the pheromonal secretion of the queen butterfly and several ω -quinoid acids (4, n=1, 2) and (5, n=1, 2), which are metabolites of polyisoprenoidquinones, were synthesized.