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Diversity of the C-C Bond Formation in the Reaction of a 5-Bromouracil Derivative with Carbanions

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Reaction of 5-bromo-1,3-dimethyluracil (1) with carbanions generated from a mixture of active methylene compounds and base was investigated. Upon treatment of (1) with diethylmalonate and sodium ethoxide, 5-substituted uracil was formed via an intermediacy of 5,6-bis (malonate-substituted)-5,6-dihydrouracil. On the other hand, when ethyl phenylacetate and benzyl cyanide were employed as a source of carbanions, 2,4-diazabicyclo (4,1,0) heptane derivatives were isolated as the sole products. The reaction of (1) with dibenzylketone generating a dicarbanion resulted in the formation of 2,4-diazabicyclo (4,3,0) nonane derivative. The formation of three type of product was significantly dependent on the nature of the carbanions.

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Photo-oxidative Decarboxylation of Phenylacetic Acids induced by Pyrimido (5,4-g) pteridine-10-oxide involving a Single-electron-transfer Process in Both Stages.

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Irradiation of phenylacetic acid derivatives (para-substituents: OMe, Me, F, H) in the presence of pyrimido (5,4-g) pteridine-10-oxide (1) with UV-visible light gave the corresponding benzaldehyde derivatives as the major product via an intermediary formation of benzyl alcohols. The present result indicated that the N-oxide (1) efficiently functions as an electron acceptor in its singlet-excited state and as agents for both oxygenation and dehydrogenation in both stages of the photoreaction.

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A Novel Ring Transformation of 5-Carbamoyluracils into Barbituric Acids

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Reaction of 5-cyano-3-methyl-1-phenyluracil with sodium hydrosulfide caused a novel ring transformation to give 5-anilinomethylene-1-methyl-4-thiobarbituric acid (1). In the above reaction, isolation of 5-thiocarbamoyluracil (2) as a reaction intermediate led to the successful extension of the ring transformation of 5-thiocarbamoyl (or carbamoyl) uracils into barbituric acids. Thus, heating of (2) and 5-carbamoyl-3-methyl-1-phenyluracils in ethanolic sodium ethoxide gave the 4-thiobarbituric acid (1) and 5-anilinomethylenebarbituric acids, respectively. Reaction of 5-carbamoyl-1,3-dimethyluracil, which has no phenyl group at the 1-position, with NaOEt under similar conditions, resulted in the recovery of the starting material. The presence of phenyl group affected upon occurrence of this ring transformation.