[*J. Org. Chem.*, **62**, 2999-3001 (1997)] [Lab. of Medicinal Chemistry]

Reactivity of Thioaldehyde: Cyclization Reaction of 6-Amino-1,3-dimethyl-5-thioformyluracil with Enamines into Pyrido[2,3-*d*]pyrimidine2,4-(1*H*,3*H*)-diones.

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The reaction of 6-amino-1,3-dimethyl-5-thioformyluracils with enamines was studied. The 6-amino-5-thioformyluracil reacted as a diene with electron-rich morphorino enamines under mild conditions to give pyrido[2,3-*d*]pyrimidine derivatives. The reactivity can be reduced by the placement of phenyl groups on the enamine. The 5-thioformyluracil would be cyclized formally as a diene with the enamines.

[*Chem. Pharm. Bull.*, **45**, 542-544 (1997)] [Lab. of Medicinal Chemistry]

Reactivities of 6-Amino-1,3-dimethyl-5-thioformyluracil toward Nucleophiles and Its Application to Synthesis of Pyrido[2,3-*d*]pyrimidines.

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Reactivity of the thioformyl group of 6-amino-1,3-dimethyl-5-thioformyluracil toward nucleophiles was investigated in comparison with that of the corresponding 5-formyluracil. The reaction of the 5-thioformyluracil with phenylhydrazine, various amines, and carbanions [$^-$CH(CN)X : X = CN, COOEt] readily afforded the hydrazone, Schiff bases, and pyrido[2,3-*d*]pyrimidines, respectively. The thioaldehyde possess much higher reactivities toward nucleophiles than the corresponding aldehyde.

[*Tetrahedron Lett.*, **38**, 399-402 (1997)] [Lab. of Medicinal Chemistry]

Chemoselective Inhibition of the Hydrogenolysis of the MPM Protective Group for Phenolic Hydroxy Functions Using a Pd/C-Pyridine Catalyst.

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It was found the addition of pyridine to the Pd/C-catalyzed reduction system inhibitted the deprotection of a MPM (4-methoxybenzyl) protective group for the phenolic hydroxy groups, although phenolic benzyl ether, Cbz, benzyl ester, nitro and olefin functions were easily hydrogenated. This is a convenient method for the selective hydrogenation of reducible functions distinguishing from the MPM group. The MPM group could be extensively applied to chemoselective hydrogenation as a protecting group for phenolic hydroxy functions by employment of the Pd/C-pyridine catalyst.

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Ribofuranose-ring Cleavage of Purine Nucleosides with Diisobutylaliminum Hydride: Convenient Method for the Preparation of Purine Acyclonucleosides.

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The reduction of 2',3'-O-isopropylidene protected purine nucleosides with diisobutylaluminum hydride (DIBAL-H) caused the cleavage of the C-1'– O-4' bond in the ribose moiety to give the corresponding 9-D-ribitylpurines. The DIBAL-H reduction of inosine, thioinosine, and their derivatives having an alkyl group at the O^6- or S^6-position proceeded in good yields, whereas the introduction of methyl group into the N^6-position of adenosine remarkably reduced the reactivity to afford ribityl derivatives in low yields. The reduction of both 5'-deoxy and 5'-chloro-5'-deoxy purine nucleosides under similar conditions gave ribityl derivatives as well as that of 5'-hydroxy derivatives. An acyclic analog of guanosine, which is biologically interesting, was prepared from the guanosine derivative in a similar way. The present methodology for the synthesis of acyclic purine nuculeosides was applied to the preparation of an acyclic analog of neplanocin A.