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[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 morpholino 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.

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[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 [ $\text{CH}(\text{CN})\text{X}$ :  $\text{X} = \text{CN}, \text{COOEt}$ ] 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.

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[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 inhibited 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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[Lab. of Medicinal Chemistry]

**Ribofuranose-ring Cleavage of Purine Nucleosides with Diisobutylaluminum 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-ribityl purines. The DIBAL-H reduction of inosine, thioinosine, and their derivatives having an alkyl group at the O<sup>6</sup>- or S<sup>6</sup>-position proceeded in good yields, whereas the introduction of methyl group into the N<sup>6</sup>-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 nucleosides was applied to the preparation of an acyclic analog of neplanocin A.