

SYNTHESIS AND REDUCING ABILITIES OF 1-SUBSTITUTED DIHYDROPYRIMIDINES

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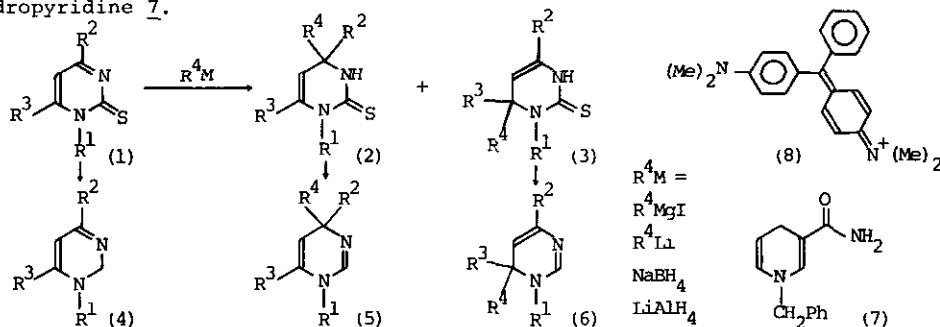
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N-Substituted pyridines have been extensively investigated as model compounds of NAD(P)H. In spite of being aza-analogues of dihydropyridines, little attention has been paid for the synthesis and properties of dihydropyrimidines, especially 1-substituted dihydropyrimidines. First we tried to synthesize 1-substituted dihydropyrimidines by desulfuration of pyrimidine-2(1H)-thiones or their dihydro-derivatives with Raney nickel.

3,4-Dihydropyrimidine-2(1H)-thiones (**2**) were treated with Raney nickel in MeOH at 50 °C for 1 h, then refluxed for 2 h to afford 1,4-dihydropyrimidines (**5**). 1,6-Dihydropyrimidines (**6**) were also obtained by the same treatment of 3,6-dihydropyrimidine-2(1H)-thiones (**3**) with Raney nickel. Furthermore, pyrimidine-2(1H)-thiones (**1**) were treated with Raney nickel for 3 h at room temperature under hydrogen atmosphere to give 1,2-dihydropyrimidines (**4**).

Since dihydropyrimidines are aza-analogues of dihydropyridines, they are expected to exhibit reducing abilities. Therefore, reducing abilities of dihydropyrimidines are compared with those of 1-benzyl-1,4-dihydronicotinamide (**7**) in the following points: (a) the measurement of oxidation potentials; (b) the measurement of rate constant for reduction by the decrease of the absorbance of malachite green (**8**); (c) the solvent effect. As a result, dihydropyrimidines show reducing abilities similarly to dihydropyridine **7**.



In conclusion, the selective synthesis of three types of dihydropyrimidine isomers is established. Further, these dihydropyrimidines exhibit reducing abilities similarly to dihydropyridines. The detailed studies on mechanism are now in progress.