

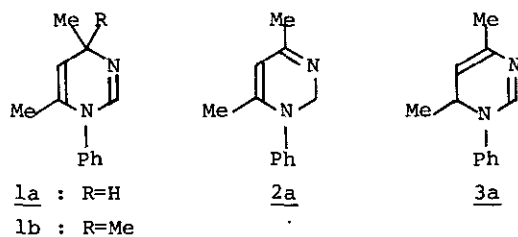
REACTION OF DIHYDROPYRIMIDINE WITH p-BENZOQUINONE

Choji Kashima, Masao Shimizu, Akira Katoh, and Yoshimori Omote

Department of Chemistry, University of Tsukuba,

Sakura-mura, Niihari-gun, Ibaraki 305, Japan

The chemistry of 1,4-dihydropyridines and their derivatives has been extensively investigated as model compounds of NAD(P)H. Although dihydropyrimidines are regarded as aza-analogs of dihydropyridines, little attention has been paid to the synthesis and reaction of dihydropyrimidines. We previously reported that three types of N-substituted dihydropyrimidine isomers were obtained from the desulfurization of pyrimidine-2(1H)-thiones and their dihydro-derivatives with Raney nickel. Then, the reaction of dihydropyrimidines with malachite green or iodine as substrates has been examined, since it was expected that dihydropyrimidines had reducing ability similar to dihydropyridines. In the course of studies on reducing ability, the reaction with p-benzoquinone as a substrate was examined.



When 1,4-dihydro-4,6-dimethyl-1-phenylpyrimidine (1a) was treated with p-benzoquinone in a buffer solution (pH = 8.5), the absorption maximum of p-benzoquinone ($\lambda_{\text{max}} = 244 \text{ nm}$) decreased and a new absorption at $\lambda_{\text{max}} = 500 \text{ nm}$ appeared. This phenomenon was also observed in both 1,2- (2a) and 1,6-dihydropyrimidines (3a) which were isomeric with compound (1a). However, in the reaction of 1,4-dihydro-4,4,6-trimethyl-1-phenylpyrimidine (1b), which has no hydrogen atom at the C-4 position of the pyrimidine ring, the decrease of p-benzoquinone was not observed. The resulting rate increased in the order of (2a) > (1a) > (3a). This order showed a good agreement with that of the reaction rate with iodine. However, the details of the study for the mechanism including the product are now in progress.