SYNTHESIS USING THE REACTION OF THE SINGLET OXYGEN WITH 1,2-DIHYDROPYRIDINES

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Reaction of the singlet oxygen with dihydropyridines such as 1-carbomethoxy-1,2-dihydropyridine and 1-benzoyl-2-benzoyloxymethyl-5-cyano-1,2-dihydropyridine produced the corresponding endocyclic peroxides, which were reactive enough in the presence of the protic substrate, acid, and the reducing reagent. Thus, sulfur, oxygen, chlorine, and nitrogen functions could be introduced into α or γ position in the pyridine ring with a certain extent of the stereochemical control, when the above-mentioned endocyclic peroxide was reacted with thiol, alcohol, hydrogen chloride, and hydrazoic acid.

5-Carbomethoxyamino-5-deoxy-dl-ribopiperidinose derivative, 5-carbomethoxyamino-5-deoxy-dl-lyxopiperidinose derivative, 5-benzamido-5-deoxy-dl-allopiperidinose methylglycoside, and 5-benzamido-5-deoxy-dl-altropiperidinose methylglycoside were synthesized by utilizing above knowledge. Furthermore, 4α-acetamido-5β-acetoxy-6α-bezoyloxymethyl-1- benzoyl-3-cyano-$\Delta^{2,3}$-piperidine was also synthesized as a possible intermediate for 2,4-diamino-2,4-dideoxyarabinoses, whose representative is an antibiotic, prumycin.