

SYNTHESIS USING THE REACTION OF THE SINGLET OXYGEN
WITH 1,2-DIHYDROPYRIDINES (CONTD.)

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A facile introduction of oxygen, nitrogen, halogen, and sulfur functional groups into the α or γ position of pyridine ring was reported last year in this Symposium by utilizing a reductive ring-opening of the singlet oxygen adduct derived from 1-acyl-1,2-dihydropyridine derivatives in the presence of various kinds of nucleophiles, such as alcohols, hydrazoic acid, hydrogen chloride, and thiols. In the continuation of this study, the synthesis of a nucleoside analogue containing an amino-sugar was attempted this time by using the knowledge obtained previously and the subsequent effort attaining a new type of carbon-carbon bond formation on a heterocyclic ring led to a finding of a novel reaction of the above $^1\text{O}_2$ adduct.

5-Methoxycarbonylamino-5-deoxy-DL- β -ribopiperidinoyluracil triacetate was synthesized by stannic chloride catalyzed condensation of 1-methoxycarbonyl-2 α -phenylthio-3 β ,4 β ,5 β -triacetoxypiperidine with bistrimethylsilyluracil, whereas the similar condensation of 5-acetoxy-1-methoxycarbonyl-2-phenylthio-1,2,5,6-tetrahydropyridine or 5-acetoxy-1-methoxycarbonyl-4-phenylthio-1,4,5,6-tetrahydropyridine afforded the same 4-uracil-substituted 1,4,5,6-tetrahydropyridine derivative.

An allyl cation generated from 5-acetoxy-1-benzoyl-6-benzoyloxymethyl-3-cyano-2-methoxy-1,2,5,6-tetrahydropyridine with stannic chloride gave the corresponding 4-aryl-1,4,5,6-tetrahydropyridine derivatives by the reaction with anisole, veratrole, dihydrosafrol, or thiophen.

The singlet oxygen adduct obtained from 1-methoxycarbonyl-1,2-dihydropyridine itself or its alkyl or methoxycarbonyl derivative was found to react with trimethylsilylacetophenone, ethyl vinyl ether, cyclohexanone piperidine enamine, indole, furan, and N-methylpyrrole by treatment with stannous chloride in a very mild condition and produced 5-hydroxy-1-methoxycarbonyl-1,2,5,6-tetrahydro- α -picolyl phenyl ketones, 5-hydroxy-1-methoxycarbonyl-1,2,5,6-tetrahydro-2-pyridylacetaldehyde diethylacetals, and 2-(3'-indolyl)-5-hydroxy-1-methoxycarbonyl-1,2,5,6-tetrahydropyridines, etc.