

A FACILE PHOTOCHEMICAL ROUTE TO C-5 AND C-6
ALLYL-SUBSTITUTED URACIL NUCLEOSIDES¹

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Summary: Irradiation of 5-iodouridine or 6-iodo-1,3-dimethyluracil in *aq.* acetonitrile in the presence of allyltrimethylsilane provided the corresponding 5- or 6-allylated product.

The synthetic method for creation of carbon-carbon bonds at C-5 or C-6 position of pyrimidine nucleosides has become increasingly important in recent years.^{2,3} Usually the substitution at C-5 of uridine has been accomplished by reaction of olefins with organo-palladium intermediates generated in situ from mercurinucleosides.² We wish to report an exceedingly facile method for the introduction of allyl group at C-5 or C-6 of uracil and uridine without using toxic mercury. Our approach is based on the photocoupling of allylsilanes to C-5- or C-6-iodouracils and has following important features: (1) the reaction may be carried out with readily available starting materials under mild neutral conditions; (2) allylation of unprotected nucleosides in *aq.* solvents can be accomplished as well, in contrast to the transition metal-catalyzed coupling where reduction of catalytic activity in the presence of water limits its use with unprotected nucleosides.

A typical procedure for the allylation of 5-iodouridine (1) is as follows. A solution of 1 (70 mg, 0.19 mmol) and allyltrimethylsilane (328 mg, 2.84 mmol) in acetonitrile-water (5:1, 50 mL) was irradiated with a 100 W high-pressure Hg lamp through Pyrex filter (8 h). Removal of the solvent followed by preparative TLC (silica gel, ethyl acetate-EtOH 10:1) gave 3⁴



