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Chemistry]

[Lab. of Pharm.

**2,6-Diphenyl-4*H*-chalcogenopyran-4-ones and 2,6-Diphenyl-4*H*-  
chalcogenopyran-4-thiones: a New Catalyst for the Baylis-Hillman Reaction.**

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2,6-Diphenyl-4*H*-chalcogenopyran-4-ones and 2,6-diphenyl-4*H*-chalcogenopyran-4-thiones, a new series of catalysts for the Baylis-Hillman reaction, were investigated. After attempting to find a good Lewis acid, the reactions proceeded smoothly in the presence of 1 mol equiv. of  $\text{TiCl}_4$  under atmospheric pressure at  $0^\circ\text{C}$ , giving adducts in moderate to high yields. Chalcogenopyranones and chalcogenopyranthiones were a more efficient kind of catalyst than  $\text{Me}_2\text{S}$ , and in most cases selenopyran-4-one gave better results than thiopyran-4-thione.

[*Chem. Commun.* 1041-1042 (1999)]

[Lab. of Medicinal Chemistry]

**Pd/C(en)-catalyzed Regioselective Hydrogenolysis of Terminal Epoxides to  
Secondary Alcohols.**

Hironao SAJIKI, Kazuyuki HATTORI, and Kosaku HIROTA\*

The preparation of the alcohol from the corresponding epoxide is normally accomplished by stoichiometric metal hydride or dissolving metal reagents, and such reductive cleavage with most reducing agents generally produces a large quantity of metal sludge. The present study describes an environmentally benign and catalytic technique using an easily handled and heterogeneous 10% Pd/C(en) catalyst that has been developed for the efficient regioselective ring-opening method of terminal epoxides to secondary alcohols. The formation of the primary alcohols could be mostly fixed. The 10% Pd/C(en) catalyst is stable and retains high efficiency during consecutive catalytic cycles (at least three times). The regioselectivity observed for terminal epoxides and the general utility of this methodology will make this simple technique an attractive addition to the range of procedures already known for this general transformation.

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[Lab. of Medicinal Chemistry]

**Regioselective Modification of the Sugar Moiety in Pyrimidine Nucleosides  
via a 4',5'-dehydro-2',3'-anhydrouridine intermediate.**

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2',3'-Epoxy pyrimidine nucleosides are a versatile building block of nucleosides modified in the sugar moiety, which through nucleophilic ring-opening reaction can function as precursors of enantiomerically pure and biologically interesting pyrimidine nucleoside derivatives, and a number of reports for the application of 2',3'-epoxy pyrimidine nucleosides have appeared in the literature. However, it is well known that the nucleophilic addition of the epoxy nucleosides gave a mixture of 2' and 3'-adducts in most cases. The present study describes a regioselective method for the synthesis of 3'-substituted pyrimidine nucleoside derivatives using easily prepared 4',5'-dehydro-5'-deoxy-2',3'-epoxyuridine as a key intermediate without the formation of the corresponding 2'-adduct. 4',5'-Dehydro-5'-deoxy-2',3'-epoxyuridine reacted regioselectively with various nucleophiles to give the corresponding 3'-adducts by the regiospecific nucleophilic attack of the nucleophiles at the highly reactive allylic 3'-position. The results, therefore, should be of interest to many organic chemists, particularly those engaged in the study of nucleic acids chemistry.

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[Lab. of Medicinal Chemistry]

**Diversity of Rearrangement of 3-Substituted 5-Carbamoyl-1-phenyluracil Derivatives.**

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Treatment of 3-substituted 5-carbamoyl-1-phenyluracil derivatives with NaH afforded 5-(*N*-substituted carbamoyl)-1-phenyluracil derivatives *via* rearrangement involving the rare C(2)-N(3) bond cleavage of a uracil ring system. Upon reaction of 5-*N*-methylcarbamoyl-1-phenyluracil derivatives and 3-methyl-1-phenyl-5-thiocarbamoyluracil (**6**) with NaH, 5-(anilinoethylene)barbituric acid derivatives formed, respectively, *via* rearrangement involving the N(1)-C(2) bond cleavage.