[Tetrahedron Lett., **35**, 4587-4590 (1994)] [Lab. Pharm. Chemistry]

Novel Benzoyl Migration of the Intermidiary 1:1 Adducts of 1,3-Dipolar Cycloaddition of Thiazolo [3,2-b] [1,2,4] triazolium N-Phenacylides with Dimethyl Acetylenedicarboxylate.

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Thiazolo[3,2-*b*][1,2,4]triazolium *N*-phenacylides **1** were generated *in situ* from the corresponding thiazolotriazolium salts and triethylamine. Reaction of the *N*-phenacylides **1** with dimethyl acetylenedicarboxylate (DMAD) gave novel compounds, 2-(1*H*-pyrrolo[2,1-*c*]-1,2,4-triazolyl)-ethenyl thiobenzoates **2** and 2-[2-(1*H*-pyrrolo[2,1-*c*]-1,2,4-triazolyl) ethenylthio]propenoates **3**. The former products **2** would be formed *via* a new type of intramolecular benzoyl migration of the intermediary 1:1 cycloadducts of *N*-ylides **1** and DMAD.

[Heterocycles, **37**, 563-570 (1994)] [Lab. of Medicinal Chemistry]

Novel Synthesis of Pyrido[3,4-*d*]pyrimidines, Pyrido[2,3-*d*]pyrimidines, and Quinazolines *via* Palladium-catalyzed Oxidative Coupling.

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The Pyrido[3,4-*d*]pyrimidines and quinazolines, deaza analogs of pteridines, have been of interest for their potential biological activities. Novel synthesis of such heterocycles using oxidative coupling reaction is described. Thus, reaction of 6-dimethylaminomethylenamino-1, 3-dimethyluracil with an electron deficient olefin such as methyl acrylate, acrylonitrile, and methyl vinyl ketone in the presence of stoichiometric amount of palladium acetate gave exclusively 6-substituted pyrido[2,3-*d*]pyrimidine-2,4-diones in good yield. Similar treatment of 1,3-dimethyl-6-carboxaldhyde dimethylhydrazone and 1,3-dimethyl-6-(2-dimethylaminovinyl)uracil gave the corresponding pyrido[3,4-*d*]pyrimidine-2,4-diones and quinazoline-2,4-diones, respectively.

[Chem. Pharm. Bull., **42**, 806-810 (1994)] [Lab. of Medicinal Chemistry]

New and Facile Synthesis of 5,6,7,8-Tetrahydro-5-deaza-5-thiapterins *via* the Aliphatic *S-N* Type Smiles Rearrangement.

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5,6,7,8-Tetrahydro-5-deaza-5-thiapterins, a thia analog of biologically important tetrahydropterins, were conveniently synthesized by the thermal condensation of 5-bromo-6-chloroisocytosine (**1**) with cysteamines *via* the aliphatic *S-N* type Smiles rearrangement in ethanolic pH 7.0 buffer solution. A special future of this method is that the construction of the tetrahydro-5-deaza-5-thiapterin ring system involves annulation of the 2,3-dihydro-1,4-thiazine ring employing appropriately substituted isocytosine derivative (**1**) as a starting material. The present result provides a novel example of *S-N* type Smiles rearrangement in the β-aminoethylarylsulfides and provides a promising method for the preparation of the 5-thia analog of tetrahydrofolic acid having a highly functionalized groups in the side-chain.