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Development of Efficient Methods for Synthesis of Nitrogen-containing Compounds Using Carbamates, Acylhydrazines, and Ammonia

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Toward efficient synthesis of divergent *nitrogen*-containing compounds of pharmaceutical and agricultural importance, development of efficient, complementary, and new synthetic methodologies is essential. One of the key subjects is how to introduce nitrogen atoms in organic molecules. Hence, our attention has been paid to the use of *carbamates*, *acylhydrazines*, and *ammonia* as nitrogen sources, since those have not been utilized frequently.

First, semicyclic *N,O*-acetals were prepared efficiently from semicyclic acetals and *carbamates*. Those undergo ring-opening reactions with various types of nucleophiles in the presence of a Lewis acid catalyst to afford ring-opened amino alcohols with high stereoselectivity. The reaction was successfully applied to syntheses of piperidine and pyrrolidine alkaloids such as (+)-isofebrifugine, an antimalarial agent.

Second, *N*-acylhydrazones, which are readily prepared *via* condensation of carbonyl compounds and *acylhydrazines*, were found to undergo allylation with allyltrichlorosilanes in the presence of neutral coordinate-organocatalysts (*NCOs*) such as sulfoxides and phosphine oxides. Highly enantioselective reactions were thus attained by using optically active *NCOs*.

Finally, ammonia was focused on as a simple, inexpensive, atom economical nitrogen source. It turned out that three-component reactions of aldehydes, allylboronates, and ammonia proceeded smoothly to give homoallylic primary amines with high selectivity. Concise and stereoselective syntheses of amino acids and amino sugars were achieved based on this reaction. Further utility of ammonia is now being pursued.

The above methodologies would provide efficient synthetic processes for useful *nitrogen*-containing compounds.