Guanidine Chemistry

○Tsutomu Ishikawa
(Dept. of Med. Org. Chem., Grad. Sch. of Pharm. Sci., Chiba Univ.)

Guanidines could be categorized to be strong organobases; however, their catalytic utilities in organic synthesis have never been discussed completely. We have extensively and systematically studied on their potential ability.

(1) Functionality as organosuperbases: A variety of chiral guanidines could be designated by introduction of chirality on the three guanidinyl nitrogens. We found that modified guanidines prepared by our original methods were effective in not only catalytic but also stoichiometric asymmetric syntheses.

(2) Role as a nitrogen source: We discovered that guanidinium salts carrying a glycinate function reacted with unsaturated aldehydes under basic conditions to give unsaturated aziridine-2-carboxylates, which were available as useful building blocks in organic synthesis because of convertible to functionalized amino acid derivatives by ring-opening reaction, together with urea compounds recyclable to the starting guanidinium salts. Introduction of chiral template to the guanidinium salt allowed us to expand the cycle aziridination reaction to asymmetric version.

(3) Affinity to proton and metal salts: Effective complexabilty of bisguanidines with either proton or metal ions in water was observed, suggesting their possible application to the removal of toxic substance from polluted water and recovery of rare elements as material sources.

(4) Potential chirality of bisguanidinobenzenes: Monoalkylation of bisguanidinobenzenes afforded a chiral alkylated product by asymmetric crystallization, indicating that bisguanidinobenzenes have a potential chiral character due to the plane asymmetry.