



Institut Ruđer Bošković

CX. Kolokvij Zavoda za organsku kemiju i biokemiju i
Sekcije za organsku kemiju Hrvatskog kemijskog društva

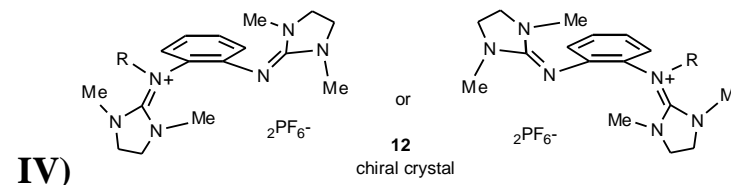
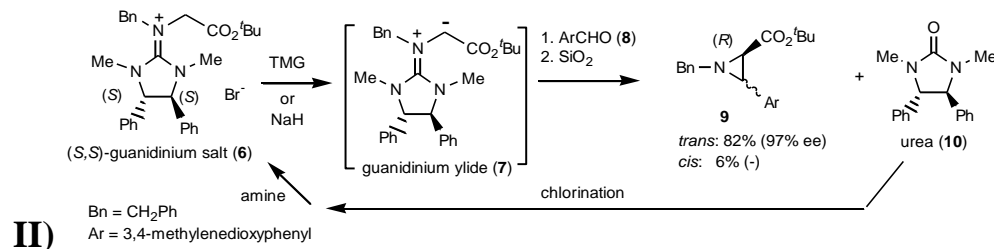
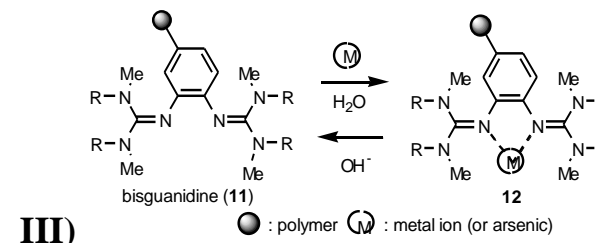
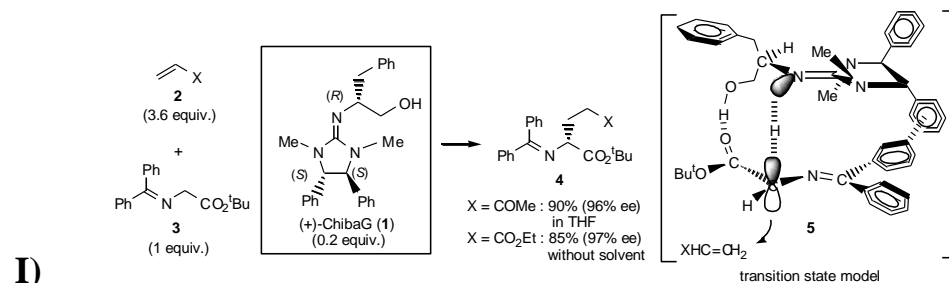


Professor Tsutomu Ishikawa
Chiba University
Japan

ponedjeljak, 10. 03. 2014.
predavaonica III. krila IRB
11:00-13:00 sati

Guanidine Chemistry

Guanidines are categorized to be strong organobases; however, their catalytic utility in organic synthesis has never been discussed completely. We extensively and systematically studied on their potential ability and focused on: (I) modified guanidines as chiral auxiliaries, (II) guanidinium ylides for aziridine formation, (III) affinity of bisguanidines to proton and metal salts, and (IV) potential chirality of bisguanidines.



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In the 1st topic guanidinium salt derived from guanidines by reaction with either acid or nucleophile plays an important role in a range of reactions as an active intermediate. ChibaG (**1**)-catalyzed Michael reaction between an active vinyl compound **2** and iminoacetate **3** satisfactorily affording an adduct **4** is exemplified in **Fig. 1**, in which a transition model **5** supposed for the effective asymmetric induction is given.

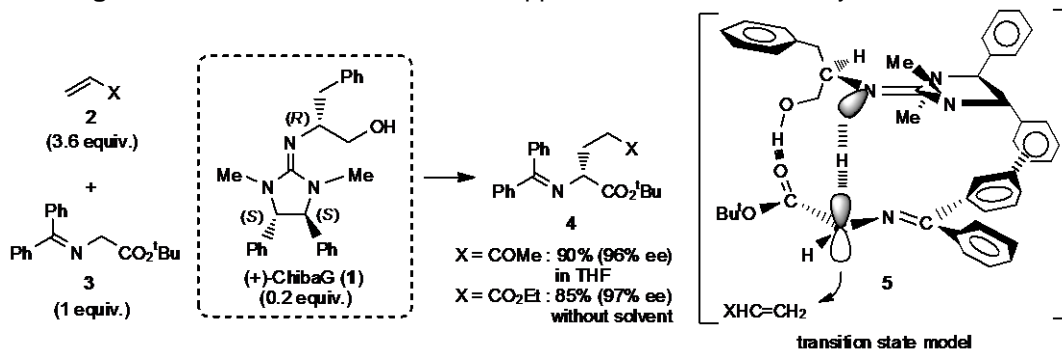


Fig. 1. Michael reaction and the supposed transition state model

In the 2nd topic, reaction of guanidinium salts **6** carrying a glycinate function with aromatic (or unsaturated) aldehydes **8** under basic conditions unexpectedly afforded aziridine-2-carboxylates **9**, which were available as useful building blocks in organic synthesis convertible to functionalized amino acid derivatives by ring-opening reaction, together with urea compounds **10** recyclable to the starting guanidinium salts **6** by chlorination. Guanidinium ylides **7** may be acted as nucleophiles in this reaction. Introduction of chiral template to the guanidinium salt allowed us to expand the cycle aziridination reaction to asymmetric version (**Fig. 2**).

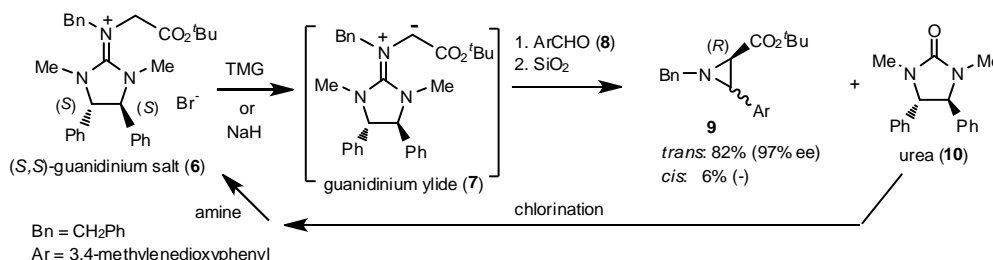


Fig. 2. Cycle asymmetric aziridination

In the 3rd topic, effective complexability of bisguanidines **11** with either proton or metal ions in water was observed, suggesting their possible application to the removal of toxic substances from polluted water and recovery of rare elements as material sources (**Fig. 3**).

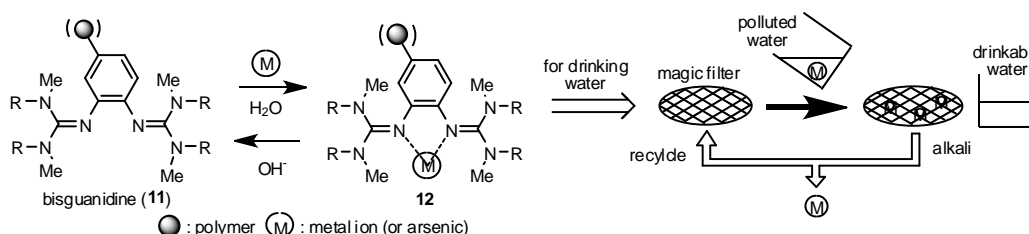


Fig. 3. Possible application of bisguanidine to green chemistry

In the last topic, monomethylation or monoethylation of bisguanidine **11** afforded a chiral product **12** by asymmetric crystallization, indicating that bisguanidines **11** have a potential chiral character due to the plane asymmetry (**Fig. 4**).

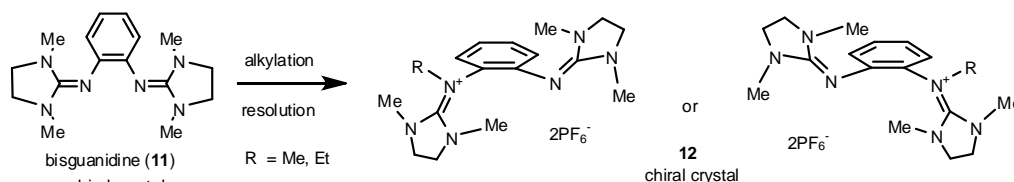


Fig. 4. Optical resolution of bisguanidine by alkylation