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SYNTHESIS OF SILACYCLIC COMPOUNDS INDUCED BY ADDITION OF IN-SITU GENERATED SILYL CATIONS TO MULTIPLE BONDS

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A silyl cation is well known to be one of the highly reactive Lewis acids, and is available for activation of unsaturated compounds. We developed a sila-Friedel–Crafts reaction, in which the addition of silyl cation to the aromatic moiety followed by deprotonation induces Si-C bond formation and applied it to synthesize various dibenzosiloles such as trisilasumanene and so on. We thought an intermediary silyl cation or its arene complex can add to multiple bonds to form -silyl cations, which undergo Friedel-Crafts reaction with an aromatic ring existed in a molecule to give the corresponding silacyclic compounds. We have investigated the reactions using dialkylbenzylhydrosilanes and dialkylhydro-1-naphthylsilanes as precursors of silyl cations, alkynes, alkenes, allenes, carbon dioxide, and aldehydes as multiply bonded compounds, trityl tetrakis(pentafluorophenyl)borate (TPFPB) as a hydride-abstracting reagent, and 2,6-di-tert-butyl-4-methylpyridine as a base. Interestingly, we have found that cyclization occurred only at the 8-position of the naphthalene ring in the reactions using dialkyl-1-naphthylsilanes and alkenes. We also studied on intramolecular version of the reactions using alkynes. Namely, we prepared aromatic compounds bearing trimethylsilyl- ethynyl and dialkylhydrosilyl groups at the neighboring position and treated them with a small amount of TPFPB to give the corresponding aromatic ring-fused siloles and disiloles via single and double intramolecular chain hydrosilylation reactions with silyl cations as chain carriers, respectively. In these reactions, -silyl cations are considered to have undergone hydride abstraction from the starting hydrosilanes instead of Friedel-Crafts reactions in the former reactions. In this presentation, we wish to report on the details of these reactions.

Biography

Takayuki Kawashima has received his DSci degree in 1974 from the University of Tokyo under the supervision of Professor Naoki Inamoto. He became a Professor of Department of Chemistry, Graduate School of Science, The University of Tokyo in 1998 via a Research Associate, a Lecturer, and an Associate Professor. From 1976 to 1978, he did Postdoctoral research with Professor J G Verkade at Iowa State University and with Professor W G Bentrude at University of Utah. In 2010, he retired and became Professor Emeritus at the University of Tokyo. He is now a Visiting Professor of Graduate School of Science and Technology, Gunma University after that of Gakushuin University. He received 2013 The Society of Silicon Chemistry, Japan Award. He has 263 original papers. He is a Member of Editorial Board of *Heteroatom Chemistry* from 2003 and International Board on International Conference on Phosphorus Chemistry from 2006.

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