

Development of New Reactions and Materials Based on the Characteristics of Unsaturated Bonds Containing Heavier Main Group Elements

(Faculty of Engineering, Gifu University) ○Toshiaki Murai

Keywords: Heavier Main Group Elements; Heavier Conjugate System; Sequential Reactions; Thiazole-based Fluorescent Molecules; Chirality Transfer Reactions

One of the most important missions of chemists is to maximize the latent properties of the elements in the third and subsequent rows of the periodic table, and to construct a new world of molecular chemistry. Among them, we have focused on compounds with C=S, C=Se, C=Te, P=S, and P=Se groups and established new synthetic reactions for novel derivatives. We categorized them into the following four topics.

1. Heavy Atom-Containing Conjugate System: Carboxylic acids are ubiquitous organic compounds. The basic skeleton of these compounds has a C=O group. We successfully synthesized derivatives in which the C=O group was replaced with a C=Se group.¹ In addition, the methylation of tellurium isologues of amides, i.e., telluroamides, led to the telluroiminium salts. We elucidated the structures of these species in solutions and in the solid state with NMR spectroscopy and X-ray structural analyses.

2. Sequential Reactions of Thioamides and Thioformates: The sequential addition of two different carbon nucleophiles to thioformamides proceeded smoothly to give tertiary amines. Two nucleophiles were incorporated into the carbon atom of the C=S group.² In contrast, two different carbon nucleophiles were introduced to the carbon and sulfur of the C=S group of thioformates. Reactions of secondary thioamides with *n*-BuLi generated carbanions adjacent to the nitrogen atom.

3. Thiazole-based Fluorescent Molecules: The combination of the new reactions shown above led to the formation of fluorescent 5-*N*-arylaminothiazoles. By selecting the combination of aryl groups and arylamino groups incorporated into the thiazole ring, we observed various emission colors from blue to red and multi-chromisms.³

4. Phosphoroselenoyl Chlorides with a Binaphthyl Group and Chirality Transfer Reaction: We developed phosphoroselenoyl chlorides with a binaphthyl group and applied them as chiral molecular tools. Notably, the reaction of a range of derivatives with nucleophiles proceeded via the transfer of the axial chirality of the binaphthyl group to the central chirality of the phosphorus atom.⁴

1) T. Murai, D. Nishi, S. Hayashi, W. Nakanishi, *Bull. Chem. Soc. Jpn.* **2014**, 87, 677. 2) T. Murai, Y. Mutoh, *Chem. Lett.* **2012**, 41, 2. 3) Y. Tsuchiya, K. Yamaguchi, Y. Miwa, S. Kutsumizu, M. Minoura, T. Murai, *Bull. Chem. Soc. Jpn.* **2020**, 93, 927. 4) Y. Maekawa, K. Kuwabara, A. Sugiyama, K. Iwata, T. Maruyama, T. Murai, *Chem. Lett.* **2017**, 46, 1068.