ORGANOHETEROATOM CHEMISTRY

Annual Research Review

(1) "Syntheses and Thermolyses of Heteracyclobutanes Containing a Highly Coordinate Main Group Element"

In the course of our study on heteracyclobutanes containing a highly coordinate main group element, we have synthesized 1,3,2$\lambda^5$-oxazaphosphetidine 1 and 1,3,2$\lambda^5$-diazaphosphetidine-4-thione 2 by cycloaddition reactions of the corresponding iminophosphorane with a ketone and an isothiocyanate, respectively. Formation of an imine and a cyclic phosphinate upon thermolysis of 1 shows that 1 is an intermediate of the aza-Wittig reaction. Compound 2 exhibited two reaction pathways upon thermolysis giving the iminophosphorane with the isothiocyanate, and a cyclic thiophosphinate with a carbodiimide, respectively. The formation of the latter two compounds suggests the bond recombination around the phosphorus atom of 2.

Tetracoordinate 1,5-dioxa-4$\lambda^4$-telluraspiro[3.3]heptane 3 bearing two 1,2-oxatelluretane rings was synthesized and crystallographically characterized. Thermolysis of 3 gave a mixture of the corresponding oxirane, olefin, and alcohol in contrast to those of other heteracyclobutanes containing a highly coordinate main group element. The reaction was found to proceed mainly via a radical pathway.


(2) "Synthesis, Structure, and Reactions of Heteracyclopropanes Containing a Highly Coordinate Main Group Element"

Three-membered ring compounds containing a highly coordinate heteroatom are interesting in view of their strained structures and the bonding properties of a polar hypervalent bond fixed in the ring system. We have succeeded in the synthesis of the first stable selenaphosphirane 4 and thiasiliranide 5 by taking advantage of the Martin ligand. Their strained molecular structures were characterized by X-ray crystallographic analysis. The characteristic solvent effect in $^{31}$P and $^{77}$Se NMR spectra of 4 revealed the existence of the polar P-Se bond. The equilibrium of 4 with the phosphorus ylide and elemental selenium has also been revealed.

The hydrolysis of 5 afforded 3,3-dimethylbutanethiol indicating the potential relationship of the thiasiliranide with an intermediate of the Brook rearrangement, while reaction with aqueous HCl gave the $\alpha$-mercaptoalkylsilane.


(3) "Synthesis of 5-Carbaphosphatranes"

The characteristics of silatranes and phosphatranes, which are known as bioactive species and basic catalysts, respectively, are strongly attributable to the transannular dative bond of nitrogen to the central atom. We have synthesized 5-carbaphosphatranes 6, in which a P→C, dative bond was replaced by the P–C covalent bond, and elucidated their structures and spectroscopic properties. The theoretical calculations indicated that the transannular bond in 6 is twice as strong as that of phosphatran and more than 3 times stronger than that of silatran, reflecting the difference between a covalent bond and the more ionic dative bonds.

A. Original Papers


C. Proceedings


D. Books
