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Phosphorus, Sulfur, and Silicon and the Related Elements

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A Personal Reflection

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■ A Personal Reflection

Professor Marian Mikołajczyk's pioneering work on heteroatom chemistry can be found in his numerous literature publications, books, and monographs, and they firmly place him in a world-class ensemble of organosulfur and organophosphorus chemists. His contributions to stereochemical and synthetic main-group chemistry have provided a mechanistic understanding, new reagents, and novel pathways in several important areas of organoelement research. For these special issues of *Phosphorus, Sulfur, and Silicon and the Related Elements*, I asked Professor Mikołajczyk to personally develop a short list of what he considers to be his most important contributions over his impressive career. His suggestions are below:

- 1) Elaboration of methods and determination of the absolute configuration of chiral phosphorus monothioacids.
- 2) Construction of the first Walden cycle for a phosphorus chiral system.
- 3) Discovery of the retention of configuration at a phosphorus in the nucleophilic substitution reaction in diastereomeric cyclic, five-membered thiophosphoryl halogenides—this result provided the first stereochemical evidence for the addition–elimination mechanism involving a pentacoordinate phosphorus intermediate (the Westheimer concept).
- 4) The first asymmetric and stereoselective synthesis of optically active trivalent phosphorus acid esters, thioesters, and amides.
- 5) The first asymmetric and stereoselective synthesis of optically active sulfinates with the sulfur atom as a sole centre of chirality.
- 6) The synthesis of thiosulfinic acids—a new class of chiral organosulfur compounds.
- 7) The stereoselective synthesis of optically active ^{16}O , ^{18}O -sulfinic acids and ^{16}O , ^{18}O -thiosulfonic acid salts.
- 8) A rigorous proof for the inversion of configuration at sulfur in the elementary methoxy–methoxy exchange reaction in sulfinates.
- 9) Discovery of a unique reaction (acid-catalyzed alcoholysis of chiral sulfinamides), which occurs with retention and/or inversion of configuration at sulfur, thus providing evidence for an addition–elimination mechanism involving sulfuranes as intermediates.

- 10) Synthesis of enantiomeric dimethoxyphosphorylmethyl *p*-tolyl sulfoxides, which are reagents of choice for the synthesis of chiral vinyl sulfoxides.
- 11) Synthesis of enantiomeric α -phosphorylvinyl *p*-tolyl sulfoxides and their use in the asymmetric cyclopropanation reactions.
- 12) The first asymmetric syntheses of α -, β -, and γ -aminophosphonic acids mediated by chiral sulfinimines.
- 13) Elaboration of new strategies for the phosphonate-mediated syntheses of bioactive and natural products (*Z*-jasnone, methylenomycin A and B, sarkomycin, isoterpenin, prostaglandin B₁, neplanocin A, cyclopentenone TEI-9826).

With my best wishes and gratitude for your contributions,

Martin D. Rudd
Editor-in-Chief