Polish J. Chem., **75**, 1089–1101 (2001) **REVIEW ARTICLE**

New Developments in Heterocyclic Chemistry of Phosphorus and Nitrogen

by T.A. Modro

Centre for Heteroatom Chemistry, Department of Chemistry,
University of Pretoria, Pretoria 0002, South Africa
e-mail: tamodro@scientia.up.ac.za

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A series of phosphoric triamides of a general structure $(R_2N)_3P{=}O$ has been prepared. The series included non-cyclic structures, as well as structures in which the phosphorus and two (monocyclic structure), or three (bicyclic structure) nitrogen atoms were incorporated in the five-membered heterocyclic ring. The molecular parameters (particularly the N-P-N bond angles and P-N bond distances) were determined by X-ray diffraction, and they were correlated with the ^{31}P NMR shielding parameters of the phosphorus nucleus. A distinct interrelation between the NMR and crystal structure data was observed and interpreted in terms of the changes in the hybridization of the P-N bonding.

In the next part, the chemistry of a new, bicyclic triamide system – 1-oxo-2,8-disubstituted-2,5,8-triaza-1λ^5-phosphabicyclo[3.3.0]octane (**3**) was extensively studied. Solvolytic cleavage under acidic conditions yielded selectively a new, eight-membered monocyclic product (**6**), while the base-catalyzed reaction proceeded with the opposite selectivity, yielding the isomeric products (**5**). The most interesting observation was that products **6** undergo spontaneous rearrangement to the five-membered cyclic products **5**. The mechanisms for the cleavage, and for the rearrangement, are discussed. Substrates **3** were also converted, through the lithiation-induced phosphorus migration from nitrogen to an aromatic carbon, to two new types of bicyclic phosphonic and phosphinic derivatives. The nucleophilic cleavage of the latter produced a new, twelve-membered cyclic phosphinic system containing three amine nitrogen atoms in the ring. Further studies on the selectivity in the cleavage of the new bicyclic systems are reported.

Compounds **3** were finally used as starting materials for the preparation of the otherwise difficult to prepare triamines of the general structure $ArNHCH_2CH_2NHCH_2CH_2NHAr$ (**11**). Amines **11** were in turn used as substrates for the preparation of the thiophosphoryl analogues of **3**, the structure and chemistry of which is currently investigated.

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Synthesis and Stereochemistry of Mono and Bicyclic 1,2-Thiaphosphacyclanes

by T.A. Mastryukova, I.L. Odinets, N.M. Vinogradova, K.A. Lyssenko and P.V. Petrovskii

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, GSP-1, Vavilova str.28, Russia
e-mail: odinets@ineos.ac.ru

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The facile synthetic route to 5- and 6-membered mono and bicyclic 3-cyano-2-oxo-1,2-thiaphosphacyclanes has been elaborated on the base of intramolecular S-alkylation in a series of mono- and bis-ω-haloalkyl substituted thiophosphorylacetonitriles. The stereochemistry of the cyclic compounds was determined by NMR as well as X-ray diffraction. The diastereomeric transformations of 3-cyano-2-oxo-1,2-thiaphosphinanes and formation of conglomerates in the case of 6-cyano-2-oxa-10-thia-1-phosphabicyclo[4.4.0]decane-1-oxide are discussed.

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Thiophosphates and Selenophosphates as Tools in the Construction of Carbon–Carbon Double Bond

by A. Skowrońska, P. Dybowski, M. Koprowski, E. Krawczyk and I. Maciągiewicz

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland

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Efficient new methodology of regio- and stereoselective synthesis of a variety of functionalized mono- and polycyclic compounds based on thio- and selenophosphates is reported. The representative examples of these compounds are: vinyl thiiranes, conjugated dienes, cycloadducts, α,β-unsaturated carbonyl compounds, allylic alcohols, α-hydroxy ketones and aromatic compounds.

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C-Phosphorylated Azoles

by A.M. Pinchuk, A.A. Yurchenko, G.V. Oshovsky, E.V. Zarudnitskii, A.O. Pushechnikov and A.A. Tolmachev

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya, 5; Kiev-94, 02094, Ukraine

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A method of phosphorylation of heterocycles incorporating 1,3-azole moiety with phosphorus(III) halides is elaborated. As a result, previously unknown azolyldihalogenphosphines are prepared. Influence of heteroatom and quantity of nitrogen atoms in a cycle on the activity of azoles is studied. Reaction of 5-aminopyrazole derivatives with phosphorus(III) halides affords novel phosphorus-containing bi- and tricyclic fused systems

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^{31}P High Resolution Solid State NMR Studies of Phosphoroorganic Compounds of Biological Interest

by M.J. Potrzebowski, K. Ganicz and S. Kaźmierski

Polish Academy of Sciences, Center of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland
E-mail marekpot@bilbo.cbmm.lodz.pl

In this review several applications of ^{31}P high resolution solid state NMR spectroscopy in structural studies of bioorganic samples is reported. The problem of pseudopolymorphism of bis[6-O,6′-O-(1,2:3,4-diisopropylidene-α-D-galactopyranosyl) phosphorothioyl] disulfide **1** and application of ^{31}P CP/MAS experiment to investigate of this phenomenon is discussed. The influence of weak C–H···S intermolecular contacts on molecular packing of 1,6-anhydro-2-O-tosyl-4-S-(5,5-dimethyl-2-thioxa-1,3,2-dioxaphosphorinan-2-yl)-β-D-glucopyranose **2** and S_P, R_P diastereomers of deoxy*xylo*thymidyl-3′-*O*-acetylthymidyl (3′,5′)-*O*-(2-cyanoethyl) phosphorothioate **3** and their implication on ^{31}P NMR spectra is shown. The final part of review describes the recent progress in structural studies of O-phosphorylated amino acids (serine, threonine, tyrosine), relationship between molecular structure and ^{31}P chemical shift parameters δ_{ii} and influence of hydrogen bonding on values of principal elements of chemical shift tensor.

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Models of Biomacromolecules and Other Useful Structures Based on the Poly(alkylene phosphate) Chains

by S. Penczek, J. Pretula and K. Kałużyński

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences,
90-363 Łódź, Sienkiewicza 112, Poland
e-mail: spenczek@bilbo.cbmm.lodz.pl

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Poly(alkylene phosphate) backbones are at the basis of two important classes of biomacromolecules, nucleic and teichoic acids. Both are known to strongly bind metal cations; teichoic acids interact specifically with Ca^{2+} and Mg^{2+} cations transporting these cations in the biological milieu. This review describes the work of this laboratory directed towards synthesis of the backbones interaction with cations and some applications in nonbiological systems, although related to the ability to interact with cations. Thus, poly(alkylene phosphates) are described as liquid membranes and in the form of block copolymers as regulating crystal growth by interacting with cations rich surface. Moreover, poly(alkylene phosphates) function as strong acids: cationation of polyaniline (doping) leading to the intermolecular complex, in which poly(pentamethylene phosphate) specifically recognize the distance between the nitrogen atoms in polyaniline.

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"No Strain, No Gain:" Studies in the Mechanism of a DNA Repair Enzyme

by G.M. Blackburn and G. Walcher

Krebs Institute, Department of Chemistry, Sheffield University, Sheffield, S3 7HF, UK
E-mail: g.m.blackburn@sheffield.ac.uk

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The presence of uracil in DNA occurs either as a result of the mis-incorporation of dUTP in place of dTTP or by deamination of deoxycytidine to give deoxyuridine and is pro-mutagenic. Some 500 such lesions are repaired per cell per day in man. The first enzyme in the repair pathway is uracil DNA glycohydrolase, UDG, which cleaves the glycosylic bond in deoxyuridine in DNA. It shows a rate acceleration of 10^{12} and specificity for uracil of at least 10^7 with respect to cytosine or thymine bases. Its mechanism of action has been revealed through the X-ray crystal structure of a transition-state analogue bound in the enzyme active site and is clearly a dissociative, S_N1 type process.