

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

New Synthetic Route to Phosphonic Acid Anhydrides

K. Diemert^a; W. Kuchen^a; D. Mootz^a; W. Poll^a; F. Sandt^a

^a Institut für Anorganische Chemie und Strukturchemie Heinrich-Heine-Universität Düsseldorf, Düsseldorf

To cite this Article Diemert, K. , Kuchen, W. , Mootz, D. , Poll, W. and Sandt, F.(1996) 'New Synthetic Route to Phosphonic Acid Anhydrides', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 111: 1, 100

To link to this Article: DOI: 10.1080/10426509608054729

URL: <http://dx.doi.org/10.1080/10426509608054729>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

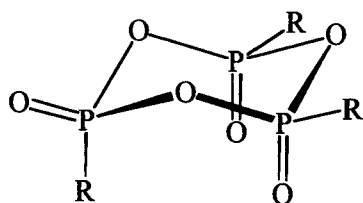
NEW SYNTHETIC ROUTE TO PHOSPHONIC ACID ANHYDRIDES

K. DIEMERT, W. KUCHEN, D. MOOTZ, W. POLL AND F. SANDT

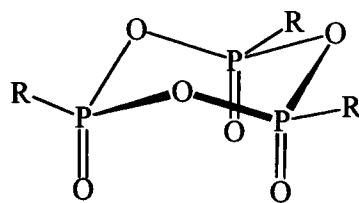
Institut für Anorganische Chemie und Strukturchemie

Heinrich-Heine-Universität Düsseldorf, D - 40225 Düsseldorf

Phosphonic acid anhydrides are useful condensation reagents in the peptide and polyamide synthesis [1,2]. A new method for the preparation of well defined anhydrides is now described and intermediates of the peptide synthesis are elucidated. Cryoscopic and mass spectrometric data confirm the suggested cyclic trimeric molecular structure and the $^{31}\text{P}\{^1\text{H}\}$ - as well as ^1H -NMR spectra can be explained with the structures:



C_s symmetry, AB_2 spin system;
 $R = 1,1$ Dimethylethyl,
 2-Methylphenyl



C_{3v} symmetry, A_3 spin system;
 $R = 2,4,6$ -Trimethylphenyl

Reaction of $t\text{-BuP}(\text{O})(\text{SiMe}_3)_2$ and PhBCl_2 yields the mixed anhydride of t -butylphosphonic and phenylboronic acid $\text{C}_{40}\text{H}_{57}\text{B}_4\text{O}_{12}\text{P}_4$. The compound forms colourless crystals and the obtained data are in agreement with a 16 membered P-O-B- ring.

By adding H_2O to a solution of the anhydride $[\text{t-BuPO}_2]_3$ [3] the hitherto unknown acid $\text{H}_2[\text{t-Bu}_3\text{P}_3\text{O}_7]$ can be obtained. This acid proved to be a strong acid and rather stable against further hydrolysis with H_2O in alcohol. Neutralisation leads to the salt $[(\text{t-Bu})_3\text{P}_3\text{O}_7]\text{Na}_2 \cdot 8 \text{H}_2\text{O}$, of which an x-ray structure was determined. Colourless, plate-like crystals; monoclinic, ($a = 1086.9$, $b = 3113.9$, $c = 912.3$ pm, $\beta = 114.59^\circ$, $P2_1/c$, $Z = 4$, $R1 = 0.040$, $wR2 = 0.119$). The first of the two independent Na^+ cations is six-coordinated by five water molecules and one oxygen atom of the anion in the form of a distorted octahedra. The coordination of the other Na^+ ion by only five water molecules can best be described as largely distorted square pyramid with an Oxygen as apex. Both polyhedra share a common edge. The anions with their polar PO_2 groups and seven of the eight independent water molecules form hydrogen bonded layers perpendicular to b . Two such layers (equivalent across a centre of symmetry) are now connected to double layers by the eighth water molecule and the embedded Na^+ cations. This polar layer is „sandwich“-like enclosed in two nonpolar layers of t -butyl groups of the triphosphonate anions. Between those „sandwiches“ only van der Waals interactions are observed.

References

1. H. Wissmann, H.J. Kleiner, *Angew. Chem.* 92, 129 (1980)
2. M. Ueda, T. Honma, *Makromol. Chem.* 190, 1507 (1989)
3. O.I. Koldyazhnyi, E.V. Grishkan, *Zh. Obshch. Kim.* 64, 1440 (1994)