

This article was downloaded by:

On: 29 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>

S,S-Diorgano Derivatives of the $P_2N_4S_2$ Ring

Rainer Vollmerhaus^a; Robert W. Hilt^a; Masood Parvez^a; Xiaoliang Gao^a; Tristram Chivers^a

^a Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada

To cite this Article Vollmerhaus, Rainer , Hilt, Robert W. , Parvez, Masood , Gao, Xiaoliang and Chivers, Tristram(1994) 'S,S-Diorgano Derivatives of the $P_2N_4S_2$ Ring', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 425 — 426

To link to this Article: DOI: 10.1080/10426509408021886

URL: <http://dx.doi.org/10.1080/10426509408021886>

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.

S,S'-DIORGANO DERIVATIVES OF THE $P_2N_4S_2$ RING: LITHIUM HALIDE ADDUCTS, UNSYMMETRICAL DERIVATIVES AND CONFORMATIONAL ISOMERS

RAINER VOLLMERHAUS, ROBERT W. HILTS, MASOOD PARVEZ, XIAOLIANG GAO AND TRISTRAM CHIVERS, Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada, T2N 1N4

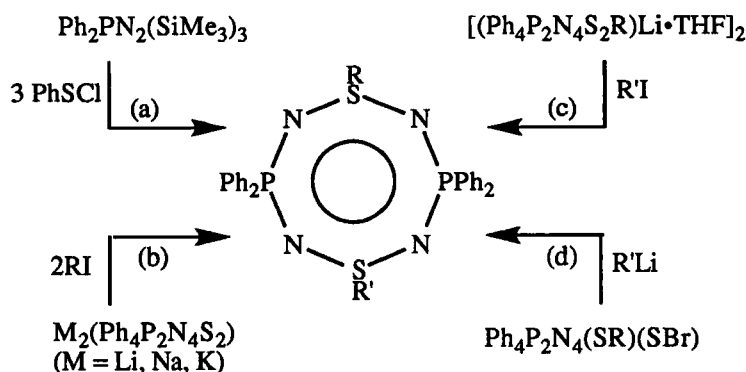
Abstract The reaction of $[Li(Ph_4P_2N_4S_2R)THF]_2$ with alkyl iodides $R'I$ produces the unsymmetrically substituted derivatives $Ph_4P_2N_4(SR)(SR')$ as lithium iodide adducts. The coordinated LiI is readily removed in CH_3CN or CH_2Cl_2 to give the eight-membered rings in a boat conformation ($\delta^{31}P = 14-17$ ppm). The boat conformers readily isomerize to the corresponding chair isomers ($\delta^{31}P = 25-29$ ppm) upon gentle heating.

INTRODUCTION

Ring systems of the type $1,5-R_4P_2N_4S_2R'_2$ are hybrids of the well known cyclotetraphosphazenes $(R_2PN)_4$ and the tetrameric cyclothiazyls $(NSR')_4$. The symmetrically substituted derivative $Ph_4P_2N_4S_2Me_2$ has been known for many years¹ and we have developed improved routes to such derivatives (see methods (a) and (b) in Scheme 1).^{2,3} These heterocycles may be useful as multidentate ligands or as precursors for hybrid PN/SN polymers. The recently discovered organolithium derivatives of the type $[Li(Ph_4P_2N_4S_2R)THF]_2$ ⁴ should be convenient reagents for the synthesis of unsymmetrically substituted derivatives $Ph_4P_2N_4(SR)(SR')$ by reaction with alkyl iodides (see method (c) in Scheme 1).

LITHIUM HALIDE ADDUCTS

The initial product of the reaction of $[Li(Ph_4P_2N_4S_2R)THF]_2$ ($R = Me, ^tBu, Ph$) with methyl or allyl iodide is the lithium iodide adduct of $Ph_4P_2N_4(SR)(SR')$. These adducts have been characterized by elemental analysis and by 1H , 7Li and ^{31}P NMR spectroscopy. Analogous $LiBr$ adducts are obtained by the alternative synthetic method (d) (see Scheme 1).



SCHEME 1 Synthetic routes to symmetrical ($R=R'$) and unsymmetrical ($R \neq R'$) $\text{Ph}_4\text{P}_2\text{N}_4(\text{SR})(\text{SR}')$

BOAT AND CHAIR CONFORMERS

The coordinated LiX in these adducts can be readily removed by dissolution in CH_3CN or CH_2Cl_2 to give the heterocycles $\text{Ph}_4\text{P}_2\text{N}_4(\text{SR})(\text{SR}')$ as the boat conformers, which are characterized by ^{31}P NMR singlets in the narrow range 14–17 ppm. The boat conformers slowly isomerize in CH_2Cl_2 or CH_3CN at room temperature (more rapidly on gentle heating) to give the thermodynamically favoured chair conformers, which exhibit characteristic ^{31}P NMR resonances at 27–29 ppm (see Figure 1). The conformational assignments have been confirmed by X-ray structures of several derivatives.

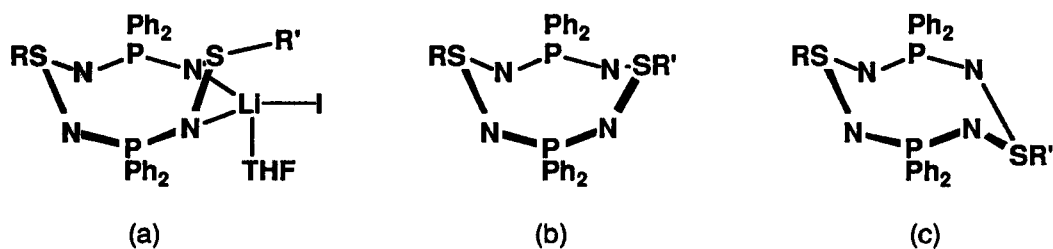


FIGURE 1 (a) LiI adducts, (b) boat and (c) chair conformers of $\text{Ph}_4\text{P}_2\text{N}_4(\text{SR})(\text{SR}')$

REFERENCES

1. R. Appel, D. Hänsgen and W. Müller, *Chem. Ber.*, **101**, 2855 (1968).
2. T. Chivers, S. S. Kumaravel, A. Meetsma, J. C. van de Grampel and A. van der Lee, *Inorg. Chem.*, **29**, 4591 (1990).
3. T. Chivers, M. Cowie, M. Edwards and R. W. Hilt, *Inorg. Chem.*, **31**, 3349 (1992).
4. T. Chivers, M. Edwards, R. W. Hilt, M. Parvez and R. Vollmerhaus, *Inorg. Chem.*, **33**, 1440 (1994).