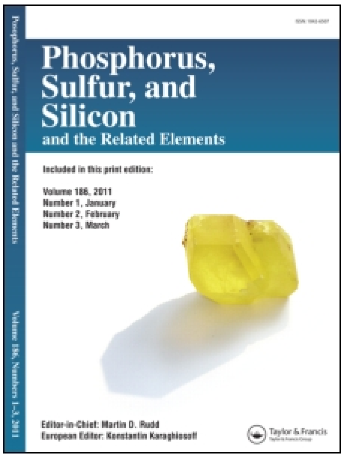

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Synthesis and Reactions of Diphosphorinanes and Diphospholanes

M. Fild[a]; T. Oehmigen[a]
[a] Institut für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig, Federal Republic of Germany

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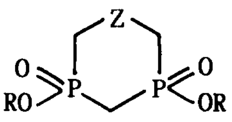
SYNTHESIS AND REACTIONS OF DIPHOSPHORINANES AND DIPHOSPHOLANES.

M. FILD, T. OEHMIGEN
Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig
Federal Republic of Germany

Abstract Reactions of XCH_2ZCH_2X ($Z=CH_2,O,S$; $X=Cl,Br$) with $(RO)_2PCH_2P(OR)_2$ gave substituted diphosphorinanes. The reduction of the cyclic esters with silanes yielded diphosphorinanes with trivalent phosphorus, whereas with $LiAlH_4$ cleavage of the ringsystem was observed, and the asymmetric substituted diphosphines $Me(H)PCH_2ZCH_2PH_2$ were formed. Reduction of acyclic esters of the type $R'(OR)P(O)CH_2ZCH_2(O)$-$P(OR)R'$ ($R'=Me,OR$; $R=Pr^1,Et$; $Z=CH_2,S$) with $LiAlH_4$ or silane gave acyclic diphosphines and diphospholanes.

The reaction of the Methanebis(phosphonous diisopropylester) with $BrCH_2ZCH_2Br$ ($Z=CH_2,S,O$) gave the corresponding diphosphorinanes, oxadiphosphorinanes and thiadiphosphorinanes (I), respectively.

(1) $$(RO)_2PCH_2ZCH_2P(OR)_2 \xrightarrow[-\ 2RX]{XCH_2ZCH_2X}$$

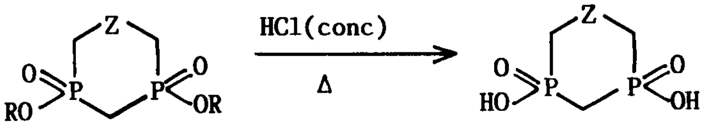


I

The compounds of the type (I) were obtained in high yields, when the reactions were conducted in highly diluted solutions at 140-150°C in Xylene as solvent. In these reactions, both isomers (cis/trans) were formed, as proved by ^{31}P-, ^{13}C- and ^{1}H- NMR spectroscopy.

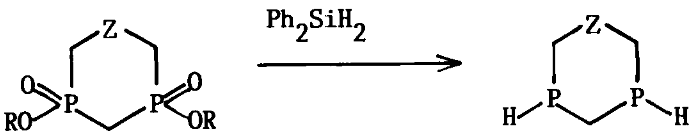
Hydrolysis of the cyclic esters with conc. hydrochloric acid led to the corresponding cyclic acids (II). Reducing the substituted diphosphorinanes (I,II) with Ph_2SiH_2, at 170-190°C, yielded the diphosphorinane (III) with trivalent phosphorus.

(2)



I II

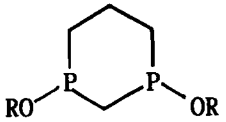
(3)



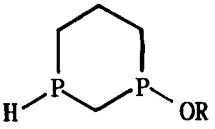
I III

From temperature- and solvent- dependent NMR spectra, it was shown that (a,a;e,e)- and (e,a)- conformers were present.

A detailed investigation by NMR- and mass spectral analysis of the reduction process for the diphosphorinane ($Z=CH_2$) showed that the reaction proceeded in a stepwise fashion. The intermediates (IV,V) were formed.



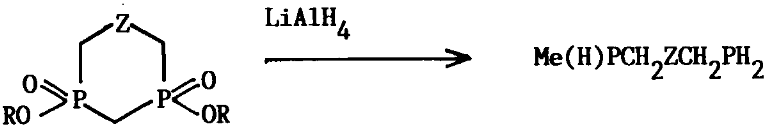
IV



V

The reaction of compounds of the type (I) with $LiAlH_4$ resulted in the cleavage of the cyclic systems to yield asymmetric substituted diphosphines (VI), no cyclic compounds being detected.

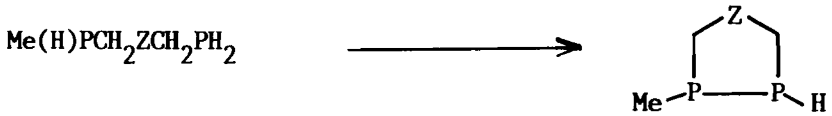
(4)



I VI

A similar cleavage reaction was observed in the reduction of $(RO)(O)\overline{PCH_2CH_2P(O)(OR)C}H_2$, which gave $Me(H)PCH_2CH_2PH_2$ Depending on the reaction conditions (temperature, work-up procedure) the acyclic diphosphines were accomponied by asymmetric substituted diphospholanes (VII).

(5)

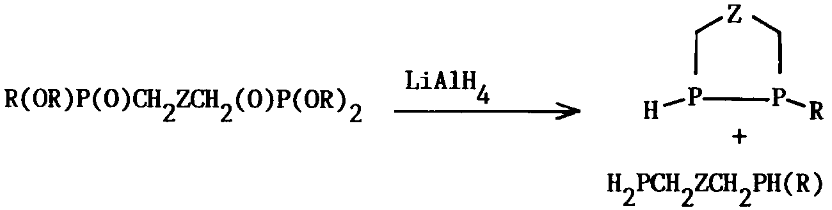


VII

Higher reaction temperature and/or basic hydrolysis of the reaction mixture substantially increased the amount of the diphospholanes relative to the diphosphines. Since this represented a separational problem, an alternative route to the diphospholanes was employed.

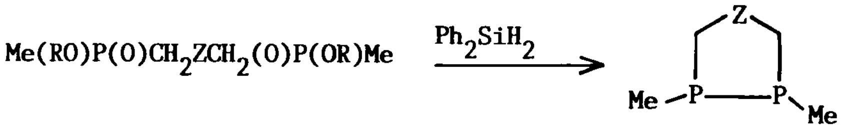
The starting material, diphosphonic or diphosphinic esters was prepared by an Arbuzov reaction. The reduction of these esters gave different results. Reduction of the esters (eq.(6)) with $LiAlH_4$, led to substituted diphospholanes and diphosphines.

(6)



If the reduction of symmetrical substituted esters was performed with diphenylsilane, only the diphospholane was obtained.

(7)



From the ^1H-, ^{13}C- and ^{31}P-NMR spectra, the stereochemistry of the diphospholanes could be unambiguously assigned.