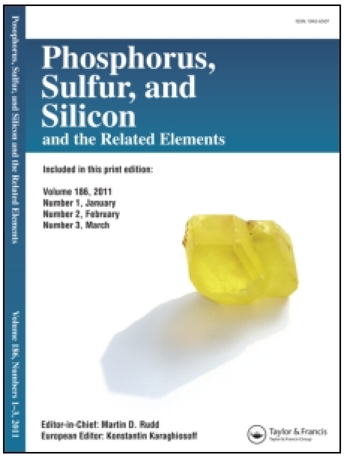

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Phospha-carba-oligo-enes, Synthesis and Reactivity

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Phospha-carba-oligo-enes, Synthesis and Reactivity

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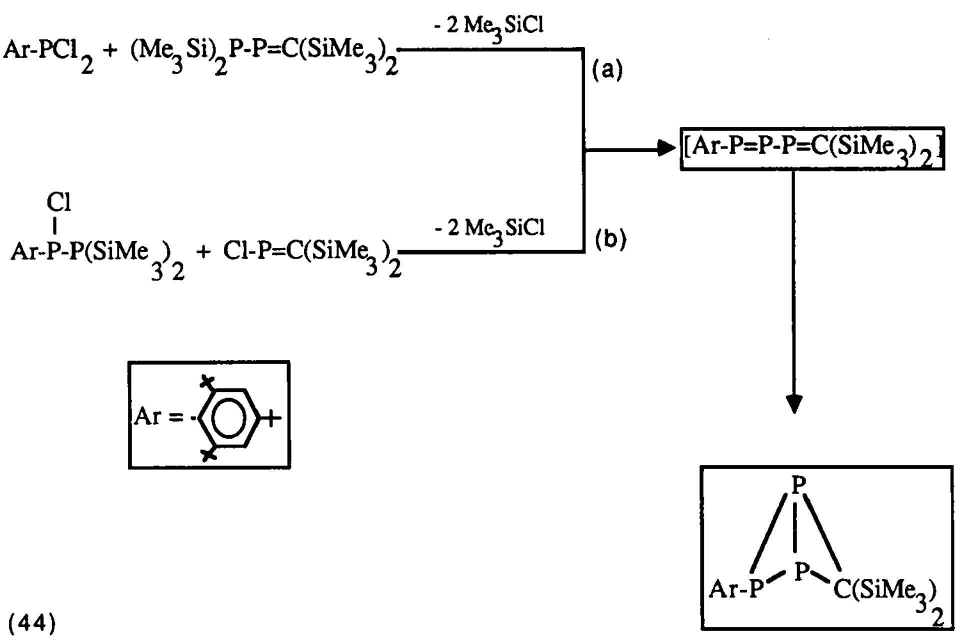
Abstract The synthesis of various mono-, di- and triphosphabutadienes, of two triphosphapentadienes and of several mono-, di- and tetraphospha-hexadienes is being reported .Their chemistry demonstrates an astonishing relationship to the corresponding olefinic compounds.

Phospha-carba-oligo-enes are deducted from aliphatic enes by means of substitution of individual CH-moieties with sp^2 hybridized phosphorus atoms, creating (PC) double bonds in conjugation with other (P=C) and (or) (C=C) sequences. These compounds can mainly be prepared by intra- and intermolecular condensation of HCl, Me_3SiCl or $(Me_3Si)_2O$ between chlorophosphanes, silylphosphanes and carboxylic acid chlorides, often followed by silyl migration reactions.

Up to now monophosphabutadienes with the phosphorus in position 1 and 2[1,2,3,4,5], three diphosphabutadiens ,the 1,3[6.7], 2,3[8,9,10,11] and 1,4 [12a]diphosphabutadienes could be prepared as stable compounds . In the series of triphosphabutadienes only the 1,2,4 -triphospha-butadiene is known[12b].The other 1.2.3-triphosphabuta-1,3-diene is suggested as an intermediate, but in an intramolecular [2+2] cycloaddition yielded the first 1,2,3-cyclobutene according to scheme 1[13,14].

A key compound for the synthesis of substances exhibiting the molecular structure of phosphapentadienes proved to be the phosphaketene Ar-P=C=O. The reaction on bis-(trimethylsilyl)phosphanes in the ratio of 2:1 leads to the class of 1,3,5-triphosphapenta-1,4-dienes [15] . Aryl-, alkyl- as well as alkenyl-bridged bis(triphosphapentadienes) - the latter after multiple addition of the phosphaketene on bis(trimethylsilylphosphanes) - are available by this method. Compounds with the skeleton of 2,3,4-triphosphapentadienes could be stabilized as Mo- and Ni-complexes[2,16].



(44)

The synthesisof 1,3,4,6-tetra- and 1,6-diphosphahexadienes have been reported at earlier meetings in Durham and Nice[17,18].These compounds show the phenomenon of a fluctuating bond skeleton which was identified as a phospha-Cope--rearrangement. That the Cope-rearrangement of these two phosphahexadienes is not an isolated affair could be verified by additional phosphahexadienes exhibiting different phosphorus-carbon -skeletons. A compound with the 1,3-diphosphahexa-1,5-diene structure could recently be prepared in a reaction of a chloro-1,3-diphospha-2-propen with 2-butenyl magnesium chloride. At temperatures above 40°C valenceisomerisation under splitting of the central PC bond takes place[19].

The behaviour of monophosphahexadienes was also included in these studies. 3-phosphahexa-1,5-dienes could be prepared in a reaction of styrylchlorophosphanes with crotyl, allyl or cinnamyl magnesium chloride. Prolonged heating to 100° C causes an irreversible rearrangement to the 1-phosphahexa-1,5-dienes[20].

All pericyclic reactions under participation of the PC double bond like [2+2] cycloadditions, Diels-Alder-reactions and Cope rearrangements proceed from the 2-coordinated to the more stable 3-coordinated phosphorus.The inverse valence isomerisation from 3 to 2coordinated phosphorus could be observed with a 3,4-diphosphahexa-1,5-diene. This valence isomerisation is supported by bulky substituents at both P atoms. While the tert.butyl substituted distyryldiphosphane does not show any tendency towards a Cope rearrangement, but the tri-tert.butylphenyl substituted compound does[21]. While warming up to room temperature the ^{31}P signals in the area of phosphanes at -15 and -21 ppm disappear and new signals in the so typical area for phosphaalkenes at 258 and 255 ppm raise. These signals are associated with the racemic and meso form of the 1,6-diphosphahexa-1,5-diene proved by X-ray analysis.

Valence isomerisation could also be observed with the phosphapropargyl system. A 3,4-diphosphahexa-1,5-diine was transformed via a thermal isomerisation into the 3,4-bis(phosphamethylene)-1-cyclobutene. Reaction of chloro(phenylethynyl)phosphane with tert.butyllithium yields 3,4-diphosphahexa-1,5-diine nearly pure with respect to diastereomeres, which can be characterized by a ^{31}P nmr signal at -41 ppm. Above 10°C the compound reacts to the cyclobutene showing a ^{31}P signal at 170 ppm. The structure could be proved by X-ray analysis [20,22].

This rection path corresponds to the preparation of 3,4-bis(methylene)cyclobutenes from 1,5-hexadiines via a thermal isomerisation. Transferring the mechanistic picture developed for this preparation on the formation of the bis(phosphamethylene)-cyclobutene primarily one gets 1,6-diphosphahexatetraene after a Cope rearrengement of 3,4-diphosphahexa-1,5-diine. A [2+2] cycloaddition follows, ending up with the cyclobutene.

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