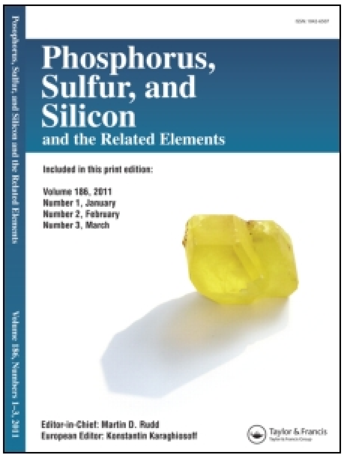

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# Pericyclic reactions with participation of the (PC)-double bond

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# PERICYCLIC REACTIONS WITH PARTICIPATION OF THE (PC)-DOUBLE BOND

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Abstract Equilibrium between the tetraphospha-bicyclo[2.2.0]hexane and tetraphosphahexadiene-structure, opening of CC-bonds in organic ringsystems by [3.3]-sigmatrope rearrangements, Diels-Alder-reactions with phosphaalkenes.

At earlier meetings in Halle[1] and Durham[2], the distinct properties of the tetraphosphahexadienes, generated in the reactions of disilylphosphanes and phosgene or isocyanide dichlorides resp., were reported. The O-silylated compounds, formed in the phosgene-reaction,react spontaneously to the bicyclohexan-skeleton, whereas the N-substituted derivates do not. Instead they show the phenomenon of a fluctuating bond skeleton which was identified as a phospha-Cope-rearrangement.(FIGURE 1) In order to elucidate the influence of the substituents at the bridge-C-atom on the course of the reaction, a tetraphosphahexadiene was synthesized, the one part of which (PCP-allene) was O-substituted whereas the other one was N-substituted. A slight variation of the reaction parameters (solvent,temperature) lead to the isolation of two isomeric compounds. The colourless one was identified as the tetraphosphabicyclohexane by x-ray structure determination and by solid-state

$^{31}$P-nmr-spectroscopy, whereas the yellow one could be recognized as the open-chained tetraphosphahexadiene. According to $^{31}$P-nmr-spectroscopic experiments in solution an equilibrium between the two species is quickly achieved. (FIGURE 2)

FIGURE 1

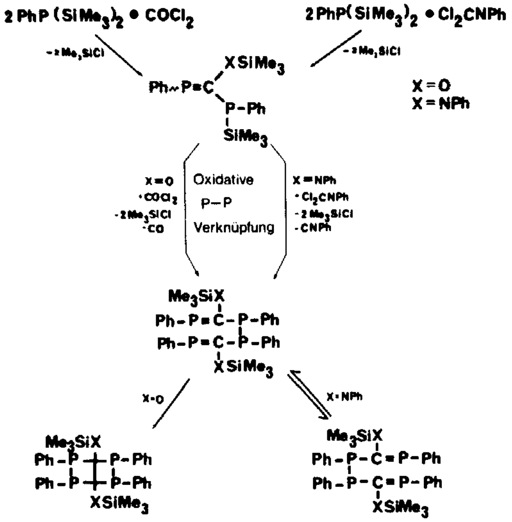
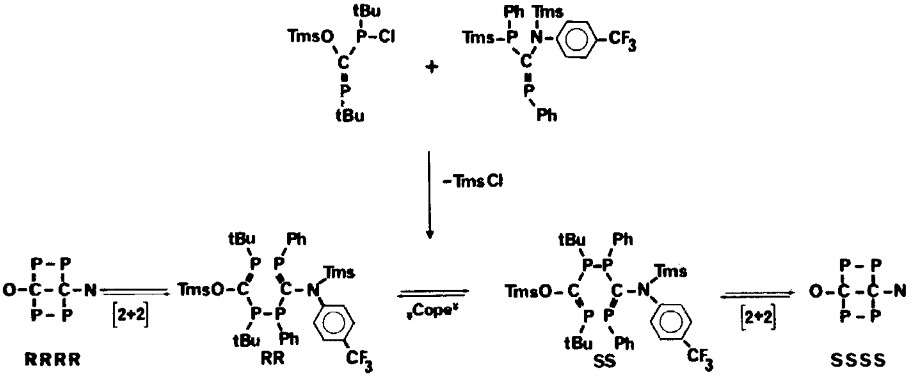


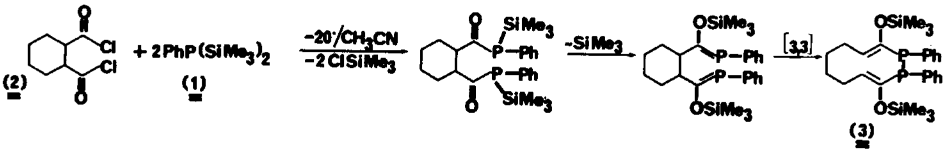
FIGURE 2

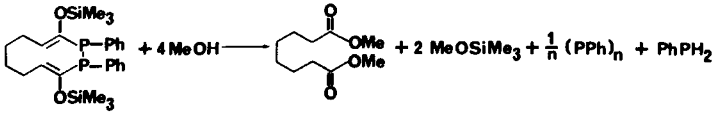


To our knowledge this is the first example of a dimerization and new formation of two (PC)-double bonds in a dynamic equilibrium of intramolecular[2+2]-cycloaddition and the retro-reaction. The fluctuating bond system, interpreted as the Cope-rearrangement could be proved by means of $^1$H-nmr temperature measurements as well in the case of the mixed O/N-substituted tetraphosphahexadiene.

In order to further remove the doubts on the phospha-Cope-rearrangement and to lay stress on the general validity of this reaction we examined the cleavage of (CC)-bonds by phospha-Cope-rearrangements in organic ring compounds in analogy to the reaction between succinyl dichloride and disilylphosphane already reported in Durham[2] .

For the first time the ring opening could be demonstrated by the reaction of phenyl(bistrimethylsilyl)phosphane with trans-1,2-cyclo-hexanedicarboxylic acid dichloride. According to equ. 3 the ten-membered ring of the 1,2-diphosphadecadiene-3,9 is obtained in a yield of 75%.





Other examples were found in the reactions of the 1,2-dicarboxylic acid dichlorides of the rings: cyclobutane, norbornene and bicyclo[2.2.2]-2,3:5,6-dibenzo-octadiene-(2,5), which proceed via[3.3]sigmatropic rearrangement, ring opening and formation of the cyclic diphosphanes.

Diels-Alder-reactions of various phospha-alkenes with dimethyl-butadiene take place easier than with olefins in high yields already at low temperatures. Two stereoisomeric 1,2,5,6-tetrahydro-$\lambda^3$-phosphorines are obtained which can be converted thermally into each other. In the case of a selective reaction the[4+2]-cycloaddition with cyclopentadiene can be used to determine the molecule-geometry (E/Z-isomeres) of the often oily phospha-alkenes via the x-ray structure determination of the crystalline additionproducts. The retro-Diels-Alder-reactions of the additionproducts with cyclopentadiene indicate a concerted reaction.

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