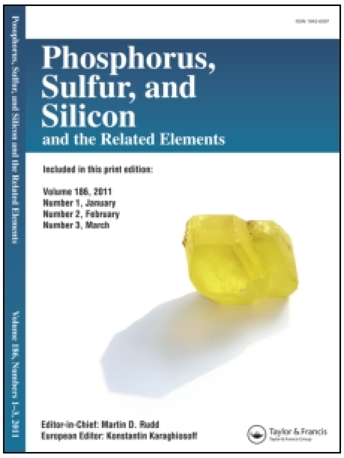

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Valence Isomerization Of Phosphaalkenes

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To cite this Article Appel, Rolf , Barth, Volker , Paulen, Wilfried and Knoch, Falk(1986) 'Valence Isomerization Of Phosphaalkenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 26: 1, 1 — 13

To link to this Article: DOI: 10.1080/03086648608084564

URL: http://dx.doi.org/10.1080/03086648608084564

Phosphorus and Sulfur, 1986, Vol. 26, pp. 1–13
0308-664X/86/2601-0001/$20.00/0

VALENCE ISOMERIZATION OF PHOSPHAALKENES

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The main topic of this lecture is valence isomerization with participation of the PC-double bond. This is a matter of intramolecular structure conversion which takes place under shifting of σ- and π-bonds. This phenomenon was at first observed in the reactions of disilylphosphanes with phosgene and isocyanide dichlorides.

As actually expected the reaction with phosgene proceeds stepwise and some of the intermediates can be isolated. The first step is a simple trimethylchlorosilane condensation. Of course, the acylphosphane is not very stable, so with a second molecule of silylphosphane it reacts to 1,3-diphosphapropene. Until lately it was not clear whether this stage was achieved by intramolecular trimethylchlorosilane condensation yielding the phosphaketene followed by an addition to the CO-bond or by an intramolecular condensation. Only recently we succeeded in finding evidence and finally in isolating the first representatives of the phosphaketenes so that this pathway could be proved (Figure 1).

The 1,3-diphosphapropenes are indeed isolable, but as highly reactive compounds, they condense with excess of phosgene at the silylated P-atom. By elimination of CO and trimethylchlorosilane an oxidative P—P-linkage forms, generating tetraphosphahexadienes, which are not stable in this particular case. They react according to the principle of a [2 + 2]cycloaddition to yield a bicyclohexane-skeleton (Figure 2). Further reaction with phosgene finally leads to destruction of the molecule forming CO and organyldichlorophosphane.

The first reaction steps with isocyanide dichlorides coincide completely. The *N*-substituted 1,3-diphosphapropenes are formed, which react with excess of isocyanide dichloride–as before with phosgene–to the P—P-bridged compounds. By trimethylchlorosilane- and isocyanide-elimination, the tetraphosphahexadienes are generated, which are now stable without showing any tendency to form cyclic products. They show interesting phenomena which can be demonstrated by ^{31}P-NMR-spectroscopy which will be discussed in detail (Figure 3).

At room temperature the ^{31}P-NMR-spectrum shows the characteristic substructure of a four-spin system of the AA′XX′-type. The left signal group at +258 ppm (low field) is assigned to the phosphorus with the coordination number two, the right group at −12.3 ppm (high field) to the tervalent diphosphane phosphorus. Additionally, a broad signal at +115.7 occurs. Cooling to −70°C results in splitting of the broad signal. In addition to the signals already present, another four-spin system of the same type appears, with the left part arising from the phosphorus of coordination number two and the right-hand signals from the diphosphane phosphorus.

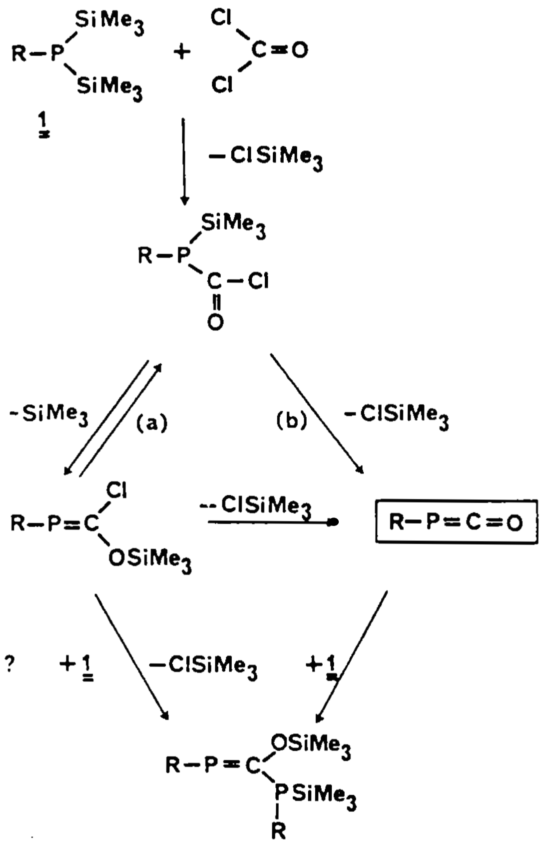


FIGURE 1

Upon cooling to −80°C or lower, the outer groups disappear completely, since this substance crystallizes at −80°C. If the crystals are filtered at low temperature and redissolved, only the spectrum of the separated form with the exterior signals is obtained. On warming, the interior groups of signals appear again and at +30°C the spectrum originally recorded at this temperature is reproduced.

These findings can be interpreted as follows. Because the compound is uniform, according to elemental analysis and molecular mass determination, the compound indicated by the broad absorption at +115.7 ppm must be of an isomeric form.

The splitting of the absorption into another AA′XX′ multiplet also indicates that this species must be a diastereoisomeric tetraphosphahexadiene derivative, since the characteristic signal groups of the phosphorus atoms with coordination number two and three appear.

The reason for the appearance of two diastereoisomers, which can be converted into one other, is that the tetraphosphahexadiene is a diphosphane with symmetrically different substituents that has two chiral centers at the threefold-coordinated phosphorus atoms and so yields a mixture–similar to tartaric acid–of the meso and the racemic forms.

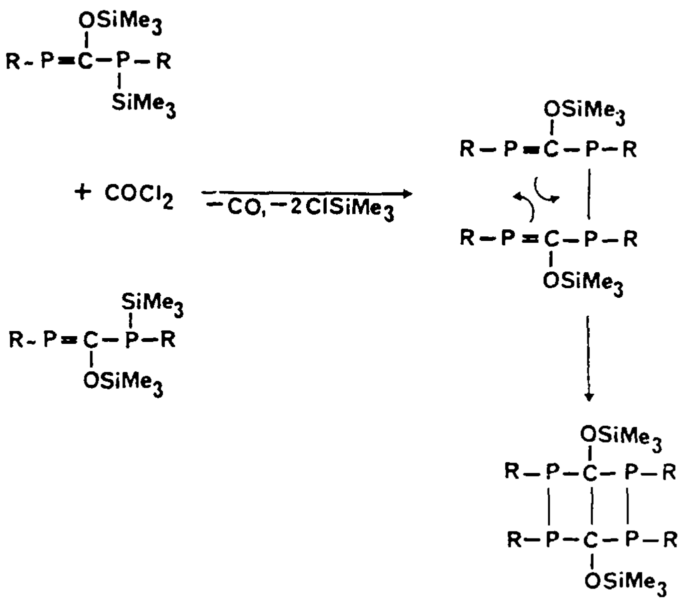


FIGURE 2

The reversible coalescence of the signal groups of the diphosphane (A′) and the methylenephosphane (X′) indicates the concerted conversion A versus X and X versus A, whereas the spectrum AA′XX′ of the other form remains unchanged. These experimental findings agree only with the hypothesis that the coalescence of the ^{31}P-NMR-spectra is due to a pericyclic reaction, which is known as the Cope rearrangement in the case of hexadiene-1,5. By [3.3]-sigmatropic rearrangement the P—P-bond closes between the phosphorus atoms, which at the beginning were twofold coordinated (Figure 4).

A centrosymmetrical coalescence of the original signals due to the phosphorus atoms with coordination number two and three occurs, because it is a degenerate rearrangement and the bond exchanges happen faster on the time scale of NMR measurement at ambient temperature.

The explanation for observing the coalescence phenomenon only with one diastereoisomeric form is obvious. Only one of the two configurations has the conformation that fulfills the stereochemical requirements for the Cope rearrangement. That is – as can be demonstrated by the model – the racemic form. So, if that is correct, the crystals filtered at low temperature which do not show the coalescence phenomenon, should represent the meso-form. This can indeed be proved. The X-ray structure determination with the crystals precipitated at low temperature confirmed the meso-form, all substituents are arranged trans to the P—P-bond.

Coming back to the starting point concerning the different reactivities of the two tetraphosphahexadienes, one realizes that the O-silylated compounds react spontaneously to the bicyclohexane structure, the *N*-substituted show the phenomenon of a fluctuating bond system. Obviously, the observed different pathways of reaction are controlled by the substituents at the bridging C-atom.

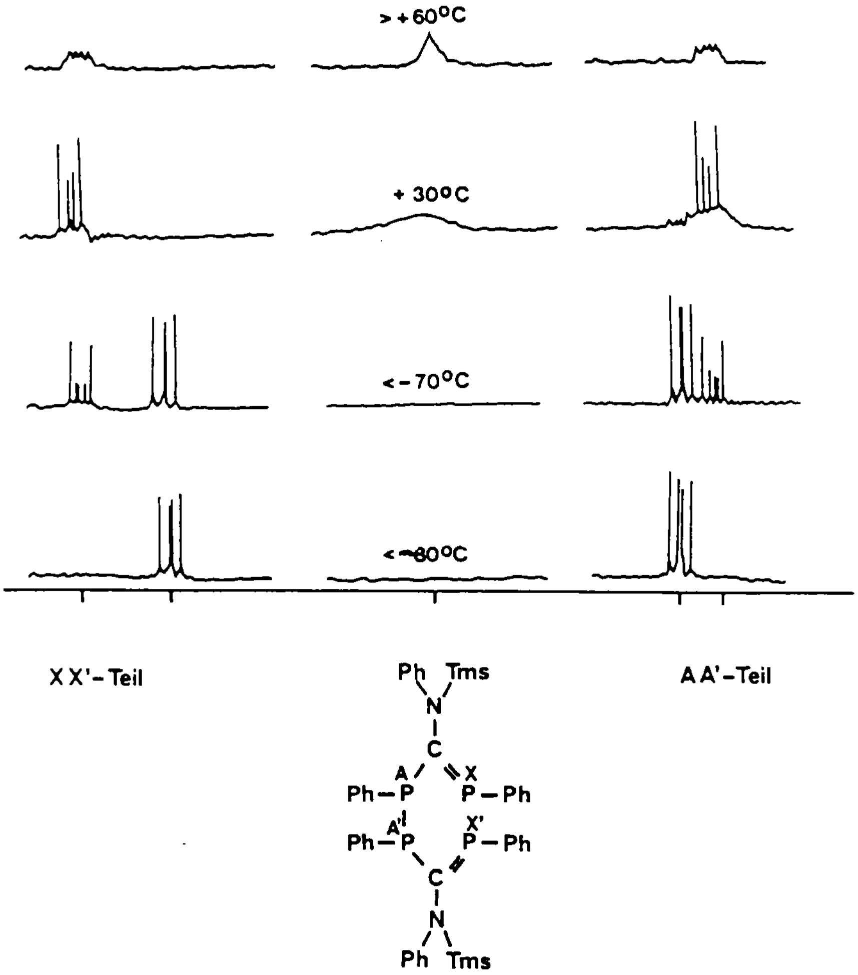


FIGURE 3

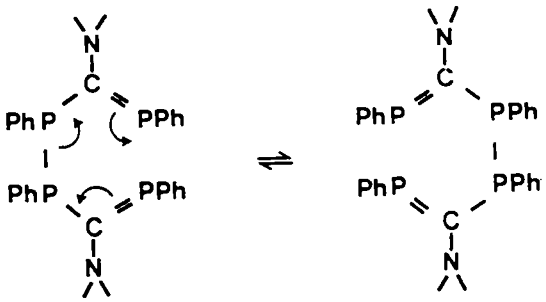


FIGURE 4

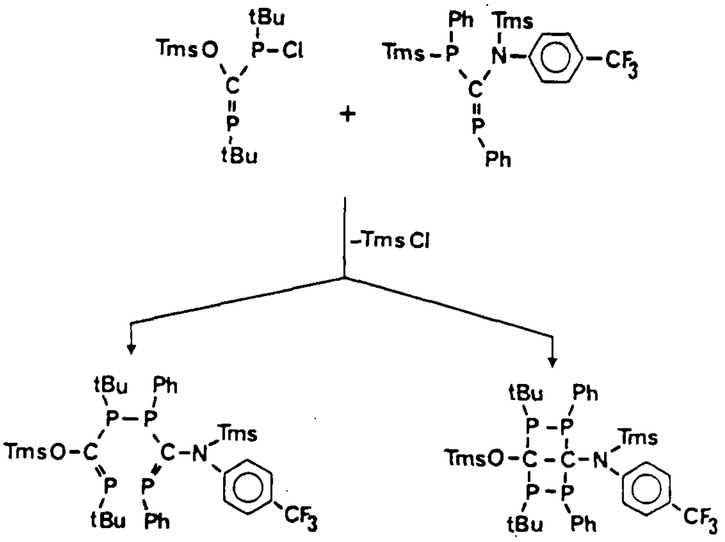


FIGURE 5

Further information regarding this question was expected from a cross experiment synthesizing a tetraphosphahexadiene which is *O*-substituted in one half and *N*-substituted in the other half. What could be expected in this case?

The difficult synthesis of this target molecule was achieved by treating the thermally very instable chlorosubstituted phosphano-methylenephosphane with the highly reactive silylphosphano-substituted methylenephosphane. Now the interesting question whether the isolated compound was a bicyclic or an open-chain substance and whether it would show the Cope rearrangement could be answered by X-ray structure determination and NMR experiments as follows (Figure 5).

The crystals obtained by this synthesis were colorless, which was an indication of the bicyclic structure. This presumption was confirmed by the X-ray structure analysis as well as by ^{31}P-NMR-spectra in the solid state; the latter did not show signals in the characteristic area for the phosphorus of coordination number two.

These findings do not agree with the NMR experiments executed in solution. Yet the intensively yellow to red-brown coloring during the dissolution process of the colorless crystals is evidence for further reactions depending upon dissolving the compound.

At ambient temperature the proton decoupled ^{31}P-NMR-spectrum shows, besides the expected four-spin system of the ABCD-type in the phosphane-area for the bicyclic compound, four additional broad signals, two in the same phosphane region and two more downfield shifted as is characteristic for phosphaalkenes (Figure 6).

If the ^{31}P-NMR-spectrum is recorded at $-60°$C, these broad signals split to a further four-spin system with ABCD character.

This four-spin system has to be attached to the tetraphosphahexadiene according to the characteristic downfield shift of the CD part and the characteristic habitus of the spectrum. The reversible broadening of the signals above $-50°$C indicates a dynamic process, which was realized as the Cope rearrangement previously.

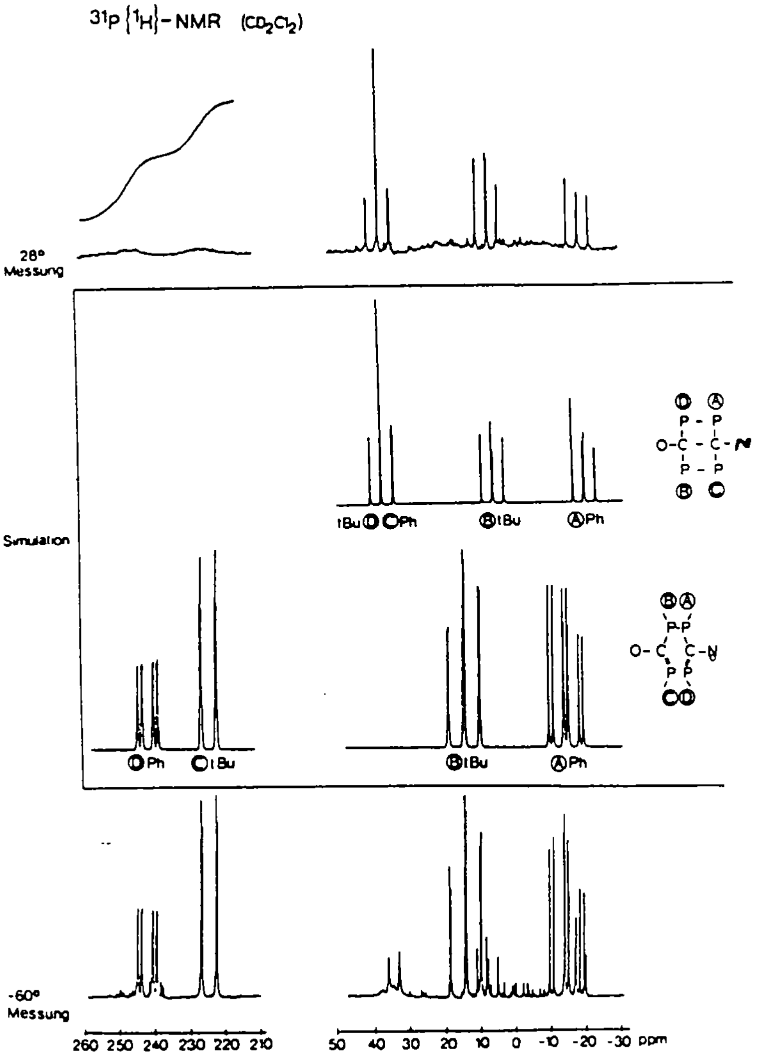


FIGURE 6

The ^{31}P-NMR-spectrum shows that the exchange is slow at ambient temperature. The experiment to find coalescence at high temperature in the ^{31}P-NMR-spectrum – so as to achieve a fast exchange – failed because the compound decomposed. However, to prove the phospha-Cope rearrangement securely with this example, we referred to a ^{1}H-NMR-temperature-run, making use of the fact that the coalescence temperature depends on the shift difference in Hz of the signals which are to collapse. The lower the temperature, the smaller the shift difference.

As confirmed by ^{31}P-decoupled ^{1}H-NMR at 90 MHz, the coalescence occurs at 22°C, equivalent to an activation energy of 14.7 ± 0.3 kcal/mol.

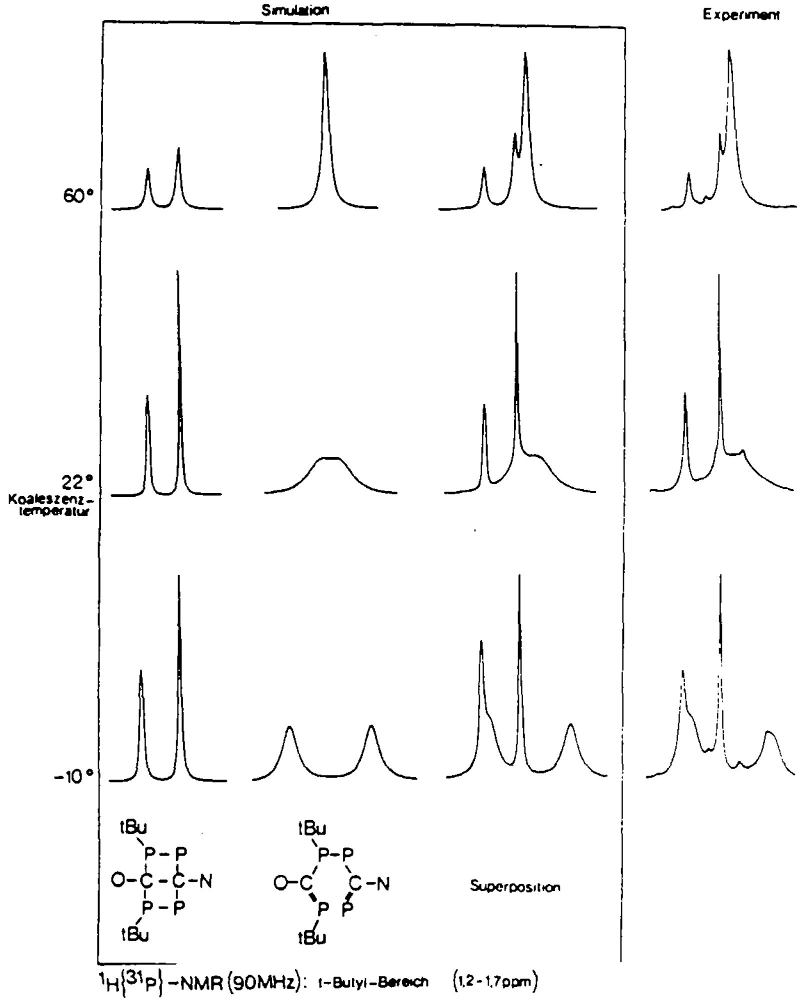
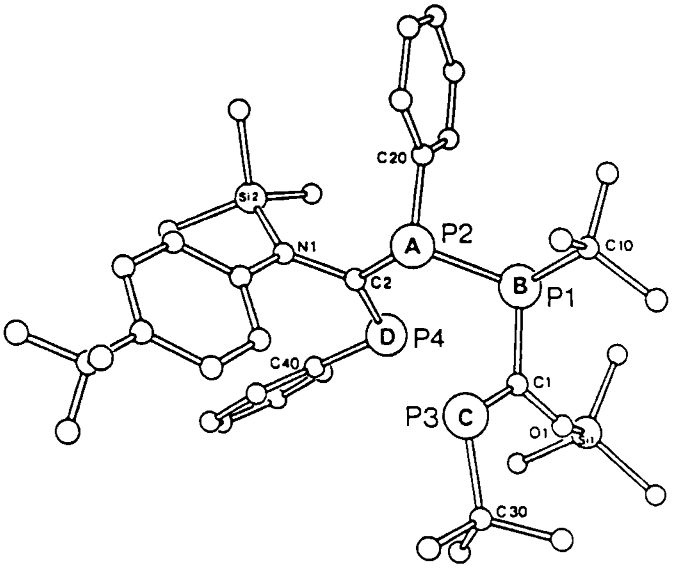


FIGURE 7

The illustration, showing only the protons of the *t*-butyl group, demonstrates the good agreement between the calculated and the experimentally observed spectrum (Figure 7).

The most impressive proof for the existence of the tetraphosphahexadiene, which exists in an equilibrium with the bicyclic form in solution, could be achieved by the isolation of the crystalline yellow isomer so that an X-ray structure analysis was possible (Figure 8).

According to the X-ray structure analysis and NMR in the solid state, the substance crystallized from benzene is homogeneous. If resolved afterwards, both forms will again be detected by ^{31}P-NMR. The same result applies to the colorless substance, which crystallized from toluene and which was shown to be the bicyclohexane derivative by X-ray analysis and NMR in the solid state.



Abstände	in pm	Winkel	in°
C1–P3	166.8(7)	O1 C1 P3	125.0(5)
C2–P4	168.1(6)	P1 C1 P3	121.4(4)
C1–P1	185.3(6)	O1 C1 P1	113.5(4)
C2–P2	186.4(6)	P4 C2 N1	127.8(4)
C1–O1	136.0(8)	P4 C2 P2	120.6(3)
C2–N1	142.7(8)	P2 C2 N1	111.3(4)
		C40 P4 C2	107.0(3)
		C30 P3 C1	108.6(4)

FIGURE 8

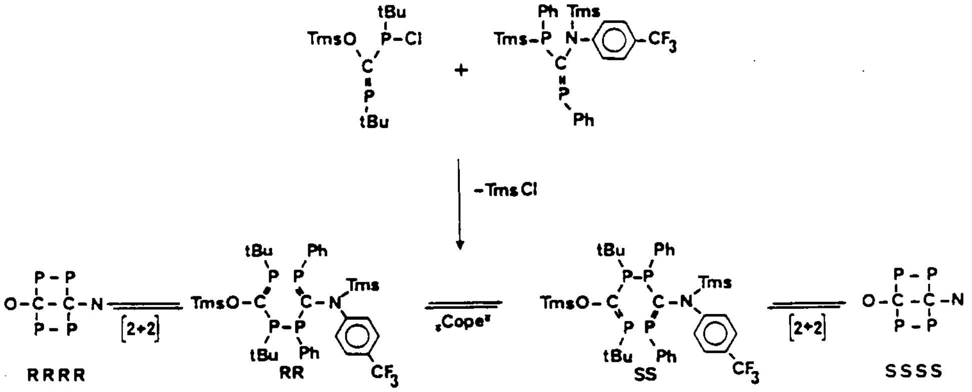


FIGURE 9

Here again, after a new dissolution, one finds both forms as well.

As a result of these experiments, we have established the first example for dimerization, or rather new formation, of two PC-double bonds by permanent change of intramolecular [2 + 2] cycloaddition and [2 + 2] cycloreversion (Figure 9). The proof for the valence isomerization is due to the convenient thermodynamic data of this system. The entropy factor is always in favor of the flexible tetraphosphahexadienic form because of the rigidity of the bicycle. Therefore, the valence isomerism is evident if the enthalpy of the bicycle is lower than the enthalpy of the hexadiene. That this is the case is shown in the energy diagram (Figure 16). By raising the temperature, the influence of the enthalpy factor becomes greater till the enthalpy process is compensated.

With these experimental findings we cannot answer the question about the reaction mechanism. We have to consider two possibilities: In addition to the concerted mechanism, in accordance with the Woodward-Hoffman rules, a nonconcerted mechanism with the 1,4-tetraphosphacyclohexanediyl radical as an intermediate. The first possibility can be checked by stereochemical analysis of educt and product in consideration of the strict stereochemical control of concerted reactions. Without photochemical influence on the reaction, one expects a geometrically difficult but symmetry-allowed [2a + 2a] process for a thermally inducted process.

According to the Woodward-Hoffman rules, tetraphosphacyclohexadiene with the same configuration at the P-atoms would be generated from the tetraphosphahexadiene with ERRE-configuration, but one of its carbon atoms changes the configuration by antarafacial attack. Indeed only the RRRR tetraphosphabicyclohexane is formed out of the ERRE tetraphosphahexadiene and corresponding to that the SSSS-bicycle out of the ESSE isomer. Therefore, the isomerization is stereospecific in a very high degree (Figure 10).

The geometry of the transition state of the analogous carbon skeletons provides an objection to a symmetry-allowed [2s + 2a] process. Based on kinetic investigations and thermodynamic estimations of the Arrhenius parameters of 1.4-cyclohexane-diyl radicals for the isomerization of bicyclo[2,2,0]hexane skeletons, many suppose a

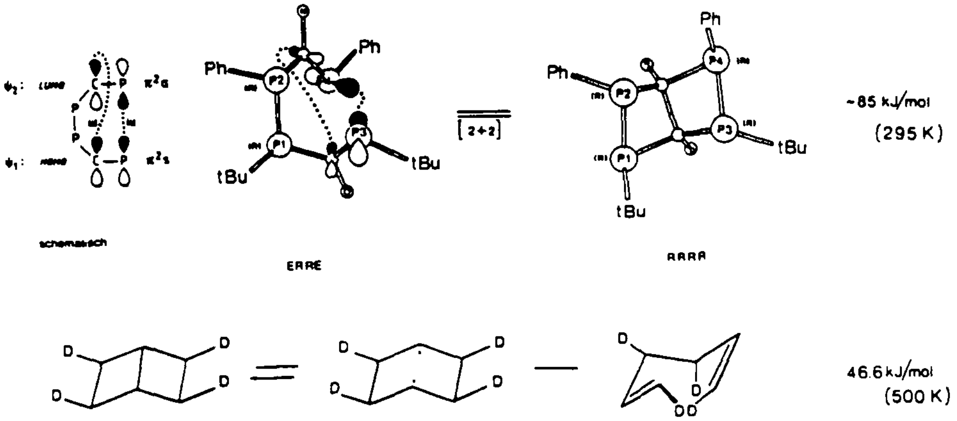


FIGURE 10

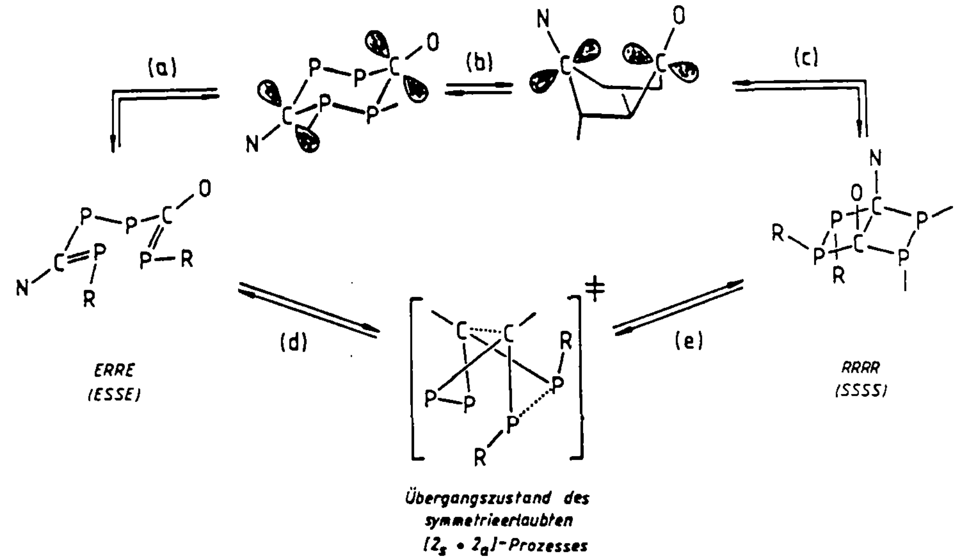


FIGURE 11

step-by-step mechanism with preliminary cleavage of the strained σ-bond, although the stereochemistry would also allow a [2s + 2a] process; however, radicals could not be demonstrated by ESR-spectroscopy or interception reactions. Also, in the case of the tetraphosphabicyclohexane, which we investigated, ESR-spectroscopy brought out no evidence for the existence of radicals.

Transfer of the conceptions derived from the carbasystem to the isomerization of the tetraphosphabicyclohexane system explains the observed stereochemistry, if the diradical generated from the tetraphosphabicyclohexane turns from the boat to chair-conformation as is shown in the upper line of Figure 11.

Experiments to allow a decision in favor of a step-by-step mechanism by considering the activation energy are based on the following calculations.

In a step-by-step mechanism the reaction starts with the cleavage of the central CC-bond. Therefore, the free activation enthalpy for this process should be comparable with the activation parameters of the analogous carbon skeleton, because the central CC-bond is cleaved first in both cases.

A comparison between the values described in the literature for the carbasystem and the experimentally found values for the tetraphosphahexadiene-system shows that the activation energy of the unsubstituted bicyclohexane is 62 J/mol more than the corresponding value of the tetraphosphabicyclohexane. To conclude from this strong difference between the carba- and the phospha-system that the valence isomerization is a concerted, symmetry allowed process is incorrect for two reasons.

Firstly, only the unsubstituted carbasystem was compared with the substituted tetraphospha-compound, though it is well known that the substituents in positions 2 and 5 lower the energy threshold essentially in comparison with the unsubstituted compound. Secondly, the value for the activation energy of the cycloreversion depends on the strain energy of the cycles concerned. The higher the strain energy, the lower is the activation energy of the cycloreversion. For the tetraphospha-bicycle the strain energy is unknown, but in comparison with the carbasystem it is probably essentially higher, because the central CC-bond is considerably longer (161.7 ppm to 157 ppm). After these briefly discussed kinetic and thermodynamic facts, a decision in favor of one of the two mechanisms considered is not possible. A way to solve this problem may be an exact X-ray analysis of the two valence-isomeric compounds of this system. One can realize that in both compounds the substituents at the N-atom are arranged in one plane. From that one can derive sp^2-hybridization for the nitrogen atoms. Thus the free electron pair is situated in a *p*-orbital perpendicular to the plane. This *p*-orbital is able to conjugate with the π-systems, if the overlapping with unsaturated systems is big enough.

As shown by the molecular model, the open-chain tetraphosphahexadiene has a nearly planar orientation to the *p*-orbitals of the aromatic substituents. The expected conjugation with the C-atom of the aromatic substituents is indicated by the bond distance shortened by 139 pm and by the diminution of the exterior angle expected by considering the VSEPR-model (Figure 12). Figure 13 shows the orientation of the *p*-orbital of the bicycle. The dieder angle of the aromatic substituent is 69°, so a conjugation with the *p*-orbital has to be excluded, which is also indicated by the normal N—C-distance of 144.5 pm and the exterior angle, which is 5° enlarged.

From the orthogonal position of the two planes Si_2, N_1, C_{50} and C_1, C_2, N_1 (89°) can be derived the mainly parallel orientation of the central CC-bond. From this an interaction with the orbitals of the C-atom in the sense of a hyperconjugation can be inferred, which is important for molecules in the transition state as Dewar found. During the homolytic cleavage of the CC-bond, the π-orbital is predestined for the stabilizing of the diradical intermediate according to its advantageous orientation.

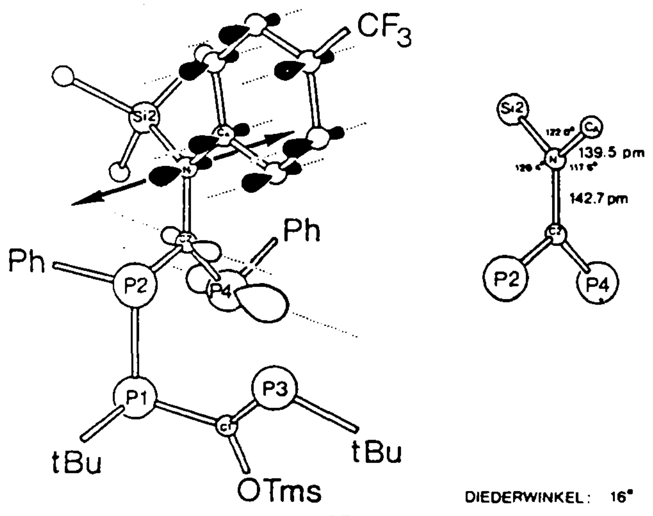
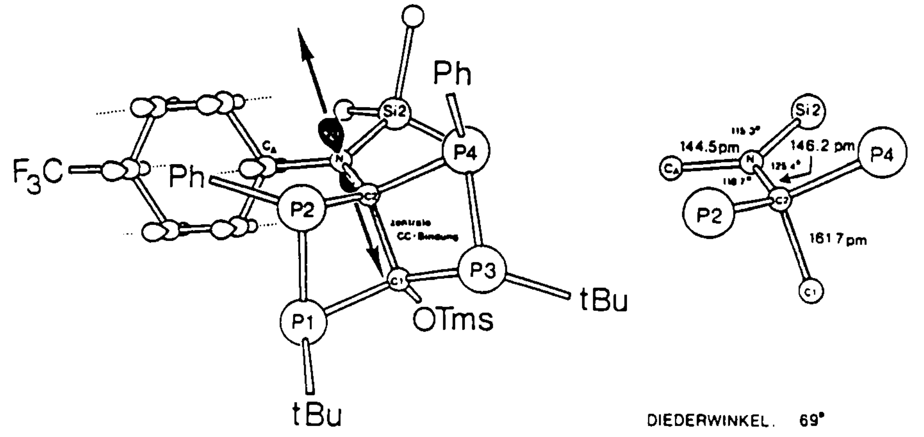


FIGURE 12



DIEDERWINKEL. 69°
EBENE C_A.N.Si_2/EBENE N.C_2.C_1: 89°

FIGURE 13

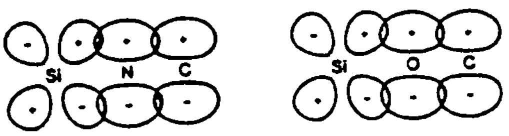


FIGURE 14

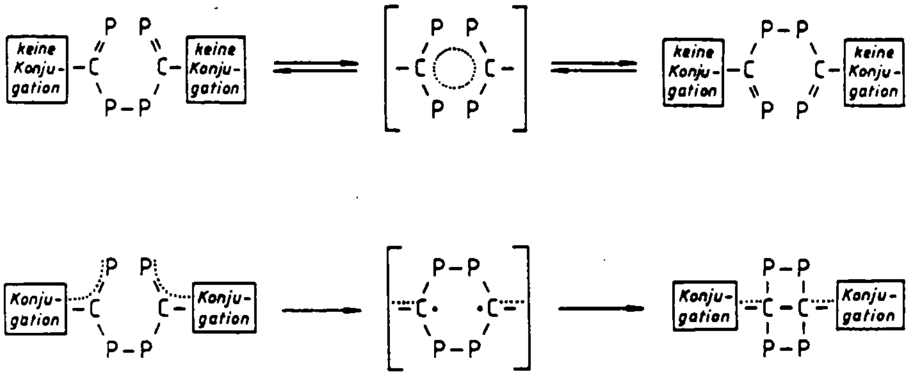


FIGURE 15

The stabilizing of the radical has to be considered as a kind of multiple-centered bond (3 centers, 3 electrons), in which free *d*-orbitals of the silicon take part as well (Figure 14). The trimethylsiloxy group has a similar stabilizing effect, because the oxygen too has a tendency to form coordinative *p*-bonds to the silicon.

Reservedly one may draw the conclusion that the [2 + 2]cycloaddition or -reversion takes place by a diradical intermediate, if the radical intermediate is substituted

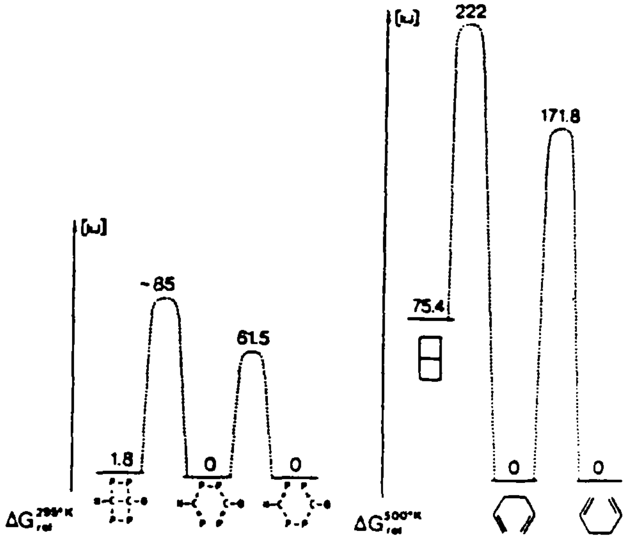


FIGURE 16

by groups which are able to stabilize it in positions 2 and 5 by mesomeric effects; if that is not the case, the equilibrium favors the tetraphosphahexadiene.

Summarizing, we can make the following statements about the interactions of the described equilibria. The substituents at the phosphorus atoms have no important influence on the reaction pathway. Decisive are the substituents at the two carbon atoms. If they are – on account of the hindered orbital overlapping – not able, to interact with the PC-double bond, a nearly aromatic transition state can be developed. If that is the case, because of the equilibrium, the tetraphosphahexadienes predominate. But if the substituents at positions 2 and 5 are able to conjugate with the PC-double bond, then – by mesomeric charge transfer into the branches of the molecule – the nearly aromatic transition state is hindered and a 1,4-tetraphosphacyclohexadiyl radical is formed on the way to the tetraphospha-Cope rearrangement, which reacts by recombination to the bicycle (Figure 15).

In Figure 16 the energy diagrams of the carba- and the tetraphosphacarba-system are confronted by one another. The comparison shows that in both systems the free activation enthalpy for the valence isomerization is essentially higher than the enthalpy for the Cope rearrangement. But it is evident too that the bicycle cannot be considered as an intermediate of the tetraphospha-Cope rearrangement. Cope rearrangement and valence isomerization are two independent equilibria with different activation energies.

For more information see: V. Barth, Dissertation Bonn 1983
W. Paulen, Dissertation Bonn 1984