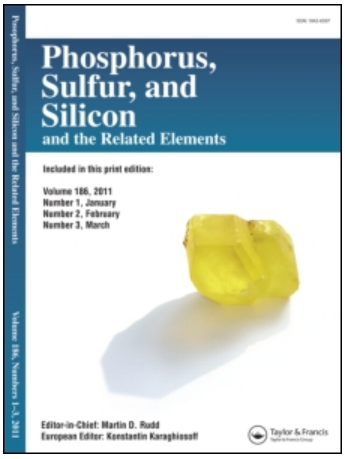


**Phosphorus, Sulfur, and Silicon and the Related Elements**
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# DYNAMIC STEREOCHEMISTRY OF SYMMETRICALLY BUT DIFFERENTLY SUBSTITUTED DIPHOSPHANES

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**To cite this Article** Appel, Rolf , Brück, Bruno , Knoch, Falk and Hünerbein, Johannes(1986) 'DYNAMIC STEREOCHEMISTRY OF SYMMETRICALLY BUT DIFFERENTLY SUBSTITUTED DIPHOSPHANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 27: 1, 55 — 64
**To link to this Article: DOI:** 10.1080/03086648608072758
**URL:** http://dx.doi.org/10.1080/03086648608072758

*Phosphorus and Sulfur*, 1986, Vol. 27, pp. 55–64
0308-664X/86/2702-0055/$15.00/0


# DYNAMIC STEREOCHEMISTRY OF SYMMETRICALLY BUT DIFFERENTLY SUBSTITUTED DIPHOSPHANES

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The main interest of our work in Bonn during the last years was in the field of phosphorus-carbon compounds with multiple bonds. Beside the synthesis of new classes of compounds we were particularly interested in the amazing analogy between the PC- and the CC-double bond, which could be proved by evidence of E/Z isomers and a clear indication of pericyclic reactions.

Among these reactions, the phospha-Cope-rearrangement with all its aspects was the one, which fascinated me most. This was first discovered with the 1,3,4,6-tetraphosphahexadiene, formed under condensation between isocyaniddichlorides and organyldisilylphosphanes.

After we had achieved some insight into the mechanism of this valence isomerisation, —I had given more details in La Tour de Carol (s. the proceedings)—there was, concerning the Cope-rearrangement, still a stereochemical problem left over.

We focused our interest upon the easy exchange of configuration between the meso- and the racemic forms, which show inversion of configuration at low temperatures. The meso compound, consisting of X-ray determinated uniform crystals, is no longer stable with respect to its configuration above $-70°C$ in solution. One detects signals due to the racemic compound, which because of the accelerating degenerated Cope-rearrangement merge at ambient temperature.

To study this problem on a less complicated system we looked for the dynamic stereochemistry of symmetrically but differently substituted diphosphanes. These compounds can be considered as simplified models of 1,3,4,6-tetraphosphahexadienes, showing also two chiral centres at the three valent P-atoms.

Indications of the less stable configuration of diphosphines with respect to the tertiary phosphanes can be found in the literature since 1966. Attempts to get insight into this phenomenon have been launched by McFarlane,[1] Lambert,[2] Albrandt,[3] Harris[4] and others in recent years. One reason given for the low stability of configuration, is the eased inversion at the chiral phosphorus atom due to bulky and mesomeric substituents. The other is a scrambling mechanism involving a cyclic transition state.

A disadvantage of these explanations based on proton and $^{31}P$ n.m.r. investigations is the lack of X-ray structure determinations of the diastereoisomers concerned. Up to now just a couple of diphosphane structures related to our problem have been investigated but in any case only one of the two possible diastereomeric compounds was isolated and proved by X-ray. The n.m.r. investigations constantly done in solvents like chloroform or methylendichloride were another disadvantage, since

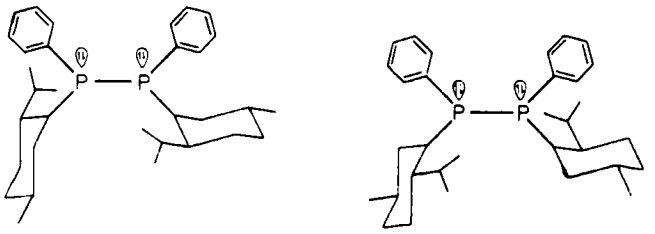


FIGURE 1

referring to a recent paper by Harris,[5] diphosphanes decompose therein within several days. The spectra of such contaminated samples are difficult to interpret.

Therefore we started to analyse this problem again under the following aspects. In order to test the exact configurations we searched for a differently but symmetrically substituted diphosphane, which crystallized at room temperature to encourage a X-ray structure determinations.

Three differently but symmetrically substituted diphosphanes which complied with the requirements are 1.2-dimethyl-1.2-diphenyl-diphosphane, 1.2-isobutyl-1.2-diphenyl-diphosphane and 1.2-di-tert-butyl-1.2-diphenyl-diphosphane.

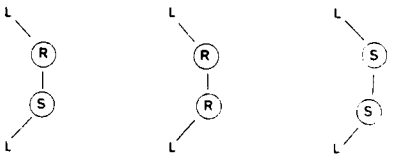
$^{31}P$ n.m.r. spectra of these compounds in solution show the expected signals for the two compounds, meso- and racemic form, but a preparative separation of the two compounds was impossible. In all cases only the meso R,S-compound crystallized from the solvent, exhibiting substituents all trans positioned.

Finally we succeeded in synthesizing a 1.2-dimethyl-1.2-diphenyl-diphospane suitable for our purpose to separate the diastereomers with the help of two additional chiral menthyl centers (Figure 1).

The number of possible isomers, which can be theoretically deducted from a synthesis of the diphosphane with two *L*-menthyl substituent exclusively are three stereoisomers similar to the tartaric acid. With respect to the P-atoms one should characterize the compound **1** as of pseudo meso, **2** and **3** of pseudo enantiomeric types (Figure 2).

The diastereoisomeric compounds synthesized according to the following scheme (Figure 3) were separated due to the different crystal habitus.

The needle like crystals, melting at 134°C exhibit the pseudo meso compound **1**, (Figure 4) the prismatic crystals, melting at 118°C, turned out to be the stereoisomer **2** showing the R,R-configuration on the P-atoms (Figure 5).



**1** **2** **3**

FIGURE 2

1.2-Di(*L* menthyl)-1.2-diphenyldiphosphane

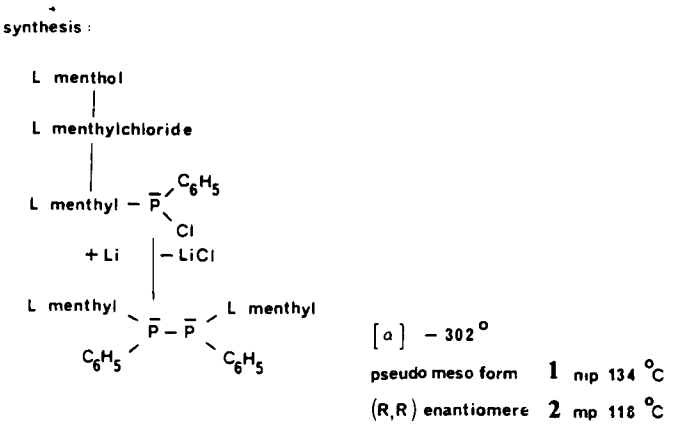


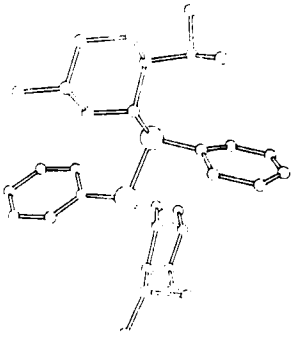

FIGURE 3



As can be seen from Figures 4 and 5, the substituents of the meso-compound are in the all trans position while the lone pairs of the racemic forms are in the trans position to each other. Expected $^{31}P$ n.m.r. spectra are compared with those actually found in this system (Figure 6).

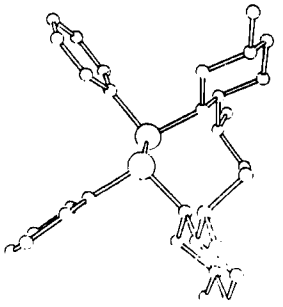
One expects an AB spin system like (a) for the P-atoms of the pseudo meso compound **1**, due to different surroundings. In contrary one expects a singulet for the R,R pseudo enantiomeric compound **2** like (b) because of identical surroundings. A different singulet like (c) should be seen for the S,S pseudo enantiomeric compound **3**, since the alternating effect works between the *L*-menthyl substituent and the P-atom of R- or S-configuration.

Solutions of the two types of crystals **1** and **2** in THF/acetone at 0°C in each case show only the expected AB-system (a) or the singulet (b) respectively. Above 5°C the interconversion of the two isomers of configuration becomes evident. The equilibrium is reached within one hour, demonstrating a ratio of 75% pseudo meso **1** to



pseudo meso form **1**

FIGURE 4



(R,R) enantiomere **2**

FIGURE 5

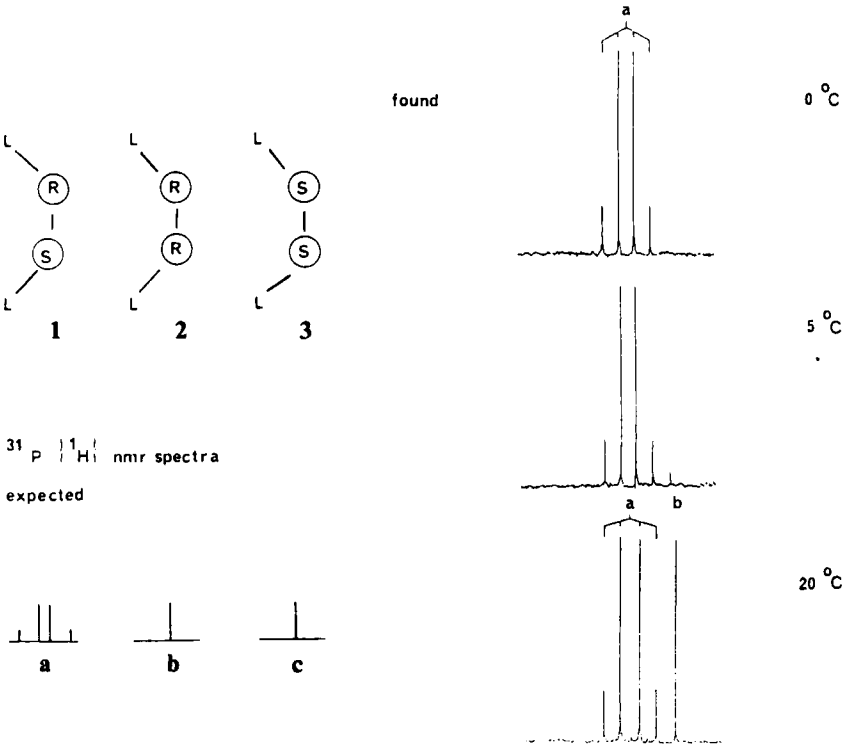



FIGURE 6



25% of the R,R-isomeric compound **2**. The signal (c) for the third compound, the S,S isomeric type **3** is absent.

The second series of experiments was carried out in exactly the same way as before with the diphosphane exhibiting *D*-menthyl substituents. As expected the difference could only be realized by measuring the optical rotation. Under equilibrium conditions this value was found to be +293° for the *D*-menthyl configurated compounds and −302° for the *L*-menthyl configurated compounds. Because of the enantiomeric correlation between **1** and **4** as well as **2** and **5** no further X-ray structure determination was undertaken.

Again one may consider the three theoretically possible isomers and their characteristic spectra. Of these isomers out of the *D*-menthyl type again only two can be detected. Compound **1** and **4** as well as **2** and **5** are enantiomeric to each other. Therefore the spectrum is identical with the one received from the *L*-menthyldiphospshane (Figure 6).

The inversion of configuration takes place at +5°C, equilibrium was established within 1 hour, like in the *L*-menthyl series. From these findings the conclusion can be drawn, that the inversion of configuration does not take place via a four centered mechanism including bond breaking. If this was the case, one should have seen beside the isomer **2** exhibiting the R,R-configuration at the phosphorus and the complementary one **3** showing the S,S-configuration (Figure 7).

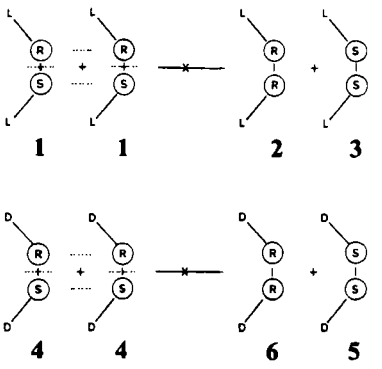



FIGURE 7

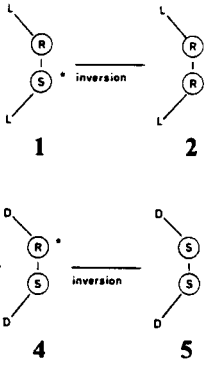



FIGURE 8

From these results we can definitely make the following statement: The P-atoms showing S-configuration in the *L*-menthyl group like **1** as well as the P-atoms of R-configuration in the *D*-menthyl group like **4** did invert with respect to their configuration (Figure 8).

Crystals of pseudo meso *L*-menthyl diphosphane **1** and of the meso *D*-menthyl diphosphane **4** have been dissolved in THF/aceton for another $^{31}P$ n.m.r. experiment. At ambient temperature only the previously and separately detected four diasteriomeric diphosphanes **1,4** and **2,5** can be seen. Assuming a four centered scrambling reaction for this system, one should expect—as elaborated in Figure 9—six additional stereoisomeric compounds: **3** and **6** as well as **7**, **8**, **9** and **10**. Therefore the theory asks for ten different stereoisomeric compounds, but because of the enantiomeric relationship only 6 should be n.m.r. detectable.

Let me explain this in a more specific way.

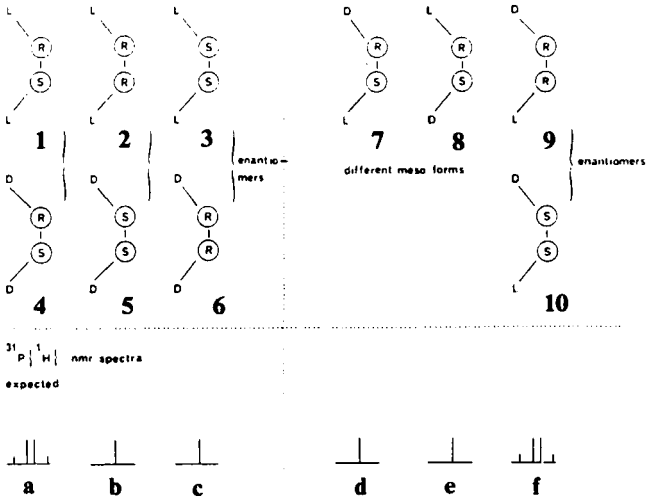



FIGURE 9

Pairs of compounds sharing a mirror relationship to each other (i.e. enantiomers) can of course not be separated by n.m.r. These are the pseudo meso compounds **1** and **4**. This can easily be understood, when **4** is turned 180° within the plane of the picture. These compounds give an $^{31}P$ n.m.r. spectrum showing only one AB spin system of four lines. The pair consisting of **2** and **5** is also enantiomeric, which can not be discriminated by n.m.r. and therefore shows up as a singulet.

The pair consisting of **3** and **6** is also a enantiomeric pair but diastereoisomeric against **2** and **5**. It should be seen in the spectrum as a signal (c) separated from (b).

The two stereoisomers **7** and **8** are real different meso compounds, because a mirror plane bisects the P—P bond rectangularly. So the $^{31}P$ n.m.r. spectrum registers two separated singulets (d) and (e) for the two diastereomeric compounds **7** and **8**.

The remaining stereoisomers **9** and **10** again form a real enantiomeric pair, which can easily be recognized turning the formula 180° within the plane of the picture. From there the $^{31}P$ n.m.r. spectrum shows four signals of a AB spin system (f).

What does the experiment prove?

No indications are to be seen in the $^{31}P$ n.m.r. spectrum for additional signals, it is identical with those gained from the single components. Therefrom we can draw the conclusion, that under the conditions like ambient temperature and in nonpolar solvents like benzene and THF/acetone no scrambling reaction takes place and no additional P-atom is converted.

A completely different situation occurs, if the experiment is carried out in deuterochloroform. Solving the crystals of the two pseudo meso compounds **1** and **4** at low temperatures, one detects in the $^{31}P$ n.m.r. spectrum first of all the signals of the AB spin system (a). Warming up to ambient temperature an additional singlet (b) appears at the expense of the signals due to the AB spin system. Up to this point the results in chloroform are consistent with those in THF. However inversion had taken place at only one P-atom (Figure 10).

After this it is very attractive to follow the time dependent change of the $^{31}P$ n.m.r. spectrum (Figure 11). Slowly additional signals come up. Within two hours the equilibrium is established as is seen in Figures 12 and 13. The analysis of the spectrum yielded 3 new compounds, two appearing as a singlet and one as a AB spin system. The additional signals can only be explained with a cleavage of the P–P bond. Adopting as an explanation the current opinion regarding the expiration of a cyclic scrambling reaction, we come to the scheme, seen in Figure 13.

Starting redistribution with **1** and **4** one ends up with compound **7** and **8** associated with the signals (d) and (e). The new AB spin system fits to the pair of enantiomeric compounds **9** and **10**, which can be generated from the diastereomers **1** and **4** in a way, demonstrated in the lower part of the figure. Out of the 10 diastereomeric compounds n.m.r. spectroscopically expected 6 are detectable but only 5 could be recognized, because **3** and **6** are absent.

Probably this combination of substituents do create stereochemical restrictions, which do hinder the necessary cyclic transition state. The control experiment, in which the diphosphane has been synthesized using racemic *D,L*-menthol with the intention to gain access to all the theoretically possible diastereomers, turned out to be in agreement with the results gained so far. Except the expected singlet of the stereoisomeric pair **3** and **6**, which again could not be observed, all other stereoiso-

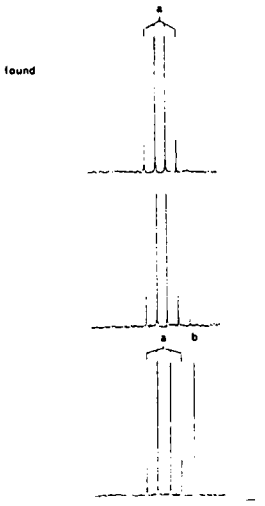



FIGURE 10

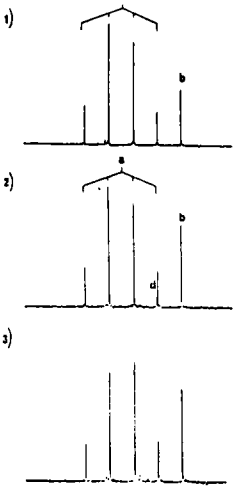



FIGURE 11

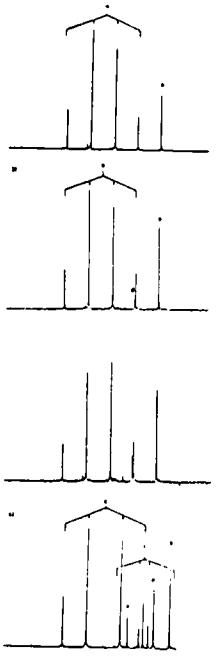


FIGURE 12



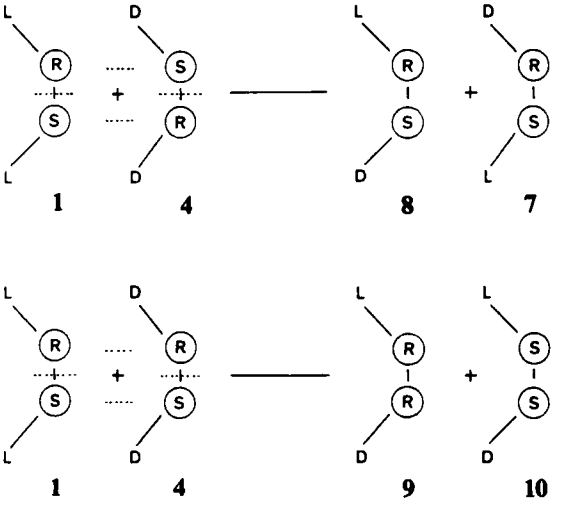



FIGURE 13

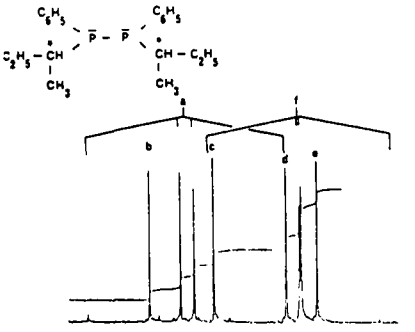


FIGURE 14

mers could be detected. The $^{31}P$ n.m.r. spectrum was identical with the one, gained via the scrambling experiment done in chloroform.

The assumption, the missing pair **3** and **6** is due to steric hindrance, could be proved indirectly by the synthesis of a 1,2-di(1-methylpropyl) 1,2-diphenyl diphosphane starting with a racemic mixture of the less bulky 1-methylpropyl substituents. Out of the 10 theoretically possible stereoisomers, the expected diastereoisomers could be correlated to the signals (a) to (f) (Figure 14).

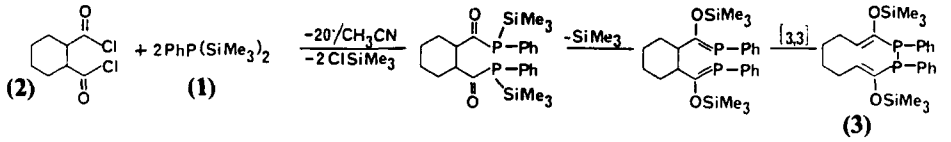


FIGURE 15

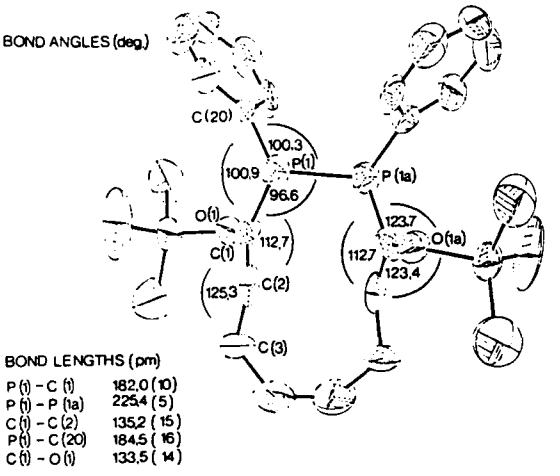



FIGURE 16

Our results can be summarized as follows: For the low stability of configuration of diphosphanes two different processes have been proved, which are solvent dependent in a characteristic way. In benzene and THF/aceton the change in configuration is due to the inversion of only one phosphorus atom. This is controlled by the stereochemistry of the substituents in so far, as only a selection of all the possible isomers may be seen.

In addition to that, a change of configuration in chlorine containing solvents like chloroform or dichloromethane takes place under scrambling reaction. There is no certain knowledge available about the mechanism of this scrambling process. So we can only speculate.

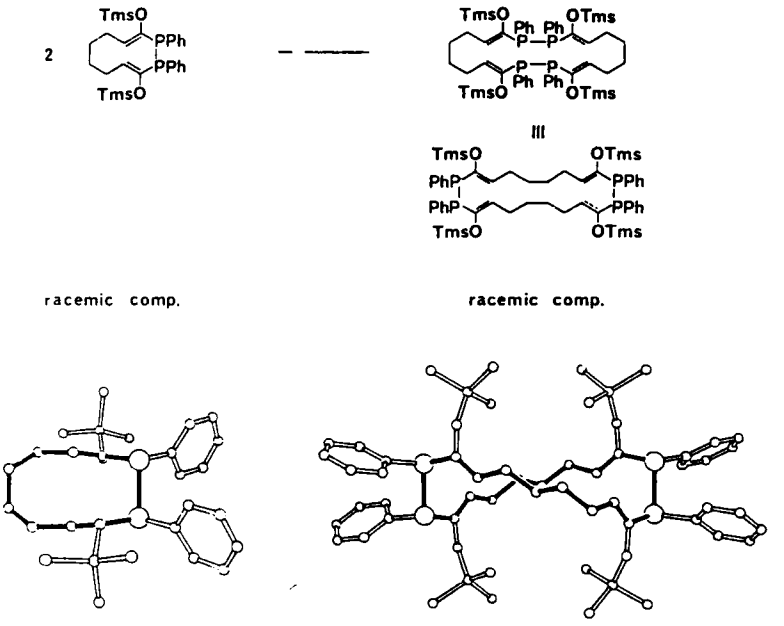



FIGURE 17

RING EXTENSION REACTIONS

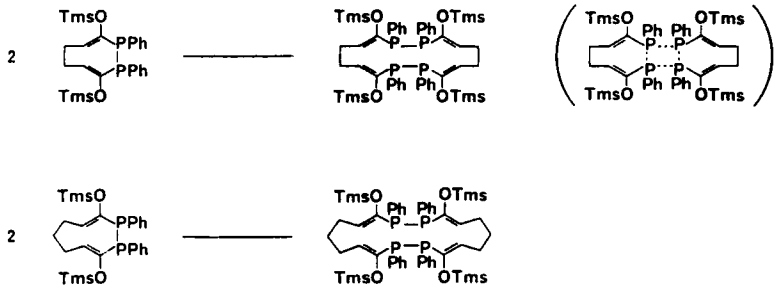



FIGURE 18

It is absolutely impossible to exclude the cleavage of the P—P bond being due to a very small amount of hydrogen chloride, particularly if one realizes the chlorine containing solvents, in which the scrambling takes place, are base sensitive splitting off hydrogen chloride very easily. In addition to that one should take into account that the P-centers, strongly shielded by bulky substituents—proved with models—are probably unable to participate in a cyclic transition state with overlapping alternating effects.

On the other hand there are of course points supporting the four centered transition state. Besides the fact, that addition of up to one third of chloroform to the THF solution does not initiate the scrambling reaction, there is evidence after all during the ring opening process of the phospha-Cope-rearrangement.

As can be seen from the Figure 15 the reaction of 1,2-cyclohexanedicarbonic chloride with organyl disilylphosphane first of all gives the diphosphaalkene, followed by a [3,3] sigmatropic rearrangement, ring opening involving a P—P combination and finally ends up with the 1,2-diphosphadecadiene-3,9, which was isolated and its structure determinated by X-ray analysis (Figure 16). This compound is not very stable in solution. Two molecules react doubling the ring size and forming the cyclic tetraphosphan (Figure 17).

Again this structure was proved by X-ray analysis. The only explanation for such a phenomenon is a four centered mechanism, in which two molecules are breaking and establishing new bonds with retention of orbital symmetry. The configuration at the double bonds are E,E orientated and the P-atoms R,R or S,S arranged respectively. Ring opening due to a phospha-Cope-rearrangement was established with two additional diphosphanes (Figure 18).

These not quite finished investigations regarding the dynamic stereochemistry of diphosphanes did strengthen one point: It is not acceptable to draw general conclusions with respect to the results collected from individual compounds. Next to the inversion at P-atoms, the scrambling mechanism may—indeed only in certain chlorine containing solvents—contribute to the amazingly easy change of configuration.



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