Thermal Ring Opening of Diphosphiranes: Experimental and Theoretical Approaches

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Thermal ring opening of diphosphiranes **1a–g** leading to 1,3-diphosphapropenes **2** by preferential P–P bond rupture is investigated. The experimental approach indicates that the regio- and stereoselectivity of the reaction depend on the nature of the ring substituents. For the unsymmetrical functionalized diphosphiranes **1a,b** only the trans-syn diphosphapropenes **2a,b** are quantitatively obtained whereas for **1c–f** the resulting trans-gauche diphosphapropenes are the major products. In addition to the trans diphosphapropenes, the corresponding cis isomers are formed for **1e,f**. The theoretical calculations (MNDO and ab initio) performed on unsubstituted derivatives reveal two preferred mechanisms involving exo-exo biradical or exo-endo radical intermediates. These two mechanisms allow the interpretation of all the experimental results.

1. Introduction

The chemistry of small, strained cycles, particularly that of cyclopropanes, has developed considerably over the last 30 years, as much in the experimental domain (cyclopropanation reactions) as in the theoretical. In the field of natural products, for example, the role of cyclopropyl groups in enzymatic mechanisms[1] has reawakened interest in ring-opening reactions.

The chemistry of phosphacyclopropanes is much younger,[2] and much theoretical and experimental work remains to be done on these new models. The introduction of one or two phosphorus atoms into the three-membered ring allows complexation by transition metals.[3] Thermal or photochemical activation leads most frequently to bond breaking at the heteroatom. Thus, opening the ring in these strained heterocycles leads to dimerizations,[4,5] to the formation of larger rings,[6–11] to thermal cycloreversions [2+1],[12–16] or to phosphapropenes.[17–20]

The investigation by Appel of phosphapropenes and of phosphacarbapolyenes in general[21] occupies an important place in heteroatom chemistry. The remarkable similarity of these compounds to pure carbon systems is most impressively demonstrated by their reactivity. They are precursors to bidentate allylic ligands,[22–26] certain of which are used as catalysts in olefin polymerization reactions.[27]

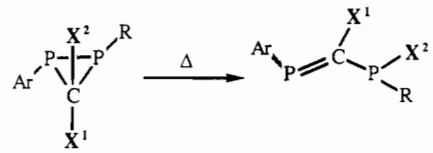

Figure 1. Diphosphirane–diphosphapropene isomerization.

The diphosphiranes being obvious precursors to 1,3-diphosphapropenes, we decided in the light of experimental results and theoretical calculations to carry out a study on thermal ring opening of these phosphorus analogues of cyclopropane (Figure 1). At this time, there exists no study on this subject. We have therefore carried out a quantum mechanical analysis in order to

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(1) Suckling, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 537.
(2) Mathey, F. *Chem. Rev.* **1990**, *90*, 997–1025.
(3) Bitterer, F.; Brauer, D. J.; Dörrenbach, F.; Stelzer, O. *J. Organomet. Chem.* **1990**, *399*, C4–C8.
(4) Baudler, M.; Saykowski, F. *Z. Naturforsch.* **1978**, *33B*, 1208.
(5) (a) Novikova, Z. S.; Prischenko, A. A.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1979**, *49*, 413–414. (b) Prishchenko, A. A.; Novikova, Z. S.; Lutsenko, J. F. *Z. Obshch. Khim.* **1980**, *50*, 689.
(6) (a) Richter, W. J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 292. (b) Richter, W. J. *Chem. Ber.* **1983**, *116*, 3293.
(7) Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001.
(8) Blatter, K.; Rösch, W.; Vogelbacher, U. J.; Fink, J.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 85.
(9) Katz, T. J.; Carnahan, J. C., Jr.; Clarke, G. M.; Acton, N. *J. Am. Chem. Soc.* **1970**, *92*, 734.
(10) Märkl, G.; Beckh, H. J.; Ziegler, M. L.; Nuber, B. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1134.
(11) Garot, C.; Etemad-Moghadam, G.; Declercq, J. P.; Dubourg, A.; Koenig, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 625.
(12) Quast, H.; Heuschmann, M. *Chem. Ber.* **1982**, *115*, 901.
(13) Mercier, F.; Deschamps, B.; Mathey, F. *J. Am. Chem. Soc.* **1989**, *107*, 9098.
(14) Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217.
(15) Toyota, K.; Yoshimura, H.; Uesugi, T.; Yoshifuji, M. *Tetrahedron Lett.* **1991**, *32*, 6879.
(16) Etemad-Moghadam, G.; Tachon, C.; Gouygou, M.; Koenig, M. *Tetrahedron Lett.* **1991**, *32*, 3687.
(17) Quast, H.; Heuschmann, M. *Liebigs Ann. Chem.* **1981**, 977.
(18) (a) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 4700. (b) Marinetti, A.; Mathey, F. *Tetrahedron* **1989**, *45*, 3061.
(19) (a) Gouygou, M.; Tachon, C.; Koenig, M.; Etemad-Moghadam, G. *New. J. Chem.* **1989**, *13*, 315. (b) Gouygou, M.; Tachon, C.; Etemad-Moghadam, G.; Koenig, M. *Tetrahedron Lett.* **1989**, *30*, 7411. (c) Gouygou, M.; Bellan, J.; Escudié, J.; Couret, C.; Dubourg, A.; Declercq, J. P.; Koenig, M. *J. Chem. Soc., Chem. Commun.* **1989**, 593.
(20) Gouygou, M.; Tachon, C.; Koenig, M.; Dubourg, A.; Declercq, J. P.; Jaud, J.; Etemad-Moghadam, G. *J. Org. Chem.* **1990**, *55*, 5750.
(21) Appel, R. In *Multiple bonds and low coordination in phosphorus chemistry*; Regitz, M., Scherrer, O. J., Eds.; Thieme Medical Publishers: New York, 1990; p 157.
(22) (a) Appel, R.; Schuhn, W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 420. (b) Appel, R.; Schuhn, W.; Knoch, F. *J. Organomet. Chem.* **1987**, *319*, 345. (c) Appel, R.; Schuhn, W. *J. Organomet. Chem.* **1987**, *329*, 179. (d) Appel, R.; Schuhn, W.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 416.
(23) (a) Karsch, H. H.; Reisacher, H. U.; Huber, B.; Muller, G.; Malisch, W.; Jorg, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 455. (b) Karsch, H. H.; Reisacher, H. U.; Huber, B.; Muller, G. *New. J. Chem.* **1989**, *13*, 319.
(24) (a) Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 357. (b) Mercier, F.; Hugel Le Goff, C.; Mathey, F. *Organometallics* **1988**, *7*, 955. (c) Mercier, F.; Mathey, F. *Organometallics* **1990**, *9*, 863.
(25) Niecke, E.; Kramer, B.; Nieger, M. *Organometallics* **1991**, *10*, 10.
(26) El Ouatib, R.; Ballivet-Tkatchenko, D.; Etemad-Maghadam, G.; Koenig, M. *J. Organomet. Chem.* **1993**, *453*, 77.
(27) Keim, W.; Appel, R.; Gruppe, S.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1012.

0020-1669/94/1333-0596$04.50/0

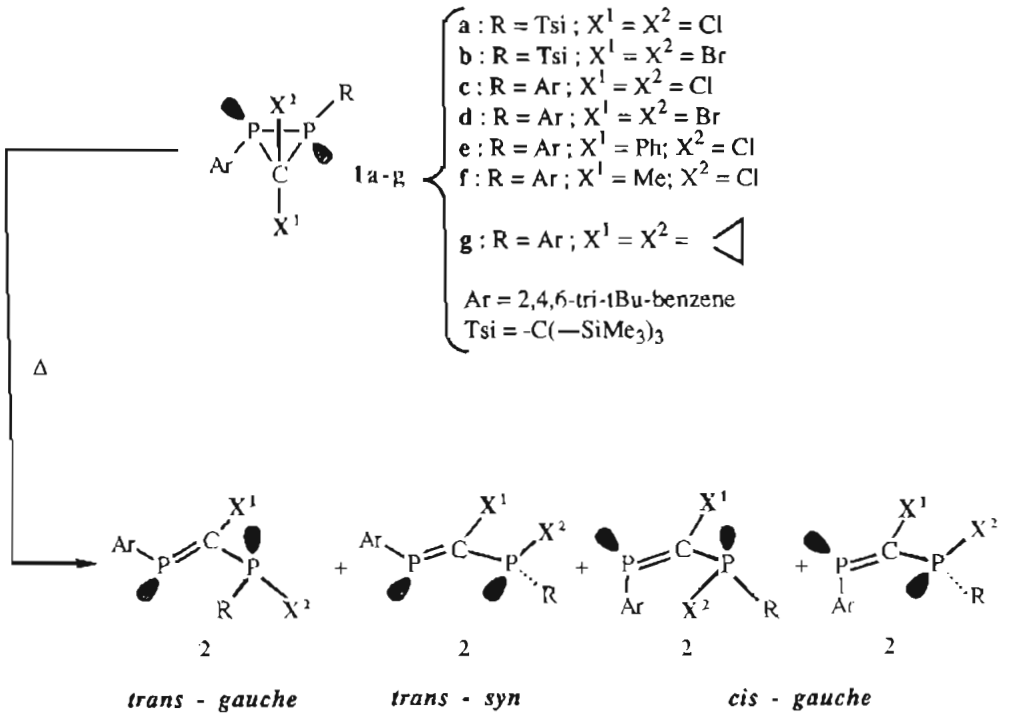

Figure 2. Thermal ring opening of diphosphirane—different compounds studied.

determine the different energy barriers involved and to discover the preferred mechanism for this "diphosphirane–diphosphapropene" isomerization. The calculations were performed on unsubstituted derivatives.

2. Calculations and Experimental Conditions

(a) Experiments. Diphosphiranes **1a–g** (Figure 2) were synthesized according to previously described methods.[28] The major products of the reaction, the 1,3-diphosphapropenes **2a–g**, as well as the stable secondary products, have already been isolated and characterized.[20] ^{31}P NMR experiments and especially $^2J_{PP}$ coupling constants allow us to distinguish the cis and trans configurations as well as the syn and gauche conformations. The structural analysis by X-ray diffraction allows the characterization of the syn and gauche conformations of the trans isomers.

General Method for Thermal Ring Opening of Diphosphiranes. A solution of a diphosphirane **1** (5×10^{-2} M < *C* < 9×10^{-2} M) in a dry previously degassed solvent is heated under argon. The progress of the ring-opening reaction and the proportions of the various isomers resulting therefrom are monitored as a function of elapsed time by ^{31}P NMR (Bruker AC 80). Whereas the thermolysis rate determinations are crude, the use of a limited scope of concentration allows us to account for the half-time value ($t_{1/2}$) without any consideration of the kinetic order of the reaction. So, for the comparative studies, we have used the diphosphirane solutions at the same concentration (ca. 9×10^{-2} M in toluene at 100 °C).

(b) Computational Details. Given the size of the problem, we chose the MNDO[29] formalism for preliminary studies. Then we carried out more elaborate calculations using the Monstergauss program[30] for SCF calculations and the CIPSI algorithm[31] for configuration interaction (CI) treatments.

(i) MNDO Calculations. The MNDO calculations were performed with the AMPAC 2.1 program. The structures of the minima were found via the D-F-P algorithm.[32] Saddle points were determined by means of the CHAIN algorithm.[33] Specific correlation effects were taken into account by a configuration interaction (CI) based on the subset of the crossing orbitals encountered along the reaction path (the two highest occupied MOs and the two lowest vacant MOs). Thus the wave function describing the singlet ground state smoothly evolves between the various minima and transition states and allows closed-shell, biradical, or zwitterionic forms along the reaction path to be distinguished.

(ii) SCF ab Initio Calculations. We used a modified 4-31G basis set in which one set of d polarization functions was added to the phosphorus ($\xi_P^d = 0.57$).[34] The molecular geometries were optimized at the SCF level with respect to all bond lengths and bond angles by a gradient method.

Table 1. Thermal Ring Opening of Diphosphiranes **1a–g** (70 mM) as a Function of the Nature of the Solvent and the Reaction Temperature

entry	compd	solvent	temp (°C)	$t_{1/2}$ (h)
1	**1a**	toluene	70	24
2		1,2-dichloroethane	70	1
3	**1b**	hexane	20	1
4	**1c**	hexane	70	*a*
5		toluene	100	14
6		1,2-dichloroethane	70	6
7		nitrobenzene	100	0.5
8	**1d**	hexane	70	46
9		toluene	100	1.5
10		1,2-dichloroethane	60	<0.5
11	**1e**	toluene	100	5.5
12		toluene[b]	100	2.5
13		1,2-dichloroethane	50	2.5
14	**1f**	toluene	100	72
15		1,2-dichloroethane	70	30
16	**1g**	toluene	100	1.5
17		toluene[b]	100	1

[a] No ring opening was observed. [b] In the presence of AIBN.

(28) (a) Etermad-Moghadam, G.; Bellan, J.; Tachon, C.; Koenig, M. *Tetrahedron* **1987**, *43*, 1793. (b) Gouygou, M.; Tachon, C.; El Ouatib, R.; Ramarijaona, O.; Etemad-Moghadam, G.; Koenig, M. *Tetrahedron Lett.* **1989**, *30*, 177.
(29) Dewarm, J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(30) Peterson, M.; Poirier, R. Monstergauss (Avril 1986). Chemistry Department, University of Toronto, Ontario, Canada. Monstergauss is a modification of the Gaussian series of programs developed by A. Pople and co-workers.
(31) (a) Huron, B.; Malrieu, J. P.; Rancurel, P. *J. Chem. Phys.* **1973**, *58*, 5745. (b) Pellissier, M. Thèse Université P. Sabatier, Toulouse, 1980.
(32) (a) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163. (b) Davidon, W. C. *Comput. J.* **1968**, *11*, 406.
(33) Liotard, D.; Penot, J. P. In *Numerical methods in the study of critical phenomena*; Della-rosa, J., Demmongeot, J.; Lacolle, B., Eds.; Springer: Weinheim, Germany, 1981; Vol. 9, p 213.
(34) (a) Ditchfield, R.; Hehre, W. H.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Kutzelnigg, W.; Wallmeier, H. *Theor. Chim. Acta* **1979**, *51*, 261.

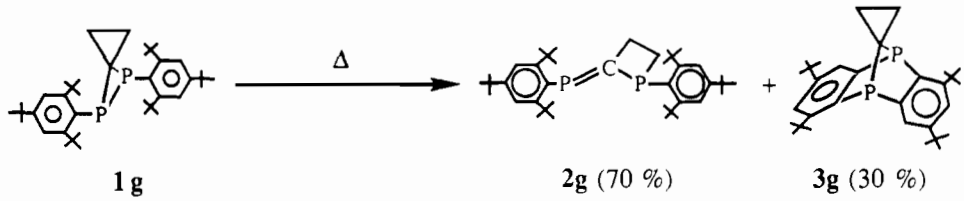

Figure 3. Ring opening of spirodiphosphirane.

The detection of transition states was carried out using the Powell algorithm.[35] Each stationary point was characterized by force constant matrix analysis. In order to obtain a correct description all along the reaction path, open-shell calculations (ROHF formalism) were carried out for the isomerizations associated with the concerted process and the singlet biradical species. We used an UHF formalism in the case of radicals. The effects of electronic correlation were estimated using a variational perturbation method (CIPSI algorithm[31]). In this formalism, a variational zeroth-order wave function is built from iterative selection of the most important determinants according to a threshold on the coefficients. The perturbative step is a multireference second-order Moller–Plesset treatment and includes all single and double excitations from the main determinants. At least 40–50 determinants were included in the variational wave function, 6×10^6–8×10^6 determinants thus being generated.

3. Results

3.1. Experimental Data for the Thermal Ring Opening of Diphosphiranes. In the absence of nucleophilic or electrophilic assistance, the thermal opening of diphosphiranes mono- and dihalogenated at the ring carbon leads to 1,3-diphosphapropenes. These 1,3-diphosphapropenes are present in the form of four major isomers (trans, gauche-trans, syn-cis, gauche) characterized in earlier work,[19,20,36] of very similar energies (Figure 2).

We distinguish the diphosphiranes with different substituents on the phosphorus atoms (R = Tsi, **1a,b**) from the ones **1c–g** with the same substituents on the phosphorus atoms (R = Ar).

The thermal ring opening of diphosphiranes **1a,b** is regioselective and stereoselective since it leads quantitatively to the trans,syn diphosphapropenes **2a,b**.[19c] On the other hand, the thermal ring opening of diphosphiranes **1c–f** is not characterized by the same stereoselectivity as that of **1a,b**. We obtain trans,gauche isomers **2** for all of the symmetric halogenated diphosphiranes **1c–f**, whereas for the monohalogenated **1e,f** we observe in addition cis isomers **2e,f** (Figure 2).

(i) Influence of the Solvents. In order to prevent solvolysis reactions, we used aprotic solvents. Ring-opening reactions are evidently accelerated by solvents of increasing polarity. For example when **1c** is heated at 70 °C in hexane ($\epsilon = 1.9$), the ring does not open at all irrespective of the duration of heating, whereas in 1,2-dichloroethane for the same temperature the half-time of the ring is 6 h. In a more polar solvent such as nitrobenzene ($\epsilon = 34.8$) a lowering of $t_{1/2}$ to 30 min has been observed (Table 1, entries 4–7).

(ii) Influence of the Substituents. (a) Substituents on the Phosphorus Atoms. While following the progress of the reaction with ^{31}P NMR, we observe that the ring opening for the diphosphiranes **1a,b** is easier than that for the homologues **1c–f**. Thus, **1a** opens 6 times faster than **1c** in 1,2-dichloroethane at 70 °C (Table 1, entries 2 and 6). This lowering of the barrier to ring opening is due to the presence of the very bulky Tsi group on the phosphorus atom, which induces further strain in the cycle (a shorter P–P bond: $d_{P-P} = 2.1$ Å for **1a**;[37] $d_{P-P} = 2.2$ Å for **1c**[20]).

(b) Substituents on the Ring Carbon. In the same way, the substituent on the ring carbon can modify the reaction rate. In toluene at 100 °C, $C = 9 \times 10^{-2}$ M, the value of $t_{1/2}$ changes from 72 h for **1f** to 1.5 h for **1d** (Table 1, entries 9 and 14). So the thermal stability of the diphosphiranes is as follows:

$$\mathbf{1f > 1c > 1e > 1d > 1a > 1b}$$

The radical nature of the ring thermolysis can be demonstrated by the addition of free-radical initiators. We have compared the ring-opening reaction rate of diphosphirane **1e** in toluene (70 mM) at 100 °C with that of a solution as concentrated as **1e** but with 5 equiv of α,α'-azoisobutyronitrile (AIBN). The same products are obtained with a decrease of the ring half-time from 5.5 to 2.5 h as is observed subsequent to the addition of this initiator (Table I, entries 11 and 12). A similar observation has been made during the ring opening of spirodiphosphirane **1g** which leads to 2-phosphaallyl-1-phosphacyclobutane **2g** (70%) and 1,4-diphosphanorbornadiene **3g** (30%) (Figure 3; Table 1, entries 16 and 17).

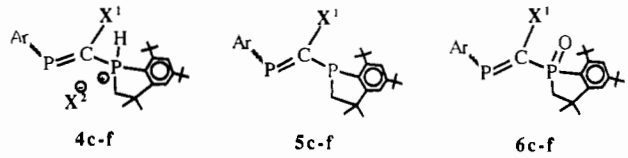

Figure 4. Secondary products obtained.

(iii) Nature of the Ring-Opening Products. The gem-dihalogenated diphosphiranes **1a–d** lead, under our experimental conditions, to trans 1,3-diphosphapropenes. Only the monohalogenated diphosphiranes **1e,f** give, after thermolysis, a cis/trans mixture, the proportions of which vary according to the nature of the solvent and the temperature. Thus in refluxing toluene the cis/trans ratios can take the values 2 and 0.5 for **1e** and **1f**, respectively. Whatever the experimental conditions, the percentage of cis isomers originating from **1e** is greater than that from **1f**.

The diphosphiranes **1a,b** lead in a stereoselective way to trans,syn 1,3-diphosphapropenes **2a,b** ($\theta = 0°$). In this case we have never detected trans,gauche isomers ($\theta = 100°$). On the contrary, during heating of **1c–f** we have observed only trans,gauche isomers.

The cis isomer appears as the kinetic product of opening. We have checked that the cis isomers have been obtained by ring opening and not after trans–cis isomerization. These cis isomers have not been detected in the cases of **1c,d**.

In addition, due to the 2,4,6-tri-*tert*-butylbenzenic substituent on the halophosphine of 1,3-diphosphapropene, secondary products have been observed; they are the result of the reactivity of this site: oxidative addition to the lone pair of **4c–f**, dehydrohalogenation to **5c–f**, and oxidation for **6c–f** (Figure 4). Nevertheless, in every case here studied, the initial cis/trans configuration at the P=C double bond is retained.

3.2. MNDO and ab Initio Analysis of the Ring-Opening Processes. We have undertaken a quantum chemical analysis in order to determine the various barriers and to further elucidate the preferential mechanism for this diphosphirane–diphosphapropene isomerization. The calculations were carried out on unsubstituted derivatives starting from *trans*-diphosphirane. During these studies we have only investigated the monomolecular processes for their ring opening. In order to specify the kinetic order of the reaction and this monomolecular character, it will

(35) Powell, M. J. D. In *Numerical methods for non linear algebraic equations*; Gordon and Breach: New York, 1991; p 87.
(36) Gouygou, M.; Koenig, M.; Hervé, M. J.; Gonbeau, D.; Pfister-Guillouzo, G. *J. Org. Chem.* **1991**, *56*, 3438.
(37) Gouygou, M.; Couret, C.; Escudié, J.; Huch, V.; Veith, M.; Koenig, M. *Bull. Soc. Chim. Fr.*, in press.

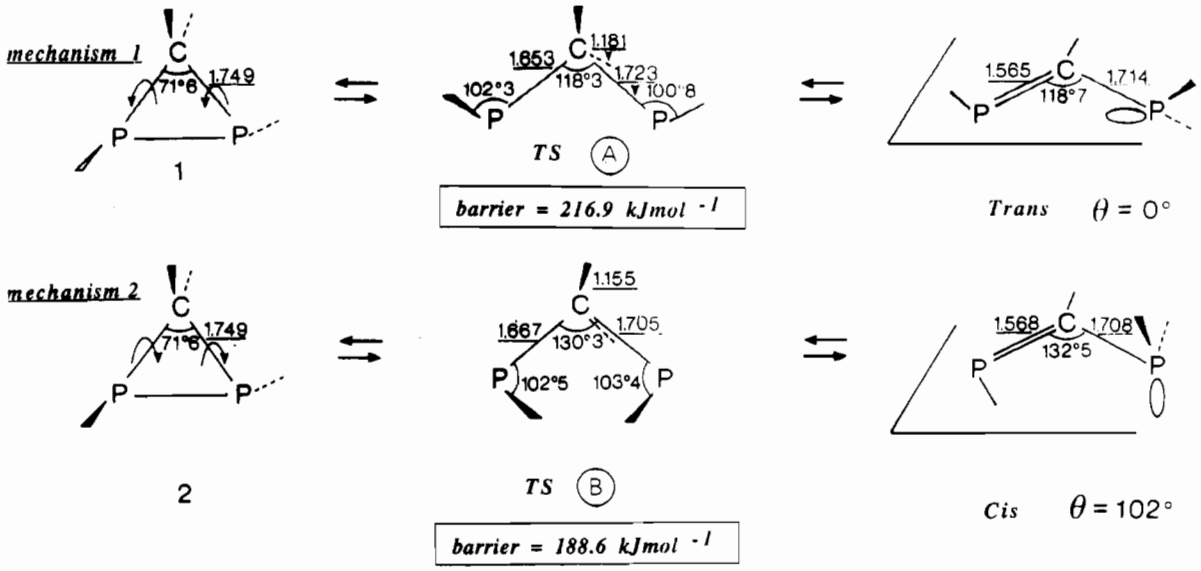

Figure 5. MNDO results: diphosphirane–diphosphapropene isomerization, ring opening and migration occurring in a concerted fashion (transition states exo-exo, endo-endo).

be necessary to undertake a detailed kinetic analysis for all the diphosphiranes.

Three mechanisms are possible for this isomerization, which corresponds to a cleavage of the P–P bond and to a halogen migration. We can consider (1) ring opening and migation occurring in a concerted fashion, (2) an initial rupture of the P–P bond with formation of a singlet biradical followed by halogen migration to form the diphosphapropene, and (3) a homolytic cleavage of the exocyclic C–X bond and P–P rupture.

Using the terminology of Woodward and Hoffmann,[38] conrotatory and disrotatory ring-opening modes should be considered; for the diphosphapropene obtained, four stable conformers of similar energy have been characterized.[36]

3.2.1. Ring Opening and Migration Occurring in a Concerted Fashion. A preliminary study was carried out in MNDO.

In the case of conrotatory opening we have characterized two transition states of appropriate structure (Figure 5):

For mechanism 1 the A transition state exo-exo is associated with a 216.9 kJ·mol^{-1} barrier. It leads directly on one hand to the trans diphosphirane and on the other hand to the trans conformer of diphosphapropene (θ = 0°).

For mechanism 2 the B transition state endo-endo is associated with a 188.6 kJ·mol^{-1} barrier. It leads directly on one hand to the trans diphosphirane and on the other hand to the cis conformer of diphosphapropene (θ = 102°).

In both cases, the essential variables are the same: the PCP angle and the dihedral angles related to the motions of the hydrogens on phosphorus. The variations of these dihedral angles are not equivalent. Similar observations have been made by Jug[39] for the cyclopropane–propene isomerization.

The geometries of the transition states show a broken P–P bond and a slight lengthening of a C–H bond (Figure 5). The migration of hydrogen begins at the transition state, but bond rupture is only completed during the final stages of the reaction path.

Endo-exo structures must be examined for disrotatory ring openings. Two transition states C and D have been characterized (Figure 6). They show a broken P–P bond and one migrating hydrogen; the lengthening of the C–H bond is more important than for mechanisms 1 and 2. Moreover, these transition states are not connected with the trans diphosphirane but with the cis, thus implying a prior trans–cis isomerization of diphosphirane. Other calculations allow us to describe these two mechanisms.

The first trans–cis isomerization of the cycle in common for mechanisms 3 and 4 corresponds to the inversion of one P–H group; the system loses symmetry but without rupture of the P–P bond; the barrier is about 170 kJ·mol^{-1}.

The second stage of diphosphapropene formation begins with the cis diphosphirane and corresponds to a conrotatory opening of the cycle. This stage shows a variation of geometrical parameters similar to that observed for mechanisms 1 and 2: the opening of the P–P bond occurs before the transition state, and the migration starts at the transition state but is only completed in the second part of the reaction pathway. We note as above nonconcerted variations of dihedral angles related to the motions of the hydrogens bonded to phosphorus.

This leads, for the mechanism 3, to a trans diphosphapropene (θ = 114°) with a 250 kJ·mol^{-1} barrier and, for the mechanism 4, to a cis rotamer with a similar barrier of 253.5 kJ·mol^{-1}.

According to these results, for a concerted process of rupture and migration, there exists no path corresponding to disrotatory opening of a trans ring which passes through a transition state of endo-exo structure. However we have characterized mechanisms associated with conrotatory opening corresponding either to a direct opening of the trans cycle or to a trans–cis isomerization followed by a conrotatory opening of the cis cycle. The preferential openings correspond, in view of the calculated barriers, to direct processes starting from the trans cycle according to mechanisms 1 and 2. It is to be noted that Jug[39] with a semiempirical formalism has determined a barrier of about 200.6 kJ·mol^{-1} for concerted cyclopropane–propene isomerization.

In order to estimate more precisely the barriers obtained in MNDO, we have undertaken an ab initio analysis of favored mechanisms 1 and 2. The two transition states found A′ and B′ (Figure 7) have geometrical structures very similar to the ones obtained in MNDO. We only observed a lengthening of bonds in the ab initio analysis due to the use of d orbitals. The same variations of geometrical parameters are observed along the reaction path: the initial phenomena observed are the opening of the P–P bond and the rotation of the P–H groups; hydrogen migration only takes place afterward and is only initiated at the level of the transition state.

The CI barriers are similar to those obtained in MNDO. The barrier to opening is slightly higher for mechanism 1 (241.7 kJ·mol^{-1}) than for mechanism 2 (213.4 kJ·mol^{-1}), but mechanism 1 must be considered in relation to the bulky substituents on the compounds experimentally studied.

(38) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(39) Jug, K. *Theor. Chim. Acta* **1976**, *42*, 303.

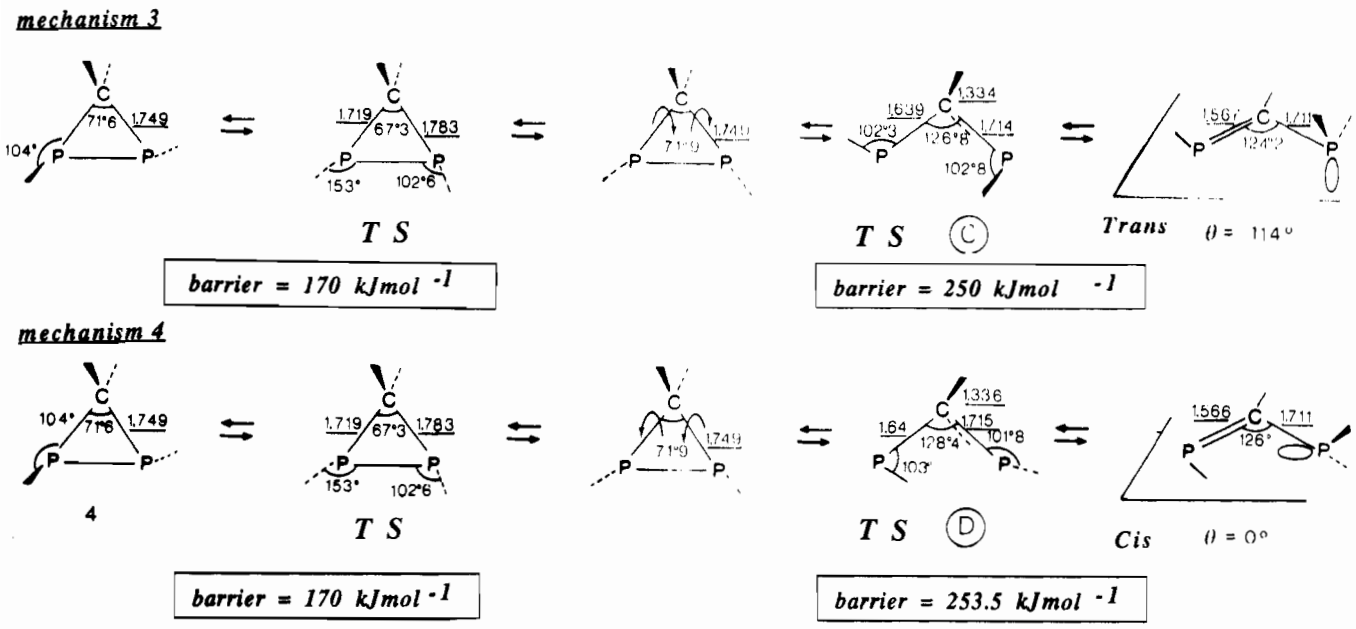

Figure 6. MNDO results: diphosphirane–diphosphapropene isomerization, Ring opening and migration occurring in a concerted fashion (transition states endo-exo).

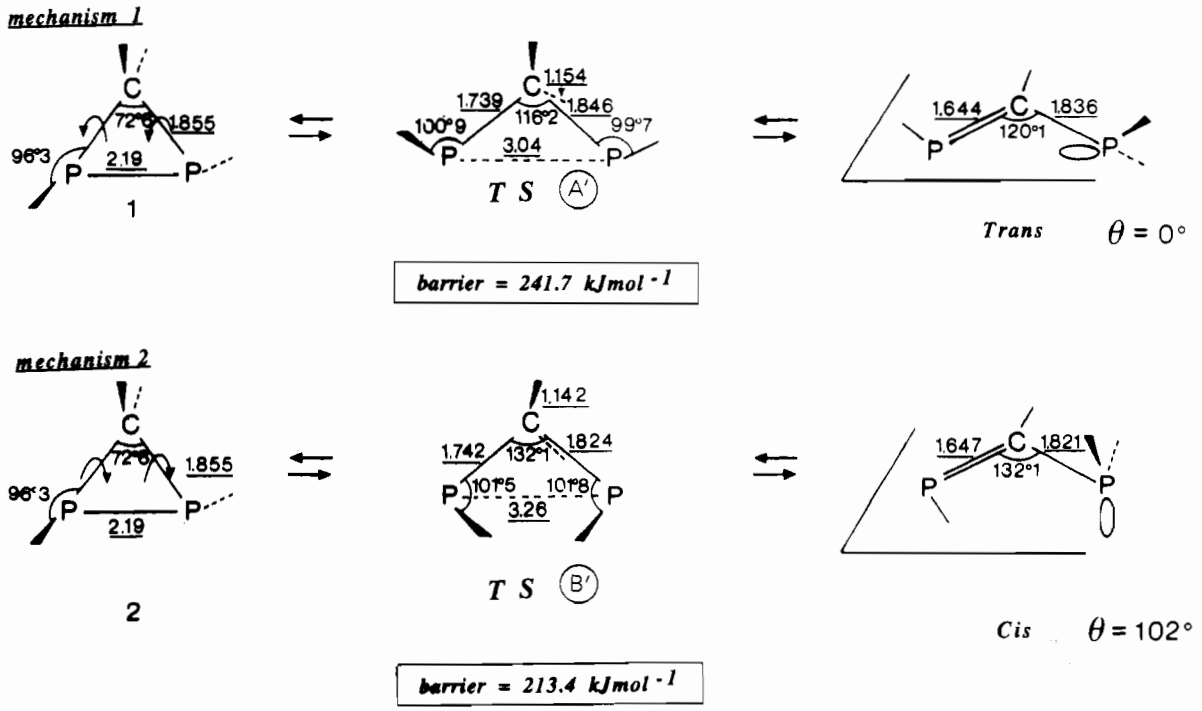

Figure 7. Ab initio results: diphosphirane–diphosphapropene isomerization, ring-opening and migration occurring in a concerted fashion (transitions states exo-exo, endo-endo).

The diphosphirane–diphosphapropene isomerization in the case of ring opening and migration occurring in a concerted fashion would thus lead via conrotatory opening to a trans diphosphapropene ($\theta = 0°$).

3.2.2. Isomerization with Formation of a Singlet Biradical Intermediate. We have investigated the possibility of a singlet biradical intermediate analogous to that postulated for the ring-opening reactions of cyclopropane,[40] oxirane, or aziridine;[41,42] the conrotatory and disrotatory ring openings have been examined.

A preliminary study has been carried out in MNDO with the analysis of exo-exo, endo-exo, and exo-endo acyclic structures.

For the conrotatory opening (mechanism 5) we have characterized an exo-exo biradical minimum and the transition state which leads to it from the diphosphirane (Figure 8). The minimum, which is planar, corresponds to a PCP angle of 108.5°. The cleavage of the P–P bond occurs before the transition state which differs from the minimum by its dihedral angle HPPH (nearly 65° for the transition state and 0° for the minimum). A barrier of 144.5 kJ·mol^{-1} is calculated for the reaction diphos-

(40) (a) Hoffmann, R.; Swaminathan, S.; Odell, B.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 7091. (b) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1972**, *94*, 638. (c) Segal, G. *J. Am. Chem. Soc.* **1974**, *96*, 7892. (d) Doubleday, C.; Camp, R.; King, H.; McIver, J. W.; Mullaly, D.; Page, M. *J. Am. Chem. Soc.* **1984**, *106*, 447. (e) Bernardi, F.; Bottoni, A.; Robb, M.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1985**, *107*, 2260. (f) Doubleday, C.; McIver, J. W.; Page, M. *J. Phys. Chem.* **1988**, *92*, 4367. (g) Rappoport, Z. In *Chemistry of the cyclopropyl group*; Patai, S., Ed.; Wiley: New York, 1987.
(41) Jean, Y.; Volatron, F.; Nguyen Trong Anh. *J. Mol. Struct.* **1983**, *93*, 167.
(42) (a) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1979**, *101*, 1101. (b) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1979**, *101*, 1095.

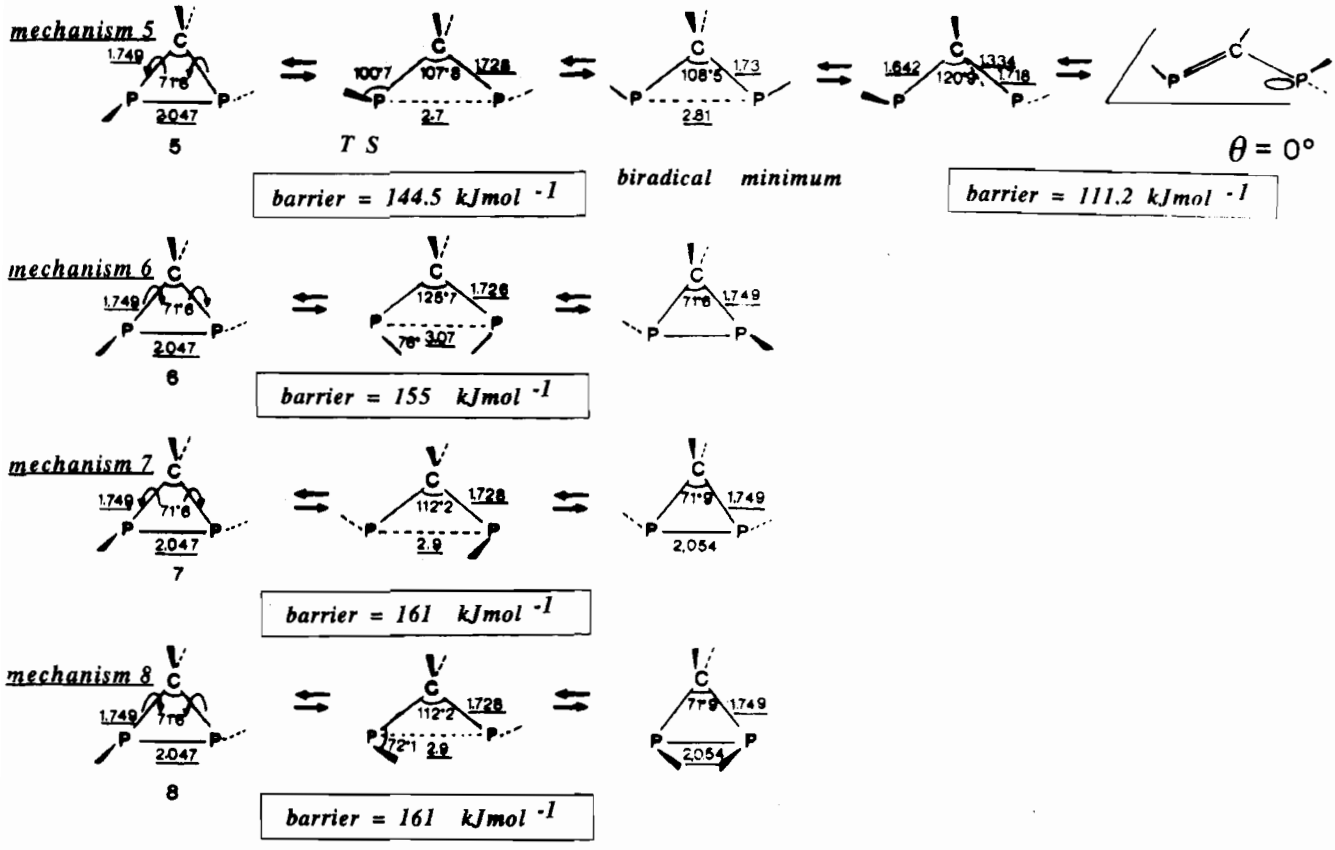

Figure 8. MNDO results: isomerization with formation of a singlet biradical intermediate.

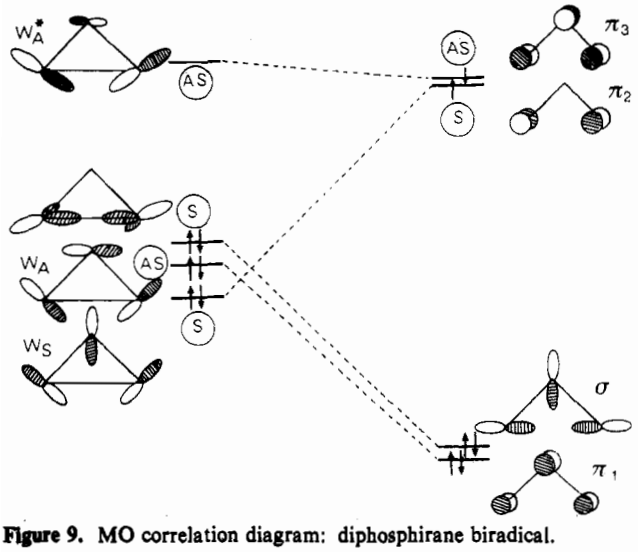

Figure 9. MO correlation diagram: diphosphirane biradical.

phirane ↔ biradical. Analysis of the orbital correlation diagram for diphosphirane ↔ singlet biradical (Figure 9) shows a crossing between orbitals of the same symmetry. The Walsh orbitals of the cycle W_S and W^*_A correlate with the π_2 and π_3 quasi-degenerate orbitals of the biradical; the W_A orbital correlates with π_1 and the HOMO with a σ orbital close to it in energy.

For the mechanism 6 the calculations do not reveal a minimum but an endo-endo transition state (Figure 8); this transition state of planar structure correlates on one hand with the trans diphosphirane and on the other hand with its optical isomer. This racemization reaction corresponds to a barrier of 155 kJ·mol^{-1}.

For the mechanisms 7 and 8 no biradical minimum of exo-endo structure has been characterized. However a transition state of this type has been determined (Figure 8) that connects directly on one hand with the trans diphosphirane and on the other hand with the cis cycle. The computed barrier is 161 kJ·mol^{-1}. This geometric isomerization of diphosphirane corresponds to a slightly lower barrier than the isomerization with inversion at phosphorus and without P–P cleavage.

Thus the conrotatory and disrotatory ring-opening barriers are not very different; however the lower corresponds to the conrotatory mechanism 5 with a biradical intermediate. For the mechanisms 6–8 the results associated with geometrical and optical isomerizations of diphosphirane are similar to those previously obtained by Salem et al.[43] for cyclopropane; in this latter case the barriers are about 200 and 250 kJ·mol^{-1}.

In order to analyze the entire diphosphirane–diphosphapropene isomerization process, it was necessary to study the hydrogen migration starting from the biradical minimum. The transition state is characterized by a considerable increase in the PCP angle, an asymmetry in the P–C bond lengths, and an increase in the C–H bond length relative to the biradical. For the second isomerization step the barrier of about 111.2 kJ·mol^{-1} is lower than for the first; it leads to trans diphosphirane ($\theta = 0°$).

We have carried out an ab initio study of mechanism 5.

A minimum was found corresponding to a singlet biradical. For this structure the exo-exo PH groups are as in MNDO in the PCP plane; for this π biradical the PCP angle is 100.3° and the P–P bond length 2.83 Å (Figure 10). The transition state leading to this minimum via conrotatory opening was also studied. The optimized value of the PCP angle is 77.5° (d_{P-P} = 2.3 Å) with a rather slight increase of about 5° in comparison with the case of diphosphirane. Thus, the breaking of the P–P bond does not occur before the transition state, as in MNDO, but after. The more important variations are relative to the dihedral angles of hydrogens on phosphorus; the disposition of the PH groups in the transition state is close to that of the biradical minimum but still far from the final planar structure; they are indeed located on the same side of the P–P bond as the carbon but the value of the HPPH dihedral angle is 133.7°.

(43) Horsley, J. A.; Jean, J.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 279.

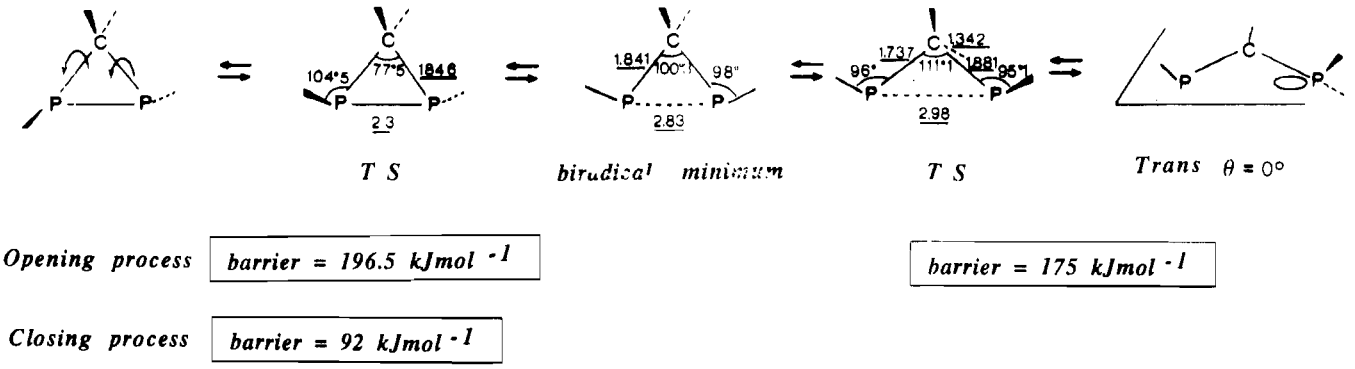

Figure 10. Ab initio results: isomerization with formation of a singlet biradical intermediate.

The barrier to attain the biradical minimum is 196.5 kJ·mol^{-1} after CI; it is lower by 45.2 kJ·mol^{-1} than the barrier of mechanism 1 corresponding to diphosphirane–diphosphapropene isomerization by concerted conrotatory opening.

The theoretical study of electrocyclic opening of cyclopropane[40a,b] and oxirane[41,42b] leads to similar barriers. On the other hand, differences appear at the barriers to closure of these biradical species. For the trimethylene biradical the stationary point corresponding to this structure has been discussed[40] in relation to the very flat potential energy surface around this point; the barrier to closure evaluated by some authors is very low (≈4 kJ·mol^{-1}).[40a,b] For oxirane the calculations allow us to unambiguously determine a local minimum associated with a biradical whose barrier to closure was evaluated to be about 56 kJ·mol^{-1}.[41] For the diphosphorus biradical a higher barrier of 92 kJ·mol^{-1} after CI was determined, showing a greater stability in regard to the closing process.

We have also analyzed by ab initio methods the hydrogen migration which leads from singlet biradical to diphosphapropene. The results concerning the transition state are close to those obtained in MNDO; we observe an opening of the PCP angle, an asymmetry of the P–C bonds, and a lengthening of the C–H bond. The barrier for this migration step of 175 kJ·mol^{-1} is slightly lower than the barrier to the first step of P–P opening. The diphosphapropene obtained shows a trans structure (θ = 0°).

From these results the diphosphirane–diphosphapropene isomerization would correspond to a two-step mechanism with a biradical intermediate.

3.2.3. Isomerization Involving Radical Species. For the thermal opening of diphosphirane, one can imagine a radical process occurring following homolytic rupture of the C–H bond.

It was initially necessary to examine the stable forms of the radical species. The ab initio calculations allow us to characterize a cyclic species and two open radicals. The $\langle S^2 \rangle$ values for the acyclic forms revealed a certain amount of mixing with states of higher multiplicity ($\langle S^2 \rangle \approx 0.8$); CI calculations were carried out on the three minima. The order of energies remains unchanged after CI with a cyclic form less stable than the two open forms (Figure 12).

The diphosphiranyl radical has shorter P–C bonds than the diphosphirane (d_{P3-C} = 1.855 Å) and, like the cyclic anion, an sp^3 carbon.[44] For this radical the spin densities showed considerable localization on the carbon; the SOMO also shows a predominant carbon localization. The diphosphaallyl radicals are planar with very similar geometric parameters (Figure 11). The spin densities and the SOMOs show for these two radicals a localization of the single electron on the two phosphorus atoms and not on the carbon as in the cyclic radical (Figure 12).

For the ring opening, it is well-known that Woodward–Hoffmann rules are not directly applicable in the case of radical

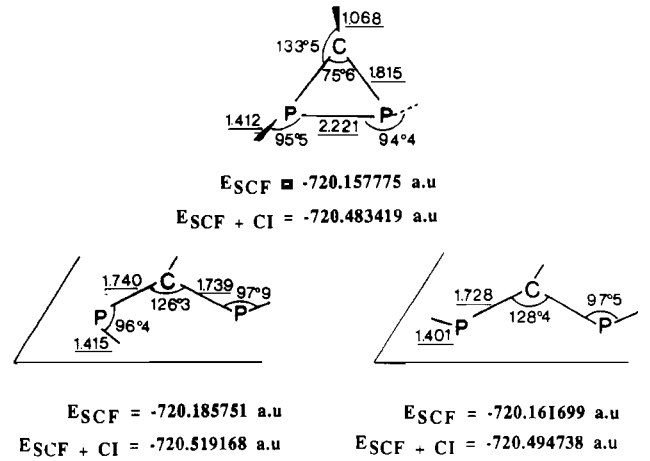

Figure 11. Radical species: optimized geometries (bond lengths in angstroms; angles in degrees)—energy values.

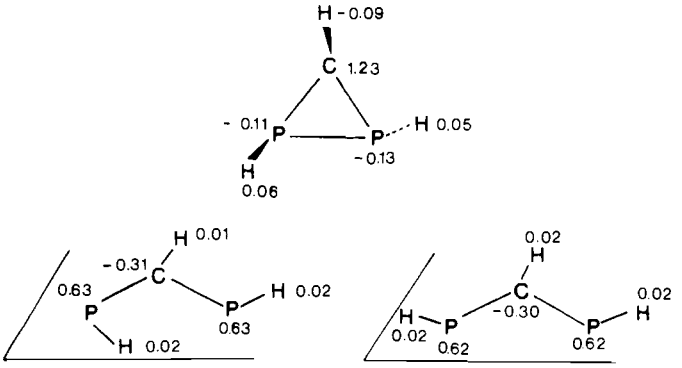

Figure 12. Radical species: spin densities.

species.[45] This is illustrated by the orbital correlation diagrams corresponding to conrotatory and disrotatory openings (Figure 13). Indeed, we observe for the conrotatory opening that the cycle's SOMO correlates with the doubly occupied π_1 orbital and, on the other hand, the doubly occupied σ_{P-P} correlates with the SOMO of the acyclic radical. For the disrotatory opening, a crossing occurs between $n_C \leftrightarrow \pi_3$ and $\sigma^*_{P-P} \leftrightarrow \pi_2$. Consequently, in every case, the ground states of the cyclic and acyclic radicals are of different symmetries and the ground state of the ring correlates with an excited state of the open-chain radical.

In order to specify the preferred mechanism, we have in each case examined the transition state and the corresponding barrier (Figure 14).

For the disrotatory opening (mechanism 9), the main coordinate is the PCP angle. The dissymmetrical transition state occurs for

(44) Tachon, C.; Gouygou, M.; Koenig, M.; Hervé, M. J.; Gonbeau, D.; Pfister-Guillouzo, G. *Inorg. Chem.* **1992**, *31*, 2414.

(45) (a) Longuet-Higgins, H. C.; Abrahamson, E. W. *J. Am. Chem. Soc.* **1965**, *87*, 2045. (b) Dewar, M. J. S. *Tetrahedron Suppl.* **1966**, *8* (Part I), 75. (c) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

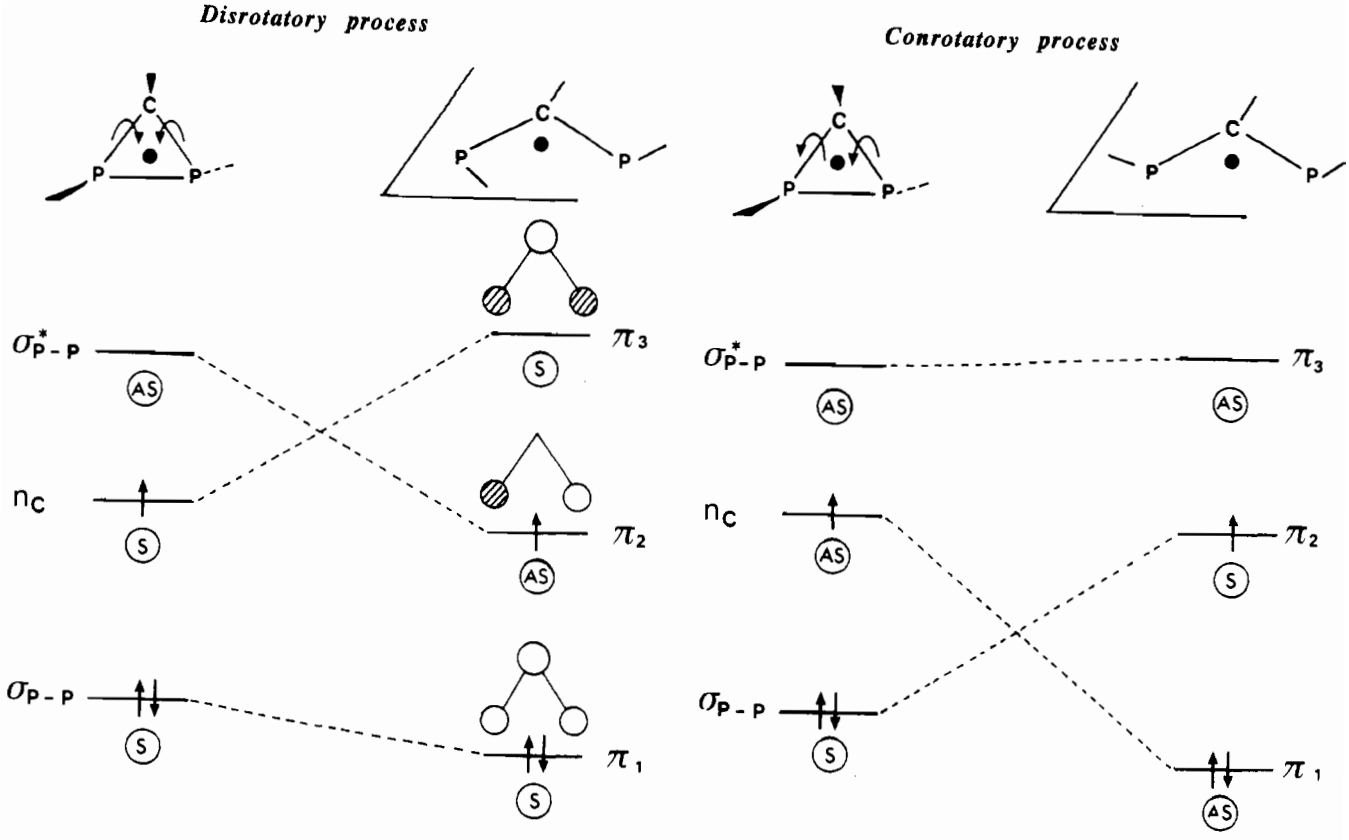

Figure 13. Radical ring opening: MO correlation diagram.

a partially broken P–P bond (2.65 Å), whereas the PH groups after a partial rotation adopt a relative disposition similar to that observed for the acyclic radical. The corresponding barrier of about 82.4 kJ·mol^{-1} is rather low relative to the previously calculated barriers. However a comparison with the other processes would imply taking into account the cleavage of the C–H (C–X) bond a priori as more energetic than the rupture of the P–P bond.

For the conrotatory opening (mechanism 10), the essential variables are the dihedral angles associated with the motions of the hydrogens on phosphorus. The transition state is dissymmetrical with an HPPH angle of 134°, very different from the 195° value associated with the initial state; the rotations of the PH groups about the P–C bonds are not equivalent, but the disposition of these groups is close to that observed in the final state. The barrier obtained, 113.3 kJ·mol^{-1}, is higher than that for the disrotatory process.

Olivella et al.[46] have determined for the cyclopropyl radical a common transition state for the conrotatory and disrotatory openings; the value of the barrier is between 93 kJ·mol^{-1} at the UHF/3-21G level and 82 kJ·mol^{-1} at the CASSCF/3-21G level.

From the performed calculations, a disrotatory opening of diphosphirane appears to be favored after homolytic rupture of the C–H bond. The endo-exo acyclic compound is susceptible to attack on either phosphorus, leading to diphosphapropene of cis or trans structure.

4. Discussion

The main results relative to the 10 mechanisms associated with the three processes examined are reported in Table 2.

Mechanisms 6–8 must be rejected because they do not correspond to the opening of diphosphirane. Similarly, mechanisms 3 and 4 need not be taken into consideration since they require a trans–cis isomerization before the P–P bond breaking; indeed, experimental results show high inversion barriers for strained cyclic phosphines greater than the barriers to opening of the cycle.[47]

For the other mechanisms 1 and 2 (concerted process), 5 (biradical process), and 9 and 10 (radical process), the comparison with experimental data allows us to propose a preferred mechanism or mechanisms.

Concerning mechanisms 1 and 2, it should be noted that if mechanism 1 leads to *trans-syn*-diphosphirane in agreement with the X-ray structure of **2a**,[19c] it corresponds to the higher energy barrier. Mechanism 2, associated with the formation of cis isomers, needs not to be considered in the case of bulky substituted experimental compounds. In addition, these concerted mechanisms should not be very sensitive to solvent and experimentally a noticeable influence of dielectric constant on the opening barrier has been observed. In view of these results, the diphosphirane–diphosphapropene isomerization does not correspond to a concerted opening and migration process.

Mechanism 5 (biradical process) can lead, like mechanism 1, to a trans-syn diphosphapropene compatible with the X-ray structure of **2a**. This mechanism in two steps (opening and migration) is however energetically favored in relation to the concerted process; it allows a rationalization for several experimental results during the thermal opening process; when the migration step is impossible (for **1g**), the formation of diphos-

(46) Olivella, S.; Sole, A.; Boffil, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2160.

(47) Lambert, J. B.; Jackson, G. F., III; Mueller, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 164.

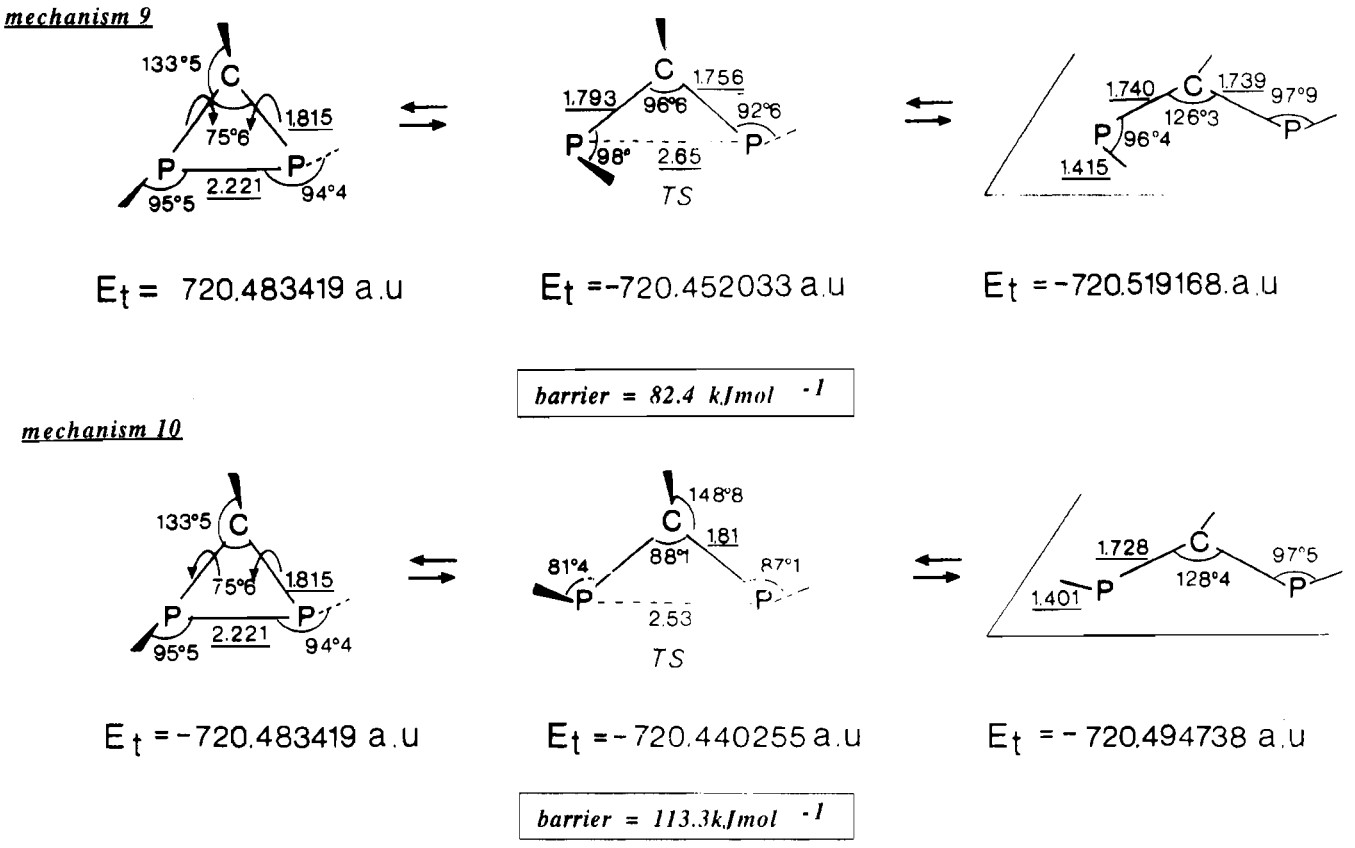

Figure 14. Ring opening of the diphosphiranyl radical.

Table 2. Thermal Ring Opening of Diphosphirane—MNDO and ab Initio Results

		Mechanism	Configuration of transition state or intermediate	Product	Angle (°)	Barrier (kJ.mol^{-1}) MNDO a	MNDO b	Ab initio a	Ab initio b
Concerted	conrotatory	1	exo-exo	trans diphosphapropene	0	216.9		241.7	
	conrotatory	2	endo-endo	cis diphosphapropene	102	188.6		213.4	
	conrotatory	3	endo-exo	trans diphosphapropene	114	170	250		
	conrotatory	4	endo-exo	cis diphosphapropene	0	170	253.5		
Biradicalar	conrotatory	5	exo-exo	trans diphosphapropene	0	144.5	111.2	196.5	175
	conrotatory	6	endo-endo	trans diphosphirane		155			
	disrotatory	7	endo-exo	cis diphosphirane		161			
	disrotatory	8	exo-endo	cis diphosphirane		161			
Radicalar	disrotatory	9	exo-endo	cis or trans diphosphapropene				82.4	
	conrotatory	10	exo-exo	trans diphosphapropene				113.3	

phanorbornadiene has been established via a biradical intermediate;[11] in addition, the dimerizations observed by Baudler[4] for diphosphiranes without substituents on carbon are in favor of this mechanism with a π biradical. This hypothesis is supported by the nonnegligible effect of radical initiators on the opening rate. This increase of the opening rate by radical initiator addition has not been observed for the thermolysis of cyclopropane.[40g] This could be due to the stability difference between the phosphorus and carbon biradicals. Actually, for the trimethylene biradical, the barrier to closure is much more lower than for the diphosphapropanyl biradical.[40] Thus, the lifetime of the latter will be higher and its concentration should be sensitive to the presence of radical initiators.

Finally, the exo-exo structure of the biradical allows us to explain the exclusive formation of trans isomers for the dihalogenated diphosphiranes; the lowering of the bond energy of C–X when a hydrogen is substituted by a halogen favors the second step of migration (mean value of a C–X bond energy 327 kJ·mol^{-1} (X = Cl), 285 kJ·mol^{-1} (X = Br); mean value of a C–H bond energy 411 kJ·mol^{-1}).[48]

(48) Huheey, J. E. *Inorganic Chemistry*; Harper and Row: New York, 1983.

From the results of calculations, the trans isomers are obtained with syn conformations; it thus appears reasonable to explain the formation of gauche conformers (diphosphiranes **1c,d**) by rotation from syn conformers in relation to the low barriers to rotation about the P–C bond. It should be noted that while this biradical mechanism takes numerous experimental results into account, it does not explain how cis isomers were obtained.

The radical process (mechanisms 9 and 10) requires an initial rupture of the extracyclic bond, leading to a cyclic diphosphiranyl intermediate, which should open relatively easily (82 kJ·mol^{-1} for the disrotatory process and 113 kJ·mol^{-1} for the conrotatory process). This radical process has been already observed during the photochemical opening of halodiphosphiranes (**1c–f**); the diphosphiranyl and diphosphapropenyl intermediates have been characterized by spin trapping in ESR.[20] The disrotatory process 9 associated with the lower barrier leads to a planar diphosphaallyl intermediate with endo-exo substituents on phosphorus; the formation of trans or cis diphosphapropene results from the attack on one of the two phosphorus atoms. Experimentally, monohalogenated diphosphiranes **1e,f** lead to trans and cis isomers, in agreement with the double possibility of evolution of the intermediate; for the monohalogenated compounds, initial cleavage of the exocyclic bond is facilitated by the lower C–X bond energy (relative to that of dihalogenated compounds).[49] The radical mechanism with a disrotatory opening is the only one which allows the explanation of the nature of the products in the case of monohalogenated diphosphiranes.

(49) The C–Cl bond order for a monohalogenated compound like **1f** is lower (0.94) than that for a dihalogenated compound like **1c** (0.98).

5. Conclusion

The theoretical analysis of the possible monomolecular processes for thermal opening of diphosphiranes has revealed two preferred mechanisms involving biradical or radical species: either conrotatory opening via an exo-exo singlet biradical leading to trans 1,3-diphosphapropenes or disrotatory opening via a radical exo-endo species leading to cis or trans diphosphapropenes. Only a disrotatory process accounts for the presence of the cis isomers.

These two mechanisms allow the interpretation of all the experimental results. All of the thermal ring openings of gem-dihalogenated diphosphiranes lead to acyclic trans isomers, while the monohalogenated diphosphiranes lead to mixtures of cis and trans isomers. In addition, the formation either of dimers in the case of nonsubstituted diphosphiranes or of diphosphanorbornadiene when the migration step is impossible is in favor of a biradical mechanism.

Acknowledgment. We thank the Direction Chimie du CNRS for the calculation time allocation on the VP 200 computer of CIRCE.