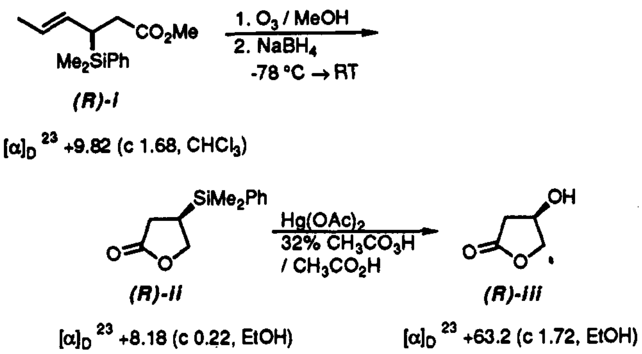
to Ms. Heather L. Nimmons and Mr. Michael Creech for performing mass spectral measurements.

Note Added in Proof. The absolute stereochemistry of the Claisen products was confirmed by the independent synthesis of the hydroxy lactone (*R*)-iii, of known absolute configuration. As illustrated in the scheme below, the (*R*)-(*E*)-crotylsilane (82% enantiomeric purity) was converted to (*R*)-(+)-3-(dimethylphenylsilyl)butyrolactone, ii. Replacement of the silicon group with a hydroxyl was accomplished using the method of Fleming [cf. refs 12a and 12b] and, as expected, occurred with complete retention of configuration to produce (*R*)-(+)-3-hydroxybutyrolactone, iii, 50% yield from (*R*)-i, [lit: $[\alpha]^{23}_D$ +77.0 (*c* 2.0, EtOH), cf. Mori, K.; Takigawa, T.; Matsuo, T. *Tetrahedron* **1979**, *35*, 933]. The discrepancy in rotation values is simply a result of enantiomeric purity of the starting (*R*)-(*E*)-crotylsilane.



Supplementary Material Available: ^{13}C and ^{1}H NMR spectra for compounds **1b,e,g,h,j–m**, **2a**, *syn*-**2b**, *anti*-**2b**, **2c,d**, *syn*-**2e**, *anti*-**2e**, and **2f–m** (47 pages). Ordering information is given on any current masthead page.

Evidence of the Rotamerism of the 1,3-Diphosphapropenes

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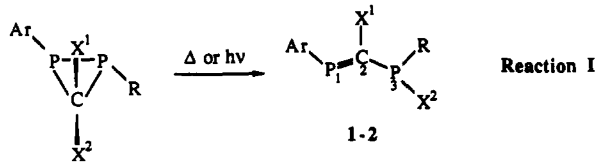
Many stereochemical problems arise from the 1,3-diphosphapropenes obtained by the ring opening of functionalized diphosphiranes. In particular, the structures of **1a** and **2a** show two different conformations. On the one hand, theoretical studies indicate these two conformers are close in energy and are separated by low rotation barrier (5 and 12 kJ·mol^{-1}). In the more stable conformer (gauche conformation), the angle between the tricoordinated phosphorus lone pair and the P–C bond, θ, is 114°, whereas the second minimum corresponds to the syn conformation (θ = 0°). On the other hand, the ^{31}P NMR experiments that we have performed to verify the existence of the two rotamers I and II give experimental barrier of the irreversible transformation **1b**(I) → **1b**(II) as 104 kJ·mol^{-1}.

Introduction

Recently, some of us have characterized new 1,3-diphosphapropenes obtained by photochemical or thermal ring opening of functionalized diphosphiranes[1,2] (Scheme I). The structural analysis by X-ray diffraction indicates that these molecules have the same trans configuration with different conformations. The diphosphapropene **1a** obtained by photochemical ring opening of the symmetrical diphosphirane (R = Ar, $X_1 = X_2$ = Cl) exists in the gauche conformation I, in which the lone pair of the tricoordinated phosphorus P_3 is roughly orthogonal to the σ-plane of the P=C double bond (θ = 100°).[1] The diphosphapropene **2a** produced by thermal ring opening of the unsymmetrical diphosphirane (R = Tsi, $X_1 = X_2$ = Cl) exhibits a syn conformation II in which the two phosphorus lone pairs are approximately in the σ-plane (θ = 12°)[2] (Figure 1).

The main difference in the ^{31}P NMR parameters, in particular the significant enhancement of the $^{2}J_{PP}$ coupling constant in the II conformation, can be explained by the difference in orientation of the respective phosphorus lone pairs. The existence of these two different conformations for the diphosphapropenes could indicate a possible rotamerism in these models. To our knowledge, this general phenomenon observed especially for unsaturated propenes[3] derivatives, amidines,[4] and ethenylphosphines[5] has not been observed for 1,3-diphosphapropenes.

Scheme I



1-2

We have undertaken a theoretical study of the internal rotation process of the phosphino group around the P–C bond and tried to obtain experimental evidence for the interconversion between the two conformers of series 1.

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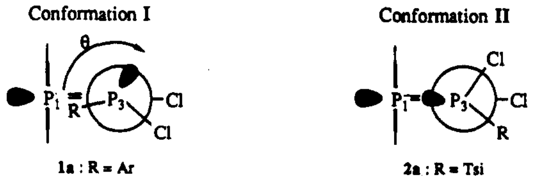

1a : R = Ar

2a : R = Tsi

Figure 1. Newman representation (P_3–C_2 axis).

Calculations and Experimental Conditions

The calculations were performed with the MONSTERGAUSS program.[6] The split valence 4-31G basis set was used and augmented by one set of d polarization functions on phosphorus ($\zeta_P{}^d = 0.57$).[7]

The molecular geometries were fully optimized at an SCF level with respect to all bond lengths and bond angles by the Broyden–Fletcher–Goldfarb–Shanno gradient method.[8] The detection of transition states was carried out by employing the Powell algorithm.[9] The stationary points were characterized by force constant analysis (number of negative eigenvalues). For the maxima a zero gradient (accuracy 10^{-3}) has been obtained.

The CI calculations were carried out using a variation perturbation method (CIPSI algorithm[10]). A zero-order variation function was constructed by the 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.

The NMR spectra (^{31}P) were run on a Bruker AC80 and mass spectra were obtained on a Ribermag R1010 (DCI/NH_3).

The 1,3-diphosphapropenes were prepared by the room temperature photolysis of the corresponding diphosphiranes **1a** ($X_1 = X_2$ = Cl, Br[11a]), **1b** ($X_1 = X_2$ = Br), **1c** (X_1 = CH_3, X_2 = Cl[11b]) in solution with degassed hexane or toluene as solvent, using a Rayonet photochemical reactor operating at 300 nm. Compounds **1a** and **1c** were obtained as yellow crystals by recrystallization from pentane whereas compound **1b** was obtained as yellow oil.[1]

1(I) → 1(II) Isomerization. 1,3-Diphosphapropene 1a(II). A solution of compound **1a**(I) (0.060 g, 0.095 mmol) in degassed 1,2-dichloroethane (2 mL) was heated at 70 °C for 7 h. Compound **1a**(II) was obtained in solution as main product (70%). ^{31}P NMR ($Cl(CH_2)_2Cl$): $\delta P_1 = 316$, $\delta P_3 = 154$, $^2J_{PP} = 485$ Hz. MS: $m/e = 635$ (M^+).

1,3-Diphosphapropene 1b(II). A degassed solution of compound **1b**(I) (0.090 g, 0.125 mmol) heated at 60 °C for 2 h in benzene-d_6 or for 30 mn in 1,2-dichloroethane led to compound **1b**(II) as main product (70%). ^{31}P NMR (C_6D_6): $\delta P_1 = 323$, $\delta P_3 = 147$, $^2J_{PP} = 488$ Hz. MS: m/e = 722 (M^+).

1,3-Diphosphapropene 1c(II). The same procedure as described for **1a**(II) was used. Starting from a solution of **1c**(I) (0.060 g, 0.098 mmol) in degassed 1,2-dichloroethane (2 mL), **1c**(II) was formed in 80% yield after 10 h at 70 °C. ^{31}P NMR ($Cl(CH_2)_2Cl$): $\delta P_1 = 316$, $\delta P_3 = 166$, $^2J_{PP} = 598$ Hz.

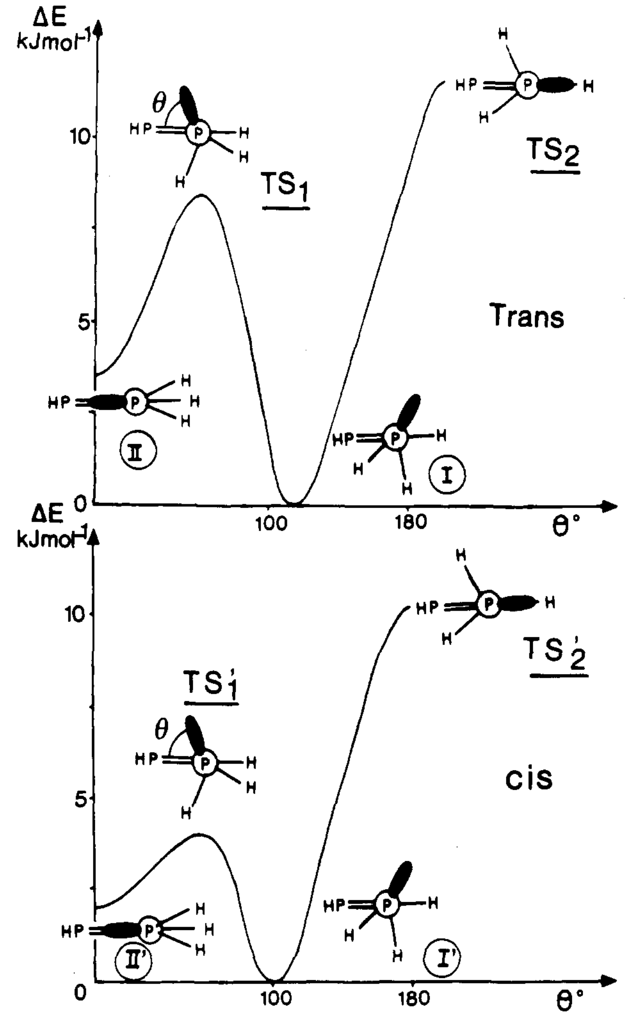

Figure 2. Rotation of the PH_2 group about the P–C bond. Relative energies as a function of θ.

In all cases, the heating of **1a–c**(I) solutions led to unidentified oligomers (20–30%) which become the main products on further heating. Compounds **1a–c**(II), unlike **2a–b**(II),[2] are only metastable in solution and all the attempts at their isolation failed. The compounds **3a–c** could be quantitatively obtained either by dilution of these solutions or after evaporation to dryness and redissolving the residue in another solvent. Compounds **3** were obtained as oil products.

3a. MS: $m/e = 599$ (M^+). ^{31}P NMR (C_6D_6): $\delta P_1 = 306$, $\delta P_3 = 19$, $^2J_{PP} = 129$ Hz, $^1J_{PH} = 597$ Hz.

3b. MS: $m/e = 642$ (M^+). ^{31}P NMR (C_6D_6): $\delta P_1 = 325$, $\delta P_3 = 20$, $^2J_{PP} = 128$ Hz, $^1J_{PH} = 599$ Hz.

3c. ^{31}P NMR (C_6D_6): $\delta P_1 = 305$, $\delta P_3 = 29$, $^2J_{PP} = 206$ Hz, $^1J_{PH} = 575$ Hz.

The isomerization reactions were followed by ^{31}P NMR spectroscopy. The changes in concentration ([1(I)] and [1(II)] with the time were determined by ^{31}P NMR using an external reference solution of known phosphorus concentration.

Results and Discussion

1. Ab Initio Analysis of the Rotation Process. The rotation process has been analyzed for the two isomers cis and trans of the 1,3-diphosphapropene HP=CHPH$_2$, by an ab initio method with a 4-31G* basis set. The calculations carried out with appropriate optimization processes

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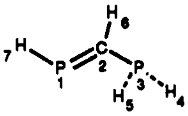
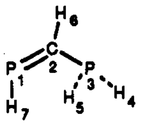
Table I. Diphosphapropene (Trans and Cis) Optimized Geometries and Total Energies (Bonds in Angstroms, Angles in Degrees): Experimental Values for 1a and 2a[1,2] in Parentheses

	trans isomer			
	II minimum	TS$_1$ saddle point	I minimum	TS$_2$ saddle point
θ	0.	59.	114. (100.)	180.
$d_{P_1=C_2}$	1.6444 (1.670)	1.6459	1.6476 (1.661)	1.6410
$d_{P_3-C_2}$	1.8366 (1.835)	1.8316	1.8265 (1.818)	1.8501
d_{P_1-H}	1.4162	1.4174	1.4186	1.4145
$d_{P_3(-H_4)-H_5(Cl)}$	1.4101 1.4100 (2.090)	1.4086 1.4071	1.4089 1.4050 (1.890)	1.4096 1.4093
$P_1C_2P_3$	120.04 (11.03)	122.56	125.09 (120.)	124.92
HP_1C_2	98.77	98.64	98.50	100.29
$H_4P_3C_2$	96.93	97.34	97.74	99.45
$H_5P_3C_2$	96.93	97.42	97.91	99.45
E_{tot} (au) SCF	−720.786206	−720.784165	−720.787597	−720.782943
E_{tot} (au) CI	−721.115417		−721.116427	

	cis isomer			
	II′ minimum	TS′$_1$ saddle point	I′ minimum	TS′$_2$ saddle point
•	0.	61.	102.	180.
$d_{P_1=C_2}$	1.6415	1.6425	1.6474	1.6430
$d_{P_3-C_2}$	1.8331	1.8330	1.8209	1.8443
d_{P_1-H}	1.4146	1.4146	1.4196	1.4186
$d_{P_3(-H_4)-H_5}$	1.4065	1.4066 1.4060	1.4077 1.4030	1.4073 1.4071
$P_1C_2P_3$	126.05	127.10	132.04	132.13
HP_1C_2	98.62	98.65	98.92	99.25
$H_4P_3C_2$	97.33	97.30	97.29	97.90
$H_5P_3C_2$	97.33	97.60	98.44	97.88
E_{tot} (au) SCF	−720.787258	−720.786421	−720.788032	−720.783883
E_{tot} (au) Cl	−721.116403		−721.116785	

display two minima and two saddle points for both the isomers (Figure 2). The two minima are located at θ = 0° and θ = 114° for the trans isomer and at θ = 0° and θ = 102° for the cis isomer, where θ is the dihedral angle between the lone pair of the P_3 phosphorus and the σ(P–C) bond.

In order to take into account the correlation effects, calculations including CI were performed for these four minima.

It is found that the cis isomer with θ = 102° is the most favored energetically. However, the energy difference between it and the trans isomer with θ = 114° is very small (about 1 kJ·mol^{-1} after CI) (Table I). It is interesting to note that the most stable conformations of I and II are in contrast to that of ethenylphosphine. For the latter, the most stable conformation corresponds to θ = 0°.[5c]

These results can be interpreted by different stabilizing interactions when θ is near 90° in the two systems. The energetic lowering of the π^* orbital from ethylene to phosphaethene involves a more important interaction for $n_p \leftrightarrow \pi^*_{P=C}$ than that for $n_p \leftrightarrow \pi^*_{C=C}$.

However, in the nonsubstituted system, the energetic differences between the privileged rotamers, trans and cis gauche forms, and the corresponding syn forms, are very small, of the order of 1–3 kJ·mol^{-1}, with CI taken into account. This is a consequence of the important pyramidalization of phosphorus atom that leads to nonnegligible interactions by stabilizing hyperconjugations $\pi^*_{PH_2} \leftrightarrow \pi_{P=C}$ and $\pi_{PH_2} \leftrightarrow \pi^*_{P=C}$ for the syn rotamer (θ = 0°).

The optimized geometric parameters for the 1,3-diphosphapropenes vary as the experimental observed modifications for **1a** and **2a** (Table I).

An increase of $P_1C_2P_3$ angle occurs from θ = 0° to θ = 114°.

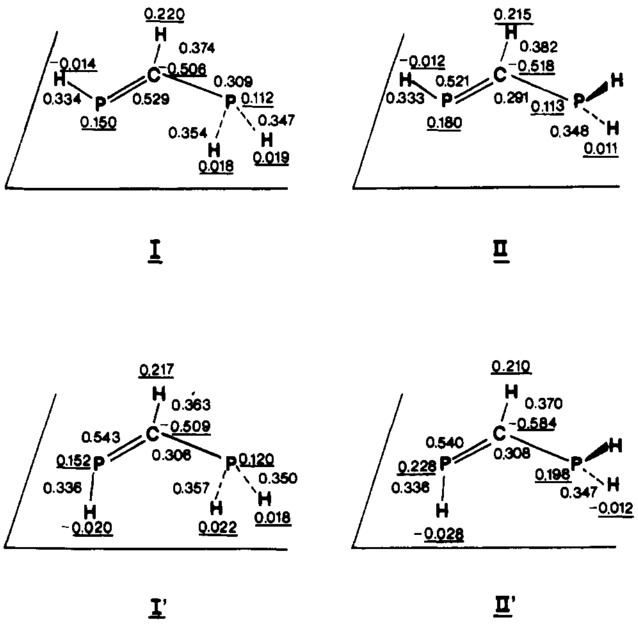


Figure 3. Mulliken population analysis, net total charges (underlined), overlap populations.

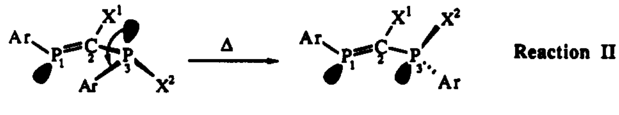
In the same way, the lengthening of P–Cl bond, 1.89 Å for **1a**, 2.09 Å for **2a**, can be compared to the calculated lengthening for P_3H_5 bond (1.405 Å for θ = 114° and 1.41 Å for θ = 0°).

Although small, the variations in length of single and double P–C bonds reveal the effect of interactions. So, we observe a shortening of P–C length and a lengthening of P=C double bond length for the privileged rotamer I in which the $n_P \leftrightarrow \pi^*_{P=C}$ interaction occurs. These deforma-

Table II. ^{31}P NMR Parameters of Compounds 1, 2, and 3

	1(I)			1(II)			2(II)			3			
	δP_2	δP_3	$^2J_{PP}$ (Hz)	δP_2	δP_3	$^2J_{PP}$ (Hz)	δP_2	δP_3	$^2J_{PP}$ (Hz)	δP_1	δP_3	$^2J_{PP}$ (Hz)	$^1J_{PH}$ (Hz)
a	276	75	106	316	154	485	328	144	457	306	19	129	597
b	293	75	109	323	147	488	343	143	487	325	20	128	599
c	273	84	143	316	166	598				305	29	206	575

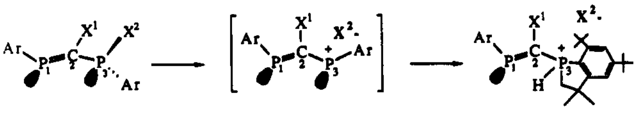
Scheme II



1a-c(I) 1a-c(II)

1a : X_1=X_2=Cl
1b : X_1=X_2=Br
1c : X_1=Cl, X_2=CH3

Scheme III



1 a-c(II) 3 a-c

Reaction III

tions are less evident in the case of the X-ray structures.

Concerning the electronic structure, the total polarity of the P=C double bond, approximately the same for the different rotamers (Figure 3), is near to that of phosphaethene. As observed for HP=CH$_2$,[12] the π-system is characterized by a quasi-symmetrical distribution.

In the electronic structure of these rotamers, the most important differences concern the orbital molecular energies related to the magnitude of the interaction between the phosphorus lone pair and the $\pi_{P=C}$ system.

The rotation barriers for the interconversion are low, 5.35–12.21 kJ·mol^{-1} for trans isomer and 2.20–10.90 kJ·mol^{-1} for cis isomer. For the models presented in this work, only the bielectronic interaction effects are taken into account for the calculated barriers.

2. Experimental Study of the Interconversion Process. In order to test the theoretical prediction of two possible rotamers for 1,3-diphosphapropene an experimental study of **1a** (conformation I) and **2a** (conformation II) by ^{31}P NMR at various temperatures was performed.

We observe, for compound **1a**, an increase of the $^2J_{PP}$ coupling constant with temperature (ΔJ = 20 Hz between −80 and 90 °C) and for compound **2a**, a slight decrease (ΔJ = 5 Hz between −70 and 70 °C). Compounds **1a–c**(I) were then heated further.

After being heated in benzene or 1,2-dichloroethane, the isomerization of compounds **1a–c**(I) yields diphosphapropenes which are found to have very different NMR parameters. Indeed, for these isomers obtained after heating, we observe an important deshielding of the chemical shift about 30–40 ppm for P$_1$ and 70–80 ppm for P$_3$, whereas the $^2J_{PP}$ coupling constant takes values ranging from 485 to 598 Hz (Table II). Since the ^{31}P NMR parameters are very close to those **2a–b** (with conformation II), we conclude that I → II isomerization takes place (Scheme II). So rotamers I and II exist in a same series of diphosphapropenes.

The notable effects observed for $^2J_{PP}$ values are a consequence of the relative positions of the phosphorus lone pairs. This phenomenon has been already observed for the diphosphinoamines in which nitrogen is sp^2 hybridized.[13] For these compounds, the $^2J_{PNP}$ values ranging from 15 to 665 Hz depend on the relative orientation of the lone pairs. For the 1,3-diphosphapropenes, the $^2J_{PP}$ values are affected by carbon C$_1$ and phosphorus P$_3$ substituents[14] ($^2J_{PP}$ decreases when the electronegativity of the substituents increases) and also strongly dependent of the relative lone pair positions. When the angle of the two lone pairs is about 100°, the $^2J_{PP}$ coupling constants vary between 106 and 143 Hz and when the two lone pairs are in the same plane, in a syn position ($\theta = 0°$), the $^2J_{PP}$ values are extremely large: 485 Hz < $^2J_{PP}$ < 598 Hz. Such values are close to the $^1J_{PP}$ coupling constant between two unsaturated phosphorus atoms in diphosphenes[15] and much larger than the values found in the literature for diphosphapropenes.[14-16] For these compounds, the inherent dependence of the $^2J_{PP}$ constant on phosphorus environment allows Karsch and co-workers to distinguish cis and trans isomers[16] ($^2J_{PP}$ trans > $^2J_{PP}$ cis), similarly this enables us to characterize different rotamers.

This explanation differs from that of Fluck[17] who considers that the increase of the $^2J_{PP}$ values can be interpreted as corresponding to an increase in the PCP bond angle. Indeed, the comparison of PCP angles for **1a** and **2a** reveals a slight decrease from 120° to 110° whereas $^2J_{PP}$ value increases from 106 to 457 Hz.

The determination of the kinetic parameters of the irreversible isomerization reaction **1b**(I) → **1b**(II) at 30 °C in deuteriated benzene solution has been carried out by ^{31}P NMR. The free enthalpy of activation is 104.5 kJ·mol^{-1}. Nevertheless, the diphosphapropenes **1a–c**(II) are less stable than **1a–c**(I). A modification of the concentration or the change of solvent leads to the formation of the corresponding phosphonium phosphaalkene **3a–c** (Scheme III). The ^{31}P NMR parameters are reported in Table II.

From the calculated values as well as from the experimental data, we note a lengthening of P–X bond (X = H, or X = Cl). The lengthening of about 10% (due to the $\pi^*_{PH_2} \leftrightarrow \pi_{P=C}$ interaction) ascribes a ionic character to the P–X bond. The partial charge attributes a phosphenium character to the phosphorus atom; consequently, all the ^{31}P chemical shifts are deshielded around 50–70 ppm (Table II). Due to the phosphorus environment, the phosphenium character makes the compounds **1a–c**(II) unstable. On dilution or after the evaporation to dryness, the change of the solvent induces the definitive breaking of P–Cl bond and the formation of the more stable phosphenium phosphaalkenes **3a–c** (Scheme III). This kind of cation **3** has been already obtained by the action

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of $AlCl_3$ on **1a–c**(I) at room temperature.[18]

Moreover, the isomerization reactions are strongly dependent on the nature of the X_1 and X_2 substituents and the polarity of the solvent.

With the 1,2-dichloroethane as solvent, the isomerization of **1b** is the quickest reaction ($t_{1/2}$ = 6 min at 60 °C) whereas **1c** is the slowest ($t_{1/2}$ = 180 min at 70 °C).

For compounds **1a–c**, the isomerization always takes place with 1,2-dichloroethane as solvent while it is never observed in hexane. Finally, only compound **1b** undergoes the isomerization reaction in benzene or toluene solution.

The rate constant of the interconversion depends on the polarity of the solvents. For the reaction **1b**(I) → **1b**(II), $t_{1/2}$ = 20 min at 60 °C in the benzene whereas $t_{1/2}$ = 6 min in the dichloroethane at the same temperature. However, in the most polar solvent used (nitrobenzene), compounds **1a–c**(I) do not undergo the expected isomerisations but one ionization reaction takes place which leads to the formation of phosphonium phosphaalkenes **3a–c**. The calculated dipolar moment for the conformation I and II of $HP{=}CHPH_2$ are respectively 0.76 and 1.25 Debye. This result is consistent with the influence of polar solvent on the isomerization reactions I → II.

The fact, that the diphosphapropenes substituted on the phosphorus by the TSi group are thermodynamically stable in the syn conformation II is probably the consequence of the difference in steric bulkiness and of the electronic effect of Tsi group which, in this case, reduces the stabilizing $n_P \rightarrow \pi^*_{P=C}$ interaction.

Conclusion

The 1,3-diphosphapropenes exist in the form of two stable rotamers; their existence predicted by a theoretical study is verified experimentally using ^{31}P NMR method. The structural deformations of these two rotamers are connected to differentiate interactions between the P=C system and the phosphino group. These structural changes manifested through different NMR parameters would result in very different reactivities for these isolated systems.

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Notes

Bromine-Catalyzed Configuration Isomerization in Bicyclic [3.2.1] Systems

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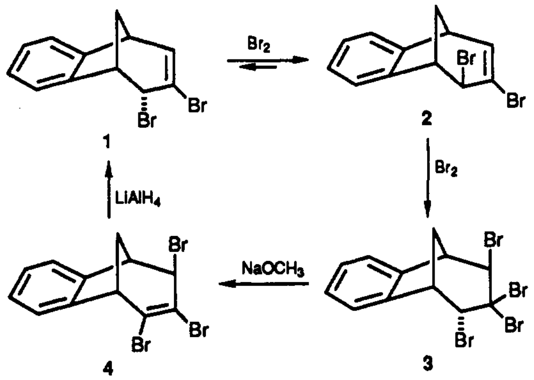
The study of ground state and photochemical solvolysis and Wagner–Meerwein rearrangements in certain bridge–ring systems containing aromatic groups and nucleofugal groups has been of considerable interest.[1,2] Study of these compounds has shown that there are stereo- and regiochemical requirements for both ionization and subsequent rearrangements. In this paper, we describe a new system where similar rearrangements have been observed. We report also an unusual configurational isomerization of *endo*-2,3-dibromo-6,7-benzobicyclo[3.2.1]-octa-3,6-diene (**1**) in the presence of bromine, which provides evidence for radical rearrangement.

Results and Discussion

The starting material **2**[3] was synthesized by addition of dibromocarbene to the readily available benzonorbornadiene,[4] as reported in the literature. The reaction of **2** with bromine[5] under radical conditions provided **3** in a yield of 65% besides six other products.[6] Treatment of **3** with 1 mol of sodium methoxide gave the tribromide **4** (Scheme I). The structure of **4** and the exo position of the bromine was determined by means of ^1H and ^{13}C NMR spectra.[7]

Scheme I



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[5] Treatment of **2** with bromine causes at first configuration isomerization in 10 min followed by addition of bromine to give **3** as the major product.

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[7] The exo configuration of bromine at C_4 has been established by analysis of the AB system arising from the bridge methylene protons H_{8e} and H_{8i}. The B part of the AB system shows a doublet. There is no further measurable coupling with the adjacent bridge head protons H_1 and H_5 due to nearly 90° dihedral angles between H_{8e} and H_1 and H_5. However, the A part of the AB system is split into triplets of doublets of doublet. The second doublet splitting ($^4J_{48i}$ = 1.5 Hz) originates from the proton on C_4 which is in the endo position. In the case of ^4J in the bicyclic systems one speaks of the M or W arrangement. The bonding arrangement of the coupled protons H_4 and H_{8i} meets M criterion. The fact that there is any coupling between H_{8i} and H_4 is an indication for the exo configuration of the bromine atom at C_4.

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