Oxyphosphoranes with an Oxaphospholene Ring: Analysis of the Activation Barriers of the Isomerization Process

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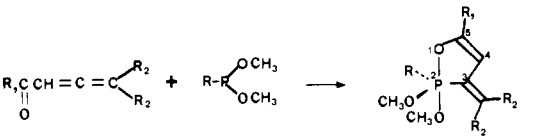
Abstract: New oxyphosphoranes containing a 1,2-oxaphospholene ring with an exocyclic double bond and an equatorial sp^2 carbon bonded to phosphorus are readily obtained by the reaction of tricoordinated compounds such as $RP(OMe)_2$ (R = Me, Ph, $CH{=}CH_2$, SMe, CN, OMe, OPh, NMe_2) or Ph_2POMe with α-allenic ketones. The trigonal-bipyramidal (TBP) structure of these phosphoranes is deduced from ^1H, ^{13}C, and ^{31}P NMR data. The regular exchange processes were studied by ^1H DNMR, and the associated free enthalpy of activation was obtained by computer simulation of the exchange patterns. The activation parameters for these phosphoranes are compared with those of analogous phosphoranes without the exocyclic double bond on the oxaphospholene ring and sp^3 carbon bonded to phosphorus. These kinetic parameters are interpreted in terms of the apicophilicity of ligands and steric effects within the assumption that the higher energy TBP topomer is energetically close to the real transition state of the isomerization pathway. Holmes' model is applied to conformational energy calculations of all the intermediates of the two possible isomerization pathways and allows us to find the most probable one. Furthermore the relative apicophilicity of Me, Ph, $CH{=}CH_2$, NMe_2, and OMe groups has been quantitatively evaluated. The CN and OPh ligands exhibit a high apicophilicity vs. the MeO group, while the SMe group presents a comparable one. A decreasing apicophilicity scale of these ligands has been set up and seems to be better correlated to the inductive constant σ_I than electronegativity.

The pseudorotation of stable oxyphosphoranes has been the topic of several studies during the last 10 years.[1] One of the main reasons for this development is the growing interest in the stereochemistry of reactions of tri- and tetracoordinated phosphorus compounds which involve pentacoordinated phosphorus intermediates. Therefore, the pseudorotation processes may have a great influence on the structure of the reaction products.[1d,2,3] In this work, we studied quantitatively the major contributions to the activation barrier of multiple pseudorotation processes occurring in a homogeneous series of monocyclic phosphoranes and determined the apicophilicity of the ligands and the steric effects. We thus studied the isomerization processes of new phosphoranes, **1a-1i**, with a 3-methyliden-Δ^4-1,2-oxaphospholene ring synthesized from trivalent compounds on α-allenic ketones,[4] particularly the 4-oxo-1,2-pentadiene.

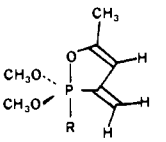
We established the trigonal-bipyramidal structure (TBP) of phosphorane **1a** by ^1H, ^{13}C, and ^{31}P NMR. The oxaphospholene ring occupies an apical-equatorial position with the sp^2 carbon bonded to phosphorus in an equatorial position, as would be expected from ring strain and electronegativity rules. The methoxy groups of compounds **1a-1i** exhibit an exchange process which can be readily followed by ^1H DNMR and which allows the determination of activation barriers associated with the isomerization process.



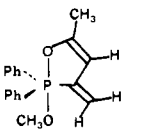
1

1a R = CH_3O, R_1 = CH_3, R_2 = H
1b R = $(CH_3)_2N$, R_1 = CH_3, R_2 = H
1c R = Ph, R_1 = CH_3, R_2 = H
1d R = CH_3, R_1 = CH_3, R_2 = H
1e R = $CH{=}CH_2$, R_1 = CH_3, R_2 = H
1f R = Ph, R_1 = iPr, R_2 = H
1g R = $(CH_3)_2N$, R_1 = iPr, R_2 = H
1h R = Ph, R_1 = tertBu, R_2 = H
1i R = Ph, R_1 = CH_3, R_2 = CH_3

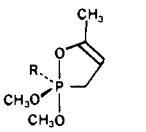
On the other hand, the NMR spectra of compounds **1j-1m**



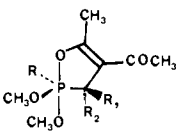
1j R = PhO
1k R = C≡N
1l R = SCH_3



1m



2a R = CH_3O
2b R = $(CH_3)_2N$
2c R = Ph



3a R_1=R=Ph, R_2=H
3b R_1=R_2=Ph, R=H
3c R=Ph, R_1=R_2=H
3d R=Ph, R_1=R_2=CH_3
3e R=OCH_3, R_1=Ph, R_2=H
3f R=OCH_3, R_1=R_2=CH_3

(1) (a) R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Georg Thieme Verlag, Stuggart, 1973; (b) F. Ramirez and I. Ugi, "Advances in Physical Organic Chemistry", Collect. Vol. 9, V. Gold, Ed., Academic Press, New York, 1971, p 25; (c) R. R. Holmes, *Acc. Chem. Res.*, **5**, 296 (1972); (d) S. Trippett, *Phosphorus Sulfur*, **1**, 89 (1976); (e) D. Hellwinkel, "Organic Phosphorus Compounds", Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, 1972, p 185-339.

(2) (a) P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem., Int. Ed. Engl.*, **12**, 91 (1973); (b) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968); (c) R. F. Hudson and C. Brown, *ibid.*, **5**, 204 (1972); (d) F. Ramirez, *Bull. Soc. Chim. Fr.*, 3491 (1970); (e) R. Burgada, *ibid.*, 407 (1975); (f) K. Mislow, *Acc. Chem. Res.*, **3**, 321 (1970); (g) R. A. Naylor and A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1908 (1976); (h) T. D. *Inch* and G. J. Lewis, *Carbohydr. Res.*, **45**, 65 (1975); (i) F. M. Richards and H. W. Wyckoff, "The Enzymes", Vol. IV, 3rd ed, P. D. Boyer, Ed., Academic Press, New York, 1971, pp 647-806, and references cited therein.

(3) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).

(4) G. Buono and G. Peiffer, *Tetrahedron Lett.*, 149 (1972).

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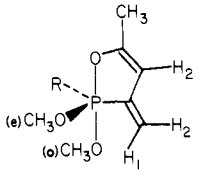
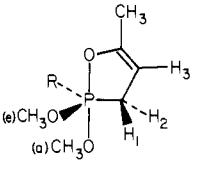
Table I. ^1H and ^{31}P NMR of Phosphorane 1 and 2[a]



1



2

compd	R	$\delta^{31}P$[b]	CH_3	$CH_3O_{(e)}$[c]	$CH_3O_{(a)}$[c]	H_1	H_2	H_3	R
1a	CH_3O	−46.4	1.74	3.50 (13.3)	3.20 (10.8)	5.98 (21.4)	5.63 (56.4)	5.36 (42.6)	3.50 (13.3)
1b	$(CH_3)_2N$	−45.7	1.78	3.48 (13.4)	3.32 (10.2)	5.66 (21.1)	5.47 (55.1)	5.32 (40.2)	2.63 (10.2)
1c	Ph	−33.7	1.64	3.59 (13.8)	3.14 (10.0)	6.07 (20.1)	5.79 (52.8)	5.43 (39.6)	7.2-7.6 (m)
1d	CH_3	−21.6	1.74	3.59 (13.9)	3.14 (10.0)	5.61 (20.7)	5.56 (53.4)	5.34 (37.9)	1.64 (16.1)
1e	$CH{=}CH_2$	−39.3	1.73	3.53 (13.9)	3.49 (9.8)			5.31 (39.4)	
1i[e]	Ph	−47.6	1.65	3.62 (13.8)	3.21 (10.4)	1.91 (1.6)	2.10 (3.1)	5.49 (34.7)	
1j	PhO	−49.6	1.65	3.51 (14.0)		6.12 (22)	5.74 (57)	5.45 (44)	
1k[d]	C≡N	−47.3	1.82	3.51 (14.5)		5.70 (20.0)	5.52 (53.1)	5.44 (39.9)	
1m[d]	Ph	−42.2	1.52		2.66 (10.2)	6.05 (20.2)	5.82 (56.1)	5.43 (39.0)	7.3 (m)
1l	SCH_3	−26.5	1.72	3.48 (13.0)		5.65 (22.6)	5.54 (57.3)	5.42 (44.0)	1.99
2a	CH_3O	−21.1	1.76	3.51 (12.3)		2.56 (19.6)		4.47 (47.8)	
2b	$(CH_3)_2N$	−22.7	1.73	3.57 (12.7)	3.24 (10.2)	2.44 (19)		4.44 (44.8)	2.64 (10.0)
2c	Ph	−11.2	1.60	3.77 (13.3)	3.13 (10.0)	2.84 (18.0)		4.48 (44.2)	7-7.3 7.5-8 (m)

[a] Numbers in parentheses indicate the coupling constants J_{HP} in hertz. For phosphorane 1 NMR data do not change with the nature of the alkyl substituent in the 5 position of oxaphospholene ring, so the values obtained for 1f, 1g, and 1h are not included. The coupling constants between the oxaphospholene ring protons are about $^2J_{H_1H_2} \simeq 2$–2.4 Hz, $^4J_{H_1H_3} \simeq 0.6$–0.8 Hz, and $^4J_{H_2H_3} \simeq 0.5$–0.6 Hz for phosphorane 1, except 1i. For 1e a complex overlapping spectrum is observed for the vinyl substituent protons at 5.5-5.65 ppm. [b] Relative to H_3PO_4; negative values indicate resonance to high field of standard. [c] The magnetic parameters of the methoxy protons have been measured below the coalescence temperature. For the other protons, these parameters have been measured at room temperature. For 1l, the average of equatorial and axial environments because intramolecular exchange was not stopped in the ^1H spectrum at lowest accessible temperature. [d] The cyano group is in apical position and the two phenyl groups are in equatorial positions. [e] The assignment of the methyl groups ($H_1 \simeq H_2 \simeq$ Me) is realized from the anisotropic effect of the phenyl group and the values of the coupling constants [$^4J_{HP}$ (trans) > $^4J_{HP}$ (cis)].

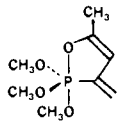
remain unaffected by temperature changes in the range −100 °C to 120 °C. However, the position of methoxy groups has been assigned on the basis of NMR parameter values (chemical shift and coupling constants with phosphorus) as well as symmetrical considerations. Thus, the relative high apicophilicity of the ligands CN, PhO, and SMe and the low apicophilicity of the phenyl group were shown.

We synthesized phosphorane **2** from addition of the same trivalent phosphorus compounds to methyl vinyl ketone. The activation barriers of the exchange process of these compounds are compared with those of phosphoranes **1**. Hence, some conclusions about the electronic and steric effects of equatorial ring carbons can be drawn.

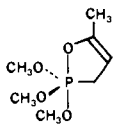
The results obtained in the two series are compared with those obtained by Gorenstein[5] on phosphorane **3** and some general trends concerning the rates of the exchange processes have been outlined.

Results and Discussions

1. Structure of Phosphorane 1. As it was shown[5] for compound **2a**, the methoxy groups of phosphorane **1a** are magnetically

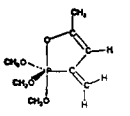


1a



2a

equivalent at room temperature ($^3J_{POCH_3}$ = 12.6 Hz) and only one doublet was observed. However, at −120 °C in deuteriotoluene, this signal splits into two doublets of relative intensities, 2:1, corresponding to two equatorial ($^3J_{POCH_3}$ = 13.3 Hz) and one apical ($^3J_{POCH_3}$ = 10.8 Hz) methoxy groups (Figure 1). These spectroscopic data suggest that at low temperature the pseudorotation is restricted and reveal a TBP structure for the molecule. The equatorial methoxy protons are shifted downfield vs. the apical protons and exhibit the highest coupling constant $^3J_{POCH_3}$ (Table I). The negative ^{31}P chemical shift −46.4 ppm vs. H_3PO_4 is typical



1a

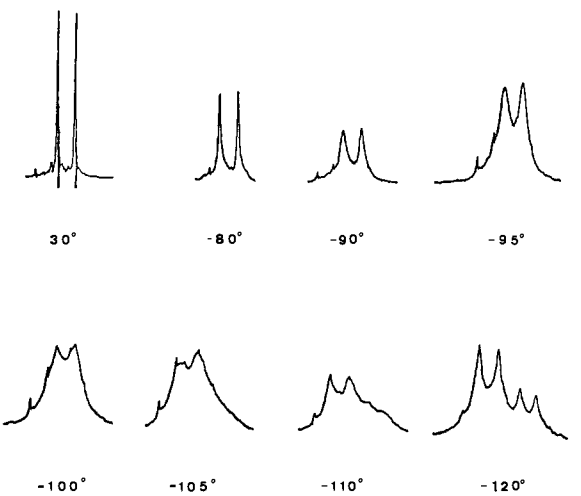


Figure 1. Temperature dependence of the ^1H NMR spectrum of the phosphorane **1a**. Exchange of the methoxy groups.

of a pentacoordinated structure, and the ^1H and ^{13}C signals of the oxaphospholene ring nuclei are unchanged with change in temperature. The oxaphospholene ring is apical equatorial in the TBP structure with the sp^2 carbon ring in the equatorial position as shown by the large coupling constant $^1J_{PC}$ = 202.0 Hz. The $^1J_{PC}$ coupling constant is closely related to the s character of the bond, so it depends upon the coordination state of phosphorus and the nature of the atoms bonded to phosphorus.[6] In the equatorial molecular plane of the TBP, the bonding could be interpreted in

(5) (a) D. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **92**, 634 (1970); (b) D. Gorenstein, *ibid.*, **92**, 644 (1970).

(6) G. Buono and J. R. Llinas, unpublished data.

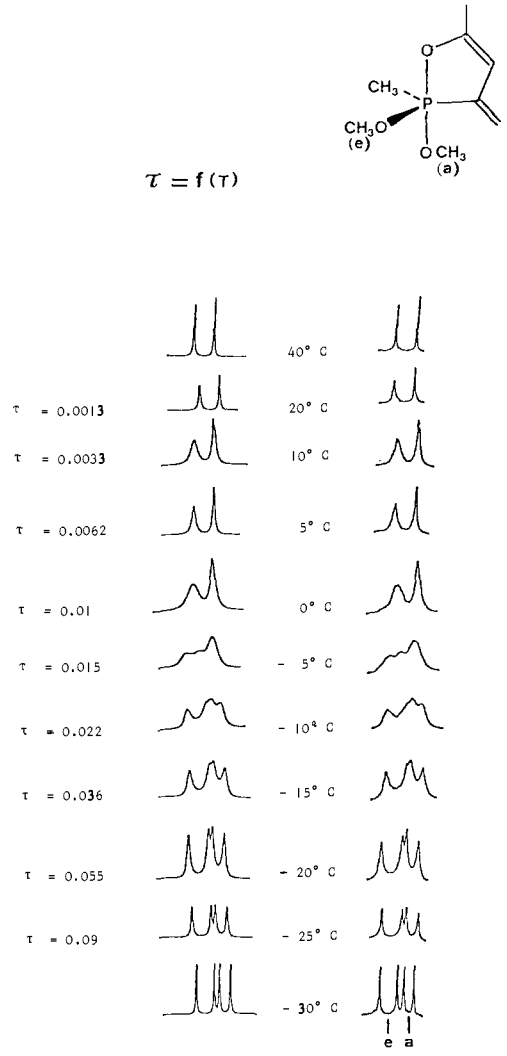


Figure 2. ^1H DNMR of compound **1d**: exchange of the methoxy groups. Experimental (right) and calculated (left) spectra at different temperatures.

terms of a sp^2 hybrid; hence, the $^1J_{PC}$ becomes greater in contrast to that of the apical bonds where the s character is weak.[7,26] The $^1J_{PC}$ for compound **1** is usually greater (50 Hz) than that of compound **2**; this can also be explained by the presence of the sp^2 carbon bonded to phosphorus in compound **1**. The same variations hold for the $^1J_{PC}$ of the extracyclic alkyl ligands (Table II), **1d** ($^1J_{PC}$ = 155.9 Hz) vs. **1e** ($^1J_{PC}$ = 192.6 Hz).

If one of the methoxy groups of compounds **1a** and **2a** is substituted by a ligand such as R = NMe_2, Ph, Me, and $CH{=}CH_2$, we observe the same exchange process between the equatorial and apical methoxy groups (Figures 2 and 3) but with a higher coalescence temperature (Table III). By analogy with spectral parameters of compounds **1a** and **2a**, we can assume for **1b–1i** and **2b–2c** a TBP structure in which the R ligand occupies an equatorial position. The assignment of methoxy groups in the TBP is made from ^1H and ^{13}C spectra on the basis of the shielding of an apical methoxy group vs. an equatorial one and the different coupling constants $^3J_{POCH_3(e)}$ (13–14 Hz) and $^3J_{POCH_3(a)}$ (10–11 Hz). On the other hand, coupling constants $^2J_{POC}$ are insensitive to the different positions of the methoxy groups in the TBP. From these considerations we ascribe an equatorial position to the methoxy groups of **1j** and **1k**. For **1k** the coupling constants $^1J_{PCN}$ = 9.3 Hz provided further support for this assignment; the $^1J_{PCN}$ is 210 Hz for the analogous spirophosphorane with dioxaphospholane and oxaphospholene rings and the CN group is compelled to span in the equatorial plane.[8] The apical position of the methoxy group in the phosphorane **1m** is inferred from NMR phenyl group equivalence, ^1H and ^{13}C NMR shielding of the methoxy, and the low coupling constant $^3J_{POCH_3}$ = 10.2 Hz. Compound **11** (R = SMe) shows only one doublet for the two methoxy groups over a temperature range −80 to 100 °C, but the SMe position cannot be deduced from averaged NMR data. This can be explained in two ways: either the exchange is too fast in the NMR time scale (therefore the SMe group is likely as apicophilic as the MeO group) or the SMe position is apical.

(7) (a) H. Shmidbaur, W. Buchner, and F. H. Köhler, *J. Am. Chem. Soc.*, **96**, 6208 (1974); (b) G. Buono and J. R. Llinas, *Tetrahedron Lett.*, 749 (1976); (c) K. I. The and R. G. Cavell, *Chem. Commun.*, 716 (1975); H. Dreeskamp, C. Schumann, and R. Schmultzer, *Chem. Commun.*, 71 (1970); J. A. Gibson and G. Y. Roschenthaler, *J. Chem. Soc., Dalton Trans.*, **1492** (1977); (f) see the text for the different coupling constant J_{PCN_a} and J_{PCN_e}.[8]

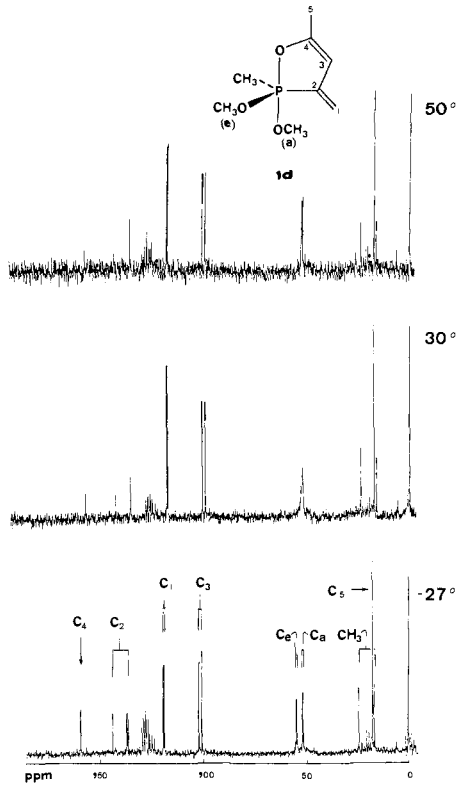


Figure 3. Temperature dependence of the ^{13}C NMR spectrum of the phosphorane **1d** (toluene-d_8 as solvent): slow exchange, coalescence, and fast exchange domains.

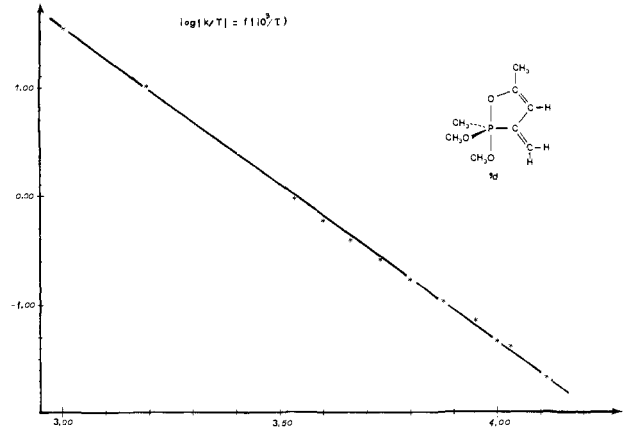
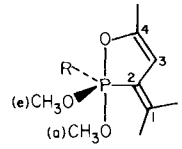


Figure 4. Determination of activation parameters associated with the exchange of the methoxy groups for the phosphorane **1d**.

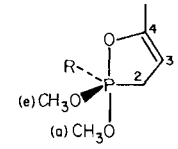
2. Exchange Process Studies. The results of ^1H DNMR studies on 11 phosphoranes are reported in Table III. The activation parameters of the exchange process have been evaluated from the simulation of experimental spectra at different temperatures by

(8) G. Buono and J. R. Llinas, presented at the Congress of the Phosphorus Chemistry, Strasbourg, France, Sept 1978.

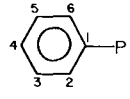
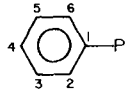
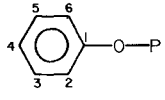
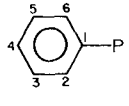
Table II. ^{13}C NMR of Phosphoranes **1** and **2**[a]



1



2

compd	R	CH_3	$CH_3O_{(a)}$[b]	$CH_3O_{(e)}$[b]	C_1	C_2	C_3	C_4	R		
1a	CH_3O	17.0 (2.2)	54.6 (10.7)		122.3 (7.3)	143.3 (202.0)	102.8 (33.2)	156.5 (9.0)			
1b	$(CH_3)_2N$	17.1	51.9 (10.5)	55.9 (10.9)	118.9 (7.3)	142.2 (194.0)	102.8 (31.9)	156.2 (7.8)	40.2 (5.7)		
1c[d]		17.5	51.6 (9.8)	55.9 (10.1)	121.5 (8.6)	141.2 (161.1)	101.6 (29.3)	158.5 (4.0)	C_1 139.3 (195.2) $C_{2,6}$ 129.6 (10.9) $C_{3,5}$ 127.7 (16.6) C_4 129.4 (3.4)		
1d	CH_3	17.4	51.9 (9.6)	54.9 (9.4)	119.1 (10.9)	141.2 (151.7)	101.1 (27.3)	159.4 (2.4)	20.1 (155.9)		
1e	$CH{=}CH_2$	17.4	51.8 (9.5)	55.1 (9.8)	120.7 (8.9)	141.8 (163.3)	101.5 (28.8)	158.6 (3.9)	135.3 (192.6)	131.2 (4.1)	
1i[c,d]		17.4	53.1 (10.1)		131.5 (10.4)	136.6 (169.7)	100.9 (29.3)	154.1 (3.3)	C_1 140.3 (194.9) $C_{2,6}$ 130.0 (10.9) $C_{3,5}$ 127.4 (16.4) C_4 129.0 (3.5)		
1j[d]		16.5 (2.4)		55.2 (10.8)	123.2 (7)	141 (203.4)	103 (33.8)	156.3 (8.5)	C_1 149 (11.4) $C_{2,6}$ 121 (4.7) $C_{3,5}$ 129 C_4 129.6		
1k[e]	C≡N	16.4 (3.4)		57.0 (10.7)	122.6 (19.2)	140.0 (159.3)	103.6 (30.1)	157.0 (5.7)	118.0 (9.3)		
1l	SCH_3	16.8	54.6 (11.9)		119.5 (8.0)	142.8 (169.4)	102.3 (32.9)	157.6 (4.6)	15.9 (7.0)		
1m[e]	Ph	16.6	51.3 (7.5)		118.8 (7.5)		100.4 (26.5)	158.3 (—)			
2a	CH_3O	16.5 (4.6)	51.5 (10.5)	55.8 (10.0)		29.0 (163.1)	91.4 (5.3)	151.7 (16.9)			
2b	$(CH_3)_2N$	16.8 (3.9)	51.2 (10.9)	56.0 (10.9)		28.5 (160.0)	91.4 (6.2)	151.5 (16.4)	39.9 (5.4)		
2c[d]		17.2 (1.9)	53.4 (9.9)			30.2 (132.3)	90.0 (5.3)	152.9 (11.3)	C_1 138.7 (183.4) $C_{2,6}$ 132.2 (9.7) $C_{3,5}$ 128.0 (15.9) C_4 129.0 (2.1)		

[a] Parts per million from ^{13}C of $(CH_3)_4Si$, positive values indicating shifts to low field of standard. Numbers in parentheses indicate the coupling constants J_{CP} in hertz. [b] For each compound the spectral parameters of methoxy groups have been measured below the coalescence temperature; for the other positions the parameters have been measured at room temperature. The assignments were deduced from compound **1m** and temperature-dependent ^{13}C NMR spectra of **2a**, yielding at low temperature two ^{13}C signals for the CH_3O groups with the relative intensity ratio 1:2. [c] Methyl attached in the cis position vs. phosphorus, 24.0 ppm (4.4 Hz); Me in the trans position, 25.5 ppm (15.2 Hz). [d] The assignment of the 2,6 and 3,5 phenyl carbons was deduced from coupling constants $^3J_{CH}$ obtained from undecoupled spectrum. Thus, we have observed two $^3J_{CH}$ coupling constants for C_2 and C_6 and only one for C_3 and C_5. For **1j** this assignment was realized by analogy with the sequence of chemical shifts found for alkoxy benzene as follows: $\delta_{C_1} > \delta_{C_3,C_5} > \delta_{C_4} > \delta_{C_2,C_6}$ and by studying[23] different spirophosphoranes with para-substituted phenoxy group. [e] The CN group is in apical position of the TBP for 1k and the two phenyl groups are in equatorial position for **1m**.

Table III. Activation Parameters of Exchange Process Determined by ^{1}H DNMR

compd	R	T_c, °C[a]	$\Delta\nu$, Hz[b]	$\Delta H^\ddagger$, kcal/mol[c]	$\Delta S^\ddagger$, eu[c]	$\Delta G^\ddagger_c$[d]	$\Delta G^\ddagger_{300}$[e]
1a	CH_3O	−99	28.2	7.9	−3.6	8.5	9.0
1b	$(CH_3)_2N$	−12	15.9	9.9	−13.0	13.3	13.8
1c	Ph	18	52.0	14.0	−1.3	14.4	14.4
1d	CH_3	−7	8.7	13.2	−2.0	13.7	13.8
1e	CH_2=CH	−9.5	8.2	10.0	−13.2	13.5	14.0
1f	Ph	20	50.0	13.3	−2.6	14.1	14.1
1g	$(CH_3)_2N$	20	30.7	9.9	−12.4	13.6	13.6
1h	Ph	30	68.0	14.2	0.1	14.1	14.2
1i	Ph	18	41.4	13.0	2.7	12.3	12.2
2a[f]	CH_3O	85		11.1		9.6	
2b	$(CH_3)_2N$	13	30.9	13.6	−1.9	14.1	14.2
2c	Ph	−10	57.4	13.1	0.1	13	13.1

[a] The coalescence temperatures, T_c, refer to the temperatures of maximum broadening of the NMR signals from the methoxy groups. [b] Difference in chemical shifts of apical and equatorial methoxy groups in the absence of exchange. [c] Calculated from line shape analysis. Calculated errors lie within ±1.5 kcal/mol for $\Delta H^\ddagger$ and within ±3 eu for $\Delta S^\ddagger$. [d] $\Delta G^\ddagger_c$ in kcal/mol calculated at coalescence temperature from the equation $\Delta G^\ddagger_c \simeq \Delta H^\ddagger - T_c\Delta S^\ddagger$ with estimated uncertainty less than 0.2 kcal/mol. Similar values were obtained (±0.1 kcal/mol) from the equation $\Delta G^\ddagger_c = 4.57 \times 10^{-3} T_c[10.32 + \log(T_c\sqrt{2}/\pi\Delta\nu)]$. [e] $\Delta G^\ddagger$ values in kcal/mol reported at 300 °K. [f] Reference 5.

analyzing the coupled ABX two-site exchange with $J_{AB} = 0$ (Figures 2 and 4). The regular exchange process may be deduced from several experimental features: (a) the energetic barriers for exchange processes do not depend either on the solvent or on the hexafluoroisopropyl alcohol added. (b) No ionic structure from the oxaphospholene ring opening has been observed by ^{31}P NMR even at high temperature (130 °C). (c) ^{1}H and ^{13}C NMR parameters of oxaphospholene ring and R ligand are unchanged with changes in temperature (Figure 3). (d) The activation entropies are near zero except where negative values were found for compounds **1b**, **1e**, and **1g** with R = Me_2N and CH_2=CH.

3. Determination of Isomerization Pathways. Different isomerization pathways describe the exchange ligand processes. These interconversion pathways may be topologically[9] depicted by the graphs as is shown[9f] in Figure 5. The topomers are associated with vertices and the elemental isomerization processes with edges. Berry pseudorotation[10] (BPR) and turnstile rotation[1b,11] (TR) mechanisms belonging to the same rearrangement mode are permutationally undistinguishable; hence, every edge represents either BPR or TR mechanisms with the respective transition state proper to these mechanisms: C_{4v} square-pyramidal and C_s TR-30° states. However, on the basis of both theoretical estimates[12] and solid state structural distorsions,[13a,b] the Berry process seems to be the most likely.

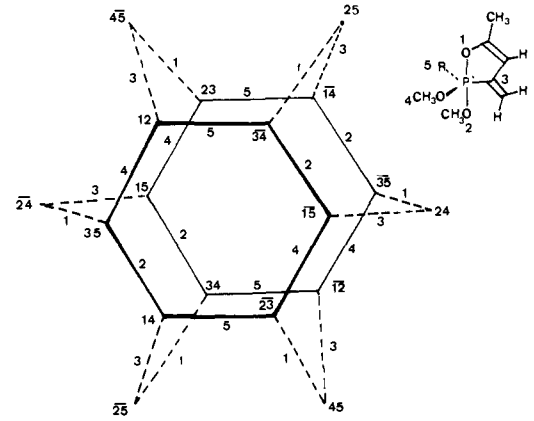


Figure 5. Topological diagram[9f] for pseudorotation, summarizing isomerization (heavy solid lines) and epimerization process (dashed lines) for compounds **1**, **2**, and **3**. Isomers are denoted by Gielen's notation.[9a]

The topomers 13 and $\overline{13}$ are ruled out of the graph because the oxaphospholene ring is unable to occupy the two apical positions of a TBP. We can deduce from this topological diagram two types of energetically possible pathways for permutational isomerizations:

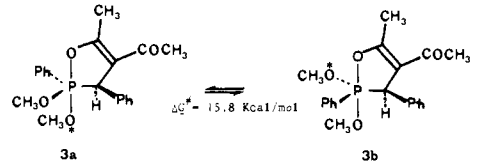
$$12 \rightleftharpoons \overline{34} \rightleftharpoons \overline{15} \rightleftharpoons \overline{23} \rightleftharpoons 14 \qquad \text{(I)}$$

$$12 \rightleftharpoons 35 \rightleftharpoons 14 \qquad \text{(II)}$$

or their respective mirror image pathways Ī and ĪĪ

$$\overline{12} \rightleftharpoons 34 \rightleftharpoons 15 \rightleftharpoons 23 \rightleftharpoons \overline{14} \quad \text{(Ī)} \qquad \overline{12} \rightleftharpoons \overline{35} \rightleftharpoons \overline{14} \quad \text{(ĪĪ)}$$

We have excluded any epimerization processes involving the high-energy topomers 24, 45, 25, $\overline{24}$, $\overline{45}$, and $\overline{25}$ in which the oxaphospholene ring is forced to span the unfavored diequatorial position of the TBP geometry; such intermediates would require more than 14 kcal/mol. This assumption is supported by the ^{1}H and ^{13}C DNMR results of analogous spirophosphoranes with identical oxaphospholene and dioxaphospholane rings.[7b,14] The exchange process of these compounds involve high-energy topomers with a diequatorial ring and indeed the free-energy activation is greater than that found on **1a** and **2a**. Furthermore, Gorenstein[5] has shown by ^{1}H DNMR that the methoxy exchange occurs between diastereoisomer phosphoranes **3a** and **3b** without epimerization of the phosphorus atom. The energetic barrier associated with isomerization is 15.8 kcal/mol, while that associated with epimerization process has been estimated above 24 kcal/mol.



3a 3b

Figure 6 describes the two low-energy isomerization pathways for the phosphoranes **2** and **3** with their own TBP and SP structure intermediates. The TBP topomers $\overline{34}$, $\overline{15}$, $\overline{23}$, and 35 are destabilized either by the apical ring carbon position or the apical R ligand position or both in an apical position. The SP structures are denoted by the labeled apical ligand; for the structures in which a ring occupies a cis dibasal position, the destabilization arises from the axial position of the methoxy group more polar than the R group. With these compounds it is not possible to distinguish by ^{1}H and ^{13}C DNMR the two isomerization pathways I and II since both belong to the same permutational isomerization operation. From the experimental $\Delta G^\ddagger$ values of exchange processes occurring in different phosphoranes, Trippett[1d,16] and Holmes[15]

(9) (a) M. Gielen, "Chemical Applications of Graph Theory", A. T. Balaban, Academic Press, New York, 1976, pp 261–298; (b) M. Gielen, "Stêreochimie dynamique", Freund Publishing House, Tel Aviv, Israël, 1974; (c) P. C. Lauterbur and F. Ramirez, *J. Am. Chem. Soc.*, **90**, 6722 (1968); (d) E. L. Muetterties, *J. Am. Chem. Soc.*, **91**, 1636, 4115 (1969); (e) D. J. Cram, J. Day, D. R. Rayner, D. M. Von Schriltz, D. J. Duchamp, and D. C. Garwood, *ibid.*, **92**, 7369 (1970); (f) K. E. De Bruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7631 (1969).

(10) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(11) I. Ugi, F. Ramirez, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *Angew. Chem.*, **82**, 766 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 725 (1970).

(12) (a) J. A. Altmann, K. Yates, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **98**, 1450 (1976); (b) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *ibid.*, **94**, 3047 (1972); (c) A. Rauk, L. C. Allen, and K. Mislow, *J. Am. Chem. Soc.*, **94**, 3035 (1972); (d) A. Strich and A. Veillard, *ibid.*, **95**, 5574 (1975); (e) P. Russegger and J. Brickmann, *Chem. Phys. Lett.*, **30**, 276 (1975); (f) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, **4**, 288 (1971); (g) S. K. Shih, S. D. Peyerimhoff, and R. J. Buenker, *J. Chem. Soc., Faraday Trans. 2*, **75**, 379 (1979).

(13) (a) R. R. Holmes and J. A. Deiters, *J. Chem. Res.* 92 (1977); *J. Am. Chem. Soc.*, **99**, 3318 (1977); R. R. Holmes, *Acc. Chem. Res.*, **12**, 257 (1979); (b) J. R. Llinas, D. Sc. *Thesis*, Aix Marseille University III, Marseille, France, 1979, pp 8–57.

(14) G. Buono and J. R. Llinas, unpublished data.

(15) R. R. Holmes, *J. Am. Chem. Soc.*, **100**, 433 (1978).

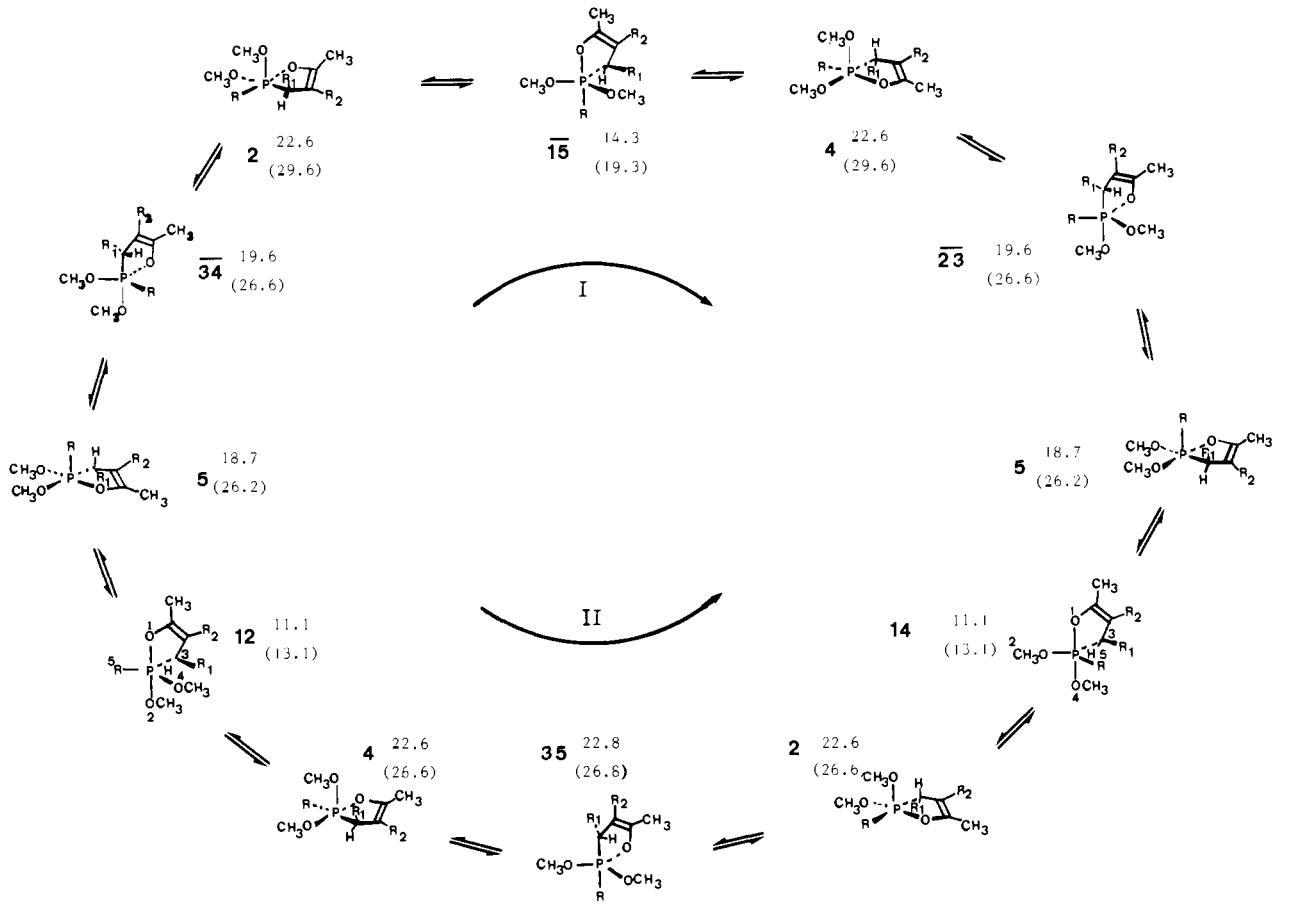
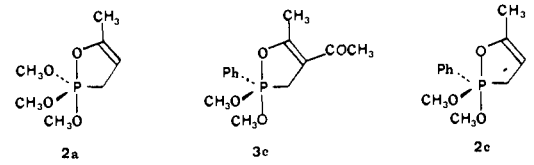


Figure 6. Isomerization pathway I and II. Estimation from Holmes' model[15] of the relative stability of all TBP and all SP isomers of phosphorane **2c** ($R_1 = R_2 = H$, R = Ph) and **3a,3b** ($R = R_1 = Ph$, $R_2 = COCH_3$). The numbers associated to each structure identify the isomer on the topological diagram shown in Figure 5 and the relative isomer energy in kcal/mol respectively for **2c** and **3a,3b** (in parentheses). The terms in Tables I, V, and VI of ref 15 have been used for these calculations.

have established models for the calculation of relative energies of transition states. Holmes' works predicted the relative stabilities of all TBP and SP stereoisomers lying on the isomerization pathway and particularly in the family of compounds **3a** and **3b**. In Figure 6 are reported the calculated energies according to Holmes' model[15] for phosphoranes **2c**, **3a**, and **3b**. The equal values of energy of the least stable structure (**35** for pathway II and **2** and **4** for I) shows that pathways I and II are equally probable for **2c**. For the compounds **3a** and **3b**, the difference in energy between the postulated transition state is about 3 kcal/mol. Holmes[15] has particularly taken into account the pathway I and TBP $\overline{15}$ as the transition state on the basis of Gorenstein's results[5] on phosphorus **2a** and **3c**, where similar $\Delta G^{\ddagger}$



$\Delta G^{\neq} = 9.6$ kcal/mol $\Delta G^{\neq} = 9.5$ kcal/mol $\Delta G^{\neq} = 13.0$ kcal/mol

values have been found for the exchange of the methoxy groups. It follows that the difference in apicophilicity between an oxygen and an intracyclic carbon atom appears to be the main factor involved in reaching the transition state.[15]

The analysis of our results (Table III) leads to a somewhat different interpretation. The 13 kcal/mol observed for **2c** shows the influence of different factors on $\Delta G^{\ddagger}$: (1) the extracyclic phenyl group: the $\Delta G^{\ddagger}$ value is 3.4 kcal/mol higher than the homologue compound **2a** with the CH_3O group; (2) the 4-acetyl group substituted on the oxaphospholene ring seems to reduce the $\Delta G^{\ddagger}$ value for **3c**.

Table IV

compd	R	$\Delta G^{\ddagger}_c$ (exp), kcal/mol	$\Delta G^{\ddagger}$ (calcd I), kcal/mol	$\Delta G^{\ddagger}$ (calcd II), kcal/mol
2a	CH_3O	9.6	8.6	8.5
2b	Me_2N	14.1	15.5	15.1
2c	Ph	13.0	11.5	11.7

The transition states are somewhat different in the two isomerization pathways. In pathway II the topomer **35** is energetically close to the neighboring SP structures **2** and **4**. In these structures the extracyclic ligand R and the carbon of the oxaphospholene ring bonded to phosphorus are trans in basal positions. On the other hand, in pathway I these substituents are in a cis position in the high-energy SP structures **2** and **4**; thus, the related interaction is the major contribution to the difference in energy between the two pathways. Therefore, we can expect pathway II to be favored when the cis interaction increases. For **2a** and **2b**, the $\Delta G^{\ddagger}$ values calculated for the two pathways from Holmes' model are close to the experimental values (Table IV). The deviation observed for **2c** may result from the evaluation of the apicophilicity term, which seems to be not only governed by the ligand electronegativity as it was postulated by Holmes.[15]

In conclusion, it appears that for phosphoranes with an oxaphospholene ring, the two pathways may be effective with a slight probability for pathway II when the steric interaction between R and the carbon bonded to phosphorus (or its substituents) becomes important. Such an interaction may arise from the exocyclic double bond in compound **1**.

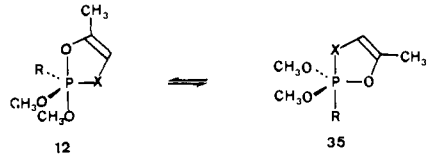
In the following discussions, we only consider the destabilized **35** as the likely transition state in the exchange process on the

(16) S. A. Bone, S. Trippett, M. W. White, and P. J. Whittle, *Tetrahedron Lett.*, 1795 (1974).

Chart I

apicophilicity scale	CN,	PhO	>	CH_3O,	CH_3S	>	$(CH_3)_2N$,	CH_3,	CH_2=CH,	Ph
electronegativities,[18] χ	3.3	3.5		3.7	2.8		3	2.3	3	3
inductive constants[19] σ_I	0.56	0.38		0.27	0.23		0.06	−0.04	0.05	0.1

assumption that all structural modifications involve nearly identical energy variations for the **35** BPT and the **2** and **4** SP structures.



12 35

4. Interpretation of Energetic Barriers: Apicophilicity and Steric Effects. Some general trends may be deduced from the results given in Table III. For phosphoranes containing the same oxaphospholene ring, the $\Delta G^{\ddagger}$ is strongly dependent upon the nature of the extracyclic ligand R which occupies an apical position in the TBP **35**. However, for the phosphoranes **1b** and **1g** (R = NMe_2) and **1e** (R = CH=CH_2), the entropy of activation is significantly negative. These $\Delta S^{\ddagger}$ values affect the $\Delta G^{\ddagger}$ by about 3–4 kcal/mol. It is worth mentioning that this occurs only for phosphorane **1**. This can be due to a reduction of the external number of symmetry and the degrees of freedom in the transition state[17] for $N(CH_3)_2$ and CH=CH_2 groups. Further, on the basis of the observed values of $\Delta H^{\ddagger}$ in these compounds, the apicophilicity of these groups would be slightly higher. Hence, it follows that in all exchange studies, it would be interesting to analyze separately the relative contributions of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the apicophilicity. This would require further accurate determination of all activation parameters on various phosphoranes and, thus, general trends may be deduced. In the following, we may regard the changes in $\Delta G^{\ddagger}$ as the relative apicophilicity of the R substituents. The difference in apicophilicity between the methoxy and the *N*-dimethylamino groups is about 4.5 kcal/mol for phosphoranes **2a–2b** and 4.8 kcal/mol for phosphoranes **1a–1b**. The phenyl group is the least apicophilic group of all the studied substituents. If we take into account the experimental assignment of the position of the ligands PhO and CN in phosphoranes **1j** and **1k**, we can classify the different substituents in order of decreasing apicophilicity (see Chart I). One can see that this apicophilicity scale does not follow the polarity rule.[20] This is most obvious for the SMe group vs. MeO and Me_2N groups. This suggests that apicophilicity is not governed only by the the electronegativity term and that some others contributions such as pπ–dπ interactions, steric effects, and polarizability of atoms must be considered.[1d,21,22] A correlation with inductive substituent constants σ_I of Hammett[23] seems to be more attractive. This was already proposed by Cavell et al.[24–26] in a series of trifluoromethylphosphoranes,

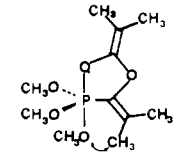
Table V

	$\Delta G^{\ddagger}$, kcal/mol		$\Delta(\Delta G^{\ddagger})$, kcal/mol
	R = Ph	R = MeO	
1a		8.5	
1c	14.4		5.9
2a		9.6[5]	3.4
2c	13		
3a, 3b	15.8[5]		
3e		11.8[5]	4
3d	17.4[5]		2.9
3f		14.5[5]	

The free enthalpies of activation depend on the structure of the oxaphospholene ring. For the same extracyclic ligand R, the $\Delta G^{\ddagger}$ values are 1 kcal/mol lower in phosphorane **1** than in phosphorane **2** except for the phenyl group where there appears a reverse effect, The two families differ only by the hybridization state of the carbon atom bonded to phosphorus and the presence of an exocyclic double bond, which can explain the observed differences: (a) The sp^2 carbon is more electronegative than the sp^3 carbon. This would decrease the energy of TBP **35** and, thus, the $\Delta G^{\ddagger}$ for compound **1**. This is not consistent with results showing that the apicophilicity difference between these two carbons are small. Further, in the ground-state topomer **1** the p orbital of the exocyclic double bond lies in the equatorial plane. Such an ideal situation according to Hoffmann[12b] stabilizes the ground-state structure and this may counterbalance the electronegativity effects. (b) The energy of the ground state must be higher in phosphorane **1** than in **2**; this is based on the steric interaction between the exocyclic double bond and the apical methoxy group. Such an interaction seems to outweigh the steric crowding induced by the apical position of the intracyclic sp^2 carbon in 35. Bentrude[27]

12 35

observed such an interaction for the phosphorane **4**, where the



4

exchange of methoxy groups could not be frozen, even at −100 °C. The $\Delta G^{\ddagger}$ of this process must be less than the 8.5 kcal/mol obtained for **1a**. This shows the important interaction between the methyl bonded to exocyclic double bond and the methoxy in the ground state.

This hypothesis was supported by studying the exchange process of compound **1i**. There is a decrease of 2.1 kcal/mol between $\Delta G^{\ddagger}$

(17) S. W. Benson, "Methods for the Estimation of Thermochemical Data and Rate Parameters", 2nd ed., Wiley-Interscience, New York, 1976. Accurate determination of the activation parameters shows that, in the spirophosphoranes with an anilo extracyclic group (PhNH), the variation in the isomerization barrier is essentially due to entropy factors. A. Klaebe, M. Sanchez, G. Caruana, and R. Wolf., *J. Chem. Soc., Perkin Trans. 2*, 976 (1980).

(18) P. R. Wells, "Progress in Physical Organic Chemistry", Collect. Vol. 6, A. Streitwieser and R. W. Taft, Ed., Interscience, 1968, p 111.

(19) J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley-Interscience, New York, 1975, p 55.

(20) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(21) J. Emsley and D. Hall, "The Chemistry of Phosphorus", Harper and Row, New York, 1976, p 65.

(22) K. E. Debruin, A. G. Padilla, and M. I. Campbell, J. Am. *Chem. Soc.*, **95**, 4681 (1973); S. Bone, S. Trippett, and P. J. Whittle, *J. Chem. Soc., Perkin Trans. 1*, 2125 (1974); R. K. Oram and S. Trippett, *ibid.*, 1300 (1973); J. Brierley, S. Trippett, and M. W. White, *ibid.*, 273 (1977); R. K. Oram and S. Trippett, *Chem. Commun.*, 554 (1972).

(23) J. R. Llinas and G. Buono, presented in part at the International Conference on Phosphorus Chemistry, Halle (GDR), Sept 1979. In the analogous spirophosphoranes, a relationship was determined between the $\Delta G^{\ddagger}_{300}$ values and either Hammett substituent constants or Swain and Lupton parameters (C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).

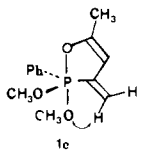
(24) R. G. Cavell, D. D. Poulin, K. I. The, and A. J. Tomlinson, *J. Chem. Soc., Chem. Commun.*, 19 (1974).

(25) D. D. Poulin and R. G. Cavell, *Inorg. Chem.*, **13**, 2324 (1974).

(26) R. G. Cavell, J. A. Gibson, and K. I. The, *J. Am. Chem. Soc.*, **99**, 7841 (1977).

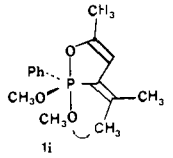
(27) W. G. Bentrude, W. D. Johnson, and W. A. Khan, *J. Am. Chem. Soc.*, **94**, 3058 (1972).

of **1c** and **1i**, which have the same ligand environment. As mentioned above, the steric crowding increases in the ground state of **1i** and thus decreases the $\Delta G^{\neq}$. Then, such steric effects must



1c

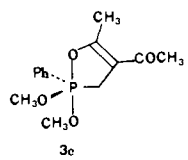
$\Delta G^{\neq} = 14.4$ kcal/mol



1i

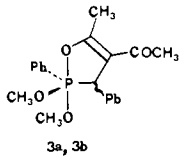
$\Delta G^{\neq} = 12.3$ kcal/mol

induce important deviations in $\Delta G^{\neq}$ values, but these contributions cannot be readily extrapolated from one model to another. Similar effects have been analyzed on **3a–3f** from Gorenstein's studies.[5]



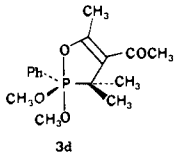
3c

$\Delta G^{\neq} = 9.5$ kcal/mol



3a, 3b

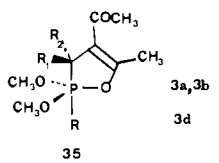
$\Delta G^{\neq} = 15.8$ kcal/mol



3d

$\Delta G^{\neq} = 17.4$ kcal/mol

The observed deviations (6.3 and 7.9 kcal/mol vs. compound **3c**) can only arise from steric crowding between ring substituents at C-3 and extracyclic ligands. In this case, these interactions are particularly strong in TBP transition state **35**, in which substituents C-3 (methyl or phenyl) and equatorial ligands are in an eclipsed position; therefore, the height of energy barrier for this exchange process is risen. Such interactions involve considerable change



3a,3b

3d

35

in ligand apicophilicity. This is outlined by the different relative apicophilicity values between methoxy and phenyl groups in our models and Gorenstein's models[5] (Table V). It appears that an apicophilicity scale must be determined from the same model's compounds and can only be extrapolated to another model's compounds if steric effects are carefully evaluated.

Furthermore, the $\Delta G^{\neq}$ values of the CH_3O exchange process are greatly affected by an acetyl group in the C-4 position, with all else about equal. We have thus observed a decrease of 3.5 kcal/mol in **3c** vs. **2c**. This can only be ascribed to the polarization of the π system and the P–O bond induced by the acetyl group. So, the apicophilicity of the oxygen ring must be lowered. From the foregoing, the effects related to the structure of oxaphospholene ring reveal to be important although this ring never spans a diequatorial position in the isomerization pathway. This can be due either to a substituent steric effect on the intracyclic carbon-3 bonded to phosphorus or to an electronic effect induced by any substituent on the π system of the oxaphospholene ring. On the other hand, a substitution at the C-5 position by bulky groups such as isopropyl or *tert*-butyl does not alter the $\Delta G^{\neq}$ values of the exchange process, and similar values have been obtained for **1c**, **1f**, and **1h**.

Experimental Section

The appropriate cares in handling moisture sensitive compounds were observed throughout this work. Solvents and commercial reagents were distilled and dried by conventional methods before use. IR spectra were measured on a Perkin-Elmer Model 457 IR spectrometer. For NMR experiments, ^{1}H NMR spectra were recorded on a Perkin-Elmer R 32 (at 90 MHz) and on a Varian XL-100 (at 100 MHz) spectrometer. Samples were studied in toluene-d_8 (15% v/v). Usual cares were taken to ensure temperature stability, slow passage, and maximum amplitude without any saturation. ^{13}C NMR spectra were recorded on a Varian NV-14 pulse Fourier transform NMR spectrometer (8192 data points) at 15.087 MHz. Lock signal was provided by the solvent (aromatic deuterons of perdeuteriotoluene, 40% v/v). All the spectra were obtained with the same set of parameters (flip angle, 40°; transients, 2000; spectral width, 3000 Hz) under proton noise decoupling. Chemical shifts are referenced against internal Me_4Si. ^{31}P NMR spectra were measured with the same samples by using the same spectrometer working in a CW mode at 24.3 MHz with proton noise decoupling. The ^{31}P NMR signals are given in parts per million vs. 85% H_3PO_4 (positive values are downfield from the reference). The variable temperature units were precalibrated with a thermocouple, ensuring an error less than 2 °C on the temperature measurement.

Materials. Allenic Ketones. 4-Oxo-1,2-pentadiene, bp 62 °C (80 mm), was prepared in 80% yield from a solution of 2,3-pentadione and dibromotriphenylphosphorane in methylene chloride followed by reaction with triethylamine and usual workup, using a modification of a method previously reported.[28] 5,5-Dimethyl-4-oxo-1,2-pentadiene, bp 48 °C (15 mm), and 5,5-dimethyl-4-oxo-1,2-hexadiene, bp 64 °C (17 mm), were prepared according to the method of Bertrand.[29] 1,1-Dimethyl-4-oxo-1,2-pentadiene, bp 62 °C (12 mm), was obtained by a recent method of Linstrumelle[30] by reaction of 3,3-dimethylallenyllithium with *N*,*N*-dimethylacetamide in 70% yield.

Trivalent Phosphorus Compounds. Dimethyl phenyl phosphite, $(MeO)_2(PhO)P$, dimethyl phenylphosphonite, $(MeO)_2PhP$, and methyl diphenylphosphinite, $(MeO)Ph_2P$, were prepared by a conventional method.[31]

Dimethyl methylphosphonite, $(MeO)_2MeP$, bp 63 °C (300 mm), and dimethyl vinylphosphonite,[33] $(MeO)_2(CH_2{=}CH)P$, bp 68 °C (158 mm), were synthesized from methanolysis of the corresponding phosphorus diamides.

Trimethyl thiophosphite $(MeS)(MeO)_2P$ was prepared as follows: to an ice-cooled stirred solution of 0.2 mol of Et_3N in 300 mL of diethyl ether was added dropwise 50 mL of Et_2O solutions of $MeSPCl_2$ (0.1 mol, bp 50 °C (8 mm)) and MeOH (0.2 mol) under nitrogen. After the addition, the reaction mixture was stirred at room temperature for 1 h. Triethylammonium chloride was removed by filtration under nitrogen. Distillation using a Vigreux column gave the liquid compound in 60% yield, bp 30–31 °C (1.5 mm). Dimethyl phosphorocyanidite $CN-(MeO)_2P$, bp 58 °C (10 mm), was prepared according to the method of Stec[34] by reaction of dimethyl chlorophosphite $Cl(MeO)_2P$ with hydrogen cyanide and triethylamine. This compound was particularly air and water sensitive and all operations using it were carried out in a dry prepurified argon or nitrogen atmosphere and in a well-ventilated hood or in a closed vacuum-line system.

Pentacoordinated Phosphorus Compounds. Phosphorane 1. One equivalent of trivalent phosphorus compound was added to a solution of α-allenic ketone (0.03 mol) in methylene chloride (50 mL) at −30 °C under nitrogen. The mixture was stirred for 3 h and the temperature was allowed to rise to room temperature. The reaction can be monitored by observing the vanishing of the IR allenic bond absorption (2000 cm^{-1}). The solvent was removed under vacuum, leaving the crude phosphorane, which was not further purified. Because of the thermal instability of some phosphoranes, analysis of these was made by ^{31}P NMR. Since only one peak was observed, these reactions are presumed to be quite quantitative. Nevertheless, some stable phosphoranes can be distilled: **1a**, bp 50–52 °C (1.5 mm); **1b**, bp 58 °C (0.2 mm); **1d**, bp 50–52 °C (1.5 mm); **1e**, Kulgelrohr distillation, bp 90 °C (0.5 mm). The major IR bands for the compound **1** are found at 2950 (CH), 1610 (C=C), and 1450 (P–O–C) cm^{-1}. The IR characteristic band at 1610 cm^{-1} (s) corresponds to the double bond of the oxaphospholene ring.

Phosphorane 2. These compounds were prepared according to the method described by Gorenstein[5] for the adduct **2a**: 1 equiv of a trivalent compound was added to freshly distilled methyl vinyl ketone (0.1 mol) in 50 mL of methylene chloride at 0 °C. The solution was stirred and allowed to stand under nitrogen at room temperature until the methyl vinyl ketone disappeared (IR monitoring). The solvent was removed under vacuum and the residue was carried out in Kulgelrohr distillation: **2a**,**2b**, bp 50–60 °C (3 mm); **2c**, 100 °C (1 mm); yield, 70–80%. These compounds have principal IR bands: 3080, 2980 (CH), 1670 (C=C), 1450 (P–O–C), 1040 (P–O–C) cm^{-1}.

Line-Shape Analysis. The rate constant k was obtained for each temperature by comparing the experimental exchanging spectra with simulated ones. Line-shape calculations and plotting were performed on a HP 2100 computer with a program adapted from the Gutowsky, McCall, and Slichter theory[35,36] for two-site exchange of the ABX type

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system ($J_{AB} = 0$). For each study, more than eight different temperatures were used. Log (k/T) was plotted against $1/T$ (see Figure 4) and a least-square treatment using the Eyring model gave enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation for the observed exchanges and the free enthalpy of activation at coalescence $\Delta G^{\ddagger}_c$.

$$\log (k/T) = 10.32 - \Delta H^{\ddagger}/4.57T + \Delta S^{\ddagger}/4.57$$

$$\Delta G^{\ddagger}_c = \Delta H^{\ddagger} - T_c \Delta S^{\ddagger}$$

For the line-shape simulation, the chemical shift difference $\Delta\nu$ between the two sites was determined for different temperatures in the low-exchange domain and this enabled us to evaluate $\Delta\nu$ at each temperature with a linear expresion: $\Delta\nu = aT + b$. The spin-spin relaxation time (T_2) was corrected at each temperature by the line-width changes deduced from a reference peak. The populations of each site were obtained by integration of ^{1}H NMR spectra. Good fits were obtained by linear regression on the Eyring equation; nevertheless, on the basis of experimental errors and linear adjustment, maximum total errors estimated for the activation parameters are about ±1.5 kcal/mol for $\Delta H^{\ddagger}$ and ±3 eu for $\Delta S^{\ddagger}$. However, as previously reported,[36] the errors associated with $\Delta G^{\ddagger}_c$ are not as important as the latter and could not exceed 0.3–0.4 kcal/mol. The reliability of $\Delta G^{\ddagger}_c$ values have been tested with the following approximated expression

$$\Delta G^{\ddagger}_c = 4.57 \times 10^{-3} T_c \left(10.32 + \log \left(T_c\sqrt{2}/\pi\Delta\nu\right)\right)$$

and a good agreement was obtained with the $\Delta G^{\ddagger}_c$ evaluated by line-shape analysis.

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Stereochemistry of Nucleophilic Addition to Cyclohexanone. The Importance of Two-Electron Stabilizing Interactions

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Abstract: A theory of charge-transfer stabilization of the transition state for nucleophilic addition to a carbonyl group by electron donors is proposed. It is postulated, using the Bell–Evans–Polanyi principle, that the feature of this transition state critical for stereoselectivity of the reaction is the existence of a low-lying vacant orbital $\sigma^*_{\ddagger}$ associated with the σ bond being formed in the reaction and that electron delocalization into that orbital will stabilize the transition state and may thereby enhance the reaction rate: the kinetic anomeric effect and the kinetic α effect are considered as the examples of such a stabilizing interaction. Stereochemistry of nucleophilic addition to cyclohexanone is determined by two factors according to this model: steric hindrance which favors the equatorial approach and electron donation from the cyclohexanone σ_{CC} and σ_{CH} bonds into the $\sigma^*_{\ddagger}$ orbital, which favors the axial approach since the carbon–hydrogen bonds are better electron donors. Consequently, nucleophile structure, metal cations complexing the carbonyl oxygen, solvent, and counterions or other solutes may influence stereoselectivity of the reaction by changing the $\epsilon(\sigma^*_{\ddagger})$. Furthermore, it is shown that this model offers a simple and consistent way to rationalize kinetic and stereochemical effects of the so-called "remote polar substituents" which cannot be explained in terms of steric or electrostatic interactions but appear to be controlled by the overlap and energy gap between the remote electron-donor orbitals and the $\sigma^*_{\ddagger}$ orbital.

For an explanation of the stereochemistry of fast irreversible nucleophilic additions to cyclohexanone such as metal hydride reductions or additions of organometallic compounds, at least two different interactions must be invoked. This necessity was pointed out 2 decades ago in the first major review of the topic, which concluded in the following way.

"...Thus, the steric direction of reaction of nucleophilic addition to the carbonyl group of cyclic six-membered ketones is determined, apparently, by two competitive factors: a factor directing the entering substituent into the axial position, and a factor opposing this, depending on steric hindrance and directing the substituent into the equatorial position. It appears probable that the first factor is determined not by thermodynamic stability of the final products but is mainly connected with the orientation of the charged...attacking agent under the action of polar influences...connected for example, with the uncompensated dipole moments of the carbon–hydrogen bonds..."[1]

The nature of the interaction, described above as the second factor, has never been questioned. It is generally agreed that if the reaction goes through an early reactant-like transition state, the steric strain between a nucleophile and the C_3 and C_5 axial hydrogen atoms destabilizes the axial transition state, thus directing a nucleophile into the equatorial position. However, after 2 decades the nature of the first interaction is still a matter of continuing discussion and in the recent reviews is described as "...some other (nonsteric) factor which provides an intrinsic preference for axial attack"[2], or as "...It is obvious that some chemical property of 4-*tert*-butylcyclohexanone directs the attack of complex metal hydrides to the axial side...".[3]

Numerous suggestions involving the arguments of thermodynamic stability, steric interactions, and frontier orbitals have been

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