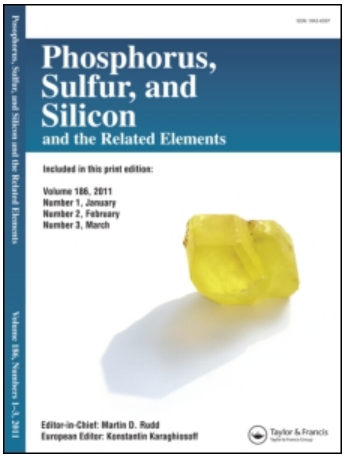

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PHOSPHOROTROPIC TAUTOMERISM IN CYCLIC PHOSPHORANES. ^{1}H, ^{13}C AND ^{31}P NMR DATA

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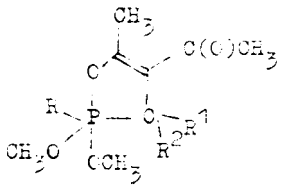
A new type of phosphorotropic tautomerism for a series of five membered monocyclic phosphoranes with an acyl group in position 4 (**1a**, **4a–c**, **5a–c**, **6a**, **7a**) has been discovered and studied. An equilibrium of two tautomeric forms with a pentacoordinated phosphorus atom (Schemes 2, 3, 4) is likely to occur via an intermediate acylic zwitterion. The values of chemical shifts ^{31}P for the compounds studied have been shown to be unchanged in the range of temperatures from 203 K to 383 K. Activation parameters of the tautomeric rearrangement have been determined by means of NMR (^{1}H and ^{13}C) spectroscopy. The proposed schemes of the tautomeric processes have been confirmed by a comparison of the temperature changes in the ^{13}C- and ^{31}P-NMR spectra of phosphoranes **6a**, **7a** and related bipolar ions **6b** and **7b**.

INTRODUCTION

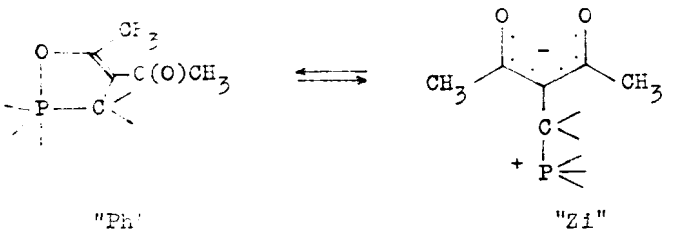
A series of cyclic phosphoranes containing an acyl group at position 4 **1a–1f**[1–5] has been prepared by condensation of trivalent phosphorus compounds with the idene derivatives of β-dicarbonyl compounds



	R	R^1	R^2
1a	OCH_3	H	C_6H_5
1b	C_6H_5	H	C_6H_5
1c	OCH_3	CH_3	CH_3
1d	C_6H_5	CH_3	CH_3
1e	C_6H_5	H	H
1f	OC_6H_5	H	C_6H_5

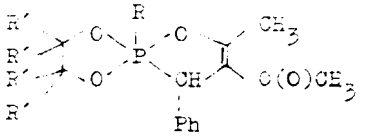
The ^{1}H NMR spectra of **1a–1f** are temperature dependent. At high temperatures various phosphoranes related to acetylacetone undergo an exchange between the two methyl groups of the acetylacetone system. The exchange has been identified in ref. 6 "as one that occurs by way of ring opening and reclosure, through an open-chain zwitterionic intermediate", although some authors[3,5] pointed out that there is an equilibrium between the cyclic phosphorane ("Ph") and an open dipolar structure ("Zi"). At the coalescence temperature the signals due to the acetyl and the methyl begin to coalesce and become a singlet. At the highest temperatures there is open dipolar structure exclusively[5] (Scheme 1).

*Author to whom all correspondence should be addressed.



SCHEME 1

Similar coalescence of signals of methyl protons of acetylacetone moiety that was observed[7a,b] in the ^{1}H-NMR spectra of 1,2-oxaphosphol-4-enes **2a–2c** at high temperatures has also been attributed to the equilibrium "Ph" ⇄ "Zi" (see Scheme 1). For analogous compounds **3a–3e** the pseudorotation processes have been discussed and it has been shown that "dissociation is not a significant factor in the variable temperature NMR experiments".[8]



2a–2c R′ = H
2a R = OCH_3
2b R = $N(C_2H_5)_2$
2c R = C_2H_5

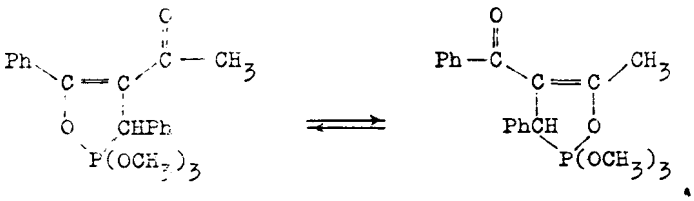
3a–3e R′ = CF_3
3a R = OCH_3
3b R = OC_2H_5
3c R = OC_4H_9
3d R = SC_2H_5
3e R = $N(CH_3)_2$

The compound formed from tris(dimethylamino)phosphine and benzil was regarded as a rapid equilibrating mixture of phosphorane and zwitterion (the structure of this substance has been examined by ^{31}P NMR spectroscopy).[3,9]

However, recent investigation[10a,b] of several condensation products of tris(amino)phosphines and α-dicarbonyl compounds by the ^{1}H, ^{13}C and ^{31}P NMR spectroscopy have shown that the problem of the structure of these products in solutions is rather complex. The authors explain the variable temperature of NMR spectra by "increased delocalization with ultimate ionization as the dielectric constant of the medium is increased".[10b]

RESULTS AND DISCUSSION

We discovered[11] that phosphorane **4a** prepared by condensation of benzylideneben-zoylacetone and trimethylphosphite in a solution at room temperature consists of a mixture of two forms, "Ph_1" and "Ph_2" in the 1 : 2 ratio.

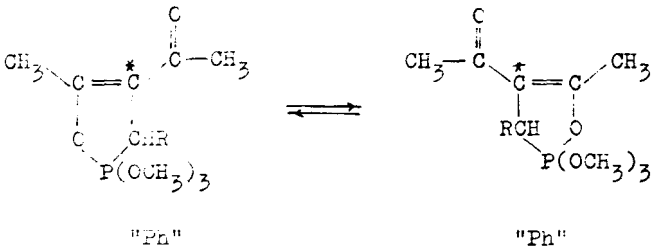


4a "Ph_1" **4a** "Ph_2"

SCHEME 2

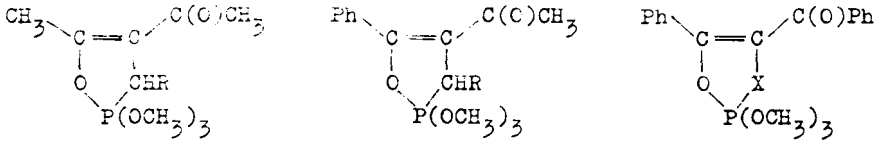
A similar behavior was observed for the phosphoranes **4b**[11d] and **4c**. The equilibrium (Scheme 2) appears to be realized via the zwitterion "Zi" not apparent in the NMR spectra since its equilibrium concentration is low.

We postulated that the phosphoranes related to acetylacetone (**1**, **5**) undergo a similar tautomeric rearrangement leading to exchange of the methyl groups of the acetylacetone system (see Scheme 3, here and below the carbon atom not participating in the exchange is starred*).



SCHEME 3

To identify and to study a new type of phosphorotropic tautomerism observed, we have used ^{1}H, ^{13}C and ^{31}P NMR spectroscopy for investigating the monocyclic phosphoranes containing 1,2-oxaphospholenic, 1,3,2-dioxaphospholenic and 1,3,2-oxazaphospholenic cycles with an acyl group at position 4.



1a R = C_6H_5
5a R = CH_3
5b R = $C_6H_4N(CH_3)_2$
5c R = $C_6H_4NO_2$

4a R = C_6H_5
4b R = $C_6H_4N(CH_3)_2$
4c R = $C_6H_4NO_2$

6a X = O
7a X = NC_6H_5

The ^{31}P NMR shifts of all investigated compounds are typical of pentacoordinated phosphorane structures (see Table I). This shift was found to be both solvent and concentration independent at all temperatures at which the described tautomeric processes were observed.

Figure 1 presents the ^{1}H-NMR spectrum of phosphorane **5a** and variable temperature spectra of the acetylacetone moiety of **5a** since the remaining spectral lines remain unchanged at higher temperatures. It can be seen that variable temperature line shapes correspond to a mutual exchange.

TABLE I

The chemical shifts of phosphoranes

Compound	**1a**	**4a**	**4b**	**4c**	**5a**	**5b**	**5c**	**6a**	**7a**
^{31}P, ppm	−37.0	−32.2	−36.1	−27.8	−27.0	−34.2	−29.0	−50.2	−51.1

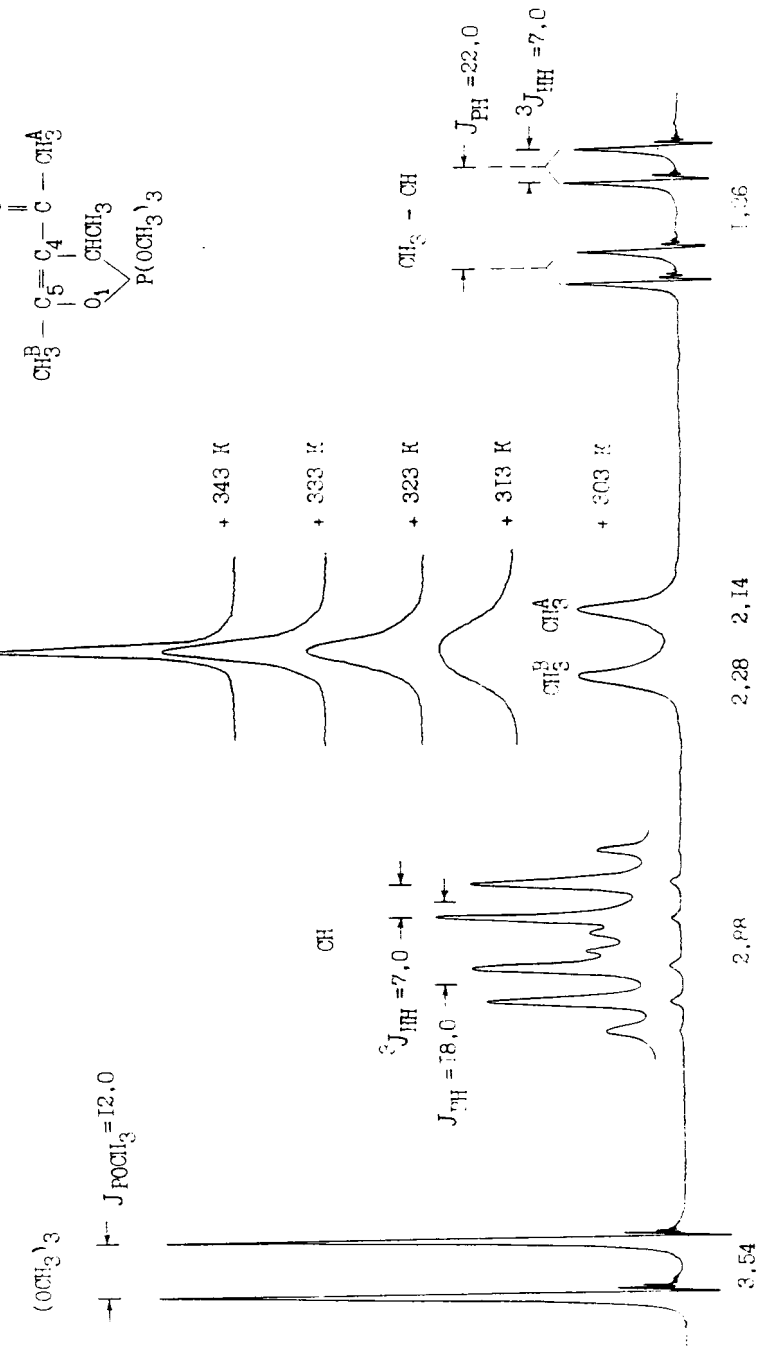


FIGURE 1 ^{1}H-NMR spectra of phosphorane **5a**. Line δ = 2.28 ppm at T < 273 K reveals splitting, $J_{P...H}$ = 0.5 Hz.

Variable temperature ^{1}H NMR spectra of phosphoranes **5b**[11c] and **1a**[2,3,5,11c] are in general the same as those of phosphorane **5a** but T_c of the methyl groups of acetylacetone moiety is much higher (see Table II).

The exchange of the methyl groups in phosphoranes **4a, b, c** (see Scheme 2) is considered to be non-mutual. Two groups of lines are observed at room temperature which correspond to two phosphorane structures, Ph_1 and Ph_2; in all cases the structure with benzoyl group at position **4** is the major compound (in the 1 : 2 ratio irrespective of the type of the solvent, which points to a small difference in the polarity of these structures). ^{1}H NMR spectra of **4a, b** at various temperatures was discussed elsewhere.[11a,c]

The activation parameters of the phosphorotropic tautomerism are given in Table II. The rate constants were determined by line shape analysis. The activation parameters were calculated in terms of the absolute rate theory.

The intramolecular exchange of the methoxy group on the phosphorus atom in compounds **4a, b**, **5a, b** is revealed in ^{1}H NMR spectra at lower temperatures, T_c 240–250 K, free energy of activation $\Delta G^{\ddagger}$ 40–45 kJ · mol^{-1}.

Figure 2 presents variable temperature ^{13}C NMR spectra of phosphorane **5a**. At 203 K both processes are slow in the ^{13}C NMR time scale. At room temperature the

TABLE II

Activation parameters for tautomeric conversions in monocyclic phosphoranes*

Comp.	Solvent	T_c (Me) K	$\Delta G^{\ddagger}$ kJ · mol^{-1}	$\Delta H^{\ddagger}$ kJ · mol^{-1}	$\Delta S^{\ddagger}$ kJ · mol^{-1}
5a	neat	313	69.4	42.8 ± 3	−85 ± 4
	CCl_4	313	69.7	42.5 ± 6	−91 ± 10
	CH_2Cl_2	293	66.5	34.1 ± 1	−111 ± 2
	C_5H_5N	313	69.4	36.8 ± 6	−104 ± 2
5b	CCl_4	not attained up to 440	> 130	—	—
5c	CCl_4	not attained up to 440	> 130	—	—
1a	CH_2Cl_2		95.7	89.0 ± 1	−16 ± 2
4a	CH_2Cl_2	398	87.5	36.6 ± 3	−128 ± 4
4b	C_6H_6	not attained up to 440**	123	—	—
4c	C_6H_6	not attained	124	—	—
6a	CH_2Cl_2	260	47.7	—	—
7a	CH_2Cl_2	240	40.8	—	—
	CH_3CN	240	40.8	—	—

*The parameters were determined from the ^{13}C-NMR spectra of the compounds **6a** and **7a** and from the ^{1}H-NMR spectra of the remaining compounds; æ = 1.

**T_c (OMe) = 358 K, T_c (NMe_2) = 353 K. In other cases T_c (Me) of the acetylacetone or benzoylacetone moiety are reported.

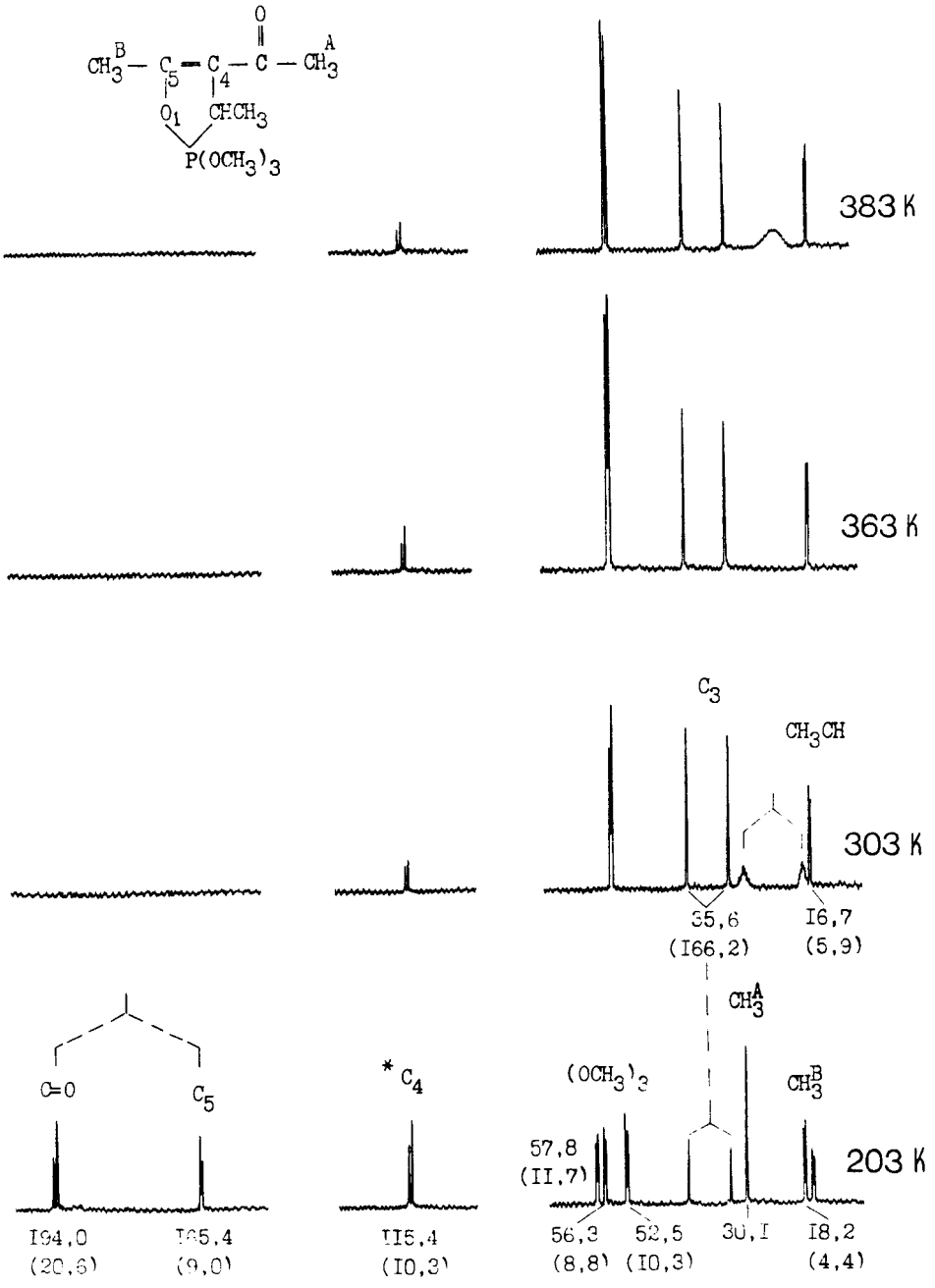


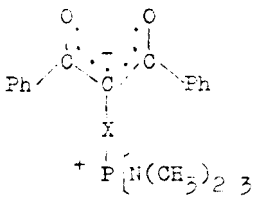
FIGURE 2 ^{13}C-NMR spectra (22.63 MHz) of phosphorane **5a** in a mixture of solvents (C_6H_6 + CH_2Cl_2 + CD_2Cl_2, 2:2:1) at different temperatures. Here and in other figures, the values of $J_{P...C}$ (Hz) are given in brackets under the chemical shift values (ppm).

lines of the carbon atoms of methyl groups of acetylacetone moiety are slightly broadened ($T_c \sim 363$ K), whereas the lines corresponding to carbon atoms of the C=O and =C–O groups already are coalesced ($T_c = 303$ K). Their absence in the spectra is readily explained since at the coalescence the magnetization is distributed over a broad frequency range ~ 660 Hz (at 22.63 MHz) and an averaged signal should be observed at high temperatures > 450 K. Symmetrical broadening and coalescing of the methyl carbon lines, temperature invariability of the atom $=C^*-$ shift and of its coupling constant $^2J_{P\ldots C}$ at all temperatures indicate mutual exchange (Scheme 3). Process 1 implies a change of the spectral parameters for all three carbon atoms ($-C=C^*-C(O)-$).

For the investigation of tautomeric transformations of **1a**, **4a, b**, **5b** the ^{13}C-NMR spectroscopy proved to be of little use and less informative than ^{1}H-NMR due to the specific features of the time scale (an efficient exchange broadening should be expected in a high temperature region in which phosphoranes are decomposed).

As noted above, the chemical shifts δ ^{31}P of all studied phosphoranes are constant at all temperatures and are independent of the solvent type. The values of chemical shifts are characteristic of the pentacoordinated structures (see Table I), which shows that the structure "Zi" is not responsible for the observed temperature dependence of NMR spectra and, consequently, is not the main component of the tautomeric equilibrium of the cyclic phosphoranes, so that Scheme 1 cannot be realized. The equilibrium takes place between two phosphorane structures.

The proposed scheme of the tautomeric transformations (2 or 3) can be strongly supported by a comparison of the temperature dependence of the ^{13}C- and ^{31}P-NMR spectra of phosphoranes **6a**, **7a** and those of related bipolar ions **6b** and **7b**.



6b X = O δ ^{31}P + 35.9 (CH_2Cl_2)
7b X = NC_6H_5 δ ^{31}P + 40.0 (CH_2Cl_2)

The comparison is quite justified since the substituents at phosphorus are removed from the indicator groups by at least three bonds and must not affect greatly the chemical shifts of their carbon atoms. With the aid of the comparison, one could attempt to find the test-signs in the ^{13}C NMR spectra pointing to the participation of "Zi" form in the equilibrium.

The ^{31}P NMR shifts of compounds **6b** and **7b** is constant at all temperatures (190–350 K) and characteristic of the bipolar structures.[12a,b] The ^{13}C NMR spectrum of **6b** in this temperature range also unchanged and corresponds to the symmetry of an "averaged" phosphonium structure realized owing to fast (in the ^{13}C-NMR scale) rotation about the C—N and N—P bonds. The methyl group carbons bonded to nitrogen were found to be a simple doublet at δ ^{13}C 37.3 ppm, $^2J_{PNC} = 4.8$ Hz. The spectrum interpretation is sufficiently simple (see Figure 3, top). The lines of aromatic carbon atoms were assigned with due regard for the fact that, in passing from one substituent to another, the ^{13}C-NMR chemical shifts in

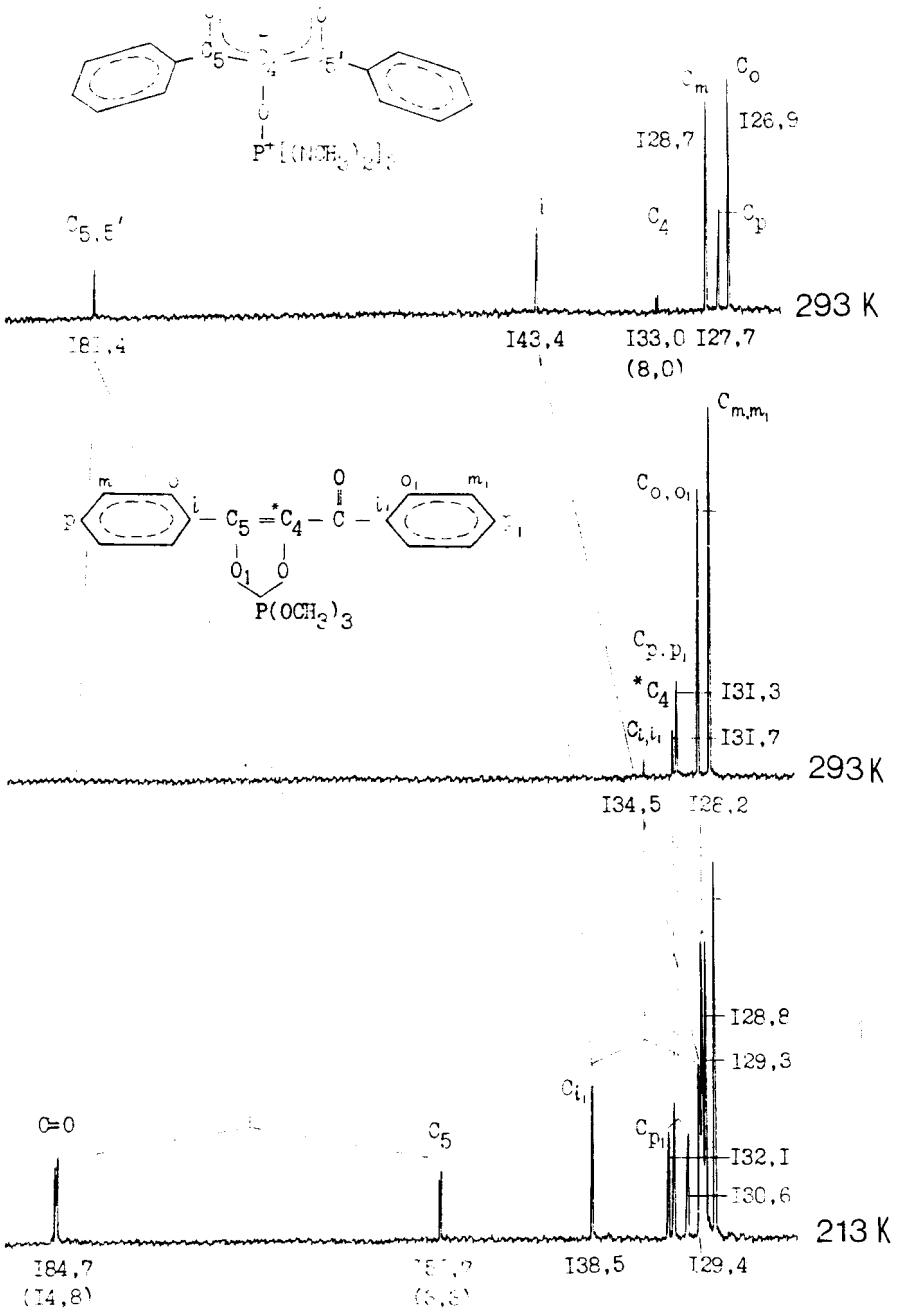
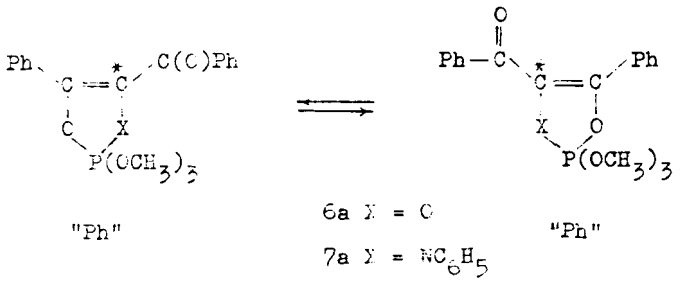


FIGURE 3 ^{13}C-NMR spectra of betaine **6b** (top) in a mixture of solvents (CD_2Cl_2 + CH_2Cl_2, 4 : 1) at T = 293 K and of phosphorane **6a** (CH_2Cl_2 + CD_2Cl_2, 4 : 1).

monosubstituted benzenes decreases in the order $C^i > C^p > C^o > C^m$ and the δ C^m value, with few exceptions, is independent of the substituent type.[13a,b]

In the ^{13}C NMR spectrum of phosphorane **6a** at 213 K, (Figure 3, bottom), two non-equivalent magnetically aromatic fragments are revealed, to which three pairs of lines correspond, the line intensities in each pair being equal. As expected, only the lines related to C^m are not resolved. The lines were assigned as in the case of compound **6b**; the exchange line pairs were identified by running the spectra through a small temperature interval (10 K). The variable temperature line shapes testify to a mutual exchange, i.e. to the fact that tautomeric equilibrium between two phosphoranes structures is established (Scheme 4).



SCHEME 4

In the ^{13}C-NMR scale the exchange becomes fast at $T > 293$ K. Scheme 4 is confirmed by the invariability of the *C carbon line. Since the coupling constants $^2J_{PO*C}$ and $^3J_{POC*C}$ in the dioxaphospholene cycle are apparently equal in magnitude and opposite in sign, the line is not split. The lack in the room temperature spectrum of the lines corresponding to the C=O and =C—O carbon atoms is due to the same reason as for compound **5a** (here $\Delta\nu \sim 2000$ Hz at $\nu_0 = 62.86$ MHz). It should be noted that these lines are displayed in the spectrum as highly broadened at 253 K with the δ ^{13}C 184 and 150 ppm.

^{13}C-NMR spectrum of the phosphorane **6a** at 350 K is identical with that at 293 K and, as can be seen from Figure 3, can neither be assigned to the betaine structure "Zi" nor be interpreted as an average in the phosphorane $\rightleftarrows$ bipolar ion exchange. Such a hypothetic exchange is presented in Figure 3 by continuous lines for atoms C^i, C^p of the aromatic ring, C=O and =C—O. The real exchange is plotted by dotted lines.

More complex ^{13}C-NMR spectra correspond to compounds **7a** and **7b**. The assignment of chemical shifts is given in Figure 4. The character of their temperature changes is the same as for pair **6a, 6b**. Keeping in mind the ^{31}P NMR data (the invariability of δ ^{31}P at 190–350 K) one can state that the tautomeric equilibrium according to Scheme 4 also takes place in this case.

Unlike above phosphoranes with 1,2-oxaphospholene cycle (**1a**; **5a, b**, **4a, b**), phosphorotropic tautomeric rearrangements in phosphoranes **6a** and **7a** are characterized by smaller values of free activation energy $\Delta G^{\ddagger}$ (see Table II).

The intramolecular exchange of the methoxy groups at phosphorus in **6a** and **7a** is not frozen on the NMR-time-scale at 190 K. The three methoxyl groups appear as a

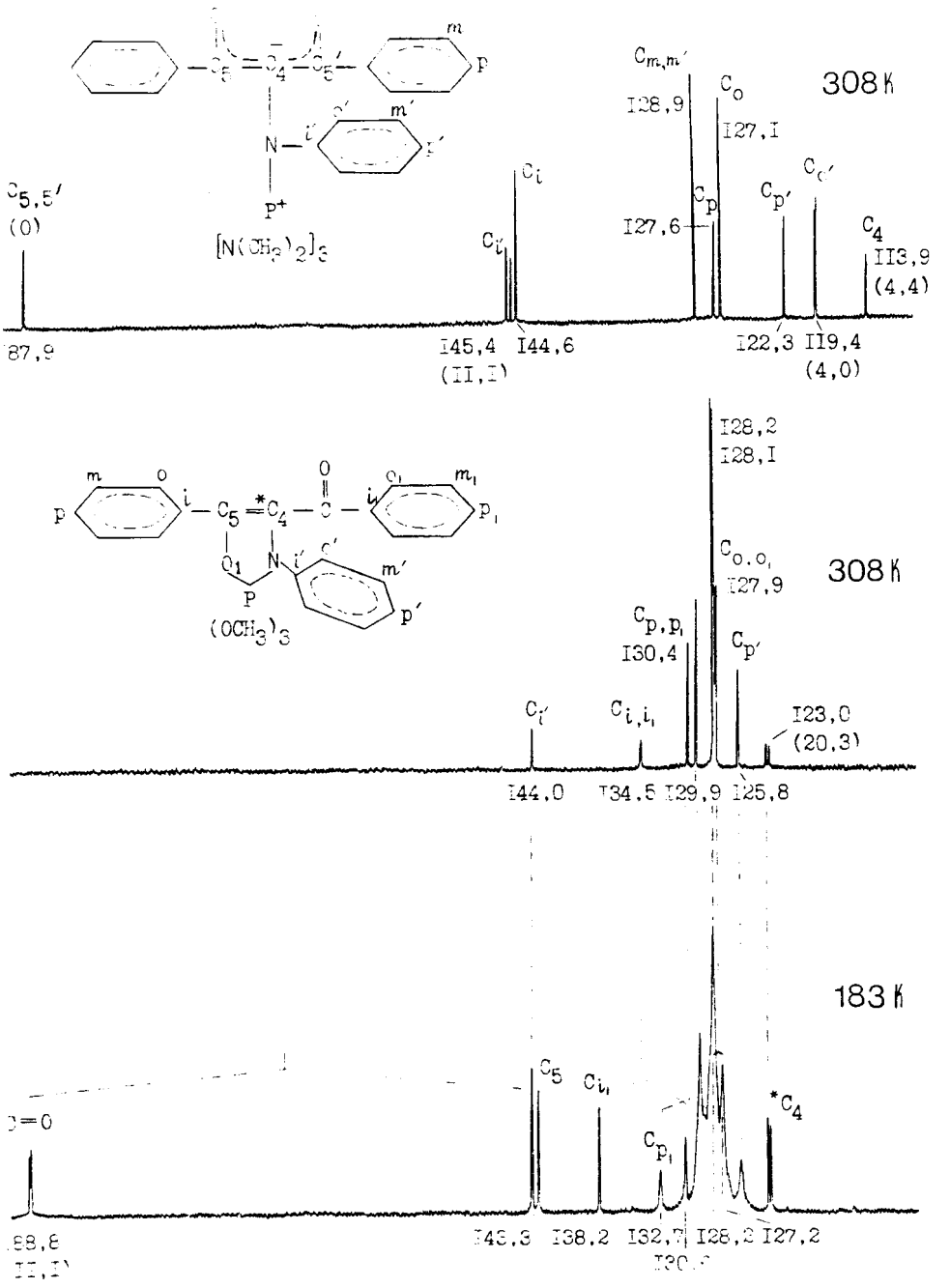


FIGURE 4 ^{13}C-NMR spectra (62.86 MHz) of betaine **7b** (top) in a mixture of solvents (CH_2Cl_2 + CD_2Cl_2, 4 : 1) and of phosphorane **7a** in the same mixture. In the spectrum of **7a** at 273 K, lines 128.2, 128.1 and 129.9 belong to C_m, C_m1 and C_m2 and are attributed presumably.

doublet with $^2J_{POC}$ (in brackets) at 56 ppm (9.9 Hz) and 55.7 ppm (11.1 Hz) at 293 K for **6a** and **7a**, respectively.

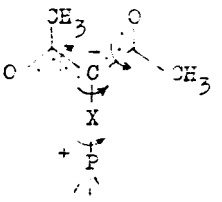
The comparison of the ^{13}C-NMR data for two different pairs of compounds **6a, b** and **7a, b**, shows how carefully one must choose test-signs, by which it is possible to detect the existence of the ionic form without detailed temperature investigations. For example, the absence of multiplicity of the *C carbon atom lines in phosphoranes **6a** and **7a** is related to the presence of the second heteroatom in the phospholene cycle: in 1,2-oxaphospha(P^V)lene **5a**, $J_{P\ldots C} = 10$ Hz. However, the multiplicity of the C=O line, that is not revealed in bipolar ions **6b** and **7b**, is apparently characteristic of the cyclic phosphoranes (**5a**, **6a**, **7a**). The C=O carbon atoms' chemical shifts show a weak alteration when one passes to ionic compounds ($C_{5,5}$i in both pairs over a range 1–3 ppm) and do not reveal general tendencies; alterations of δ ^{13}C of C_4 are also irregular. This may be due to the fact that ^{13}C shifts may not be uniquely related to the charge density on the carbon atoms. The chemical shifts of C^i and C^p atoms of aromatic fragments are more informative since they are changed significantly and not in a similar manner: the C^i lines are displaced to weak field, whereas those of C^n— to strong ones. The differences in chemical shifts δ $C^i - \delta$ $C^n = \Delta\delta$ ("Zi") in the ionic form (15.7 and 17.0 ppm for **6b** and **7b**, respectively) exceed considerably the values of $\Delta\delta$ ("Ph") = $\delta C^i - \delta C^n$ in the averaged spectrum of the corresponding phosphoranes (3.5 and 4.1 ppm for **6a** and **7a**).

Thus, the data of the ^{1}H-, ^{13}C- and ^{31}P-NMR spectra of monocyclic phosphoranes containing 1,2-oxaphospholene, 1,3,2-dioxaphospholene and 1,3,2-oxazaphospholene cycles with an acyl group at position 4 make it possible to conclude that phosphorotropic tautomerism does take place in these compounds and is described by Schemes 2, 3 or 4 but not by Scheme 1.

A similar interpretation should apparently be applied to the analogous variable temperature spectra of compounds **1a–1f**, **2a–2c** described in the introduction.

The above phosphorotropic tautomeric rearrangements and intramolecular ligand exchange on the pentacoordinated phosphorus atom (permutative isomerization) have quite different consequences for the NMR spectra and are thus distinct. The temperatures at which these processes take place can be close or differ greatly depending on the phospholene cycle type and substituent nature. The connection between these processes is rather vague and most probably indirect.

The NMR-spectra of phosphorane **5a** in various solvents were studied. As seen from Table II, the activation enthalpy decreases as the dielectric constant of the medium increases while free activation energy shows a lack of dependence on the solvent type. This fact may be explained by some published data[10b], which show that ionization degree rises with increasing dielectric constant of solvent. Moreover, assumption about participation of a intermediate of "Zi" type in the equilibrium described by Schemes 2–4 is quite logical. The strongly polar form of "Zi" type, which appears in the course of a relative motion of the molecule fragments, is a barrier form. As is seen from Scheme 5, the rupture of the endocyclic P—O bond with subsequent closure of the phosphorane cycle at another oxygen atom is accompanied by various processes: redistribution of electron density in the β-dicarbonyl fragment and rotation about the P—X, X—C and C—C bonds.



SCHEME 5

At least in the P—X—C fragment the rotation is not free and the total process includes, undoubtedly, more than one stage. This fact is confirmed indirectly by the absence of epimerization of phosphorane **1b**[5] at the coalescence temperature T_c of signals of the methyl groups of acetylacetone moiety. This is also indicated by large negative values of activation entropy $\Delta S^{\ddagger}$ and by the fact, that $\Delta G^{\ddagger}$, which is determined by the rate constant of total process does not essentially depend upon the solvent type.

Information on the activation parameters of the described tautomeric processes is scant and does not make it possible to estimate unambiguously the part of different additive contributions. Nevertheless, the role of steric properties of substituents at position 3 may easily be traced in the series of compounds **1a**, **4a–c**, **5a–c**.

It is possible that phosphorotropic tautomery proceeds by intramolecular replacement at P^{V} intermediate with P^{VI}. However, no data are as yet available to support this hypothesis.

EXPERIMENTAL

^{1}H-NMR-spectra were run on a Varian Model HA-100D spectrometer equipped with a variable-temperature accessory V-4341/V-6057. ^{13}C-NMR spectra were run on a Bruker-Physik Model WH-90 and WM-250 spectrometers equipped with a variable-temperature unit B-VT-1000. ^{31}P NMR shifts were reported in ppm relative to 85% phosphoric acid (external), $-\delta$ upfield and were measured by the double heteronuclear resonance ^{1}H-{^{31}P} accessory[14] on a HA-100D spectrometer with an accuracy of ± 1 ppm and also by direct observation of ^{31}P-resonance on a WM-250 spectrometer. ^{1}H-chemical shifts are reported relative to TMS (internal), ^{13}C are reported also relative to TMS (± 0.5 ppm). The absolute values of coupling constants were measured with an accuracy of ± 0.1 Hz (J_{HH}, J_{PH}) and ± 0.2 Hz ($J_{P\ldots C}$). All samples were prepared under conditions preventing their hydrolysis by atmospheric moisture. Concentration of samples used was about 20% by volume.

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