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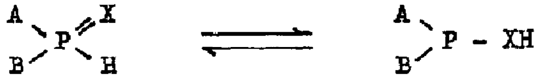
DIADIC PHOSPHORUS-CARBON TAUTOMERISM

T.A.Mastryukova*, I.M.Aladzheva, I.V.Leont'eva,
P.V.Petrovski, E.I.Fedin, M.I.Kabachnik

Institute of Organo-Element Compounds of the USSR Academy
of Sciences, Vavilova 28, Moscow 117813, USSR

Among the diadic tautomeric systems the organophosphorus diads which principal representatives are the dialkylphosphites attract the greatest attention.



(X = O, S, NR)

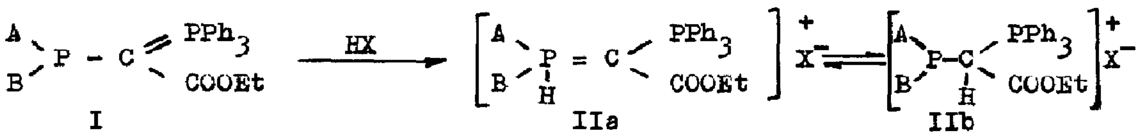
To this type of tautomerism should be also referred the diadic phosphorus-carbon system:

(a)   (b)

This kind of equilibrium which has not been observed previously is the subject of the present study.

In general the equilibrium position in the tautomeric systems depends upon the relative acidities of the individual forms[1]. It is well known that alkyl phosphites, alkyl phosphinites and tertiary alkyl phosphines usually exist in the CH-form (b). This means, that the acidity of the "ylidic" PH-form (a) in these compounds is much higher than that of the CH-form (b). An increase in the CH-acidity caused, for instance, by inserting electronegative substituents at the carbon atom (two alkoxycarbonyl groups, two sulfonic groups u s.w.) has not resulted in the formation of the "ylidic" form (a)[2]. It has been found recently[3], that only by introduction of two very strong electronegative substituents at C-atom (triphenylphosphonium groups) the acidity of the

CH-form can be enhanced to such extent, that the equilibrium is completely shifted to the PH-form. Therefore one might expect that if the central carbon atom is bonded to one ethoxycarbonyl and one triphenylphosphonium group the CH- and PH-acidities should become approximately equal and both forms (a) and (b) should exist in the solution. This, indeed, has been confirmed experimentally.



The tertiary (triphenylphosphonioethoxycarbonyl)methyl phosphine salts II were prepared by the action of acids on the corresponding ylides I, produced according to the method of Issleib and Lindner[4]. It was found that treatment of the dibuthyl derivative I (A=B=Bu) with an excess of hydrogen chloride or hydrogen bromide at -80°C in CH_2Cl_2 or with trifluoroacetic acid (20°) gives only the product of P-protonation (IIa). The latter exists at -80° in two conformations - cisoid and transoid - as the result of hindered rotation about the partial double C-C-bond (Table I):

Table 1. ^{31}P-NMR parameters of the chlorides II in CH_2Cl_2

A, B	Temp (°C)	Form	$\delta_{P(Ph_2H)}$ ppm (d)	$\delta_{P(Ph_3)}$ ppm (d)	J_{PP} Hz	J_{PH} Hz
Bu	-80	a	5.7 2.4	19.4 21.8	32 32	460 480
Ph	-90	a	0.5 -2.4	21.4 23.7	42 39	460 460
		b	-15.6[7]	23.1	88	-

Similar conformational isomerism was also observed for ylides I[5] and for other alkoxycarbonylsubstituted ylides[6].

A different picture is observed with the diphenyl derivative II (A=B=Ph) obtained in CH_2Cl_2 solution in the presence of 3 mol hydrogen chloride at -90°. Besides the signals corresponding to the cisoid and transoid conformers of the PH-form in the ^{31}P-NMR spectrum the signals with chemical shifts only slightly different from those of the original ylide but with much smaller P-P coupling constants are also present (Table I, Figure I). We ascribe this grou

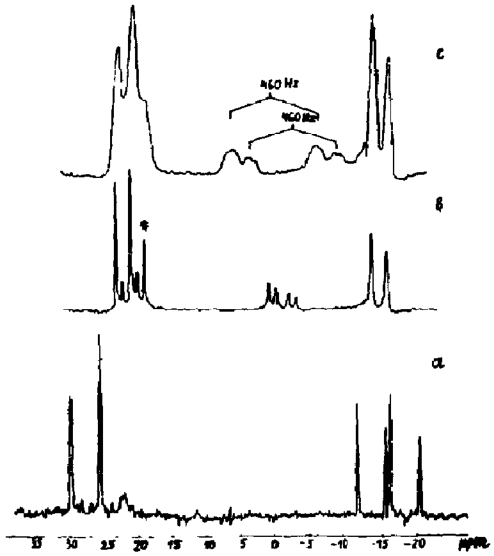


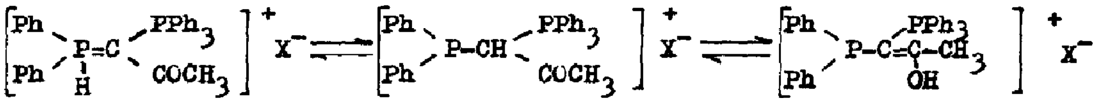
Figure I. ^{31}P-NMR spectra in CH_2Cl_2: a - ylide I (A=B=Ph) at -70°; b,c - HCl protonated ylide I (A=B=Ph) at -90° (proton decoupled and proton undecoupled spectra); *) signal of the degradation product $Ph_3\overset{+}{P}CH_2COOEt\ Cl^-$.

of signals to the CH-form (b) since it is known[8], that the conversion of phospinosubstituted ylides into the corresponding phosphonium salts leads to similar changes in δP^{III} and J_{PP}.

This conclusion is confirmed by ^{13}C-NMR spectral data obtained under conditions when only the CH-form is present[9]. The signal of the central carbon atom (δ=38.1 ppm) is a doublet due to the CH coupling (J_{CH} 139.7 Hz), each line of the doublet is a doublet of doublets due to CP coupling ($J_{CP(Ph_3)}$57 Hz and $J_{CP(Ph_2)}$ 48 Hz).

Thus in CH_2Cl_2 at -90° chloride salt II (A=B=Ph) exists both in the CH- and PH-forms. A further study has shown that both forms are in a mobile tautomeric equilibrium. The relative percentage of the forms in solution depends upon the temperature and the polarity of the medium. The relative percentage of CH-form is increased when the temperature rise or by increasing of solvent polarity. In trifluoroacetic acid as solvent only PH-form is present[10].

A similar study was carried out for the corresponding acetyl derivative:



In this case the usual keto-enol tautomerism occurs as well as the diadic phosphorus-carbon tautomerism.

Thus, the known examples of oxygen, sulfur and nitrogen organophosphorus diadic tautomeric systems can now be supplemented by phosphorus-carbon diadic tautomerism.

References and Notes

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5. $^{31}P-\{^{1}H\}$-NMR parameters of ylides I: A=B=Bu, CH_2Cl_2, -80°, $\delta_{P(Ph_2)}$ -31.5, -38.3 ppm, $\delta_{P(Ph_3)}$ 27.3 ppm, J_{PP} 154, 161 Hz. A=B=Ph, CH_2Cl_2, -70°, $\delta_{P(Ph_2)}$ -13.5, -19.2 ppm, $\delta_{P(Ph_3)}$ 28.0, 28.1 ppm, J_{PP} 178, 183 Hz.
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7. $\delta_{P(Ph_2)}$ of the CH-form IIb.
8. M.C.Hussain, H.Schmidbaur, Z. Naturforsch., 31b, 721 (1976); E.Appel, G.Erbelding, Tetrahedron Lett., 1978, 2689.
9. In CH_2Cl_2-CH_3CN solution (10:1), at -80°.
10. In a large excess of hydrogen chloride (10 mol) at -90° both forms are transformed to the dication $[Ph_2\overset{+}{P}(H)CH(\overset{+}{P}Ph_3)COOEt]\ 2Cl^-$. ^{31}P-NMR parameter (CH_2Cl_2-CH_3CN, 10:1): $\delta_{P(Ph_2H)}$ 5 ppm, J_{PP} 7.3 Hz, J_{PH} 520 Hz; $\delta_{P(Ph_3)}$ 23 ppm, J_{PP} 7.3 Hz.

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