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X-RAY PHOTOELECTRON SPECTRA OF PHOSPHORUS YLIDES. PROBING THE PHOSPHORUS-CARBON YLIDE BOND

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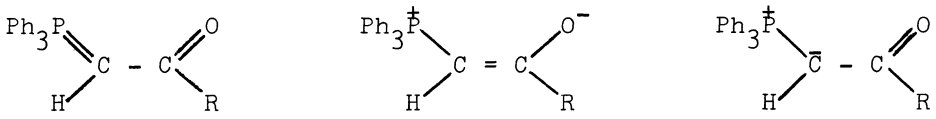
The nature of the phosphorus-carbon ylide bond was investigated by means of XPS. The binding energies of P-2p electrons of $Ph_3P{=}CHCOR$ (R=p-nitrophenyl, phenyl, p-methoxyphenyl) were found to be lower than that of $Ph_3P{=}CHCOOMe$. The binding energies of ylides are lower than those of the corresponding salts. These results are qualitatively consistent with IR data and ^{31}P-nmr data.

The term phosphorus ylide is used to describe organic phosphorus compounds which have the general structure illustrated in Ia or Ib.

Ia Ib

The P-C bond character shown in Ia and Ib has been discussed on the basis of the spectroscopic data and the information as for the stabilities, reactivities and equilibria of isomers of the ylides. Especially, the degree of $d\pi$-$p\pi$ interaction would be important in phosphorus ylides. However, the nature of bonding has not definitely been explained yet, and by means of X-ray photoelectron spectroscopy(XPS), ^{31}P-nmr and IR(C=O), the analysis of the bond character was performed. Particularly, XPS seems to be useful for determination of the charge density on phosphorus atom.[1] The compounds used for the present investigation are the ylides $Ph_3P{=}CHCOR$, and the corresponding salts; several related compounds were also examined for comparison. The possible resonance structures of the ylides are shown below.



IIa IIb IIc

It has been reported for these resonance-stabilized ylides that the charge on the carbon atom is definitely influenced by the property of the substituent R as revealed by measurements of pKa and reactivity.[2)]

The results of the present investigation are given in Table I.

Table I IR(C=O), ^{31}P-nmr and XPS Data of Ylides and Related Compounds

	IR(C=O)cm^{-1}	^{31}P-nmr ppm	XPS P-2p eV	Rate of reaction[b)] with Ph-CHO k,l/mol·sec	pKa[b)]
Ph_3P		+ 5.6 [a)]	131.3		
$Ph_3P{=}O$		-24.7 [a)]	131.5		
$Ph_3P{=}S$		-39.9 [a)]	131.6		
$Ph_3P{=}CHCO$-C$_6$H$_4$-NO_2	1540-1500	-16.8	130.8	6.45×10^{-6}	4.2
$Ph_3P{=}CHCO$-C$_6$H$_5$	1527	-16.2	131.2	1.21×10^{-4}	6.0
$Ph_3P{=}CHCO$-C$_6$H$_4$-OMe	1503	-16.7	131.3	4.10×10^{-4}	6.7
$Ph_3P{=}CHCO{-}OMe$	1620	-17.4	131.7	1.45×10^{-2}	8.8
$[Ph_3\overset{+}{P}{-}CH_2CO$-C$_6H_4$-$NO_2]\bar{B}r$	1689	-20.5	131.8		
$[Ph_3\overset{+}{P}{-}CH_2CO$-C$_6H_5]\bar{B}r$	1662	-20.6	132.0		
$[Ph_3\overset{+}{P}{-}CH_2CO$-C$_6H_4$-OMe$]\bar{C}l$	1652	-20.4	132.0		
$[Ph_3\overset{+}{P}{-}CH_2CO{-}OMe]\bar{B}r$	1725	-20.5	132.5		

a)M.M.Crutchfield, C.H.Dungan, J.H.Letcher, V.Mark and J.R.V.Wazer, "Topics in Phosphorus Chemistry", Vol. 5, John Wiley & Sons, New York, (1967) p. 227.
b)S.Fliszar, R.F.Hudson and G.Salvadori, Helv. Chim. Acta, 172, 1580 (1963).

In the XPS measurements, the phosphorus 2p binding energies were recorded with reference to the C-1s line at 284eV. The aluminum Kα and the magnesium Kα radiations were used as X-ray excitation source and the powdered samples were dispersed on a surface of aluminum plate. The spectrometers used were a JASCO ESCA-1 and a McPherson ESCA 36.*

IR measurements

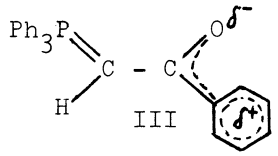
It was deduced from the X-ray single crystal analysis that the resonance structure IIb contributes largely in the phosphorus ylide with phenyl group as a substituent.[3,4)] Thus, the IR band due to the C=O stretching of the ylides shifts

*It was operated in Department of Chemistry, Faculty of Science, University of Tokyo, by Mr.Y.Tada and Prof. H.Kuroda, to whom the authors' thanks are due.

to lower wave numbers than those of usual carbonyl compounds. Further, the lower wave numbers were found for the ylides with more electron releasing substituents, indicating the increase in the contribution of structure IIb. It was also reported from the measurement of ^{13}C-nmr that the resonance structure IIc contributes largely in the ylide of R=OMe.[5] Accordingly, the wave number of the C=O band of this ylide would be higher than others (R=p-nitrophenyl, phenyl, p-methoxyphenyl), because the contribution of the double bond structure in the carbonyl group of this ylide is greater than others. Actually, the present data are consistent with these considerations.

XPS measurements

The results of XPS measurement are consistent with those of IR measurement. The binding energy of the ylide of R=OMe is the highest among four ylides. This result is reasonable, because the contribution of resonance structure IIc is considered to be the highest as mentioned above. The lowering binding energies are found in the order, R=p-methoxyphenyl, phenyl, p-nitrophenyl, as expected from the substituent effect on IR C=O band. This result would suggest the large contribution of resonance structure IIb and III.



III

An interesting result was obtained when the data for the ylides were compared with those for their salts; that is, the binding energies of the salts are higher than those of the corresponding ylides. This result is consistent with an information that the phosphorus atoms of quaternary phosphorus salts have more positive charge. This seems to indicate conversely that the differences of the charge density in these and related compounds can be detected by XPS. The substituent of the ylides has some effect on the value of the binding energy. The binding energy of $Ph_3P=CHCOOMe$ is higher than those of $Ph_3P=O$ and $Ph_3P=S$. It is plausible from this result that the contribution of polarized bond of ylide(R=OMe) is larger than those of $Ph_3P=O$ and $Ph_3P=S$, and this supports the usual explanation that the ylide has a dipolar structure.

^{31}P-nmr measurements

The differences of the chemical shift of ^{31}P-nmr peak are not large among the ylides investigated, but the differences between the ylides and their salts are distinct. This result is consistent with XPS data.

Comparison of XPS data with reactivity

It was already discussed that the overall rate and stereochemistry of the Wittig reaction depend on k_1 in the following sequence.[3)]

$$\text{ylide} + \text{aldehyde} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{betain} \xrightarrow{k_2} \text{product}$$

$$\text{rate of reaction} = k_1(\text{ylide})(\text{aldehyde})/(1 + k_{-1}/k_2)$$

Since $k_{-1} \simeq k_2$

$$\text{rate of reaction} = k_1(\text{ylide})(\text{aldehyde})/2$$

The initial bimolecular, nucleophilic step would be affected by the electronic effect as well as the steric one. With respect to a series of ylides used here, Hudson has demonstrated a linear relationship between the ylide basicity(pKa) and the rate of reactin (log k_1).[2)] It is, therefore, of interest to compare XPS data with pKa or log k_1. As shown in Table I, the binding energy is parallel with the basicity and the rate of reaction.

In conclusion, it was made clear that the results of XPS agree well with the results of the spectroscopic and kinetic measurements.

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