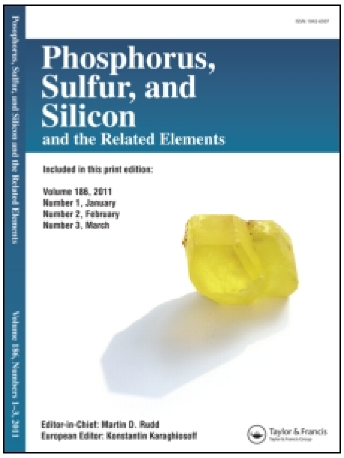

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Enolization of the Phosphoryl Group

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ENOLIZATION OF THE PHOSPHORYL GROUP

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Abstract The ability of the phosphoryl group to undergo enolization has been studied. The introduction of strongly electronegative substituents at the α-carbon atom is shown to increase CH- acidity greately and result in the enolization of the P=O group.

As is known the carbonyl group readily undergoes enolization. As far as the phosphoryl group is concerned, the corresponding data had been lacking until quite recently. From 1976 to 1982, Kolodyazhnyi[1] and we[2,3] reported the first examples of this kind:

/A/  /B/

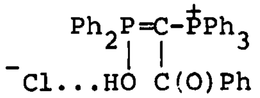
where $Y=Y'=SO_2Ph$[1] or $Y=Y'=Ph_3P^+X^-$ and $Y=Ts$, $Y'=Ph_3P^+X^-$ [2,3]. In all the three compounds, the central carbon atom had acidifying substituents (Y and Y') and for this reason, the acidity of the CH from (A) was higher than that of the P-OH one (B), and the proton migrated to the phosphoryl group.

In this work various electronegative groups, $Y=Ph_3P^+X^-$, PhCO, CN, Ts, MeCO, COOEt and $CONEt_2$, were used in combination with the same Y' substituent, $Y'=Ph_3P^+X^-$. This enabled us to vary CH acidity of form (A) smoothly. In the series of studied compounds, the degree of the enolization of the P=O group changed from 100% to zero.

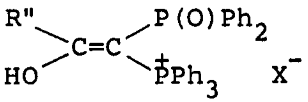
CRYSTALLINE STATE

According to IR evidence the biphosphonium salt ($Y=Ph_3P^+X^-$) occurs as phosphaenol (B) in crystals. A strong acidifying action of two phosphonium groups causes proton transfer to the P=O group. The benzyl derivative (Y=PhCO) chloride[4] has the phosphaenol structure (B) as follows from its IR spectrum and the X-ray diffraction data. The chloro anion participates in the stabilization of the phosphaenol structure (B):

/B/



$$^{-}Cl\cdots HO-\overset{|}{P}Ph_2=\overset{|}{C}(C(O)Ph)-\overset{+}{P}Ph_3$$



/C/

R" = Me or Ph

As to the perchlorate and borofluoride, they are enolized at the carbonyl group (C). The cyano derivative (Y=CN) has the phosphaenol structure (B)[5] stabilized by strong H-bonds between OH groups and bromo anions. In perchlorates, the formation of strong H-bonds is practically impossible, and the phosphaenol form (B) is stabilized by the interaction with one more base molecule to produce a basic salt (dimer) of the type BHB^+ with equivalent pairs of bonds:

$$CN(ClO_4^- \; {}^{+}PPh_3)C{=}\overset{|}{\underset{|}{P}}{-}O{-}H\cdots O{=}\overset{|}{\underset{|}{P}}{-}C{=}PPh_3(CN)$$

The tosyl derivative (Y=Ts) bromide[3] has the phosphaenol structure (B) according to the X-ray and IR data. It is stabilized by the H-bonds $P-OH\cdots Br^-$. The perchlorate has the BHB^+ structure. The acetyl derivatives (Y=MeCO)[4] are enolized at the carbonyl group (C) irrespective of the anion (Cl^-, Br^-, or ClO_4^-). The carboethoxyl derivative (Y=COOEt)[6] whose COOEt group has a weaker acidifying action exists as phosphaenol (B) in the presence of chloro anions and a typical CH- phosphoryl derivative (A) with perchlorato groups as counterions. Lastly, the carbamoyl derivative ($Y=CONEt_2$) contains the weakest acceptor group of all studied. Even its chloride occurs as CH- phosphoryl derivative (A) rather than phosphaenol (B). It folloes that although the structure of molecules in crystals depends on many factors, the effect of electronegativity of Y appears to prevail.

SOLUTIONS

Solutions in CH_2Cl_2, $CHCl_3$, CH_3CN, CH_3NO_2, EtOH, and CF_3COOH were studied using the IR and ^{31}P, ^1H and ^{13}C NMR spectroscopy. With most compounds there is, in principle, the possibility of the A $\rightleftharpoons$ B tautomerism in solutions. The acetyl and benzoyl derivatives can exist as A, B, and C tautomers. Bisphosphonium compounds (Y=$Ph_3P^+X^-$) have been found to be phosphaenols (B) irrespective of the anion. With Y=CN, the bromide and perchlorate exist as phosphaenols at -80 to +30°C; the CH- form is, however, stabilized in CF_3COOH. The tosyl derivative (Y=Ts) shows a similar behaviour. With the benzoyl group for Y, practically no enolization of the CO group is observed. The solution mainly contains phosphaenol (B), doubtless stabilized by H-bonds between P-OH and chloro anions. Bromo anions form weaker H-bonds, and the percentage of phosphaenol (B) is decreased, while that of the phosphoryl CH-form increased, from the chloride. In the acetyl derivative chloride (Y=MeCO), the enol form (C) predominates whereas the corresponding bromide has the phosphoryl CH- structure (A). The percentage of phosphaenol (B) is lower in both salts than with the benzoyl derivative. Tautomeric equilibria are also characteristic of the carboethoxyl derivative, Y=COOEt. In aprotic media, the percentage of phosphaenol (B) decrease as the dielectric properties of medium increase: $CH_2Cl_2 > CH_2Cl_2 + MeNO_2$ (4:1) $> MeNO_2$. Chloroform solvates P=O groups and favours the formation of the structure (A). Lastly, the weakest acidifying substituent, the carbamoyl group (Y=$CONEt_2$), strongly shifts the equilibrium on the side of the phosphoryl form (A). It follows that the acidifying action of Y substantially affects equilibria in the systems under consideration.

The ability of the phosphoryl group to undergo enolization also depends on the nature of the substituents at phosphorus, R and R'. Thus the tosyl derivative bromides form phosphaenols (B) in the crystalline state when R and R' are Bu, Et, and Ph. With EtO and PhO for R and R', the compounds have the phosphoryl structure (A). All the perchlorates except the Ph derivative also have the phosphoryl structure (A). With diphenyl derivatives, the dimers BHB^+ are formed.

There is studied also question concerned with the experimental acidity and the enolization of compounds investigated.

Conclusion. The phosphoryl group can indeed indergo enolization. This requires the presence of sufficiently strong acidifying substituents at the central carbon atom and donor substituents at phosphorus. The ability of the P=O group to undergo enolization is also influenced by other factors such as H-bonds, the nature of solvents, and temperature. On the whole, the enolization of the P=O group follows general patterns of acid-base protolytic tautomeric equilibria.

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