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A SPECTRAL STUDY OF TAUTOMERISM IN β-OXOPHOSPHONIUM SALTS

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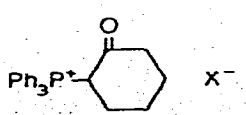
Summary

β-Oxoalkyltriphenylphosphonium salts, $Ph_3P^+—CH_2COR\ X^-$, display keto-enol tautomerism. The keto—enol equilibrium was studied by ^{31}P and ^1H NMR and IR methods. The enol fraction in solution increases with a decrease in the size of the substituent R. The equilibrium is strongly influenced by hydrogen bonding between the anion X^- and the enol hydroxyl.

Introduction

Tautomerism of ketones containing onium groups has not been the subject of much study; the phosphonium case has only been discussed in a few papers. Kabachnik, Mastryukova et al. [1,2] found that the diacylmethyltriphenylphosphonium salts $Ph_3P^+—CH(COR)COR'\ X^-$, in the solid state or in $CHCl_3$, are enols exclusively. Cyclic β-ketophosphonium salts such as 3,3,5,5-tetraphenyl-3,5-diphosphacyclohexanone salts, regardless of the anion, are enolised completely in the crystal state and in $CHCl_3$, CH_3CN, DMSO, and display a keto—enol equilibrium in CH_3OH or CF_3COOH [3,4]. The most interesting results [5] deal with the salts $Ph_2P(CH_3)—CH_2—C(O)—CH_2P(O)Ph_2$ X(I) (X = a, Cl; b, BPh_4; c, ClO_4; d, BF_4; e, CF_3COO). The NMR and IR data [5] suggest that in the solid state all the salts are ketones. In chloroform, Ia and Ie are equilibrium keto—enol mixtures. The salts Ib—1d, which contain complex anions, are not enolised.

The anion effect may also be observed in salts of the type



IR spectra suggest [6] that the solid salt is an enol with X = Cl and a ketone with

X = Br. Both salts are isomer mixtures in solution.

To sum up the literature data, all phosphonium keto salts capable of giving reasonable amounts of enol in solution either contain enol-stabilising C=O or P=O groups or are derivatives of a highly enolisable compound e.g. cyclohehexanone.

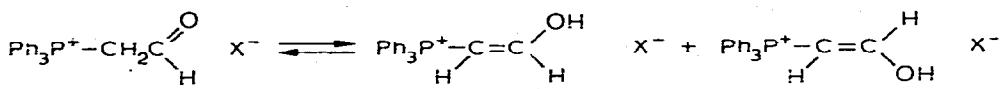
The simplest carbonyl compounds of the type $Ph_3P^+—CH_2—C(O)—R\ X^-$ (II) were thought [1,5] to be hardly capable of any enolisation. In the IR spectra of some solutions of β-oxophosphonium salts we noticed an intense band at 1620 cm^{-1}; which we tentatively assigned to the enol double C=C bond. This was the starting point of the investigation we describe below.

Previously, in a short communication we reported [7,8] the presence of keto—enol tautomerism in solutions of II and the X^- effect upon the equilibrium. In the present paper, we describe extensive data obtained for a larger set of R substituents in II and discuss the equilibrium as a function of the substituent.

Results

A. Tautomersim in formylmethyltriphenylphosphonium salts

The ν(C=O) frequency lies at 1720—1670 cm^{-1} in all the simplest phosphonium salts having an oxo group on the β-carbon [9—11]. The IR spectrum of the solid IIIa contains an intense band at 1620 cm^{-1}; this and the absence of absorption in the 1700 cm^{-1} region suggest that IIIa is an enol in the crystal state. Solutions of the salt contain practically nothing but the enol form, as follows from the IR and NMR data.



(IIIa, IVa) (IIIb, IVb) (IIIc, IVc)

III, X = Cl; IV, X = BF_4

An IR spectrum of IIIa in chloroform (Table 1) displays two bands (1601 and 1609 cm^{-1}) assignable to the >C=C< bonds of the *cis*- and *trans*-isomeric enols. A very intense band observed at 2700—2200 cm^{-1} suggests that there is strong hydrogen bonding between the hydroxyl group and the anion [12].

The presence of enolic isomers of IIIa agrees with the NMR $^{31}P — \{^1H\}$ data: two singlets, at δ — 18.9 and —13.9 ppm. Relative chemical shifts will be discussed in more detail below. An NMR $^1H—\{^{31}P\}$ spectrum of IIIa in $CDCl_3$ contains signals assignable to the *cis*- and *trans*-isomers of the enol. For the *trans*-isomer of $Ph_3P^+—CH_a=C(H_b)OH\ Cl^-$, δ($CH_a$) is 5.6 ppm, $J(H_a—H_b)$ 12 Hz and $J(PH_a)$ 13.5 Hz; for the *cis*-isomer, δ(CH_a) is 4.6 ppm, $J(H_a—H_b)$ 6.8 Hz and $J(PH_a)$ 18 Hz. In both isomers the spectrum contains an hydroxyl signal; δ 10.1 ppm. The spectral data are summarised in Table 1.

An IR spectrum of a solution of formylmethyltriphenylphosphonium bromide reveals bands characteristic of an enol and aldehyde. The bromide is subject to an equilibrium, which has a pronounced shift to the aldehyde with BF_4 as anion (salt IV). An increase in solvent polarity shifts the equilibrium towards

TABLE 1

IR AND NMR $^{31}P-\{^1H\}$ DATA FOR FORMYLMETHYLTRIPHENYLPHOSPHONIUM SALTS $Ph_3P^+-CH_2C(O)H\ X^- \rightleftharpoons Ph_3P^+-CH=C(OH)H\ X^-$

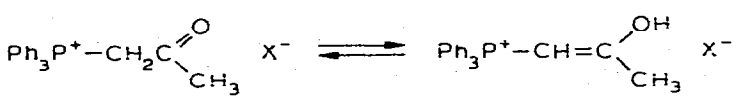
X	Solvent	^{31}P (δ, ppm)			Content (%)			IR spectra $\nu(cm^{-1})$
		Ketone	Enol		Ketone	Enol		
			trans	*cis*		*trans*	*cis*	
Cl	$CHCl_3$	—	−18.9	−13.9	0	64	36	1601 [a], 1609 [a], 2200—2800, 3400; 3680
	KBr							1615
	Nujol							1620, 2400—2700
Br	$CHCl_3$							1720, 1635, 1600, 2200—2800
BF_4	$CHCl_3$	−19.5	−18.5	−13.4	34	56	10	1725 [a], 1645 [a], 1612 [a], 3670, 3470, 3280, 2200—2800
	CH_3CN	−18.9	−18.3	−12.4	48	36	16	
	CH_3OH	−19.6	—	—	100	0	0	
	Nujol							1723, 1615w

[a] Similar bands were observed in dichloroethane or CH_2Cl_2.

the aldehyde. In the crystal state the salt IV is an aldehyde. Consequently, formylmethyltriphenylphosphonium salts (except for those with complex anions) prefer the enol structure.

B. Tautomerism in acylmethyltriphenylphosphonium salts

IR, PMR, and ^{31}P NMR methods helped us to study tautomerism of the simplest ketophosphonium cation V.



(V) (VI)

Va, VIa, X = BF_4; Vb, VIb, X = Br; Vc, VIc, X = Cl; Vd, VId, X = CF_3COO

The solid salts (Va—Vd) were found to have ketone structures. The IR spectra (Fig. 1) recorded in methylene chloride or chloroform contain, along with the ν(C=O) band at 1720 cm^{-1}, an intense band at 1620 cm^{-1} (ν(C=C)). The latter band is absent from the solutions in methanol and from the tetrafluoroborate Va solutions. Its intensity grows on going from the bromide to the chloride and, further, to the trifluoroacetate. IR spectra of the Vb, Vc, Vd solutions display bands at 2800—2200 cm^{-1} characteristic of a hydroxyl group with strong hydrogen bonding [12]. Therefore, the IR data demonstrate that there is keto—enol tautomerism in solutions of acetonyltriphenylphosphonium salts and that hydrogen bonding plays a role in stabilising the enol (no enol with X = BF_4; an increase in the enol content in going from Br to Cl to CF_3COO). The solvent polarity effect is normal; a polar solvent (methanol) shifts the equilibrium markedly towards the ketone. The trifluoroacetate (Vd) or bromide (Vb) solutions

in chloroform become red on addition of ferric chloride, although to a smaller extent with bromide.

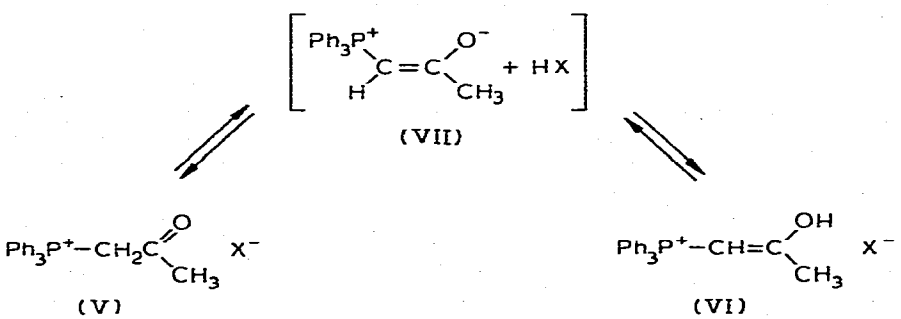
The NMR $^{31}P-\{^1H\}$ spectra were obtained using pulse methods. The fact that the relative intensities are invariable on variation in the pulse sequence frequency leads one to believe that the ketone/enol ratios of Table 2 are close to the real ones.

An ^{31}P NMR spectrum of the trifluoroacetate (Vd) solution contains two singlets at δ —19.6 and —13.4 ppm (Fig. 2), the latter signal being much more intense in methylene chloride and considerably less intense in methanol (very low enol content). The enol signal, absent from the tetrafluoroborate spectrum, is of low intensity in the bromide (V) spectrum.

PMR spectra recorded for all the salts at low temperatures reveal proton signals assignable to the ketone and the enol forms (Table 3).

The Vd hydroxyl proton signal obtained at —20°C is broadened and remains broadened even at —60°C. The ketone/enol ratio is 28 : 72 judging from the Vd PMR spectrum in chloroform. Both forms are also quite pronounced for the chloride Vc in chloroform, the ketone/enol ratio being 64 : 36. However, with the bromide, the enol content is very low.

A natural intermediate in the ketone—enol transformation is the ylide VII, therefore addition of the ylide to the reaction mixture should not alter the equilibrium but should accelerate the equilibration, the ylide also being a possible proton carrier.



(VII)

(V) (VI)

Indeed, a 10% solution of ylide added to the solution of Vd in methylene chloride resulted in only one broadened signal (Fig. 2); cooling the probe down to —10°C gives two singlets, which become narrower at —30°C. The ylide signal lies at δ —14.7 ppm, close to the enol signal [14].

The data discussed above demonstrate that even a small amount of the enol may be indicated by the 1620 cm^{-1} band; e.g., the bromide Vb produces 6% enol in $CHCl_3$ and below 1% enol in DMSO, nevertheless the IR band is quite observable. Consequently, further work in this area was done in some cases without NMR spectroscopy since the absence of a band at 1620 cm^{-1} was a good proof of the absence of enol. Also, when phosphonium trifluoroacetate was exclusively or almost exclusively in the ketone form the bromide or tetrafluoroborate were not studied since they could be reasonably assumed to be even more ketonic.

A similar arsonium salt, $Ph_3As^+-CH_2COCH_3$ CF_3COO^-, exists exclusively

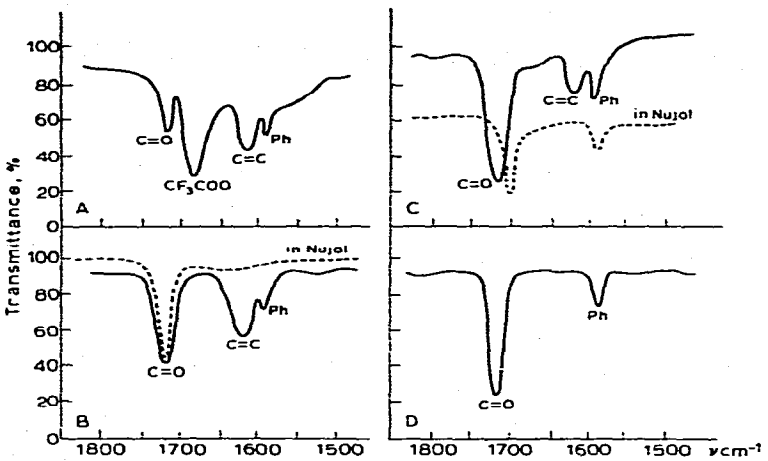


Fig. 1. IR spectra of Ph_3P^+—CH_2COCH_3 X^- in $CHCl_3$. X is: A, CF_3COO; B, Cl; C, Br; D, BF_4.

in the ketone form. Its IR spectrum recorded in dichloroethane or in Nujol contains two bands: 1715 cm^{-1} (ν(C=O)) and 1650 cm^{-1} (ν(C=O) in CF_3COO^-).

C. Tautomerism in other acylmethylphosphonium salts

To visualise the effect of the R substituent in the acyl group of the phospho-

TABLE 2

IR AND NMR ^{31}P—$\{^1H\}$ DATA FOR ACETONYLMETHYLTRIPHENYLPHOSPHONIUM SALTS Ph_3P^+—$CH_2C(O)CH_3$ X^- ⇌ Ph_3P^+—CH=$C(OH)CH_3$ X^-
(V) (VI)

X	Temp. (°C)	Solvent	^{31}P (δ, ppm)		Content (%)		IR spectra ν(cm^{-1})
			Ketone	Enol	Ketone	Enol	
CF_3COO	−30	CH_2Cl_2	−19.6	−13.1	28	72	
	−10	$CHCl_3$			36	64	
	20	$CHCl_3$	−19.6	−13.4	46	54	1720, 1675; 1622, 2800—2200; 3425, 3675
	20	CH_3OH	−19.3	−12.6	88	12	
	20	Nujol					1715, 1675
Cl	20	$CHCl_3$	—	—	71	29 [a]	
	20	CH_2Cl_2	—	—			1718, 1608, 2800—2200; 3360; 3675
	20	CH_3OH	—	—			1722
	20	Nujol		—			1705
Br	20	$CHCl_3$	−19.6	−12.6	93	7	1720, 1620, 2800—2400, 3425; 3660
	20	CH_3OH	−19.2	−12.2	95	5	
	20	DMCO	−19.2	−11.8	>99	<1	1718, 1620
	20	Nujol					1710
BF_4	20	$CHCl_3$	−19.4	—	100	0	1722
	20	Nujol					1718

[a] Based on ^{13}C NMR data [13].

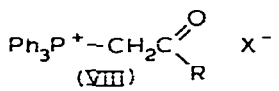
TABLE 3

PMR DATA FOR ACETONYLTRIPHENYLPHOSPHONIUM SALTS IN CHLOROFORM [a] $Ph_3P^+-CH_2C(O)CH_3X^- \rightleftharpoons Ph_3P^+-CH{=}C(OH)CH_3X^-$

X	Temp. (°C)	δ(CH_2) (ppm)	J(CH_2–P) (Hz)	δ(CH) (ppm)	J(CH–P) (Hz)	δ(CH_3) (ppm)	δ(OH) (ppm)	Intensity ratios (I)
CF_3COO	−60	5.54 d	12.75	4.53 d	21	2.25 s	14.7 s	$CH_2/CH/CH_3/OH$ = 2.2 : 3 : 12.8 : 2.8
CF_3COO	20	—	—	—	—	2.3 s	—	
Cl [b]	25	6.12 d	11.6	4.75 d	19.5	2.50 s	12.82	$CH_2/CH/OH$ = 3.86 : 1.10 : 1.00
Br	−30	5.83 d	10.5	4.53 d	18	2.28 s	11.0	
Br	20	5.60 d	12	—	—	2.30 s	—	CH_2/CH_3 = 2 : 3
BF_4	20	5.0 d	12	—	—	2.33 s	—	CH_2/CH_3 = 2 : 3

[a] The chemical shifts were recorded in $CHCl_3$, δ-scale: s, singlet; d, doublet. [b] These data were kindly provided for us by T.A. Mastryukova and I.M. Aladzheva.

nium salts under study, we synthetised, the following phosphonium salts:



(VIII)

VIIIa, R = C_2H_5;
VIIIb, R = CH_2Cl; VIIIc, R = $C(CH_3)_3$;
VIIId, R = C_6H_5; VIIIe, R = p-$C_6H_4OCH_3$;
VIIIf, R = p-$C_6H_4NO_2$

and studied them using IR and ^{31}P NMR spectroscopy. Table 4 lists the results obtained.

Table 4 demonstrates that when C_2H_5 or CH_2Cl replaces CH_3 in Vd the enol content decreases from ca. 70—30% VIIIa, or 70—45% VIIIb. In the t-butyl case, there is no enol in solution, even with trifluoroacetate. The same is true for aryl groups; replacing methyl by aryl groups reduces the enol content to zero or

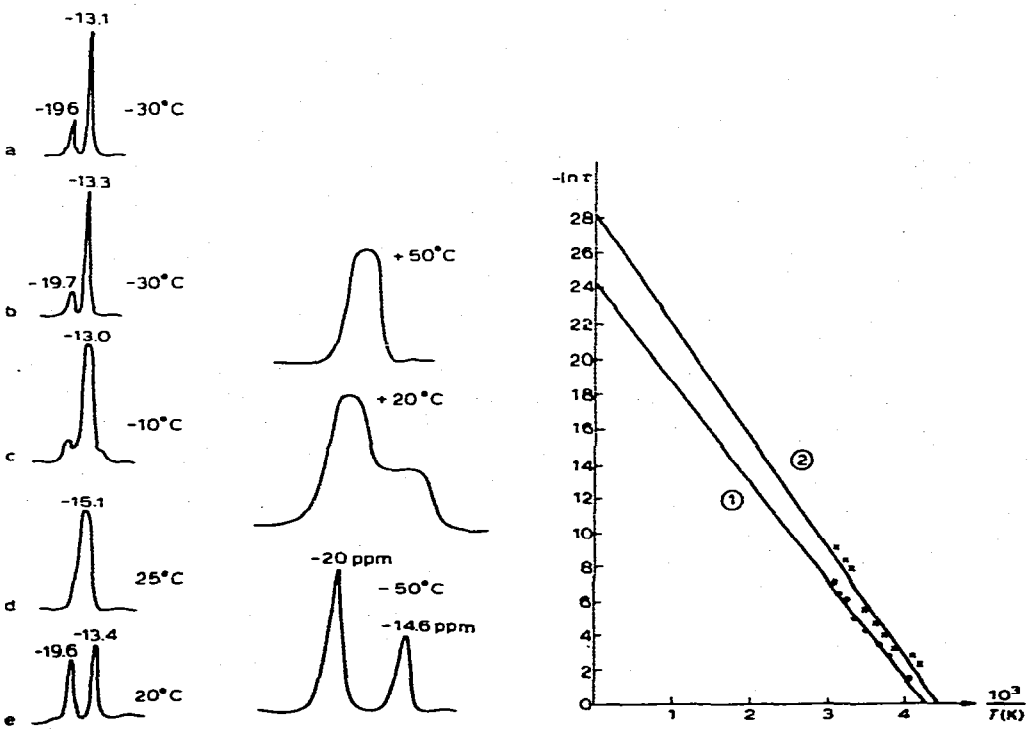


Fig. 2. ^{31}P NMR spectra of Ph_3P^+—$CH_2C(0)CH_3$ CF_3COO^- (chemical shifts in ppm): a, in CH_2Cl_2; b, c, d, in CH_2Cl_2, 10% ylide added; e, in $CHCl_3$.

Fig. 3. Temperature variable NMR spectra of Ph_3P^+—CH_2COEt CF_3COO^- and Ph_3P^+—CH_2COCH_2Cl CF_3COO^-, in $CHCl_3$.

Fig. 4. Arrhenius plots for calculation of transformation energies: (1) Ph_3P^+—CH_2COEt CF_3COO^-, (2) Ph_3P^+—CH_2COCH_2Cl CF_3COO^-.

TABLE 4

IR AND NMR $^{31}P-\{^1H\}$ DATA FOR ACYLMETHYLTRIPHENYLPHOSPHONIUM SALTS: $Ph_3P^+-CH_2C(O)RX^-$ (VIII)

R	X	Temp. (°C)	Solvent	^{31}P (δ, ppm)		Content (%)		IR spectra ν(C=O) (cm^{-1})
				Ketone	Enol	Ketone	Enol	
C_2H_5	CF_3COO	−40	$CHCl_3$	−20	−14.6	70	30	1720, 1670, 1605, 2200–2800; 3350; 3650
	CF_3COO	20	Nujol	–	–	–	–	1708, 1680
	Cl	25	$CHCl_3$	−19.9	−14	96	4	1720, 1608, 2400–2800; 3340, 3650
	Cl	20	CH_2Cl_2	–	–	–	–	1718; 1610
	Cl	20	Nujol	–	–	–	–	1710, 1612vw.
CH_2Cl	CF_3COO	−40	$CHCl_3$	−20	−14.3	55	45	
	CF_3COO	20	$CHCl_3$	–	–	–	–	1740, 1680, 1615, 2200–2800
	CF_3COO	20	Nujol	–	–	–	–	1720, 1620
	Cl	25	$CHCl_3$	−20	−13.9	96	4	1715, 1610, 2800–2400; 3350, 3650
	Cl	20	Nujol	–	–	–	–	1740, 1612w
$C(CH_3)_3$	CF_3COO	25	CH_2Cl_2	−21.8	–	100	0	–
	CF_3COO	20	$CHCl_3$	–	–	–	–	1710, 1685
	Br	20	CH_2Cl_2	–	–	–	–	1705
C_6H_5	CF_3COO	20	$CHCl_3$	−21	–	100	0	–
	CF_3COO	−20	$CHCl_3$	−23.4	−16.8	98	2	–
	Br	20	$CHCl_3$	–	–	–	–	1670
	Br	20	DMCO	−21.0	–	100	0	1675
	Br	20	Nujol	–	–	–	–	1660
p-$CH_3OC_6H_4$	CF_3COO	25	$CHCl_3$	−21.6	–	100	0	1670, 1600, 1590 } Ph
	CF_3COO	−50	$CHCl_3$	−21.5	–	100	0	
	CF_3COO	20	Nujol	–	–	–	–	1680, 1650, 1600, 1590 } Ph
	Br	25	$CHCl_3$	−21.9	–	100	0	1670, 1600, 1590 } Ph
		25	Nujol	–	–	–	–	1650, 1600, 1590 } Ph
p-$NO_2C_6H_4$	Br	25	$CHCl_3$	−21.3	–	100	0	1690; 1610(Ph) 1520(NO_2)
	Br	20	Nujol	–	–	–	–	1675; 1605(Ph) 1520(NO_2)

below 1% regardless of the *para*-substituent in the ring, VIIId—VIIIf.

^{31}P NMR ketone and enol signals can be observed for VIIIa and VIIIb only at —40°C. Heating the mixture leads to rapid interconversion of the ketone and enol species and at 50°C only one averaged signal is observed in the spectra (Fig. 3).

The Arrhenius equation was solved at 10°C intervals using $^{31}P—\{^1H\}$ NMR data recorded at —40°C to +50°C, to give the transformation energies; —11.25 kcal/mol for VIIIa and —12.27 kcal/mol for VIIIb. The plots are shown in Fig. 4.

Discussion

I. Effect of the anion X^- on keto—enol equilibrium

The β-oxophosphonium salts under discussion differ from the usual keto—enol tautomeric compounds in that they: (a) Contain no C=O or P=O groups capable of hydrogen bonding with the enol hydroxyl; (b) Have quaternary phosphonium ions in their molecules and (c) Contain an anion, X^-.

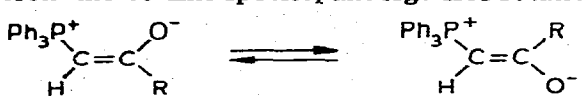
The data in Tables 2 and 4 demonstrate very clearly that the ability of X^- to enter into hydrogen bonding plays a very important role in shifting the equilibrium towards the enol, the effect decreases in the series $CF_3COO^- > Cl^- >> Br^- >> BF_4^-$.

Strong hydrogen bonds $X^-\cdots HO$ in some of the compounds are confirmed by IR and PMR spectra, e.g., the spectrum of acetonyltriphenylphosphonium trifluoroacetate (Va) contains a very intense band at 2900—2200 cm^{-1}, characteristic of a hydroxyl group subject to strong hydrogen bonding [3,5,12]. In going from CF_3COO^- to Cl^- to Br^-, this band becomes weaker, and disappears completely with the tetrafluoroborate Vd. The downfield shifts observed for the hydroxyl proton (δ(OH) 11 for Vb, 12.8 for Vc and 14.7 ppm for Vd, Table 3) also suggests strong hydrogen bonding in the salts under consideration [16,17].

Consequently, an increase in the anion basicity lowers the OH acid (enol) strength compared with the CH acid (ketone), since $K_T = K_a(k)/K_a(e)$ * in a given solvent, i.e. strong hydrogen bonding lowers the enol K_a. A methanol solvent, polar and protic, shifts the equilibrium towards ketone owing, probably, to a weakening of the enol hydroxyl—anion hydrogen bond. A similar effect is observed on adding trifluoroacetic acid to a solution of the trifluoroacetate Vd in chloroform. The resulting PMR intensity ratio is $I(CH_2)/I(CH_3)$ 2 : 3 that is, the equilibrium is almost completely on the ketone side.

II. Stereochemistry of the enols

Ylides of the type IX or X, whose structure has a significant contribution from the betaine species, undergo free rotation [18,19].



(IXA, XA) (IXB, XB)

IX, R = H; X, R = Alk, Ar

* K_T is the tautomeric equilibrium constant, $K_a(k)$ is ketone ionisation constant, $K_a(e)$ is enol ionisation constant.

Spin—spin couplings found for formylmethylenetriphenylphosphorane (J(PH)*trans* 4.0 Hz, J(PH) *cis* 39.0 Hz) allowed ^{31}P NMR signal to be assigned as —19.1 ppm for the *trans*-isomer; —15 ppm for the *cis*-isomer [18,19]. The A/B ratio was close to 1 : 1 in the IX solution. If, however, hydrogen was replaced by a different group (Alk, Ar), the betaine existed as the *cis*-isomer exclusively owing, appearently, to steric hindrance caused by Ph_3P—R interaction in X B [20—22].

These data, and the PMR data obtained for formylmethyltriphenylphosphonium chloride (III, Table 1), allow us to conclude that the III ^{31}P—{^{1}H} NMR signal obtained in $CHCl_3$ and lying at δ —14 ppm may be assigned to the *cis*-isomer and the one lying at ca. δ —19 ppm to the *trans*-isomer. Thus, the salt III is a 36 : 64 *cis/trans* mixture. With the tetrafluoroborate IV the signals of the geometric isomers are accompanied by a signal at δ —19.5 ppm assignable to the aldehyde species. The ratio of stereoisomers changes in favour of the *trans*-isomer, 56 : 10. An increase in the solvent polarity shifts the equilibrium towards the ketone and IV in methanol is aldehyde exclusively, $\delta(^{31}P)$ —19.6 ppm.

Naturally, ^{31}P NMR spectra alone would hardly allow one to distinguish between the aldehyde and the *trans*-enol species since their δ values are very close. However the IR spectrum of III, (R = H, X = Cl) shows no band attributable to a carbonyl group.

When hydrogen is replaced by CH_3 (in acetonyltriphenylphosphonium salts (V)) the enol exists only as the *cis*-isomer (δ —12 to —13 ppm, Table 2). In other phosphonium salts (VIIIa, VIIIb), containing the enol form in solution, the enol exists as the *cis*-isomer in all cases (Table 4).

III. Effect of R on the equilibrium constant

We have already mentioned that compounds of the type Ph_3P^+—CH=C(R)O^- (X) are very sensitive to spatial effects of the substituent R. Indeed, when R = H in IX is replaced by R = Alk or Ar the *cis*-isomer exists exclusively [19.21]. Apparently, the triphenylphosphonium group is large enough to hinder the *cis*-arrangement of groups as small as alkyls. The polar effects play a less important role in this transformation; they are probably in part weakened, owing to the donor—acceptor (O^-—P^+) *trans*-arrangement favoured by conjugation and to the *cis*-arrangement of the charged atoms favoured by Coulomb interaction.

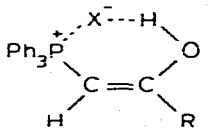
In the compounds we studied, spatial effects of the kind are also prominent. The aldehyde salts (IV, R = H) are almost exclusively enols, whereas the ketones (V, R = CH_3) display a equilibrium close to the 50 : 50 case with X = Cl or CF_3COO^-. Further increase in the size of R, from C_2H_5 to $C(CH_3)_3$ lowers the enol content in solution to zero. This could have been explained by an increase in the $+I$ effect over the series $H < CH_3 < C_2H_5 < C(CH_3)_3$, but this explanation would disagree with known properties of these systems, in which phenyl is a stronger electron acceptor than methyl since phenacyltriphenylphosphonium salts are much more acidic than acetonyltriphenylphosphonium salts [23,24]. Nevertheless, the enol content in a solution of phenacyltriphenylphosphonium trifluoroacetate (VIIId) in $CHCl_3$ is only 2% and there is no enol in solutions of the trifluoroacetate (VIIIe, R = *p*-$C_6H_4OCH_3$) or the bromide (VIIIf, R = *p*-$C_6H_4NO_2$). We failed to synthesise the trifluoroacetate VIIIf because attempts to isolate it resulted in loss of CF_3COOH and formation of the ylide. It should be em-

phasised that in the salts VIIIa and VIIIb, containing the substituents CH_2CH_3 and CH_2Cl which possess oppposite induction effects and similar sizes, the enol content is markedly lower than it is in the salts V, R = CH_3 (Tables 2 and 4). Thus in these cases the equilibrium is governed only by the steric effects of the R substituents.

Since $pK_T = pK_a(k) - pK_a(e)$, a comparison of substituent polar effect on $pK_a(k)$ with that on $pK_a(e)$ is important. The effect may, however, be levelled out by the fact that the number of bonds between the substituent and the enol hydroxyl proton is equal to the number of bonds between R and the ketonic CH_2 protons.

The steric effect may be visualised as follows. At a large enough R, the *cis*-enol is more favourable, owing to the Ph_3P—R interaction. The C—O—H angle is, however, ca. 105°, so the hydroxyl hydrogen should enter into steric interaction with the large Ph_3P group or (in the other conformation) with the substituent R. Both the interactions should raise the enol energy and weaken the OH···X hydrogen bond.

A chelate structure for the enol, would not agree with the R steric effect



mentioned. The conformation pictured above is also incompatible with the fact that formylmethyltriphenylphosphonium chloride (III) as enol in solution is a *cis/trans* mixture, *trans*-isomer being dominant although it cannot exist in chelate form.

Experimental

Acylmethylphosphonium trifluoroacetates were obtained via two methods.

Method A. A mixture of equimolar amounts of ylide and trifluoroacetic acid was left overnight in dry benzene. The precipitate was filtered and washed with hexane.

Method B. Phosphonium chloride or bromide in dry CH_3OH was treated with an equimolar solution of silver trifluoroacetate. The AgCl precipitate was filtered off, the filtrate evaporated in vacuo and the residual crystals were twice reprecipitated from dichloroethane by hexane and carefully dried in vacuo.

Acylmethyltriphenylphosphonium tetrafluoroborates

A solution of acylmethylphosphonium bromide in water was treated with an excess of an aqueous solution of NH_4BF_4. The precipitate was filtered, dried, and reprecipitated twice from chloroform by ether.

Acetonyltriphenylarsonium trifluoroacetate

The compound was obtained via Method B. The solvent was removed and the residue was washed several times with hexane. The yield was 60%, m.p. 116—118°C. Found: C, 57.78; H, 4.36. $C_{23}H_{20}AsF_3O_3$ calcd.: C, 57.99; H, 4.23%.

TABLE 5. PHOSPHONIUM SALTS $Ph_3P^+-CH_2C(O)RX^-$

Compound No.	R	X	Yield (method) (%)	M.p. (°C)	Found (calcd.) (%)			
					C	H	P	Hal
III	H	Cl	55	214 [a] (212–216 [25])	—	—	—	—
IV [b]	H	BF_4	90	76–77 [c]	59,46 (59,50)	5,23 (4,90, 5,08)	—	17,92 (18,03)
Vd	CH_3	CF_3COO	80(A)	195–196	63,68 (63,89)	4,66 (4,66)	7,31 (7,16)	—
Vc	CH_3	Cl	85	238 [a] (237–238 [26])	—	—	—	—
Vb	CH_3	Br	80	229 [a] (226 [27])	62,96 (63,17)	5,10 (5,05)	7,65 (7,76)	20,09 (20,01)
Va	CH_3	BF_4	95	154	61,76 (62,09)	4,81 (4,96)	7,68 (7,62)	18,72 (18,71)
VIIIa	C_2H_5	CF_3COO	93(B)	119–120	64,57 (64,68)	4,96 (4,82)	—	—
VIIIa [28]	C_2H_5	Cl	63	217–218 [d]	71,64 (71,63)	6,01 (6,89)	8,39 (7,97)	—
VIIIb	CH_2Cl	CF_3COO	86(B)	95	59,17 (59,09)	4,10 (4,07)	6,63 (6,65)	
VIIIb	CH_2Cl	Cl	65	213 [e] (210–212 [29])	—	—	—	—
VIIIc	$C(CH_3)_3$	Br	67	217–218 [a] (217–219 [30])	—	—	—	—
VIIIc	$C(CH_3)_3$	CF_3COO	64(A)	140 [a]	65,64 (65,81)	5,47 (5,52)	6,75 (6,53)	—
VIIId	C_6H_5	CF_3COO	75(A)	132	68,04 (68,01)	4,57 (4,48)	6,23 (6,26)	—
VIIId	C_6H_5	Br	80	271–273 [a] (269–271 [26])	—	—	—	—
VIIIe	p-$C_6H_4OCH_3$	CF_3COO	90(B)	173–174	66,41 (66,05)	4,61 (4,47)	5,90 (5,74)	—
VIIIe	p-$C_6H_4OCH_3$	Br	74	221 [a] (222 [31])	—	—	—	—
VIIIf	p-$C_6H_4NO_2$	Br	70	149–150 [e] (150 [30])	—	—	—	—

[a] Reprecipitated from $CHCl_3$ by ether. [b] Crystallises with a CH_3OH molecule. [c] Reprecipitated from $CHCl_3$ by ether. [d] Reprecipitated from dichloroethane/

p-Nitrobenzoylmethylenetriphenylphosphorane

The compound was obtained according to a literature method [31]. The precipitate was washed with methanol and water, m.p. 157—158°C. After recrystallisation from aqueous alcohol and careful drying, the melting point was 191—192°C (lit. [31] 147.5—148.5°C). Found: C, 73.09; H, 4.88; P, 7.18. $C_{26}H_{20}NO_3P$ calcd.: C, 73.41; H, 4.74; P, 7.28%.

Spectral studies

IR spectra were measured on an IKS-22A spectrometer. NMR spectra were recorded on Bruker HX-90 36.43 MHz ($^{31}P-\{^1H\}$), RYa-2305 60 MHz and Hitachi Perkin—Elmer R-20 60 MHz (^1H), machines. Mathematical treatment of experimental data was carried out on a PDP-12 computer.

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