The k_1/k_2 ratios determined using Eqs. (1) and (2) differed by a few percent since these results imply that $k_3[ND]_0 > k_5([I]_{SS} + [II]_{SS})$ and $k_4[ND]_0 > k_6([I]_{SS} + [II]_{SS})$ for the Cl_4 -PhCH₂X (X = Br and Cl) systems. The k_1/k_2 ratios given in Table 1 are the average values of three independent experiments. The relative error was not greater than $\pm 10\%$.

CONCLUSION

The rate constants for the abstraction of bromine from $PhCH_2Br$ and of chlorine from CCl_4 by $M(CO)_5$ and $M(CO)_4PPh_3$ species (M = Cr, Mo, and W) are two orders of magnitude greater than the rate constants for chlorine abstraction from $PhCH_2Cl$; the difference in the rates of chlorine abstraction from CCl_4 and C_2Cl_6 by these species is within an order of magnitude.

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TAUTOMERISM OF $\beta\text{-}DICARBONYL$ COMPOUNDS CONTAINING A TRIPHENYLARSONIUM GROUP

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In our previous work [1-3], we showed that β -oxoalkylphosphonium salts (I) may exist in ketonic and enolic forms and the extent of enolization in solution depends significantly on the basicity of the anion, specifically, on the strength of the OH···X⁻ hydrogen bond, which decreases in the series CF₃CO₂⁻ > Cl⁻ >> Br⁻ >> Br₄⁻. Enolization also depends on the substituent R. K_T drops in the series H >> Me > Et >> Ar [3].



On the whole [4-6], β -dicarbonyl compounds with a triphenylphosphonium substituent at the central carbon atom have been found to be more enolized than the unsubstituted dicarbonyl compounds, while K_T strongly depends on the basicity of the anion. The enol form has the noncyclic trans configuration.

We have studied the tautomerism of β -ketoarsonium salts and triphenylarsonic-substituted β -diketones using PMR and IR spectroscopy. In CD₂Cl₂, Ph₃As⁺-CH₂COMeX⁻ salts (II) (X = CF₃CO₂⁻ and Cl⁻) exist virtually entirely in the ketone form, while the phosphorus analogs (I) contain 60 [3] and 30% enol form [7]. This discrepancy is apparently a result of the low electron-withdrawing capacity of the Ph₃As⁺ group and the related lower CH-acidity of the arsonium salts in comparison with the phosphonium salts [8].

M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1152-1155, May, 1987. Original article submitted July 8, 1986. TABLE 1. PMR and IR Spectral Data for Triphenyl (diacylmethyl)arsonium salts

COMe

	Ph_3	As+-C	н	X-≠	Ph ₃ As+		0		
			COR			C=C	`н .	•	
	_,				CO	R	Me	X-	
	PMR spectrum, CD2Cl2, 6, ppm					IR spectrum, CH ₂ Cl ₂ , \vee ,			
d	ket	tone		eno1		ketane	enol		
Compound	Me	MeO	Me	MeO	онх	C=0	C=C	C=0	онх
(IVa) (IVb) (IVc)	2,55 2,43	$_{3,47}^{-}$	$2,71 \\ 2,71 \\ 2,50$	$3,02 \\ 3,01 \\ 3,06$	13,80 12,54 11,81	1740 1720 4740	1580 1580 1580	1710 1715 †	1900–2700 2200–2800 3100–3300
(IX) (Va)	2,27		$1,43 \\ 2,12$	2,91	$17,61 \\ 13,66$	1680	1' 1580	$\begin{array}{c} 700 \\ 1640 \end{array}$	‡ 1900–2700
(Vb)	2,31	-	2,14	-	12,38	1720 1680 1720	1600	1640	2200-2800
(Va)	2,19	_	1,94	-	12,47	1680 1720		1640	3100-3300
(VIa) (VIb)	$2,52 \\ 2,53$	-	2,33 * 2,33 *		13,80 12,86	172 0 172 0	1580 1580	$1640 \\ 1640$	2200 - 3300 2200 - 2800
(VIc)	2.43		2.25 *	-	13,34	1725	1590	-	1 -

*The signals for the methyl protons of the enolized and ketonic acetyl groups coincide. +Coincides with the ketone C=O band. +Total increase in the background at 1100-1440 cm⁻¹.

 β -Dicarbonyl compounds with the triphenylarsonium group are obtained by the addition of HX acids to the corresponding ylids:



For all the salts, $X = C1^{-}(a)$, $Br^{-}(b)$, and $BF_{4}^{-}(c)$.

The spectral characteristics of the salts obtained are given in Table 1.

The IR spectra of the arsonium salts virtually do not differ from those of the analogous phosphonium salts and their PMR parameters are very similar [4, 6].

The assignment of the signals for the MeCO group to the ketone or enol form was made by comparison of the integral intensities of the signals for the OH and the various Me groups in the PMR spectra and by comparison of the PMR and IR spectra of the chlorides, bromides, and tetrafluoroborides (IV)-(VI).

The ratios of the ketone and enol forms as indicated by PMR spectroscopy are given in Table 2, which shows that the effect of the anion in the arsonium salts on the position of the equilibrium is very significant as in the case of phosphonium salts. Chlorides (IVa), (Va) and (VIa) in CD_2Cl_2 are predominantly in the enol form, while tetrafluoroborides (IVc), (Vc), and (VIc) are predominantly in the ketone form. The bromides occupy an intermediate position. The IR spectra of vaseline mulls indicate that, in the solid state, salts (IVc), (VIa) and (VIb) are ketones, while the other compounds are enolized. There is a broad vOH···X band for all the enolized salts at from 1900 to 3300 cm⁻¹. The bands for the stretching vibrations of the OH groups are shifted toward lower frequencies with increasing strength of the hydrogen bond. In the PMR spectra, an increase in the strength of the hydrogen bonding is indicated by higher δ values.

	Enol, %						
Compound	$E = As (CD_2Cl_2)$	E == P [5] *	$ROC - CH_2 - COR' \dagger [9]$				
(IVa) (IVb) (IVc)	100 83 23	100 100 100	75 (CHCl ₃)				
(Va) (Vb) (Vc)	87 43 5	100 90 45 (MeNO ₂)	94,5 (CCl ₄) 90,5 (CDCl ₃)				
(VIa) (VIb) (VIc)	60 30 5	$ \begin{array}{c} 100 \\ 50 \\ - \end{array} $	94 (CCl ₄)				

TABLE 2. Enolization of β -Diketones Ph_3E^+ -

COR

COR

COR

X-COR'

*Determined by $^{3\,1}\mathrm{P}$ NMR spectroscopy for the phosphonium salts in CHCl_3.

†PMR data.

+Data supplied T. A. Mastryukova and I. M. Aladzheva.

TABLE 3. Triphenyl(diacylmethyl)arsonium Salts Ph₃As+-CH X-

Com- pound	mp,°C	Found, %				Calculated, %		
		С	н	E	Chemical formula	С	H	E
(IVa)	122-123	59.83	4.81		CasHasAsClOa	60.48	4.85	
(IVb)	115,5-116,5	55,42	4,55	-	$C_{23}H_{22}AsBrO_3$	55,11	4,42	_
(IVc)	144-145	53,81	4,35	14,97 (a)	$\mathrm{C}_{23}\mathrm{H}_{22}\mathrm{AsBF_4O_3}$	54,36	4,36	14,95
(Vc)	155 - 156	60,17	4,11	13,48 (ъ)	$C_{28}H_{24}AsBF_4O_2$	60,68	4,36	13,52
(VIc)	138-138.5	56.28	4.62	I	CarHanAsBE/Oa	56 13	4.54	

*Melting points, °C: (VIa), 120-121; (VIb), 138-138.5; (Va), 132-133; (Vb), 142-143; (IX), 152.5-153.5. E = F (a) and As (b).

It is interesting to note that while phosphorus analog of (VIIa) in $CHCl_3$ contains more than 50% enol form [5], the arsonium salt is hardly enolized as indicated by IR spectroscopy and the enol fraction is difficult to determine by PMR spectroscopy. IR spectroscopy indicates that the enol content in solutions of (VIIIa) is also very low. Bromides and tetrafluoroborides (VII) and (VIII) are presented only by the ketone form.

Comparison of arsonium salts (IV)-(VIII) with the corresponding unsubstituted β -dicarbonyl compounds shows their considerable difference. Of the unsubstituted compounds, dibenzoylmethane is the most enolized and ethyl acetoacetate is the least enolized. The position is reversed upon the introduction of the arsonium group. These differences are apparently related to a change in the configuration of the enol form of the diketone upon the introduction of the onium group, which was demonstrated by the x-ray diffraction structural analysis of several phosphonium salts [5, 10]. While the cyclic "chelate" structure is characteristic for the enol forms of unsubstituted dicarbonyl compounds, the introduction of a bulky phosphonium or arsonium group makes this structure disadvantageous due to the steric interaction of the Ph_3E⁺ group with the two adjacent substituents. The enols examined have open configuration with OH···X⁻ hydrogen bond, which stabilizes the enol form.

Comparison of the phosphonium and arsonium salts shows that the enolization of the former is greater in all cases. This behavior is related to the greater electron-withdrawing capacity of the Ph_aP^+ group.

These results indicate that the salts containing an acetyl group which undergoes enolization are most enolized. In this case, the methyl group, according to Mastryukova et al. [4] and the PMR data obtained in our laboratory (see Table 1), is in the position trans to the Ph_3As^+ group.

We should note the special properties of tetrafluoroboride (IVc). This salt is obtained by the action of excess HBF_4 on the corresponding ylid and is a ketone in the solid state while it is 30% enolized in CD_2Cl_2 . The addition of an equimolar amount of the corresponding starting ylid (III) gives (IX), which formally contains two ylid molecules per HBF_4 molecule.



The enol form of the salt in the complex obtained is stabilized by the strong hydrogen bond with the ylid oxygen which is indicated by x-ray diffraction structural analysis of the phosphorus analog [5]. Upon the addition of excess HBF_4 , (IX) is converted to the ordinary salt (IVc). This does not occur in the case of the phosphorus analog of (IX).

EXPERIMENTAL

Chlorides and bromides (IV)-(VIII) were obtained by passing dry HCl or HBr through a solution of 1 mmole ylid in benzene until there is no further precipitate formation. The precipitate was filtered off, washed with benzene and reprecipitated from $CHCl_3$ by the addition of ether.

Tetrafluoroborides (IV)-(VIII) were obtained by the addition of 0.5 ml 45% aqueous HBF₄ to a solution of 1 mmole ylid in CH_2Cl_2 . The mixture was stirred for 5 min. The organic layer was separated and dried. The solvent was distilled off in vacuum. The precipitate was reprecipitated from CH_2Cl_2 by the addition of ether. The product yields in all cases were quantitative.

All the experiments were carried out in absolute solvents. The IR spectra were taken on a UR-20 spectrometer in CH_2Cl_2 . The PMR spectra were taken on a Bruker WP-200SY spectrometer in CD_2Cl_2 at -90°C relative to CH_2Cl_2 converted to TMS. The characteristics of the compounds obtained are given in Table 3.

CONCLUSION

l. The enolization of triphenylarsoniodiacylmethylene salts depends significantly on the basicity of the anion. The enol form is stabilized by the $OH \cdots X^-$ bond.

2. Triphenylarsoniodiacylmethylene salts are less enolized than their phosphorus analogs and their enol forms have identical structure.

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REACTION OF TETRACOORDINATED PHOSPHORUS

CHLOROCYANIDES WITH PROTON DONORS

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The development of a method for the synthesis of P(III) chlorocyanides [1] permitted us to study the relative reactivity of the chlorine atom and cyano group bound to one phosphorus atom. The reaction of ethyl chlorocyanophosphite with nucleophilic reagents such as alcohols, mercaptans and amines proceed under mild conditions with substitution of the CN group and the formation of trivalent phosphorus acid chlorides



It is interesting to note that substitution of the chlorine atom occurs when the chlorophosphite molecule contains the NCO pseudohalide group in reactions with alcohols and amines [2].

We have previously found the facile substitution of the CN group by a chlorine atom in P(III) dicyanides by the action of HCl [1]. Hence, we may propose that chlorophosphites are formed in the reactions of chlorocyanophosphites with HZ either by the direct substitution of the cyano group (pathway 1) or through the intermediate substitution of the chlorine atom (pathway 2):



In order to clarify this question, experiments were designed to model the possible intermediate steps of this reaction. Thus, diethyl chlorophosphite was isolated in good yield upon bubbling dry HCl into diethyl cyanophosphite. However, the reaction of O-ethyl-N,Ndiethylamidocyanophosphite with HCl proceeds with retention of the P-CN bond and substitution of the more basic Et_2N group.



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