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Spectroscopic Investigations of α-Keto Phosphorus Compounds

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The NMR, IR, and UV spectra of some α-keto phosphorus compounds, $(C_2H_5)_2PCOR$, $(C_2H_5)_2P(S)COR$, and $[(C_2H_5)_2CH_3PCOR]^+I^-$ ($R=C_6H_5$ and CH_3), were measured. The carbonyl stretching frequency and the n-π^* transition show considerable red shifts, but the shifts are smaller than those of α-keto organosilicon compounds. The lowering of the carbonyl π^* level, which resulted from the interaction with a vacant d orbital of the phosphorus atom, was found to be largely responsible for the red shift of the n-π^* transition in the α-keto phosphorus compounds, particularly in $[(C_2H_5)_2CH_3PCOR]^+I^-$. The rise in the n level of the carbonyl group was found to be rather small.

Two of the characteristic properties of the α-keto derivatives of organometalloids are a large red shift of the n-π^* transition and a low carbonyl stretching frequency relative to those of the carbon analogs.[1,2] To explain these unusual red shifts of the n-π^* transition, several suggestions, especially for silicon compounds, have been put forward:

a) A large π^*-d splitting and a slight rise in the n level of the carbonyl oxygen caused by an inductive effect of the triorganosilyl group have been suggested on the basis of molecular orbital considerations.[3,4]

b) The simultaneous operation of the σ-donor and π-acceptor effects of the triorganosilyl group has been proposed.[5] Bock *et al.*[6] deduced, from a variety of experimental measurements, that the unusual red shift is due to the strong inductive rise in the n level as well as to considerable excited-state interactions, $Si \leftarrow \pi^*$.

c) The inductive rise in the n level is considered to be the primary cause of the long-wavelength shift of the n-π^* transition.[7-10] Agolini *et al.*[11] have drawn the conclusion, from simple and extended Hückel molecular orbital calculations with and without d orbitals, that it is the σ-donor properties of silicon which are primarily responsible for the observed spectral shift, and that any possible p_π-d_π interactions are of minor importance.

These studies, however, were mainly made on α-keto derivatives of Group IVb organometalloids, which are very limited in organophosphorus derivatives.[12-15] In

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the present report, the effects of the organophosphorus group on the UV and IR spectra of the carbonyl group have been studied. For this purpose, three types of α-keto organophosphorus compounds, $(C_2H_5)_2PCOR$, $(C_2H_5)_2P(S)COR$, and $[(C_2H_5)_2CH_3PCOR]^+I^-$ (R= C_6H_5 and CH_3), have been prepared. Because the valence state of the phosphorus atom is different in these compounds, some distinguishable effects on the spectra of the carbonyl group can be expected. The internal chemical shift of the ethyl group was also measured for these compounds.

Experimental

All the experiments were performed in an oxygen-free dry nitrogen atmosphere. The solvents were purified in a stream of nitrogen prior to use.

Preparation. Benzoyldiethylphosphine (I), Benzoyldiethylmethylphosphonium Iodide (III), Acetyldiethylphosphine (IV), and Acetyldiethylmethylphosphonium Iodide (VI): These substances were synthesized by Issleib's method.[16] I, bp 102—103 °C /2.5 mmHg) (reported 98—100 °C/2 mmHg). III, mp 68—69 °C (reported 68 °C). IV, bp 58 °C/11 mmHg (reported 168 °C/760 mm and 53—54 °C/10 mmHg[14]). VI, mp121°C (reported 122 °C).

Benzoyldiethylphosphine Sulfide (II). I (2.70 g, 13.9 mmol) and trimethylstibine sulfide, $(CH_3)_3SbS$[17] (2.76 g, 13.9 mmol), were treated in dichloromethane at room temperature for 12 hr. The trimethylstibine formed was removed with a solvent *in vacuo*, and the residual liquid was extracted with *n*-hexane. After the removal of the solvent *in vacuo*, 2.63 g (83%) of II were obtained as a viscous liquid, which was then gradually hydrolyzed by moisture in the air (Found: C, 58.27; H, 6.90%. Calcd for $C_{11}H_{15}OSP$: C, 58.39; H, 6.68%.). The compound could not be distilled below 100 °C under a high vacuum (1.3×10^{-3} mmHg), and it decomposed at a higher temperature. In the treatment of I with equimolar amounts of sulfur powder in tetrahydrofuran at room temperature, an exothermic reaction occurred immediately. The liquid obtained after the removal of the solvent contained II, with significant amounts of impurities.

Acetyldiethylphosphine Sulfide (V). As in the case of II, equimolar amounts of IV and trimethylstibine sulfide were treated, the liquid thus obtained was then distilled *in vacuo*, yielding 85% of V (bp 47 °C /1.1×10^{-3} mmHg); it was a faintly pale yellow liquid and was readily hydrolyzed in air (Found: C, 43.88; H, 8.05%. Calcd for $C_6H_{13}OSP$: C, 43.89; H, 7.98%.). A similar reaction took place between IV and sulfur, yielding 25% of V.

Diethylphosphine Sulfide. Soon after the mixing of diethylphosphine[18] (2.0 g, 22.2 mmol) and sulfur powder (0.64 g, 20.0 mmol) in dry ether, a vigorous reaction occurred and the sulfur powder disappeared. After the removal of the solvent, the residue was distilled *in vacuo*, yielding 1.95 g (80%) of the product (bp 57 °C/1 mmHg), which was readily hydrolyzed in air. Found: C, 39.03; H, 8.86%. Calcd for $C_4H_{11}SP$: C, 39.33; H, 9.08%. IR spectrum (neat) ν_{PH} 2297, ν_{PS} 586 cm^{-1}.

Physical Measurements. The infrared spectra in dichloromethane were measured on a Hitachi 225 grating spectrophotometer in airproof cells provided with KRS-5 windows. The electronic spectra were obtained by means of a Hitachi 124 spectrophotometer in 1 cm quartz airproof cells in cyclohexane, dichloromethane, and acetonitrile. The NMR spectra were recorded on JNM-3H-60 and JNM-PS-100 spectrometers operating at 60 and 100 MHz, respectively, at 25 °C in dichloromethane.

Analysis of the NMR Spectra. The NMR spectra of ethyl protons of I and IV were analyzed by the use of Corio's theoretical formula[19] of A_3B_2X. In other cases, the first-order analysis was performed. The reliability of the internal chemical shifts of the ethyl group was found to be ±0.02 ppm at most.

Results and Discussion

NMR Spectra. As can be seen from Table 1, the values of the internal chemical shift of the ethyl group and the indirect spin-spin coupling constants between the ethyl protons and the phosphorus nucleus increase in the following order for I—VI; tertiary phosphine<phosphine sulfide<phosphonium iodide in both benzoyl and acetyl series. The results are quite similar to those obtained for organophosphorus compounds without the keto group.[20-22] The electron-withdrawing effect on the internal chemical shift of these phosphorus compounds is considered to increase

TABLE 1. NMR SPECTRAL DATA OF α-KETO PHOSPHORUS COMPOUNDS IN DICHLOROMETHANE

	Compound	H_β[a]		H_α[a]		$\varDelta$[b]	$J_{H_\alpha H_\beta}$	$PCOCH_3$		PCH_3	
		δ ppm	$^3J_{PH}$ Hz	δ ppm	$^2J_{PH}$ Hz	ppm	Hz	δ ppm	$^3J_{PH}$ Hz	δ ppm	$^2J_{PH}$ Hz
I	$(C_2H_5)_2PCOC_6H_5$	1.02	14.2	1.74	2.9	0.72	7.60				
II	$(C_2H_5)_2P(S)COC_6H_5$	1.19	19.5	2.20	11.8	1.01	7.7				
III	$[(C_2H_5)_2CH_3PCOC_6H_5]^+I^-$	1.31	20.4	3.14	12.5	1.81	7.7			2.59	13.8
IV	$(C_2H_5)_2PCOCH_3$	1.08	14.2	1.76	3.5	0.68	7.62	2.26	5.3		
V	$(C_2H_5)_2P(S)COCH_3$	1.15	19.6	1.97	11.6	0.82	7.7	2.61	4.7		
VI	$[(C_2H_5)_2CH_3PCOCH_3]^+I^-$	1.32	19.3	2.88	13.5	1.56	7.7	3.09	5.4	2.44	14.0

a) H_β and H_α are methyl and methylene protons, respectively, of the ethyl group.

b) $\varDelta = \delta_{H_\alpha} - \delta_{H_\beta}$

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TABLE 2. CARBONYL STRETCHING FREQUENCIES OF α-KETO PHOSPHORUS COMPOUNDS IN DICHLOROMETHANE (cm^{-1})

Compound	ν_{CO}
$(CH_3)_3CCOC_6H_5$[a]	1680
$(CH_3)_3SiCOC_6H_5$[b]	1618
I	1635
II	1646
III	1663
$(CH_3)_3CCOCH_3$[c]	1718
$(CH_3)_3SiCOCH_3$[b]	1645
IV	1652
V	1687
VI	1707

a) Ref. 24.
b) Ref. 9.
c) Ref. 6.

in the above order.[23] The internal chemical shifts of I—VI are always larger than those of the corresponding phosphorus compound not containing the keto group. This is considered to be due mainly to the difference in the electron withdrawing property of the ethyl and the keto groups, although there might be some contributions of the magnetic anisotropy of the carbonyl group.

One of the most notable results is that the $^3J_{PH}$ value for the acetyl group in IV—VI is very small compared with that of the methyl protons in the ethyl group; it is almost the same for the three compounds.

IR Spectra. The carbonyl stretching frequency of I—VI is shown in Table 2, together with the carbon[6,24] and silicon[9] analogs. The low-frequency shift of the carbonyl stretching of the α-keto organosilicon compounds relative to the carbon analogs is considered to be due mainly to a small electronegativity of silicon.[1] The stretching frequency of I—VI is smaller than that of carbon analogs, but larger than that of silicon, and it increases as in the internal chemical shift in this order: I<II<III and IV<V<VI. The results are considered to be due to the increase in the electron withdrawing property of the phosphorus group. In spite of the large effective electronegativity of the phosphorus atom in III and VI relative to that of carbon as revealed from NMR spectra, the stretching frequency is a little smaller than that of the carbon analogs. These results seem to suggest that there are some p_π-d_π interactions[25] in the ground state in III and VI.

TABLE 3. ELECTRONIC SPECTRA OF α-KETO PHOSPHORUS COMPOUNDS (cm^{-1})

Compound	Solvent	A	B	C	D	E	F
		ν_{max} (ε_{max})	ν_{max} (ε_{max})	ν_{max} (ε_{max})	ν_{max} (ε_{max})	ν_{max} (ε_{max})	ν_{max} (ε_{max})
$(CH_3)_3CCOC_6H_5$[a]	n-C_6H_{14}	31250(103)	36500(600)	42000(8800)			50300(25400)
$(CH_3)_3SiCOC_6H_5$[a]	n-C_6H_{14}	23650(119)	35400(1140)	40000(11300)			50000(19450)
I	cyc-C_6H_{12}	26300(268)	35000sh	39100(12700)			——[d]
	CH_2Cl_2	26200(687)	——[d]	——[d]			——[d]
	CH_3CN	26600(595)	36200(3500)	41400(10500)			49500(14500)
II	cyc-C_6H_{12}	24600(403)	34800sh	39200(10900)		——[d]	——[d]
	CH_2Cl_2	25100(613)	——[d]	——[d]		——[d]	——[d]
	CH_3CN	25300(674)	35000sh	39200(13500)		44400(5000)	47200(11000)
III[b]	CH_2Cl_2	26400(369)		——[d]	——[d]		——[d]
	CH_3CN	27400(110)		37500(12100)	41300(16700)		48300(14700)
$(CH_3)_3CCOCH_3$[c]	n-C_7H_{16}	34800(23)					53800(1100)
$(CH_3)_3SiCOCH_3$[c]	n-C_6H_{14}	26900(126)					51200(4200)
IV	cyc-C_6H_{12}	30100(379)	40500(1350)				——[d]
	CH_2Cl_2	30000(608)	——[d]				——[d]
	CH_3CN	30500(517)	40800(2780)				48700(3100)
V	cyc-C_6H_{12}	28000(306)	37900(550)			——[d]	——[d]
	CH_2Cl_2	28400(287)	39100(442)			——[d]	——[d]
	CH_3CN	28600(329)	38900(477)			42700(6100)	48400(16000)
VI[b]	CH_2Cl_2	30700(297)			——[d]		——[d]
	CH_3CN	32000(152)			41700(14000)		48800(23700)
$(C_2H_5)_2P(S)H$	cyc-C_6H_{12}					45000(7900)	
	CH_3CN					47800(4100)	

a) Ref. 6.
b) The data in cyclohexane solution were not obtained because of insolubility.
c) Ref. 11.
d) Not measured.

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23) If we use the relation between the internal chemical shift of the ethyl group and the electronegativity of the atom bonded to this group proposed by Narasimhan and Rogers (*J. Amer. Chem. Soc.*, **82**, 5983 (1960)), the effective electronegativities of the phosphorus and silicon atoms are found to be 2.2, 2.5, 2.8, and 1.8 for $(C_2H_5)_3P$, $(C_2H_5)_3PS$, $(C_2H_5)_4P^+$, and $(C_2H_5)_4Si$ respectively.

24) J. I. Adelfang, P. H. Hess, and N. H. Cromwell, *J. Org. Chem.*, **26**, 1402 (1961).

25) Hoffmann *et al.* have indicated that, in Extended Hückel MO calculation, the large charge separation is considerably reduced by the inclusion of the P 3d orbital in phosphonium ylide (R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, **92**, 3929 (1970)).

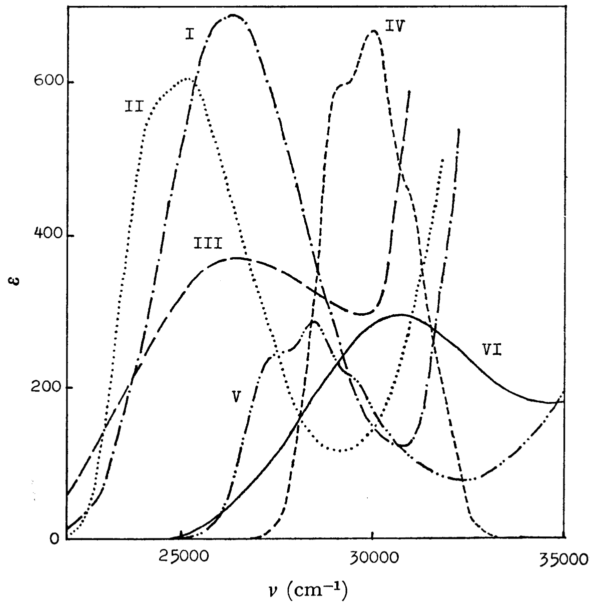

Fig. 1. The absorption bands of the n-π^* transition measured in dichloromethane.

UV Spectra. The positions and intensities of the absorption maxima of I—VI are summarized in Table 3. The values of the carbon and silicon analogs are added for the sake of comparison. Each compound exhibits several absorption bands in the 23000—50000 cm^{-1} region, these bands can be classified into six types depending on their positions and intensities. The band at the lowest frequency (A) shows a blue shift as the polarity of solvent increases, and, as is shown in Fig. 1, it has somewhat fine structure. One of the most remarkable results is that the intensity of the band is rather large as compared with that of carbon analogs. This band is presumably due to the n-π^* transition involving the carbonyl group. The band with a medium intensity or the shoulder (B) at 35000—36000 cm^{-1} in I and II is probably due to the ^1L_b band.[26] The band (B) in III may be hidden by a strong band, C. The origin of the absorption band (B) at 38000—41000 cm^{-1} in IV and V is not clear. A possible assignment of this band is a transition of the n electrons on phosphorus and sulfur to the π^* orbital of the carbonyl group. The intense band (C) at 38000—42000 cm^{-1} in I—III is probably due to the allowed ^1L_a band with an intramolecular charge-transfer character of the benzoyl group.[26] The intense band (D) at 41000—42000 cm^{-1} in III and VI was assigned tentatively to an intramolecular charge-transfer transition from the carbonyl n level to the vacant d orbitals of the phosphorus atom, because, in these compounds, the energy level of the d orbitals seems to be considerably lowered as a result of a net positive charge on the molecule. The band with medium intensity (E) at 43000—45000 cm^{-1} in II and V may be due to the P–S group, because a similar band was observed in diethylphosphine sulfide. Finally, in the highest frequency region, an intense band (F) was observed in all the compounds. The band in I—III is probably due to the intramolecular charge-transfer band with the ^{1}B-band character.[26] The nature of the band not containing the phenyl group IV—VI has never been definitely established. This band may be due to either the π-π^* transition or the n-σ^* transition of the carbonyl group. One notable result of this band is that, in V and VI, the intensity is very large compared with that of pinacolone or acetyltrimethylsilane.

As can be seen from Table 3, the n-π^* transition band of I—VI shows a large red shift as compared with that of the carbon analogs, but the shift is smaller than that of the silicon analogs. II and V show the largest red shift among the phosphorus compounds. The red shifts of I and III, and those of IV and VI, relative to the carbon analogs are almost the same, although the valence state of the phosphorus atom is different. As has been shown in connection with the NMR and IR spectra, the electron withdrawing property of the phosphorus group is larger than that of the silyl group. Therefore, the inductive rise in the n level of the carbonyl group may be smaller in I—VI, particularly in III and VI, than in α-keto silicon compounds. The red shift of the n-π^* transition band in III and VI may be largely responsible for the lowering of the π^* level of the carbonyl group as a result of interaction with the vacant d orbital of the phosphorus atom. In I and IV, in addition to the lowering of the carbonyl π^* level, there may be some contribution of the n level rising to the red shift. The largest red shift in II and V is also considered to be due to the large lowering of the carbonyl π^* level by the interaction with that of the P=S group. The lowering of the π^* level in the phosphorus compounds is partly supported by the following fact. In spite of the smaller red shift of the n-π^* transition in the phosphorus compounds relative to that of the silicon, the red shifts of the π-π^* transitions are larger in phosphorus compounds (see Table 3). These results seem to reveal that the d-π^* interaction occurs more easily in α-keto organophosphorus compounds than in organosilicon compounds.

We wish to express our hearty thanks to Professor Rokuro Okawara for his continuous encouragement throughout this study. We are also grateful to Drs. Masanori Wada and Yoshio Matsumura of Osaka University for their helpful discussions. The calculations needed for obtaining the NMR parameters were carried out on an NEAC-2200 at the Computation Center of Osaka University.

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