

DIFFICULTIES IN THE INTERACTION OF THE FREE
ELECTRON PAIR IN DIACETOPHOSPHIDES
AND DIACETAMIDES

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Reasoning from the low, mesomerically positive capacity of the phosphorus atom and the ready availability of its vacant d-orbitals, we assume that the obstacles to amide-type resonance and $p_{\pi}-d_{\pi}$ interaction which are observed in monoacetophosphides [1] will appear to an even greater degree when diacetophosphides and amides are compared. The introduction of a second acyl group into the acetophosphides should not weaken the $p_{\pi}-d_{\pi}$ interaction (conjugation with the two d-orbitals), but the resonance should be weakened in the amides because of the simultaneous conjugation of the electron pair with the two substituents.

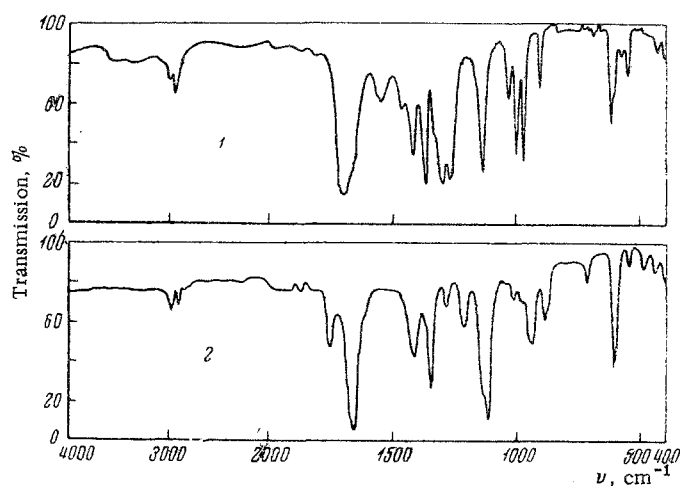


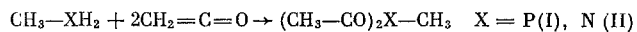
Fig. 1. Infrared spectra. 1) Methyl diacetamide; 2) methyl diacetophosphide.

TABLE 1

Compound	IR spectra		UV spectra		PMR spectra			
	$\nu_{\text{CO}}, \text{cm}^{-1}$	$\Delta\nu_{\text{CO}}, \text{cm}^{-1}$	$\lambda_{\text{max}}, \text{nm}$ (n-heptane)	$\Delta\lambda, \text{nm}$	$\delta_{\text{CH}_3}, \text{p.p.m.}$	$\delta_{\text{CH}_2, \text{CO}}, \text{p.p.m.}$	$J_{\text{PCH}}, \text{Hz}$	$J_{\text{PCCH}}, \text{Hz}$
$\text{CH}_3\text{CON}(\text{CH}_3)_2$ (I)	1650		195,3 $n \rightarrow \pi^*$ [3]		2,94; 2,78 (2,86)	1,89	—	—
		50		20,4				
$(\text{CH}_3\text{CO})_2\text{NCH}_3$ (II)	1700		215,7 $n \rightarrow \pi^*$		3,23	2,37	—	—
$\text{CH}_3\text{COP}(\text{CH}_3)_2$ (III)	1660		223,5 $n \rightarrow \pi^*$		1,33	2,14	—	4,60
	1758		347,0 $n \rightarrow \pi^*$					
		3		-3,0 $n \rightarrow \pi^*$ 5,0 $n \rightarrow \pi^*$				
$(\text{CH}_3\text{CO})_2\text{PCH}_3$ (IV)	1657		220,5 $n \rightarrow \pi^*$		1,49	2,50	1,14	5,00
	1758		342,0 $n \rightarrow \pi^*$					

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We synthesized and studied methyldiacetophosphide (I) and methyldiacetamide (II):



The conclusions reached above were confirmed by the following data.

The ν_{CO} band in the IR spectrum of (I) (Fig. 1, Table 1) is analogous to that in $\text{CH}_3\text{C(O)P(CH}_3)_2$ (III) [1]. In (II), the ν_{CO} band is shifted 50 cm^{-1} towards higher frequencies in comparison with $\text{CH}_3\text{C(O)N(CH}_3)_2$ (IV). A similar regularity is noted on comparison of the benzoyl derivatives [2]: ν_{CO} of $\text{C}_6\text{H}_5\text{COP(CH}_3)_2$ and $(\text{C}_6\text{H}_5\text{CO})_3\text{P}$ are 1645 and 1663 cm^{-1} , respectively ($\Delta\nu = 18$), and ν_{CO} of $\text{C}_6\text{H}_5\text{CON(CH}_3)_2$ and $(\text{C}_6\text{H}_5\text{CO})_3\text{N}$ are 1655 and 1697 cm^{-1} , respectively ($\Delta\nu = 42$).

In the UV spectrum of (I), the position of the $\pi \rightarrow \pi^*$ transition is practically the same as for (III) [1]. However, this transition in (II) has a bathochromic shift of 20 nm in comparison with (IV) [3]; the reason for this lies in the decrease in the energy of the antibonding molecular orbital as the orbital expands. In contrast to (II), the spectra of (I) [as well as of (III)] [1] have an $n \rightarrow \pi^*$ chromophoric transition in which the phosphorus atom takes part. An analogous transition is found in the spectra of diphenylbenzophosphide ($\lambda_{\text{max}} 404 \text{ nm}$) and tribenzophosphide ($\lambda_{\text{max}} 384 \text{ nm}$) [2].

In the PMR spectra of (III) and (I) (Fig. 2, Table 1), $\delta_{\text{CH}_3\text{CO}}$ lies at weaker fields than $\delta_{\text{CH}_3\text{P}}$. In the corresponding compounds (IV) and (II), conversely, $\delta_{\text{CH}_3\text{CO}}$ lies at stronger fields than $\delta_{\text{CH}_3\text{N}}$. While $\delta_{\text{CH}_3\text{P}}$ is nearly constant in the series $(\text{CH}_3)_3\text{P}$, (III), and (I) ($\Delta\delta = 0.1 \text{ p.p.m.}$), it changes considerably in the nitrogen series $(\text{CH}_3)_3\text{N}$, (IV), and (II) ($\Delta\delta = 0.72$ and 0.37 p.p.m. , respectively). This shows that, in spite of the introduction of substituents having a strong $-I$ effect ($\sigma_I = 0.29$), shielding of the methyl protons by the phosphorus remains practically constant. Consequently, an effective negative charge appears on the phosphorus atom. This is in contrast to the nitrogen atom, which carries an effective positive charge. The shift of δ_{CH_3} towards weaker fields on going from the mono- to the diaceto derivative is probably caused by the changing $-I$ effect of the nitrogen and phosphorus groups.

In the mass spectrum of (IV), the formation of fragment (a) is shown by the failure of the peak at $m/e = 72$ to shift in the mass spectrum of $\text{CD}_3\text{CON(CH}_3)_2$:

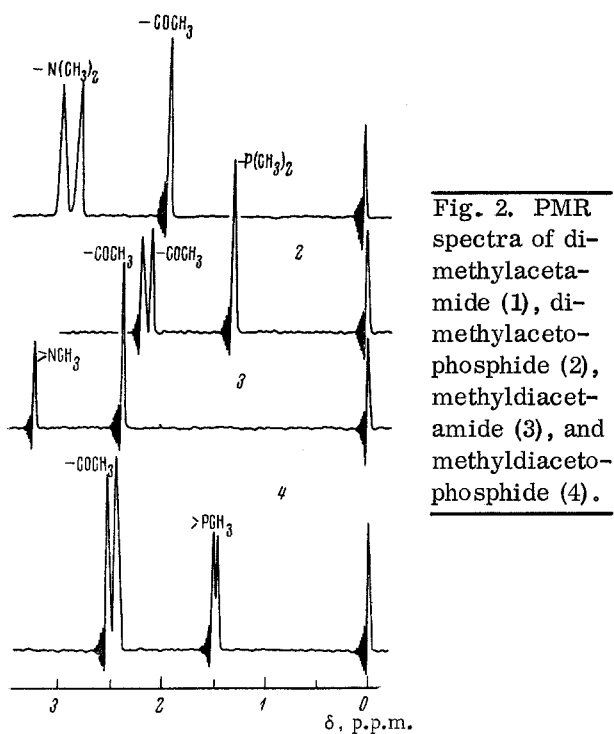
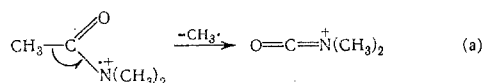


Fig. 2. PMR spectra of dimethylacetamide (1), dimethylacetophosphide (2), methyldiacetamide (3), and methyldiacetophosphide (4).

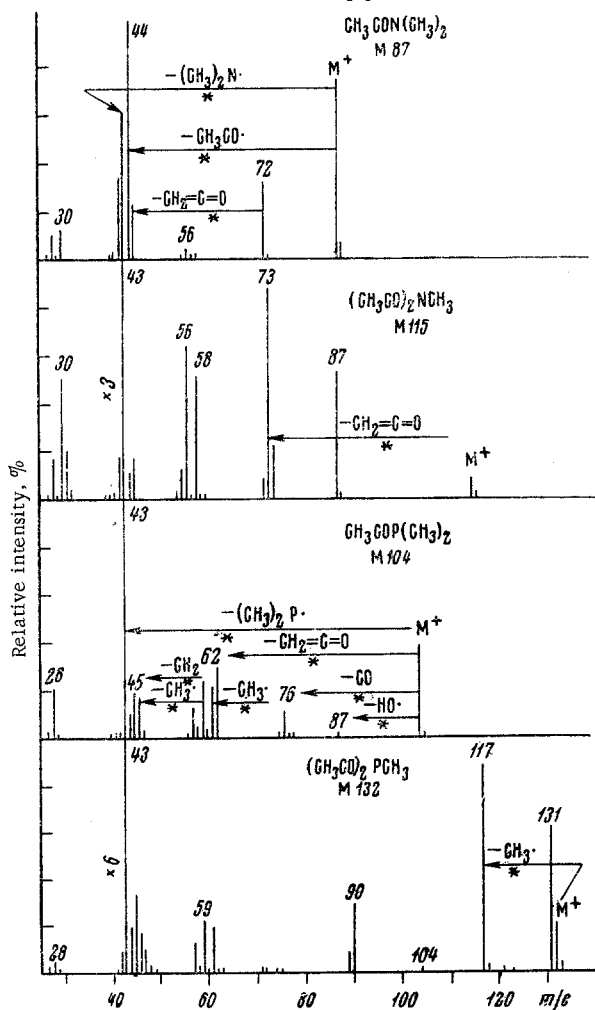
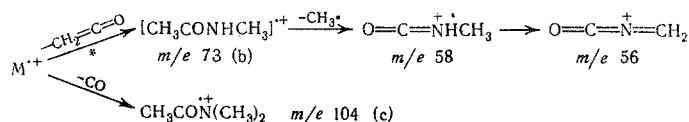
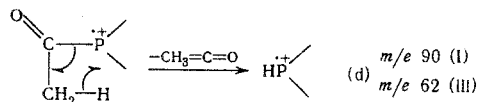


Fig. 3. Mass spectra of dimethylacetamide, methyldiacetamide, dimethylacetophosphide, and methyldiacetophosphide.

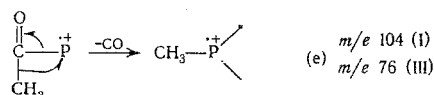
The absence of fragments like type (a) in the mass spectrum of (III) (Fig. 3) is an indication of the weakness of the stabilization; this poor stability is the result of the free electron pair on the phosphorus atom [4]. The decomposition of (II) proceeds according to the scheme:



The process, $\text{M} \rightarrow (b)$ is also observed during the fragmentation of acetophosphides:



Fragment (c) corresponds to the elimination of CO from the molecular ion. An analogous fragmentation has been described for piperlongumine, which contains the diacylamino group [5]. Elimination of CO is also observed during the decomposition of acetophosphides:



In the spectrum of (I), the presence of the intense fragments $\text{M}-1$ and $\text{M}-15$ may be explained by the high degree of charge delocalization, which results because of the efficient dispersion of the electron density from the two carbonyl groups into the d-orbitals of the phosphorus atom.

EXPERIMENTAL

The spectra were obtained as described in [6].

Methyldiacetophosphide (I). A solution of 10.0 g methylphosphine in 300 ml absolute ether was treated with 17.5 g ketene at -50 to -40° in an argon atmosphere. After separation of the ether, the residue was distilled. The product was a viscous, light yellow liquid which oxidizes in air. The yield of (I) was 14.47 g (52.9%); bp $92.5-94^\circ$ (21 mm); n_D^{20} 1.5095; d_4^{20} 1.0880. Found%: C 45.71, 45.72; H 6.93, 6.99; P 22.84, 22.95. $\text{C}_5\text{H}_9\text{O}_2\text{P}$. Calculated%: C 45.46; H 6.87; P 23.44.

Methyldiacetamide (II). This compound was obtained by alkylation of 3.0 g methylamine with excess ketene in ether at room temperature. The yield was 45%; bp $31-32^\circ$ (1 mm); n_D^{20} 1.4508; d_4^{20} 1.0589. According to the literature [7], the boiling point is 192° .

Dimethylacetophosphide (III). A solution of 8.70 g dimethylphosphide in 50 ml absolute ether was treated with 3.70 g ketene at -20 to -15° in an argon atmosphere. After separation of the ether, the residue was distilled. The product was a colorless liquid which ignites spontaneously in air. The yield of (III) was 8.11 g (88.4%); bp 58° (58 mm); n_D^{20} 1.4750; d_4^{20} 0.9841. Found%: C 45.71, 46.08; H 8.61, 8.61; P 30.22, 30.41. $\text{C}_4\text{H}_9\text{OP}$. Calculated%: C 46.16; H 8.71; P 29.76.

CONCLUSIONS

1. The IR, PMR, and mass spectra of mono- and diacetamides and phosphides were studied.
2. Conjugation of the two carbonyl groups with the nitrogen atom in methyldiacetamide weakens the amide resonance in comparison with dimethylacetamide.
3. The conjugation of the carbonyl groups with the phosphorus atom does not change on going from dimethylaceto- to methyldiacetophosphide. This is due to the interaction of the π -electrons of the carbonyl groups with the d-orbitals of the phosphorus atom.

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