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HINDERED LONE PAIR CONJUGATION IN THE Vth GROUP ELEMENTS—I

ACETOPHOSPHIDES

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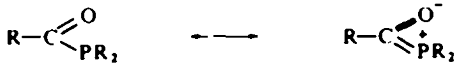
Abstract—Dimethyl-and diphenylacetophosphides have been prepared by the reaction of ketene with the corresponding disubstituted phosphines. In the IR spectra two bands of $\nu_{C=O}$ refer to the two conformations having different conjugation energies. In the UV spectra of these compounds the longwave absorption corresponding to the $n \rightarrow \pi^*$ transition was discovered in which the atom of phosphorus participated. The mass and PMR spectra of acetophosphides have been investigated. The data obtained indicate the absence of amide-type resonance and the evidence of p_π-d_π conjugation in these compounds.

HOFFMAN was the first to display an interest in phosphorus analogues of amides but the first specimen of these systems was synthesized only in 1952.[1,2] Issleib *et al.*[3,4] came to the conclusion that these compounds were analogous to amides, the amide-type resonance taking place in phosphides:



Recently we have studied hindered amide resonance in ethyleneamides[5] caused by an increased inversion barrier in ethyleneimine (E 10 kcal/mole,[6] 12 kcal/mole[7]) as compared to ammonia (E 4·9 kcal/mole[8]) and amines. A considerably higher inversion barrier in phosphines (PH_3 E 15 kcal/mole;[8] Me_3P E 22 kcal/mole;[9] C_3H_7MePPh E 30 kcal/mole[16]) provides a still greater hindrance to the phosphorus transition into the coplanar configuration which is necessary for the amide-type resonance.

We have synthesized and investigated acetophosphides:

$$CH_2{=}C{=}O + HPR_2 \cdot Me\ C(O)\ PR_2,\ R = Me(I);\ Ph\ (II)$$

In the PMR spectrum of I the following signals were found: δMeP 1·33 ppm; δMeCO 2·14 ppm; *J* PCCH 4·6 c/s; the ^{31}P NMR data: 22·2 ppm. On the other hand II exhibits δMeCO 2·10 ppm; the IR data: $\nu_{C=O}$ 1664 and 1758 cm^{-1} (the $\nu_{C=O}$ in $MeCONPh_2$ was observed at 1662 cm^{-1}). In the reaction of I with atmospheric oxygen the high activity of the lone pair on phosphorus was established. The PMR data for $MeC(O)P(O)Me_2$ (III): δMeP 1·18 ppm; *J* PCH 12 c/s; δ MeCO 1·77 ppm; in the mass spectrum the fragments at *m/e* 77 and 43 (100%) were found. The I was quaternized at room temperature; the PMR data for $MeC(O)\overset{+}{P}Me_3\ I^-$ (IV): δ MeP 1·83 ppm; *J* PCH 16·5 c/s; δ MeCO 3·27 ppm (multiplet). The reactions of oxidation, quaternization and complex formation with $CoBr_2$ were also reported by Issleib[3,4] for phosphides.

The above data indicate an absence of amide-type resonance in I which was also proved by the equivalence of Me protons in the PMR spectrum of I (MeP—singlet at 1·35 ppm).

In the IR spectra of I–IV (Fig. 1, also see Table 1) the shift of $\nu_{C=O}$ into the region of amide I band described earlier[4] may be explained by means of p_π–d_π interaction and by the following resonance:

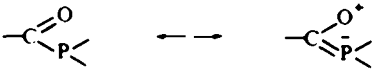
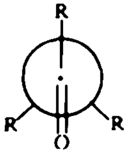


TABLE 1.

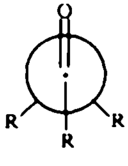
Compound	IR spectra		$\nu_{C=O}$ cm^{-1}	UV spectra (in n-heptane)	
	Pure specimen	In MeCN	In $C_2H_4Cl_2$	λ_{max} (mμ)	lg ε transition
MeC(O)PMe$_2$	1660 1758	1660 1755	1664 1755	223·5 347·0 359·5 371·0 (sh)	1·75 $\pi \to \pi^*$ 0·96 0·95 $n \to \pi^*$ 0·80
MeC(O)NMe$_2$	1650	1655	1652	–	–
MeC(O)P(O)Me$_2$	1723 1760	1725 1758	1718 1760	224·5 277	1·75 $\pi \to \pi^*$ 1·08 $n \to \pi^*$
MeC(O)$\dot{P}$Me$_3$J$^-$	1772[a]	1720	—	325[b]	1·66 $n \to \pi^*$

[a] in KBr pellet
[b] in MeCN

The considerably lower shift of $\nu_{C=O}$ in the case of diphenylbenzo-(1645 cm^{-1} [11]) and tribenzophosphide (1663 cm^{-1} [12]) in respect to the corresponding amides (diphenylbenzamide 1655 cm^{-1} [4] and tribenzamide 1697 cm^{-1} [12]) may be accounted for the high capacity of the d orbitals in phosphorus. Two intensive bands in the region 1760–1660 cm^{-1} in spectra of I–III may be explained by existence of conformers A and B (the persistence of high intensity for both bands in solvents of different polarity excludes the possibility of Fermi-resonance):



A



B

The same effect was evidently observed in the case of diphenylbenzophosphide but the second band at 5·85 μ was erroneously interpreted as that for benzaldehyde absorption.[11] The low frequency band may be referred to the conformer A, considerably gaining in resonance energy. The single band in the IR spectrum of IV is explained by the equality of energies of A and B, and in the case of other phosphides the single carbonyl band[4] is associated with steric hindrance to the generation of isomer B due to the size of the substituent R.

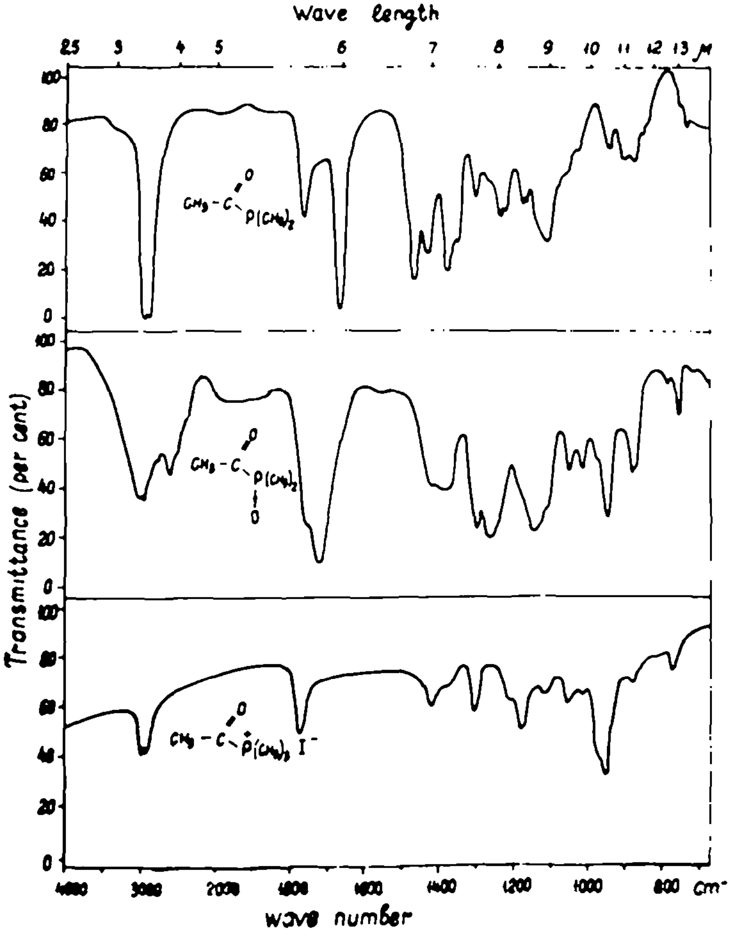


FIG. 1.

In the spectra of III and IV lone pair bonding causes a shift of $\nu_{C=O}$ to an area of high frequency because the −I-effect of phosphonium and phosphonic groups increases in respect to the original −I-effect of dimethylphosphine group ($\sigma_I = -0{\cdot}12$).[13] Thus, for example, the conversion of 2,2,6-trimethylquinuclidone-7 into its methyliodide shifts $\nu_{C=O}$ from 1756 to 1827 cm^{-1}.[14]

In ketones Me—C(O)—MPh$_3$ where an element with vacant d orbitals has no lone pair, an analogous shift of the carbonyl band to a low frequency region ($\nu_{C=O}$ for Si 1644, Ge 1669, Sn 1670 cm^{-1} [15]) was observed. In the UV spectra of these compounds the $n \rightarrow \pi^*$ transition due to participation of heteroatom responsible for the yellow colour of these compounds was elucidated ($Ph_3SiC(O)Me$ has λ_{max} 372 mμ).[16] The compound II was also of yellow colour (λ_{max} 375 mμ, 1 g ε 1·86). The same transition can be seen in diphenylbenzophosphide and tribenzophosphide spectra (λ_{max} 404[11] and 384 mμ).[12] In the UV spectrum of II benzene absorption displayed a fine structure (λ_{max} 256, 261·4, 274 mμ; 1 g ε 2·08, 2·18, 2·05) which was absent in the triphenylphosphine spectrum.[17] Thus the carbonyl group being a stronger donor competitively "cuts off" the phenyl substituents from interaction with phosphorus. The UV spectra of I, III, IV (see Table) showed the $n \rightarrow \pi^*$ band corresponded to the chromophorous transition with participation of phosphorus, as well as the $\pi \rightarrow \pi^*$ transition in the spectra of I and II (in dimethylformamide at 205 mμ).[19]

The interaction of carbonyl group with phosphorus determined from the frequency of the $n \rightarrow \pi^*$ transition decreases in the following order: I > IV > III.

In the mass spectrum of I (Fig. 2) low intensity at *m/e* 61 (which is evidently entirely

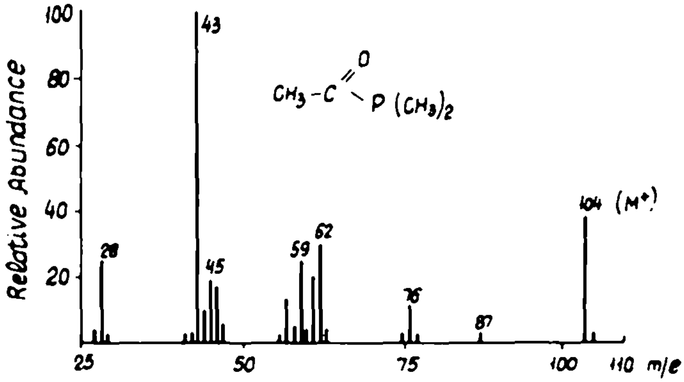


FIG. 2.

that of Me_2P^+) was observed, testifying the weak stabilization of the ion fragment by the lone pair on the phosphorous atom unlike the nitrogen [in the mass spectrum of dimethylacetamide the amine fragment ($Me—\overset{+}{N}H{=}CH_2$) has the maximum intensity].

The p_π–d_π interaction in phosphides is in a good agreement with the properties of cyanophosphides (the $\nu_{C\equiv N}$ band is not seen in the IR spectra, the shielding of phosphorous nucleus increases according to the ^{31}P NMR data[19]), vinylphosphides (the double bond is polarized in the reverse direction than that in enamine[20]) and phospholes (the lone pair does not participate in aromatic sextet[21]) as well as with the data on high electron attracting capacity of phosphine group.[14, 19, 20, 22–26]

Thus, all spectral and chemical features of phosphides may be interpreted from the view of p_π–d_π interaction of the carbonyl group with the phosphorous atom.

EXPERIMENTAL

The IR spectra of all compounds were taken using an Hitachi EPI-S2 apparatus in an airproof cell provided with KRS-5 windows. The UV spectra were obtained by means of CF-4 Optika spectrophotometre in a quartz airproof cell. PMR and ^{31}P NMR spectra were recorded with a JNM-3H-60 spectrometre, TMS and 85% H_3PO_4 were used as internal and external standards. The mass spectra were taken on a MX-1303 apparatus at room temp ($U = 30$ eV, $I = 0·75$ mA). The preparation of all the specimens was performed in an airtight box under a stream of dry argon.

1. *Tetramethyldiphosphine disulphide*. To the Grignard reagent [from 97·0 g (4 mole) Mg turnings and 568·0 g (4 mole) MeI in 1500 ml dry ether] 208·0 g (1·23 mole) of $PS\,Cl_3$ was slowly added dropwise with vigorous stirring at 3–5°. After the intensive reaction was complete the temp was increased to the room level and the mixture was heated for 1 hr on a water bath. The excess Grignard reagent was decomposed with 2N H_2SO_4 (1 l.) at 0°. The ether was evaporated and the white crystalline ppt was filtered off, washed with a large amount of water and recrystallized from alcohol–toluene mixture (1 : 3).

85·0 g (74·4%) of the product was obtained, m.p. 226–227·5°. Lit. m.p. 226·5 227·5°.[27]

2. *Dimethylphosphine*. To the mixture of 20·64 g (0·111 mole) tetramethyldiphosphine-disulphide and 8·0 g (0·210 mole) LAH, 80 ml dry dibutyl ether was added dropwise in an argon atmosphere. The temp was gradually allowed to rise to 70° and the dimethylphosphine evolved was collected in a receiver cooled with acetone–dry ice mixture; 11·64 g (84·7%) of the product was obtained, b.p. 21°, lit. b.p. 25°.[28]

3. *Dimethylacetophosphide*. A soln of 8·7 g (0·140 mole) dimethylphosphine in 50 ml dry ether was treated while stirred with 3·70 g (0·088 mole) gaseous ketene at $-20°$– $-15°$ under an argon atmosphere. The reaction was accompanied by marked heat evolution and by a change in colour to bright yellow. After removal of the solvent the residue was twice distilled *in vacuo* yielding 8·11 g (88·4%) of product, b.p. 58° (57 mm), n_D^{20} 1·4750, d_4^{20} 0·9841 which was a colourless clean liquid inflammable in air. (Found: C, 45·71, 46·08; H, 8·61, 8·61; P, 30·22, 30·41. Calc. for C_4H_9OP: C, 46·17; H, 8·72; P, 29·77%).

4. *Dimethylacetophosphineoxide*. A soln of 4·0 g (0·0375 mole) dimethylacetophosphide in 10 ml CH_2Cl_2 was treated with dry O_2 during 3 hr until evolution of white fumes stopped. During the reaction heat was evolved and the colour changed to yellow. After removal of the solvent the residue was distilled *in vacuo*, yielding 2·21 g (49·0%) of product, b.p. 103–104° (12 mm), n_D^{20} 1·4362, d_4^{20} 1·0794, which was a yellow clean liquid, readily hydrolysed in air. (Found: C, 39·06, 39·15; H, 7·72, 7·93; P, 26·06, 26·11. Calc. for $C_4H_9O_2P$: C, 40·02; H, 7·56; P, 25·80%).

5. *Trimethylacetophosphonium iodide*. To a soln of 1·75 g (0·0171 mole) dimethylacetophosphide in 3 ml dry ether, a soln of 4·84 g (0·034 mole) MeI in 10 ml of the same solvent was added under an argon atmosphere. The solid ppt was filtered off and recrystallized from MeOH–ether yielding 4·20 g (quantitative) of product, m.p. 139–140°. (Found: C, 24·54, 24·59; H, 5·34, 5·26; P, 12·43, 12·75. Calc. for C_5H_{12} OPJ: C, 24·41, H, 4·92, P, 12·59%).

6. *Diphenylacetophosphide*. A soln of 11·88 (0·0639 mole) diphenylphosphine in 150 ml dry ether was treated while stirred with 2·80 g (0·0666 mole) gaseous ketene at $-20°$ under an argon atmosphere. The reaction was accompanied by evolution of heat as well as by change in colour to yellow. After removal of the solvent the residue was distilled *in vacuo* yielding 9·66 g (66·3%) of product, b.p. 133° (1 mm), n_D^{20} 1·6630, d_4^{20} 1·1294, as a thick light-yellow liquid which oxidized in air.

Diphenylacetophosphide was also obtained[3] from diphenyl sodiumphosphide and acetyl chloride in 49·9% yield, b.p. 139–141° (1·5 mm), n_D^{20} 1·6222.

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