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The spectral properties of the acetophosphides $R_2P-C(O)-R'$ may be explained on the basis of the existence of two conformers having different energies [1, 2]. Examination of the vibrational spectrum of acetophosphide shows that there is a large difference in the valence-bond vibrations of the carbonyl group that can be used to estimate the proportions of the cis and trans isomers by the intensity of ν_{CO} . The predominant factor stabilizing isomers of this type in the liquid phase is steric interaction [3]. It has been shown with Stewart-Briegleb models that the introduction of very different substituent at R', such as methyl or phenyl, makes the existence of the cis isomer sterically impossible.

In order to confirm the hypothesis discussed above, we have synthesized dimethyl- (I) and diphenyl-hexafluoroisobutyrophosphide (II) by the scheme

$$R_2PH + (CF_3)_2C = C = O \rightarrow R_2P - C(O) - CH(CF_3)_2$$
$$R = CH(D) - CH(U)$$

$$\mathbf{n} = \mathbf{Cn}_3(\mathbf{i}), \ \mathbf{C}_{\mathbf{6}\mathbf{n}_5}(\mathbf{i}\mathbf{i})$$

The structures of the compounds obtained were confirmed by their NMR spectra (Fig. 1 and Table 1).

TABLE 1

Compound	v _{co} ,	^δ CH,	J.	Hz
	cm ⁻¹	p.p.m.	HCCF	PCCH
$\begin{array}{c} ({\rm CH}_3)_2{\rm PC}({\rm O}){\rm CH}_4({\rm CF}_3)_2 \\ ({\rm C}_6{\rm H}_5)_2{\rm PC}({\rm O}){\rm CH}({\rm CF}_6)_2 \\ ({\rm CH}_3)_2{\rm NC}({\rm O}){\rm CH}({\rm CF}_3)_2 \ [4] \\ ({\rm C}_2{\rm H}_5)_2{\rm PC}({\rm O}){\rm CH}_3 \end{array}$	1685 1682 1680 1665 1758	4,87 4,36 4,45	7,70 7,50 7,20	8,31 8,10

In accordance with the reasons previously expressed, there is only one absorption peak $\nu_{\rm CO}$ in the IR spectra of (I) and (II) corresponding to the trans isomer, (Fig. 2 and Table 1). Thus the low-frequency absorption peak corresponds to the trans isomer, and in both cases studied it is nearly at the frequency of the amide-I band of the corresponding amide. In the IR spectrum of diethylacetophosphide two absorption peaks are observed for the carbonyl group, the high-frequency peak assigned to the cis isomer, that is, the increased

volume of the substituent on phosphorus does not produce steric hindrance (Fig. 3 and Table 1). The steric position of the unshared pair of the phosphorus relative to the carbonyl group of the trans isomer excludes any kind of interaction between them in this case. However it must be noted that increased conjugation of the carbonyl group with the phosphorus atom is observed here.

Thus steric repulsion of the substituents and the $p\pi - d\pi$ interaction in the acetophosphides leads to two isomers, of which the trans isomer has the lower free energy.

EXPERIMENTAL

The IR and NMR spectra were taken as in [2].

Dimethylhexafluoroisobutyrophosphide (I). A solution of 2.00 g of dimethylphosphine in 50 ml of absolute ether was treated with 2.00 g of hexafluorodimethylketene at -10 to -5° C under an argon atmosphere. After removal of the solvent, the residue was distilled. This gave 1.61 g (60%) of a product with bp 61° (62 mm); n_D^{20} 1.3955; d_4^{20} 0.9408; a colorless liquid rapidly oxidized in air. Found %: C 30.24; 30.41; H 3.07, 3.11; P 13.09, 13.24. $C_6H_7OPF_6$. Calculated %: C 30.02, H 2.93, P 12.90.

<u>Diphenylhexafluoroisobutyrophosphide</u> (II). A solution of 4.07 g of diphenylphosphine in 50 ml of absolute ether was treated with 4.25 g of hexafluorodimethylketene at 0° in an argon atmosphere. After removing the ether, the residue was distilled. This gave 5.24 g (66.0%) of a product with bp 114-115° (1 mm); n_D^{20} 1.5241; d_4^{20} 1.3945; a thick transparent liquid oxidizing slowly in air. Found %: C 52.88, 52.92; H 3.12, 3.18; P 8.77, 8.82. C₁₆H₁₁OPF₆. Calculated %: C 52.76, H 3.04, P 8.50.

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Fig. 1. NMR spectra of diphenyl- (1), dimethylhexafluoroisobutyrophosphide (2), and dimethylhexafluoroisobutyramide (3).



Fig. 2. IR spectrum of dimethylhexafluoroisobutyrophosphide



Fig. 3. IR spectrum of diethylacetophosphide.

Diethylacetophosphide (III). This was obtained by a method similar to that for dimethylacetophosphide [2]; yield 83.5%; bp 53-54° (10 mm). Literature data [5]: bp 165-170°

CONCLUSIONS

1. The introduction of a bulky substituent at the carbonyl group in acetophosphides invokes steric hindrance to the existence of the cis isomer.

2. The low-frequency peak $\nu_{\rm CO}$ in the IR spectra of acetophosphides is due to the trans isomer.

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