IMIDE—AMIDE REARRANGEMENT UNDER THE INFLUENCE OF BORON TRIFLUORIDE ETHERATE

V. A. Gilyarov, B. A. Kvasov,
T. M. Shcherbina, and M. I. Kabachnik

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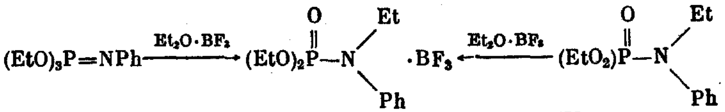
It is known that triphenylphosphine alkylimines [1, 2] and triphenylphosphine imine [3] form complexes with BF_3, these complexes having the proposed structure $Ph_3P{=}N^+(X){-}BF_3^-$ (X = R or H).

In attempting to prepare analogous complexes of triethyl N-phenylphosphorimidate (I) by reaction with BF_3 etherate, we observed imide—amide rearrangement with formation of a complex of BF_3 with O,O-diethyl-N-ethyl-N-phenyl-phosphoramidate (III), which was also obtained by an authentic route starting from the amide (II)



$$(EtO)_3P{=}NPh \xrightarrow{Et_2O\cdot BF_3} (EtO)_2\overset{O}{\overset{\|}{P}}{-}N(Et)(Ph)\cdot BF_3 \xleftarrow{Et_2O\cdot BF_3} (EtO_2)\overset{O}{\overset{\|}{P}}{-}N(Et)(Ph)$$

(I) (III) (II)

The purity and identity of (III) were confirmed by GLC, IR spectra, and comparison of constants (Table 1). Complex (III) is a colorless liquid which distils under vacuum without decomposing. The complex (V) obtained from O,O-diethyl N,N-diethylphosphoramidate (IV) and BF_3 has similar properties (see Table 1). The P=O vibration bands in the IR spectra of (III) and (V) are shifted to 1245 and 1225 cm^{-1} compared with 1270 and 1265 cm^{-1} for amides (II) and (IV), respectively. This suggests that complex formation occurs through the phosphoryl oxygen atom rather than the nitrogen atom, as is also the case in the complex of Hexametapol with BF_3 [6, 7].

According to molecular weight data (ebullioscopy in benzene), complex (III) is monomeric.

The $^{31}P{-}\{^1H\}$ NMR spectrum of (II) contains a singlet with $\delta = 5.45$ ppm, while those of complexes (III) and (V) contain quadruplets with $\delta = 1.07$ and 5.3 ppm, respectively, with a splitting between the components of ~10 Hz. These quadruplets become broader when the temperature is lowered to —30°C, evidently due to the increase in the viscosity of the sample. When the temperature is increased to 70°C, the quadruplet structure is lost and the ^{31}P signal becomes narrower. This may be due to fast intermolecular exchange of BF_3.

The ^{19}F spectrum contains a doublet at $\delta = 68.8$ ppm (at low field relative to CF_3COOH) with the same splitting [9.0 Hz for (III) and 9.3 Hz for (V)], indicating that the quadruplets in the ^{31}P spectra are due to J_{P-F} spin—spin coupling through the $P{=}O\cdot BF_3$ coordination

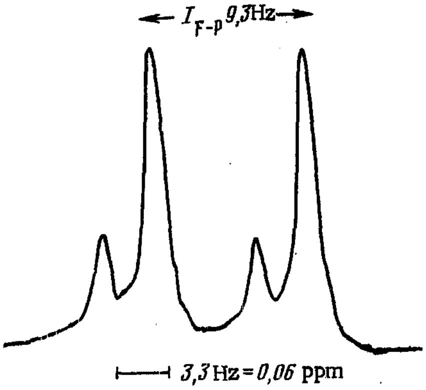


Fig. 1. The ^{19}F NMR spectrum of the complex of O,O-diethyl-N,N-diethylphosphoramidate with BF_3 (V).

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TABLE 1

Formula	Yield, %	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	Found P, %	Empirical formula	Calculated, P, %
$(EtO)_2P(O)N(Et)Ph \cdot BF_3$	65 *	126 (0,06)	1,4607	1,2243	–	–	9,5	$C_{12}H_{20}BF_3NO_3P$	9,5
	59	120 (0,04)	1,4589	1,2201	–	–	9,4		
$(EtO)_2P(O)NEt_2 \cdot BF_3$ †	83	110 (0,03)	1,4009	1,1705	–	–	11,1	$C_8H_{20}BF_3NO_3P$	11,2
$(MeO)_2P(O)N(Me)Ph$ ‡	76	80–82 (0,03)	1,5120	1,1961	53,98	54,03	14,6	$C_9H_{14}NO_3P$	14,4
$(EtO)_2P(O)N(Et)Ph$ **	75	90–91 (0,6)	1,4948	1,1001	68,29	67,88	12,0	$C_{12}H_{20}NO_3P$	12,1
$(PrO)_2P(O)N(Pr)Ph$	75	94–95 (0,03)	1,4880	1,0492	82,20	81,69	10,6	$C_{15}H_{26}NO_3P$	10,4
$(BuO)_2P(O)N(Bu)Ph$	65	125–126 (0,05)	1,4833	1,0165	95,97	95,12	9,4	$C_{18}H_{32}NO_3P$	9,3
$(BuO)_2P(O)N(Bu)C_6H_4Me$-*p*	80	133–134 (0,01)	1,4839	1,0067	101,00	100,22	8,7	$C_{19}H_{34}NO_3P$	8,7
$(BuO)_3P{=}NC_6H_4Me$-*p*	74	134–135 (0,03)	1,4897	0,9933	103,41	103,03	8,6	$C_{19}H_{34}NO_3P$	8,7

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*Prepared from phosphorimidate (I). Found: F 17.7%, mol. wt. 293. Calculated: F 17.5%, mol. wt. 325.

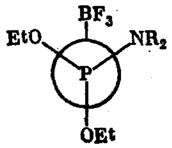
†Found: F 20.3%. Calculated: F 20.6%.

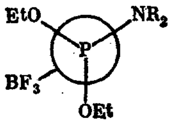
‡Constants cf. [4].

**Constants cf. [5].

bond. So far as we know, this kind of J_{P-F} coupling through a coordination bond has never been observed before [6, 8-10].

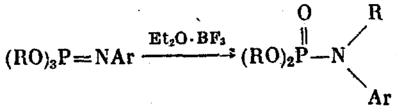
A more detailed investigation of the ^{19}F NMR spectra of compounds (III) and (V) shows the presence of two doublets with chemical shifts differing by only $\Delta\delta = 0.06$ ppm, with the same J_{P-F} value, and with an intensity ratio of ~ 5 for (III) and ~ 3 for (V) (the smaller doublet being at lower field, Fig. 1). This may be due to the existence of two conformers, and the intensity ratio is evidently connected both with purely statistical preference and





with a difference in the energies of the nonbonded interactions between the BF_3 group and the N and O atoms.

In studying the reaction of trialkyl N-aryl-phosphorimidates (VI) with $Et_2O \cdot BF_3$, it was found in [11] that imide—amide rearrangement of (VI), which is normally effected by heating with alkyl halides or by thermal isomerization [5, 12], goes to completion under relatively mild conditions (60-65°C) in the presence of catalytic amounts of $Et_2O \cdot BF_3$, resulting in the formation of O,O-dialkyl-N-alkyl-N-arylphosphoramidates (VII)



$$(RO)_3P{=}NAr \xrightarrow{Et_2O \cdot BF_3} (RO)_2\overset{O}{\overset{\|}{P}}{-}N\begin{matrix} \diagup R \\ \diagdown Ar \end{matrix}$$

(VI) (VII)

The completeness of the rearrangement of (VI) was monitored by the disappearance of absorption at 1380 cm^{-1} (P=N) in the IR spectrum. Table 1 summarizes the yields and constants of the synthesized phosphoramidates (VII), the purity of which was confirmed by GLC. It is interesting to note that tributyl N-phenylphosphorimidate is only 50% isomerized (according to GLC) when boiled with butyl bromide for 10 h, whereas isomerization is complete in the presence of $Et_2O \cdot BF_3$.

EXPERIMENTAL

The IR spectra of the pure substances were obtained with a UR-20 instrument. The $^{31}P-\{^1H\}$ NMR spectra of the pure substances were obtained with a Bruker HX-90 spectrometer (36.43 MHz) at temperatures from —30 to 70°C, using 85% H_3PO_4 as external standard. Low-field shifts were reckoned as positive. The ^{19}F NMR spectra were recorded with a Hitachi R-20 spectrometer (56.4 MHz) at 34°C. The chemical shifts were measured relative to CF_3COOH as external standard.

The GLC analysis of complex (III) was performed with glass columns containing 3% silicone elastomer XE-60 on Chromosorb W (80/100 mesh) at 145°C, using He as carrier gas (40 ml/min) and a flame-ionization detector.

The analysis of phosphoramidates (VII) was performed with a column containing 2.4% polyethylene glycol adipate on Chromosorb. Depending on the substituent attached to P (MeO, EtO, PrO, or BuO), the column temperature was 185, 190, 195, or 200°C, respectively. The sample was injected directly into the column, and a flame-ionization detector was used. The retention time of the compounds was not more than 10 min.

Complex of O,O-Diethyl-N-ethyl-N-phenyl-phosphoramidate with BF_3 (III). a) Freshly distilled $Et_2O \cdot BF_3$ (2.84 g) was added to 5.11 g of triethyl N-phenyl-phosphorimidate (I) (equimolar quantities). A slight exothermic effect was observed. The mixture was heated at 50-60°C for 2 h. Distillation yielded 4.25 g of (III).

b) A 2.84 g portion of $Et_2O \cdot BF_3$ was added to 5.11 g of O,O-diethyl-N-ethyl-N-phenylphosphoramidate (II). The mixture was heated at 60-65°C for 2 h. Distillation yielded 3.84 g of (III).

Complex of O,O-Diethyl-N,N-diethyl-phosphoramidate with BF_3 (V). This was prepared similarly from 4.19 g of O,O-diethyl-N,N-diethyl-phosphoramidate and 2.84 g of $Et_2O \cdot BF_3$ (heating for 3 h). The yield was 4.56 g.

O,O-Dimethyl-N-methyl-N-phenyl-phosphoramidate. Ten drops of freshly distilled $Et_2O \cdot BF_3$ were added to 6.45 g of trimethyl N-phenyl-phosphorimidate at 0°C. The colling was withdrawn and the temperature increased to 46°C. The mixture was then heated at 60-65°C for 6 h. Distillation yielded 4.96 g of the phosphoramidate.

The other phosphoramidates (VII) were prepared similarly. Tributyl N-(p-tolyl)-phosphorimidate was prepared from 7.5 g of tributyl phosphite and 4.0 g of p-tolyl azide in 20 ml of abs. benzene at 30-40°C. The yields and constants are given in Table 1.

CONCLUSIONS

1. Reaction of triethyl N-phenyl-phosphorimidate with BF_3 etherate yields a complex of O,O-diethyl-N-ethyl-N-phenyl-phosphoramidate with BF_3.

2. The ^{31}P and ^{19}F NMR spectra of the complexes of O,O-diethyl-N-ethyl-N-phenyl-phosphoramidate and O,O-diethyl-N,N-diethyl-phosphoramidate with BF_3 have been studied, and J_{P-F} coupling through the $P{=}O \cdot BF_3$ coordination bond has been detected.

3. It has been discovered that trialkyl N-aryl-phosphorimidates undergo imide—amide rearrangement under the influence of catalytic amounts of BF_3 etherate.

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