A GC-MS investigation of the mechanism of imide-amide rearrangement

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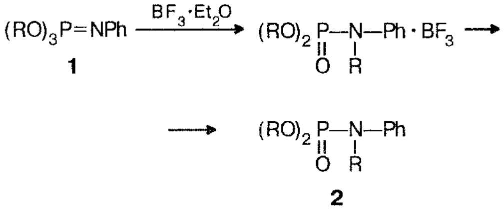
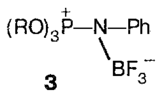
The products of imide-amide rearangement of trialkyl (arylimido)phosphates were studied by the GC-MS method. An ionic chain mechanism was suggested for this reaction.

Key words: capillary gas chromatography, mass spectrometry, imide-amide rearrangement, trialkyl (arylimido)phosphates, ionic chain mechanism.

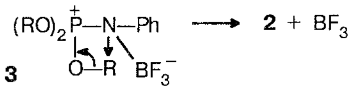
Previously[1] we showed that the imide-amide rearrangement of *N*-phenylimidophosphates occurs under the catalytic action of boron trifluoride etherate:



It seemed quite probable[2] that this catalytic action is due to the formation of adduct **3**,



which acts as a strong alkylating agent and decomposes during homoalkylation:[2]



However, when an equimolar mixture of two imidophosphates **1** and **4** is treated with $BF_3 \cdot Et_2O$ (Scheme 1, Table 1), along with two homoalkylation products, **2** and **5**, two cross-alkylation products **6** and **7**[3,4] are produced.

It may be suggested that products **6** and **7** result from an exchange of functional groups between compounds **2** and **5** under the action of $BF_3 \cdot Et_2O$. However, a special experiment carried out with **2** and **5** showed that this exchange does not take place. Thus, the products of cross-alkylation arise during the rearrangement, which occurs, at least partly, according to an intermolecular mechanism.[4]

Scheme 1

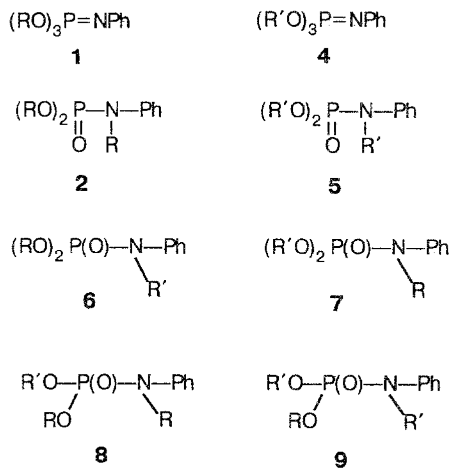


Table 1. The ratio between the products of the imide-amide rearrangement in a mixture of imides **1** and **4** (rel %).

Run	Starting compounds		Reaction products					
	1, R	**4**, R′	**2**	**5**	**6**	**7**	**8**	**9**
A	Me	C_2D_5	11.0	20.2	10.1	31.5	18.1	9.1
B	CD_3	Et	10.8	31.9	13.9	28.5	7.3	7.6
C	CD_3	Bu	20.0	31.5	5.0	30.3	10.0	3.2
D	Et	*i*-Pr	30.5	20.5	27.5	20.5	0.5	0.5
E	Et	Bu	18.2	26.1	23.3	31.4	0.6	0.4
F	C_2D_5	Bu	24.5	18.8	15.1	21.0	12.0	8.6

To investigate the imide-amide rearrangement in more detail, we studied the products of the reaction of an equimolar mixture of two imidophosphates having different alkyl groups at the phosphorus atom and equimolar mixtures of their two deuterated analogs by GC-MS. This substantially improved chromatographic separation of the isomers (Fig. 1) and allowed us to identify six components: two homo-alkylation products,

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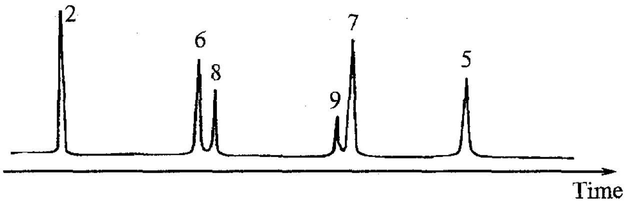


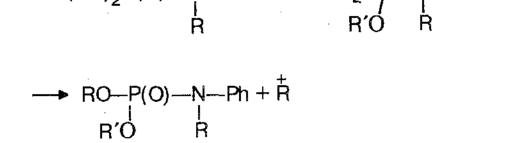
Fig. 1. Chromatogram of the reaction products of run F.

2 and **5**, two cross-alkylation products, **6** and **7**, and two compounds having different substituents at the phosphorus atom, **8** and **9**.

As can be seen from Table 1, which lists the ratios between the products of the imide-amide rearrangement of a mixture of imides **1** and **4**, the amount of compounds **8** and **9** is considerably higher in the case of the deuterated imidophosphate (*cf.* run F and run E). The proportion of homo-rearrangement products increases somewhat (from 30 % to 50 %) as the alkyl substituent in the starting compound becomes more complex, and the amount of the products of cross-rearrangement varies from 40 % to 50 %.

The ratios observed apparently correspond to an ionic chain mechanism of the imide-amide rearrangement initiated by boron trifluoride etherate (Scheme 2).

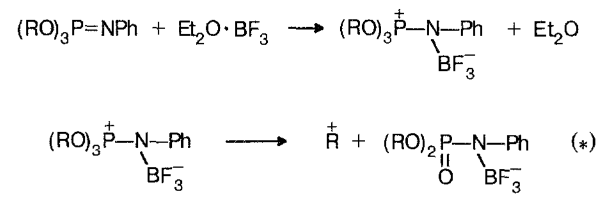
In the experiments with compounds **1** and **4**, along with the chain homo-rearrangement, an attack of the «alien» imidophosphate **4** by cation R^+ occurs to afford compound **7** and a new cation R'^+, which continues the chain. Since concentrations of the starting imides **1** and **4** are equal, the probabilities of the formation of products **2**, **5**, **6**, and **7** should be close to each other. Differences may arise for the most part due to different rates of diffusion of cations R^+ and R'^+ into the bulk. Thus, homo-rearrangement occurs within a solvent cage, whereas cross-rearrangement is only possible when R^+ and R'^+ come out to the bulk and, consequently, its characteristics depend on the mass of the cation, which increases in the order: $Me^+ < CD_3^+ < Et^+ < C_2D_5^+ < i\text{-}Pr^+ < Bu^+$ (see Table 1). The reasons for high yields of compounds **8** and **9** in the experiments with deuterated compounds are still unclear. Transalkylation at the phosphorus atom may occur when the P=O group of the rearrangement product is attacked by the R^+ or R'^+ cation:



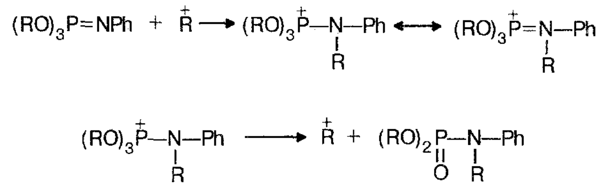
In a specially carried out experiment, the reagents, $(BuO)_3PO$ and $(PrO)_3PO$, were treated in the same way as imides **1** and **4**, however, as in the run with compounds **2** and **5**, no products of the above-mentioned transalkylation were detected. This makes it possible to conclude that transalkylation at the phosphorus atom only occurs during imide-amide rearrangement.

Scheme 2

1) chain initiation:

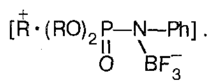


2) chain growth:

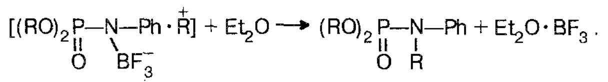


3) chain termination:

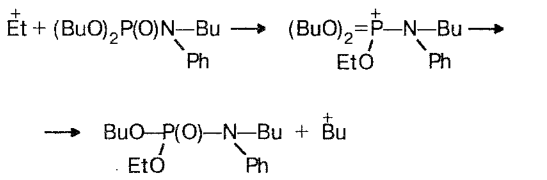
* Formation of the ion pair is possible



Chain termination in this case occurs through the following reaction:



Taking into account the fact that boron trifluoride etherate does not affect the mixture of homo-rearrangement products **2** with R = Et and **5** with R′ = Bu (owing to the absence of alkyl cation R^+), we studied the action of $BF_3 \cdot Et_2O$ on an equimolar mixture of $(EtO)_3P{=}NPh$ and $(BuO)_2P(O)N(Bu)Ph$ and obtained a mixture of the following compounds: homo-rearrangement product, 45.4 %; the starting butyl amidoester $(BuO)_2P(O)N(Bu)Ph$, 48.1 %, *i.e.*, 93.5 % normal products, and, in addition, 1.6 % $(EtO)_2P(O)N(Bu)Ph$ (which indicates that the Bu^+ cations arise in the course of the reaction), and 4.2 % $(BuO)_2P(O)N(Et)Ph$ as well as two products with replaced alkyl substituents at the phosphorus atom: EtO(BuO)P(O)—N(Et)Ph (0.5 %) and EtO(BuO)P(O)—N(Bu)Ph (0.2 %). These products are likely to result from the action of the Et^+ and Bu^+ cations on the starting and final compounds. The Bu^+ cation is produced according to the following scheme:



Mass spectra of the compounds obtained in runs A, B, E, and F exhibit intense molecular ion peaks (Table 2). The structures of the compounds were determined from the character of their fragmentation and the type of $[M-R'NPh]^+$ and $[R'NPh]^+$ fragment ions which arise as a result of P—N bond cleavage.[6] Further decomposition occurs with the loss of two or four ethylene molecules to give a fragment (responsible for a highly intense peak) with m/z 186 ($C_8H_{10}NO_2P$), which is converted to a fragment with m/z 155 (C_8H_8NOP) by the loss of two methyl groups. The other intense peaks in the spectra correspond to ions with m/z 79 (PO_3^+), 93 (PO_3N^+), and 77 ($C_6H_5^+$). In runs C and D all of the compounds exhibit fragments with m/z 120 ($C_8H_{10}N$) and 125 ($C_8D_5H_5N$) (Fig. 2).

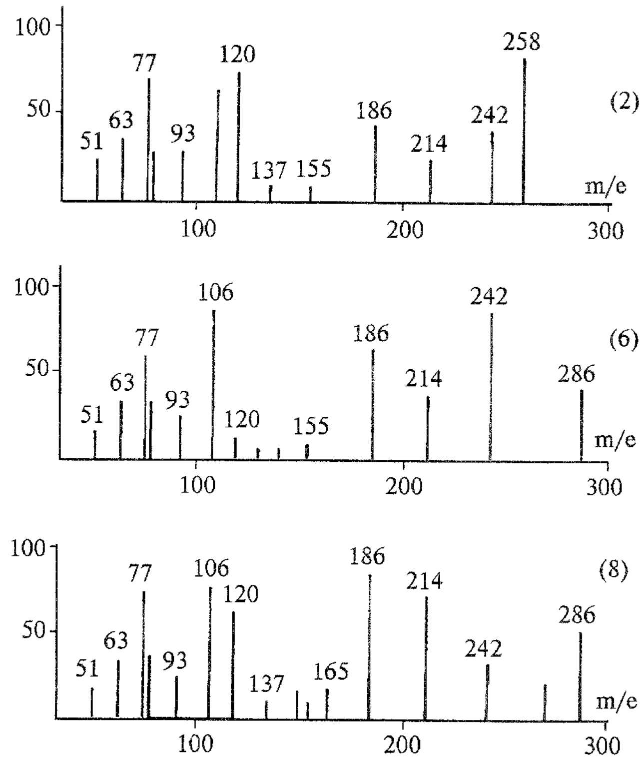


Fig. 2. Mass spectra of compounds **2**, **6**, and **8**, run F.

Experimental

The starting compounds $(RO)_3P{=}NPh$ with R = Me, Et, and Bu were prepared according to the known procedure,[5] the synthesis of $(RO)_3P{=}NPh$ with R = CD_3 and C_2D_5 and the procedure of the imide-amide rearrangement have been described previously.[4]

The GC-MS investigations were carried out on a Varian 3400 chromatograph with a DB-5 capillary column (25 m). Chromatographic analysis was carried out with temperature programming from 60 °C (3 min) to 230 °C at a rate of 4° min^{-1}, the injector temperature was 220 °C. A Finnigan MAT AT 800 ion trap served as the detector. The ionization energy was 70 eV.

Table 2. Mass numbers and relative intensities of the peaks for the products of the imide-amide rearrangement (% of I_{max})

Reaction products	Mass number	Run A	Run B	Run E	Run F
		Starting compounds			
		1, R = Me; **4**, R′ = C_2D_5	**1**, R = CD_3; **4**, R′ = Et	**1**, R = Et; **4**, R′ = Bu	**1**, R = C_2D_5; **4**, R′ = Bu
2	M^+	216(100)	225(100)	258(100)	273(100)
	$[M-R'NPh]^+$	109(42)	115(42)	137(7)	147(2)
	$[R'NPh]^+$	106(54)	109(55)	120(64)	125(60)
5	M^+	273(100)	258(100)	342(100)	342(25)
	$[M-R'NPh]^+$	147(2)	137(14)	193(3)	193(2)
	$[R'NPh]^+$	125(7)	120(43)	148(6)	148(8)
6	M^+	235(100)	236(50)	286(46)	296(48)
	$[M-R'NPh]^+$	109(44)	115(46)	137(7)	147(2)
	$[R'NPh]^+$	125(22)	120(40)	148(5)	148(5)
7	M^+	254(100)	247(100)	314(20)	319(100)
	$[M-R'NPh]^+$	147(4)	137(5)	193(2)	193(4)
	$[R'NPh]^+$	106(55)	109(82)	120(27)	125(33)
8	M^+	235(100)	236(100)	286(39)	296(100)
	$[M-R'NPh]^+$	128(6)	126(8)	165(2)	170(4)
	$[R'NPh]^+$	106(55)	109(55)	120(49)	125(30)
9	M^+	254(100)	247(39)	314(48)	319(100)
	$[M-R'NPh]^+$	128(7)	126(11)	165(3)	170(4)
	$[R'NPh]^+$	125(25)	120(42)	148(10)	148(8)

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