

GC-MS STUDY OF THE IMIDE—AMIDE REARRANGEMENT

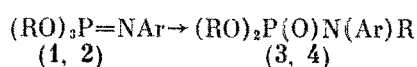
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The imide—amide rearrangement of trialkyl arylimidophosphates by the action of catalytic amounts of boron trifluoride etherate proceeds at least partially by an intermolecular mechanism.

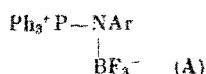
Keywords: capillary gas-liquid chromatography/mass spectrometry, imide—amide rearrangement, trialkyl arylimidophosphate.

In previous work [1, 2], we showed that the imide—amide rearrangement of trialkyl arylimidophosphates proceeding by the action of catalytic amounts of boron trifluoride etherate leads to the formation of O,O-dialkyl N,N-alkylaryl amidophosphates.

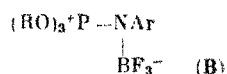


where Ar = Ph, R = Me (1, 3), Et (2, 4).

A study of the structure of complexes of triphenylphosphinarylimines with BF₃ indicated phosphonium species (A)

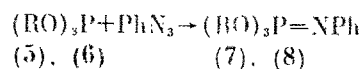


and the formation of analogous complexes (B)



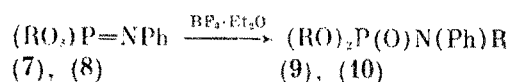
by the action of BF₃ on trialkyl arylimidophosphates [3]. Such complexes are naturally extremely unstable and decompose to form products of imide—amide rearrangement. In the present work, we studied the mechanism of the imide—amide rearrangement.

Samples of trideuteromethyl phenylimidophosphate (7) and trideuteroethyl phenylimidophosphate (8) were prepared by the action of phenyl azide on trideuteromethyl phosphite (5) and trideuteroethyl phosphite (6), which were obtained according to the procedure used for the synthesis of trialkyl phosphites, namely, the reaction of CD₃OD or C₂D₅OD with phosphorus trichloride in the presence of dimethylaniline in absolute ether [4].



where R = CD₃ (5, 7), C₂D₅ (6, 8).

The products of the imide—amide rearrangement, namely, O,O-dideuteromethyl N,N-deuteromethyl phenylamidophosphate (9) and O,O-dideuteroethyl N,N-deuteroethyl phenylamidophosphate (10) were obtained by the action of catalytic amounts of boron trifluoride etherate on imidophosphates (7) and (8) [2].



where R = CD₃ (9) and C₂D₅ (10).

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TABLE 1. Indices for 5-10

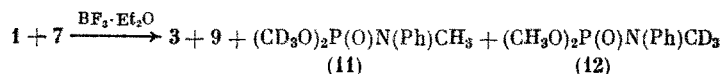
Compound	Yield, %	Bp, °C (p, torr)	n_D^{20}	d_4^{20}	Found Calculated, %	Empirical formula	^{31}P NMR spectrum (δ , ppm)
(CD_3O) ₃ P (5)	68	65-66(100)	1.4100	1.1325	$\frac{23.6}{23.3}$	$\text{C}_3\text{D}_9\text{O}_3\text{P}$	97.0
($\text{C}_2\text{D}_5\text{O}$) ₃ P (6)	76	50-51(12)	1.4220	1.0402	$\frac{13.2}{13.4}$	$\text{C}_6\text{D}_{15}\text{O}_3\text{P}$	139.3
(CD_3O) ₃ P=NPh (7)	82	70-71(0.06)	1.5222	1.2163	$\frac{13.9}{13.8}$	$\text{C}_8\text{H}_5\text{D}_9\text{O}_3\text{NP}$	-3.1
($\text{C}_2\text{D}_5\text{O}$) ₃ P=NPh (8)	84	80-81(0.04)	1.5040	1.1322	$\frac{11.2}{11.4}$	$\text{C}_{12}\text{H}_3\text{D}_{15}\text{O}_3\text{NP}$	-4.0
(CD_3O) ₂ P(O)N(CD ₃)Ph (9)	78	105-106(1)	1.5135	1.2374	$\frac{13.8}{13.8}$	$\text{C}_8\text{H}_5\text{D}_9\text{O}_3\text{NP}$	8.8
($\text{C}_2\text{D}_5\text{O}$) ₂ P(O)N(C ₂ D ₅)Ph (10)	80	89-90(0.07)	1.4955	1.1634	$\frac{11.8}{11.4}$	$\text{C}_{12}\text{H}_{13}\text{D}_{15}\text{O}_3\text{NP}$	6.0 *

*In benzene.

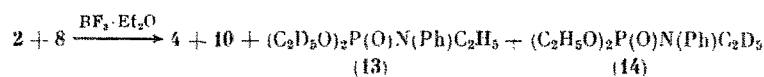
The structures of **8-10** were indicated by the IR spectra: $\nu_{\text{P}=\text{N}}$ 1380 for **7** and **8** and $\nu_{\text{P}=\text{O}}$ 1280 cm^{-1} for **9** and **10**. The indices for **5-10** are given in Table 1.

The purity of the samples of **7-10** was indicated by their GC-MS data.

The imide–amide rearrangement of an equimolar mixture of trimethyl phenylimidophosphate **1** and imidophosphate **7** and an equimolar mixture of triethyl phenylimidophosphate **2** and imidophosphate **8** in the presence of catalytic amounts of boron trifluoride etherate in benzene solution was carried out in order to study the mechanism of this rearrangement by the action of catalytic amounts of the indicated catalyst. The products of the imide–amide rearrangement were studied by GC-MS. In both cases, four products were detected in 1:1:1:1 ratio. In the case of imidophosphates **1** and **7**, O,O-dideuteromethyl N,N-methyl phenylamidophosphate (**11**) and O,O-dimethyl N,N-deuteromethyl phenylamidophosphate (**12**) were observed in the reaction mixture in addition to amidophosphates **3** and **9**.



In the case of imidophosphates **2** and **8**, the reaction mixture contained both amidophosphates **4** and **10** as well as O,O-dideuteroethyl N,N-ethyl phenylamidophosphate (**13**) and O,O-diethyl N,N-deuteroethyl phenylamidophosphate (**14**).



Products **11-14** are the result of an imide–amide rearrangement proceeding through an intermolecular mechanism. The formation of amides **3** and **9** or **4** and **10** may occur by either a monomolecular or bimolecular mechanism.

Treatment of a mixture of amides **3** and **9** with catalytic amounts of boron trifluoride etherate leads to the formation of new compounds, which excludes the possibility of the exchange of the alkyl groups at the nitrogen atom in amides **3** and **9**.

EXPERIMENTAL

The reaction mixture was studied by GC-MS on a Varian 3400 chromatograph with a 25-m DB-5 capillary column and Finnegan MAT AT 800 ion trap detector manufactured in the USA. The ionization energy was 70 eV. The chromatographic analysis was carried out with temperature programming at a rate of 4°C/min from 60°C (3 min) to 230°C. The injector temperature was 220°C. The mass spectrometric data were published in our previous work [5].

The IR spectra of the pure substances were obtained in a UR-20 instrument, in a thin layer. The $^{31}\text{P}\{-^1\text{H}\}$ spectra of the pure substances were taken in a Bruker WP-200 SY instrument (80.96 MHz) with 85% H_3PO_4 as an external standard.

Imide–Amide Rearrangement of a Mixture of Trimethyl Phenylimidophosphate (1) and Trideuteromethyl Phenylimidophosphate (7). Five drops of boron trifluoride etherate were added to a solution of 60 mmoles imidophosphate **1** and 60 mmoles imidophosphate **7** in 5 ml absolute benzene. The mixture was heated at 50°C for 2 h. Benzene was distilled off in vacuum. The residue was dissolved in 5 ml absolute ether and 10 drops triethylamine were added. The mixture was placed in a refrigerator for 24 h. The solution was decanted from the oily precipitate of the triethylamine complex with boron trifluoride and evaporated in vacuum. The residue was distilled at 105–106°C (1 mm) to give 2.1 g of a mixture of amidophosphates **3**, **9**, **11**, and **12** (81% yield). The imide–amide rearrangement of an equimolar mixture of imidophosphates **2** and **8** and the rearrangements of individual imidophosphates **1**, **2**, **7**, and **8** were carried out by analogous procedures. The experiment with amides **3** and **9** was carried out under the same conditions.

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