MS/GC STUDY OF THE IMIDE-AMIDE REARRANGEMENT

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In previous works [1,2], we showed that the imide-amide rearrangement in trialkyl arylimidophosphates, catalyzed by boron trifluoride etherate, leads to the formation of O,O-dialkyl N,N-alkylarylamidophosphates. However, it was not clear whether this rearrangement is intra- or intermolecular. In order to answer this question, we synthesized $(CD_3O)_3P{=}NC_6H_5$ (I), which is a deuterated analog of $(CH_3O)_3P{=}NC_6H_5$ (II). Each of these compounds and their mixture was treated with a catalytic amount of boron trifluoride etherate in benzene. The reaction products were studied by MS/GC. The isomerization of (I) was found to lead to $(CD_3O)_2P(O)N(CD_3)C_6H_5$ (III), while the isomerization of (II) was found to give $(CH_3O)_2P(O)N(CH_3)C_6H_5$ (IV). The isomerization of an equimolar mixture of (I) and (II) gave (III), (IV), $(CD_3O)_2P(O)N(CH_3)C_6H_5$ (V), and $(CH_3O)_2P(O)N(CD_3)C_6H_5$ (VI). The structures of these compounds were indicated by their mass spectra (Table 1).

Thus, the formation of amides (V) and (IV) is a result of an intermolecular alkyl group exchange. Products (III) and (IV) may result either from a bimolecular or intramolecular reaction.

TABLE 1. Mass Spectral Data for $(RO)_2P(O)N(R^1)C_6H_5$

Compound	R	R^1	m/z (I_{rel}, %)		
			$[M-1]^+$	$[M-(R^1NC_6H_5)]^+$	$[R^1NC_6H_5]^+$
(III)	CD_3	CD_3	223(74)	115(52)	109(100)
(IV)	CH_3	CH_3	214(65)	109(50)	106(100)
(V)	CD_3	CH_3	220(59)	115(46)	106(100)
(VI)	CH_3	CD_3	217(53)	109(100)	109(100)

LITERATURE CITED

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