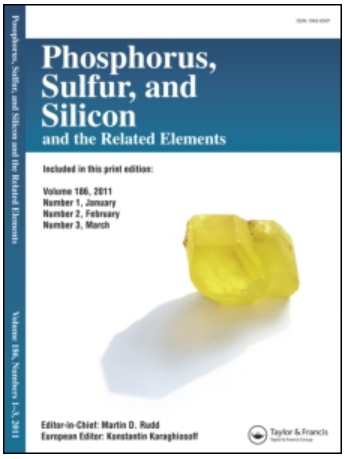

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Phosphorus-Containing N'-Trifluoromethylcarbodiimides and N'-Trifluoromethylfluoroformamidines in Reactions with Nucleophilic Reagents

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PHOSPHORUS-CONTAINING N'-TRIFLUOROMETHYLCARBODIIMIDES AND N'-TRIFLUOROMETHYLFLUOROFORMAMIDINES IN REACTIONS WITH NUCLEOPHILIC REAGENTS

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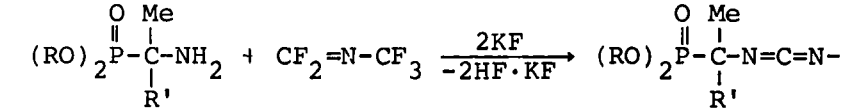
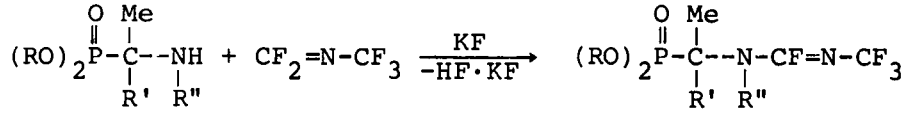
The presence of highly reactive fluorine containing groups in molecules of phosphorus compounds results in unusual and unpredictable chemical properties of these compounds. This work describes the synthesis and chemical properties of ealier unknown phosphorus-containing N'-trifluoromethylcarbodiimides and N'-trifluoromethylfluoroformamidines. The studied conversions of these compounds allowed us to develop the new approaches to the synthesis of fluorine containing α-aminoalkylphosphorylic compounds, which have drawn attention of researchers in the field of physiologically active substances in last years.

The α-(N'-trifluoromethylcarbodiimido)alkylphosphonates (1) and α-(N'-trifluoromethylfluoroformamidimo)alkylphosphonates (2) were obtained by interaction of α-aminoalkylphosphonates with CF_2=N-CF_3 at -30 ÷ -10°C in the presence of 1-2.5 equivalents of KF.[1,2]

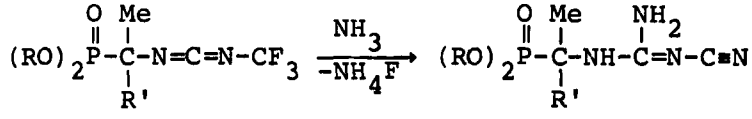


(1)



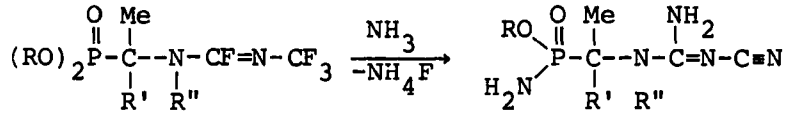
(2)

The compounds (1) and (2, R = H) react with NH_3 in ether or acetonitrile exothermically to yield 1-(2-cyanoguanidino)phosphonates (3).[2,3]



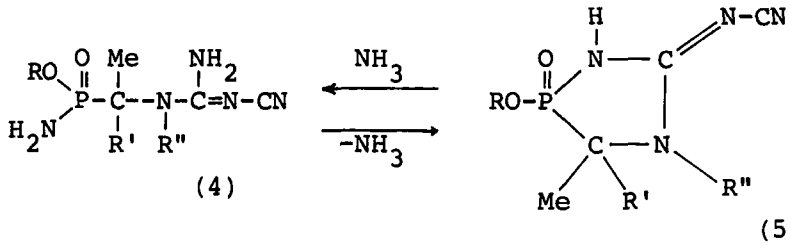
(1) (3)

N-Alkylated analogs (2, R = Alk) interact with NH_3 under more severe conditions (Excess of NH_3 in sealed tube) to form phosphonates (4) (δ_p 35 ppm).[4]



(2) (4)

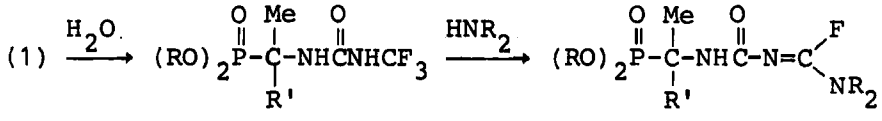
This reaction differs from the previous one, since alkoxygroup in compounds (4) is formally replaced by amino-group. In course of separation (80°C) phosphonates (4) eliminate a NH_3-molecule and convert into 1,4,2-diazaphosphol (5) (δ_p 56 ppm). The heterocycle (5) opens readily in liquid NH_3.



(4) (5)

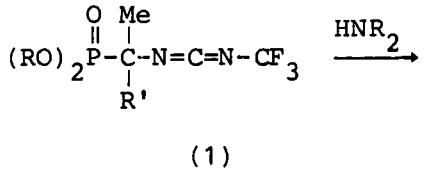
It is interesting, that in the ^{31}P NMR spectrum of the mixture of (4) and (5) only a singlet is present at room temperature. Its position lies in the interval 35-56 ppm depending on the mixture composition.

Phosphorus-containing carbodiimides (1) react easily with H_2O to form corresponding N'-trifluoromethylureas (6). By treatment with secondary amines the ureas (6) convert into phosphorus-containing carbamoylated fluoroformamidines (7).[5,6]

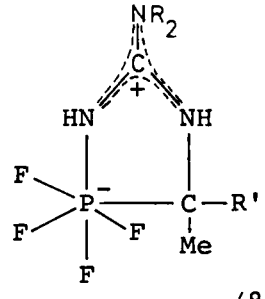


(6) (7)

The 10-hour heating of equimolar quantities of α-(N'-trifluoromethylcarbodiimido)alkylphosphonates (1) with dialkylamines at 65-70°C yields instead of α-quanidinophosphonates, as to be expected, an earlier unknown type of compounds of hexacoordinated phosphorus: $1\lambda^4,4,2\lambda^6$-diazaphosphoratoles (8).[2, 7-10]



(1)



(8)

Phosphorates (8) were also obtained by interaction of dialkylamines with phosphonates (2, R = H).

Structure of diazaphosphoratoles (8), the first neutral monocyclic phosphorates with the P--C bond in cycle, was proved by X-ray analysis and confirmed by NMR spectra. The formation of phosphorates (8) from compounds of tetracoordinated phosphorus is unusual.

Five-member cycle of phosphorates (8) has a planar envelope conformation with a tip at atoms P or C[3]. The bond lengths of planar guanidinic fragment indicates on π-delocalization at C=N formal double bond. Endocyclic P-C bond is in (8) practically equal on length - 1.770 Å - and normal covalent odinary bond and preceptibly shorter than in all other early structurally studied compounds of hexacoordinated phosphorus, bond lengths P-N in those were 1.885-1.98 Å.

We also studied the interaction of phosphorus-containing cyanoguanidines (3) and 1,4,2-diazaphospholes (5) with hexafluoroacetone and N-acylimines of hexafluoroacetone; molecular structure of some products of these interactions has been discussed[11,12].

Authors express a hope, that the obtained results concerning the developing of new methods of the synthesis of

fluoro-containing α-aminoalkylphosphorylic compounds on the basis of phosphorus-containing α-(N'-trifluoromethylcarbodiimido)- and α-(N'-trifluoromethylfluoroormamidino)alylphosphonates, and these compounds themselves have attracted attention both of chemists and biochemists, because the number of obtained compounds has a different type of physiological activity.

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