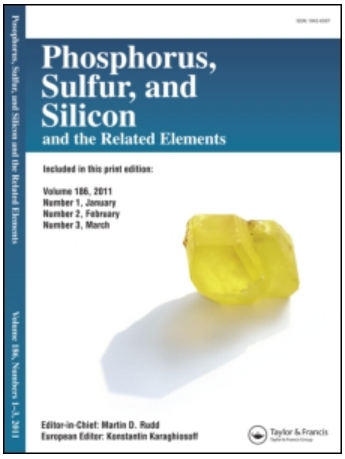

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Oxidative Addition of Hexafluoroacetone, Perfluorinated 1,2-Diketones and Tetrachloro-O-Benzoquinone to Compounds of Low-Valent Phosphorus-New Modes of Addition and Unusual Products

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OXIDATIVE ADDITION OF HEXAFLUOROACETONE, PERFLUORINATED 1,2-DIKETONES AND TETRACHLORO-o-BENZOQUINONE TO COMPOUNDS OF LOW-VALENT PHOSPHORUS - NEW MODES OF ADDITION AND UNUSUAL PRODUCTS

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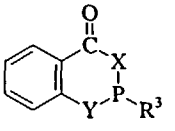
Abstract The reaction of hexafluoroacetone (HFA) with the benzoxazaphosphorinone **1** leads to the λ^5-oxazaphosphepinone **2**. In several cases unusual products, **3**, **8 - 14**, **16**, and **17**, were isolated in the reactions of **1**, **4 - 7**, and **15** with HFA, tetrachloroorthobenzoquinone (TOB) and perfluorinated 1,2-diketones. X-Ray crystal structure analyses were carried out for the derivatives **2**, **3**, and **8 - 10**.

Key Words: Oxidative Addition; N-Alkylation; Phosphoranes, bicyclic; Phosphoranes, tricyclic; Single Crystal X-Ray Structure Determination.

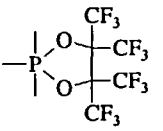
INTRODUCTION

Benzoxaza- and diazaphosphorinones of type **A** are known to react with nucleophiles either with displacement of the P-bonded substituents (usually chlorine) or with cleavage of the phosphorinone ring [1-8]. Many phosphorus(III) compounds have been reported to undergo oxidative addition reactions with HFA with formation of phosphoranes involving the structural element **B** [9,10].

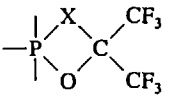


X = O Y = NR^1
X = O Y = O
X = NR^2 Y = O
X = NR^2 Y = NR^1
R^1 = Me R^2 = Alkyl, Aryl
R^3 = Hal, Amino, Alkoxy

A



B



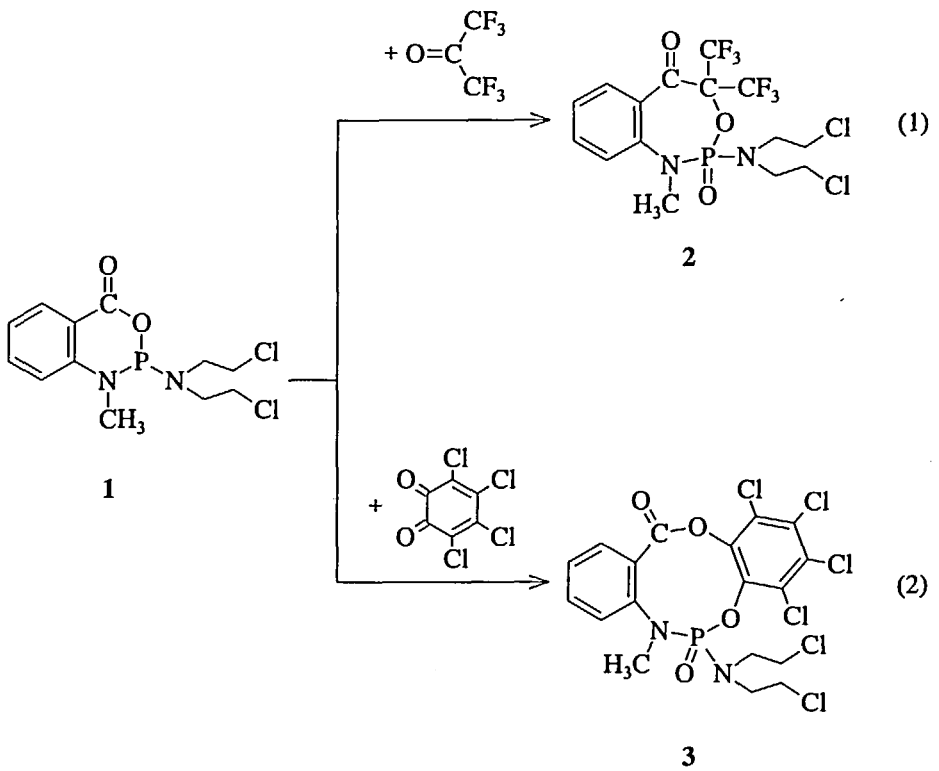
X = CH_2, CHCl, NR^1
R^1 = Alkyl, Aryl

C

The reaction of phosphorus(III) compounds with HFA was found to lead to λ^5-oxaphosphetane derivatives of structure **C** when CH_3, CH_2Cl, or NHR substituents were bonded to P(III) [10-12].

RESULTS AND DISCUSSION

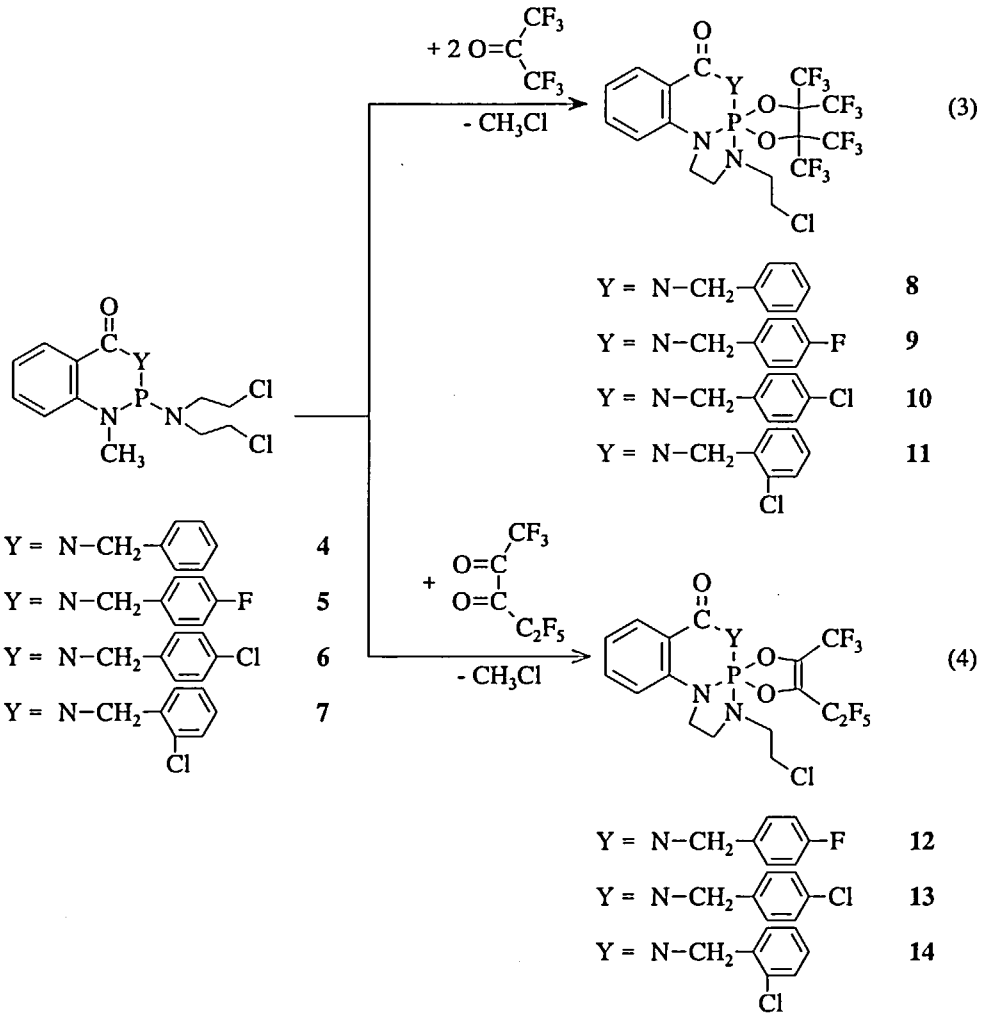
The reaction of the bis(2-chloroethyl)amino-1,3,2-oxazaphosphorinone derivative **1** with HFA and TOB did not lead to the expected spirocyclic products by oxidative addition of HFA or the quinone system to the λ^3-P-atom. Instead, cleavage and expansion of the heterocyclic ring system with formation of the oxazaphosphepinone **2** and the tricyclic derivative **3** was found to occur (Eq. (1) and (2)).



1 **2** **3**

The structures of **2** and **3** were confirmed by single crystal X-ray structure determination [5,11]. The derivatives **4** - **7** reacted with HFA and trifluoromethyl-pentafluoroethyl-1,2-diketone (TMPE) in an unexpected fashion. The oxidative addition of HFA and TMPE to the P(III) compounds was invariably accompanied by an unusual N-alkylation reaction, involving one of the two CH_2CH_2Cl-groups bonded via nitrogen to the

phosphorus atom. The alkylation reaction leads to ring closure and formation of the tricyclic phosphorane ring systems **8** - **11** and **12** - **14** (Eq. (3) and (4)).

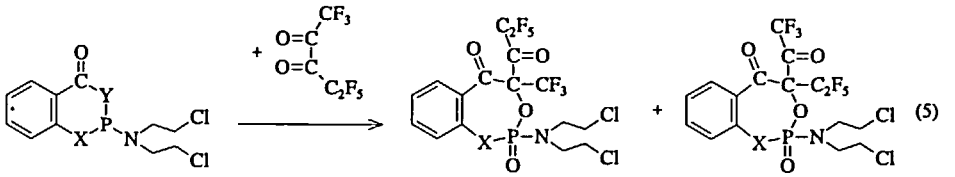


(3)

(4)

The structures of the tricyclic n-benzyl-, p-fluorobenzyl-, and p-chlorobenzyl-phosphorane derivatives **8** - **10**, involving the phosphorus atom as a spiro center, linking one six-membered and two five-membered rings together, were confirmed by single crystal X-ray structure determinations [13].

In the reaction of **1** and **15** with TMPE, insertion of the diketones into the heterocycle of **1** and **15** with formation of **16** and **17**, involving dioxa- and oxazaphosphepine ring systems, was found to take place. Compounds **16** and **17** were obtained as mixtures of the isomers **16a** and **16b**, and **17a** and **17b** (Eq.(5)).



X = Y = O 1 16a X = NCH_3 16b

X = NCH_3, Y = O 15 17a X = O 17b

(5)

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We thank Dr. A. A. Kadyrov for the synthesis of the oxazaphosphepinones **16** and **17** and Dipl.-Chemiker R. Sonnenburg for drawing the formulae.

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