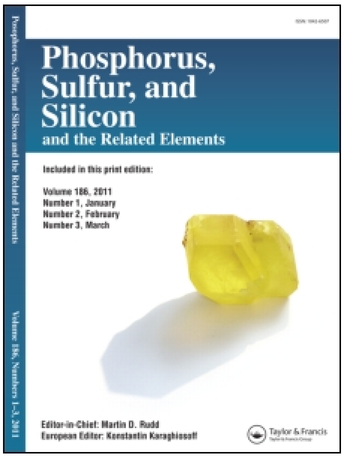

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A New Approach to The Synthesis of Phosphoranes Based on the Reaction of Benzo[*d*]-1,3,2-Dioxaphospholes, Having β- or γ-Unsaturated Group in a Substituent, with Compounds Containing Multiple Bonds

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A New Approach to The Synthesis of Phosphoranes Based on the Reaction of Benzo[*d*]-1,3,2-Dioxaphospholes, Having β- or γ-Unsaturated Group in a Substituent, with Compounds Containing Multiple Bonds

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We developed a new approach to the synthesis of phosphoranes and carbaphosphatranes on the basis of the reaction of benzo[d]-1,3,2-dioxaphospholes, having β- or γ-unsaturated group in a substituent, with such compounds containing multiple bonds, such as hexafluoroacetone, chloral, and diethylacetylenedicarboxylate.

Keywords Phosphorane; benzo-1,3,2-dioxaphosphole derivatives; hexafluoroacetone; chloral; diethylacetylenedicarboxylate; carbaphosphatranes; X-ray analysis

INTRODUCTION

It is known that the P–(III) derivatives, containing such a group as NCO, NCS, C≡CR, RC = CR_2 bonded with phosphorus, easily react with carbonyl compounds or imines to give various P-heterocycles.[1,2] The formation of the intermediate P^+—C—O^- or P^+—O—C^- bipolar ions and the intramolecular attack of anionic moiety on unsaturated substituent at phosphorus are postulated in these reactions and lead to the final P-heterocycles. Here, we attempted to extend this approach to

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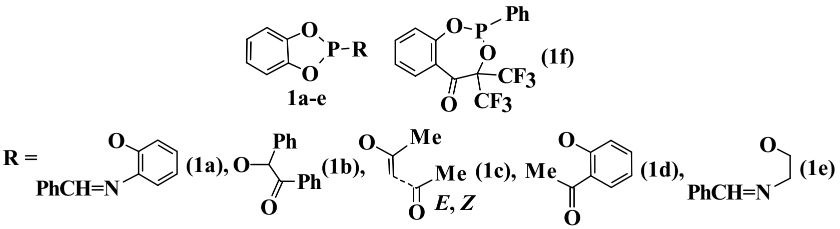
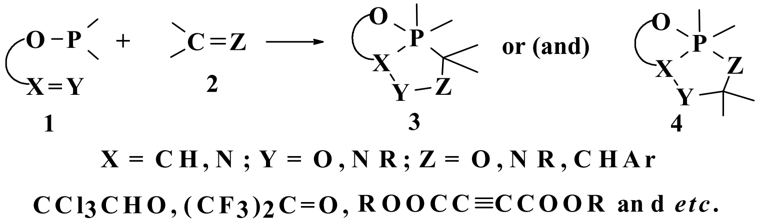
the relatively stable P-(III) derivatives **1a–e**, containing a substituent not bonded directly with phosphorus (Scheme 1). Derivatives **1a–e**, containing C = O or C = N bond in β- or γ-position, were obtained by the phosphorylation of 2-N-benzylidenaminophenol, benzoine, acetylacetone, and some other hydroxycarbonyl compounds in presence of a base.



SCHEME 1

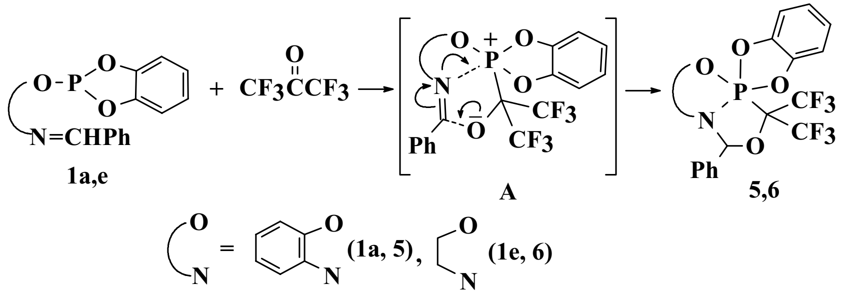
We believed that the various types of phosphoranes **3, 4** could be obtained in the reaction of compounds **1a–e** with such unsaturated derivatives **2** as chloral, hexafluoroacetone, acetylenedicarboxylic acid diethyl ester, and others (Scheme 2). We found that the anionic moiety of intermediate P^{+}—C—O^{-} or P^{+}—O—C^{-} bipolar ions will attack the unsaturated substituent at phosphorus via an intramolecular method.



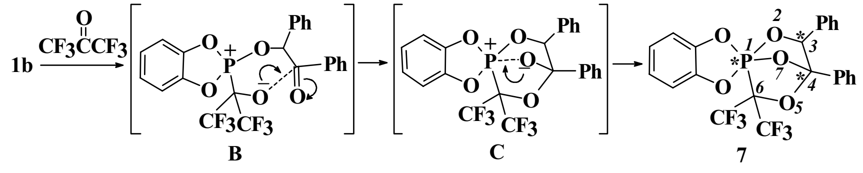
SCHEME 2

The suggestion mentioned above was firstly verified using the P(III)derivatives **1a**, **e**, containing N = C bond in γ-position, and hexafluoroacetone. The tricyclic phosphoranes 5 (*m/z* 501 $[M]^{+\bullet}$, δ_P −3.1 ppm) and 6 (*m/z* 453 $[M]^{+\bullet}$, δ_P −3.5 ppm), having phosphorus–carbon bond were obtained with the yields of 47 and 87%. The reaction is likely to include an intermediate formation of bipolar ion **A** with P–C bond and intramolecular interaction of O^{-} with C=N bond (Scheme 3).[3]

We obtained closely related results in the reaction of phosphole **1b**, having a carbonyl group in the β-position.[4] Phosphorane **7** (*m/z* 516 $[M]^{+\bullet}$, δ_P −21.5 ppm) was isolated as a single diastereoisomer, and the



SCHEME 3

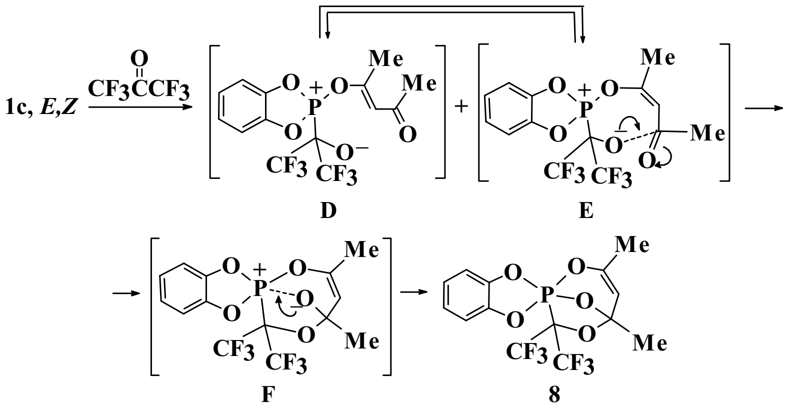


SCHEME 4

configuration of phosphorus and carbons has been determined by single crystal X-ray diffraction (racemate, $C^3_RC^4_SP^1_R/C^3_SC^4_RP^1_S$, d_{P-C} 1.891(3) Å). The reaction probably involves the initial formation of a bipolar ion with P—C bond **B** (Scheme 4), in which an intramolecular attack of the alkoxide anion at the carbonyl group then occurs to give the betaine **C**. The latter is stabilized by attacking the phosphorus atom to give spirophosphorane **7** as the end product formed with a high stereoselectivity.

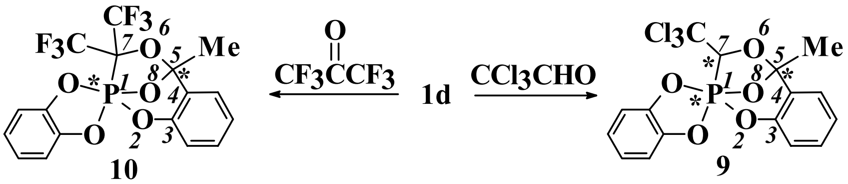
We found that the isomeric mixture of compound **1c**, containing a carbonyl group at the γ-position to the phosphorus atom in the exocyclic substituent was capable of reacting with hexafluoroacetone by the intramolecular cyclization involving this group[4] (Scheme 5).

Although the geometrical situation in the *E*-isomer does not favor the reaction with hexafluoroacetone occurring as intramolecular cyclization, both isomers react to give a single compound **8** (*m/z* 404 $[M]^{+\bullet}$, δ_P −25.0 ppm, d_{P-C} 1.894(4) Å). We assume that the reaction begins with nucleophilic interaction of the phosphorus atom and the carbonyl group of hexafluoroacetone to give bipolar ions **D** and **E**. Presumably, bipolar ion **D** can be transformed into ion **E**, which is removed from the equilibrium mixture due to fast intramolecular attack at the exocyclic carbonyl group to give bipolar ion **F**. The subsequent intramolecular attack of the alkoxide anion at the phosphorus atom results in phosphorane **8** as the final product (its crystal structure



SCHEME 5

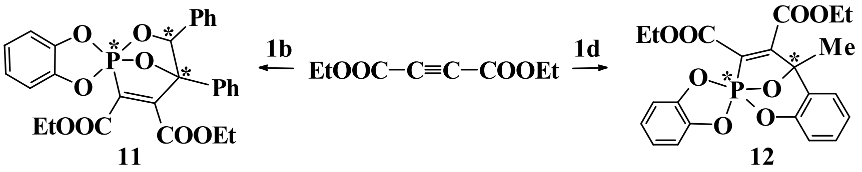
is shown in Figure 1). Phosphorylated derivative **1d** obtained from 2-hydroxyphenylmethylketone reacts with chloral and hexafluoroacetone to gives phosphoranes **9** (*m/z* 420 $[M]^{+\bullet}$, δ_P −25.9 ppm), **10** (*m/z* 440 $[M]^{+\bullet}$, δ_P −23.6 ppm, d_{P-C} 1.926(3) Å) with carbon–phosphorus bond with high stereoselectivity (Scheme 6). The configuration of phosphorus and carbons in compound **9** has been determined by single crystal X-ray diffraction (racemate, $C^{5}_{S}C^{7}_{S}P^{1}_{R}/C^{5}_{R}C^{7}_{R}P^{1}_{S}$, d_{P-C} 1.856(2) Å). The geometry of the molecule **10** is shown in Figure 2. The reaction is likely to involve the formation of the intermediates that are similar to those mentioned above.



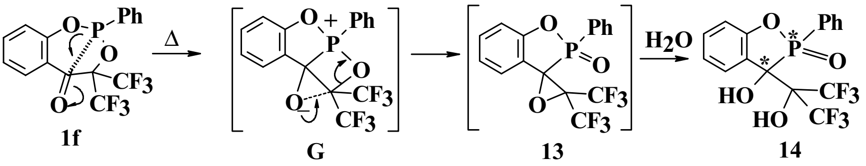
SCHEME 6

Acetylenedicarboxylic acid diethyl ester was found to react with phospholes **1b**, **1d** to give spirophosphoranes **11** (*m/z* 520 $[M]^{+\bullet}$, δ_P −18.0 ppm), **12** (*m/z* 444 $[M]^{+\bullet}$, δ_P −25.4 ppm) (Scheme 7). Here, the formation of phosphorus–carbon and carbon–carbon bonds occurs.

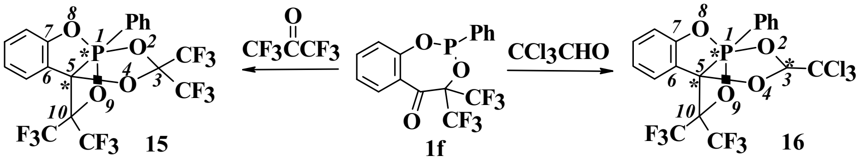
Benzophosphepine **1f** contains an endocyclic carbonyl group activated by two trifluoromethyl substituents at the β-position. This compound is relatively stable in the ordinary conditions, however it is subjected to the unusual transformation under heating (Scheme 8).



SCHEME 7



SCHEME 8



SCHEME 9

Intermediate spiran structure **13** is unstable and the epoxy cycle easily opens under the action of water to form dihydroxyphosphole **14** (*m*/*z* 412 $[M]^{+\bullet}$, δ_P 60.4 ppm). Intramolecular attack of phosphorus on carbonyl group of phosphonite **1f** is likely to occur and gives intermediate

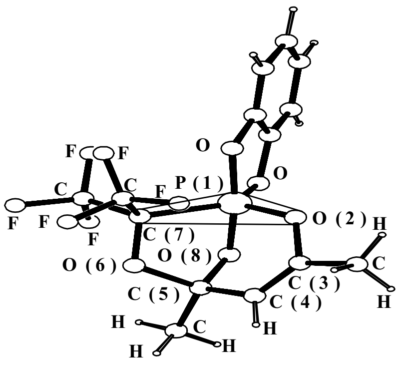


FIGURE 1 Geometry of molecule 8.

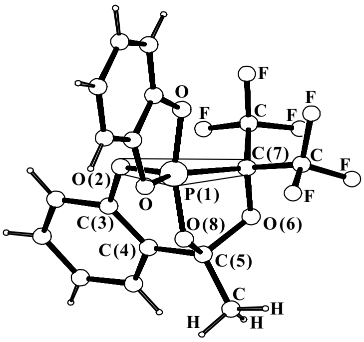


FIGURE 2 Geometry of molecule 10.

betaine **G** containing five- and four-membered heterocycles, annelated along the P–C bond.

The unusual propeller-like carbaphosphatranes **15** (*m/z* 560 $[M]^{+\bullet}$, δ_P 9.0 ppm), **16** (δ_P 4.6 ppm) were obtained in the reaction of **1f** with hexafluoroacetone and chloral (Scheme 9). These structures contain three small cycles, annelated along the P—C bond. The phosphorus atom and endocyclic carbonyl group take part simultaneously in the course of the reaction.

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