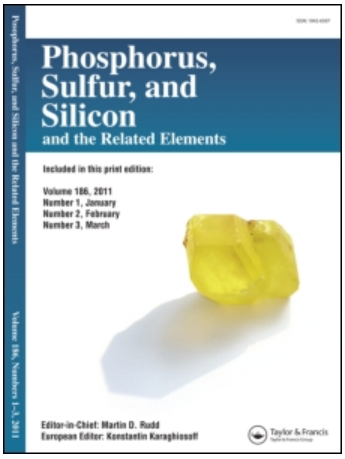

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USE OF TIN DERIVATIVES FOR THE SYNTHESIS OF POLYPHOSPHAZENES FEATURING PHOSPHORUS-CARBON BONDS

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Abstract Palladium(0) catalyzed gem-dimethylation of hexachlorocyclotriphosphazene with tetramethylstannane, as well as the allylation of N-dichlorophosphoryl-P-trichloromonophosphazene and of poly(dichloro)phosphazene by allyltrialkylstan-nane under irradiation are described.

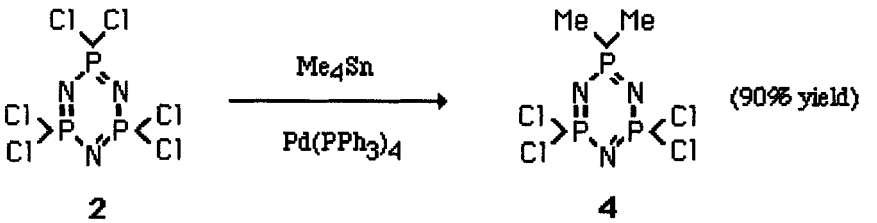
INTRODUCTION

In recent years one of the most rapidly expanding branches of materials science has been the area of inorganic polymers.[1] Phosphazene polymers are the most highly developped, surpassing the silicones in structural variety.[1,2] Their chemical and physical properties are due to their backbone of alternating phosphorus and nitrogen, but are greatly influenced by the nature of the side groups.[1,2] The synthesis of high-polymeric phosphazenes with alkyl or aryl side groups is of primary importance since it is expected that the stability of the P-C bonds will enhance the thermal and chemical stability of the polymers which would be isoelectronic/isostructural to polysiloxanes.[3] A few synthetic methods have been reported,[4] but none of them are effective from the only really available precursor, namely the poly(dichlorophosphazene) **1**.
Here we report the gem-dimethylation of hexaachlorocyclotriphosphazene, and the allylation of N-dichlorophosphoryl-P-trichloromonophosphazene and poly(dichloro)-phosphazene using tin reagents.

RESULTS AND DISCUSSION

Derivatives of the types R_4Sn or R_3SnR' are known to react with carbon-halogen bonds, in the presence of a catalytic amount of zerovalent palladium complexes, with the formation of carbon-carbon bonds.[5] The halophilicity of tin is, of course, the driving force of these reactions. A very few transformations of this type have already been reported in phosphorus chemistry but none of them were selective.[6]

The substitution reactions of polymers are often complex. Thus, it is useful to carry out initial studies with small molecule model compounds. In the field of polyphosphazenes two models can be used before attempting the method on poly(dichloro)phosphazene **1** : the hexachlorocyclotriphosphazene **2**[7] and the N-dichlorophosphoryl-P-trichloromonophos- phazene **3**.[8] Both of them are precursors of **1**. We first performed the palladium-catalyzed methylation of **2** which appeared to occur at 120 °C. After 16 hours, total conversion of **2** was observed and the gem-dimethyltetrachlorocyclotriphosphazene **4**[9] was obtained after purification as a white solid in 90 % yield.

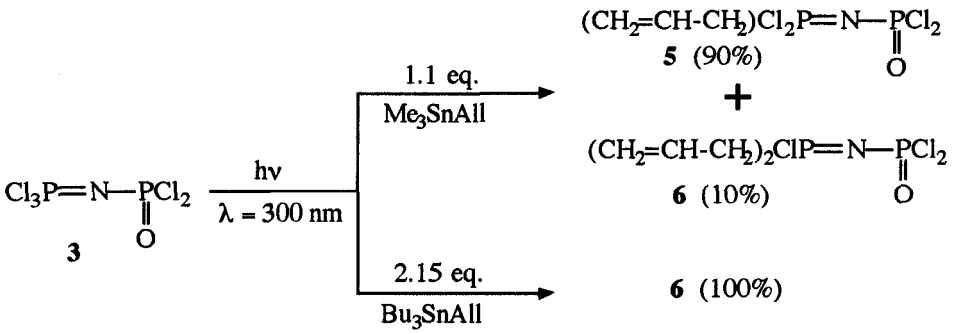


2 **4**

Unfortunately, all attempts to generalize this synthetic approach to poly(dichloro)phosphazene **1** or even to N-dichlorophosphoryl-P-trichloromonophospha- zene **3** failed. After a few minutes, a black precipitate was observed indicating the destruction of the catalyst with formation of palladium metal.

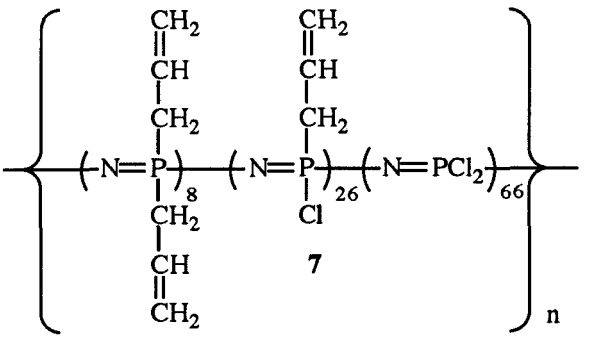
Since allyltrialkylstannanes are known to transfer the allyl group by a radical process,[10] we tried to react hexachlorocyclotriphosphazene **2** with allyltrimethylstannane in the presence of a radical initiator. No clean reaction occured. However, in marked contrast, when N-dichlorophosphoryl-P-trichloromonophosphazene **3** was photolysed at 300 nm in the presence of 1.1 equivalent of allyltrimethylstannane, a 90/10 mixture of dichlorophosphoryl-P-allyldichloromonophosphazene **5** and dichlorophosphoryl-P-diallylchloromonophosphazene **6** was obtained. After distillation in the presence of irganox, **5** was isolated in 81% yield. In the same way, the use of 2.2 equivalents of allyltributylstannane allowed the synthesis of the disubstituted derivative **6** in 85 %

isolated yield (Scheme 1). The radical mechanism of these reactions was clearlydemonstrated since no substitution occurs in the presence of a radical inhibitor (benzoquinone), whereas **5** and **6** were also obtained by heating the reaction mixture in the presence of azobisdiisobutyronitrile.



(SCHEME 1)

These results prompted us to try the photochemical reaction of allyltributylstannane with poly(dichlorophosphazene) **1**. It quickly appeared that 0.75 equivalent of tin reagent per chlorine atom was a maximum, otherwise cross-linking, giving rise to unsoluble material, took place. Three signals were present on the ^{31}P NMR spectrum at -19, +8 and + 18 ppm in a 33/13/4 ratio. These signals can be assigned to PCl_2, AllPCl and All_2P groups respectively, and thus the structure of the polymer **7a** obtained is of type:



Of particular interest the comparison of the value of the intrinsec viscosity of this partially allyl-substituted polymer **7** (η = 27 mL/g) with that of the starting material (η =

14 mL/g) shows that the skeleton has not been destroyed.

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