Tetrahedron Letters, Vol. 33, No. 52, pp. 8095-8098, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

Use of Tin Derivatives for Selective Allylation and Methylation of Halogenophosphorus Compounds

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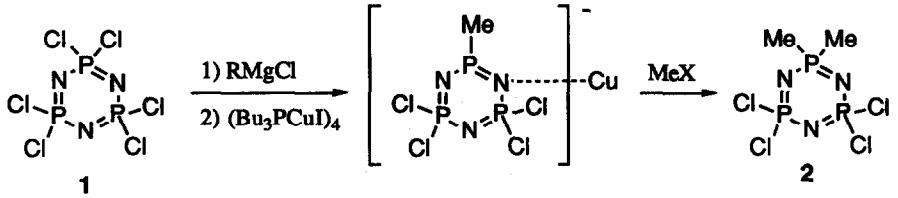
Abstract: Palladium(0) catalyzed gem-dimethylation of hexachlorocyclotriphosphazene with tetramethylstannane is described as well as the high yield monoallylation of halogenophosphorus or -boron compounds by allyltrialkylstannanes under photolytic conditions.

It is well known that tin derivatives of the types R_4Sn or R'_3SnR react with carbon-halogen bonds, in the presence of a catalytic amount of zerovalent palladium complexes, with the formation of carbon-carbon bonds.[1]

The formation of phosphorus-carbon bonds is a crucial problem especially in the field of polyphosphazenes.[2] A considerable amount of fundamental and applied research has been conducted on hexachlorocyclotriphosphazene **1**, the polymerization of which affords the starting material for the synthesis of a variety of polyphosphazenes.[3] The substitution of the chlorine of **1** by amino, alkoxy or aryloxy groups is quite easy, but in contrast, the alkylation of **1** is very difficult.[2] Organometallic reagents such as methyllithium cause rupture of the ring with formation of acyclic "ring opened" phosphazenes.[4] So far, only one reaction pathway has been satisfactory developed as illustrated in the following scheme.[5]



Here we report the straigthforward synthesis of gem-dimethylcyclotriphosphazene, as well as some examples of monoallylation of polyhalogenophosphanes and -boranes.

The palladium-catalyzed methylation of hexachlorocyclotriphosphazene **1** was carried out as follows: A THF solution (5 mL) of **1** (3.64 g, 10.4 mmol), tetramethylstannane (10.37 g, 58 mmol), and tetrakis(triphenylphosphane)palladium (0.24 g, 0.2 mmol) was heated in a bomb at 120 °C for 16 hours. Total conversion of **1** was observed. The gem-dimethyltetrachlorocyclotriphosphazene **2** precipated as a white solid which was purified by several washings with THF at 0°C (90% yield). The spectroscopic data for **2** were in agreement with those reported in the literature.[5] No further substitution occured even when the Me_4Sn / **1** ratio was increased to 20.

$$\mathbf{1} \xrightarrow[Pd(PPh_3)_4]{Me_4Sn} \mathbf{2} \quad (90\%\ \text{yield})$$

This favourable result led us to reinvestigate the well-known reaction of P-X bonds with R_4Sn.[6] Surprisingly, under the same experimental conditions, simple chlorophosphanes were not methylated. Moreover, we were not able to transfer the ethynyl group (otherwise known to be the easiest one to transfer)[1] using the tin-palladium(0) method.

However, we discovered that heating chlorodiphenylphosphane oxide **3** with allyltrimethyltin led to the corresponding allyldiphenylphosphane oxide **4**[7] along with trimethylchlorostannane. Since this reaction was faster in the presence of a radical initiator (AIBN) and blocked by a radical inhibitor (benzoquinone), the radical character of the substitution was clear.[8] Therefore, it appears that the best results were obtained under photolytic conditions. In a typical experiment, a degassed toluene solution (10 mL) of trimethyl- or tributylallylstannane (1 mmol) and the halogenophosphorus derivatives **3**, **5**, **7**, **9**, or **11** (1 mmol) was irradiated at 300 nm for 8 to 70 hours. Removal of the solvent followed by fractional distillation afforded derivatives **6**,[9] **8**,[10] **10**,[11] **12**[11] in 75 to 92 % isolated yields; allyldiphenylphosphane oxide **4** was obtained as a white solide after filtration and several washings with pentane at 0 °C, in near quantitative yield. The choice of the tin allylating reagent depends on the boiling point of the product (Table).

Table: Monoallylation of phosphorus and boron derivatives.

substrate	tin reagent	product	yield (%)
$Ph_2P(O)Cl$ **3**	$Me_3SnAllyl$	$Ph_2P(O)Allyl$ **4**	95
Cl_3P **5**	$Bu_3SnAllyl$	$Cl_2PAllyl$ **6**	75
$Cl_3P(O)$ **7**	$Bu_3SnAllyl$	$Cl_2P(O)Allyl$ **8**	85
Cl_2PCHCl_2 **9**	$Bu_3SnAllyl$	$Cl_2CHP(Cl)Allyl$ **10**	92
$Cl_2PN(iPr)2$ **11**	$Bu_3SnAllyl$	$(iPr)_2NP(Cl)Allyl$ **12**	85
$PhBCl_2$ **13**	$Bu_3SnAllyl$	$PhB(Cl)Allyl$ **14**	90

Some advantages of this method have to be underlined: better yields are obtained for the already known monoallyl phosphorus compounds **6** and **8**; selective allylation at phosphorus in the case of **9**; reactions are easily carried out and can be monitored by ^{119}Sn NMR ($Me_3SnAllyl$ -2.5; $Bu_3SnAllyl$ -18.2; Me_3SnCl +145.6; Bu_3SnCl +150.7 ppm). Lastly, it should be noted that the reaction is also efficient for chloroborane: allylphenylchloroborane **14**[11] was obtained after distillation in 90% yield (Table).

Acknowledgment: This work was supported by the CNRS and by ATOCHEM (Groupe Elf-Aquitaine).

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11. Analytical data for new compounds. (Dichloromethyl)allylchlorophosphane **10** bp : 135°C / 6 mm Hg; ^{31}P NMR $\{^1H\}(C_6D_6)$: δ = 88.0 (s) ppm; ^1H NMR (C_6D_6) : δ = 2.38 (dd, J_{HH} = 7.70 Hz, $^2J_{HP}$ = 8.73 Hz, 2H, $-CH_2-$), 4.85-4,96 (m, 2H, $=CH_2$), 5.28 (d,$^2J_{HP}$ = 7.40 Hz, 1H), 5.35-5.56 (m, 1H, =CH-). ^{13}C NMR $\{^1H\}(CDCl_3)$: δ = 35.7 (d, $^1J_{CP}$ = 35.1 Hz ,$-CH_2-$), 70.9 (d, $^1J_{CP}$ = 59.6 Hz, $CHCl_2$), 120.5 (d, $^3J_{CP}$ = 8.3 Hz, $CH_2=$), 128.1 (d, $^2J_{CP}$ = 6.3 Hz, =CH). Anal. Calcd. for $C_4H_6Cl_3P$: C, 25.08; H, 3.14. Found: C, 25.01; H, 3.08. Diisopropylamino)allylchlorophosphane **12** bp : 50°C / 0.2 mm Hg; ^{31}P NMR $\{^1H\}(C_6D_6)$: δ =129.2 (s) ppm; ^1H NMR (C_6D_6) : δ = 1,05 (d, J_{HH} = 12 Hz, 6H, CH_3), 1.18 (d, J_{HH} = 12 Hz, 6H, CH_3), 2.82 (m, 2H, $-CH_2-$), 3.50 (m, 2H, CH-N), 5.01-5.23 (m, 2H, $=CH_2$), 5.42-5.62 (m, 1H, =CH-). ^{13}C NMR $\{^1H\}(CDCl_3)$: δ = 24.1 (d, $^3J_{CP}$ = 6.3 Hz, CH_3), 41.4 (d, $^1J_{CP}$ = 28.5 Hz ,$-CH_2-$), 45.3 (d, $^2J_{CP}$ = 7.6 Hz , N-CH), 118.9 (d, $^3J_{CP}$ = 11.3 Hz, $CH_2=$), 131.2 (d, $^2J_{CP}$ = 12.8 Hz, =CH-). Anal. Calcd. $C_9H_{19}NClP$: C, 52.05; H, 9.16; N, 6.75. Found: C, 51.98; H, 9.11; N, 6.80. Allylphenylchloroborane **14** bp : 80°C / 3 mm Hg; ^{11}B NMR (C_6D_6) : δ = 72,9 (s) ppm. ^1H NMR (C_6D_6): δ = 2.47 (d , J_{HH} = 7.13 Hz , 2 H, $-CH_2-$), 4.90-5.10 (m, 2 H, $=CH_2$), 5.74-6.16 (m, 1 H, =CH-), 7.15 (m, 2 H, *o*-H), 7.88 (m, 3 H, *p,m*-H); ^{13}C NMR $\{^1H\}(C_6D_6)$: δ = 28.2 (s ,$-CH_2-$), 116.4 (s, $CH_2=$), 128.2 (s, =CH-), 133.8 (s, *p*-C), 134.2 (s, *m*-C), 136.3 (s, *o*-C). Anal. Calcd. for $C_9H_{10}ClB$: C, 65.73; H, 6.09. Found: C, 65.70; H, 6.08.

(Received in France 21 September 1992)