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

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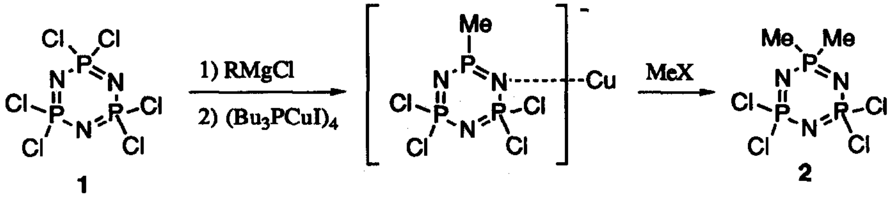
Abstract: Palladium(0) catalyzed gem-dimethylation of hexachlorocyclotriphosphazene with tetramethylstannane is described as well as the high yield monoallylation of halogenophosphorus or -boron compounds by allyltrialkylstannanes under photolytic conditions.

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.

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

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 (%)
$\mathrm{Ph_2P(O)Cl}$ **3**	$\mathrm{Me_3SnAllyl}$	$\mathrm{Ph_2P(O)Allyl}$ **4**	95
$\mathrm{Cl_3P}$ **5**	$\mathrm{Bu_3SnAllyl}$	$\mathrm{Cl_2PAllyl}$ **6**	75
$\mathrm{Cl_3P(O)}$ **7**	$\mathrm{Bu_3SnAllyl}$	$\mathrm{Cl_2P(O)Allyl}$ **8**	85
$\mathrm{Cl_2PCHCl_2}$ **9**	$\mathrm{Bu_3SnAllyl}$	$\mathrm{Cl_2CHP(Cl)Allyl}$ **10**	92
$\mathrm{Cl_2PN(iPr)2}$ **11**	$\mathrm{Bu_3SnAllyl}$	$\mathrm{(iPr)_2NP(Cl)Allyl}$ **12**	85
$\mathrm{PhBCl_2}$ **13**	$\mathrm{Bu_3SnAllyl}$	$\mathrm{PhB(Cl)Allyl}$ **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 ($\mathrm{Me_3SnAllyl}$ -2.5; $\mathrm{Bu_3SnAllyl}$ -18.2; $\mathrm{Me_3SnCl}$ +145.6; $\mathrm{Bu_3SnCl}$ +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).

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References and Notes

1. (a) Stille, J. K. *Pure and Appl. Chem.* **1985**, *57*, 1771; (b) Stille, J. K. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508.
2. (a) Neilson, R. H.; Wisian, P. *Chem. Ber.* **1988**, *88*, 541; (b) Allcock, H. R.; Chu, C. T. *Macromolecules* **1979**, *12*, 551; (c) Allcock, H. R.; Desorcie, J. L.; Harris, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 2814; (d) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *8*, 541.
3. For examples, see: (a) Zeldin, M.; Wynne, K. J.; Allcock, H. R. "Inorganic and Organometallic Polymers", *ACS Symposium Series*, **1988**; (b) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351; (c) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, **1972**.
4. (a) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119; (b) Harris, P. J.; Fadeley, C. L. *Inorg. Chem.* **1982**, *22*, 561.
5. Allcock, H. R.; Harris, P. J.; Connoly, M. S. *Inorg. Chem.* **1981**, *20*, 11.
6. Bmagilov, R. K.; Razumov, A. I.; Yafavava, R. L. *Zh. Obshch. Khim.* **1972**, *42*, 1248; Vinokurava, G. M. *Zh. Obshch. Khim.* **1967**, *37*, 1652; Novikova, Z. S.; Efimova, E. A.; Lutsenko, I. F. *Zh. Obshch.*

Khim. **1968**, *38*, 2345; Proskurina, M. V.; Novikova, Z. S.; Lutsenko, I. F. *Dokl. Akad. Nauk. SSSR* **1964**, *159*, 619; Hartmann, H. *Ann. Chem.* **1968**, *714*, 1; Siebert, W.; Davidsohn, W. E.; Henry, M. C. *J. Organomet. Chem.* **1969**, *17*, 65; Ashe, A. J., III *J. Am. Chem. Soc.* **1971**, *93*, 3293.

7. (a) Arbuzov, A. E.; Nikonorov, K. V. *Zh. Obshch. Khim.* **1948**, *18*, 2008; (b) Martin, J. D.; Griffin, E. G. *J. Org. Chem.* **1965**, *30*, 4034; (c) Mastryukova, T. A.; Genkina, G. K.; Kalayanova, R. M.; Shchubina, T.M.; Petrovskii, P. V.; Kabachnik, M. I. *Zh. Obshch. Khim.* **1978**, *48*, 263.
8. (a) Grignon, J.; Servens, C.; Pereyre, M. *J. Organometal. Chem.* **1975**, *96*, 225; (b) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829.
9. (a) Razumov, A. I.; Liober, B. G.; Gazizov, M. B.; Khammatova, Z. M. *Zh. Obshch. Khim.* **1964**, *34*, 1851; (b) Razumov, A. I.; Liober, B. G.; Zykova, T. V.; Bambushek, I. Ya. *Zh. Obshch. Khim.* **1970**, *40*, 1704.
10. (a) Knunyants, I. L.; Neimysheva, A. A. *Zh. Obshch. Khim.* **1964**, *34*, 1851; (b) Morita, T.; Okamoto, Y.; Sakurai, H. *Chem. Lett.* **1980**, 435.
11. Analytical data for new compounds. (Dichloromethyl)allylchlorophosphane **10** bp : 135°C / 6 mm Hg; ^{31}P NMR {^{1}H}(C_6D_6) : $\delta = 88.0$ (s) ppm; ^{1}H NMR (C_6D_6) : $\delta = 2.38$ (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 {^{1}H}($CDCl_3$) : $\delta = 35.7$ (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 {^{1}H}(C_6D_6) : $\delta = 129.2$ (s) ppm; ^{1}H NMR (C_6D_6) : $\delta = 1{,}05$ (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 {^{1}H}($CDCl_3$) : $\delta = 24.1$ (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) : $\delta = 72{,}9$ (s) ppm. ^{1}H NMR (C_6D_6): $\delta = 2.47$ (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 {^{1}H}(C_6D_6) : $\delta = 28.2$ (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.

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