Synthesis of New *gem*-Dialkyltetrachlorocyclophosphazenes *via* 'Metallophosphazene' Intermediates

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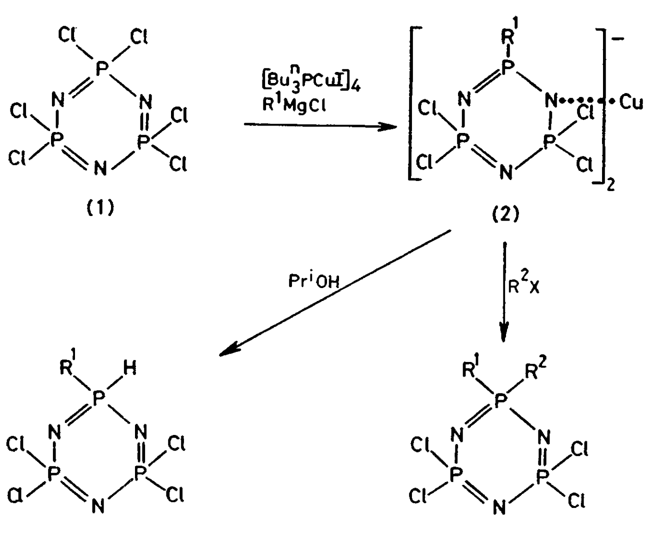
Summary New alkylhalogenocyclophosphazenes, including those with unsaturated alkyl groups, have been prepared by the interaction of hexachlorocyclotriphosphazene with Grignard reagents and $[Bu^n_3PCuI]_4$, followed by treatment with alkyl halides.

IN an earlier communication[1] we described the synthesis of hydridocyclophosphazenes, $N_3P_3Cl_4HR$ (**3**) by the interaction of $(NPCl_2)_3$ (**1**) with alkylmagnesium halides in the presence of $[Bu^n_3PCuI]_4$. This reaction was presumed to proceed through the formation of a metallophosphazene intermediate (**2**), which has not yet been isolated. However, we have now demonstrated the broad utility of (**2**) as a synthetic intermediate by the preparation in high yield of a range of hitherto inaccessible *gem*-dialkylcyclotriphosphazenes (**4**). This method is a powerful addition to the available methods[2] for the attachment of organic residues to a phosphazene skeleton through carbon–phosphorus bonds.



Compounds (**4**) are prepared as follows. Hexachlorocyclotriphosphazene (**1**) (5·0 g, 14·37 mmol) and [Bu$^n_3$-PCuI]$_4$ (4·0 g, 2·53 mmol) were stirred in tetrahydrofuran (150 ml) at −80 °C, and the Grignard reagent (56 mmol) was then added dropwise. The reaction mixture was allowed to warm slowly to 25 °C and was then stirred for 14 h to optimize the yield of (**2**). The mixture was then cooled to 0 °C, the alkyl halide (42 mmol) was added, and stirring was continued at 25 °C for a further 20 h. The product (**4**) was isolated in > 70% yield [based on the amount of (**1**)] after recrystallization from n-hexane. All compounds (**4**) were characterized by i.r. and ^{1}H, ^{13}C, and ^{31}P n.m.r. spectroscopy, mass spectrometry, and elemental analyses.

TABLE. Products $N_3P_3R^1R^2Cl_4$ (**4**) formed from copper–phosphazene intremediates.

Grignard reagent R^1MgCl R^1	Organic halide R^2X	R^2 or $R^{2\prime}$ in phosphazene (**4**)[a]
Me	MeI	Me
Me	CH_2=$CHCH_2Br$	CH_2=$CHCH_2$–
Me	CHMe=$CHCH_2Br$	CH_2=CHCHMe–
Me	CH≡CCH_2Br	CH_2=C=CH–
Et	MeI	Me
Pr^n	MeI	Me
Bu^n	MeI	Me
Pr^i	MeI	Me
Pr^i	CH_2=$CHCH_2Br$	CH_2=$CHCH_2$–
Bu^t	MeI	Me
Bu^t	CH_2=$CHCH_2Br$	CH_2=$CHCH_2$–
CH_2=$CHCH_2$–	MeI	Me
CH_2=$CHCH_2$–	CH_2=$CHCH_2Br$	CH_2=$CHCH_2$–

[a] $R^{2\prime}$ = rearranged side chain. R^1 is the same as in the Grignard reagent R^1MgCl.

The versatility of this synthesis is shown by the Table. Of particular interest is the observation that 1-bromobut-2-ene and prop-2-ynyl bromide react with (**2**) by a 1,4-addition route behaviour typical of many organo-copper reagents.[3] Thus, although the structure of (**2**) has not yet been determined unambiguously, its reactivity patterns are compatible with an 'organo-copper'-type intermediate, as suggested in the structure shown.

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