

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

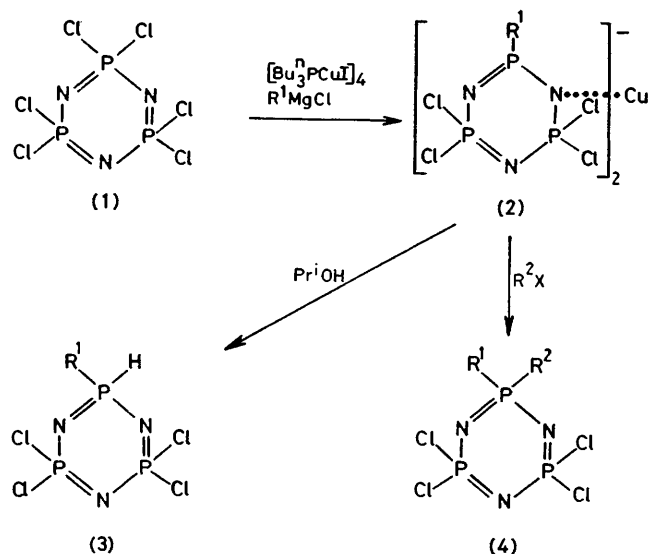
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Summary New alkylhalogenocyclophosphazenes, including those with unsaturated alkyl groups, have been prepared by the interaction of hexachlorocyclotriphosphazene with Grignard reagents and $[\text{Bu}^n_3\text{PCuI}]_4$, followed by treatment with alkyl halides.

In an earlier communication¹ we described the synthesis of hydridocyclophosphazenes, $\text{N}_3\text{P}_3\text{Cl}_4\text{HR}$ (**3**) by the interaction of $(\text{NPCl}_2)_3$ (**1**) with alkylmagnesium halides in the presence of $[\text{Bu}^n_3\text{PCuI}]_4$. 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*-dialkylcyclotripphosphazenes (4). This method is a powerful addition to the available methods² for the attachment of organic residues to a phosphazene skeleton through carbon-phosphorus bonds.



Compounds (4) are prepared as follows. Hexachlorocyclotripphosphazene (1) (5.0 g, 14.37 mmol) and $[\text{Bu}_3\text{PCu}]_4$ (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 ^1H , ^{13}C , and ^{31}P n.m.r. spectroscopy, mass spectrometry, and elemental analyses.

TABLE. Products $\text{N}_3\text{P}_3\text{R}^1\text{R}^2\text{Cl}_4$ (4) formed from copper-phosphazene intermediates.

Grignard reagent R^1MgCl	Organic halide R^2X	R^2 or $\text{R}^{2'}$ in phosphazene (4) ^a
Me	MeI	Me
Me	$\text{CH}_2=\text{CHCH}_2\text{Br}$	$\text{CH}_2=\text{CHCH}_2-$
Me	$\text{CHMe}=\text{CHCH}_2\text{Br}$	$\text{CH}_2=\text{CHCHMe}-$
Me	$\text{CH}\equiv\text{CCH}_2\text{Br}$	$\text{CH}_2=\text{C}=\text{CH}-$
Et	MeI	Me
Pr^n	MeI	Me
Bu^n	MeI	Me
Pr^i	MeI	Me
Bu^i	$\text{CH}_2=\text{CHCH}_2\text{Br}$	$\text{CH}_2=\text{CHCH}_2-$
Bu^i	MeI	Me
$\text{CH}_2=\text{CHCH}_2-$	$\text{CH}_2=\text{CHCH}_2\text{Br}$	$\text{CH}_2=\text{CHCH}_2-$
$\text{CH}_2=\text{CHCH}_2-$	MeI	Me
	$\text{CH}_2=\text{CHCH}_2\text{Br}$	$\text{CH}_2=\text{CHCH}_2-$

^a $\text{R}^{2'}$ = 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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