Ligand Exchange with Organophosphazenes

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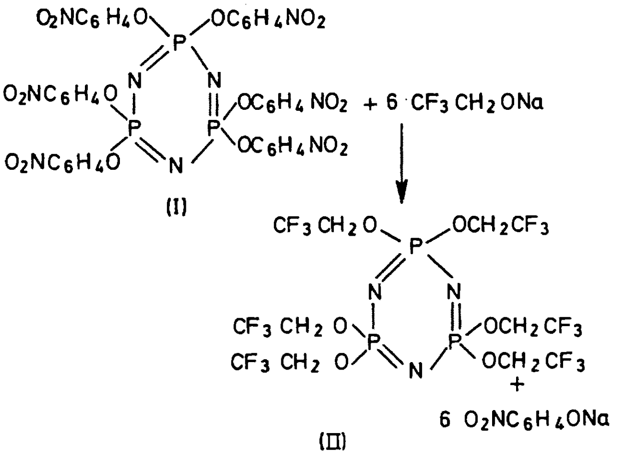
Summary A novel series of displacement reactions between organic nucleophiles and organophosphazenes provides a versatile route for the synthesis of new phosphazenes.

ALTHOUGH much is known about the nucleophilic replacement of halogeno-groups from halogenocyclophosphazenes (phosphonitrilic halides) by ammonia,[1] amines,[2] alkoxides,[3] aryloxides,[4,5] or other halide ions,[6,7] relatively little work has been reported on the displacement of organic ligands from phosphazenes by nucleophiles. Hydrolysis studies reported recently show that hydroxide ion can displace alkoxy- or aryloxy-groups from organophosphazenes,[8,9] but the effects of organic nucleophiles on organophosphazenes have not previously been explored.



Exchange of ligands with various organophosphazenes

	$O_2NC_6H_4O^-$	NH_2^-	$CF_3CH_2O^-$	PhO^-	EtO^-	MeMgI[b]	PhMgI[b]	PhLi[b]	MeLi[b]	$PhNH^-$
$[NP(OC_6H_4NO_2\text{-}p)_2]_3$ (I)[a]	c	+	+	+	+	+	+	+	+	+
$[NP(OCH_2CF_3)_2]_4$	—	—	c	+	+	+	+	+	+	+
$[NP(OCH_2CF_3)_2]_3$ (II)	—	—	c	—[d]	+	—[d]	+[e]	+[e]	+[e]	+
$[NP(OC_6H_5)_2]_3$	—	—	—	c	—	—	—	—	+	+
$[NP(NHC_6H_5)_2]_3$	—	—[f]	—	—	—	—	—	—	—[g]	c

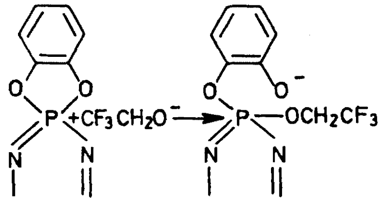
[a] The *o*-nitrophenoxy-derivative behaved in a similar manner to the *p*-nitro compound. [b] With Grignard and organolithium reagents, ring cleavage accompanied ligand exchange. [c] Although exchange of identical ligands was not followed, evidence for the related halogen–halogen exchange process[6] suggests that side-group exchange may occur in these cases also. [d] Exchange occurred but at a much slower rate than with the appropriate tetramers, and reaction times of 48—72 h at 65° are required before the displaced ligand is detected. [e] The tetramer reacts much faster than the trimer. [f] Metallation of the phosphazene NH group apparently occurred without ligand cleavage taking place. [g] Methane evolution occurred before hydrolysis, but the original phosphazene was recovered in a 99% yield.

We now report that displacement reactions occur between organic nucleophiles and organophosphazenes. The ligand exchange reaction is typified by the interaction of sodium 2,2,2-trifluoroethoxide with hexakis-(*p*-nitrophenoxy)cyclotriphosphazene (I) in tetrahydrofuran solvent at 65° to provide a 70% yield of hexakis-(2,2,2-trifluoroethoxy)-cyclotriphosphazene (II). Exchange also takes place at 25°. Cyclophosphazenes which contain both ligands have been isolated from this reaction at 25 and 65°. Sodium phenoxide also reacts with (I) to yield hexakis(phenoxy)-cyclotriphosphazene and mixed phenoxy-*p*-nitrophenoxy-derivatives, and anilide ion interacts with (II) to yield a mixed anilino-trifluoroethoxy-cyclotriphosphazene.

Two series of exchange reactions have been examined; those which involve cyclophosphazenes with two independent ligands at each phosphorus, such as (I) or (II), and those where each phosphorus atom forms part of an exocyclic ring. For the first group, oxy-anions were found to be better nucleophiles toward phosphorus than uncharged primary amines, and substantial differences were observed between the effects of different nucleophiles and different leaving-groups. These differences are illustrated in the Table, where + indicates that exchange occurred with a particular nucleophile within 24 hr. at 65° in tetrahydrofuran and — indicates that no exchange was detected. For the phosphazenes shown, the ease of leaving-group displacement roughly parallels the decrease in basicity of the displaced ligands.

Organometallic reagents such as methylmagnesium iodide, phenylmagnesium bromide, methyl-lithium, or phenyl-lithium displace ligands from $[NP(OC_6H_4NO_2\text{-}p)_2]_3$ (I), $[NP(OC_6H_4NO_2\text{-}o)_2]_3$, $[NP(OCH_2CF_3)_2]_3$ (II), $[NP(OCH_2CF_3)_2]_4$, or $[NP(OPh)_2]_3$ (see Table), but substitution is accompanied by rapid phosphazene ring cleavage to give linear derivatives. These products were identified on the basis of n.m.r. and i.r. spectra. Both lithium and Grignard reagents which contain the same organic grouping apparently give the same ring-cleavage product after hydrolysis. High polymers participate in these reactions in a similar manner to cyclic trimers and tetramers. For example, methyl-lithium displaces piperidine from $[NP(NC_5H_{10})_2]_n$.

When a 5-membered exocyclic ring exists at phosphorus, ring opening and ligand exchange occur readily with a wider variety of reagents. Thus, trifluoroethoxide ion, n-propylamine, diethylamine, and piperidine readily replaced one aryloxy-bond from each phosphorus in tris-(*o*-phenylenedioxy)cyclotriphosphazene, $[NP(O_2C_6H_4)]_3$, as shown in the sequence:



In this reaction, exchange was followed by i.r. and mass spectra and by Schiff base formation with 4-aminoantipyrine.[10] Similar exchanges were observed with tris-(*o*-phenylenediamino)cyclotriphosphazene, $[NP(NH)_2C_6H_4]_3$, but not with tris-(2,2′-dioxybiphenyl)cyclotriphosphazene, $[NP(O_2C_{12}H_8)]_3$, which contains a 7-membered exocyclic ring. This enhanced reactivity in the presence of a 5-membered exocyclic ring is reminiscent of the results of hydrolysis reactions[8] and degradation reactions with *o*-aminophenol.[5]

All these reactions illustrate that particular care must be exercised when examining halogen replacement patterns in organohalogenophosphazenes. It is also clear that displacement reactions such as these provide a valuable new route to the synthesis of a wide variety of hitherto inaccessible organophosphazenes.

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