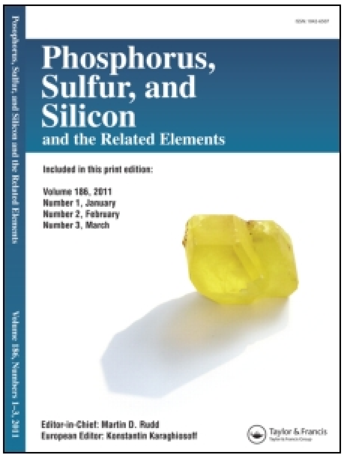

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REACTIONS OF THE HYDROLYZED PHOSPHAZENE $N_3P_3(OCH_2CF_3)_5ONa$

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$N_3P_3(OCH_2CF_3)_5ONa$ reacts readily with compounds which have an active chloride. Examples are *p*-toluenesulfonyl chloride, benzoyl chloride and triphenyldichlorophosphorane. The *p*-toluenesulfonate undergoes further reaction with sodium salts. These reactions describe a novel approach to the synthesis of new substituted phosphazenes.

Stable hydrolysis products of $N_3P_3(OCH_2CF_3)_6$ have been known for a number of years[1] but their reactions have not been investigated. This brief report shows that $N_3P_3(OCH_2CF_3)_5ONa$ (I) reacts with compounds which have active chloride to produce new substituted cyclotriphosphazenes.

RESULTS AND DISCUSSION

Reaction of I with sulfonyl chlorides produced reactive intermediates as the *p*-toluenesulfonate, II, *p*-nitrobenzenesulfonate, III, and the methanesulfonate, IV. Good crystalline material was obtained only after slow crystallization (weeks). If refluxing during synthesis was continued for an extended period $N_3P_3(OCH_2CF_2)_5Cl$ was formed by a reaction of the NaCl by-product with the sulfonate. To illustrate the utility of sulfonated phosphazenes, II was allowed to react with $NaOCH_2CF_3$, $NaOCOCH_3$ and I to form $N_3P_3(OCH_2CF_3)_6$, VII and IX phosphazene products. Reaction of II with *t*-butyl lithium produced *t*-butyl alcohol and a phosphazadiene.

The products of reactions with organic acid chlorides produced a benzoate, V, a toluate, VI, and a terephthalate, X. It was hoped that these would be stable polymer model compounds; however, in the case of the terephthalate, decomposition began to produce phosphazadiene and precipitate acid as soon as the oily products were separated from mixtures. Reaction products of I with isophthaloyl and adipoyl chloride exhibited the same decomposition characteristics and were not characterized.

Table I gives analytical results yields and melting points for pure products. Table II gives IR, ^1H and ^{31}P NMR spectra. The ^{31}P NMR spectra for ring P atoms were sometimes AB_2 type and sometimes ABX type.

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TABLE I

Elemental Analysis, Melting Points and Yields

For $N_3P_3(CH_2CF_3)_5R$		Calc., %			Found, %				
No.	R	C	H	P	C	H	P	M.P., °C	% Yield
II.	$OSO_2C_6H_4CH_3$-*p*	25.46	2.12		25.63	2.21		43	76
III.	$OSO_2C_6H_4NO_2$-*p*	23.09	1.70	11.16	22.97	1.51	11.27	60	75
IV.	OSO_2CH_3	18.22	1.81	12.81	18.39	2.05	12.66	36	
V.	$OCOC_6H_5$	27.18	2.02	12.37	27.47	2.02	12.27	oil	75
VI.	$OCOC_6H_4CH_3$-*p*	28.25	2.24	12.14	28.32	2.41	11.86	oil	85
VII.	$OCOCH_3$							oil	
VIII.	ONa.DIGLYME	23.92	3.02	11.57	23.98	3.04	11.63	94–6	83
Products of different formula									
IX.	$[N_3P_3(OCH_2CF_3)_5]_2O$							oil	
X.	$[N_3P_3(OCH_2CF_3)_5O]_2[COC_6H_4CO]$							oil	
XI.	$[N_4P_3(OCH_2CF_3)_5O]P(C_6H_5)_3$							oil	

TABLE II

Spectroscopic Properties of Products

No.	IR[a], cm^{-1}		^1H NMR[f]		^{31}P NMR[b,e]	
II.	PN	1244 s	CH_4[b,e]	2.49 s	$P(OCH_2CF_3)(OSO_2—)$	8.9 (d o t)
	OSO_2	1400 m	OCH_2CF_3	4.25 m	$P(OCH_2CF_3)$	17.1 (d o d)
				4.38 m	$J_{PP} = 72.84$	
			C_6H_4	7.61 m		
III.	PN	1260 s	OCH_2CF_3[c]	4.31 m	$P(OCH_2CF_3)(OSO_2—)$[c]	13.0 (d o t)
	OSO_2	1400 m	C_6H_4	8.25 m	$P(OCH_2CF_3)_2$	17.3 (d o d)
	NO_3	1560 s			$J_{PP} = 60.80$	
IV.	PN	1260 s	CH_3	3.26 s	$P(OCH_2CF_3)(OSO_2—)$	8.9 (d o t)
	SO_2	1400 m	OCH_2CF_3	4.31 m	$P(OCH_2CF_3)_2$	16.6 (d o d)
					$J_{PP} = 63.76$	
V.	PN	1240 s	OCH_2CF_3[c]	4.32 m	$P(OCH_2CF_3)(O_2C—)$	13.1 (d o t)
		1260 sh	C_6H_5	7.75 m	$P(OCH_2CF_3)_2$	17.5 (d o d)
	CO	1760 s			$J_{PP} = 60.78$	
VI.	PN	1245 s	CH_3[c]	2.48 s		
		1265 s	OCH_2CF_3	4.32 m		
			C_6H_4	7.60 m		
	CO	1755 s				
VII.	PN	1255 s				
	CO	1720 s				
VIII.			OCH_3[d]	3.36 s		
			OCH_2CH_2O	3.58 q		
			OCH_2CF_3	4.32 m		
				4.45 m		
IX.	PN	1260 s	OCH_2CF_3	4.31 m	N_2POPN_2	8.4 (d o t)
					$P(OCH_2CF_3)_2$	16.4 (d o d)
					$J_{PP} = 63.76$	
X.	PN	1250 s	OCH_2CF_3	4.31 m	$P(OCH_2CF_3)(OCO—)$	13.1 (d o t)
					$P(OCH_2CF_3)_2$	17.3 (d o d)
	CO	1690 s	C_6H_4	8.22 m		
XI.[c]			OCH_2CF_3	4.16 m	N_2PO	3.6 t
				4.30 m	$P(CH_2CF_3)_2$	14.4 d
			C_6H_5	7.62 m	$J_{PP} = 50$	
					$P(O)_2(C_6H_5)_3$	32.3 s

[a] In CCl_4 between sodium chloride plates.
[b] In $CDCl_3$.
[c] In CCl_4.
[d] In CD_3COCD_3.
[e] Bruker WP 200.
[f] Varian T-60 unless otherwise specified.

EXPERIMENTAL

All reagents were purchased from Sigma or Aldrich chemical companies and used as received unless otherwise noted. Acetone was dried over anhydrous sodium sulfate before use. Infra-red spectra were obtained on a Perkin-Elmer 727B spectrophotometer. Some ^1H NMR spectra were recorded on a Varian T-60 while other NMR spectra were recorded on a Bruker WP 200 spectrometer[3] operating at 200 MHz (^1H) and 81 MHz (^{31}P). Tetramethylsilane was used as an internal reference for the ^1H measurements and 85% phosphoric acide was used as an external reference for ^{31}P measurements. Elemental analyses were performed by Huffman Laboratories, Inc., Wheat Ridge, CO. Starting materials, $N_3P_3(OCH_2CF_3)_6$ and (I), were prepared by previously reported procedures.[2,4]

Typical Reaction of (I) with active chlorides. A 50 mL acetone solution of *p*-toluenesulfonylchloride (1.45 g, 0.0076 mol) was added dropwise to a 50 mL acetone solution of I (5.00 g, 0.0075 mol). The mixture was stirred for 1 h at 25°C and then refluxed for 4 h. Sodium chloride was filtered from the cooled reaction mixture and the solvent was evaporated under reduced pressure. The residue was dissolved in 20 mL of ethanol, filtered and the filtrate chilled to 0°C before addition of 40 mL of chilled water to cause precipitation. The precipitate was filtered and dried to give 4.79 g (76% yield) of a white crystalline product, $N_3P_3(OCH_2CF_3)_5OSO_2C_6H_5CH_3$-*p*, II.

Typical Reaction of II with metal salts. A 40 mL anhydrous diethyl ether solution of II (0.15 g, 0.00061 mol) was added dropwise to a 50 mL diethyl ether solution of sodium trifluoroethoxide (0.0027 mol). When the addition was complete, the solution was refluxed for 3 h. The cooled solution was filtered into a clean 100 mL beaker and then transferred to a separatory funnel containing 50 mL of cold water. The mixture was thoroughly shaken and 5 mL of saturated sodium chloride solution was added to break the emulsion that formed. The ether layer was collected in a 250 mL Erlenmeyer flask. Anhydrous sodium sulfate (about 5 g) was added and the solution was allowed to stand for 15 min before filtering into a round bottom flask. Ether was evaporated under reduced pressure and the residue was recrystallized from *n*-pentane to give 0.11 g (80% yield) of a white crystalline material, $N_3P_3(OCH_2CF_3)_6$.

Other reactions were conducted in acetone solutions.

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