Phosphonitrilic chloride: 37. Reaction of 1,1-diamino-3,3,5,5-tetrakis (2,2,2-trifluoroethoxy) cyclotriphosphazene with organosilanes

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The Spiro compound $N_3P_3(OCH_2CF_3)_4(NH)_2Si(CH_3)_2$ formed by reaction of 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene $N_3P_3(OCH_2CF_3)_4(NH_2)_2$ and dimethyldichlorosilane $Cl_2Si(CH_3)_2$ is a yellow or orange coloured oil soluble in organic solvents, vapourized at 160°C without decomposition, and not hydrolysed appreciably in boiling water. Linear compounds are formed by reaction of $N_3P_3(OCH_2CF_3)_4(NH_2)_2$ with diphenyldichlorosilane or phenyltrichlorosilane owing to hindrance of the phenyl radical. These compounds are amorphous or tacky solids, soluble in organic solvents and stable to water.

INTRODUCTION

Kireev[1], Zhivukhin[2] and Kajiwara *et al.*[3] reported the formation of rubber or glass like polymers by polycondensation of cyclotriphosphazene and organosilane compounds. Emblem[4] noted the good thermal stability of plastic materials obtained by reaction of dichlorocyclotriphosphazene and various silanol compounds. The break strength of asbestos laminates made with them did not change on heating for long periods at 500°C. Recently, Kajiwara[5] reported a cyclotriphosphazene compound having a four-membered exocyclic Spiro ring. This paper describes the synthesis of cyclotriphosphazene derivates of 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy) cyclotriphosphazene and organochlorosilanes.

EXPERIMENTAL

1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene, $N_3P_3(OCH_2CF_3)_4(NH_2)_2$, prepared from 1,1-diamino-3,3,5,5-tetrachlorocyclotriphosphazene and fluoroethoxide by the method of Lenton[6] was reacted with organosilanes as follows.

(1) $N_3P_3(OCH_2CF_3)_4(NH_2)_2$ (0.02 mol), dimethyldichlorosilane (0.02 mol) and triethylamine (0.01 mol) in 100 ml THF were heated together with vigorous stirring for 2 h at 60° or 20°C. The extent of the reaction was measured by the amount of triethylamine hydrochloride formed. The reaction mixture was separated by filtration, and on vacuum distillation the filtrate gave a yellow or orange coloured oil soluble in organic solvents.

(2) $N_3P_3(OCH_2CF_3)_4(NH_2)_2$ (0.1 mol) and dichlorodiphenylsilane (0.1 mol) were vigorously stirred together in dry N_2 for 140 h at 160°C. The reaction mixture was separated by column chromatography using active α-Al_2O_3 and the product was an amorphous, transparent, adhesive material, soluble in most organic solvents.

(3) $N_3P_3(OCH_2CF_3)_4(NH_2)_2$ (0.062 mol) in 150 ml of dry benzene heated to 40°C was added to 30 ml of benzene containing 0.62 mol of trichlorophenylsilane and the mixture heated at 80°C in dry N_2 for 24 h. The reaction mixture was filtered and the filtrate reacted with 2 g of ethanol and 5 ml of triethylamine at 50°C for 3 h. The product was filtered and distilled and the residue separated by column chromatography.

Molecular weights were measured with a Hitachi Model-117 type osmometer using benzene as solvent. I.r. spectra were recorded on a Shimazu Model-450 type spectrometer (4000–200 cm^{-1}) using the pressed KBr disc technique. ^{31}P n.m.r. and ^{1}H n.m.r. spectra were recorded on a Niphon Denshi Model-100 type spectometer. Viscosity was measured with a Tokisangyo E type viscometer.

RESULTS AND DISCUSSION

The formula of the product (1), obtained by molecular weight and chemical analysis, corresponds to $N_5P_3SiC_{10}F_{12}O_4$. The N–H frequency appears in the region of 3250 cm^{-1} and 1540 cm^{-1}, and the P–N frequency in the P_3N_3 ring appears in the region of 1410 cm^{-1}. The ^{31}P n.m.r. spectrum was typical of an AB_2 system with four

Table 1 The chemical shift and the area ratio of H atom

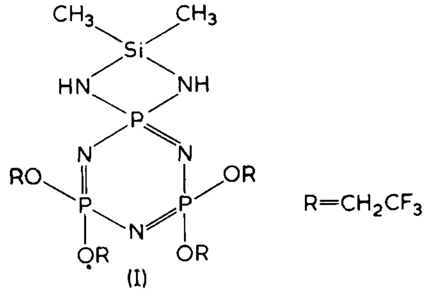
Sample	ArH	$POCH_2CF_3$	$SiOCH_2CH_3$	PNH_2	PNHP	SiOH	$SiCH_2CH_3$
II	2.30–3.30 (m 20H)	5.60–6.30 (m 16H)			6.35–6.70 (m 3H)	6.50 (s 2H)	
III	2.10–3.30 (m 15H)	5.55–6.50 (m 16H)	6.32 (q 2H)	7.10–7.35 (m 2H)	8.80–9.20 (m 3H)	6.85 (s 3H)	8.80 (t 3H)

s, singlet; t, triplet; q, quartet; m, multipet peaks (2.2, 3.3, 4.6, 4.8 ppm) belonging to $P(OCH_2CF_3)_2$, and three peaks (5.2, 6.7, 7.0 ppm) belonging to $P(NH)_2Si$. The substitution reaction can be written as follows:

$$N_3P_3(OCH_2CF_3)_4(NH_2)_2 + Cl_2Si(CH_3)_2 + 2(Et)_3N \longrightarrow$$

$$N_3P_3(OCH_2CF_3)_4(NH)_2Si(CH_3)_2 + 2(Et)_3NHCl$$

The proposed structure of the product (I) is:



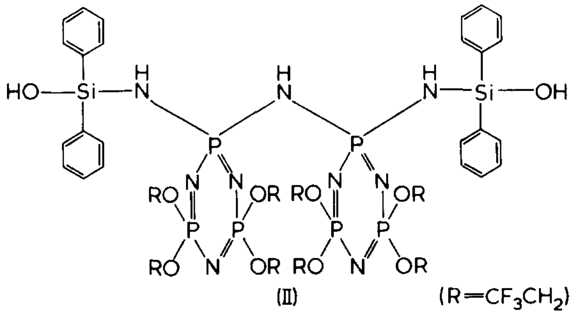
(I)

The variation of the viscosity of the product (I) with temperature corresponds to an activation energy ΔE_{vis} of about 15 kcal/mol. It is reported by Kajiwara[7] that the value of the ΔE_{vis} of some hexaalkoxycyclotriphosphazenes $N_3P_3(OR)_6$ (R = Et, n-Pr, n-Bu) was about 5–7 kcal/mol, and thus it may be presumed that the intermolecular forces are much stronger for the product (I). The product is vapourized at 160°C and is not hydrolysed appreciably in boiling water.

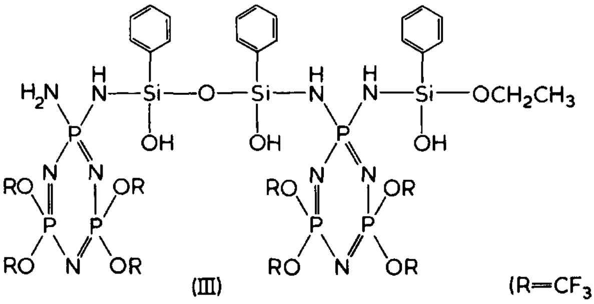
When $N_3P_3(OCH_2CF_3)_4(NH_2)_2$ is reacted with dichlorodiphenylsilane, $Cl_2Si(C_6H_5)_2$, hydrogen chloride evolution is complete at 35% reaction. Ammonium chloride is also produced by reaction of the chloride of dichlorodiphenylsilane and ammonia formed by homocondensation of $N_3P_3(OCH_2CF_3)_4(NH_2)_2$[8]. The infra-red absorption of product (II) showed P–NH and –OH frequencies 3400–3300 cm^{-1} and 1550 cm^{-1}, C_6H_5 at 3050 cm^{-1} and 1590 cm^{-1}, CH_2 at 2960 cm^{-1}, Si–N at 1170 cm^{-1}, P–O–R at 1080 cm^{-1}, P–N at 1240 cm^{-1} and 870 cm^{-1}, respectively. The maximum absorption frequency and the absorption coefficient at 210 nm and 24 000 corresponded to four phenyl groups per molecule. The experimental formula obtained from chemical analysis and molecular weight measurement by g.p.c. is $N_9P_6Si_2C_{40}H_{41}F_{24}O_{10}$. The chemical shift and the area ratio of H atom is shown in *Table 1*. The extent of the reaction between $N_3P_3(OCH_2CF_3)_4(NH_2)_2$ and trichlorophenylsilane, calculated from the amount of triethylamine hydrochloride formed, is about 84%.

The experimental formula of the product (III) obtained by further reaction with ethanol is $N_{10}P_6Si_3C_{36}H_{44}F_{24}O_{13}$. The infra-red absorption spectrum is similar to that of the product (II) and the maximum in the ultra-voilet absorption occurs at 214 nm and the maximum absorption coefficient is about 13 000 corresponding to three phenyl groups per molecule. The chemical shift of the H atom and the area ratio is given in *Table 1*.

Consequently, the structures of the products (II) and (III) are assumed to be:



(II)



(III)

The Spiro ring product such as (A) is easily formed at room temperature when $N_3P_3(OCH_2CF_3)_4(NH_2)_2$ is reacted with dichloromethylsilane or dichlorodimethylsilane, but under the same conditions dichlorodiphenylsilane or trichlorophenylsilane do not react owing to the steric hindrance of the phenyl radical. However, at temperatures above 100°C, products such as (II) or (III) are formed.

REFERENCES

1 Belykh, S. I., Zhiklin, S. M., Krieev, V. V. and Kolenniskov, H. S. *Vysokomol. Soedin. (A)* 1969, **11**, 625

2 Zhinvklin, S. M., Tolstozuzov, V. B. and Yakobson, F. I. *Vysokomol. Soedin.* 1966, **8**, 717

3 Kajiwara, M., Sakamoto, A. and Saito, H. *Angew. Makromol. Chem.* 1975, **46**, 63

4 Emblem, G. H., Oxley, E. C. and Trow, A. S. *Br. Polym. J.* 1970, **2**, 83

5 Kajiwara, M., Makihara, M. and Saito, H. *J. Inorg. Nucl. Chem.* 1975, **37**, 2576

6 Lenton, M. V. and Lewis, B. *J. Chem. Soc. (A)* 1960, p 665

7 Kajiwara, M., Mori, Y. and Saito, H. *Polymer* 1976, **17**, 898

8 Kajiwara, M., Nakashima, K. and Saito, H. *J. Macromol. Sci. (A)* 1977, **11**, 449