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Spiro, ansa-derivatives of cyclotetraphosphazenes with a tetrafluorobutane-1,4-diol

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ABSTRACT

The reaction of the octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ (**1**), in three stoichiometries (1:1, 1:2 and 1:3) with the sodium derivative of the fluorinated diol, 2,2,3,3-tetrafluorobutane-1,4-diol (**2**), in THF solution at room temperature produced seven products, whose structures have been characterized by elemental analysis, mass spectrometry, ^1H, ^{19}F, ^{31}P NMR spectroscopy and by X-ray crystallography, where suitable single crystals were obtained: the mono-spiro compound, $N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)$ (**3**), its ansa isomer (**4**), *cis*- and *trans*-bis-spiro derivatives $N_4P_4Cl_4(OCH_2CF_2CF_2CH_2O)_2$ (**5 and 6**), tris-spiro compound $N_4P_4Cl_2(OCH_2CF_2CF_2CH_2O)_3$ (**7**), its mono-spiro-bis-ansa isomer (**8**) and tetrakis-spiro compound $N_4P_4(OCH_2CF_2CF_2CH_2O)_4$, (**9**). X-ray crystallographic studies confirmed that the structure of the mono-spiro-bis-ansa isomer (**8**) has been reported as a first example in the literature. The results of all reactions were compared with previous work on the reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ with the sodium derivative of the diol (**2**), in a 1:1.2 mole ratio in the in the same solvent, THF, and with the reaction of octafluorocyclotetraphosphazene, $N_4P_4F_8$, with the silyl derivative of the diol (**2**), $(Me_3SiOCH_2CF_2)_2$, in a 1:0.4 mole ratio in THF.

1. Introduction

The reactions of cyclophosphazenes, $N_3P_3Cl_6$ and $N_4P_4Cl_8$ (**1**), with difunctional reagents have been of significant interest especially from the perspective of observing regioisomerism in substitution reactions: spiro, ansa, bridged derivatives and their mixture [1]. The octachlorocyclotetraphosphazatetraene, tetramer (**1**), is more reactive than the hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, the former can also, in principle, give rise to a much larger number of products, and hence determination of structure is also more difficult [2–4] and because of this substitution reactions of tetramer with polyfunctional reagents is relatively limited in the literature [1,2,5–8]. Reaction of **1** with 1,3-propane- and 1,4-butane-diols (in the presence of pyridine to neutralize the HCl formed) predominantly gave spiro derivatives for both of diols, whereas ansa-derivatives were not formed [2]. When the tetramer were reacted with 2,2′-dioxybiphenol, spiro derivatives also obtained [5]. Reaction of **1** with amino-alcohols, di-amines, their –NMe and –NPr^i derivatives, again showed a preference for spiro derivatives, when the linking $–(CH_2)_n–$ group of the reagent consisted of $n = 2, 3$ moieties [2,6,8]. On the other hand, the reactions of 1,1′-ferrocene diol with $N_4P_4Cl_4$ have been investigated [7] and lead to the formation of mono-ansa product 2,4-$N_4P_4Cl_6(FcO_2)$ on the contrary the reactions with the corresponding dithia or diselena derivatives afford monospirocycles [7].

Reaction of octafluorocyclotetraphosphazatetraene, $N_4P_4F_8$, with the dilithiated diol, $CH_2(CH_2OLi)_2$, at −80 °C yielded spiro and ansa-derivatives in the ratio *ca.* 1:5, whereas the reaction of the silyl derivative of 2,2,3,3-tetrafluorobutane-1,4-diol (**2**), $(Me_3SiOCH_2CF_2)_2$, with $N_4P_4F_8$ afforded two products; the mono-spiro derivative, $N_4P_4F_6(OCH_2CF_2CF_2CH_2O)$ and the singly-bridged compound, $(N_4P_4F_7)_2(OCH_2CF_2CF_2CH_2O)$ [1]. However, in our previous work, the reaction of hexachlorocyclotriphospazene, $N_3P_3Cl_6$, with sodium derivative of 2,2,3,3-tetrafluorobutane-1,4-diol (**2**) have leaded six products including spiro and ansa moieties [9] contrast to the reaction of $N_3P_3Cl_6$ with silyl derivative of same diol [10]. The purpose of the present study is to investigate the reaction of the sodium derivative of 2,2,3,3-tetrafluorobutane-1,4-diol (**2**) with $N_4P_4Cl_8$ (**1**) and to compare the results with those obtained previously for the reaction of $N_4P_4F_8$ with the silyl reagent of **2** [1] and the reaction of $N_3P_3Cl_6$ with the reagent **2** [9].

2. Experimental

2.1. Materials

Octachlorocyclotetraphosphazatetraene (Otsuka Chemical Co. Ltd.) was purified by fractional crystallization from *n*-hexane. NaH (Merck, 60% dispersion in mineral oil) was removed by washing with dry *n*-heptane followed by decantation. The following chemicals were obtained from Merck; *n*-hexane (>96%), THF (>99.0%), dichloromethane (>99.0%), *n*-heptane (>99.0%), and acetonitrile (>99.0%). 2,2,3,3-Tetrafluoro-1,4-butanediol was obtained

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from Aldrich and used as received. THF was distilled over a sodium–potassium alloy under argon atmosphere. All reactions were performed under argon atmosphere. THF-d_8 and $CDCl_3$ used for NMR spectroscopy were obtained from Merck.

2.2. Methods

Thin layer chromatography (TLC) was performed on Merck Silica gel plates (Merck 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck 60, 0.063–0.200 mm; for 3 g crude mixture, 120 g silica gel was used in a column of 3 cm in diameter and 110 cm in length). Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. Mass spectra were obtained by a Bruker MicrOTOF LC/MS spectrometer using electro spray ionization (ESI) method; ^{35}Cl values were used for calculated masses. ^{1}H, ^{19}F and ^{31}P NMR in $CDCl_3$ for **3–8,** in THF-d_8 solutions for **9** spectra were recorded on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^{1}H, $CFCl_3$ as an internal reference for ^{19}F and 85% H_3PO_4 as an external reference for ^{31}P NMR measurements. Differential Scanning Calorimetry (DSC) of compounds **9** was performed on a Mettler Toledo DSC 822 instrument from 25 °C to 350 °C at a heating rate of 10 °C/min.

2.3. X-ray structure determinations

Crystallographic data was collected on a Bruker Kappa APEXII diffractometer using Mo Kα radiation (λ = 0.71073 Å). Absorption correction by multi-scan has been applied [11]. Structure was solved by direct methods and refined by full-matrix least squares against F^2 using all data [12]. All non-H atoms were refined anisotropically, while H atoms were generally fixed in idealized positions with their displacement parameters riding on the values of their parent atoms. The crystal quality of compound **8** was extremely poor and the crystal used in the experiment was a small needle of dimensions 0.12 × 0.05 × 0.03, which diffracted weakly and only achieved a data completeness of 77%, despite 150 s exposure times for each image. Although β angle is found as 90°, crystal structure could be achieved only in monoclinic *P*21 asymmetric unit. The general-purpose crystallographic tool PLATON [13] was used for the structure analysis and presentation of the results. The figures were drawn with DIAMONS (Version 3.1) [14].

2.4. Reaction of *1* with 2 at 1:1 ratio

Octachlorocyclotetraphosphazene (1.391 g, 3 mmol) and 2,2,3,3-tetrafluoro-1,4-butanediol (0.486 g, 3 mmol) were dissolved in 100 mL of dry THF under argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (0.24 g, 6 mmol) in 15 mL of dry THF was quickly added to a stirred solution under argon atmosphere. The reaction mixture was stirred for 24 h at room temperature and the reaction followed on TLC silica gel plates using *n*-hexane–dichloromethane (2:1) as the mobile phase. Three products were observed except for starting compound, (**1**). The reaction mixture was filtered to remove the sodium chloride formed and any other insoluble material. The solvent removed under reduced pressure and the resulting colourless oil which composed of 64% **3**, 18% **5**, 7% **6**, 4% **1** and 3% **4** shown by ^{31}P NMR was subjected to column chromatography, using *n*-hexane-dichloromethane (2:1) as the mobile phase. Un-reacted tetramer (**1**) (0.04 g, 3%) was eluted first from the column. The first product is the mono-spiro derivative $[N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)]$ (**3**) (0.82 g, 49%, mp 113 °C). The compound **3** was re-crystallized from *n*-hexane–dichloromethane (2:1). *Anal.* Calc. for $C_4H_4Cl_6F_4N_4O_2P_4$: C, 8.69; H, 0.73; N, 10.14%, M, 552.7. Found: C, 8.67; H, 0.73; N, 10.08%, $[M+Na]^+$, 574.9. ^{1}H NMR, $CDCl_3$, 298 K; complex multiplet, 4.39 ppm, 4H, 2× (OCH_2). The second product is the isomeric mono-ansa derivative $[N_4P_4Cl_6(OCH_2CF_2CF_2CH_2O)]$ (**4**), (0.02 g, 1%, oily). *Anal.* Found: C, 8.68; H, 0.71; N, 10.10%. $[M-H]^-$, 551.5. ^{1}H NMR, $CDCl_3$, 298 K; complex multiplies, 4.50 and 4.62 ppm, 4H, 2× (OCH_2). The third product eluted from the column is the bis-spiro derivative(s) $[N_4P_4Cl_4(OCH_2CF_2CF_2CH_2O)_2]$ (**5 and 6**) shown to exist as a mixture of two products by ^{31}P NMR spectroscopy. It is known that there are two possible geometric isomers for bis-spiro compound, which have *cis*- and *trans*-arrangements. The bis-spiro products (**5** and **6**) could be separated by fractional crystallization from *n*-hexane–dichloromethane (3:1). *Anal.* Calc. for isomers $C_8H_8Cl_4F_8N_4O_4P_4$: C, 14.97; H, 1.26; N, 8.73%, M, 641.9 (**5**) (0.18 g, 9%, mp 155 °C). Found: C, 14.95; H, 1.25; N, 8.62%. $[M+Na]^+$, 663.5. ^{1}H NMR, $CDCl_3$, 298 K; complex multiplet, 4.25 ppm, 8H, 4× (OCH_2) (**6**) (0.08 g, 4%, 174 °C), Found: C, 14.96; H, 1.27; N, 8.60%, $[M+Na]^+$, 663.5. ^{1}H NMR, $CDCl_3$, 298 K; complex multiplet, 4.25 ppm, 8H, 4× (OCH_2).

2.5. Reaction of *1* with *2* at 1:2 ratio

Compounds **1** (1.391 g, 3 mmol) and **2** (0.972 g, 6 mmol) were dissolved in 100 mL of dry THF under argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (0.48 g, 12 mmol) in 15 mL of dry THF was quickly added to a stirred solution under argon atmosphere. The reaction mixture was stirred for 24 h at room temperature and the reaction followed by TLC on silica gel plates using *n*-hexane–dichloromethane (1:1). Only one new product was observed except for mono-spiro and bis-spiro derivatives and no starting material (**1**) was detected by TLC. The reaction mixture was filtered to remove the sodium chloride formed and any other insoluble material. The solvent removed under reduced pressure and the resulting colourless oil which composed of 43% **5**, 24% **6**, 23% **7** and 6% **3** shown by ^{31}P NMR was subjected to column chromatography, using *n*-hexane–dichloromethane (1:1) as the mobile phase. The mono-spiro product was obtained by yield of 3%. The bis-spiro products (0.95 g, 49%) were taken together from column chromatography. The third product is the tris-spiro derivative $[N_4P_4Cl_2(OCH_2CF_2CF_2CH_2O)_3]$ (**7**), (0.32 g, 15%, mp 198 °C), a colourless solid, which was re-crystallized from THF–acetonitrile (1:1). But the crystals were very small and did not diffract X-rays. *Anal.* Calc. for $C_{12}H_{12}Cl_2F_{12}N_4O_6P_4$: C, 19.72; H, 1.65; N, 7.66%, M, 731.0 Found: C, 19.70; H, 1.65; N, 7.53%, M^+, 730.9. ^{1}H NMR, $CDCl_3$, 298 K; complex multiplet, 4.22 ppm, 12H, 6× (OCH_2).

2.6. Reaction of *1* with *2* at 1:3 ratio

Compounds **1** (1.391 g, 3 mmol) and **2** (1.458 g, 9 mmol) were dissolved in 100 mL of dry THF under argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (0.72 g, 18 mmol) in 20 mL of dry THF was quickly added to a stirred solution under argon atmosphere. The reaction mixture was stirred for 24 h at room temperature and the reaction followed by TLC on silica gel plates using *n*-hexane–dichloromethane (1:1). The reaction mixture was filtered to remove the sodium chloride formed and any other insoluble material. Only one product was observed by TLC and ^{31}P NMR of reaction mixture. The white solid which could be solved little in dichloromethane was obtained after the reaction solvent removed under reduced pressure. Then white solid was washed thoroughly with dichloromethane to remove the soluble materials in this solvent and residue solid was solved in THF. The product was the tetrakis-spiro derivative $[N_4P_4(OCH_2CF_2CF_2CH_2O)_4]$ (**9**), (1.48 g, 60%, mp 324 °C, DSC on 3.48 mg), a colourless solid, which was re-crystallized from THF–acetonitrile (1:1). *Anal.* Calc. for $C_{16}H_{16}F_{16}N_4O_8P_4$: C, 23.43; H, 1.97; N, 6.83%, M, 820.2. Found: C,