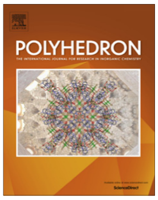
Polyhedron 81 (2014) 777–787

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Reactions of ansa fluorodioxy cyclotriphosphazene derivatives with phenol

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ARTICLE INFO

Article history:
Received 11 June 2014
Accepted 16 July 2014
Available online 9 August 2014

Keywords:
Cyclophosphazene
Fluorodiol
Ansa ring
Crystal structure
Reaction mechanism

ABSTRACT

The reactions of mono ansa fluorodioxy cyclotriphosphazenes {$N_3P_3Cl_4[OCH_2(CF_2)_nCH_2O]$ ($n = 3$, **1a**; $n = 4$, **1b**)} with the sodium salt of phenol in THF solution at different molar ratios were investigated in order to determine the reaction pathways and the mechanism of the nucleophilic substitution at the PCl_2 and PCl(OR) phosphorus atoms by phenol and for a comparison with previous work on the reactions of the same starting compounds **1a** and **1b** with the sodium salt of methanol. Fourteen new products were formed, namely mono-phenoxy derivatives (**2a**–**4a**, **3b**), di-phenoxy derivatives (**5a**–**7a**, **5b**), tri-phenoxy derivatives (**8a**–**10a**, **8b**) and tetra-phenoxy derivatives (**11a**, **11b**). These products, which could be separated, have been characterized by elemental analysis, mass spectrometry, ^1H and ^{31}P NMR spectroscopy. A similar result to the reaction with methanol was observed in the first stage of the reaction of compound **1a**, containing the 10-membered ansa-ring, with the reaction occurring competitively at both the PCl_2 and P(OR)Cl moieties with an approximate 8:1 preference for the PCl_2 group. In the second stage of the reaction of compound **1a**, the bis non-geminal *cis* compound (**7a**) formed as the major product, whilst the major product was the bis gem compound in the similar reaction of **1a** with sodium methoxide. Consequently, the tris non-geminal *cis* compound (**9a**) might be formed beside the tris geminal compound (**8a**) in the third stage of the reaction of compound **1a** with phenol, unlike the methanol reaction. All the reactions of compound **1b**, containing the 11-membered ansa-ring, with the sodium salt of phenol occurred at the PCl_2 group before the P(OR)Cl moiety. X-ray crystallographic studies of two compounds (**7a** and **8b**) showed that nucleophilic substitution reactions with the sodium salt of phenol at the ansa-ring PCl(OR) phosphorus atoms of the mono ansa fluorodioxy cyclotriphosphazene compounds **1a** and **1b** occurred with retention of the configuration.

1. Introduction

Cyclophosphazenes continue to attract attention with their intriguing complex nature and organic type reactivity [1–4]. Nucleophilic substitutions reactions are an interest center for investigations in cyclophosphazene chemistry due to the complexity and variability of the reaction mechanisms and the broad range of regio- and stereo- chemical outcomes of these reactions [4–35]. However, the focus of mechanistic studies has been almost extensively directed towards the reactions of a nucleophile with chlorocyclophosphazenes [1,5,7,8,10,11,30]. There are fewer studies on the directing effect of substituents already present on the cyclophosphazene ring to the incoming nucleophile [9,36–41].

We have previously investigated the reactions of fluorodioxy cis-ansa derivatives of cyclotriphosphazene, {$N_3P_3Cl_4[OCH_2(CF_2)_3CH_2O]$ (**1a**) and $N_3P_3Cl_4[OCH_2(CF_2)_4CH_2O]$ (**1b**)}, with the sodium salt of methanol at different molar ratios (1:1, 1:2.5 and 1:excess) [40] and important details were obtained about the reaction mechanisms and pathways from these reactions. In this paper we examined the reactions of compounds **1a** and **1b** with phenol under the same conditions to compare with the analogous reactions with methanol. Phenol is an aromatic alcohol, its sodium salt is a weaker nucleophile than sodium methoxide and it is more bulky than methanol. Furthermore, the phenoxy substrate is important since its reactions with $N_3P_3Cl_6$ have been studied extensively [42–45].

The reactions of compound **1a** with the sodium salt of phenol resulted in ten new products whereas the reactions of compound **1b** with same aryloxide resulted in only four products. The formation of both geminal and non-geminal products increased the diversity of products in the reactions of compound **1a**, especially in the second and third stages of the reaction. However the two

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http://dx.doi.org/10.1016/j.poly.2014.07.043
0277-5387/

P–Cl bonds of the PCl_2 group are more reactive than those of the P(OR)Cl moiety in the compound **1b**, so that only geminal products were formed. On the other hand, X-ray crystallographic evidences show that the nucleophilic substitution reactions of both cyclophosphazene derivatives lead to the retention of the configuration at the ansa-ring PCl(OR) phosphorus atoms.

2. Experimental

2.1. Materials and methods

Hexachlorocyclotriphosphazene (Aldrich) was purified by fractional crystallization from *n*-hexane. 2,2,3,3,4,4-Hexafluoro-1,5-pentanediol (Aldrich), 2,2,3,3,4,4,5,5-octofluoro-1,6-hexanediol (Aldrich) and phenol (Merck) were used as received. Tetrahydrofuran (THF) (Merck) was distilled over a sodium/potassium alloy under an atmosphere of dry argon. For sodium hydride, 60% dispersion in mineral oil (Merck), prior to use the oil was removed by washing with dry hexane (Merck) followed by decantation. All reactions were performed under a dry argon atmosphere. $CDCl_3$ for NMR spectroscopy was obtained from Merck. Analytical Thin Layer Chromatography (TLC) was performed on Merck silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 70–230 mesh; for 3 g crude mixture, 100 g silica gel were used). Elemental analyses were obtained using an Elementar Vario MICRO Cube. Mass analyses were recorded on a Bruker MicroTOF LC/MS spectrometer using the electro spray ionization (ESI) method; ^{35}Cl values were used for calculated masses. ^{1}H and ^{31}P NMR spectra were recorded for all compounds in $CDCl_3$ on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^{1}H and 85% H_3PO_4 as an external reference for the ^{31}P NMR measurements.

2.2. X-ray crystallography

Intensity data were recorded on a Bruker APEX II QUAZAR diffractometer using mono-chromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were performed by the multi-scan method implemented in SADABS [46] and space groups were determined using XPREP implemented in APEX2 [47]. The structures were determined using the direct methods procedure in SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97 [48]. All non-hydrogen atoms were refined with anisotropic displacement factors and C–H hydrogen atoms were placed in calculated positions and allowed to ride on their parent atom. The final geometrical calculations were carried out with PLATON [49] and MERCURY [50] programs and the molecular drawings were done with the DIAMOND [51] program.

2.3. Synthesis

Compound **1a** [33] and **1b** [34] were prepared as in the literature.

2.3.1. Reaction of *1a* with phenol in a 1:1 ratio

Ansa-$[N_3P_3Cl_4(OCH_2(CF_2)_3CH_2O)]$ (**1a**) (0.341 g, 0.70 mmol) and phenol (0.066 g, 0.70 mmol) were dissolved in 15 mL of dry THF in a 50 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.03 g, 0.70 mmol) in 10 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction was stirred for a further 24 h at room temperature and followed by TLC on silica gel plates using *n*-hexane–dichloromethane (1:1) as the mobile phase. One product was observed. The reaction mixture was filtered to remove the sodium chloride and any other insoluble material. The solvent was removed under reduced pressure and the crude product was subjected to column chromatography using *n*-hexane–dichloromethane (1:1) as the mobile phase. Firstly, the unreacted starting compound **1a** was eluted from the column. The second eluent contained a mixture of the isomer compounds **2a** and **3a** (0.18 g, 47%, oil). The pure compounds could not be isolated because of the similarity of the R_f values of two compounds.

Anal. Calc. for **2a** and **3a**; $C_{11}H_9Cl_3F_6N_3O_3P_3$: C, 24.27; H, 1.67; N, 7.72, M, 544.5. Found: C, 23.91; H, 1.45; N, 6.93%, $[M+H]^+$, 545.2.

2.3.2. Reaction of *1a* with phenol in a 1:2 ratio

Ansa-$[N_3P_3Cl_4(OCH_2(CF_2)_3CH_2O)]$ (**1a**) (0.487 g, 1.0 mmol) and phenol (0.188 g, 2.0 mmol), were dissolved in 35 mL of dry THF in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.08 g, 2.0 mmol) in 10 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction was stirred for a further 24 h at room temperature and followed by TLC on silica gel plates using *n*-hexane–THF (7:1) as the mobile phase. Two products were observed. The reaction mixture was filtered to remove the sodium chloride and any other insoluble material. The solvent was removed under reduced pressure and the crude product was subjected to column chromatography using *n*-hexane–THF (7:1) as the mobile phase. The first eluent was the mixture of two bis-phenoxy derivatives, the bis-geminal phenoxy compound (**5a**) and bis-non-geminal *trans*-phenoxy compound (**6a**). The second product was the bis-non-geminal *cis*-phenoxy compound (**7a**). The compound **7a** was crystallized from *n*-hexane–dichloromethane (3:1) and obtained as white crystals.

Anal. Calc. for **5a**–**7a**; $C_{17}H_{14}Cl_2F_6N_3O_4P_3$: C, 33.91; H, 2.34; N, 6.98, M, 602.14.

5a and **6a**: (0.21 g, 35%, oil). Found: C, 33.07; H, 2.02; N, 6.54%, $[M-H]^+$, 601.98.

7a: (0.19 g, 32%, mp. 126 °C). Found: C, 33.62; H, 2.07; N, 6.60%, M^+, 603.82. ^{1}H NMR, $CDCl_3$, 298 K, δ: 6.90–7.30 (m, 5H, aromatic protons), 4.89 (m, 1H), 4.75 (m, 1H), 4.39 (m, 2H, $-C\boldsymbol{H}_2$).

2.3.3. Reaction of *1a* with phenol in a 1:3 ratio

Ansa-$[N_3P_3Cl_4(OCH_2(CF_2)_3CH_2O)]$ (**1a**) (0.487 g, 1.00 mmol) and phenol (0.282 g, 3.00 mmol) were dissolved in 40 mL of dry THF in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.12 g, 3.00 mmol) in 10 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction was stirred for a further 24 h at room temperature and followed by TLC on silica gel plates using *n*-hexane–dichloromethane (1:1) as the mobile phase. Three products were observed. The reaction mixture was filtered to remove the sodium chloride and any other insoluble material. The solvent was removed under reduced pressure and the crude product was subjected to column chromatography using *n*-hexane–dichloromethane (1:1) as the mobile phase. The first product was the tris-geminal phenoxy compound (**8a**), the second product was the tris-*cis* phenoxy compound (**9a**) and the last product was the tetra-phenoxy compound (**11a**). Compounds **9a** and **11a** were crystallized from *n*-hexane–dichloromethane (3:1) and obtained as white crystals.

Anal. Calc. for **8a** and **9a**; $C_{23}H_{19}ClF_6N_3O_5P_3$: C, 41.87; H, 2.90; N, 6.37, M, 659.79.

Anal. Calc. for **11a**; $C_{29}H_{24}F_6N_3O_6P_3$: C, 48.55; H, 3.37; N, 5.86, M, 717.44.

8a: (0.26 g, 40%, oil). Found: C, 41.47; H, 2.42; N, 6.02%, $[M+H]^+$, 660.42. ^{1}H NMR, $CDCl_3$, 298 K, δ: 6.90–7.30 (m, 5H, aromatic protons), 4.69 (m, 1H), 4.40 (m, 1H), 4.21 (m, 1H), 4.09 (m, 1H; $-C\boldsymbol{H}_2$).