Synthesis of bridged fluorophenoxycyclotriphosphazene

Jiamei Zhu and Weimin Liu*

State Key Laboratory of Solid Lubrication, Lanzhou Institution of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P.R. China

The title compound has been synthesised by reaction of partially substituted hexachlocyclotriphosphazene with hydroquinone in moderate yield.

Keywords: bridged fluorophenoxycyclotriphosphazene

The cyclic trimer (**1**) (Fig.1) and linear phosphazenes (**2**) composed of alternating phosphorus and nitrogen atoms are a well-established class of compound.[1] Phosphazenes have received increasing interest, not only because of their importance in synthetic chemistry, but also due to their wide spectrum of chemical and physical properties. Various phosphazenes have been successfully developed as lubricants, fire-resistant polymers, biomaterials, and elastomeric materials.[2-5] Typically, the design and synthesis of cyclic trimer and linear polyphosphazenes have been extensively studied in recent years.[6-8] However, only a few examples of bridged cyclophosphazenes (**3**), containing two cyclophosphazene molecules linked together through the bifunctional reagent, have been documented.[9,10] Cyclotriphosphazenes containing fluorinated phenoxy groups are useful as lubricants, and for surface coatings in magnetic tapes and other applications due to their chemical inertness and oxidative and thermal stability.[11,12] Accordingly, we supposed that bridged fluoroaryloxy-substituted cyclotriphosphazenes might have scientific and technological applications and the present article deals with the synthesis of bridged fluorophenoxycyclotriphosphazenes (Scheme 1).

Initially, the preparation of bridged cyclophosphazenes, using the substitution reaction of hexachlocyclotriphosphazene (2 equiv.) by hydroquinone (1 equiv.) in phase-transfer catalysis, was attempted and described by Chen-Yang,[13] but failed with the formation of several inseparable products. We believe that the mono-substituted product of hexachlocyclotriphosphazene is very sensitive to heat and moisture and undergoes facile decomposition, as referred to in the literature.[14] Thus we used the route shown in Scheme 1 to synthesise the bridged cyclotriphosphazene. The method is characterised by simple reaction conditions and moderate yield.

Experimental

^{31}P NMR spectra were recorded on a Bruker AC400 (162MHz) in $CDCl_3$. ^{31}P NMR chemical shifts are related to 85% H_3PO_4 as an external reference, with the positive shift valued downfield from the reference. The IR spectra were obtained on a Bio-Rad Win-IR spectrometer. Elemental analyses were conducted on a CE-1106 microanalyser.

Hexachlocyclotriphosphazene was prepared according to described procedures[15] and 3-trifluoromethyl phenol (Aldrich) was used as received. All other chemicals used were analytical reagents. Acetone was dried over standard drying agent and freshly distilled prior to use. TLC was used to monitor the reactions. Chromatographic purification was performed with silica gel 60 (100–200 mesh).

Synthesis of $N_3P_3Cl(OC_6H_4CF_3\text{-}m)_5$ (**1**): To a solution of hexachlocyclotriphosphazene (1.44 mmol, 0.50 g) in 1,2-dichloroethane (10 ml) was added a 10 ml aqueous solution containing 3-trifluoromethyl phenol (7.90 mmol,1.28 g), sodium hydroxide (15.80 mmol, 0.63 g), and tetrabutylammonium bromide (TBNB) (0.04 mmol, 0.012 mg), as phase-transfer catalyst. The reaction mixture was stirred vigorously and refluxed for 1.5 h. After reaction the organic layer was separated from the aqueous layer, washed with water and dried over Mg_2SO_4, filtered, and evaporated. The product

* Correspondence. E-mail: wmliu@ns.lzb.ac.cn

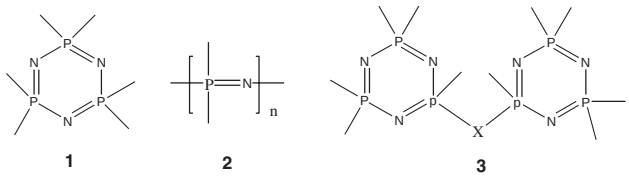
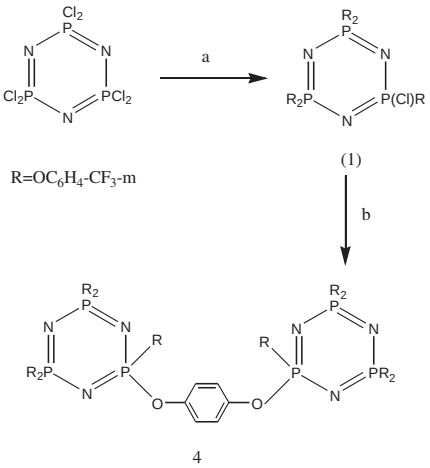


Fig. 1 Phosphazene structures.



Scheme 1 Reagents and conditions: a; 3-trifluoromethyl phenol, $(CH_2Cl)_2$, H_2O, NaOH, TBNB, reflux; b; hydroquinone, K_2CO_3, acetone, reflux.

was isolated as a colorless oil. ^{31}P NMR spectroscopy revealed traces of the hexa-substituted phosphazene. The impurity was removed after subsequent reaction with nucleophiles. The residue was purified on a column chromatograph (with the ratio of petrol:ethyl acetate to be 19:1) to give compound **1** (1.10 g, 80%). IR (δ_{max}, cm^{-1}): 3083(Ph–H), 1596(Ph), 1326(CF_3), 1180(–P=N–), 963(P–O), 621(P–Cl); ^{31}P NMR (162 Hz; $CDCl_3$):δ(ppm) 6.60(d, 2P), 21.54(t, 1P), J_{pp}=85.5 Hz. Elemental analysis Calc (%), for $C_{35}H_{20}F_{15}N_3O_5P_3Cl$: C, 43.05; H, 2.05; N, 4.30. Found (%): C, 42.75; H, 2.16; N, 4.39.

Synthesis of $N_3P_3(OC_6H_4CF_3\text{-}m)_5[OC_6H_4O]N_3P_3(OC_6H_4CF_3\text{-}m)_5$ (**4**): A mixture of compound 1 (1.64 mmol, 1.60 g), hydroquinone (0.82 mmol, 0.09 g), and anhydrous potassium carbonate (2.00 g) in acetone (20 ml) was refluxed for 3 h, and then filtered. After removal of the solvent, the pasty residual was treated with ether (20 ml), and the ether layer was washed with 0.1 N NaOH, dried, and concentrated. The residue oil was chromatographed on silica gel (with the ratio of petrol:ethyl acetate 6:1) to afford compound **4** as a clear and colourless oil (0.90 g, 55%). IR (ν_{max}, cm^{-1}): 3083(Ph–H), 1595(Ph), 1326(CF_3), 1180(–P=N–), 962(P–O); ^{31}P NMR (162 Hz; $CDCl_3$): δ(ppm) 8.32 (s). Elemental analysis Calc (%), for $C_{76}H_{44}F_{30}N_6O_{12}P_6$: C, 45.87; H, 2.21; N, 4.22. Found (%): C, 45.56; H, 2.42; N, 4.22.

The authors would like to thank the National Natural Science Foundation of China (Grant No. 50275142) and Chinese Academy of Sciences for financial support.

Received 23 March 2003; accepted 7 January 2004
Paper 03/1847

References

1 H.R. Allcock, *Phosphorus-Nitrogen Compound*, New York: Academic, 1972.
2 H.R. Allcock, R.S. Pucker and G.A. Scopelianos, *Macromolecules*, 1994, **27**, 1.
3 Y.G. Yang and J.X. Wen, *Chin. Chem. Lett.*, 1998, **9**, 727.
4 R.D. Jaeger and M. Gleria, *Prog. Polym. Sci.*, 1998, **3**, 179.
5 H.R. Allcock, *Poly. Prepr.*, 2000, **14**, 553.
6 X. Ku, N.D. Day and C.A. Angell, *Inorg. Chem. Commun.*, 1999, **2**, 261.
7 K.L. Rule, I.I. Selvaraj and R.L. Kirchmeier, *J. Fluorine Chem.*, 2001, **112**, 307.
8 C.F. Ye, W.M. Liu, Y.X. Chen and Z.W. Ou, *Organic Preparations and Procedures International*, 2001, **33**, 376.
9 A.H. Alkubaisi, H.G. Parkes and R.A. Show, *Heterocycles*, 1989, **28**, 347.
10 V. Chandrasekhar, M.G.R. Muralidhara, and I.I. Selvaraj, *Heterocycles*, 1990, **31**, 2231.
11 B.S. Nader, K.K. Kar, T.A. Morgan, et al. *Tribo. Trans.*, 1992, **35**, 37.
12 D.J. Perettie, T.A. Morgan, Q. Zhao, et al. *J. Magn. Magn. Mater.*, 1999, **193**, 318.
13 Y.W. Chen-Yang, S.J. Cheng and B.D. Tsai, *Ind. Eng. Chem. Res.*, 1991, **30**, 1314.
14 C.W. Allen and J.A .Mackay, *Inorg. Chem.*, 1986, **25**, 4628.
15 G.M. Sulzer, B. Joseph, et al. US Patent, 4656018, 1987.