Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2014, 24, 154–155

Mendeleev Communications

Synthesis of hexakis(hydroxyaryloxy)cyclotriphosphazene based on bisphenol A

Ivan V. Terekhov,*[a] Evgeniy M. Chistyakov,[a] Sergey N. Filatov,[a] Roman S. Borisov[b] and Vyacheslav V. Kireev[a]

[a] *D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation. Fax: +7 499 978 9444; e-mail: ivan.vl.terekhov@gmail.com*

[b] *A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

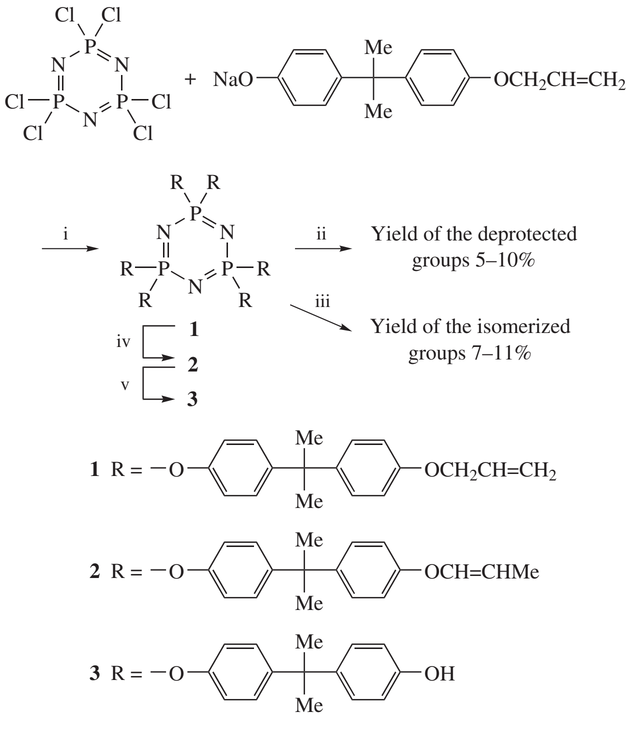
DOI: 10.1016/j.mencom.2014.04.009

Hexasubstituted derivative of cyclotriphosphazene containing hydroxyaryloxy moieties was obtained from bisphenol A using allyl protection of phenolic groups.

The preparation of phosphazene derivatives containing free hydroxy groups is of extreme importance in modern phosphazene research,[1,2] since these compounds are of practical interest.[3–17] In the first studies in this field hexakis(4-hydroxyphenoxy)cyclotriphosphazene was obtained by treatment of hexakis(4-methoxyphenoxy)cyclotriphosphazene with HBr/AcOH/H_2O mixture[18] or with BBr_3.[19] Among other known methods, there are usage of protective groups,[3–6] reduction of the aldehyde groups in the hexakis(4-formylphenoxy)cyclotriphosphazene,[7–9] the nucleophilic substitution of chlorine atoms of hexachlorocyclotriphosphazene, including replacement with discriminate binucleophiles,[10] or partial replacement with mononucleophiles, followed by further replacement of the remaining chlorine atoms with binucleophiles.[11]

Earlier we have reported the synthesis and epoxidation of hexaallyloxy derivative of aryloxycyclotriphosphazene **1** from the bisphenol A monoallyl ether and hexachlorocyclotriphosphazene.[16] In this work, allyl group in compound **1** was regarded as protective group for one of the hydroxy groups in bisphenol A (Scheme 1), which provided an access to a new cyclotriphosphazene derivative.

One of the most effective methods of deprotection of allyl ethers is their isomerization into prop-1-enyl derivative followed by hydrolysis.[20] Attempted isomerization in derivative **1** using Pd/C was unsuccessful, as well as isomerization with *in situ* acidic removal hydrolysis of the prop-l-enyl derivative. Potassium *tert*-butoxide-promoted isomerization[†] at room temperature was complete only in 20–25 h; however, raising temperature to 70 °C shortened the reaction time to 3–5 h. ^{31}P, ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry showed the absence of side products.



Scheme 1 *Reagents and conditions*: i, diglyme, 130 °C, 10 h; ii, TsOH (cat.), Pd/C, anhydrous MeOH, reflux, 20 h; iii, Pd/C, benzene, reflux, 12 h; iv, Bu^{t}OK, DMSO, 70 °C, 3 h; v, HCl, THF, H_2O, 50 °C, 3 h.

For the removal of prop-1-enyl group in derivative **2**, four methods were tested: the use of hydrochloric acid,[‡] the use of $HgCl_2$ and HgO, the use of I_2, and oxidation with $KMnO_4/OH^-$.

[†] ^{31}P and ^{1}H NMR spectra were recorded in acetone-d_6 solutions on a Bruker CXP-200 spectrometer operating at 81 and 200 MHz, respectively. Melting point analyses of compounds were performed on a Mettler Toledo DSC-822e differential scanning calorimeter at a heating rate 20 °C min^{-1} under argon flow. Mass spectra were obtained on a Bruker Auto Flex II spectrometer using MALDI-TOF method.

Isomerization of double bond in hexaallyloxy derivative of aryloxycyclotriphosphazene **1**. Allyloxy derivative **1** (10 g, 0.0057 mol) was added to a 0.5 M solution of Bu^{t}OK (5.1 g, 0.046 mol) in DMSO. After complete dissolution of compound **1**, the mixture was stirred at 70 °C for 3 h. The mixture was poured into distilled water, the precipitated product was centrifuged, washed with water and dried *in vacuo* at 80 °C for 6 h. Yield 8.2 g (82%). ^{1}H NMR (acetone-d_6) δ: 7.17–7.05 (br. d, 16 H, aromatic), 6.92–6.80 (br. d, 16 H, aromatic), 6.49–6.38 (d, 6 H, O–CH=), 4.92–4.74 (br. m, 6 H, C=CH–C), 1.68–1.62 (d, 18 H, =CMe), 1.60 (s, 36 H, CMe_2). ^{31}P NMR (acetone-d_6) δ: 7.92 (s). MS (MALDI-TOF), *m/z*: 1738 [M + H]$^+$ (calc., *m/z*: 1737).

[‡] *Hydrolysis of prop-1-enyl derivative* **2**. Compound **2** (8 g, 0.0046 mol) was dissolved in THF (30 ml) and 10% aqueous HCl solution (20 ml) was added dropwise with stirring. The mixture was stirred at 50 °C for 3 h, followed by addition of 10% aqueous KOH solution (20 ml). The solvents were removed *in vacuo*, the dry residue was dissolved in distilled water and treated with activated charcoal. Solution of HCl (10%) was added dropwise to reach a slightly acidic pH. The resulting precipitate was filtered off, washed with water and dried *in vacuo* at 80 °C for 6 h. Yield 6 g (87%), T_g = 103–111 °C. ^{1}H NMR (acetone-d_6) δ: 7.11–6.97 (dd, 16 H, aromatic), 6.87–6.77 (d, 8 H, aromatic), 6.76–6.66 (d, 8 H, aromatic), 1.57 (s, 36 H, Me). ^{31}P NMR (acetone-d_6) δ: 7.88 (s). MS (MALDI-TOF), *m/z*: 1500 [M + H]$^+$ (calc., *m/z*: 1497).

In the case of mercuric chloride or iodine the reaction proceeded quickly; however, ^{31}P NMR spectra of the product showed that the process is accompanied by the partial destruction of the phosphazene cycle. Oxidative hydrolysis with $KMnO_4$ at room temperature for 24 h provided removal of only 1 to 3 of protective groups per molecule of derivative **2**. HCl-Promoted hydrolysis proved to be the most promising: at 50 °C all four prop-1-enyl groups were removed within 3 h and yield of the purified product **3** was 87%. A singlet peak in the ^{31}P NMR spectrum of derivative **3** indicated that no adverse reactions involving the phosphazene ring occurred in the course of hydrolysis.

In conclusion, we synthesized a new hexahydroxy derivative of aryloxycyclotriphosphazene from bisphenol A. This compound seems prospective for the preparation of various polymer hybrid compositions, which, unlike analogue,[12] can possess improved mechanical properties due to the presence of isopropylidene bridge in their structure.[21]

References

1 M. Gleria and R. De Jaeger, *J. Inorg. Organomet. Polym*., 2001, **11**, 1.
2 S. Lu and I. Hamerton, *Prog. Polym. Sci*., 2002, **27**, 1661.
3 N. N. Reed and K. D. Janda, *Org. Lett*., 2000, **2**, 1311.
4 H. R. Allcock and C. G. Cameron, *Macromolecules*, 1994, **27**, 3125.
5 H. R. Allcock, C. G. Cameron and D. E. Smith, *US Patent, 5464932*, C08G, 1995.
6 H. R. Allcock and S. Kwon, *Macromolecules*, 1988, **21**, 1980.
7 K. Inoue, S. Negayama, T. Itaya and M. Sugiyama, *Macromol. Rapid Commun*., 1997, **18**, 225.
8 J. Y. Chang, H. J. Ji and M. J. Han, *Macromolecules*, 1994, **27**, 1376.
9 W. Yuan, X. Tang, X. Huang and S. Zheng, *Polymer*, 2005, **46**, 1701.
10 F. F. Stewart and M. K. Harrup, *J. Appl. Polym. Sci*., 1999, **72**, 1085.
11 D. Mathew, C. P. R. Nair and K. N. Ninan, *Polym. Int.*, 2000, **49**, 48.
12 G. Facchin, L. Guarino, M. Modesti, F. Minto and M. Gleria, *J. Inorg. Organomet. Polym.*, 1999, **9**, 133.
13 G. Fantin, A. Medici, M. Fogagnolo, P. Pedrini, M. Gleria, R. Bertani and G. Facchin, *Eur. Polym. J*., 1993, **29**, 1571.
14 G. Facchin, M. Gleria, F. Minto, R. Bertani, M. Guglielmi and G. Brusatin, *Macromol. Rapid Commun.*, 1995, **16**, 211.
15 H. R. Allcock and J. R. Taylor, *US Patent, 6093758*, C08K, C07F, 2000.
16 V. V. Kireev, E. M. Chistyakov, S. N. Filatov, R. S. Borisov and B. M. Prudskov, *Polym. Sci., Ser. B*, 2011, **53**, 412 (*Vysokomol. Soedin., Ser. B*, 2011, **53**, 1142).
17 H. R. Allcock, S. R. Pucher, R. J. Fitzpatrick and K. Rashid, *Biomaterials*, 1992, **13**, 857.
18 E. H. Kober, H. F. Lederle and G. F. Ottmann, *US Patent, 3462518*, C07D, C07F, C10M, 1969.
19 A. Medici, G. Fantin, P. Pedrini, M. Gleria and F. Minto, *Macromolecules*, 1992, **25**, 2569.
20 F. Guibe, *Tetrahedron*, 1997, **53**, 13509.
21 V. A. Sergeev, U. E. Doroshenko and V. V. Korshak, *Vysokomol. Soedin., Ser. B*, 1967, **9**, 688 (in Russian).

Received: 7th November 2013; Com. 13/4243