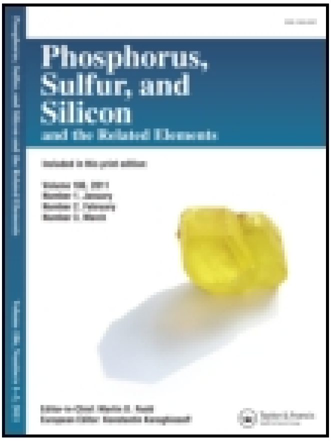

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis of New Ortho-Hydroxy Aryl Phosphonate Monomers

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SYNTHESIS OF NEW ORTHO-HYDROXY ARYL PHOSPHONATE MONOMERS

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Commercially available bridged bis-phenols react with diethylphosphite to give bis-phosphates, which are easily transformed by LDA, in good yields, to bis-ortho hydroxy aryl phosphonates. These new monomers are of great relevance for the synthesis of novel macrocycles and for thermal resistant polycondensates containing phosphonate moieties.

Keywords: Phosphonate monomers for macrocycles; NMR and MS-FAB; Fire proofing material

INTRODUCTION

Monomers that are based on a Ar_2Z moiety have been utilized intensively during the last few decades, because they play an important role in forming macrocyclic ligands as receptors for ionic or uncharged organic molecules.[1] Organo-phosphorus compounds are widely used in agrochemistry[2] as herbicides and antifungal agents, in farmacology[3] as antibiotics, in diagnostic medicine[4] as screening agents, once complexed with lanthanides, and as fire proofing or flame retardant materials[5]. Furthermore, the presence of the phosphonic moiety increases the solubility of such derivatives in organic solvents and solubility in water can be achieved also by hydrolizing them to the corresponding phosphonic acids. Therefore, considering the interest and the wide application of such compounds we wish

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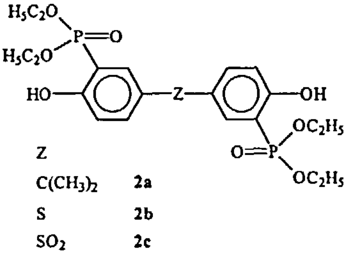
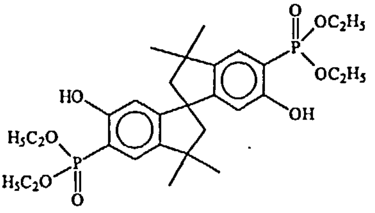
* Corresponding author.

to report here the synthesis of new monomers **2a-c** and **3** which contain the C-P bonds, in the aromatic ring.



Z	
$C(CH_3)_2$	2a
S	2b
SO_2	2c



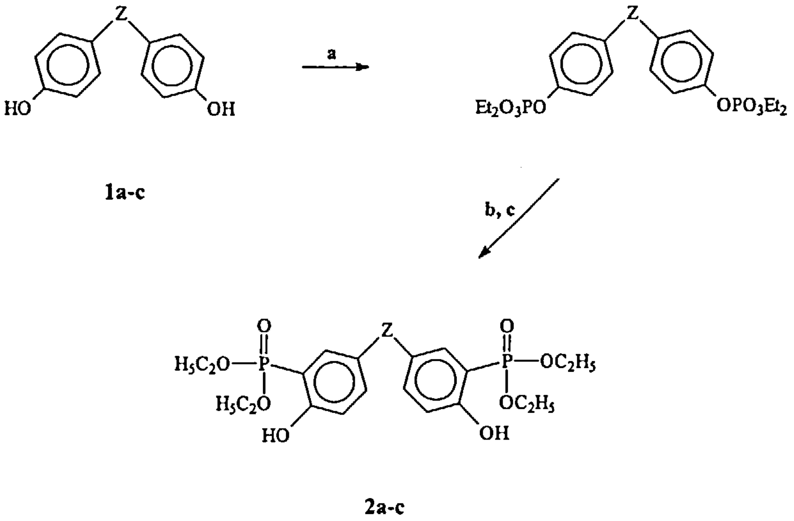
3

Such monomers are of great relevance for the synthesis of novel macrocycles and for polycondensates containing phosphonate moieties. More intriguing, phosphonate **3** is a preorganised dissymetric molecule and thus exists as a pair of enantiomers; it follows, that **3** can be used as a chiral template[6] which provides the necessary symmetry conditions for building chiral polycondensates or inducing chirality in replicating strands.

RESULTS AND DISCUSSION

Treatment of available bis-phenols with diethyl-phosphonic esters in carbon tetrachloride as solvents in presence of a base, *i.e.*, triethylamine or potassium carbonate as acid acceptor, yields the corresponding bis-phosphate derivatives which, in the presence of a stoichiometric ammount of lithium diisopropylamide (LDA), at low temperature, enter in [1,3]-sigmatropic rearrangment that involve the fission of an oxygen-phosphorus bond and the formation of a new carbon-phosphorus bond, yielding dialkyl-(2-hydroxyaryl) diphosphonates (Scheme 1). The synthesis is conceptually based on the monophosphoazylation of phenols followed by their rearrangment with lithium salts as described by Redmore *et al.*,[7] and, in our case, provides in good yields diphosphonate monomers which are synthetically very useful starting materials.

The first step proceedes in almost quantitative yield, the second one which represents the crucial step occurs with a 70–85% yield, which is satisfactory considering that a double lithiation reactions occurs. These compounds, which are good monomers for preparing polycondensates bearing phosphonic moieties in the chain, and having oxygen bridging groups between the aromatic nuclei, were also used by us in order to synthesize



SCHEME 1 Reagents: a) $HP(O)(OC_2H_5)_2/CCl_4$, $N(C_2H_5)_3$, 0 °C; b) LDA/THF, – 78 °C; c) saturated NH_4Cl/H_2O

macrocyclic systems[8] by condensing them with dihalo-methyl-derivatives in CH_3CN as solvent and in the presence of K_2CO_3 as base. In other words, the OH functionalities present high reactivity and some model reactions are now in progress in order to extend the possible use of such monomers.

In summary, a practical and easy procedure for the synthesis of a new class of monomers containing two phosphonic moieties in the ring is reported. By macrocyclization reactions novel macrocycles useful for host-guest studies and for the synthesis of new materials by polycondensation reactions are now in progress.

EXPERIMENTAL

Phenols, diethyl phosphite, triethyl amine, *n*-butyl lithium 1.6 M solution in hexane, diisopropyl amine as well as other chemicals and solvents used were high purity commercial products from Aldrich. All syntheses were performed under a dry N_2 atmosphere.

^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded in $CDCl_3$, with TMS as an internal standard, and H_3PO_4 85 % as external standard, using a Varian-Inova instrument operating at 500 MHz.

Mass spectra were obtained using a double focusing Kratos MS 50S instrument equipped with a standard FAB source and DS 90 data system. 3-Nitro-benzylalcohol was used as matrix.

Melting points were determined on a Büchi 530 melting point apparatus and are uncorrected.

General Synthetic Procedure

In a typical procedure, to a stirred mixture of bis-hydroxyphenyl derivatives (0.05 mol) and diethyl phosphite (0.11 mol), in carbon tetrachloride (100 mL) cooled at 0 °C, was added triethylamine dropwise and the temperature of the reaction was maintained below 10 °C by external cooling. The mixture was stirred overnight at room temperature, then the ammonium salt formed was filtered off and the organic solution was washed with 2 N sodium hydroxide, water and dried over anhydrous Na_2SO_4. Removal of solvent in vacuum left the bis-phosphate precursor as a colorless oil; a part (0.02 mol) of which in a THF solution (50 mL) was added from a dropping funnel to a lithium diisopropylamide (LDA) (0.08 mol) solution in 100 mL of THF at – 78 °C. After the addition was completed, the reaction mixture was stirred at – 78 °C for three additional hours, then the reaction mixture was quenched with 200 mL of saturated aqueous ammonium chloride. The organic mass was extracted with ether and chloroform, dried over anhydrous Na_2SO_4; after evaporation of the solvents at reduced pressure a white solid was left, which was purified by column chromatography on silica gel using as eluent a gradient of ethyl acetate in cyclohexane to give the pure desired dialkyl-(2-hydroxyaryl) diphosphonate.

Data for compound **2a**, *2,2-Bis(3-diethylphosphono-4-hydroxyphenyl)-propane*. White needles from cyclohexane/ethyl acetate mixture, yield 75%, m.p. 103–104 °C; ^{1}H-NMR ($CDCl_3$) δ: 10.07 (s, 2H, ArOH), 7.24 (m, 4H, ArH), 6.86 (m, 2H, ArH), 4.05 (m, 8H, OCH_2), 1.62 (s, 6H, CH_3), 1.28 (t, 12H, $^3J_{HH} = 7$ Hz); $^{13}C\{^1H\}$-NMR δ: 160.10 (d, $^2J_{CP} = 7.4$ Hz), 141.35 (d, $^3J_{CP} = 12.8$ Hz), 134.04, 128.71 (d, $^2J_{CP} = 2.7$ Hz), 117.30 (d, $^3J_{CP} = 8.3$ Hz), 107.95 (d, $^1J_{CP} = 178.7$ Hz), 62.54 (d, $^2J_{CP} = 4.4$ Hz), 41.61, 30.64, 16.08 (d, $^3J_{CP}$= 6.4 Hz); $^{31}P\{^1H\}$-NMR δ: 21.24; FAB-MS: m/z 501 $[M + H]^+$ base peak.

Data for compound **2b**, *Bis-(3-diethylphosphono-4-hydroxyphenyl) sulfide.* White needles from cyclohexane/ethyl acetate mixture, yield 70%, m.p. 119–120 °C; ^1H-NMR ($CDCl_3$) δ: 10.4 (brs, 2H, ArOH), 7.39 (m, 4H, ArH), 6.90 (m, 2H, ArH), 4.07 (m, 8H, OCH_2), 1.27 (t, 12H, $^3J_{HH} = 7$ Hz); $^{13}C(^1H)$-NMR δ: 161.45 (d, $^2J_{CP} = 7.3$ Hz), 138.26 (d, $^4J_{CP} = 2.4$ Hz), 134.39 (d, $^2J_{CP} = 6.6$ Hz), 126.03 (d, $^3J_{CP} = 14.6$ Hz), 118.82 (d, $^3J_{CP} = 12.6$ Hz), 110.02 (d, $^1J_{CP} = 178.4$ Hz), 62.85 (d, $^2J_{CP} = 4.4$ Hz), 16.07 (d, $^3J_{CP} = 6.4$ Hz); $^{31}P\{^1H\}$-NMR δ: 19.55; FAB-MS: m/z 491 $[M + H]^+$ base peak.

Data for compound **2c**, *Bis-(3-diethylphosphono-4-hydroxyphenyl) sulfone.* White prisms from water/acetic acid mixture, yield 85%, m.p. 130–131 °C; ^1H-NMR ($CDCl_3$) δ: 10.93 (brs, 2H, ArOH), 8.01 (dd, 2H, $^3J_{HP} = 14.6$ Hz, $^4J_{HH} = 2.4$, ArH), 7.83 (dd, 2H, $^3J_{HH} = 8.9$ Hz, $^4J_{HH} = 2.3$, ArH), 7.04 (dd, 2H, $^3J_{HH} = 8.8$ Hz, $^4J_{HP} = 5.8$, ArH), 4.11 (m, 8H, OCH_2), 1.33 (t, 12H, $^3J_{HH} = 7$ Hz); $^{13}C\{^1H\}$-NMR δ: 165.69 (d, $^2J_{CP} = 8.2$ Hz), 133.88 (d, $^4J_{CP} = 1.9$ Hz), 132.65 (d, $^3J_{CP} = 14.3$ Hz), 132.9 (d, $^2J_{CP} = 7.3$ Hz), 118.90 (d, $^3J_{CP} = 11.5$ Hz), 110.26 (d, $^1J_{CP} = 181.5$ Hz), 63.39 (d, $^2J_{CP} = 4.9$ Hz), 16.12 (d, $^3J_{CP} = 6.4$ Hz); $^{31}P\{^1H\}$-NMR δ: 18.06; FAB-MS: m/z 523 $[M + H]^+$ base peak.

Data for compound **3**, *Bis-(5,5′-diethylphosphono)-6,6′-dihydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobiindane.* White needles from cyclohexane, yield 77%, m.p. 144–146 °C; ^1H-NMR ($CDCl_3$) δ: 10.5 (brs, 2H, ArOH), 7.14 (d, $^3J_{HP} = 14.3$ Hz, 2H, ArH), 6.38 (d, $^4J_{HP} = 6.1$ Hz, 2H, ArH), 4.13 (m, 8H, OCH_2), 2.30 (q, 4H, CH_2), 1.37 (s, 6H, CH_3), 1.35 (t, $^3J_{HH} = 7.16$ Hz, 12H, CH_3), 1.31 (s, 6H, CH_3); $^{13}C\{^1H\}$-NMR δ: 161.62 (d, $^2J_{CP}$= 8.53 Hz), 158.41, 143.82 (d, $^3J_{CP} = 13.1$ Hz), 124.48 (d, $^2J_{CP} = 6.53$ Hz), 112.90 (d, $^3J_{CP}$= 13.4 Hz), 107.47 (d, $^1J_{CP} = 179.2$ Hz), 62.65 (d, $^2J_{CP} = 4.5$ Hz), 62.51 (d, $^2J_{CP} = 4.6$ Hz), 58.89, 57.78, 43.03, 31.81, 30.22, 16.15 (d, $^3J_{CP}$= 6.5 Hz); $^{31}P\{^1H\}$-NMR δ: 22.12; FAB-MS : m/z 581 $[M + H]^+$ base peak.

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