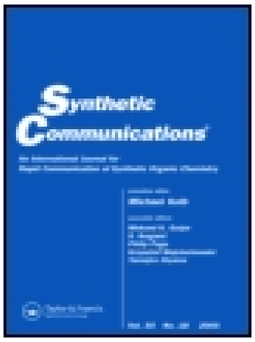

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AN IMPROVED SYNTHESIS OF PHOSPHA-CROWN ETHERS

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ABSTRACT : A synthetic and convenient pathway to phospha-crown ethers is presented involving the condensation of dichlorophenylphosphineoxide with polyethylene glycols under conditions that avoid polymerization.

Since phosphorus is a well established atom for stabilization of low oxidation state transition metal complexes[1,2], crown ethers incorporating phosphorus atoms in different valences, have become a growth area for chemistry[3-9]. Thus, very little is known about their ionophoric properties and fundamental questions remain to be probed, namely how the ring size, the combinations of donor atoms, the relative crown distribution as well as the relative stereochemistry within the macrocycles, can modify these properties.

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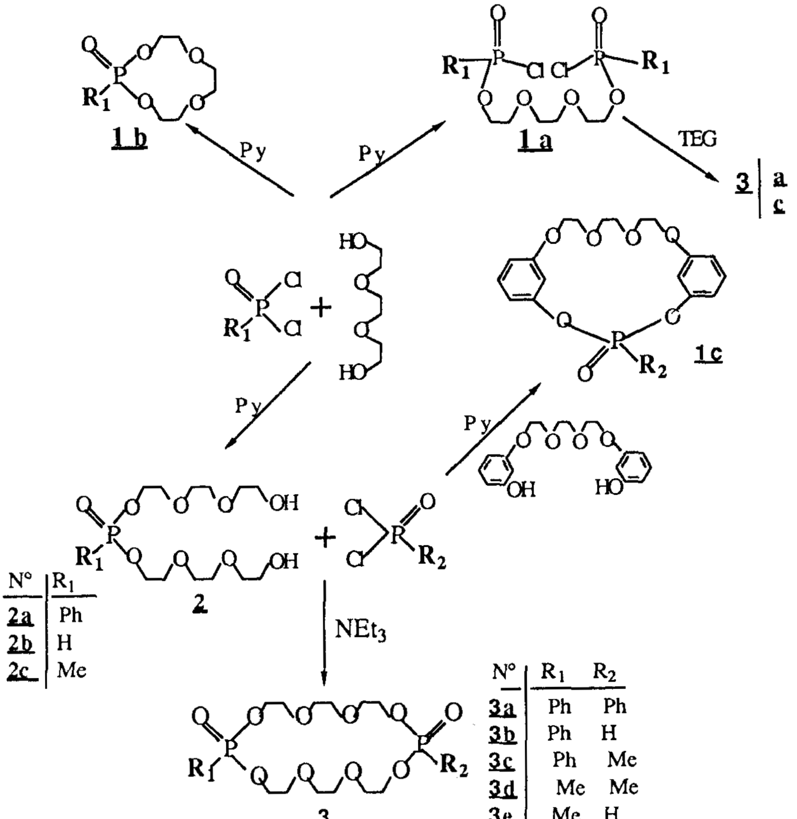
To answer these questions, we thought that the macrocycle must be systematically modified by changing only one variable at the time. In this regard, we wish to report a general synthesis of homogeneous series of diphosphacrown ethers via the reaction of dichlorophenylphosphine oxide with polyethylene glycols in which the cavity size is taken unchanged (scheme-I).



N°	R1
2a	Ph
2b	H
2c	Me

N°	R1	R2
3a	Ph	Ph
3b	Ph	H
3c	Ph	Me
3d	Me	Me
3e	Me	H

Scheme-1

In the course of our investigation on the former condensation, we found that within a range of precursor concentrations (lower than 10^{-5}M) , the reaction led to the open isolable phosphonite **2**, which structure was confirmed by elemental analysis and ^{31}P NMR spectroscopy, while the near molar stoechiometric amounts led to the cyclic phosphonite **1b**, contaminated with small amount of **1a** (5-10%), which is a key intermediate for polymerization .However, the condensation of equivalent amount of Triethylene glycol (TEG) gave **3** and hence confirm the structure of **1a**. On the other hand , subsequent coupling of **2** with dichlorophenylphosphine oxide in triethylamine gave the diphosphacrowns **3**.

Experimental

All manipulations involving air-sensitive specises were carried out in Schlenk apparatus under dry nitrogen ^{1}H.n.m.r. and^{13}C spectra were recorded on a Brucker AC-100 instrument with $CDCl_3$ as the solvent; the chemical shifts were reported in ppm, by reference to Me_4Si . ^{31}P chemical shifts were reported in ppm, from H_3PO_4 (85%) as external reference .Column chromatography was performed by using Merck Kiesegel 60 (230-400 mesh, ASTM).

General procedures; Compound 2a .To a solution of 5.30ml (27 mmol) of dichlorophenylphosphine oxide (Aldrich) in 300ml of N_2-purged pyridine and cooled to 0°C , was added 7.20ml (54 mmol) of triethylene glycol over a 30- min periode . The mixture is then stirred (at 0°C) for 1hr , and at ambiant temperature for 3hours . Subsequent to filtration of pyridinium chloride and distillation of the solvent in vacuo, the product was purified by column chromatography, silica gel, eluting with 3 : 2 acetone : methanol solvent mixture. Removal of the solvent resulted in the product **2a** (R_1 = Ph) in 52 % recovered yield, anal. Found (Calcd), C, 48.41 (49.09) ; H, 7.53 (7.55) P7.04 P(7.03), m/e 459. Spectral data ($CDCl_3$, d) : ^{1}H, 3.36 - 4.25 (m, CH_2, 24), 7.65 - 7.88 (m, Ar, 5) ; ^{13}C, 61.23, 70.35, 71.91 (CH_2) ; 129.15, 130.60, 131.21, 134.21 Ph), ^{31}P,18.83.

Compoud 3a .To a mixture of (7.10 mmol) of dichlorophenylphosphine oxide in 150ml of triethylamine , was added at O°C (7.10 mmol) of **2a** in 30ml of

Table 1. Spectroscopic and analytical data for new compounds.
R_1 ; R_2 ; Yield ; anal found (Calcd), MW.

1c (R_2= Ph) 48% ; C, 60.76 (60.50) ; H, 5.73 (5.45) ; P, 6.53 (6.42), 474.
^{1}H 3.50 - 3.80 (m, 8H , OCH_2) ; 4.10 - 4.21 (m, 4H , OCH_2) ; 6.60 - 6.75 (m, 6H, aromH) ; 7.15 - 7.30 (m, 5H, aromH) ; 7.90 - 8.10 (m, 2H, aromH).
^{13}C, 69.35 ; 69.42 ; 70.62 (OCH_2) ; 112.80 ; 118.14 ; 121.15 ; 121.18 ; 128.30 ; 131.30 ; 131.70 ; 131.78 ; 135.60 ; 148.10.
^{31}P 51.12.

2c 62% ; C, 41.27 (41.00) ; H, 8.26 (8.30) ; P, 8.18 (8.04), 378.
^{1}H 3.12 (CH_3) ; 3.55 - 4.12 (m, CH_2).
^{13}C 20.0 (CH_3) ; 61.3 ; 70.2 ; 71.8[b].
^{31}P 4.2.

3b[a] **Ph; H**; 31%; C, 45.90(46.16), H, 6.40(6.45), P, 13.10(13.22), 469.
^{1}H 3.56; 4.25 (m, CH_2) ; 7.50-7.80 (m, Ph).
^{13}C 62.32, 71.28, 72.70 (CH_2) ; 129.94, 132.32, 132,36, 134.16 (Ph)
^{31}P 3.76 (PH) ; 19.83 (PPh).

3c **Ph; Me**; 54%;
^{1}H 3.57; 4.14 (m, CH_2) ; 3,50 (Me) ; 7.52 - 7.61 (Ph).
^{13}C 61.32, 70.35, 71.03 (CH_2) ; 129.84, 131.0, 131.26, 134.12 (Ph).
^{31}P 4.91 (PMe); 19.82 (PPh).

3d **Me; Me**; 62%; C, 40.00(40.08) ; H 7.19(7.18) ; P 14.73(14.72)
^{1}H 3.14 (CH_3); 3.60, 4.14 (m, CH_2).
^{13}C 21.0 (CH_3); 61.77, 70.70, 72.27 (CH_2).
^{31}P 4.91

3e **Me; H**; 54%
^{1}H 0.95 (d, PH, J_{PH} = 657 Hz)) ; 3.74 (CH_3); 3.57; 4.21 (m, CH_2).
^{13}C 61.45, 70.83, 72.36 (CH_2).
^{31}P 3.75 (PH); 4.90 (PMe).

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[a] The PH resonance was not observed in the NMR spectrum.

[b] The rest of Carbon-resonances are centered around this value.

Triethylamine and stirred at O°C for 1 h and at ambiant temperature for 2hours. The triethylamine hydrochloride was filtered and the solvent removed in vacuo. Purification of the product by column chromatography, silica gel, elution with a 1 : 1 acetone : methanol solvent mixture, yielded the macrocycle **3a** ($R_1 = R_2 = Ph$) in 48% yield. Anal. m/e = 545 ; found (calcd) C, 48.08 (48.16) ; H, 6.69 (6.74) ; P 10.34 (10.35). Spectral data ($CDCl_3$, d), ^1H, 3.56 - 4.25 (CH_2, 24), 7.56 - 7.75 (m, Ph, 10) ; ^{13}C, 61.22, 70.31, 71.18 (CH_2), 127.92, 128.47, 129.94, 130.42, 132.15, 134.08 (Ph), ^{31}P, 19.19.

Compound 1c. The corresponding intermediate Bis- Benzocathecol was prepared from resorcinol through known procedures[8]. The cyclisation was performed in the same conditions as for **1b** in 48% after chromatography over silica gel .

These synthetic procedures were readily extended to other related diphospha-crowns, Table 1. Is stems from our studies on their ionophoric properties, that the phosphoryl groups make the main contribution to the stability of the complex , its decisive role in complex formation has been demonstrated[11].

References

1. Higgins, S.J., Taylor, R and Shaw, B.L., J.organom. Chem., 1987,**325**, 285.
2. Kyba, E.P., Davis, R.E., Fox, M.A., Clubb, C.N., Liu, S.T, Reitz, G.A., Scheuler, V.J and Kashyap, R.P., Inorg. Chem., 1987, **26** , 1647
3. Cristau, H.J., Chiche, L., Fallouh, F., Hullot, P., Renard, G. and Cristol.H., Nouv. J. Chim., 1984, **8** , 191.
4. Wei ,L., Bell , A., Williams , I.D and Lippard , S.J., J . Am . Chem . Soc.1986, **108** , 9302 .

5. Chaykovskaya, A.A., Kudrya, T.N. and Pinchuk, A.M., Zhur. Obshch. Khim., 1987, **57** , 671.

6. Tsvetkov, E.N., Bovin, A.N. and Syundrukova, V.Kh., RUSS. Chem. Rev., 1988, **57**, 776. and references cited therein.

7. Dutasta, J.P., Declercq, J.P., Esteban-Calderon, C and Tinant. B., J.Am.chem .Soc., 1989, **111**, 7136.

8 . Dutasta, J.P and Simon, P. , Tet . Lett ., 1987, **28** , 3577 .

9. Gonce, F . , Caminade, A.M ., Majoral, J.P .,Jaud, J., Vignaux, P ., Bull. Soc . Chim . Fr ., 1992 , **129** , 237 .

10 . Habata ,Y and Akabori , S ., Tet . Lett .,1992,**33** 5815 .

11. El Malouli bibout, M. , Hannioui, A. , Peiffer, G. , Samat, A. and Pannell, K.H. , Bull. Soc. Chim. Fr. , 1993 (under press).

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