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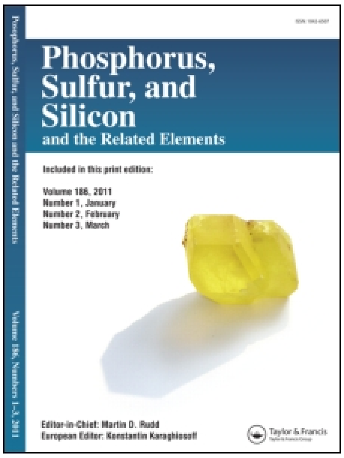

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BICYCLOPHOSPHORANES CONTAINING MACROCYCLES

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Abstract : Pentacovalent Phosphorus containing Macrocycles, **1,2,7** have been obtained by a general method applicable to all α– ω diols.

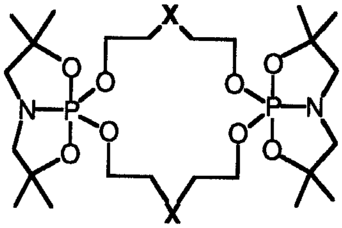
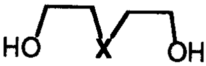
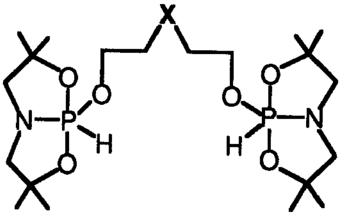
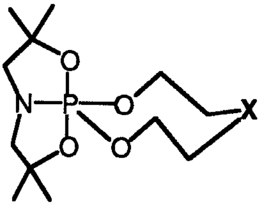
INTRODUCTION

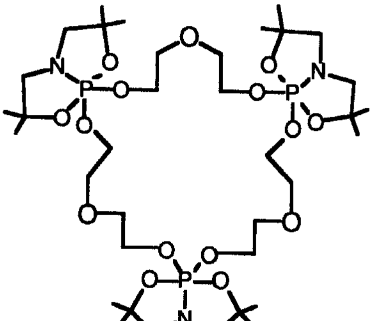
This work is motivated by the hope that a macrocycle containing conventional atoms (O,N, ...) and a Lewis acid centre could be able to recognize both cation and anion. Two recent papers (1, 2) convince us that such a target could be achieved using pentacovalent phosphorus containing macrocycles.We plan to gather in the same molecule a cation complexation site (macrocycle) and an anion capture site, the pentacovalent phosphorus that gives an hexacoordinated phosphorus anion. Only recently such an approach has been developped in two different works, using boron (3) or ammonium (4) as electrophilic centres.

Here we report the results of our attempts to prepare crown ethers including two pentacovalent phosphorus atoms as acidic centres.

EXPERIMENTAL RESULTS

The synthetic scheme involves two steps : the first is the preparation of the bis (hydridobicyclophosphoranes) **3, 4** by the addition of the corresponding 1-5 pentane diol **a, b** on the bicyclophosphane **8** (5). The second step is an Atherton- Todd reaction between **3** and **a, 4** and **b**, using the experimental conditions recently described (6,7).

X =	O	N-Bu
	1	2
	a	b
	3	4
	5	6



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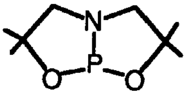

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The bis(hydridobicyclophosphorane) **3** is obtained in quantitative yield after 15 mn stirring of the acetonitrile solution of **a** and **8** at room temperature: δ ^{31}P = -39,8 ppm ; $^{1}J_{P-H}$ = 800 Hz. The Atherton-Todd reaction is then performed by addition of an acetonitrile solution of **a**, CCl_4 and Et_3N (relative concentrations 1,1,2). The reaction monitored by ^{31}P NMR, is achieved after 48 h. stirring at room temperature. The amount of triethylammonium chloride, precipitated by addition of ether, corresponds to that expected. The ^{31}P NMR spectrum of the reaction mixture contains 5 peaks : - 42.9 ppm (5%) , -44.6 ppm (30 %) , - 45.2 ppm (11%) , - 45.4 ppm (2 %) , - 45.6 ppm (27%) and two other minor peaks at 20.3 and -11.3 ppm (traces).

A chromatographic separation (silicagel 60 ACC, 70-230 mesh ; 1,2 x 20 cm column, ethyl acetate-cyclohexane as eluent , fractions monitored by ^{31}P NMR) allows the isolation, in pure form, of the compounds corresponding to the two first peaks. A third fraction of 20 / 80 composition (-44.6 and -45.1 ppm) was also isolated. The structure of the separated compounds was determined using mass spectroscopy (chemical ionization by NH_3) , ^{13}C and ^{1}H NMR. Worth to notice is the ease to differentiate the compounds with NMR, as shown for example on the ^{13}C chemical shifts in the sequence **5**, **1**, **7** (8, 16 and 24 membered rings) :

		5	**1**	**7**
δ 13C	(P)O-$^{13}CH_2$-	69,0	67,1	67,3
δ 13C	CH_2-O-$^{13}CH_2$	73, 0	71,1	71,5

We have established that the expected macrocycle **1** corresponds to the -44.6 ppm fraction. Peaks at -42.8 ppm and -45.1 ppm correspond respectively to the eight membered ring **5** and to the 24 membered ring **7**. The yields in pure compounds are very poor, 1% for each, referred to the used amount of **a** and **8**. Obviously the chromatographic separation of these macrocycles needs to be optimized.

Yields are better in the condensation of **4** (δ ^{31}P = -38.9 ppm, $^{1}J_{PH}$ = 792.4 Hz) with **b**. Following the same proceedure we isolated and characterized **2** ($\delta^{31}P$: -45.0 ppm, 14.4% of the mixture, quantitatively separated by chromatography) and **6** ($\delta^{31}P$: -42.9 ppm, 25% of the mixture, separated with 30 % yield).

In conclusion we have performed the first step of our target i.e. the obtention of pentacovalent phosphorus containing macrocycles. These compounds are very stable. This stability, very likely due to the bicyclic structure introduced on the phosphorus atom, contrast with that of the large-ring dioxytriphenyl phosphoranes, not enough stable to be isolated (8).

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