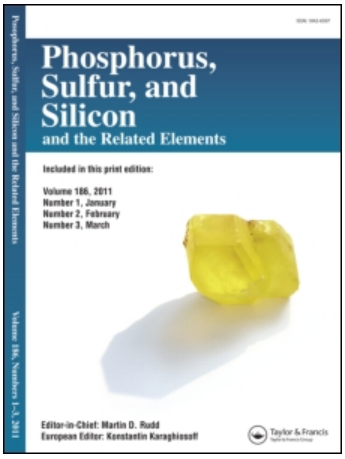


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# ON THE EXTENSION OF THE ATHERTON-TODD REACTION TO THE PENTACOORDINATED PHOSPHORUS COMPOUNDS. SYNTHESIS OF NEW BICYCLOPHOSPHORANES CONTAINING MACROCYCLES

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# ON THE EXTENSION OF THE ATHERTON-TODD REACTION TO THE PENTACOORDINATED PHOSPHORUS COMPOUNDS. SYNTHESIS OF NEW BICYCLOPHOSPHORANES CONTAINING MACROCYCLES

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The three macrocycles **5**, **6**, **7** with 10, 16 and 22 links, bearing two bicyclophosphoranes moieties are synthesized by the Atherton-Todd reaction carried out with the bis(hydridobicyclophosphoranes) **2**, **3**, **4**. This result confirms the generality of this reaction leading to new families of bis(bicyclophosphoranes) containing macrocycles.

Les trois macrocycles **5**, **6**, **7** à dix, seize et vingt deux chaînons, comportant deux motifs bicyclophosphoraniques ont été synthétisés par application de la réaction d'Atherton-Todd aux bis(hydridobicyclophosphoranes) **2**, **3**, **4**. Ce résultat confirme le caractère général de cette réaction qui permet l'accès à de nouvelles familles de macrocycles bis(bicyclophosphoraniques).

*Key words:* Bis(hydridobicyclophosphoranes); Atherton-Todd reaction; bicyclophosphoranes; macrocycles.

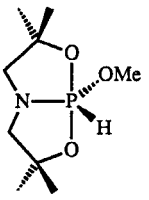


## INTRODUCTION

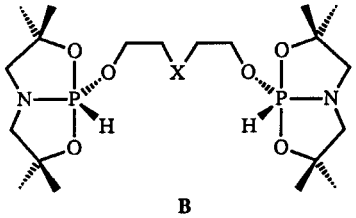
We have recently extended the so-called Atherton-Todd reaction to the 1-hydrido 1-methoxybicyclophosphorane **A**.[1]

This reaction has been used with a variety of bis(hydridobicyclophosphoranes) (**B**) (X=O, N—Bu, N—tBu, N—Ph) which have been condensed with the same binucleophile $HO(CH_2)_2X(CH_2)_2OH$ leading to the first bicyclophosphoranes containing macrocycles.[2]

Recent publications[3–5] convince us that the presence of a Lewis acid i.e., a pentacovalent phosphorus atom, in a conventional atoms (O, N) containing macrocycles would confer interesting properties to such molecules. The purpose of this paper is to report on a successful synthesis of symmetrical bicyclophosphoranes containing macrocycles starting from three readily available diols. We present now three macrocycles with 10, 16 and 22 units.




**A**




**B**

## RESULTS AND DISCUSSION

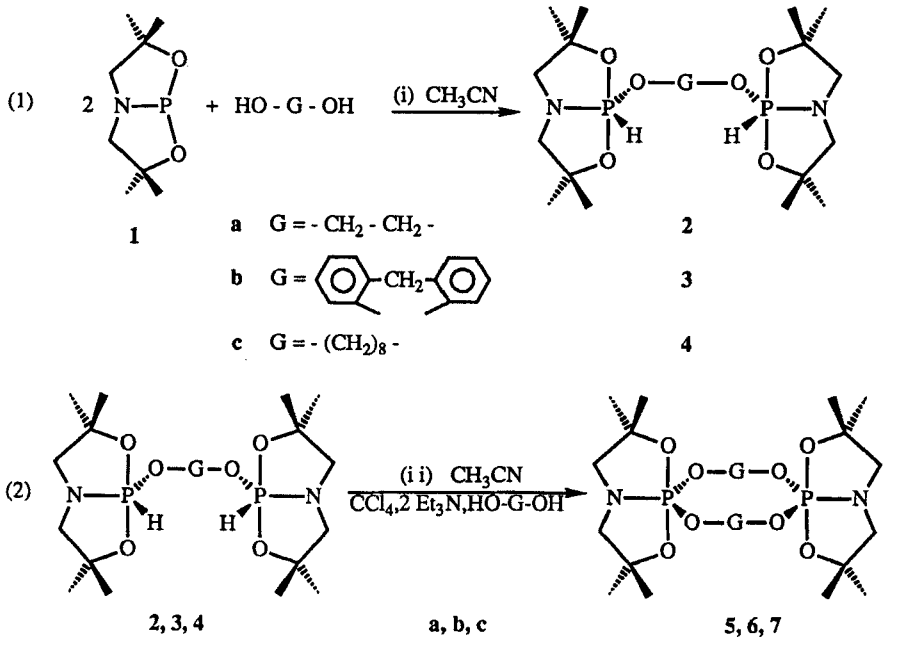
The synthetic procedure involves two steps: (i) the preparation of the bis(hydridobicyclophosphoranes) **2**, **3** and **4** by the oxidative addition of the corresponding diol (**a**, **b** and **c**) on the bicyclophosphane **1**.[2] (ii) an Atherton-Todd reaction between **2** and **a**; **3** and **b**; **4** and **c**, using the experimental conditions recently described.[1]

The bis(hydridobicyclophosphoranes) **2**, **3** and **4** have been obtained in quantitative yield after 30 minutes stirring of the acetonitrile solution of **1** with the corresponding diols at room temperature. They have been fully characterized by NMR [$^{31}P$, $^{1}H$ and $^{13}C$ (see EXPERIMENTAL)].

The Atherton-Todd reaction is then performed in acetonitrile as solvent, at room temperature, with the same binucleophile **a**, **b** or **c**. The molar ratio of the reactants was always approximatively: bis(hydridobicyclophosphorane)/$CCl_4$/$Et_3N$/NuH = 1/1/2/1.

The $^{31}P$ NMR spectrum of the reaction mixture contains two or three signals at c.a: $-40$ ppm, one of them being predominant, accompanied by minor peaks corresponding to tetracoordinated phosphorus compounds. The treatment of the crude product depends on the experiment.

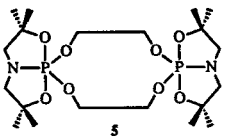
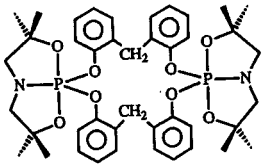
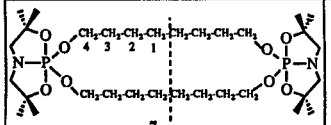
In the case of **2** + **a** and **4** + **c**, the major compounds **5** and **7** have been precipitated by addition of ethylacetate and acetonitrile respectively. For **3** + **b** a flash chromatography induces the elimination of the tetracoordinated phosphorus compounds. The resulting material has been subjected to a chromatographic separation on silica block (eluent:cyclohexane/ethylacetate 3/1) leading to the pure compound, **6**; the three derivatives **5**, **6** and **7** correspond to the [1 + 1] condensation




SCHEME 1

TABLE I

NMR parameters of macrocycles **5**, **6**, **7**

| | $^{31}P$ [δ ,ppm] | $^{1}H$ [δ, ppm J(Hz)] | $^{13}C$ [δ, ppm J(Hz)] |
|---|---|---|---|
|  **5** ($C_6D_6$) | - 43,5 (s) | 1.3 (s, 24H, $CH_3$)<br>2.7 (d, 8H, $^3J_{HP}$ = 13.2, N-$CH_2$)<br>4.1 (m, 8H, $OCH_2$) | 28.6 (d, $^3J_{CP}$ = 3.8, $CH_3$)<br>55 (d, $J_{CP}$ = 20.6, N-$CH_2$) [a]<br>67.9 (d,d, $J_{CP}$ = 9.4 and $J_{CP}$ = 5, 0 O-$CH_2$)<br>69.8 [s, -C-(Me)2] |
|  **6** ($CDCl_3$) | - 48.4 (s) | 1.1 (s, 24H, $CH_3$)<br>2.9 (d, 8H, $^3J_{HP}$ = 13.7, N-$CH_2$)<br>4.0 (m, 4H, $CH_2$)<br>6.8<δ<7.3 (m, 16H, $C_6H_5$) | 28.6 (d, $^3J_{CP}$ = 4.3, $CH_3$)<br>33.6 (s, $CH_2$)<br>54.9 (d, $^2J_{CP}$ = 20.8, N-$CH_2$) [a]<br>70.9 [s, -C-(Me)2]<br>122 (d, $J_{CP}$ = 5.9)<br>123.5 (d, $J_{CP}$ = 2.2)<br>126.6 (d, $J_{CP}$ = 1.8)<br>129.8 (d, $J_{CP}$ = 2.3) } $C_{ar}$-H<br>133.4 (d, $^3J_{CP}$ =3.9, $C_{ar}$-$CH_2$)<br>152.9 (d, $^2J_{CP}$ =10.4, $C_{ar}$-O-P) |
|  **7** ($CDCl_3$) | - 45.1 (s) | 1.3 (s, 24H, $CH_3$)<br>1.2<δ<1.4 (m, 16H ($_1CH_2$-$_2CH_2$)4]<br>1.7(q, 8H,$^3J_{HH}$ = 6.9,$_3CH_2$)<br>2.5(d, 8H,$^3J_{HP}$ = 12.8,N-$CH_2$)<br>4.1(dt, 8H,$^3J_{HH}$=6.9 and $^3J_{HP}$=6.8,O-$CH_2$) | 26.7 (s, $CH_2$-1)<br>29.0 (d, $^3J_{CP}$ = 3.9, $CH_3$)<br>30.1 (s, $CH_2$-2)<br>31.7 (d, $^3J_{CP}$ = 9.0 $CH_2$-3)<br>55.4 (d, $J_{CP}$ = 20.5, N-$CH_2$) [a]<br>67.8 (d, $^2J_{CP}$ = 9.9, O-$CH_2$-4)<br>69.3 [s, (-C-(Me)2] |

[a] $^aJ_{CP} = \frac{1}{2}[^2J_{CP} + {}^3J_{CCOP}]$

as it is depicted in the reaction (2). Their structures have been established by NMR (see Table I) and mass spectroscopy

**5**: $m/z^+$ = 499 $(M + 1)^+$ 20%;
250 $(M/2 + 1)^+$ 40% (FAB, glycerol and $CDCl_3$)

**6**: $m/z^+$ = 775 $(M + 1)^+$ 0, 1%;
388 $(M/2 + 1)^+$ 100% (chemical ionisation by $NH_3$)

**7**: $m/z^+$ = 667 $(M + 1)^+$ 100% (chemical ionisation by $NH_3$).

For all these compounds, the NMR parameters are consistent with the following characteristics: the center of the macroring whose mean conformation is nearly plane, is a symmetry centre of the molecule and the equatorial plane of the trigonal bipyramidal bicyclophosphorane group, which contains the mean macroring plane is also a symmetry plane of the molecule.

No others products have been separated by chromatography.

## CONCLUSION

The related results establish the general character of this reaction which can lead to new bis(bicyclophosphoranes) containing macrocycles of different sizes; this reaction opens a new way, towards unusual macrocycles incorporating two pentacoordinated phosphorus atoms.

Our project is to demonstrate that these phosphoranes, analogues of crown ethers can be selective towards cations; the oxygen atoms bound to phosphorus centers could have a specific role in the complexation.

## EXPERIMENTAL

*Synthesis of bis(hydridobicyclophosphoranes).* The preparation is identical for the three bis(hydridobicyclophosphoranes). The compound **2** has been previously described. We present the synthesis of **3** and **4**.

*Compound* **3**: A solution of 0.761 g ($4.10^{-3}$ mole) of bicyclophosphane **1** in 3 ml of toluene is added to a solution of 0.404 g ($2.10^{-3}$ mole) of bis(2-hydroxyphenyl)methane **b** in 1 ml of toluene. The reaction is almost instantaneous and slightly exothermic. The mixture is stirred during half an hour and analyzed by NMR.

$^{31}$P NMR (32.44 MHz, $CDCl_3$): $-38.5$ $^1J_{PH}$ = 822 Hz.
$^1$H NMR (250.13 MHz, $CDCl_3$): 1.09 (s, 12H, $CH_3$); 1.26 (s, 12H, $CH_3$); 2.82 and 2.87 [2 q AB, 8H (ABX part) $^2J_{HH}$ = $-8.5$ Hz, $^3J_{HP}$ = 11.2 Hz and $^3J_{HP}$ = 18.2 Hz, N—$CH_2$]; 4.02 (s, 2H, —$CH_2$—); 7.1 (m, 8H, $C_6H_4$); 7.3 (d, 2H, $^1J_{HP}$ = 823 Hz, H-P).
$^{13}$C NMR (62.89 MHz, $CDCl_3$): 29.5 (s, $CH_3$), 29.6 (s, $CH_3$); 30.0 (s, $CH_2$); 54.7 [d, $J_{CP}$ = $\frac{1}{2}$($^2J_{CNP}$ + $^3J_{CCOP}$) = 19.3 Hz, N—$\underline{C}H_2$]; 71.1 [s, $\underline{C}(Me)_2$]; 121.5 (d, $^3J_{CP}$ = 4.6 Hz, $\underline{C}_{ar.}$—$CH_2$—); 122.9, 126.4, 130.6, 132.1 (s, $\underline{C}$ar—H); 152.4 (d, $^2J_{CP}$ = 9.3 Hz, $\underline{C}_{ar.}$—O—P).

*Compound* **4**: We add 0.336 g ($2.3.10^{-3}$ mole) of the solid octanediol to a solution of 0.870 g ($4.6.10^{-3}$ mole) of bicyclophosphane **1** in 3 ml of acetonitrile. After extraction of the solvent the product is colorless oil characterized by NMR.

$^{31}$P NMR (32.44 MHz, $CH_3CN$): $-37.8$ $^1J_{PH}$ = 791 Hz.
$^1$H NMR (250.13 MHz, $CDCl_3$): 1.15 (s, 12H, $CH_3$); 1.18 (s, 12H, $CH_3$); 1.32 < $\delta$ < 1.46 (m, 12H, —$(CH_2)_6$—); 2.66 and 2.7 [2 q. AB (ABX part), 8H, $^2J_{HH}$ = $-8$ Hz, $^3J_{HP}$ = 14.7 Hz, $^3J_{HP}$ = 12.5 Hz, N—$CH_2$—]; 3.72 (dt, 4H, $^3J_{HH}$ = 6.9 Hz, $^3J_{H-P}$ = 9 Hz, O—$CH_2$—); 6.6 (d, 2H, $^1J_{HP}$ = 792 Hz, H—P).
$^{13}$C NMR (62.89 MHz, $CDCl_3$): 25.7 (s, —$CH_2$—); 28.7 (s, $CH_3$); 29.2 (d, $^3J_{CP}$ = 4.7 Hz, $CH_3$); 30.8 (d, $^3J_{CP}$ = 8.5 Hz, —$CH_2$—), 32.6 (s, —$CH_2$—); 55.1 [d, $J_{CP}$ ($\frac{1}{2}$($^2J_{CNP}$ + $^3J_{CCPO}$) = 18.6 Hz, N—$\underline{C}H_2$]; 66.2 (d, $^2J_{CP}$ = 7.3 Hz, O—$\underline{C}H_2$—); 70.3 [d, $^2J_{CP}$ = 4.8 $\underline{C}(Me)_2$].

*Syntheses of macrocycles:* **5**, **6** *and* **7**. We realize the Atherton-Todd reaction with the three bis(hydridobicyclophosphoranes). The general procedure is the following. The acetonitrile solution of one equivalent of bis(hydridobicyclophosphorane), two equivalents of dry carbon tetrachloride, four equivalents of triethylamine and one equivalent of nucleophile (diol) is stirred at room temperature. The reaction monitored by $^{31}$P NMR is achieved after two or three days. The amount of triethylammonium chloride precipitated by addition of diethylether corresponds to that expected. After evaporation under vacuum of the solvent and volatile products, the crude mixture is purified as depicted above.

*Macrocycle* **5**: Bis(hydridobicyclophosphorane) **2**: 1.28 g ($2.86.10^{-3}$ mole); $CCl_4$: 0.882 g ($5.73.10^{-3}$ mole), triethylamine: 1.16 g ($1.14.10^{-2}$ mole) ethyleneglycol **a**: 0.18 g ($2.86.10^{-3}$ mole) $CH_3CN$: 30 ml.

*Macrocycle* **6**: Bis(hydridobicyclophosphorane) **3**: 1.16 g ($2.10^{-3}$ mole), $CCl_4$: 0.657 g ($4.10^{-3}$ mole); $Et_3N$: 0.813 g ($8.10^{-3}$ mole), bis(2-hydroxyphenyl)methane **b**: 0.404 g ($2.10^{-3}$ mole); $CH_3CN$: 30 ml.

*Macrocycle* **7**: Bis(hydridobicyclophosphorane) **4**: 1.2 g ($2.3.10^{-3}$ mole) $CCl_4$ 0.708 ($4.6.10^{-3}$ mole), $Et_3N$: 0.929 g ($9.2.10^{-3}$ mole) octanediol **c**: 0.336 g ($2.3.10^{-3}$ mole); $CH_3CN$ 30 ml. Elemental analysis: $C_{32}H_{64}N_2O_8P_2$: M = 666; Calc.: %C: 57,65; N: 4.20; H: 9.61. Found: %C: 56.9; N: 4.3; H: 9.3.

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