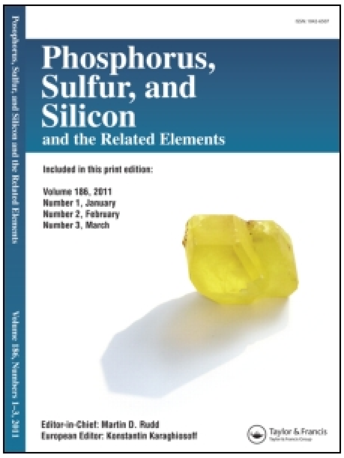

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NEW MACROCYCLES CONTAINING BICYCLOPHOSPHORANE MOIETIES IV[1]. MACROCYCLES ISSUED FROM POLYETHYLENEGLYCOLS AND TRIETHANOLAMINE

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To cite this Article Houalla, Douraid , Moureau, Loeticia , Skouta, Saïd and Mazieres, Marie-Rose(1995) 'NEW MACROCYCLES CONTAINING BICYCLOPHOSPHORANE MOIETIES IV[1]. MACROCYCLES ISSUED FROM POLYETHYLENEGLYCOLS AND TRIETHANOLAMINE', Phosphorus, Sulfur, and Silicon and the Related Elements, 103: 1, 199 — 204

To link to this Article: DOI: 10.1080/10426509508027378

URL: http://dx.doi.org/10.1080/10426509508027378

Phosphorus, Sulfur, and Silicon, 1995, Vol. 103, pp. 199–204
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NEW MACROCYCLES CONTAINING BICYCLOPHOSPHORANE MOIETIES IV[1]. MACROCYCLES ISSUED FROM POLYETHYLENEGLYCOLS AND TRIETHANOLAMINE

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Dedicated to Professor Reinhard Schmutzler on the occasion of his
60th birthday

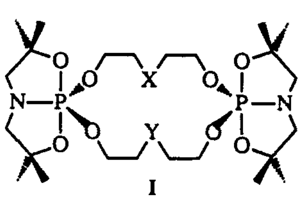
(Received October 5, 1994; in final form November 29, 1994)

New symmetric and mixed macrocycles containing bicyclophosphorane moieties **3**, **4**, **5**, **6**, **9** and **10** have been obtained by a Todd reaction between the precursors **1**, **2**, and diethyleneglycol DEG, triethyleneglycol Tri.EG and tetraethyleneglycol Tet.EG. The reaction of the precursor **11** with triethanolamine Tri.EA afforded the first cryptand bearing pentacoordinated phosphorus atoms **12**.

Key words: Polyethyleneglycols, pentacovalent phosphorus macrocycles.

INTRODUCTION

Recently we have described the synthesis of the first macrocycles containing 2 (**I**), 3 (**II**) and 4 (**III**) bicyclophosphorane moieties. All these compounds are synthesized from the corresponding 1,5-pentanediols according to the following two steps

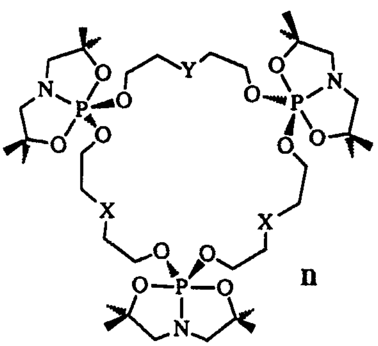


I

X = Y = O, N-Bu, N-tBu, N-Ph.

X = O, Y = S; X = N-Ph, Y = N-tBu

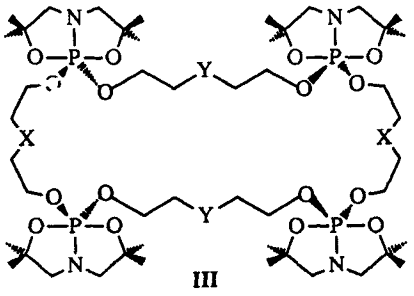
X = N-Me, Y = O; X = N-Me, Y = N-Ph



II

X = Y = O

X = S, Y = N-tBu X = O, Y = S



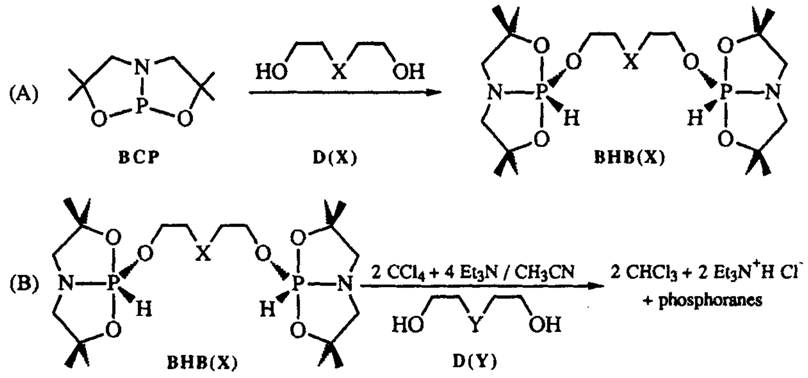
III

X = Y = O

X = S, Y = N-tBu

X = N-Ph, Y = N-tBu

synthetic scheme involving (i) the preparation of the precursor bis(hydridobicyclophosphorane)BHB(X) (reaction A) (ii) the Todd reaction of this

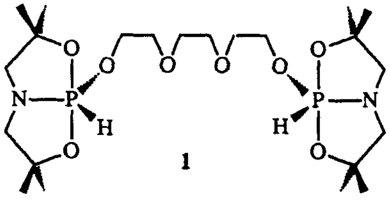


latter with the binucleophile D(Y) (reaction B). This last reaction has led to a mixture of several new P^V compounds from which the macrocycles **I**, **II** and **III** have been chromatographically separated.[2-6]

In order to extend the potential complexing properties of such macrocycles, we have attempted to prepare similar compounds derived from triethyleneglycol HO-$(CH_2O)_2$-CH_2OH, Tri.EG and tetraetyleneglycol HO-$(CH_2O)_3$-CH_2OH, Tet.EG, on one hand and a cryptand like compound issued from triethanolamine $N(CH_2$-$CH_2OH)_3$, Tri.EA, on the other hand.

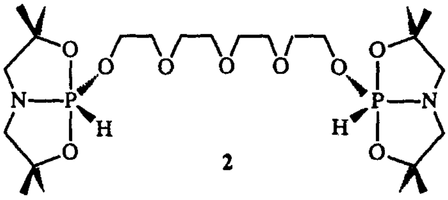
RESULTS

Starting from the precursors **1** and **2** obtained according to reaction (A) we have carried out two symmetric (1 + Tri.EG; 2 + Tet.EG) and two non-symmetric (2



1

$\delta\ ^{31}P = -36.6\ ^{1}J_{PH} = 800$ Hz

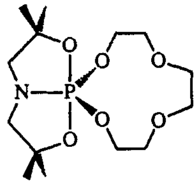


2

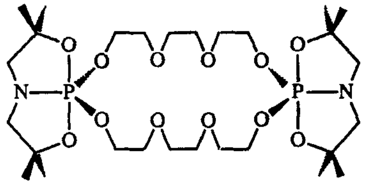
$\delta\ ^{31}P = -36.5\ ^{1}J_{PH} = 800$ Hz

+ DEG; 2 + Tri.EG) Todd reactions. As it was always observed in the previous reactions,[2-6] the reaction mixtures contained several new phosphoranes. The chromatographic separations[4] allowed the isolation of compounds **3–10** which have been fully characterized by NMR and mass spectroscopy.

1 + Tri.EG

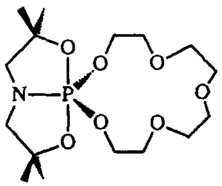


3 $\delta^{31}P$ = - 45.2

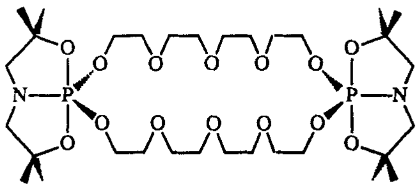


4 $\delta^{31}P$ = - 44.8

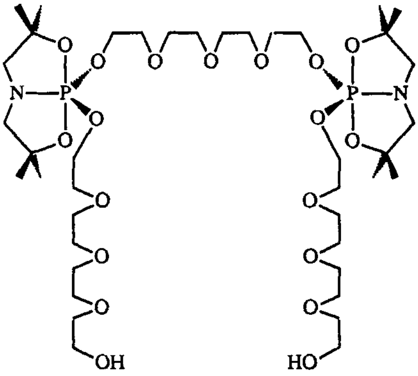
2 + Tet.EG



5 $\delta^{31}P$ = - 45.2



6 $\delta^{31}P$ = - 45.0

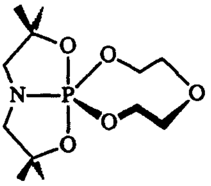


7 $\delta^{31}P$ = - 45.4

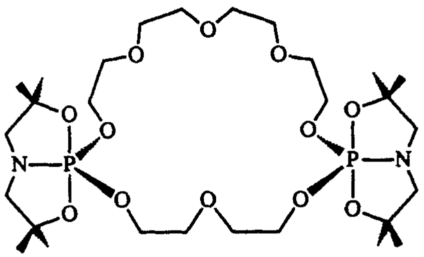
The formation of the acyclic compound **7** as well as that of the tricyclic monophosphoranes **3**, **5** and **8** derived from the starting diol D(X) and from the incoming binucleophile D(Y) (non-symmetric condensations) strongly support the synthetic pathway we have previously proposed.[5] The non eluted compounds could be noncyclic compounds similar to **7** and/or higher macrocycles.

The condensation of the precursor tris(hydridobicyclophosphorane)THB (Tri.EA) **11** derived from triethanolamine with the same trinucleophile has led to a reaction mixture which also contained several new phosphoranes. With the chromatographic

2 + DEG

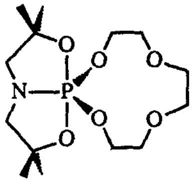


8 $\delta^{31}P = -42.9$

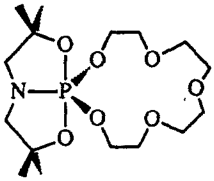


9 $\delta^{31}P = -44.9$

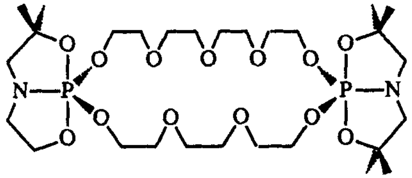
2 + TriEG



3 $\delta^{31}P = -45.2$

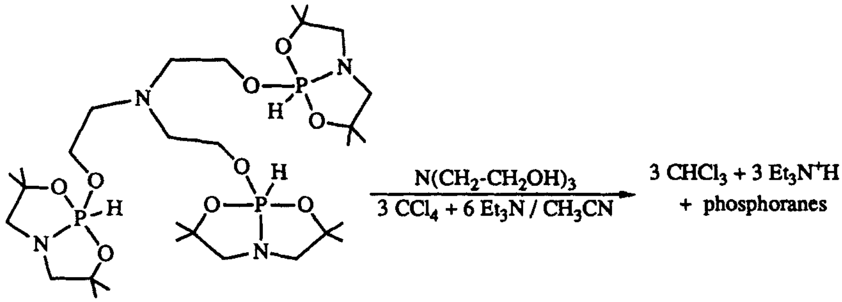


5 $\delta^{31}P = -45.2$



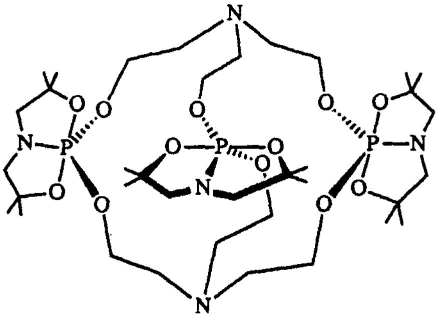
10 $\delta^{31}P = -45.0$

experimental conditions used till now, we have been unable to separate any compound. An appropriate treatment of the reaction mixture afforded the precipitation of a white solid which was identified as the bicyclic macrocycle **12** by means of NMR and mass spectroscopy. To the best of our knowledge **12** is the first cryptand



$$\xrightarrow[3\ CCl_4\ +\ 6\ Et_3N\ /\ CH_3CN]{N(CH_2\text{-}CH_2OH)_3} 3\ CHCl_3 + 3\ Et_3N^+H\ Cl^- + \text{phosphoranes}$$

11 $\delta^{31}P = -38.5$ $^1J_{PH} = 792$ Hz



12

$\delta^{31}P = -44.9$

containing pentacoordinated phosphorus atoms. All attempts to isolate other compounds were unsuccessful.

EXPERIMENTAL

I. Synthesis

The precursors BHB (Tri.EG), BHB (Tet.EG) and THB (Tri.EA) have been obtained by the routine procedure[7] i.e. the oxidative addition of the corresponding polyol on the bicyclophosphane BCP.[8] The removal of the solvent afforded an oily compound whose purity was checked by NMR. They were used as neat products.

The Todd reactions have been carried out following the previously described procedure.[2] The chromatographic separations of the reaction mixtures have been performed using silica gel or alumina as support and a mixture of solvents as eluent. The ^1H and ^{13}C NMR parameters of compounds **1–12** are in perfect agreement with the proposed structures. They will not be described.

I.1 BHB (Tri.EG) **1**

The reaction was carried out with 0.618 g (4.12 mmole) of Tri.EG, 0.779 g (4.12 mmole) of BCP in 15 mL of CH_3CN. Elemental analysis for $C_{22}H_{46}N_2O_8P_2$ calc.% C 49.99, H 8.77, N 5.30. found% C 49.6, H 8.8, N 5.4.

I.2 BHB (Tet.EG) **2**

The reaction was performed with 0.766 g (3.95 mmole) of Tet.EG and 0.747 g (3.95 mmole) of BCP in 15 mL of CH_3CN. Elemental analysis for $C_{24}H_{50}N_2O_9P_2$ calc.% C 50.34, H 8.80, N 4.89. found% C 50.4, H 9.0, N 4.9.

I.3 THB (Tri.EA) **11**

The reaction was carried out with 0.231 g (1.55 mmole) of Tri.EA, 0.882 g (4.66 mmole) of BCP in 10 mL of CH_3CN

I.4 Condensation BHB (Tri.EG) + Tri.EG

Amounts of reagents: BHB (Tri.EG): 1.397 g (2.6 mmole), Tri.EG: 0.397 g (2.6 mmole), CCl_4: 0.814 g (5.3 mmole), Et_3N: 1.069 g (10.6 mmole) CH_3CN: 20 mL 3 days at room temperature. ^{31}P NMR of the final reaction mixture: $\delta = -44.8$ (20%), -45.2 (2%), -45.4 (27%), -45.5 (48%). Chromatography on alumina with toulene as eluent. Only two compounds have been separated:

—*Tricyclic monophosphorane* **3**. White solid $\delta\,^{31}P = -45$. Mass spectroscopy (DCI/NH_3) m/z$^+$: 338 $(M_3 + 1)^+$ 100%; 355 $(M_3 + 18)^+$ 1.15%.
—*Macrocycle* **4**.$\delta\,^{31}P = -45.2$. Pale yellow solid. Mass spectroscopy (FAB/mNBA) m/z$^+$: 675 $(M_4 + 1)^+$ 7.2%; 713 $(M_4 + K)^+$ 26.9%[9]

I.5 Condensation BHB (Tet.EG) + Tet.EG

Amounts of reagents: BHB (Tet.EG): 1.514 g (2.6 mmole), Tet.EG: 0.514 g (2.6 mmole), CCl_4: 0.814 g (5.3 mmole), Et_3N: 1.069 g ((10.6 mmole), CH_3CN: 20 mL 4 days at room temperature. Chromatography on alumina with toluene as eluent. ^{31}P NMR of the final reaction mixture: $\delta = -45.0$ (15%), -45.2 (7%), -45.4 and -45.5 (78%). Three fractions have been eluted:

—*Tricyclic monophosphorane* **5**. White solid $\delta\,^{31}P = -45.2$. Mass spectroscopy (DCI/NH_3) m/z$^+$: 382 $(M_5 + 1)^+$ 100%; 399 $(M_5 + 18)^+$ 30%.
—*Macrocycle* **6**. White solid $\delta\,^{31}P = -45.0$ Mass spectroscopy (DCI/NH_3) m/z$^+$: 382 $(M_{6/2} + 1)^+$ 100%; 763 $(M_6 + 1)^+$ 5.3%
—*Acyclic compound* **7**. Visquous liquid $\delta\,^{31}P = -45.4$. Mass spectroscopy (FAB/mNBA) m/z$^+$: 382 $(M_5 + 1)^+$ 100%; 763 $(M_6 + 1)^+$ 1.3%; 979 $(M_7 + Na)^+$ 2.1%[9]

I.6 Condensation BHB (Tet.EG) + DEG

Amounts of reagents: BHB (Tet.EG): 1.27 g (2.2 mmole), DEG: 0.235 g (2.2 mmole), CCl_4: 0.683 g (4.4 mmole), Et_3N: 0.897 g (8.9 mmole), CH_3CN: 20 mL 3 days at room temperature. ^{31}P NMR of the final reaction mixture $\delta = -42.8$ (2%), -44.8 (6%), -45.2 (39%), -45.3 (40%) Chromatography on silica gel with a variable mixture of ethyl acetate and cyclohexane as eluent. Eluted fractions

—*Tricyclic monophosphorane* **8**. $\delta\ ^{31}P = -42.9$ characterized by means of its NMR parameters which are identical to those of the same compound previously prepared.[2]

—*Tricyclic monophosphorane* **5**. $\delta\ ^{31}P = -45.2$ also identified by comparison with the same compound described above.

—*Macrocycle* **9**. White solid $\delta\ ^{31}P = -44.9$. Mass spectroscopy (DCI/NH_3) m/z$^+$: 675 $(M_9 + 1)^+$ 100%, 692 $(M_9 + 18)^+$ 36%.

I.7 Condensation BHB (Tet.EG) + Tri.EG

Amounts of reagents: BHB (Tet.EG): 2.41 g (4.2 mmole), Tri.EG: 0.63 g (4.2 mmole), CCl_4: 1.292 g (8.4 mmole), Et_3N: 1.7 g (16.8 mmole), CH_3CN: 30 mL 5 days at room temperature. ^{31}P NMR of the final reaction mixture: $\delta = -45.0$ (13%), -45.2 (10%), -45.4 (26%), -45.5 (51%). Chromatography on alumina. Eluent toluene. Eluted fractions:

A mixture of the tricyclic monophosphoranes **3** and **5** evidenced by the ^1H NMR spectra

—*Macrocycle* **10**. White solid $\delta\ ^{31}P = -45.2$. Mass spectroscopy (DCI/NH_3) m/z$^+$: 719 $(M_{10} + 1)^+$ 100%; 736 $(M_{10} + 18)^+$ 8.1%

I.8 Condensation THB (Tri.EA) + Tri.EA

Amounts of reagents: THB (Tri.EA): 1.114 g (1.55 mmole), Tri.EA: 0.231 g (1.55 mmole), CCl_4: 0.719 g (4.67 mmole), Et_3N: 0.943 g (9.34 mmole), CH_3CN: 20 mL 7 days at room temperature. ^{31}P NMR of the final reaction mixture: $\delta = -43.1$ (5.4%), -43.4 (11.2%), -44.1 (10.4%), -44.4 (20.6%), -44.5 (23.5%), -45.0 (13.%), -45.1 (15.9%). Compound **12** precipitated by addition of CH_3CN to the oily reaction mixture obtained after filtration of the triethylammonium chlorhydrate and removal of the solvent. It was recrystallized in acetonitrile. White solid. $\delta\ ^{31}P = -44.9$. Mass spectroscopy (DCI/NH_3) m/z$^+$: 860 $(M_{12} + 1)^+$ Elemental analysis for $C_{36}H_{72}N_5O_{12}P_3$. calc.% C 50.29, H 8.38, N 8.15. found% C 49.5, H 8.4, N 8.0 ^1H NMR (200.13 MHz, C_7D_8, 363°K[10], δ, J): 1.26 (s, 36H, CH_3); 2.97 (td, 12H, N—CH_2, $^3J_{HH'} = 5$, $^4J_{HP} = 2.6$); 4.24 (td, 12H, OCH_2, $^3J_{HP} = 5.1$). ^{13}C NMR (50.32 MHz, C_7D_8, δ, J): 29.1 (d, CH_3, $^3J_{CP} = 4$); 55.8 (d, CH_2N—P, $1/2(^2J_{C-N-P} + ^3J_{C-C-O-P}) = 20.5$; 59.8 (d, N—$CH_2$, $^3J_{CP} = 10.6$); 69.2 (s, $C(CH_3)_2$); 69.8 (d, OCH_2, $^2J_{CP} = 10.3$)

ACKNOWLEDGEMENTS

Ms. N. Rousseau is gratefully acknowledged for her technical assistance during the preparation of the manuscript. Also acknowledged is the staff of Groupe Régional de Mesures Physiques de Midi Pyrénées: G. Commenges, F. Lacassin, G. Pelletier for the NMR measurements, Mrs. Bourdil for elemental analysis and Mrs. S. Richelme for mass spectroscopy determinations.

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7. B. Duthu, D. Houalla and R. Wolf, *Canad. J. Chem.*, **66**, 2965 (1988) and references cited therein.
8. Correct nomenclature: 3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phospha^{III}bicyclo(3,3,0)octane.
9. In mass spectroscopy using FAB technique, the presence, in the vessel, of traces of metallic salts, leads to the formation of the $(M + \text{metal})^+$ ion, if the studied compounds has the ability to complex the metallic cation. This observation accounts for the presence of $(M_4 + K)^+$ and $(M_7 + Na)^+$. Therefore **4** and **7** are strongly expected to bind respectively K^+ and Na^+.
10. Due to the conformational lability of the bicyclic frame, the OCH_2 and NCH_2 protons give rise to broad signals at room temperature. These signals are resolved only at 363°K.