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### Alditols in Organophosphorus Chemistry. Synthesis of New Monomeric, Oligomeric and Bis-Spirophosphoranes

Lydia Lamandé<sup>a</sup>; Aurelio Munoz<sup>a</sup>

<sup>a</sup> Unité associée au CNRS N° 454 - Université Paul Sabatier, Toulouse Cedex, France

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## ALDITOLS IN ORGANOPHOSPHORUS CHEMISTRY. SYNTHESIS OF NEW MONOMERIC, OLIGOMERIC AND BIS-SPIROPHOSPHORANES

LYDIA LAMANDÉ, AURELIO MUNOZ  
Unité associée au CNRS N° 454 - Université Paul Sabatier  
118 route de Narbonne - 31062 Toulouse Cedex - France

Abstract New mono, bis and polyspirophosphoranes have been prepared condensing alditols with aminophosphines  $P(NR_2)_3$ .

### INTRODUCTION

In previous papers, we related about poly and bis-spirophosphoranes prepared from reactions between tartaric acid and phosphorus trichloride<sup>1</sup>. Following these researchs, we studied the condensation of aminophosphines  $P(NR_2)_3$  ( $R = Me, Et$ ) with alditols, expecting to obtain similar phosphoranes.

### RESULTS AND DISCUSSION

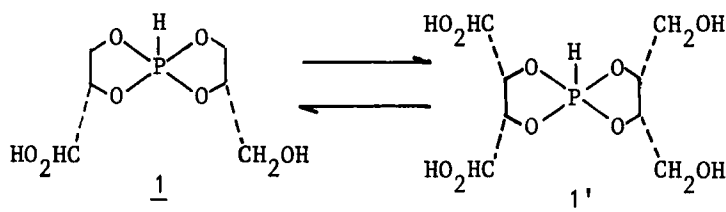
We tried glycerol, tetritols (threitol, erythritol), pentitols (xylitol, ribitol, arabinitol (L-)) and hexitols (mannitol (D+), glucitol (D+), galactitol). Many reactional routes can be conceived according to the stoichiometry. We selected the following aminophosphine/alditol ratios : 1/2, 1/1 (for the all alditols), 5/4 (only for the pentitols), 3/2 (only for the hexitols).

#### 1. Reactions $P(NR_2)_3 + 2$ alditols

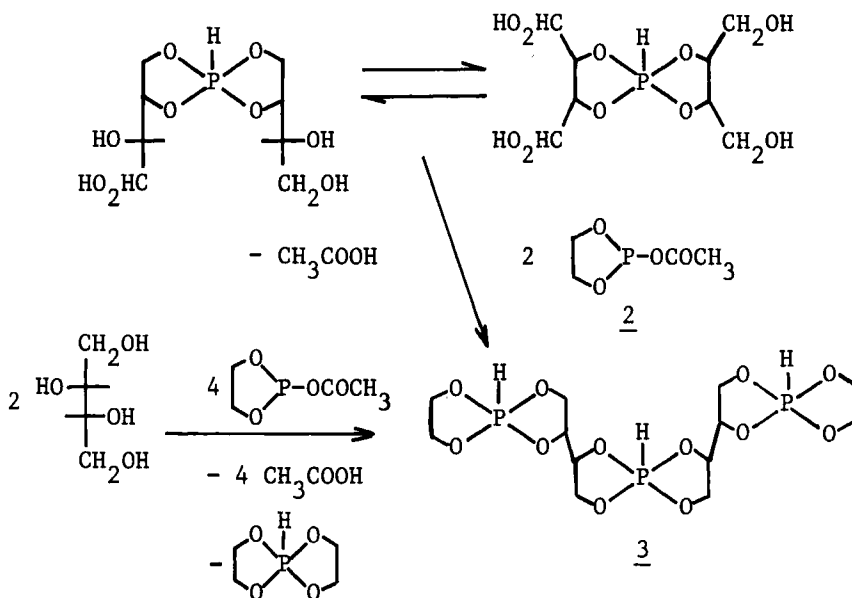
Phosphoranes 1 were prepared, with good yields, as rather unstable and thick oil, or hygroscopic powders (scheme 1). They exist as equilibrium  $1 \rightleftharpoons 1'$ , whose sense depends on alditol and solvent basicity. They react with mixed anhydrides 2 giving generally " perspirophosphoranes". Thus, with threitol derivatives, we

isolated the compound 3 (scheme 2). This last phosphorane is also obtained reacting the anhydride 2 ( $R = H$ ) with threitol (scheme 2).

Reactions  $P(NR_2)_3 + 2$  alditols gave, as side products, trisphosphates with hexacoordinated phosphorus atom, worked out from three alditol moieties. These compounds have been identified in solution, by their  $^{31}P$  NMR parameters.



Scheme 1

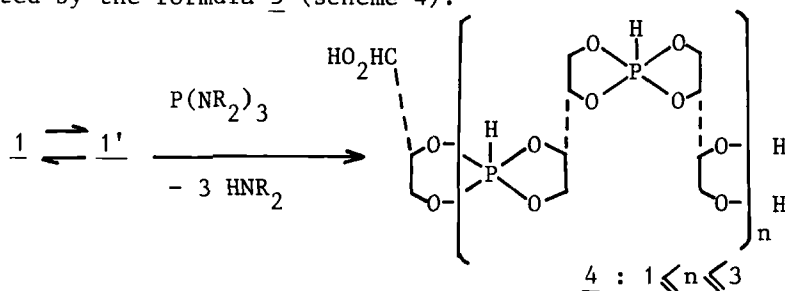


Scheme 2

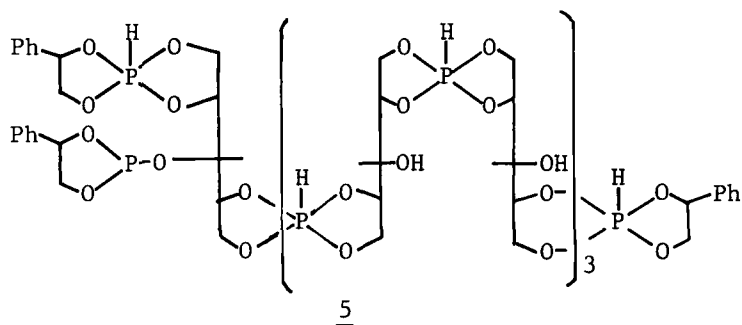
## 2. Reactions 1 $P(NR_2)_3 + 1$ alditol

The purest materials were obtained from the reactions 3, which also obey to the stoichiometry 1/1 (scheme 3). Compounds 4 react with anhydrides 2, giving new polyphosphoranes. Thus, starting from ribitol phosphoranes, we isolated compounds properly repre-

sented by the formula 5 (scheme 4).



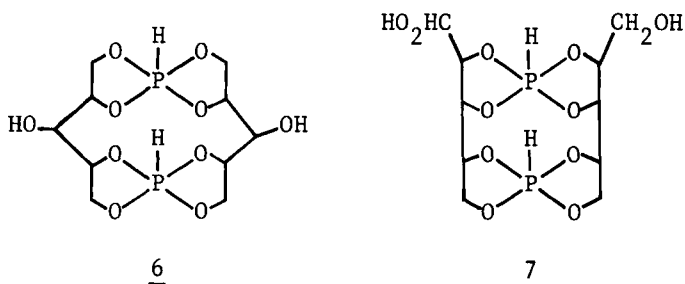
Scheme 3



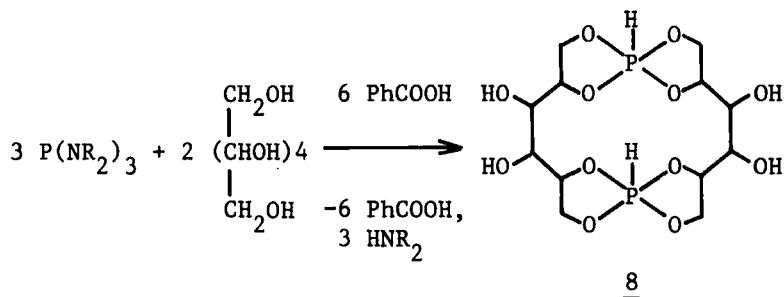
Scheme 4

### 3. Reactions 5 $P(NR_2)_3$ + 4 pentitols

These reactions led, with good yields, to bis-spirophosphoranes 6, 7. The stablest compounds were obtained from ribitol. They exhibit the structure 6, while the arabinitol phosphoranes likely present the structure 7. Concerning xylitol and arabinitol, we characterized, as side products, polycyclic phosphorous esters.



Performed under mild experimental conditions (5 hours at 40°C), these reactions gave polyspirophosphoranes (galactitol) or bis-spirophosphoranes 8 (mannitol (D+), glucitol (D+)). These last compounds were also obtained carrying out the reactions at room temperature and trapping the N,N dimethyl(or diethyl)amine with benzoic acid (scheme 6).



Scheme 6

### CONCLUSION

Reactions 1 - 6 allow us to obtain, with good yields, spirophosphoranes which can be considered as new protecting groups of alditols. On the other hand, they represent suitable starting materials to prepare poly or bis-phosphoric esters of alditols which can play a part in metabolic phenomena. Thus, recently, it was reported that dinucleotides inhibit RNA polymerase<sup>2</sup>.

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