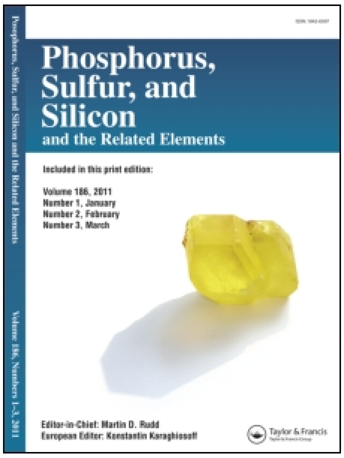


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Per-phosphoranylation of Alditols and Cyclitols

Brigitte Duthu[a]; Douraid Houalla[a]; Marie Christine Duriez[a]; Robert Wolf[a]
[a] Université Paul Sabatier, Toulouse, France

To cite this Article Duthu, Brigitte , Houalla, Douraid , Duriez, Marie Christine and Wolf, Robert(1987) 'Per-phosphoranylation of Alditols and Cyclitols', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 319 — 322
To link to this Article: DOI: 10.1080/03086648708080585
URL: http://dx.doi.org/10.1080/03086648708080585

Phosphorus and Sulfur, 1987, Vol. 30, pp. 319–322
Photocopying permitted by license only

PER-PHOSPHORANYLATION OF ALDITOLS AND CYCLITOLS.

BRIGITTE DUTHU,DOURAID HOUALLA,MARIE CHRISTINE DURIEZ AND ROBERT WOLF.

Université Paul Sabatier,Unité associée au C.N.R.S. n°454
118 Route de Narbonne 31062 Toulouse France.

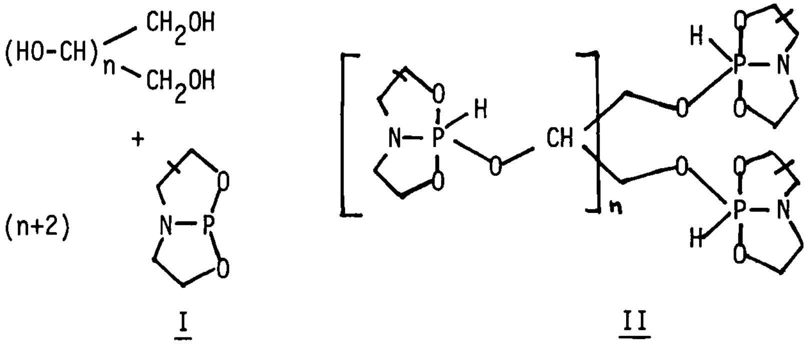
Abstract Reaction of bicyclophosphanes I with alditols,from diol to hexol,and cyclitol-myoinositol-,leads to the corresponding per-alkoxybicyclophosphoranes II which are in tautomeric equilibrium with the phosphites forms.Some chemical properties have been investigated.

INTRODUCTION

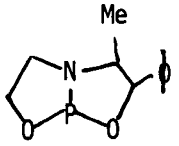
This communication concerns molecules containing the alkoxybicyclo phosphorane III as functional group.Our research has two purposes: 1)to demonstrate if it is possible to phosphoranylate all the OH groups in a polyol to obtain II ;2)to explore the reactivity of these polyphosphoranes in connection with some naturally occuring molecules.

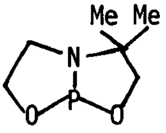
SYNTHESIS

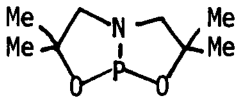
To prepare alditol and cyclitol perphosphoranes we used the reaction

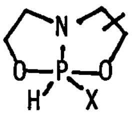


of the polyols with the constrained phosphanes I.We first studied the kinetics of the reaction of the t.butyl alcohol with Ia[1] Subsequently we investigated the reaction of Ib with six polyols : HO-$CH_2(CH\text{-}OH)_nCH_2OH$ including :glycol,(n=0);glycerol,(n=1) ;


Ia


Ib


Ic


III (X=OR)

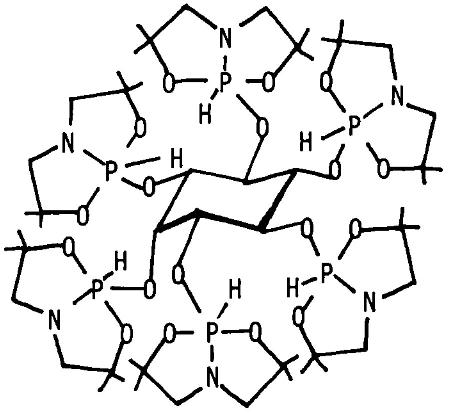
mesoerythritol,(n=2);arabitol,(n=3);dulcitol,(n=4)[2];also pentaerythritol : $C(CH_2OH)_4$ .We used the stoechiometry of one Ib for each OH group in the polyols.The progress of the reaction is followed by ^{31}P N.M.R.The peak of Ib (δ=148 p.p.m.) desappears and is simultaously replaced by the phosphoranes doublets (^1J H-P ca 800 Hz) centered close to -40 p.p.m. In addition signals observed between 133 and 143 p.p.m. correspond to new tricovalent phosphorus entities The relative intensities of -40 p.p.m.and 133-143 peaks are as follows:

Polyols	n=0	n=1	n=2	n=3	n=4
P^V/P^{III}	99/1	97/3	87/13	80/20	76/24

The regular increase of the P^{III}forms suggests the presence in such compounds of a tautomeric equilibrium between phosphoranes and phosphites ,a characteristic already known in spirophosphoranes [3,4]. We tested this hypothesis by ^{31}P variable temperature N.M.R. measurements and observed the decrease of the peaks at -40 p.p.m. and the increase of the peaks at 133-143 p.p.m. while temperature increases from 30 to 90°C (cycle 30,60,90,60,30°C).We conclude that the perphosphoranylation of alditols has occured.In addition we synthetised a new series of polyphosphoranes starting with phosphane Ic .Two simplifications were expected and actually observed:

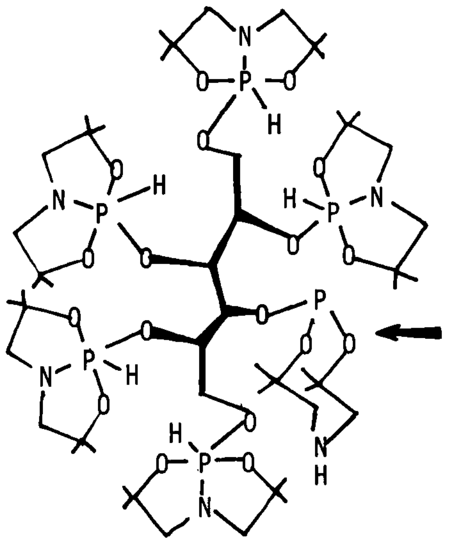
1)a lowering of the phosphite concentration,due to the influence of four methyl groups instead of two (Ingold-Thorpe rule)

2)a decrease in the number of diastereoisomers present,because Ib contains a phospho-chiral center,but not Ic which has a plane of symmetry.



Myoinositol hexa phosphoranes

M.S. : M^+ : 1314.



Dulcitol hexaphosphoranes : one tautomer.

The concentration of phosphite tautomer is reduced as follows : glycol (0%);glycerol(0%);mesoerythritol(1,4%);arabitol(5,9%);dulcitol(13,7%).The reduce number of ^{31}P peaks allowed us effectively to detect bicyclophosphoranes attached to a primary or a secondary alcohol and to show that the later is more liable to ring opening . With dulcitol hexaphosphoranes the likely structure of the main tautomer is illustrated.

We extended these results by reacting Ic with the myoinositol $\chi(CHOH)_6$ expecting to obtain the perphosphoranylated derivative.In the product mixture 90% of the phosphorane form illustrated above is present . (N.M.R.^{31}P :phosphoranes: ,from -39 to -42 p.p.m.;phosphites forms: 134 p.p.m.;the peak of the reagent Ic (M.W.189) at 163 p.p.m. has desappeared;M.S.Field Desorption: M^+: 1314; $(M-189)^{+;}$ $(M-2x189)^+$.

Three chemical properties of these coumpounds are currently studied mainly on the myoinositol perphosphoranyl derivative (mpp).

a)partial phosphorylation;a1)by using different stoechiometry between Ic and the myoinositol;a2)by removing phosphoranyl groups in mpp,using methyl alcohol.We have indeed preliminary demonstrated that CH_3OH reacts with III (X=i.PrO)to give III (X=MeO).

b)The oxydation by t.BuOOH in D.M.S.O.occurs quickly at room temperature to give a mixture of the corresponding phosphates triesters(with eight member ring) and 2 Oxo-Oxaza phospholanes.The acid hydrolysis of the mixture leads to myoinositol phosphates we attempted to separate by HPLC.

c)The sulfuration reaction appears to be promising as sulfur reacts quickly;for example with glycerol tris phosphoranes we obtain the corresponding tris thio compond.($\delta\ ^{31}P$:84,3 ppm;MS,F.D. $[2\ M - n\ 221]^+$ n = 1,2,3 : 1290, 1069, 848)

We point out that this investigation is closely relates with our research on III (X=Ar,Alk)[5], (X=H)[6],a type of ligands extensively used in coordination chemistry by J.Riess et al.[7]and I.Tkatchenko[8].

REFERENCES

1.O.S.Diallo,J.F.Brazier,A.Klaebe and R.Wolf,Phosphorus and Sulfur,22 p.93 (1985)
2.D.Houalla,A.Munoz,H.Ramdane and R.Wolf,Tetrhedron Lett. 26 p.2003 (1985)
3.a)M.Sanchez,R.Wolf,R.Burgada and F.Mathis,Bull.Soc.Chim. de France p.773 (1968).b)R.Wolf,J.F.Brazier,D.Houalla and M.Sanchez Colloques Intern.C.N.R.S.n° 182,p.167 (1970)
4.T.J.Atkins and J.E.Richman Tetrahedron Lett.p.5149 (1978)
5.A series of articles from: D.Houalla,J.F.Brazier,M.Sanchez and R.Wolf,Tetrahedron Lett.p.2969 (1972) to C.Bonningue,J.F.Brazier, and D.Houalla,Phosphorus and Sulfur 5 p.291 (1979)
6.D.Houalla,H.Ramdane and R.Wolf,Nouv.J.Chim. 9 p.189 (1985)
7.Last article quoted from J.R. et al.:J.Febvay,F.Casabianca and J.Riess,Inorg.Chem.24 p.3235 (1985).
8)Last article quoted from I.T. et al.:D.Ballivet-Tkatchenko, M.C.Bonnet,R.Faure and H.Loiseleur,J.amer.Chem.Soc.107 ,p.2994 (1985).