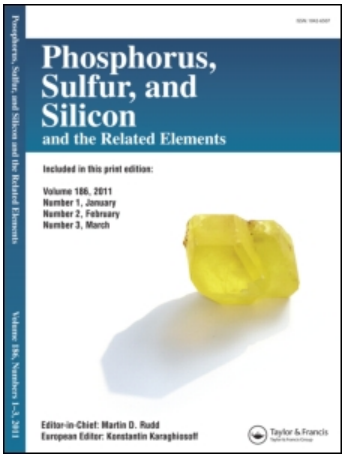


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# ALKALINE HYDROLYSIS OF β-AND γ-FUNCTIONAL PHOSPHONIUM SALTS

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**To cite this Article** Cristau, Henri-Jean and Mouchet, Patrick(1995) 'ALKALINE HYDROLYSIS OF β-AND γ-FUNCTIONAL PHOSPHONIUM SALTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 107: 1, 135 — 144
**To link to this Article: DOI:** 10.1080/10426509508027929
**URL:** http://dx.doi.org/10.1080/10426509508027929

*Phosphorus, Sulfur, and Silicon*, 1995, Vol. 107, pp. 135–144
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# ALKALINE HYDROLYSIS OF β- AND γ-FUNCTIONAL PHOSPHONIUM SALTS

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*(Received June 22, 1995)*

A model study of alkaline hydrolysis of β- and γ-heterosubstituted phosphonium salts has been made and used as a synthetic method to obtain diphosphine dioxides affording additional coordination sites in an alkyl chain linked to phosphorus. After synthesis of the corresponding salts, anomalous fragmentations, such as inversion in cleavage selectivity or participation of the reaction solvent, have been pointed out in alkaline hydrolysis of β-functional phosphonium salts. A mechanism is suggested to account for the presence of all compounds detected. In the case of γ-functional phosphonium salts, the alkaline hydrolysis leads only to predicted compounds corresponding to the usual selective cleavage of one phenyl group. The results observed have been used to synthesize symmetric and asymmetric diphosphine dioxides with ether substituted side chains.

*Key words:* Phosphonium salt, phosphine oxide, diphosphine dioxides, alkaline hydrolysis, cleavage, mechanism.



## INTRODUCTION

Diphosphine dioxides are useful ligands for the extraction of actinides from aqueous solution.[1] The use of a recurrent synthetic method, based on the repetition of a sequence of three reactions (alkylation of phosphine, alkaline hydrolysis of phosphonium salt and reduction of the resulting phosphine oxide),[2] gives us the possibility to synthesize analogs of Lariat crown-ethers[3] affording additional coordination sites in the side chain which can participate to the complexation of cations, particularly of actinides cations for the reprocessing of nuclear wastes.[4]

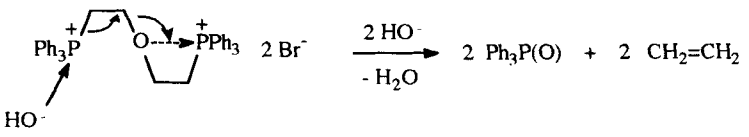
## RESULTS AND DISCUSSION

Alkaline hydrolysis of phosphonium salts have been widely studied.[5] The reaction generally leads to the selective cleavage of a carbon-phosphorus bond following the departure order:

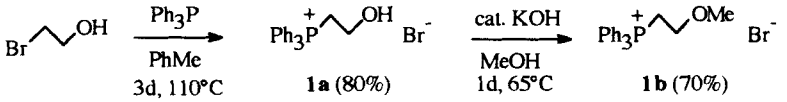
$$PhCH_2 \geq CH_2{=}CH{-}CH_2 > Ph, Ar > Alkyl$$

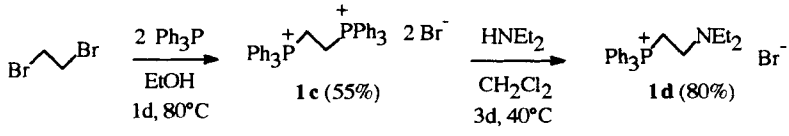
Yet, surprising fragmentation had already been pointed out, certainly due to electrostatic interactions between oxygen and phosphorus atoms in the β-position[2] (Scheme I).

The theoretical interest of this abnormal cleavage order of fragmentations and its practical interest for our synthesis of Lariat compounds have caused us to make a model study of the alkaline hydrolysis of β- and γ-heterosubstituted alkyl phosphonium salts.

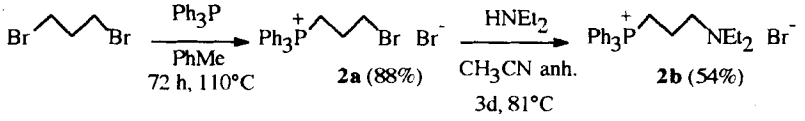


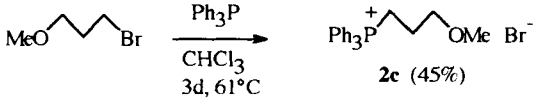
SCHEME I Anomalous fragmentation of a bisphosphonium salt.





SCHEME II Synthesis of β-functional phosphonium salts **1**.





SCHEME III Synthesis of γ-functional phosphonium salts **2**.

Thus, β-functional (**1a–d**) and γ-functional (**2a–c**) phosphonium salts were first synthesized by direct quaternization with functional halogenated alkylating agents for **1a,c** and **2a,c**[6] or by extrapolating methods described in the literature for **1b**,[7] **1d**,[8] **2b**[9] (Schemes II and III).

After alkaline hydrolysis in ethanol or toluene, the analysis of the crude reaction mixture has been achieved using GC/MS and $^{31}$P-NMR (ridded of the Nuclear Overhauser Effect to allow the quantitative determination of the various phosphorus products).

### *Hydrolysis of* β-*Functional Phosphonium Salts* **1**

After alkaline hydrolysis, numerous phosphine oxides are detected and their ratios depend on the nature of the functional Z group and on the reaction conditions, in particular on the reaction solvent (Tables I and II).

On the basis of studies reported in the literature,[5] it is possible to suggest a general mechanism which can account for the presence of all compounds observed after

TABLE I

Alkaline hydrolysis of β-functional phosphonium salts **1** in toluene

| Salt | Z group | $Ph_3P(O)$ | $Ph_2P(O)CH_2CH_2Z$ | $Ph_2P(O)CH_2CH_2OH$ | $Ph_2P(O)CH=CH_2$ | $Ph_2P(O)CH(Ph)CH_3$ |
|---|---|---|---|---|---|---|
| | | **3** | **4a-d** | **4a** | **5** | **6** Ph |
| **1a** | OH | 11 | 18 | * | 71 | 0 |
| **1b** | OMe | 24 | 56 | 7 | 7 | 6 |
| **1d** | $NEt_2$ | 10 | 90 | 0 | 0 | 0 |

* 18%, identical to the $Ph_2P(O)$-$(CH_2)_2$-Z obtained compound in this case.

TABLE II

Alkaline hydrolysis of β-functional phosphonium salts **1** in ethanol

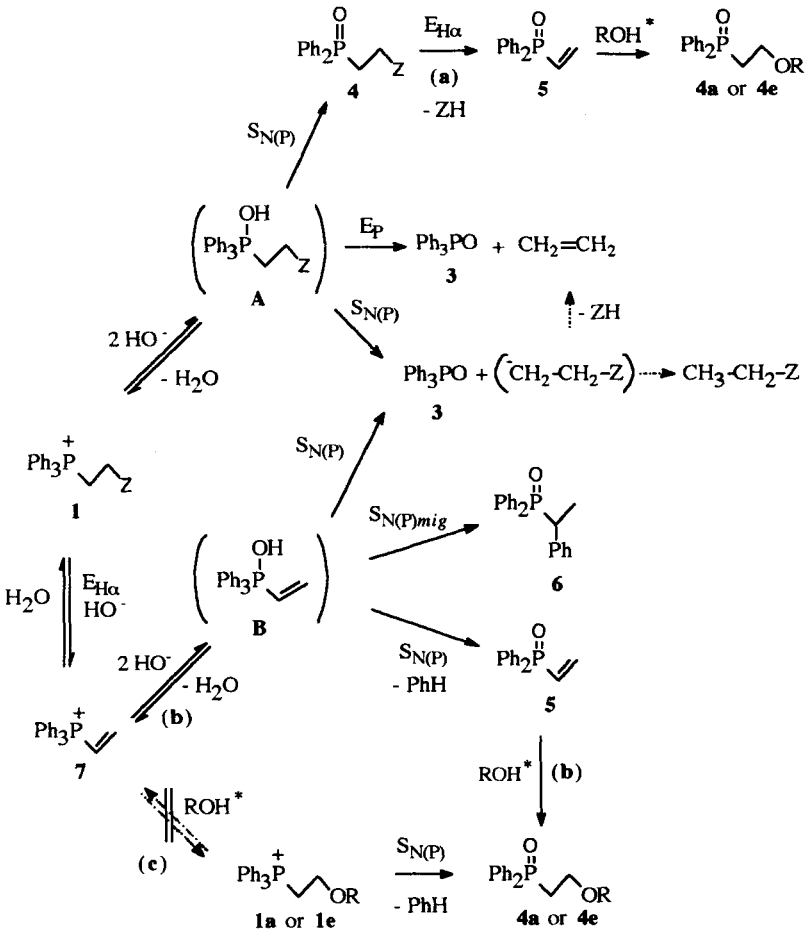
| Salt | Z group | $Ph_3P(O)$ | $Ph_2P(O)CH_2CH_2Z$ | $Ph_2P(O)CH_2CH_2OEt$ | $Ph_2P(O)CH=CH_2$ |
|---|---|---|---|---|---|
| | | **3** | **4a-d** | **4e** | **5** |
| **1a** | OH | 7 | 0 | 90 | 3 |
| **1b** | OMe | 7 | 73 | 20 | 0 |
| **1d** | $NEt_2$ | 14 | 0 | 82 | 1 |

alkaline hydrolysis of the β-heterosubstituted alkyl phosphonium salts **1** (Scheme IV).

It should be pointed out that, except phosphine oxide **6** which results from the $S_{N(P)mig}$ mechanism[10] corresponding to pathway (b), the phosphine oxides **3**, **4** and **5** could be obtained through several pathways. Thus, the addition of ethanol, either on the triphenylvinylphosphonium salt **7** and/or on diphenylvinylphosphine oxide **5** can give the diphenyl(2-ethoxyethyl)phosphine oxide **4e** corresponding to a change of the initial Z group during the reaction. Indeed, the two vinylic compounds **5** and **7** have been detected (in the final reaction mixture in the case of the vinylic phosphine oxide **5**, and by acidic quenching after one minute in the case of the vinyl phosphonium **7**). The sole presence of the starting phosphonium salt **1** and of the vinylphosphonium **7** excludes the pathway (c) since instantaneous hydrolysis of the eventual phosphonium salts **1a** (R = H) or **1e** (R = Et) seems very unlikely because transformation of the analogous salts **1a–d** is never instantaneous.

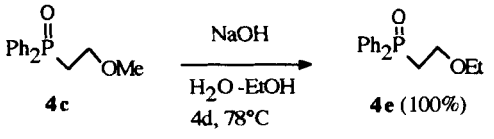
It is not possible to determine if the phosphine oxide **4e** is obtained through pathway (b) after alkaline hydrolysis of the corresponding vinylphosphonium salt **7**, and/or through pathway (a) since a verification experiment shows that the alkaline hydrolysis of **4b** (Z = OMe) in ethanol gives pure **4e** (Z = OEt) (Scheme V).

The formation of triphenylphosphine oxide **3** as a secondary product (7 to 24%) in all cases, whatever the β-substituent Z concerned or the solvent used, demonstrates the lack of selectivity in the P—C bonds cleavage.



* R = H in $H_2O$-Toluene and R = Et in $H_2O$-EtOH.

SCHEME IV Suggested mechanism for the alkaline hydrolysis of β-functional phosphonium salts **1**.



SCHEME V Exchange of alkoxy substituents in β-functional phosphine oxide **4c**.

It can be assumed that the competition phenyl/alkyl is controlled mainly, in the evolution of the intermediate phosphorane **A** (through $E_P$ or $S_{N(P)}$ mechanisms[11]), by the presence of the Z group in β-position: This group enhances the cleavage of alkyl chain, certainly due to a stabilizing electrostatic or orbital interaction between the phosphonio group and the oxygen or nitrogen donor atom in β-position, which increases the possibility for such alkyl groups to be in axial nucleofugal position in

the trigonal bipyramide structure of the hydroxyphosphorane **A**.[12] In this regard, the coordinating ability of each Z group should be in relation with their basicity, their steric requirements and also their solvatation (as well as with the solvatation of the phosphonio group). Further, it must be pointed out that triphenylphosphine oxide **3** can also be obtained through $S_{N(P)}$ cleavage of the intermediate vinylphosphonium salt **7**, whose formation depends directly on the nucleofugal ability of the Z substituent acting as a leaving group, and accordingly indirectly on the solvatation of this group.

Thus, it seems difficult to find a simple relation between Z groups and quantities of triphenylphosphine oxide **3** formed, as well as other products **4–6**.

The use of toluene as organic solvent (Table I) produces systematically some amounts (18–90%) of the expected products **4a–d**, whereas it is not always the case when ethanol (Table II) is used as solvent. Indeed, in this last case, ethanol is mainly incorporated (20–90%) in the product to give **4e** (Z = OEt). Furthermore, it must be pointed out that the reaction achieved with salt **1d** (Z = $NMe_2$) in toluene-water gives a cleaner crude mixture (90% of phosphine oxide **4d**) than with other Z groups. After improvement of the reaction conditions, our recurrent method[2] should probably allow the synthesis of diaza macrocycles with P—C—C—N linkage in the bridge between phosphorus atoms and/or compounds with N-coordinating side chains.



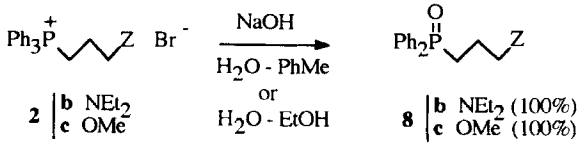
### *Hydrolysis of γ-Functional Phosphonium Salts* **2**

The cleavage selectivity and conversion rate reach 100% for the alkaline hydrolysis of γ-functional phosphonium salts **2b,c**, corresponding to a specific phenyl group departure (Scheme VI).

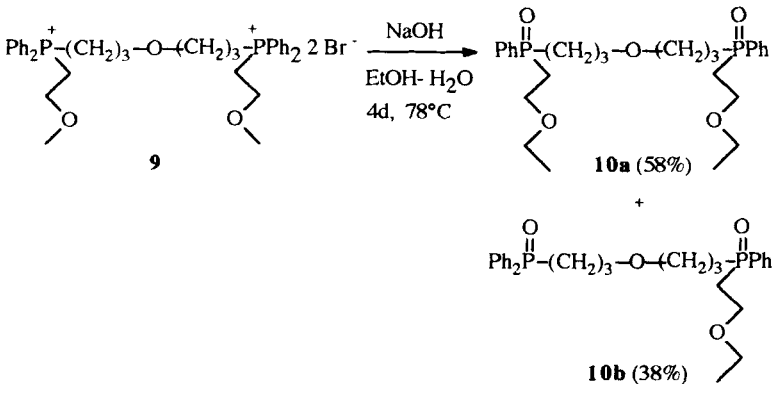
Thus alkaline hydrolysis can be used as an elimination step for the recurrent synthesis of macrocyclic diphosphine dioxides with P—C—C—C—Y (Y = O, N) structural units in the bridge between two phosphorus, since the presence of three carbon atoms prevents all fragmentation possibilities encountered with the β-substituted phosphonium salts **1**.

### *Synthetic Applications*

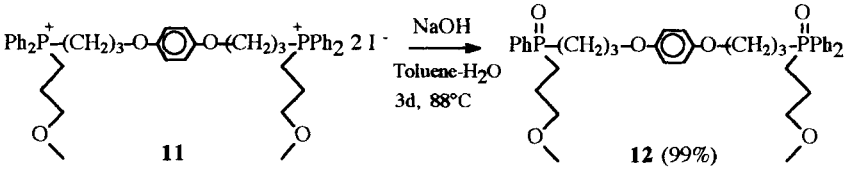
In order to quantify the influence of one or two coordinating chains on actinides extraction properties of the compounds synthesized with our recurrent method,[4] we have prepared the diphosphine dioxides **10a** or **10b** by substituting during the alkaline hydrolysis of bis(β-functional)phosphonium salt **9**, one (**10b**) or two (**10a**) phenyl groups by —$(CH_2)_2$—OEt thanks to the lack of specificity in the cleavage of the P—C bond: as expected from the model study, the departure of the alkyl chain instead of the phenyl group and the substitution of methoxy by ethoxy group




SCHEME VI Alkaline hydrolysis of γ-functional phosphonium salts **2**.




SCHEME VII Alkaline hydrolysis of bis(β-functional)phosphonium salt **9**.




SCHEME VIII Alkaline hydrolysis of bis(γ-functional)phosphonium salt **11**.

occur as well as the preservation of the bridge between the two phosphorus exhibiting the P—C—C—C—O linkage (Scheme VII).

In the case of the bis (γ-functional) phosphonium salt **11**, the specificity of cleavage leads, after departure of two phenyl groups, to the expected linear diphosphine dioxide **12** affording coordinating groups in the γ-position (Scheme VIII).

The diphosphine dioxides obtained have been first tested in liquid-liquid extraction of actinides (Pu, Np, Am).[4] The results obtained show the effect of the additional coordination sites in alkyl chains and the improvement of the extractant properties with a hydroquinone group bridging the two phosphorus. Transport experiments were carried out using liquid membranes technology; they showed the ability of such bidentate linear compounds to remove efficiently Pu and Np from radioactive contaminated liquid wastes.[4]

## EXPERIMENTAL

Melting points were determined using a METLER FP5 or a Wild LEITZ 350 apparatus. Infrared spectra were recorded on the PERKIN-ELMER 377 spectrophotometer (IR samples were prepared as KBr pellets unless noted otherwise): Spectral bands are reported in $cm^{-1}$ and the band intensity is noted vw = very weak; w = weak; m = medium; s = strong; vs = very strong. $^1$H-NMR spectra were run on either BRUKER Ac 250 or BRUKER Ac 200: the chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) in Hertz (Hz). The spin multiplicity is noted s = singlet; d = doublet; t = triplet; q = quartet; m = muliplet. Proton decoupled $^{13}$C and $^{31}$P-NMR spectra were collected on a BRUKER Ac 200. Chemical shifts are reported from internal tetramethylsilane for $^1$H and $^{13}$C or from external 85% phosphoric acid for $^{31}$P. Microanalyses were carried out by the "Service Central de Microanalyse CNRS, Montpellier." Mass spectral data were collected on a JEOL JMS-DX 300 spectrometer.

*Note*: Obtention of the phosphonium salts as iodides required anion exchange, carried out by repeated washing of a solution of phosphonium salts in $CH_2Cl_2$ or $CHCl_3$, with aqueous solutions of NaI. This operation will not be cited again below.

*Synthesis of Phosphonium Salts*

*Direct Alkylation of Triphenylphosphine*

A mixture of appropriate halogenated reagent and 1 equivalent of triphenylphosphine (2 eq. for **1c**) is refluxed under nitrogen. After cooling, precipitation in ether (volumes ratio $CHCl_3/Et_2O$:1/10) in the case of **2c**, the solid obtained is recrystallized.

*2-hydroxyethyltriphenylphosphonium Bromide* **1a**

Reaction conditions: 3 days in toluene (110°C). Yield = 80%. mp = 218°C (MeOH/AcOEt) (lit.[7] 216–217°C). $^{31}$P-NMR ($CDCl_3$, c = 0.2 M): 24.5 (s). $^1$H-NMR ($CDCl_3$, c = 0.2 M): 3.73 (dt, 2H, $^3J_{HH}$ = 6, $^2J_{HP}$ = 12, $CH_2$—P); 3.90–4.10 (m, 2H, $CH_2$—O); 5.15 (s, 1H, OH); 7.55–7.80 (m, 15H, aromatic).

*1,2-ethylene bis(triphenylphosphonium)Dibromide* **1c**

Reaction conditions: 1 day in ethanol (80°C). Yield = 55%. mp = 292–294°C (Leitz, MeOH/AcOEt) (lit.[8] 297–300°C). $^{31}$P-NMR ($CDCl_3$, c = 0.13 M): 25.6 (s). $^1$H-NMR ($CDCl_3$, c = 0.13 M): 3.93 (d, $^2J_{PH}$ = 5, 4H, $CH_2$—P); 7.70–8.00 (m, 30H, aromatic).

*3-bromopropyltriphenylphosphonium Bromide* **2a**

Reaction conditions: 16 h in toluene (100°C). Yield = 88%. mp = 228°C (lit.[13] 229°C (xylene)). $^{31}$P-NMR ($CDCl_3$, c = 0.15 M): 24.64 (s). $^1$H-NMR ($CDCl_3$, c = 0.15 M): 2.12 (s, 2H, C—$CH_2$—C); 3.70–3.95 (m, 4H, $CH_2$—P et $CH_2$—Br); 7.50–7.90 (m, 15H, aromatic).

*(3-methoxypropyl)triphenylphosphonium Bromide* **2c**

Reaction conditions: 3 days in chloroform (62°C). Yield = 45%.[14] mp = 196°C. Anal. Calcd for $C_{22}H_{24}BrOP$: C, 63.63; H, 5.82; O, 3.85; Br, 19.24. Found: C, 63.40; H, 5.80; O, 3.49; Br, 19.25. $^{31}$P-NMR ($CDCl_3$, c = 0.18 M): 25.2 (s). $^1$H-NMR ($CDCl_3$, c = 0.18 M): 1.9 (s, 2H, C—$CH_2$—C); 3.21 (s, 3H, $CH_3$); 3.60 (t, $^3J_{HH}$ = 6, 2H, $CH_2$—O); 3.70–3.90 (m, 2H, $CH_2$—P); 7.55–7.85 (m, 15H, aromatic).

*Modification of Phosphonium Salts*

*(2-methoxyethyl)triphenylphosphonium Bromide* **1b**

Reaction conditions: 1 day in methanol (65°C).[7] Yield = 70%. mp = 206°C ($CHCl_3$/AcOEt) (lit.[7] 207–209°C). $^{31}$P-NMR ($CDCl_3$, c = 0.13 M): 26.1 (s). $^1$H-NMR ($CDCl_3$, c = 0.13 M): 3.0 (s, 3H, $CH_3$); 3.82 (dt, 2H, $^3J_{HH}$ = 6, $^2J_{HP}$ = 22, $CH_2$—P); 4.14 (dt, $^3J_{HH}$ = 6, $^3J_{HP}$ = 12, 2H, $CH_2$—O); 7.55–7.90 (m, 15H, aromatic).

*(2-ethoxyethyl)triphenylphosphonium Bromide* **1e**

Reaction conditions: 1 day in ethanol (80°C).[7] Yield = 86%. mp = 179°C ($CHCl_3$/AcOEt) (lit.[7] 179–180°C). $^{31}$P-NMR ($CDCl_3$, c = 0.17 M): 25.9 (s). $^1$H-NMR ($CDCl_3$, c = 0.17 M): 0.77 (t, $^3J_{HH}$ = 7, 3H, $CH_3$); 3.11 (q, $^3J_{HH}$ = 7, 2H, $CH_2$—Me); 3.81 (dt, 2H, $^3J_{HH}$ = 6, $^2J_{HP}$ = 23, $CH_2$—P); 4.05 (dt, $^3J_{HH}$ = 6, $^3J_{HP}$ = 11, 2H, $CH_2$—O); 7.55–7.80 (m, 15H, aromatic).

*(2-diethylaminoethyl)triphenylphosphonium Bromide* **1d**

Prepared by extrapolation of methods described in literature.[7,8]

Reaction conditions: 3 days in dichloromethane (40°C). Yield = 80%. mp = 181°C (Acetone) (lit.[8] 178–182°C). $^{31}$P-NMR ($CDCl_3$, c = 0.13 M): 26.5 (s). $^1$H-NMR ($CDCl_3$, c = 0.13 M): 0.70 (t, $^3J_{HH}$ = 7, 6H, 2 $CH_3$); 2.39 (q, $^3J_{HH}$ = 7, 4H, $CH_2$—Me); 2.88 (dt, 2H, $^3J_{HH}$ = 6, $^2J_{HP}$ = 20, $CH_2$—P); 3.88 (dt, $^3J_{HH}$ = 6, $^3J_{HP}$ = 12, 2H, $CH_2$—O); 7.55–7.90 (m, 15H, aromatic).

*(3-diethylaminopropyl)triphenylphosphonium Bromide* **2b**

Prepared according to the literature.[9a]

Reaction conditions: 3 days in anhydrous acetonitrile, under nitrogen. Yield = 54%. mp = 202°C (Acetone) (lit.[9b] 208–210°C). $^{31}$P-NMR ($CDCl_3$, c = 0.13 M): 25.3 (s). $^1$H-NMR ($CDCl_3$, c = 0.13 M):

0.82 (t, $^3J_{HH}$ = 7, 6H, 2 $CH_3$); 1.55–1.75 (m, 2H, C—$CH_2$—C); 2.32 (q, $^3J_{HH}$ = 7, 4H, N—$CH_2$—Me); 2.56 (t, $^3J_{HH}$ = 6, 2H, $CH_2$N); 3.55–3.75 (m, 2H, $CH_2$—P); 7.60–7.75 (m, 15H, aromatic).

*Alkaline Hydrolysis of β-functional Phosphonium Salts* **1**

Alkaline hydrolysis of *β*-functional phosphonium salts is achieved using 10 equivalents of sodium hydroxide (5 N) with an organic solvent (homogeneous: ethanol; heterogeneous:toluene). After concentration (if ethanol is used) and extraction of the aqueous phase with dichloromethane, the organic phases are combined, washed with water to neutrality, dried with $Na_2SO_4$, then concentrated. The study of the crude reaction mixture is achieved using GC/MS and $^{31}$P-NMR techniques (ridded of the Nuclear Overhauser Effects to allow the quantitative determination of the various phosphorus products) (Tables I and II).

*(2-methoxyethyl)diphenylphosphine Oxide* **4b**

Reaction conditions: hydrolysis of **1a**, 6 days in methanol (65°C). Purified by crystallization after a flash-chromatography on $SiO_2$ (AcOEt/MeOH-95/5). Yield = 22%. mp = 102–103°C (benzene/hexane). Anal. Calcd for $C_{15}H_{17}O_2P$: C, 69.22; H, 6.58; O, 12.29. Found: C, 69.15; H, 6.79; O, 12.12. $^{31}$P-NMR ($CDCl_3$, c = 0.2 M): 30.1 (s). $^1$H-NMR ($CDCl_3$, c = 0.13 M): 2.61 (dt, 2H, $^3J_{HH}$ = 8, $^2J_{HP}$ = 12, $CH_2$—P); 3.21 (s, 3H, $CH_3$); 3.66 (q, $^3J_{HH}$ = 8, $^3J_{HP}$ = 8, 2H, $CH_2$—O); 7.30–7.60 (m, 6H, *meta* and *para*); 7.65–7.80 (m, 4H, *ortho*). $^{13}$C-NMR (50.3 MHz) ($CDCl_3$, c = 0.5 M): 30.61 (d, $^1J_{CP}$ = 71, $CH_2$—P); 58.39 (s, $CH_3$—O); 65.83 (s, $CH_2$—O); 128.53 (d, $^3J_{CP}$ = 11.8, *meta*); 130.57 (d, $^2J_{CP}$ = 9.6, *ortho*); 131.70 (d, $^4J_{CP}$ = 2.8, *para*); 132.78 (d, $^1J_{CP}$ = 99.9, *ipso*). GC/MS (injector: 300, detector: 280, hoven: 60 to 300): $M^{+\cdot}$ = 260.

*(2-ethoxyethyl)diphenylphosphine Oxide* **4c**

Reaction conditions: "alkaline hydrolysis" of oxide **4c**, 4 days in ethanol (78°C). Yield = 100%. mp = 69°C (lit.[15] 69–70°C). $^{31}$P-NMR ($CDCl_3$, c = 0.20 M): 30.3 (s). $^1$H-NMR ($CDCl_3$, c = 0.20 M): 1.03 (t, $^3J_{HH}$ = 7, 3H, $CH_3$); 2.50–2.70 (m, 2H, $CH_2$—P); 3.35 (q, $^3J_{HH}$ = 7, 2H, O—$CH_2$—Me); 3.71 (dt, $^3J_{HH}$ = 8, $^3J_{HP}$ = 9, 2H, $CH_2$—O); 7.30–7.50 (m, 6H, *meta* and *para*); 7.65–7.80 (m, 4H, *ortho*). $^{13}$C-NMR (50.3 MHz) ($CDCl_3$, c = 0.5 M): 14.84 (s, $CH_3$); 31.20 (d, $^1J_{CP}$ = 71, $CH_2$—P); 63.63 (s, $CH_2$—O); 66.13 (s, $CH_2$—O); 128.50 (d, $^3J_{CP}$ = 11.8, *meta*); 130.52 (d, $^2J_{CP}$ = 9.5, *ortho*); 131.70 (d, $^4J_{CP}$ = 2.8, *para*); 132.72 (d, $^1J_{CP}$ = 100.2, *ipso*). GC/MS (injector: 300, detector: 280, hoven: 60 à 300): $M^{+\cdot}$ = 274.

*Alkaline Hydrolysis of γ-functional Phosphonium Salts* **2**

The study of the crude mixture shows the presence of a sole compound.

*3-diethylaminopropyldiphenylphosphine Oxide* **8b**

Reaction conditions: 16 h in toluene (88°C). Yellow oil. Yield = 100%. $^{31}$P-NMR ($CDCl_3$, c = 0.18 M): 33.5 (s). $^1$H-NMR ($CDCl_3$, c = 0.15 M): 0.88 (t, $^3J_{HH}$ = 7, 6H, 2 $CH_3$); 1.55–1.75 (m, 2H, C—$CH_2$—C); 2.17–2.27 (m, 2H, $CH_2$—P); 2.37 (q, $^3J_{HH}$ = 7, 4H, N—$CH_2$—Me); 2.41 (t, $^3J_{HH}$ = 6, 2H, $CH_2$N); 7.30–7.45 (m, 6H, *meta* and *para*); 7.60–7.75 (m, 4H, *ortho*). GC/MS (injector: 315, detector: 280, hoven: 60 to 315): $M^{+\cdot}$ = 315.

*3-methoxypropyldiphenylphosphine Oxide* **8c**

Reaction conditions: 2 days in toluene (88°C). White oil. Yield = 100%. $^{31}$P-NMR ($CDCl_3$, c = 0.15 M): 33.4 (s). $^1$H-NMR ($CDCl_3$, c = 0.15 M): 1.80–1.95 (m, 2H, C—$CH_2$—C); 2.25–2.45 (m, 2H, $CH_2$—P); 3.24 (s, 3H, $CH_3$); 3.39 (t, $^3J_{HH}$ = 6, 2H, $CH_2$—O); 7.35–7.55 (m, 6H, *meta* and *para*); 7.65–7.80 (m, 4H, *ortho*). GC/MS (injector: 300, detector: 280, hoven: 60 to 300): $M^{+\cdot}$ = 274.

*Alkaline Hydrolysis of Bisphosphonium Salts*

*4-oxa-1,7-heptamethylene bis-(2'-ethoxyethyl)phenylphosphine Dioxide* **10a**

Reaction conditions: four days in EtOH/$H_2O$ (78°C). Yield = 58%. mp = 73–74°C (Leitz). Rf = 0.23 ($SiO_2$; AcOEt/MeOH: 70/30-UV). IR: 1000vw, 1012m, 1035w, 1050w, 1070m, 1113vs, 1127vs, 1165vs, 1220m. Anal. Calcd for $C_{26}H_{40}O_5P_2$: C, 63.15; H, 8.15; O, 16.18. Found: C, 63.22; H, 8.29; O, 16.06. $^{31}$P-NMR ($CDCl_3$, c = 0.25 M): 39.6 (s). $^1$H-NMR ($CDCl_3$, c = 0.25 M): 1.11 (t, $^3J_{HH}$ = 7, 3H, $CH_3$); 1.12 (t, $^3J_{HH}$ = 7, 3H, $CH_3$); 1.60–2.40 (m, 12H, C—$CH_2$—C and $CH_2$—P); 3.25–3.80 (m, 12H,

$CH_2$—O); 7.20–8.00 (m, 10H, aromatics). $^{13}$C-NMR (50.3 MHz) ($CDCl_3$, c = 0.25 M): 14.85 (s, $CH_3$); 21.62 (d, $^2J_{PC}$ = 3.9, C—$CH_2$—C); 27.04 (d, $^1J_{PC}$ = 69.8, $CH_2$—P(O)); 31.06 (d, $^1J_{PC}$ = 67.4, $CH_2$—P(O)); 63.52 (d, $^2J_{PC}$ = 1.9, $CH_2$—O); 66.05 (s, Me—$CH_2$—O); 70.29 (d, $^3J_{PC}$ = 14.8, $CH_2$—O); 128.42 (d, $^3J_{PC}$ = 11.3, *meta*); 130.12 (d, $^2J_{PC}$ = 9.0, *ortho*); 131.44 (d, $^4J_{PC}$ = 2.7, *para*); 132.15 (d, $^1J_{PC}$ = 83.8, *ipso*). $M^{+\cdot}$ = 494.

*4-oxa-1,7-heptamethylene(2'-ethoxyethyl)phenylphosphine Diphenylphosphine Dioxide* **10b**

Reaction conditions: four days in EtOH/$H_2O$ (78°C). White oil. Yield = 38%. Rf = 0.37 ($SiO_2$; AcOEt/MeOH: 70/30-UV). IR: 1000w, 1025w, 1075m, 1106vs, 1112vs, 1183s. $^{31}$P-NMR ($CDCl_3$, c = 0.25 M): 33.3 (s); 39.5 (s) (both signals have the same intensity). $^1$H-NMR ($CDCl_3$, c = 0.25 M): 1.07(t, $^3J_{HH}$ = 7, 3H, $CH_3$); 1.55–2.40 (m, 10H, C—$CH_2$—C and $CH_2$—P); 3.25–3.80 (m, 8H, $CH_2$—O); 7.20–8.00 (m, 15H, aromatics). $^{13}$C-NMR (50.3 MHz) ($CDCl_3$, c = 0.25 M): 14.86 (s, $CH_3$); 21.65 (d, $^2J_{PC}$ = 3.9, C—$CH_2$—C); 21.77 (d, $^2J_{PC}$ = 3.6, C—$CH_2$—C); 26.20 (d, $^1J_{PC}$ = 73.0, $CH_2$—P(O)); 27.02 (d, $^1J_{PC}$ = 69.7, $CH_2$—P(O)); 31.06 (d, $^1J_{PC}$ = 67.4, $CH_2$—P(O)); 63.51 (d, $^2J_{PC}$ = 2.1, $CH_2$—O); 66.08 (s, Me—$CH_2$—O); 70.20 (d, $^3J_{PC}$ = 14.6, $CH_2$—O); 70.29 (d, $^3J_{PC}$ = 14.8, $CH_2$—O); 128.47 (d, $^3J_{PC}$ = 10.6, *meta*); 128.48 (d, $^3J_{PC}$ = 11.6, 2 *meta*); 130.13 (d, $^2J_{PC}$ = 9.1, *ortho*); 130.56 (d, $^2J_{PC}$ = 9.3, 2 *ortho*); 131.49 (d, $^4J_{PC}$ = 3.0, *para*); 131.55 (d, $^4J_{PC}$ = 2.9, 2 *para*); 132.08 (d, $^1J_{PC}$ = 93.7, *ipso*); 132.74 (d, $^1J_{PC}$ = 98.5, 2 *ipso*). $M^{+\cdot}$ = 498.

*1,4-bis[3-(3'-methoxypropyl)phenylphosphinylpropoxy]benzene* **12**

Reaction conditions: 3 days in toluene/$H_2O$ (88°C). White oil. Yield = 99%. IR: 1027vw, 1049w, 1062w, 1107vs, 1157w, 1187vw, 1212m. $^{31}$P-NMR ($CDCl_3$, c = 0.25 M): 41.2 (s). $^1$H-NMR ($CDCl_3$, c = 0.25 M): 1.60–2.30 (m, 16H, C—$CH_2$—C and $CH_2$—P); 3.00–3.50 (m, 10H, $CH_2$—O and $CH_3$—O); 3.70–4.00 (m, 4H, $CH_2$—O); 6.60–6.80 (m, 4H, hydroquinonic H); 7.20–8.00 (m, 10H, aromatic H). $^{13}$C-NMR (50.3 MHz) ($CDCl_3$, c = 0.25 M): 21.68 (d, $^2J_{PC}$ = 3.8; C—$CH_2$—C); 26.58 (d, $^1J_{PC}$ = 69.3, $CH_2$—P(O)); 26.70 (d, $^1J_{PC}$ = 69.8, $CH_2$—P(O)); 58.35 (s, O—$CH_3$); 68.14 (d, $^3J_{PC}$ = 13.9, $CH_2$—O); 72.30 (d, $^3J_{PC}$ = 14.2, $CH_2$—O); 115.26 (s, hydroquinonic CH); 128.60 (d, $^3J_{PC}$ = 11.2, *meta*); 130.35 (d, $^2J_{PC}$ = 8.9, *ortho*); 131.55 (d, $^4J_{PC}$ = 2.8, *para*); 131.93 (d, $^1J_{PC}$ = 93.0, *ipso*); 152.80 (s, hydroquinonic C—O). $M^{+\cdot}$ = 586.



## ACKNOWLEDGEMENTS

We thank Alix Contreras and Christian Consolino for their contribution to this work supported by the Centre National de Recherche Scientifique and the Commissariat à l'Energie Atomique (C.E.N. de Cadarache).

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