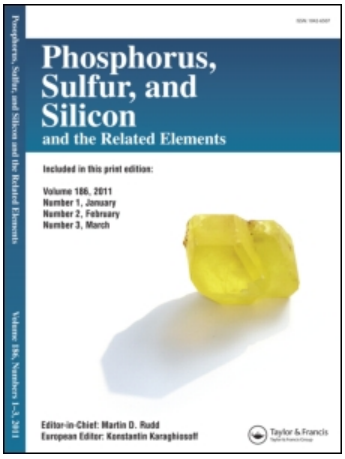

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NEW TRI-COORDINATED AND PENTACOORDINATED PHOSPHORUS COMPOUNDS AND A BORON SPIRANE INVOLVING AN ENOLPYRUVATE MOIETY. SYNTHESIS OF A HYDROXYPHOSPHORANE MODEL OF INTERMEDIATE PHOSPHORANES IN NUCLEOPHILIC SUBSTITUTION REACTIONS ON PHOSPHORIC ESTERS OF ENOLPYRUVIC ACID

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NEW TRI-COORDINATED AND PENTA-COORDINATED PHOSPHORUS COMPOUNDS AND A BORON SPIRANE INVOLVING AN ENOLPYRUVATE MOIETY. SYNTHESIS OF A HYDROXYPHOSPHORANE MODEL OF INTERMEDIATE PHOSPHORANES IN NUCLEOPHILIC SUBSTITUTION REACTIONS ON PHOSPHORIC ESTERS OF ENOLPYRUVIC ACID

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Hydrido and hydroxyspirophosphoranes, cyclic tri-coordinated phosphorus compounds and a boron spirane involving a phenylenolpyruvate moiety were prepared from reactions between phenylpyruvic acid and phosphorus trichloride, or (and) chloro-2-dioxaphospholane 1,3,2, or (and) chloro-2-oxo-2-phenyl-4,5-dioxaphospholane 1,3,2, or (and) boric acid. The hydroxyphosphorane is a good model of the intermediate postulated in the hydrolysis of enolpyruvate phosphoric esters.

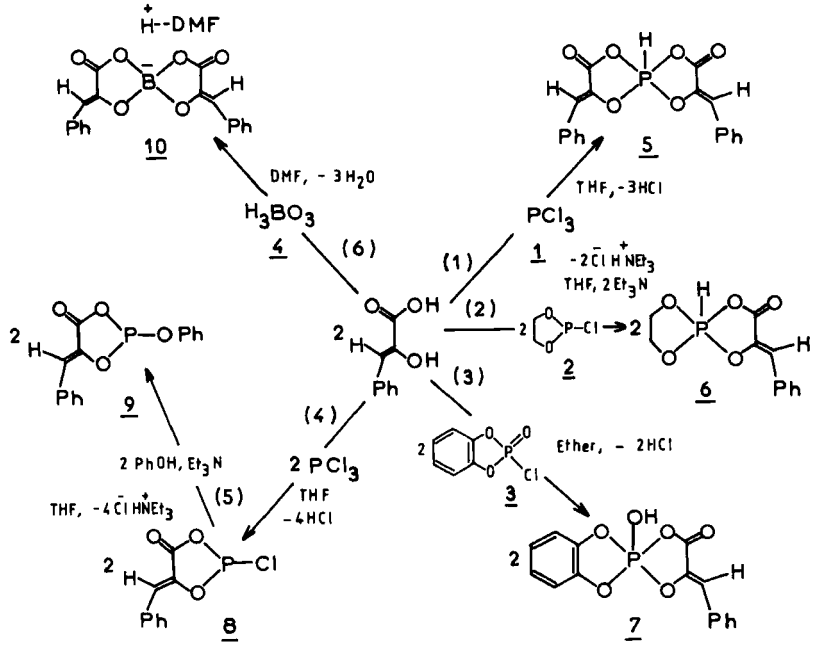
INTRODUCTION

For almost thirty years, hydroxyphosphoranes have been postulated as intermediates in reactions involving phosphate esters of biological interest.[1] Recently, some stable hydroxyphosphoranes were synthesized.[2–5] Despite of the recent preparation of penta-coordinated phosphoenolpyruvates,[6] hydroxyphosphoranes similar to those postulated as intermediate in the hydrolysis of enolpyruvate phosphoric esters[7] have, not as yet, been isolated. We report here the synthesis of hydroxy and hydrido-spirophosphoranes, of cyclic tri-coordinated phosphorus compounds, and of a boron spirane, involving the enolpyruvate ligand.

RESULTS AND DISCUSSION

In their enolic form α-ketoacids can be considered as α-hydroxyacids which have been used in the synthesis of acyloxy-spirophosphoranes,[2,8,9] and of boron spiranes.[10] Thus, we expected to obtain similar compounds upon condensing α-keto-acids and the phosphorus or boron derivatives, **1–4** (scheme 1).

For the first time, we have chosen phenylpyruvic acid whose ^{1}H, ^{13}C NMR and IR spectra are consistent with an α-enol acid: ^{1}H NMR (CD_3CN, 60 MHz): 8.2 (s, HO)8–7.3 (m, C_6H_5) 6.6 (s, H—C=C—). ^{13}C NMR (dioxane,



SCHEME 1

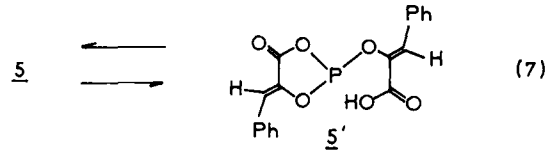
15.08 MHz): 166·5 (s, O=C—OH) 140.15 (s, —O—C=C—Ph) 134.65–127.34 (m, C_6H_5) 110.57 (s, Ph—C=C—O—). IR (KBr disk): 3460 (ν_{OH}) 1695 (ν_{COOH}) 1625 ($\nu_{C=C}$).

Spirophosphoranes **5–7**: *Synthesis and properties*

Phenylpyruvic acid reacts fast with **1–3**. In the reaction with **2**, hydrogen chloride was trapped by an equivalent of triethylamine (Equation (2), Scheme 1). Microcrystalline white powders were isolated. They are rather unstable at room temperature and very sensitive to moisture. Nevertheless, in an argon atmosphere at −20°C they can be keeped pure. The elemental analyses were in accord with **5–7**, despite slight deviations in the carbon percentages (see experimental part). ^{31}P NMR spectra were consistent with the presence of acyloxy-spirophosphoranes.[2,8] ^1H NMR spectra exhibit a deshielded doublet resulting from long-distance coupling, $^4J_{P-O-C=C-H}$, suggesting an enolpyruvate moiety, connected to a phosphorus atom[6] (table). Thus, structures **5–7** are proposed.

Besides the P–H doublet, the ^{31}P NMR spectrum of compound **5** exhibits a singlet corresponding to a compound of three-coordinated phosphorus (table). Its intensity strongly decreases at low temperatures whilst the intensity of the doublet increases. This phenomenum is characteristic of an equilibrium between the spirophosphorane **5** and an isomeric derivative with three-coordinated phosphorus. It is, effectively known that such equilibria are largely desplaced, at low temperatures, towards the species of five-coordinated phosphorus.[11] The presence, in the ^1H NMR spectrum, of a singlet at low field ($\delta = 9.60$), corresponding to an acidic proton, rules out a compound with three-coordinated

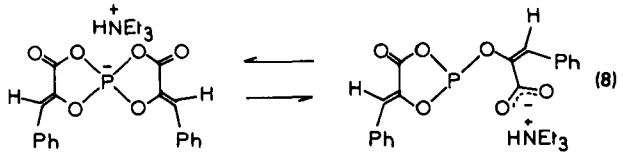
phosphorus with a ketonic open chain. Thus, we only have to consider the tautomeric form **5'** (Equation (7)).



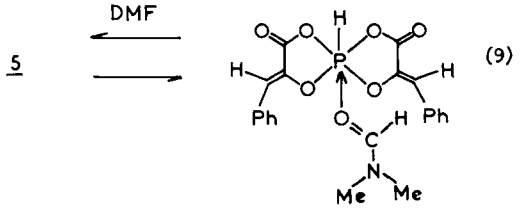
(7)

Compound **5** reacts with triethylamine: the ^{31}P NMR spectrum of an equimolecular mixture (**5** + Et_3N) exhibits, at +25°C, a sharp singlet at $\delta = 77$. This phenomenon can be interpreted by the equilibrium (8).[12] On the other hand, the ^{31}P NMR spectrum of phosphorane **5** in DMF solution, shows, at high field, P–H doublets consistent with the presence of adducts with six-coordinated phosphorus, the chemical shift of these signals varying with temperature: −116, $J_{P-H} = 921$ Hz (broad), −120, $J_{P-H} = 904$ Hz (sharp), at +25°C. −126, $J_{P-H} = 880$ Hz (broad), −140, $J_{P-H} = 904$ Hz (sharp), −141, $J_{P-H} = 880$ Hz (sharp), at −25°C. Catechol and acyloxy-spirophosphoranes gave similar complexation with pyridine or triethylamine, but not with DMF.[11,12] By analogy, we can propose the equilibrium (9), strongly displaced towards the six-coordinated phosphorus adduct. The observed multiplicity can be explained by the existence of many isomers.

The equilibrium (9) underlines the relatively strong Lewis acidity of the phosphorus atom in compound **5**.



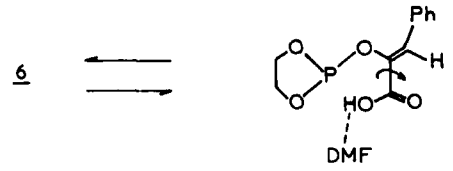
(8)



(9)

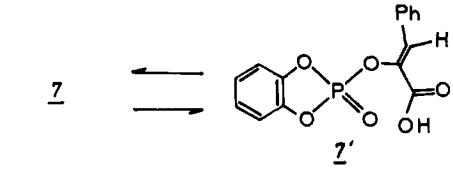
The ^{31}P NMR spectrum of compound **6** in DMF solution was found to exhibit two signals which were not observed in methylene chloride solution. Their chemical shifts ($\delta = 131.5$ and 130.3) are consistent with the presence of compounds of three-coordinated phosphorus with dioxaphospholane 1,3,2 moiety.[13] These results are explained by the tautomeric equilibrium (10). Similar equilibria were observed in the case of catechol phosphoranes and acyloxyphosphoranes.[11] The presence of two signals at low field in the ^{31}P NMR spectrum is very likely connected with the existence of rotamers. At low temperature only one peak is observed ($\delta = 130.5$). We think that free rotation is

sufficiently reduced to displace the equilibrium between rotamers towards the thermodynamically more stable derivative.



(10)

The $\delta^{31}P$ value of compound **7** varies with temperature: −35.4 (+50°C), −36.9 (+25°C), −39.3 (0°C), −40.4 (−30°C). This phenomenon is due to a dynamic equilibrium between the phosphorane **7** and tautomeric phosphoric ester **7'**[2] (Equation (11)), this equilibrium being shifted towards the hydroxy-phosphorane. The ^1H NMR spectrum reveals an important deshielding of the OH proton which suggests strong acidity. Thus, concerning the hydroxy-phosphoranes postulated as intermediate in the hydrolysis of enolpyruvate phosphoric esters, we have to expect an important Brønsted's acidity.



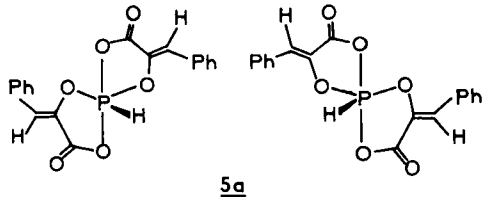
(11)

Stereochemistry

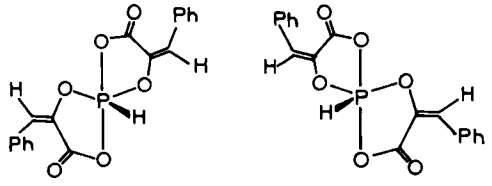
We can assume that the phosphorus atom of phosphoranes **5–7** is at center of a trigonal bipyramid. According to Muetterties rules,[14] the carboxylic groups are expected to occupy the apical positions.[8b] Thus, we can expect three (compound **5**) or two (compounds **6**, **7**) enantiomeric pairs of isomers (schemes 2 and 3). The observation in the ^{31}P NMR spectra of a single P–H doublet (**5**, **6**) or a singlet (**7**) shows that only one anantiomeric pair of phosphoranes is isolated. Nevertheless, two weak doublets were observed, close to the principal one, in the spectrum of crude phosphorane **5**. They certainly correspond to other enantiomeric pairs which were eliminated after purification. The presence in the ^1H NMR spectra of a single doublet, for the P—O—C=C—H proton, allows to discard the enantiomeric pair **5c**. We do not know unambiguously which isomer was isolated. If the W rule, concerning the $^4J_{H\cdots H}$ or $^4J_{P\cdots H}$ coupling is applied,[15] we would assign the NMR signals to compounds **5a–7a** (schemes 2, 3). Labaudinière *et al.* have reported $^4J_{P-O-C=C}$ (H(1)/H(2)) coupling for both protons (1) and (2).[6] In conclusion, and expecting a structure determination by X ray diffraction, we will state that reactions (1)–(3) (schemes 1) led to an enantiomeric pair of spirophosphoranes, **5a–7a** or **5b–7b** (schemes 2, 3).

Compounds **8** *and* **9**:

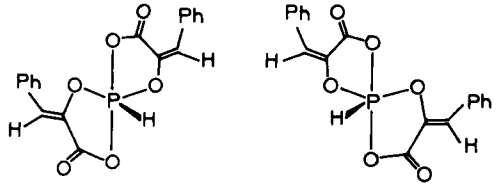
The reaction between phosphorus trichloride and phenylpyruvic acid, in equimolecular stoichiometry, conducted over 24 hours, led to the formation of sticky crystals whose ^{31}P NMR spectrum was found to exhibit a sharp singlet, in accord



5a

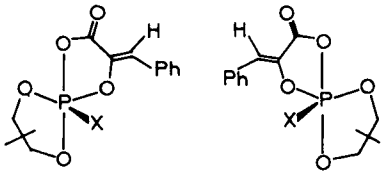


5b

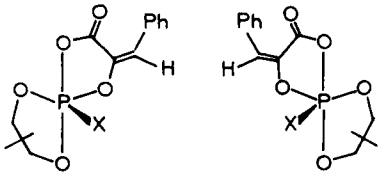


5c

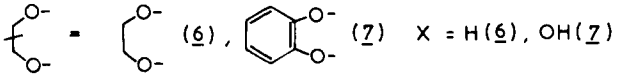
SCHEME 2



6,7a



6,7b



SCHEME 3

with a chloro-2-dioxaphospholane-1,3,2[13] (table). The ^1H NMR spectrum also showed the characteristic doublet of a dioxaphospholane-1,3,2 ring originating from phenylpyruvic acid (table and Equation (4) in scheme 1). Upon reacting with the stoichiometric quantity of phenol and triethylamine compound **8** gave the corresponding phenoxy derivative **9** (Equation (5) in scheme 1).

It is interesting to note that the phosphorochloridite **8** was isolated while, in our knowledge, homologous derivatives have not, as yet, been prepared from α-hydroxyacids. By contrast, acyloxy-spirophosphoranes of phenylpyruvic acid are less stable than similar α-hydroxyacids phosphoranes.

TABLE I

Characteristic NMR parameters of compounds **5–9**

Compound	**5**	**6**	**7**	**8**	**9**
$\delta^{31}P$ ppm (32, 44 MHz)	−47.9, J_{P-H} = 967 Hz (80%) 117, 5 (20%) (THF)	−34, 5, J_{P-H} = 898 Hz (THF)	−36, 9 (THF)	164, 7 ($CDCL_3$)	110, 8 (THF)
δ^1H (80, 13 MHz) H—C=C—O—P ppm	6, 84	6, 56	6, 27	7, 00	6, 49
$^4J_{P-O-C=C-H}$ Hz	2, 4	1, 5	1, 2	2, 5	1, 81

Boron spirane **10**

In DMF solution, boric acid readily reacted with phenylpyruvic acid. A yellow hygroscopic powder was isolated. Its ^{11}B NMR spectrum is in accord with a boron spirane of α-hydroxy-acid:[10] $\delta = 10.2$. The ^1H NMR spectrum exhibits for the H—C—Ph proton a singlet shielded towards this proton signal in the free phenylpyruvic acid. The acidic proton is strongly deshielded, this fact revealing an important increasing of its acidity. It is solvated by about one DMF molecule. The ^{13}C NMR spectrum is similar to the free acid one. Although, the singlets of the O=C and —C=C—O—B atoms are shielded, while the signal of the C—O—B atom is deshielded. These data are consistent with phenylpyruvate moieties connected to a central boron atom (compound **10**, Equation (6) in scheme 1). Effectively, a boron compound having an open chain should present a more complex ^{13}C NMR spectrum with, particularly, at least two signals for the O=C, —C=C—O—B atoms.

CONCLUSION

Our results provide additional evidence of the existence of intermediate hydroxy-phosphoranes in the hydrolysis of phosphoric esters of enol-pyruvic acid. They

complement the knowledge concerning the mechanism of nucleophilic substitution, involving phosphoric esters of biological interest.

On the other hand, the facile preparation of phosphorochloridite, **8**, should allow the synthesis of new varied phosphoenolpyruvate compounds, involving several different coordination numbers of phosphorus. Besides, the isolation of the boron spirane, **10**, shows that phenylpyruvic acid can be an interesting ligand in the preparation of compounds with other heteroatoms.

EXPERIMENTAL

Microanalyses were carried out by "Le Service Central D'Analyses du CNRS, BP 22, 69390 Vernaison". Consistently low values were obtained for carbon percentages. This has frequently been observed with organophosphorus compounds, and particularly with those having aromatic substituents.[2]

A Bruker AC 80 (80.13 MHz) and a Varian T 60 (60 MHz) instruments were used for the ^{1}H NMR measurements. Me_4Si was the internal reference. The ^{31}P NMR spectra were recorded on a Perkin–Elmer R 32 with F.T. (32.44 MHz) and a Bruker AC 80 (3244 MHz) instruments. H_3PO_4 was used as electronic reference. Chemical shifts were noted negatively for signals located at high field towards the peak of phosphoric acid. Bruker AC 80 apparatus was used for the ^{11}B NMR measurements (28.88 MHz). BF_3, Et_2O adduct was used as internal reference. Chemical shifts were noted positively at low field towards the peak of preceding adduct. The ^{13}C NMR spectra were recorded on a Bruker WP 60 (15.08 MHz) instrument. Me_4Si was used as internal reference. IR spectra were recorded on a Perkin–Elmer 283 instrument.

All the syntheses were carried out under argon protection.

Synthesis of spirophosphorane **5**. PCl_3 and phenylpyruvic acid (0.69 g, 5 mmole and 1.64 g, 10 mmole) are dissolved in 10 mL of THF. A slightly exothermic reaction takes place. ^{31}P NMR spectrum after 20 min.: 118.1 (≈10%), −46.7, J_{P-H} = 996 Hz (weak), −47.4, J_{P-H} = 966.4 Hz (~90%), −48.6, J_{P-H} = 970 Hz (weak). **5** is reprecipited with a mixture of 30 mL of pentane and 10 mL of ether, and isolated by centrifugation under argon. Yield: 60%. ^{31}P NMR (table). IR (KBr disk) cm^{-1}: 3460 (ν_{OH}), 1675 ($\nu_{C=O}$), 1645 ($\nu_{C=C}$). (sol. CH_2Cl_2; CaF_2, 0.1 mm): 3460 (ω_{OH}), 2460 (ν_{PH}), 1770 ($\nu_{C=O}$) ofthe ring part), 1710 ($\nu_{C=O}$ of the open chain), 1670 ($\nu_{C=C}$). ^{1}H NMR (CD_3CN, 80.13 MHz): 9.60 (s, HO) 8.13 (d, H–P, J_{H-P} = 967 Hz) 7.78–7.31 (m, C_6H_5) 6.84 (d, P—O—C=C—H, $^4J_{P-O-C=C-H}$ = 2.4 Hz) 6.51 (s, P—O—C=C—H of the open chain). Analysis ($C_{18}H_{13}O_6P$) Calc. %: C 60.67, H 3.65, P 8.70. Found: C 58.20; H 3.97; P 8.73.

Synthesis of spirophosphorane **6**. Phosphorochloridite **2** and phenylpyruvic acid (0.64 g, 5 mmole and 0.82 g, 5 mmole) are dissolved at −50°C in 15 mL of THF. 0.5 g (5 mmole) of Et_3N are quickly added. Triethyl-ammonium chloride precipitates and is removed by centrifugation. The strongly concentrated filtrate leaves a white precipitate which is dissolved by adding 10 mL of CH_2Cl_2. Spirophosphorane **6** is precipitated with 20 mL of pentane and isolated by centrifugation. Yield: 58%. ^{31}P NMR (table). IR (CH_2Cl_2, CaF_2, 0.1 mm): 3450 (ν_{OH}) (weak) 2440 (ν_{PH}) 1745 ($\nu_{C=O}$ of the ring part) 1705 ($\nu_{C=O}$ of the open chain) 1670 ($\nu_{C=C}$). ^{1}H NMR ($CDCl_3$, 80.13 MHz): 9.08 (s, HO) 7.58 (d, H–P, J_{H-P} = 899 Hz) 7.71–7.11 (m, C_6H_5) 6.64 (d, P—O—C=C—H, $^4J_{P-O-C=C-H}$ = 1.5 Hz) 6.46 (s, P—O—C=C—H of the open chain) 4.45–3.80 (m, CH_2—CH_2). Analysis ($C_{11}H_{11}O_5P$) Calc.%: C 51.96; H 4.72; P 12.20. Found: C 50.00 H 4.81 P 11.92.

Synthesis of spirophosphorane **7**. Phosphorochloridate **3** and phenylpyruvic acid (0.95 g, 5 mmole and 0.82 g, 5 mmole) are dissolved in 10 mL of ether. ^{31}P NMR after 15 min.: 11.3 (30%), −37 (70%). After removing ether under vacuum a thick yellow powder is obtained which is treated with 10 mL of CH_2Cl_2. Phorphorane **7** remains in suspension as a white precipitate which is separated by centrifugation. Yield: 42%. ^{31}P NMR (table). IR (KBr disk): 3300–2400 (ν_{OH} and ν_{P-OH}, broad) 1680 ($\nu_{C=O}$) 1635 ($\nu_{C=C}$). ^{1}H NMR (DMSo-d_6, 80.13 MHz): 13.47 (s, HO) 8.04–7.19 (m, C_6H_5) 6.81 (m, C_6H_4) 6.27 (d, P—O—C=C—H, $^4J_{P-O-C=C-H}$ = 1.2 Hz) 5.82 (s, P—O—C=C—H of the open chain, weak). Analysis ($C_{15}H_{11}O_5P$) Calc.% C 56.60 H 3.45 P 9.74. Found: C 54.99: H 3.54: P 9.67.

Synthesis of phosphorochloridite **8**. PCl_3 and phenylpyruvic acid (1.66 g, slight excess of 10 mmole, 1.64 g, 10 mmole) are dissolved in 15 mL of THF. This solution is left at room temperature in a sealed flask. ^{31}P NMR after 24 hours: 218 (weak), 177 (weak) 161.4 (60%), 118 (weak), −47.4,

J_{P-H} = 965 Hz (30%). THF is removed ($12/10^{-2}$ torr) and phosphorochloridite **8** is extracted by 30 mL of pentane/10 mL of ether. Oily white crystals are finally obtained. Yield: 60%. ^{31}P NMR (table). ^1H NMR ($CDCl_3$, 60 MHz): 8.00–7.30 (m, C_6H_5) 7.02 (d, P—O—C=C—H, $^4J_{P-O-C-C-H}$ = 2.5 Hz).

Synthesis of compound **9**. To phosphorochloridite **8** (0.76 g, 3 mmole), dissolved in 5 mL of THF and cooled to −50°C, phenol and Et_3N (0.28 g and o.33 g, 3 mmole), dissolved in 5 mL of THF, are added. Triethyl-ammonium chloride precipitates and is removed by centrifugation. Compound **9** is isolated as a thick yellow oil, after evaporation of THF ($12/10^{-2}$ torr). Yield: 88%. ^{31}P NMR (table). ^1H NMR (CD_3CN, 80.13 MHz): 7.84–6.86 (m, C_6H_5); 6.49 (d, P—O—C=C—H, $^4J_{P-O-C-C-H}$ = 1.81 Hz).

Synthesis of spirane **10**. Boric acid and phenylpyruvic acid (0.31 g, 5 mmole and 1.64 g, 5 mmole) are dissolved at 40°C in 5 mL of DMF. The temperature is lowered to 25°C and water formed in reaction is removed at 12 torr. After 5 h. the residual solution is treated with 30 mL of ether and left 5 h. at −20°C. A thick yellow oil separates which is decanted and dried at 60°C–80°C, at 10^{-2} torr. A very hygroscopic yellow powder is finally obtained. Yield: 80%. ^{11}B NMR ($CDCl_3$, 28.88 MHz): 10.2. ^1H NMR (CD_3CN, 60 MHz): 14 (s, H^+); 7.8 (s, H—C=O); 7.6–6.8 (m, C_6H_5); 5.8 (s, B—O—C=C—H); 2.8 and 2.7 (s, s, $(CH_3)_2N$). ^{13}C NMR (dioxane, 15.08 MHz): 168.25 (s, O=C—O—B) 164.23 (s, O=C—NMe_2); 144.82 (s, —C=C—O—B); 134.98 – 126.63 (m, C_6H_5); 103.26 (s, —C=C—O—B); 37.49 and 31.99 (s, s, $(CH_3)_2N$—). Analysis ($C_{21}H_{20}NO_7B$) Calc. %: C 61.61; H 4.88; N 3.42; B 2.68. Found: C 59.34; H 5.20; N 3.86; B 2.69.

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