The Synthesis and Reactivity of Phosphinous Acid-Boranes

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Received 3 January 2005

Abstract: Phosphinic acid chlorides are converted directly into phosphinous acid-boranes in a process utilizing BH_3·THF complex as a reducing agent. The process is general and affords phosphinous acid-boranes in good to very high yields. Phosphinous acid-boranes have been found to react readily with alkylating, acylating, reducing, halogenating and deborating agents to produce the corresponding phosphinous acid-borane esters, phosphinous acid-borane anhydrides, *sec*-phosphine oxides, *sec*-phosphine boranes and phosphinic acid halides, respectively. The efficient procedures for these conversions have been developed and their scope has been outlined.

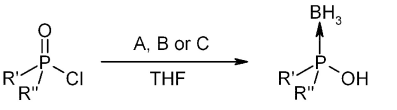
Key words: phosphorus, boron, alkylation, acylation, halogenation

Phosphine-boranes of general formula $R_3P{\cdot}BH_3$ constitute a unique class of organophosphorus compounds in respect to their reactivity and applications in organic synthesis.[1] A large number of very useful preparations have been developed with phosphine-boranes as the key reagents.[2] Especially useful in this respect proved to be borane complexes of functionalized phosphines bearing leaving groups at phosphorus.[3] Among them, phosphinite-boranes which can be formally considered as esters of phosphinous acid-boranes have become most valuable as precursors to chiral tertiary phosphines.[4] Despite the importance of these derivatives of phosphinous acid-boranes, the parent acids, their synthesis and chemistry have remained practically unexplored. Perusal of chemical literature has revealed identification of only one sodium salt[5] and two free phosphinous acid-boranes[3h,6] on record.

In our earlier work[7] on the use of borane complexes for the reduction of secondary phosphine oxides we have observed that the desired reduction process was sometimes accompanied by the competitive formation of phosphinous acid-boranes. This observation led consequently to the development of the first general procedure for the synthesis of phosphinous acid-boranes from secondary phosphine oxides.[8]

In this paper we wish to demonstrate that by taking advantage of the reducing properties of borane, the scope of the viable substrates for the synthesis of phosphinous acid-boranes can also be extended to readily available phosphinic acid halogenides. It will be demonstrated that readily available phosphinic acid chlorides react with borane complexes to directly produce phosphinous acid-boranes. The synthesized phosphinous acid-boranes have been subsequently utilized in a model reactivity study that revealed the basic reactivity pattern of phosphinous acid-boranes towards alkylating agents, halogenating agents, reducing agents as well as strong acids and acid chlorides.

In the course of our studies on phosphinous acid-boranes and the use of borane as the mild reducing agent in phosphorus chemistry, we turned our attention to phosphinic acid chlorides as potential substrates. We envisaged that reduction of their P–Cl bonds under boranating conditions could be expected to lead directly to the formation of phosphinous acid-boranes. The viability of this idea was checked in a preliminary experiment utilizing *tert*-butylphenylphosphinic chloride as substrate. It was treated with an excess of $BH_3{\cdot}SMe_2$ complex (3 equiv) in THF at room temperature and the reaction was found to furnish the desired phosphinous acid-borane in excellent yield. We selected then a short series of phosphinic acid chlorides **1a–e** and reacted them with three different borane reagents (BH_3·THF, $BH_3{\cdot}SMe_2$ and $BF_3{\cdot}NaBH_4$) in order to generalize the synthesis and to check for possible optimal conditions. The results are presented in Scheme 1 and Table 1.



1 **2**

A - $BH_3{\cdot}SMe_2$ (3 equiv), r.t., 24 h
B - BH_3·THF (3 equiv), reflux, 2 h
C - BF_3 (4 equiv)/$NaBH_4$ (3 equiv), reflux, 2 h

Scheme 1

As can be seen from Table 1, the highest yields of boranatophosphinous acids were obtained when the complex BH_3·THF was used as the reducing agent. $BH_3{\cdot}SMe_2$ complex gave good yields of phosphinous acid-boranes only in the case of *tert*-butylphenylphosphinic chloride (**1a**). Other studied phosphinic halides reacted very sluggishly with this complex. Similarly, $BF_3/NaBH_4$ mixture generating BH_3 in situ was found effective only in the case of **1a**. It thus appears that BH_3·THF complex is the reagent of choice for the synthesis of phosphinous acid-boranes from phosphinic chlorides. The developed synthetic protocol constitutes a valuable complement to the previously described synthesis of phosphinous acid-boranes from

SYNTHESIS 2005, No. 8, pp 1279–1290
Advanced online publication: 17.03.2005
DOI: 10.1055/s-2005-861878; Art ID: Z00505SS

Table 1 The Synthesis of Phosphinous Acid-Boranes from Phosphinic Acid Chlorides

Entry	Product	R′	R″	Method used	Isolated yields (%)
1	**2a**	Ph	*t*-Bu	A	90
2	**2a**	Ph	*t*-Bu	B	95
3	**2a**	Ph	*t*-Bu	C	96
4	**2b**	Ph	Ph	A	23
5	**2b**	Ph	Ph	B	92
6	**2c**	Ph	$PhCH_2$	B	74
7	**2d**	Ph	Me	B	79
8	**2d**	Ph	Me	C	28
9	**2e**	Ph	2-$NpCH_2$[a]	B	67

[a] Np = naphthyl.

secondary phosphine oxides, especially in cases where secondary phosphine oxides are difficult to access or are unstable.[9]

Attempted conversion of diethyl chlorophosphate into the corresponding acid-borane under developed conditions was unsuccessful. Inspection of the ^{31}P NMR spectrum of the crude reaction mixture revealed no trace of the desired product. The major product formed in this case was diethyl phosphite.

The developed efficient synthetic access to phosphinous acid-boranes have made it possible to consider these compounds as a new class of potential synthetic intermediates in organophosphorus chemistry. As the chemistry of phosphinous acid-boranes was practically unexplored before, we decided to study the basic reactivity of these compounds towards typical alkylating, acylating, reducing and halogenating agents. For this study we selected phosphinous acid-boranes **2a–c**, **g** and **h** as model substrates representing diaryl-, alkylaryl-, and dialkyl-substitution patterns of different steric demand (Figure 1). Phosphinous acid-boranes **2a–c** were synthesized in the course of this work. **2g** and **2h** were available from the previous study.[8]

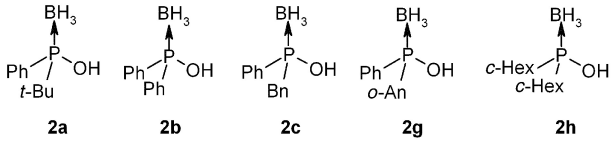
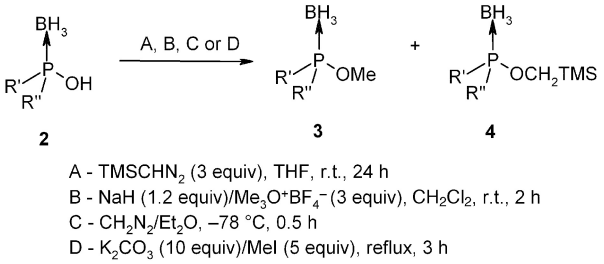


Figure 1

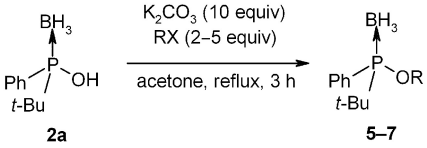
Since the esters of phosphinous acid-boranes are valuable synthetic intermediates we decided to explore their synthesis via simple *O*-alkylation of the parent acids. For the synthesis of the corresponding methyl esters of **2a–c**,**g**,**h** we tested $TMSCHN_2$, Me_3OBF_4, CH_2N_2 and MeI/K_2CO_3 as the methylating agents. The results of this screening are displayed in Scheme 2 and Table 2.



Scheme 2

In reactions of **2a–c**,**g**,**h** with trimethylsilyldiazomethane the formation of two products was always observed. Typically, methyl esters **3a–c**,**g** were formed as the minor products and trimethylsilylmethyl esters **4a–c**,**g** were formed as the major products (Entries 1–4, Table 2), except for acid **2h** (Entry 5, Table 2), which decomposed during the reaction. In reactions with Meerwein's salt (Entries 6–9, Table 2) the corresponding methyl esters were formed only with low to moderate yields (28–52%). It is noteworthy to mention, that evolution of a gas, most probably methane, was observed during these reactions. The presence of some amounts of the corresponding secondary phosphine oxides resulting from deboration of starting acid was accordingly detected in the ^{31}P NMR spectra of the crude reaction mixtures. Methylations with diazomethane (Entries 10–14, Table 2) and with MeI/K_2CO_3 (Entries 15–18, Table 2) both gave moderate to very good yields of methyl esters of acids **2**.

Encouraged by the results of methylation with the MeI/K_2CO_3 system, we also checked alkylations with other electrophiles under the same conditions using acid **2a** as the model substrate (Scheme 3, Table 3).



Scheme 3

As shown in Table 3, primary alkyl halides reacted smoothly with phosphinous acid-borane **2a** to form the corresponding esters nearly quantitatively. Even allyl ester **7** could be obtained with excellent yield (Entry 3) without affecting the borane and the alkenyl moieties. On the other hand, secondary alkyl halides did not react under these conditions at all.

Next, we moved to the reactions of phosphinous acid-boranes with acylating agents in order to explore the ability of phosphinous acid-boranes to form mixed anhydrides. First, we examined the reactivity of acids **2a–c**,**g**,**h** towards carboxylic acid chlorides. The results of this screening are presented in Scheme 4 and Table 4.

Table 2 The Reactivity of Phosphinous Acid-Boranes toward Methylating Agents

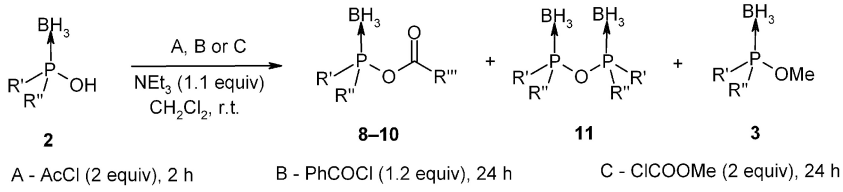
Entry	Substrate	Substituents		Reaction conditions	Isolated yields (%)	
		R′	R″		**3**	**4**
1	**2a**	Ph	*t*-Bu	A	18	55
2	**2b**	Ph	Ph	A	25	39
3	**2c**	Ph	Bn	A	32	40
4	**2g**	Ph	*o*-An	A	25	38
5	**2h**	*c*-Hex	*c*-Hex	A	0	0
6	**2a**	Ph	*t*-Bu	B	52	–
7	**2b**	Ph	Ph	B	28	–
8	**2c**	Ph	Bn	B	47	–
9	**2h**	*c*-Hex	*c*-Hex	B	37	–
10	**2a**	Ph	*t*-Bu	C	83	–
11	**2b**	Ph	Ph	C	80	–
12	**2c**	Ph	Bn	C	58	–
13	**2g**	Ph	*o*-An	C	56	–
14	**2h**	*c*-Hex	*c*-Hex	C	89	–
15	**2a**	Ph	*t*-Bu	D	89	–
16	**2b**	Ph	Ph	D	71	–
17	**2c**	Ph	Bn	D	71	–
18	**2g**	Ph	*o*-An	D	49	–

Table 3 Synthesis of Esters of *tert*-Butylphenylphosphinous Acid-Borane

Entry	Substrate	Electrophile	Product	Isolated yields (%)
1	**2a**	$PhCH_2Br$	**5**	95
2	**2a**	CH_3CH_2Br	**6**	99
3	**2a**	$CH_2=CHCH_2Br$	**7**	94
4	**2a**	*c*-$C_6H_{11}Br$	–	0
5	**2a**	*i*-C_3H_7Br	–	0

All acids **2a–c**,**g**,**h** reacted smoothly with acetyl chloride forming the expected mixed anhydrides **8a–c**,**g**,**h** with good to excellent yields (Entries 1–5, Table 4). In the reaction of acids **2** with benzoyl chloride, the mixed anhydrides **9** were also formed in good to excellent yields except for acid **2b**, in which case the formation of **9b** was accompanied by the generation of phosphinous acid anhydride-bis(borane) **11b** with overall decrease in yields. The results of reactions of acids **2** with methyl chloroformate were not uniformly good either. Acids **2a**,**g**,**h** gave the expected mixed anhydrides **10a**,**g**,**h**, respectively, in good to excellent yields (Entries 11–15, Table 4) whereas acids **2b** and **2c** underwent instead conversions to phosphinous acid anhydride-bis(borane) **11b** and methyl phosphinite-borane **3b**, and phosphinous acid anhydride-bis(borane) **11c**, respectively.

The observed differences in behavior of acids **2** towards benzoyl chloride and methyl chloroformate are likely to originate from differences in stability of the resulting mixed anhydrides, which is dependent on the nature of **2**. Acids with bulky groups at phosphorus like **2a**,**g**,**h**, appear



Scheme 4

Table 4 The Reactivity of Phosphinous Acid-Boranes towards Carboxylic Acid Halides

Entry	Substrate	Substituents			Method used	Isolated yields			
		R′	R″	R‴		**8–10**		**11**	**3**
1	**2a**	Ph	*t*-Bu	Me	A	**8a**	94	0	–
2	**2b**	Ph	Ph	Me	A	**8b**	76	0	–
3	**2c**	Ph	Bn	Me	A	**8c**	76	0	–
4	**2g**	Ph	*o*-An	Me	A	**8g**	99	0	–
5	**2h**	*c*-Hex	*c*-Hex	Me	A	**8h**	98	0	–
6	**2a**	Ph	*t*-Bu	Ph	B	**9a**	99	0	–
7	**2b**	Ph	Ph	Ph	B	**9b**	20	25	–
8	**2c**	Ph	Bn	Ph	B	**9c**	76	0	–
9	**2g**	Ph	*o*-An	Ph	B	**9g**	74	0	–
10	**2h**	*c*-Hex	*c*-Hex	Ph	B	**9h**	94	0	–
11	**2a**	Ph	*t*-Bu	OMe	C	**10a**	99	0	0
12	**2b**	Ph	Ph	OMe	C	**10b**	0	28	27
13	**2c**	Ph	Bn	OMe	C	**10c**	0	53	0
14	**2g**	Ph	*o*-An	OMe	C	**10g**	74	0	0
15	**2h**	*c*-Hex	*c*-Hex	OMe	C	**10h**	94	0	0

to form stable sterically protected mixed anhydrides, whereas acids with smaller substituents at phosphorus as in **2b** and **2c** yield more labile mixed anhydrides which readily enter consecutive trasformations under the reaction conditions. It is worthy of noting, however, that the synthesized mixed anhydrides **8**–**10** and the anhydrides **11** exhibit remarkable stability, which allows for their routine isolation and flash chromatography on silica gel practically without any loss of the product.

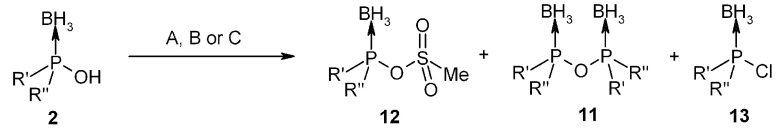
The reactivity of phosphinous acid-boranes **2** towards sulfonic acid chlorides was studied next. Mesyl chloride was chosen as a model chloride for this study. The results are collected in Scheme 5 and Table 5.

As can be seen from Table 5 only in the case of **2a** we were able to obtain the desired mixed anhydride **12a** in good yield (Entry 1). In all other cases either the corresponding phosphinous acid anhydride-bis(boranes) **11** or chlorophosphine-boranes **13** were isolated instead in moderate yield, except for chlorophosphine-borane **13h** which was isolated in excellent yield (Entry 7). It should be also noted that even in the case of acid **2a** the reaction could be completely driven to the selective production of chlorophosphine-borane **13a** by increasing the temperature and the concentration of the chloride ions (Entry 2).

Alternatively, upon changing the base and the solvent, it could selectively lead to anhydride **11a** as the sole product

Table 5 The Reactivity of Phosphinous Acid-Boranes towards Mesyl Chloride

Entry	Substrate	Substituents		Method used	Reaction time (h)	Isolated yields (%)		
		R′	R″			**11**	**12**	**13**
1	**2a**	Ph	*t*-Bu	A	6	0	86	0
2	**2a**	Ph	*t*-Bu	B	6	0	0	58
3	**2a**	Ph	*t*-Bu	C	66	54	0	0
4	**2b**	Ph	Ph	A	6	34	0	0
5	**2c**	Ph	Bn	A	5	56	0	0
6	**2g**	Ph	*o*-An	A	8	0	0	40
7	**2h**	*c*-Hex	*c*-Hex	A	3	0	0	94



A - NEt_3 (1.2 equiv), MsCl (2 equiv), CH_2Cl_2, r.t.
B - NEt_3 (1.2 equiv), MsCl (2 equiv), NEt_3-HCl (5 equiv), CH_2Cl_2, reflux
C - K_2CO_3 (10 equiv), MsCl (2 equiv), MeCN, r.t.

Scheme 5

(Entry 3). Other tested sulfonic acid chlorides like tosyl chloride and camphorosulfonyl chloride failed to form mixed anhydrides even with **2a**. Apparently, with the possible exception of **12a**, the mixed phosphinous acid-borane sulfonic acid anhydrides are very labile compounds whose undergo further transformations upon formation.

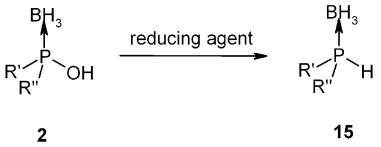
The possibility of easy removal of protecting borane group from phosphine-boranes to yield trivalent phosphorus derivatives is one of the cornerstones of their advantageous use as synthetic intermediates. In the case of phosphinous acid-boranes the deprotection would lead to secondary phosphine oxides, a valuable synthetic intermediates *per se*.

14a	R' = Ph	R'' = *t*-Bu	96%
14b	R' = Ph	R'' = Ph	91%
14c	R' = Ph	R'' = Bn	78%
14g	R' = Ph	R'' = *o*-An	96%
14h	R' = *c*-Hex	R'' = *c*-Hex	67%

Scheme 6 The synthesis of secondary phosphine oxides from phosphinous acid-boranes

We found that this transformation can be conveniently achieved by utilizing tetrafluoroboric acid as deboranating agent according to the protocol described by McKinstry and Livinghouse.[10] The studied examples of highly efficient conversion of phosphinous acid-boranes **2** into secondary phosphine oxides **14** are presented in Scheme 6. It is interesting to juxtapose the developed procedure to our recent finding that secondary phosphine oxides can be efficiently converted into phosphinous acid-boranes by treatment with $NaH{\cdot}BH_3$ (or BF_3/$NaBH_4$).[8] The two transformations complement each other and make the mutual conversion of these two classes of compounds a synthetically reversible process.

Another useful transformation of phosphinous acid-boranes which we wanted to develop was their reductive conversion into secondary phosphine-boranes. We have tested several reducing systems to probe the susceptibility of phosphinous acid-boranes to undergo P–O bond cleavage and the results of the performed representative experiments are collected in Scheme 7 and Table 6.



Scheme 7

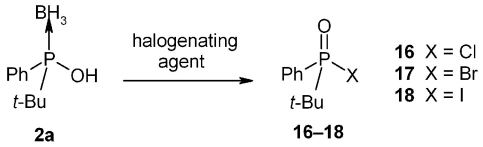
The reduction of acids **2** to secondary phosphine-boranes proved to be a difficult task. Lithium aluminium hydride, a powerful reducing agent, appeared to be completely ineffective in the case of **2**. Trichlorosilane performed somewhat better but the yields of the obtained secondary

Table 6 Conversion of Phosphinous Acid-Boranes into Secondary Phosphine–Boranes

Entry	Compound	Substituents		Reducing agent (equiv)	Reaction conditions	Isolated yields of **15**
		R′	R″			
1	**2a**	Ph	*t*-Bu	$SiHCl_3$ (5)	PhMe, reflux, 45 h	30
2	**2a**	Ph	*t*-Bu	$SiHCl_3$ (5)	NaH (1.2 equiv), PhMe, PhMe, 130 °C, 5 h	38
3	**2a**	Ph	*t*-Bu	$SiHCl_3$ (5)	NaH (1.2 equiv), PhMe, r.t., 24 h	0
4	**2a**	Ph	*t*-Bu	$LiAlH_4$ (3)	THF, r.t., 48 h	0
5	**2a**	Ph	*t*-Bu	$BH_3{\cdot}THF$ (6)	THF, r.t., 48 h	11
6	**2h**	*c*-Hex	*c*-Hex	$BH_3{\cdot}THF$ (6)	THF, r.t., 48 h	38
7	**2h**	*c*-Hex	*c*-Hex	$BH_3{\cdot}THF$ (6)	THF, reflux, 48 h	13

phosphine-borane were only modest (Entries 1 and 2, Table 6). Also modest yields of secondary phosphine-boranes were obtained with BH_3 as the reducing agent (Entries 5–7, Table 6). Interestingly, however, somewhat better yields of secondary phosphine-boranes **15** were achieved when the reduction was carried out at room temperature than when heating was applied (cf. Entries 6 and 7).

In this paper, we have demonstrated already that phosphinous acid-boranes could be readily obtained from phosphinic acid halides. We became interested in accomplishing also the reverse conversion. We chose again *tert*-butylphenylphosphinous acid-borane **2a** as a model substrate. The results of our screening are displayed in Scheme 8 and Table 7.



Scheme 8

Table 7 The Synthesis of *tert*-Butylphenylphosphinic Halides from *tert*-Butylphenylphosphinous Acid-Borane (**2a**)

Entry	Halogenating agent (equiv)	Conditions	Compd	Isolated yields
1	PPh_3 (1)/CCl_4	CCl_4, reflux, 21 h	**16**	85
2	$CCl_3C(O)CCl_3$ (5)	NaH (1.2 equiv), Et_2O, r.t., 3 h	**16**	77
3	$(COCl)_2$ (3)	PhH, r.t., 21 h	**16**	85
4	CBr_4 (5)	NaH (1.2 equiv), Et_2O, r.t., 3 h	**17**	64
5	$(COBr)_2$ (3)	PhH, r.t., 16 h	**17**	60
6	I_2 (3)	Et_2O, r.t., 24 h	**18**	90

Table 7 reveals a remarkably high propensity of phosphinous acid-boranes to undergo the transformation into phosphinic acid halides. Each of the three phosphinic acid halides **16–18** could be obtained in good to excellent yields by the action of a variety of reagents including even PPh_3·CCl_4, which we originally hoped would secure conversion of acids **2** into the corresponding chlorophosphine-boranes.

We have demonstrated herein that phosphinous acid-boranes can be directly obtained from phosphinic acid chlorides by action of BH_3·THF complex in THF. Phosphinous acid-boranes, have been shown to react readily with alkylating, acylating, reducing, halogenating and deborating agents to efficiently produce the corresponding phosphinous acid-borane esters, phosphinous acid-borane anhydrides, *sec*-phosphine oxides, *sec*-phosphine boranes and phosphinic acid halides, respectively. They have been practically neglected before, but the unraveled basic reactivity pattern of phosphinous acid-boranes makes them now begin to emerge as a new class of phosphorus reagents of potential utility in the preparative organophosphorus chemistry. When non-symmetrically substituted, they are chiral at phosphorus and their synthesis in the nonracemic forms and stereochemistry of their transformations is now under active investigation.

All experiments were carried under inert atmosphere. The solvents were dried prior to use. ^1H, ^{13}C and ^{31}P NMR were measured with a Varian AC-200 (200 MHz) and Bruker AM-500 (500 MHz) in $CDCl_3$ with Me_4Si or 85% H_3PO_4 as internal standard. Phosphinic acid chlorides were prepared by literature methods.[11] Diethyl chlorophosphate was commercially available.

Phosphinous Acid-Boranes from Phosphinic Acid Chlorides and BH_3·THF; General Procedure

In a flask equipped with a magnetic stirrer and a reflux condenser was placed phosphinic acid chloride (1.0 mmol) in anhyd THF (15 mL). Then, BH_3·THF complex (1.5 mmol) was added through a syringe. After addition of borane was completed, the reaction mixture was refluxed for 2 h and after this time it was allowed to cool to r.t. Next, aq HCl (3 M) was added to the reaction mixture and then it was extracted several times with CH_2Cl_2. The organic phases were combined and dried ($MgSO_4$). The solvents were evaporated and the residue was purified by column chromatography (silica gel; hexane–EtOAc, 2:1).

***tert*-Butylphenylphosphinous Acid-Borane (2a)**

Yield: 95%.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.00–1.70 (br m, 3 H), 1.14 (d, J_{PCCH} = 14.66 Hz, 9 H), 4.52 (br s, 1 H), 7.41–7.89 (m, 3 H), 7.69–7.85 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.85, 23.92, 31.31, 32.13, 127.82, 128.03, 131.20, 131.26, 131.46.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 114.39 (m).

Anal. Calcd for $C_{10}H_{18}BOP$: C, 61.27; H, 9.26. Found: C, 61.26; H, 9.08.

Diphenylphosphinous Acid-Borane (2b)

Yield: 92%.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.20–1.90 (br m, 3 H), 4.35 (br s, 1 H), 7.40–7.57 (m, 6 H), 7.70–7.86 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 128.35, 128.57, 130.65, 130.82, 130.88, 131.52, 132.40, 133.71.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 95.62 (m).

Anal. Calcd for $C_{12}H_{14}BOP$: C, 66.72; H, 6,53. Found: C, 66.96; H, 6.70.

Benzylphenylphosphinous Acid-Borane (2c)

Yield: 74%.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.07–1.65 (br m, 3 H), 3.38 (d, J_{PCH} = 10.22 Hz, 2 H), 4.90 (br s, 1 H), 7.01–7.13 (m, 2 H), 7.21–7.34 (m, 3 H), 7.40–7.75 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.41, 40.14, 126.68, 126.74, 127.98, 128.03, 128.08, 128.28, 129.95, 130.04, 130.19, 130.41, 131.06, 131.13, 131.18, 131.51, 131.56, 132.32.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 101.64 (m).

Anal. Calcd for $C_{13}H_{16}BOP$: C, 67.87; H, 7.01. Found: C, 68.02; H, 6.95.

Methylphenylphosphinous Acid-Borane (2d)
Yield: 79%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.05–1.65 (br m, 3 H), 1.73 (d, J_{PCH} = 9.34 Hz, 3 H), 6.20 (br s, 1 H), 7.43–7.60 (m, 3 H), 7.75–7.90 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.31, 18.20, 128.37, 128.58, 139.73, 129.96, 131.45.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 99.61 (m).

Anal. Calcd for $C_7H_{12}BOP$: C, 54.61; H, 7.96. Found: C, 55.04; H, 7.86.

(2-Naphthylmethyl)phenylphosphinous Acid-Borane (2e)
Yield: 67%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.05–1.72 (br m, 3 H), 3.52 (d, J_{PCH} = 9.98 Hz, 2 H), 3.60 (br s, 1 H), 7.11–7.21 (m, 1 H),7.36–7.56 (m, 5 H), 7.56–7.89 (m, 6 H)

^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.64, 40.36, 125.71, 126.02, 127.39, 127.50, 127.68, 128.12, 128.25, 128.46, 128.64, 128.77, 128.89, 130,261, 130.48, 131.73, 131.77, 132.22.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 103.16 (m).

Anal. Calcd for $C_{17}H_{18}BOP$: C, 72.99; H, 6.48. Found: C, 73.04; H, 6.53.

Methylation and Alkylation of Phosphinous Acid-Boranes; General Procedures

With Trimethylsilyldiazomethane (A)
In a flask equipped with a magnetic stirrer and an argon inlet, phosphinous acid-borane (0.3 mmol) in anhyd Et_2O (15 mL) was placed. Then, a solution of trimethylsilyldiazomethane (0.9 mmol) was added into the reaction mixture through a syringe. The reaction mixture immediately changed color to yellow. The reaction mixture was allowed to stay at r.t. for 24–72 h. Next, aq HCl (3 M) was added to the mixture, the biphasic mixture was extracted with CH_2Cl_2, the organic phase was dried ($MgSO_4$) and evaporated to dryness. The residue was subjected to separation (silica gel, hexane–EtOAc, 6:1).

With Meerwein Salt (B)
In a flask equipped with a magnetic stirrer and an argon inlet, phosphinous acid-borane (0.3 mmol) in anhyd Et_2O (15 mL) was placed. Then, sodium hydride (0.36 mmol) was added in one portion. When the evolution of hydrogen ceased, Meerwein salt (0.9 mmol) was added to the reaction mixture at r.t. The mixture was allowed to stand for 2 h, then aq HCl was added. The biphasic mixture was extracted with CH_2Cl_2, the organic phase was dried ($MgSO_4$) and then evaporated to dryness. The residue was subjected to separation (silica gel; hexane–EtOAc, 6:1).

With Diazomethane (C)
In a flask equipped with a magnetic stirrer and an argon inlet, phosphinous acid-borane (0.3 mmol) in anhyd Et_2O (15 mL) was placed. The reaction flask was cooled then to – 78 °C. In another flask equipped with magnetic stirrer, distillation head and reflux condenser DIAZALD (3 mmol) was placed in Et_2O (30 mL) and MeOH (10 mL). To this mixture, aq KOH (3 mmol) was added. After 5 min, an ethereal solution of diazomethane was distilled straight into the flask containing phosphinous acid–borane. The reaction mixture was maintained at –78 °C for 0.5 h, allowed to warm to r.t. and quenched with aq HCl. The mixture was extracted with CH_2Cl_2, the organic phase was dried ($MgSO_4$) and then evaporated to dryness. The residue was subjected to separation (silica gel; hexane–EtOAc, 6:1).

With Potassium Carbonate in Acetone (D)
In a flask equipped with a magnetic stirrer and an argon inlet, phosphinous acid-borane (0.3 mmol) in acetone (15 mL) was placed. Then, anhyd potassium carbonate (3 mmol) was added. After 5 min, alkyl halide (2–5 equiv) was added and the reaction mixture was refluxed for 3 h. Then, the reaction mixture was allowed to cool to r.t., inorganic salt was filtered off and the filtrate was evaporated to dryness. The residue was subjected to separation (silica gel; hexane–EtOAc, 6:1).

Methyl *tert*-Butylphenylphosphinite-Borane (3a)
Yields: 18, 52, 83 and 89%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.05–1.64 (br m, 3 H), 1.13 (d, J_{PCCH} = 14.24 Hz, 9 H), 3.73 (d, J_{POCH} = 11.07 Hz, 3 H), 7.41–7.61 (m, 3 H), 7.61–7.77 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.13, 24.19, 31.67, 32.54, 54.57, 54.74, 128.01, 128.20, 131.36, 131.41, 131.72, 131.98.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 127.62 (m).

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{20}BONaP$ (M + Na^+): 233.1237; found: 233.1235.

Methyl Diphenylphosphinite-Borane (3b)
Yields: 25, 28, 80 and 71%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20–1.90 (br m, 3 H), 3.78 (d, J_{POCH} = 12.06 Hz, 3 H), 7.44–7.62 (m, 6 H), 7.71–7.84 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 54.05, 54.09, 128.43, 128.64, 131.03, 131.26, 132.76, 131.81.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 109.02 (m).

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}BONaP$ (M + Na^+): 253.0924; found: 253.0947.

Methyl Benzylphenylphosphinite-Borane (3c)
Yields: 32, 47, 58 and 71%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.00–1.70 (br m, 3 H), 3.35 (d, J_{PCH} = 10.30 Hz, 2 H), 3.65 (d, J_{POCH} = 11.86 Hz, 3 H), 6.95–7.07 (m, 2 H), 7.20–7.28 (m, 3 H), 7.39–7.66 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 38.63, 39.42, 54.36, 126.77, 126.82, 128.01, 128.06, 128.26, 128.46, 130.01, 130.10, 130.90, 131.12, 131.90.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 115.67 (m).

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}BONaP$ (M + Na^+): 267.1032; found: 267.1027.

Methyl *o*-Anisylphenylphosphinite-Borane (3g)
Yields: 25, 56 and 49%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20–1.90 (br m, 3 H), 3.67 (s, 3 H), 3.78 (d, J_{POCH} = 12.10 Hz, 3 H), 6.82–7.17 (m, 3 H), 7.22–7.34 (m, 1 H), 7.40–7.60 (m, 3 H), 7.71–7.91 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 53.98, 55.53, 111.52, 111.62, 115.20, 120.66, 120.87, 127.93, 128.15, 129.55, 130.92, 131.16, 133.74, 133.97.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 107.34 (m).

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}BO_2NaP$ (M + Na^+): 283.1030; found: 283.1051.

Methyl Di-*c*-hexylphosphinite-Borane (3h)
Yields: 37 and 89%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.41–1.25 (br m, 3 H), 1.15–1.60 (m, 10 H), 1.60–2.00 (m, 12 H), 3.69 (d, J_{POCH} = 10.75 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.06, 25.11, 26.00, 26.17, 26.43, 26.63, 26.72, 35.14, 35.92, 56.08, 56.15.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 133.69 (m).

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{28}BONaP$ (M + Na^+): 265.1863; found: 265.1853.

Trimethylsilylmethyl *tert*-Butylphenylphosphinite-Borane (4a)
Yield: 55%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.05–1.60 (br m, 3 H), 0.17 (m, 9 H), 1.13 (d, J_{POCH} = 14.24 Hz, 9 H), 3.60 (m, 2 H), 7.41–7.61 (m, 3 H), 7.61–7.77 (m, 2 H).

Trimethylsilylmethyl Diphenylphosphinite-Borane (4b)
Yield: 39%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.29–1.90 (br m, 3 H), 0.14 (m, 9 H), 3.64 (d, J_{POCH} = 6.01 Hz, 2 H), 7.41–7.60 (m, 6 H), 7.69–7.82 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –3.23, 60.23, 60.46, 128.34, 128.55, 131.07, 131.29, 131.55, 131.60.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 108.55 (m).

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{24}BONaPSi$ (M + Na^+): 325.1319; found: 325.1335.

Trimethylsilylmethyl Benzylphenylphosphinite-Borane (4c)
Yield: 40%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.05–1.85 (br m, 3 H), 0.10 (m, 9 H), 3.21–3.45 (m, 2 H), 3.51 (m, 2 H), 6.95–7.07 (m, 2 H), 7.20–7.30 (m, 3 H), 7.36–7.62 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –3.28, 38.71, 39.50, 60.55, 60.72, 126.65, 126.71, 127.87, 127,92, 128.15, 128.34, 129.32, 130.09, 130.17, 131.03, 131.24, 131.73, 131.78.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 115.22 (m).

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{26}BONaPSi$ (M + Na^+): 339.1438; found: 339.1445.

Trimethylsilylmethyl *o*-Anisylphenylphosphinite-Borane (4g)
Yield: 38%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20–1.92 (br m, 3 H), 0.14 (m, 9 H), 3.61 (dd, J_{POCH} = 5.80, J_{HCH} = 2.92 Hz, 2 H), 3.65 (s, 3 H), 6.82–6.94 (m, 1 H), 7.04–7.16 (m, 1 H), 7.38–7.56 (m, 4 H), 7.69–7.92 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –3.25, 55.29, 59.59, 59.75, 111.26, 111.36, 120.50, 120.71, 127.76, 127.97, 130.96, 131.02, 131.25, 133.76, 133.98.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 107.07 (m).

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{26}BO_2NaPSi$ (M + Na^+): 355.1425; found: 355.1449.

Benzyl *tert*-Butylphenylphosphinite-Borane (5)
Yield: 95%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.10–1.65 (br m, 3 H), 1.17 (d, J_{PCCH} = 14.56 Hz, 9 H), 4.80–5.19 (m, 2 H), 7.32–7.64 (m, 8 H), 7.68–7.83 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.16, 24.22, 31.88, 32.74, 69.05, 69.12, 127.46, 128.02, 128.21, 128.43, 129.93, 130.83, 131.43, 131.48, 131.79, 131.98.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 126.45 (m).

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{24}BONaP$ (M + Na^+): 309.1550; found: 309.1554.

Ethyl *tert*-Butylphenylphosphinite-Borane (6)
Yield: 99%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.05–1.65 (br m, 3 H), 1.13 (d, J_{PCCH} = 14.44 Hz, 9 H), 1.36 (t, $J_{HC\text{-}H}$ = 7.10 Hz, 3 H), 3.85–4.23 (m, 2 H), 7.42–7.60 (m, 3 H), 7.66–7.80 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.59, 16.71, 24.04, 24.10, 31.51, 32.38, 63.82, 63.90, 127.90, 128.09, 128.74, 129.57, 131.23, 131.28, 131.63, 131.83.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 123.80 (m).

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{22}BONaP$ (M + Na^+): 247.1394; found: 247.1412.

Allyl *tert*-Butylphenylphosphinite-Borane (7)
Yield: 94%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.05–1.65 (br m, 3 H), 1.16 (d, J_{PCCH} = 14.52 Hz, 9 H), 4.27–4.65 (m, 2 H), 5.22–5.47 (m, 2 H), 5.90–6.09 (m, 1 H), 7.41–7.61 (m, 3 H), 7.68–7.81 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.09, 24.15, 31.75, 32.61, 68.04, 68.11, 117.04, 127.97, 128.17, 129.08, 130.06, 131.38, 131.43, 131.68, 131.88, 133.56, 133.69.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 126.07 (m).

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{22}BONaP$ (M + Na^+): 259.1394; found: 259.1385.

Mixed Phosphorus-Carboxylic Anhydrides; General Procedure
In a flask equipped with a magnetic stirrer and drying $CaCl_2$ tube phosphinous acid-borane (0.3 mmol) in CH_2Cl_2 (15 mL) was placed. Then, Et_3N (0.33 mmol) was added and 5 min later the RC(O)Cl (0.36–0.60 mmol) was added through a syringe. Then the reaction mixture was allowed to stand at r.t. for 2–24 h. Next, the reaction mixture was filtered to remove the formed triethylammonium salt, the filtrate was evaporated to dryness and the residue was separated by flash chromatography (hexane–EtOAc, 2:1 or 6:1).

Acetic *tert*-Butylphenylphosphinous-Borane Anhydride (8a)
Yield: 94%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.10–1.82 (br m, 3 H), 1.20 (d, J_{PCCH} = 14.72 Hz, 9 H), 2.31 (d, J_{POCCH} = 1.10 Hz, 3 H), 7.42–7.63 (m, 3 H), 7.63–7.78 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.20, 22.25, 24.16, 24.21, 31.76, 32.51, 128.03, 128.15, 128.35, 131.43, 131.64, 131.88, 131.94, 166.40.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 126.62 (m).

Anal. Calcd for $C_{12}H_{20}BO_2P$: C, 60.54; H, 8.47. Found: C, 60.56; H, 8.50.

Acetic Diphenylphosphinous-Borane Anhydride (8b)
Yield: 76%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35–2.10 (br m, 3 H), 2.29 (d, *J* = 1.24 Hz, 3 H), 7.45–7.64 (m, 6 H), 7.77–7.90 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.30, 22.34, 128.50, 128.72, 128.97, 130.19,131.52, 131.75, 132.23, 132.28.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 106.12 (m).

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}BO_2NaP$ (M + Na^+): 281.0873; found: 281.0886.

Acetic Benzylphenylphosphinous-Borane Anhydride (8c)
Yield: 76%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.15–1.95 (br m, 3 H), 2.23 (d, J_{POCCH} = 1.18 Hz, 3 H), 3.56–3.78 (m, 2 H), 6.94–7.06 (m, 2 H), 7.17–7.30 (m, 3 H), 7.40–7.73 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.22, 22.26, 36.96, 37.60, 127.12, 127.18, 127.50, 128.14, 128.19, 128.31, 128.52, 130.01, 130.10, 130.21, 131.14, 131.36, 132.45, 132.50, 167.00, 167.16.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 113.18 (m).

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{18}BO_2NaP$ (M + Na^+): 295.1030; found: 295.1010.

Acetic *o*-Anisylphenylphosphinous-Borane Anhydride (8g)
Yield: 99%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.30–2.10 (br m, 3 H), 2.29 (d, J_{POCCH} = 1.24 Hz, 3 H), 3.70 (s, 3 H), 6.87–6.98 (m, 1 H), 7.08–7.20 (m, 1 H), 7.40–7.63 (m, 4 H), 7.73–8.02 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.21, 55.53, 111.37, 111.46, 117.93, 120.91, 121.15, 128.02, 128.24, 129.60, 130.90, 131.03, 131.26, 131.58, 131.63, 134.09, 134.39, 134.50.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 105.37 (m).

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{18}BO_3NaP$ (M + Na^+): 311.0979; found: 311.0997.

Acetic Di-*c*-hexylphosphinous-Borane Anhydride (8h)
Yield: 98%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.32–1.41 (br m, 3 H), 1.17–1.65 (m, 10 H), 1.65–2.00 (m, 10 H), 2.05–2.31 (m, 2 H), 2.20 (d, J_{POCCH} = 0.87 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.19, 22.23, 25.76, 25.85, 25.90, 26.32, 26.37, 26.57, 35.09, 35.68, 167.39, 167.58.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 137.18 (m).

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{28}BO_2NaP$ (M + Na^+): 293.1812; found: 293.1821.

Benzoic *tert*-Butylphenylphosphinous-Borane Anhydride (9a)
Yield: 99%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.15–1.93 (br m, 3 H), 1.33 (d, J_{PCCH} = 14.70 Hz, 9 H), 7.44–7.64 (m, 5 H), 7.64–7.83 (m, 3 H), 8.07–8.22 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.45, 24.51, 32.20, 32.95, 127.06, 127.99, 128.19, 128.40, 128.75, 128.91, 130.35, 130.47, 131.32, 131.15, 131.72, 131.94, 131.99, 134.22, 162.27.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 128.14 (m).

Anal. Calcd for $C_{19}H_{18}BO_2P$: C, 68.03; H, 7.39. Found: C, 67.91; H, 7.34.

Benzoic Diphenylphosphinous-Borane Anhydride (9b)
Yield: 20%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.30–2.20 (br m, 3 H), 7.40–7.80 (m, 11 H), 7.80–8.00 (m, 3 H), 8.07–8.14 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 128.65, 128.85, 130.46, 131.64, 131.88, 132.33, 132.37, 134.27.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 107.83 (m).

Benzoic Benzylphenylphosphinous-Borane Anhydride (9c)
Yield: 76%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.15–2.00 (br m, 3 H), 3.40–3.94 (m, 2 H), 6.87–7.12 (m, 2 H), 7.12–7.31 (m, 3 H), 7.45–7.82 (m, 8 H), 8.00–8.09 (m, 1 H), 8.18–8.26 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 37.30, 37.94, 127.13, 127.19, 128.17, 128.22, 128.39, 128.58, 128.75, 130.10, 130.19, 130.27, 130.37, 130.40, 131.19, 131.34, 131.41, 132.49, 132.54, 134.25, 134.40, 162.98.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 114.68 (m).

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}BO_2NaP$ (M + Na^+): 357.1186; found: 357.1196.

Benzoic *o*-Anisylphenylphosphinous-Borane Anhydride (9g)
Yield: 99%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.40–2.20 (br m, 3 H), 3.61 (s, 3 H), 6.86–6.97 (m, 1 H), 7.11–7.22 (m, 1 H), 7.44–7.73 (m, 7 H), 7.86–7.99 (m, 2 H), 7.99–8.18 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.49, 111.36, 111.45, 120.95, 121.20, 128.15, 128.38, 128.55, 129.09, 130.03, 135.35, 131.16, 131.41, 131.68, 131.72, 133.93, 134.25, 134.52, 160.60, 160.46.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 107.45 (m).

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}BO_3NaP$ (M + Na^+): 373.1135; found: 373.1154.

Benzoic Di-*c*-hexylphosphinous-Borane Anhydride (9h)
Yield: 94%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.20–1.38 (br m, 3 H), 1.17–2.09 (m, 20 H), 2.25–2.50 (m, 2 H), 7.43–7.59 (m, 2 H), 7.59–7.71 (m, 1 H), 8.00–7.13 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.78, 25.99, 26.03, 26.37, 26.50, 26.59, 35.37, 35.95, 128.56, 130.33, 134.05, 163.02.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 138.85 (m).

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{30}BO_2NaP$ (M + Na^+): 355.1969; found: 355.1988.

***O*-Methylcarbonic *tert*-Butylphenylphosphinous-Borane Anhydride (10a)**
Yield: 99%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.12–1.86 (br m, 3 H), 1.21 (d, J_{PCCH} = 14.92 Hz, 9 H), 3.84 (s, 3 H), 7.46–7.65 (m, 3 H), 7.65–7.82 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.08, 24.16, 32.24, 32.98, 55.97, 128.19, 128.39, 131.42, 131.64, 132.10, 132.15.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 135.21 (m).

Anal. Calcd for $C_{12}H_{20}BO_3P$: C, 56.73; H, 7.93. Found: C, 56.83; H, 7.91.

***O*-Methylcarbonic *o*-Anisylphenylphosphinous-Borane Anhydride (10g)**
Yield: 74%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20–1.90 (br m, 3 H), 3.67 (s, 3 H), 3.83 (s, 3 H), 6.89–7.22 (m, 2 H), 7.38–7.67 (m, 4 H), 7.67–8.07 (m, 3H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.55, 55.79, 111.49, 111.58, 120.89, 121.13, 128.06, 128.28, 130.99, 131.23, 131.87, 134.19, 134.47, 134.81, 160.62, 160.65.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 112.63 (m).

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{18}BO_4NaP$ (M + Na^+): 327.0928; found: 327.0946.

***O*-Methylcarbonic Di-*c*-Hexylphosphinous-Borane Anhydride (10h)**
Yield: 94%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.29–1.41 (br m, 3 H), 1.18–1.64 (m, 10 H), 1.64–2.01 (m, 10 H), 2.01–2.26 (m, 2 H), 3.86 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.54, 25.75, 26.09, 26.32, 26.53, 26.58, 35.22, 35.83, 55.82, 151.05.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 145.60 (m).

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{28}BO_3NaP$ (M + Na^+): 309.1761; found: 309.1782.

Diphenylphosphinous Acid Anhydride-Bis(borane) (11b)
Yield: 28%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20–1.85 (br m, 3 H), 7.38–7.61 (m, 6 H), 7.65–7.82 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 128.43, 128.55, 128.65, 131.59, 131.72, 131.83, 132.37.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 114.85 (m).

HRMS (ESI): *m*/*z* calcd for $C_{24}H_{26}B_2ONaP_2$ (M + Na^+): 437.1548; found: 437.1559.

Benzylphenylphosphinous Acid Anhydride-Bis(borane) (11c)
Yield: 53%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20–1.90 (br m, 3 H), 3.31–3.70 (m, 2 H), 6.86–6.94 (m, 1 H), 6.96–7.04 (m, 1 H), 7.12–7.30 (m, 3 H), 7.30–7.62 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.64, 39.86, 40.33, 40.55, 127.10, 128.15, 128.23, 128.36, 128.45, 130.21, 130.31, 130.41, 131.17, 131.28, 131.40, 131.52, 132.50, 132.61.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 122.21 (m).

HRMS (ESI): *m*/*z* calcd for $C_{26}H_{30}B_2ONaP_2$ (M + Na^+): 465.1749; found: 465.1764.

Reaction Between Phosphinous Acid-Boranes and Mesyl Chloride; General Procedure
In a flask equipped with a magnetic stirrer and a drying $CaCl_2$ tube, phosphinous acid-borane (0.3 mmol) was placed in CH_2Cl_2 or MeCN (15 mL). Then, Et_3N (0.36 mmol) or anhyd K_2CO_3 (3 mmol) was added and after 5 min mesyl chloride (0.60 mmol) was added through a syringe. The reaction mixture was allowed to stand at r.t. for 3–66 h or was refluxed for 6 h. Then, the reaction mixture was filtered to remove triethylammonium salt, the filtrate was evaporate to dryness and residue was separated by flash chromatography (hexane–EtOAc, 6:1).

Methanesulfonic *tert*-Butylphenylphosphinous-Borane Anhydride (12a)
Yield: 86%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.16–1.94 (br m, 3 H), 1.22 (d, J_{PCCH} = 15.62 Hz, 9 H), 3.49 (s, 3 H), 7.48–7.68 (m, 3 H), 7.78–7.92 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.94, 24.01, 33.46, 34.13, 47.17, 126.22, 127.17, 128.28, 128.48, 131.69, 131.90, 132.62, 132.67.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 144.69 (m).

Anal. Calcd for $C_{11}H_{20}BO_3PS$: C, 48.20; H, 7.35; S, 11.70. Found: C, 48.09; H, 7.37; S, 11.57.

***tert*-Butylphenylphosphinous Acid Anhydride-Bis(borane) (11a)**
Yield: 54%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.10–1.60 (br m, 3 H), 1.26 (dd, J_{PCCH} = 15.39, J_{PCCH} = 15.34 Hz, 9 H), 7.35–7.60 (m, 3 H), 7.65–7.90 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.70, 24.83, 33.92, 34.69, 127.57, 127.68, 127.79, 127.97, 128.17, 132.34, 132.45, 132.55, 132.83, 132.94, 133.05.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 137.00 (m) and 138.83 (m).

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{34}B_2ONaP_2$ (M + Na^+): 397.2163; found: 397.2183.

***tert*-Butylphenylchlorophosphine-Borane (13a)**
Yield: 58%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.30–2.00 (br m, 3 H), 1.25 (d, J_{PCCH} = 16.50 Hz, 9 H), 7.42–7.68 (m, 3 H), 7.84–7.97 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.50, 24.59, 35.11, 35.51, 128.19, 128.40, 132.23, 132.28, 132.38, 132.60.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 121.87 (m).

***o*-Anisylphenylchlorophosphine-Borane (12g)**
Yield: 40%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.30–1.95 (br m, 3 H), 3.71 (s, 3 H), 6.90–7.01 (m, 1 H), 7.09–7.20 (m, 1 H), 7.37–8.04 (m, 7 H).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 92.20 (m).

Di-*c*-hexylchlorophosphine-Borane (12h)
Yield: 94%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.13–1.55 (br m, 3 H), 1.21–1.70 (m, 10 H), 1.70–2.17 (m, 12 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.40, 25.46, 25.67, 26.14, 26.26, 26.35, 26.53, 36.56, 36.96.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 129.54 (m).

Anal. Calcd for $C_{10}H_{14}BClP$: C, 54.49; H, 9.60; Cl, 13.50. Found: C, 54.34; H, 9.52; Cl, 13.59.

Conversion of Phosphinous Acid-Boranes into Secondary Phosphine Oxides; General Procedure
In a flask equipped with a magnetic stirrer and an argon inlet, phosphinous acid-borane (0.3 mmol) in CH_2Cl_2 (15 mL) was placed. Then, ethereal complex of tetrafluoroboric acid (1.5 mmol) was added through a syringe. The reaction mixture was allowed to stand at r.t. for 1.5 h. Then, aq sodium carbonate was added, and after 10 min the reaction mixture was extracted with CH_2Cl_2, the organic phase was dried ($MgSO_4$), evaporated to dryness and the residue was purified by flash chromatography (EtOAc–MeOH, 20:1).

***tert*-Butylphenylphosphine Oxide (14a)**
Yield: 96%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.16 (d, J_{PCCH} = 16.62 Hz, 9 H), 7.04 (d, J_{PH} = 454 Hz, 1 H), 7.42–7.80 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.48, 23.52, 31.34, 32.71, 127.86, 128.21, 128.27, 128.51, 130.70, 130.90, 132,33, 132.38.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 47.72.

HRMS (ESI): *m*/*z* calcd for $C_{10}H_{15}ONaP$ (M + Na^+): 205.0777; found: 205.0755.

Diphenylphosphine Oxide (14b)
Yield: 91%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.44–7.64 (m, 6 H), 7.65–7.80 (m, 6 H), 8.08 (d, J_{PH} = 481 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 128.64, 128.90, 130.28, 130.45, 130.67, 132.29, 132.42, 132.47.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 22.73.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{11}ONaP$ (M + Na^+): 225.0440; found: 225.0449.

Benzylphenylphosphine Oxide (14c)
Yield: 78%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.29–3.60 (m, 2 H), 7.50 (dt, J_{PH} = 476 Hz, 1 H), 7.03–7.15 (m, 2 H), 7.23–7.33 (m, 3 H), 7.40–7.64 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 38.15, 39.39, 127.03, 127.11, 128.39, 128.63, 128.69, 129.53, 129.64, 129.83, 130.04, 132.41, 132.46.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 35.49.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{13}ONaP$ (M + Na^+): 239.0596; found: 239.0608.

o-Anisylphenylphosphine Oxide (14g)
Yield: 96%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 6.87–6.99 (m, 1 H), 7.07–7.19 (m, 1 H), 7.43–7.61 (m, 4 H), 7.70–7.89 (m, 3 H), 8.19 (d, J_{PH} = 499 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.45, 110.66, 110.78, 120.92, 120.16, 128.30, 130.23, 130.47, 131.91, 131.97, 132.85, 132.99, 134.32, 134.36.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 14.51.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}OP$ (M + H^+): 233.0726; found: 233.0731.

Di-c-hexylphosphine Oxide (14h)
Yield: 67%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.13–1.51 (m, 10 H), 1.55–2.10 (m, 12 H), 6.33 (dm, J_{PH} = 438 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.84, 24.91, 25.69, 25.84, 25.99, 26.09, 26.29, 33.95, 35.23.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 53.87.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{23}ONaP$ (M + Na^+): 237.1379; found: 237.1389.

Reduction of Phosphinous Acid-Boranes into Secondary Phosphine-Boranes; General Procedure
In a flask equipped with a magnetic stirrer, an argon inlet and a reflux condenser (if needed), phosphinous acid-borane (0.3 mmol) in solvent (15 mL) was placed. Then, reducing agent (0.9–1.8 mol) was added (in Entries 2 and 3 after addition of base) and the reaction mixture was refluxed or was allowed to stand at r.t. for 5–48 h. Then, aq HCl (3 M) was added and the resulting biphasic mixture was extracted with CH_2Cl_2, the organic phase was dried ($MgSO_4$) and then evaporated to dryness. The residue was purified by flash chromatography (hexane–EtOAc, 6:1).

***tert*-Butylphenylphosphine-Borane (15a)**
Yields: 30, 38 and 11%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.05–1.65 (br m, 3 H), 1.21 (d, J_{PCCH} = 14.8 Hz, 9 H), 5.13 (dq, J_{PH} = 368 Hz, 1 H), 7.41–7.73 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.51, 26.57, 28.14, 124.24, 125.26, 128.44, 128.64, 131.47, 131.52, 133.80, 133.95.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 31.99 (m).

Anal. Calcd for $C_{10}H_{15}BP$: C, 66.71; H, 10.08. Found: C, 66.83; H, 10.21.

Di-c-hexylphosphine-borane (15h)
Yields: 38 and 13%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.45–1.50 (br m, 3 H), 1.20–1.59 (m, 10 H), 1.64–2.02 (m, 12 H), 4.15 (dq, J_{PH} = 348 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.65, 26.21, 26.43, 26.63, 27.60, 28.48, 29.15, 29.21, 29.27.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.94 (m).

Anal. Calcd for $C_{12}H_{23}BP$: C, 67.95; H, 12.35. Found: C, 68.21; H, 12.35.

***tert*-Butylphenylphosphinic Halides; General Procedure**
In a flask equipped with a magnetic stirrer, an argon inlet and a reflux condenser (if needed), phosphinous acid-borane (0.3 mmol) in solvent (15 mL) was placed. Then halogenating agent (0.9–1.5 mmol) was added to the reaction mixture (in Entries 2 and 4 after addition of base). Then, the reaction mixture was allowed to stand at r.t. or at reflux for 3–24 h. The reaction was quenched by addition of aq HCl (3 M), then the mixture was extracted with CH_2Cl_2, the organic phase was dried ($MgSO_4$) and evaporated to dryness. The residue was purified with flash chromatography (hexane–EtOAc, 2:1).

***tert*-Butylphenylphosphinic Acid Chloride (16)**
Yields: 85, 77 and 85%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.26 (d, J_{PCCH} = 19.10 Hz, 9 H), 7.45–7.70 (m, 3 H), 7.79–7.96 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.12, 38.15, 39.70, 128.12, 128.37, 132.35, 132.55, 132.79, 132.84.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 74.25.

***tert*-Butylphenylphosphinic Acid Bromide (17)**
Yields: 66 and 60%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.29 (d, J_{PCCH} = 19.70 Hz, 9 H), 7.46–7.68 (m, 3 H), 7.84–7.98 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.31, 40.07, 41.46, 128.10, 128.35, 132.41, 132.61, 132.85, 132.92.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 73.73.

***tert*-Butylphenylphosphinic Acid Iodide (18)**
Yield: 90%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.26 (d, J_{PCCH} = 20.34 Hz, 9 H), 7.47–7.66 (m, 3 H), 7.82–7.96 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.33, 41.52, 42.71, 127.91, 128.16, 132.07, 132.27, 132.76, 132.82.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 63.13.

Acknowledgment

Financial support of this study by the State Committee For Scientific Research, Poland, through the grant 3 T09A 119 26 is gratefully acknowledged.

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