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Hydrophosphination of α,β-Unsaturated Esters by Primary Phosphine-Boranes; a Useful Entry to Symmetrical and Unsymmetrical Phosphine-Boranes

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Abstract: The reactivity of primary phosphine-boranes $RPH_2 \cdot BH_3$ (R = Ph and Me) towards $CH_2=CHCO_2Me$ and $CH_2=CHP(O)(OMe)_2$ is discussed. Hydrophosphination is the major process. The presence of the free phosphine (0-20%) in the crude media indicates that a competitive hydroboration reaction also occurs. The *P-H* addition was found to be controllable to give, in reasonable yields, either the mono or the bis-adducts. All the adducts are stable and are fully characterized. The preparation of an unsymmetrical bis-adduct is also presented.

Addition of free phosphines to Michael acceptors is a well known process.[1] Most of the reactions are achieved under basic conditions, but reactions in the presence of radical initiators have also been described. These approaches are usually effective[2] but often suffer from lack of selectivity and from the sensitivity of products towards oxidation. As it was shown recently, phosphine-boranes can bring an alternative to these drawbacks.[3] Thus, hydrophosphination of aldehydes and α,β-unsaturated carbonyl compounds by secondary phenylphosphine-boranes are achieved in basic media under mild conditions.[4,5] BH_3 acts as a protecting group towards oxidation ; at the end of the reaction the free phosphine adducts can be recovered, if needed, after ligand exchange with a Lewis base. We have recently shown that the unfunctionalized primary derivatives can also be considered as useful building blocks. The more striking property is the possibility to perform the *P-H* addition onto aldehydes and ketones *without any catalyst.*[6] This methodology allowed us to acceed after decomplexation to the corresponding free mono- and bis-adducts which are not easily available by conventional procedures. In a continuing work, we report here the results bearing on the *P-H* addition of representative primary phosphine-boranes onto α,β-unsaturated carboxylic and phosphonic esters. Conditions for the obtention of an unsymmetrical bis-adduct are also precised.

Phosphine-boranes **1a** and **1b** are prepared in a two step sequence which involves the reduction of dichlorophenylphosphine or diethylmethylphosphonate with $LiAlH_4$ followed by the complexation of the free phosphine with $Me_2S \cdot BH_3$[6]. Methyl acrylate and vinyl phosphonate are selected as representative Michael acceptors. Addition reactions are performed in toluene under neutral gas in absence of catalyst[7] and are monitored by ^{31}P NMR. When addition is completed, adducts are purified by chromatography on silica and are characterized by ^{31}P, ^{1}H, ^{13}C and ^{11}B NMR spectroscopies and by HRMS. All the isolated products show a good stability. The main results are displayed in table 1.[8] The mono-hydrophosphination (ratio phosphine-borane/ester : 1/1.1)) occurs at room temperature. Under these conditions, the formation of a small amount of bis-adduct (0-12%) cannot always be avoided. Heating at 60°C allows completion of the reaction between

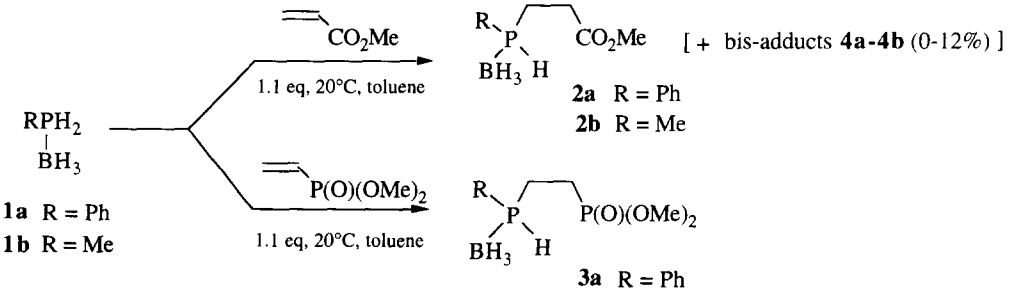
$MePH_2{\cdot}BH_3$ and methylacrylate within a reasonable period (entry 4). Bis-adducts **4a-b** (ratio phophine-borane/ester : 1/2.5 eq.) are obtained when the reactions are performed at 60°C. Adduct **5a** (ratio phophine-borane/ester : 1/2.1 eq.) is formed at room temperature in absence of solvent. Thus, by changing the reaction conditions, either the mono or the bis adducts can be selectively formed and isolated in a reasonable yield after purification by chromatography.

Competition between hydrophosphination and hydroboration already observed in the reaction between carbonyl derivatives and primary phosphine-boranes[6] also exists when Michael acceptors are involved. The lower ratio of the free phosphine observed in these last examples is in a good agreement with the weaker reactivity of alkenes towards hydroboration as compared with that of carbonyl compounds[9]. The reduction products were not isolated.

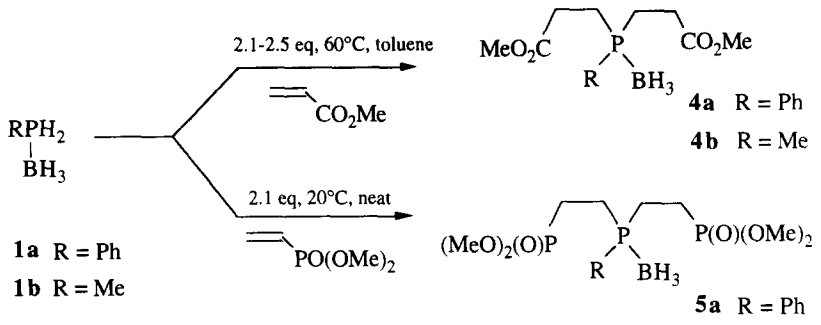
Table 1. Reactivity of phosphine-boranes **1a** and **1b** towards carboxylic and phosphonic esters[a].

Entries	Reagents	Substrats	Conditions[b]	Monoadducts [c] (isolated yield)	Bis-adducts[c] (isolated yield)	Free phosphines
1	**1a**	$CH_2{=}CHCO_2Me$	1.1 eq, 7 d, 20°C	**2a** : 80 (55)	**4a** : 5	$PhPH_2$: 15
2	**1a**	$CH_2{=}CHP(O)(OMe)_2$	1.1 eq, 19 d, 20°C	**3a** : 81 (75)	**5a** : 0	$PhPH_2$: 19
3	**1b**	$CH_2{=}CHCO_2Me$	1.1 eq, 30 d, 20°C	**2b** ; 88 (40)	**4b** : 12	$MePH_2$: 0
4	**1b**	$CH_2{=}CHCO_2Me$	1.1 eq, 6h, 60°C	**2b** : 75 (35)	**4b** : 5	$MePH_2$: 20
5	**1a**	$CH_2{=}CHCO_2Me$	2.5 eq, 21h, 60°C	**2a** : 0	**4a** : 94 (75)	$PhPH_2$: 6
6	**1a**	$CH_2{=}CHP(O)(OMe)_2$	2.1 eq, 4 d, 20°C	**3a** : 0	**5a** : 97 (72) [d]	$PhPH_2$ <3
7	**1b**	$CH_2{=}CHCO_2Me$	2.5 eq, 2h, 60°C	**2b** : 0	**4b** : 95 (60)	$MePH_2$ <5

a) All new products are characterized by ^{11}B, ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy and HRMS spectrometry[8] ; b) eq of ester ; c) ratio (% determined by ^{31}P NMR) of the different compounds for reactions occuring at the mentioned temperature in the reaction conditions ; d) reaction at room temperature in absence of solvent.

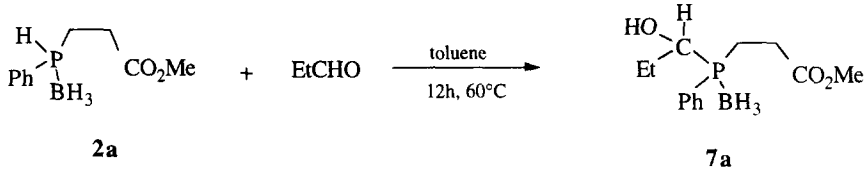


Scheme 1



Scheme 2

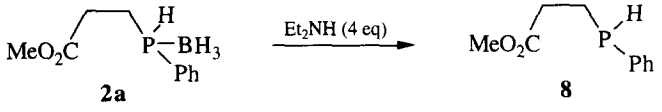
To our knowledge, unsymmetrical adducts of free primary phosphines have never been mentioned in the literature. We have obtained the mixed-adduct **7a** upon heating complex **2a** at 60°C in the presence of propionaldehyde (3 eq) . The two isomers (65% isolated yield) were separated by chromatography. Their stereochemistry was not defined.



2a **7a**

Scheme 3

Phosphine-borane adducts can be considered as protected free phosphines.[6] As an exemple, the secondary free phosphine **8** is recovered by treatment of complex **2a** with an excess of diethylamine[3,4] (Scheme 4). This product was identified by NMR spectroscopy.



2a **8**

Scheme 4

The selected NMR data of phosphine-boranes **1** and those of the corresponding mono- and bis-adducts are collected in table 2. As expected, the $^{1}J_{P-H}$ coupling constant (367-380 Hz) is strongly enhanced by the complexation. The ^{11}B chemical shift of the different adducts and the value of the corresponding $^{1}J_{B-P}$ coupling constants are weakly dependant on the nature of the phosphine substituents.

In conclusion, the uncatalyzed hydrophosphination of vinylic esters allows a selective access to mono-adducts and to symmetrical or unsymmetrical bis-adducts. All these compounds, which can be considered as protected free phosphines, are easily purified. This methodology should be useful for the preparation of free phosphines bearing various functional groups, especially for new 1-4 di- or triphosphines which are important ligands in organometallic chemistry.

Table 2 : Selected NMR data of phosphine-boranes **1-7**

Phosphine-boranes	$\delta\ ^{31}P\ (^{1}J_{P\text{-}H})$ [ppm (hertz)]	$\delta\ ^{11}B\ (^{1}J_{B\text{-}P})$ [ppm (hertz)]
1a	- 47 (370)	- 42.2 (38)
1b	- 66.7 (367)	- 41.3 (42)
2a	- 3.7 (380)	- 41.8 (58)
2b	- 18.8 (369)	- 40.8 (54)
3a	0.9 (373)	- 42 [a]
4a	17.1	- 42.1 (68)
4b	13.3	- 41 (66)
5a	21	- 42 (65)
7a	23.2 and 24.3	- 44.3 (50.2) and - 42.9 (51.4)

a) unresolved B-P coupling

References and notes

1. For a review, see Wolfsberger, W. *Chem. Zeit.* **1988,** *112,* 53-68
2. See in particular : King, R.B.; Masler, W.F. *J. Am. Chem. Soc.*, **1977**, *99*, 4001-4008 and references cited therein.
3. See for exemple Imamoto, T.; Oshiki, T., Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.*, **1990**. *112* 5245-5252
4. Imamoto, T.; Kusumoto, T.; Susuki, N. ; Sato, K. *J. Am. Chem. Soc.*, **1985**, *107*, 5301-5303 and references cited therein.
5. Gourdel, Y.; Pellon, P.; Toupet, L.; Le Corre, M. ; *Tetrahedron Lett.*, **1994,** *35*, 1197-1201
6. Bourumeau, K.; Gaumont, A.C.; Denis, J.M.; J. Organomet. Chem. **1997,** in press.
7. Typical experiment : *Mono-adducts :* The appropriate Michael acceptor (≈ 1.1 equivalents) was slowly added under nitrogen to the phosphine-borane **1a** or **1b** (7 mmol) in a benzene or a toluene solution (1.3M for **1a** and 2 M for **1b**). The mixture was stirred at room temperature or at 60°C. The reaction was monitored by ^{31}P NMR. When all the precursor was consumed, the solvent was removed under vacuum and the new product purified by silica-gel chromatography.
   Bis-adducts: A small excess of the appropriate Michael acceptor (2.1-2.5 equivalents) was slowly added under nitrogen to phosphine borane **1a** or **1b** (7 mmol) in a benzene or a toluene solution (1.3 M for **1a** and 2 M for **1b**). The mixture was stirred at 25 or 60°C. The reaction was monitored by ^{31}P NMR. When all the precursor was consumed, the solvent was removed under vacuum and the new product was purified by silica-gel chromatography.
   Unsymmetrical bis-adduct: An excess of propionaldehyde (3 equivalents) was slowly added under nitrogen to phosphine-borane **2a** (7 mmol) in a benzene or a toluene solution (0.4 M). The mixture was stirred at 60°C for 10 h. Then, the solvent was removed under vacuum and compound **7a** was purified by silica-gel chromatography. The two diastereomers were not separated.
8. The NMR data of the following derivatives are representive of the different mono and bis-adducts : **3a** ^{31}P NMR ($CDCl_3$) δ: -0.9 (ddm, $^{1}J_{PH}$ = 373 Hz, $^{3}J_{PP}$ = 55 Hz), 32.1 (d, $^{3}J_{PP}$ = 55 Hz) . ^{11}B NMR ($CDCl_3$) : δ -42.0 (qm, $^{1}J_{BH}$ = 98 Hz). ^{1}H NMR ($CDCl_3$): δ 0.75 (m), 1.7-2.0 (m), 2.0-2.3 (m), 3.6 (d, $^{3}J_{PH}$ = 2.7 Hz), 3.7 (d, $^{3}J_{PH}$ = 2.9 Hz). 5.5 (dm, $^{1}J_{PH}$ = 373 Hz), 7.3-7.5 (m), 7.5-7.7 (m). ^{13}C NMR ($CDCl_3$): δ 16.0 (tdd, $^{1}J_{CH}$ = 133 Hz, $^{1}J_{CP}$ = 35 Hz, $^{2}J_{CP}$ = 5.4 Hz), 18.2 (dt, $^{1}J_{CP}$ = 143 Hz, $^{1}J_{CH}$ = 135 Hz), 51.7 (qd, $^{1}J_{CH}$ = 148 Hz, $^{2}J_{CP}$ = 6.4Hz), 123.1 (dm, $^{1}J_{CP}$ = 56 Hz), 124.5 (d, $^{1}J_{CP}$ = 46.7 Hz), 126.1 (d, $^{1}J_{CP}$ = 47 Hz), 128.5 (dd, $^{1}J_{CH}$ = 161.3 Hz, $^{3}J_{CP}$ = 9.6 Hz, C_{meta}), 128.2 (ddm, $^{1}J_{CH}$ = 163 Hz, $^{3}J_{CP}$ = 10 Hz), 131.2 (ddm, $^{1}J_{CH}$ = 162 Hz, $^{4}J_{CP}$ = 2.5 Hz), 131.9 (ddm, $^{1}J_{CH}$ = 163 Hz, $^{2}J_{CP}$ = 9 Hz). **4b** ^{31}P NMR ($CDCl_3$) δ: 13.3 (q, $^{1}J_{PB}$ = 66 Hz). ^{11}B NMR ($CDCl_3$) : δ -41.0 (qd, $^{1}J_{BH}$ = 100 Hz). ^{1}H NMR ($CDCl_3$): δ 0.4 (m), 1.68-1.99 (m), 1.25 (d, $^{2}J_{PH}$ = 10.3 Hz), 1.8-2.0 (m),2.4-2.6 (m), 3.6 (s). ^{13}C NMR ($CDCl_3$): δ 8.1 (qd, $^{1}J_{CH}$ = 131 Hz, $^{1}J_{CP}$ = 36 Hz), 19.4 (td, $^{1}J_{CH}$ = 131 Hz, $^{1}J_{CP}$ = 33 Hz), 26.5 (tm, $^{1}J_{CH}$ = 130 Hz), 51.1 (q, $^{1}J_{CH}$ = 147 Hz), 171.6 (dm, $^{3}J_{CP}$ = 13 Hz). **7a** ^{31}P NMR ($CDCl_3$) δ: 23.2 (m). ^{11}B NMR ($CDCl_3$) : δ -44.3 (dm, $^{1}J_{BP}$ = 50.2 Hz). ^{1}H NMR ($CDCl_3$) : δ 0.7 (m), 1.0 (t, $^{3}J_{HH}$ = 7.4 Hz), 1.2 (m), 1.6 (td, $^{3}J_{HH}$ = 7.4 Hz, $^{3}J_{HH}$ = 6.9 Hz), 1.9 (broad s), 2.4 (m), 3.6 (s), 4.0 (td, $^{3}J_{HH}$ = 6.9 Hz, $^{2}J_{PH}$ = 3.1 Hz), 7.4-7.6 (m), 7.7-7.75 (m). 13C NMR ($CDCl_3$): δ 10.8 (d, $^{3}J_{CP}$ = 10.9 Hz), 17.2 (d, $^{1}J_{CP}$ = 36.9 Hz), 25.5 (d, $^{2}J_{CH}$ = 7.3 Hz), 27.6 (s), 52.1 (s), 72.3 (d, $^{1}J_{CP}$ = 41.4 Hz), 125.8 (d, $^{1}J_{CP}$ = 50 Hz), 129.1 (d, $^{3}J_{CP}$ = 9.7 Hz), 132.0 (d, $^{4}J_{CP}$ = 2.4 Hz), 132.6 (d, $^{2}J_{CP}$ = 8.4 Hz), 173 (d, $^{3}J_{CP}$ = 14.8Hz).
9. Pelter, A.; Smith, K.; Brown H.C.; "Borane reagents", Academic Press, Harcourt Brace Jovanovitch Publishers, London, 1988.

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