Pergamon

Tetrahedron Letters, Vol. 38, No. 19, pp. 3405-3408, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00647-3

A Practical Synthesis of Chiral and Achiral Phosphonium Salts from Phosphine Borane Complexes

Jacques Uziel, Nadège Riegel, Benoît Aka, Pierre Figuière and Sylvain Jugé*

Equipe "Réactivités spécifiques" - Université de Cergy-Pontoise - 5 mail Gay Lussac

95031 Cergy-Pontoise - France

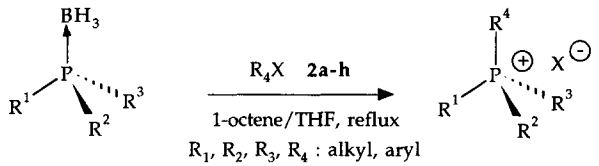
Fax : 33 1 34 25 70 67 ; E-mail : juge@u-cergy.fr

Abstract : Phosphine borane complexes are transformed under mild conditions, in presence of an olefin, into quaternary phosphonium salts by reaction with an alkyl (or aryl) halide. In the case of the reaction of (*R*)-PAMP.BH_3 **1e** with benzyl bromide, the enantiomerically pure phosphonium salt **3h** is obtained. © 1997 Published by Elsevier Science Ltd.

Phosphine borane complexes are versatile compounds generally crystalline and easily purified,[1] which have proved useful in the asymmetric synthesis of phosphine ligands [2]. Although their decomplexation with an amine (diethylamine,[3a] DABCO [3b] or HBF_4[3c]) proceeds quantitatively, the manipulation and storage of air-sensitive trivalent phosphorus compounds is not always convenient. This prompted us to investigate the direct use of phosphine boranes as synthetic equivalents.

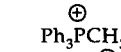
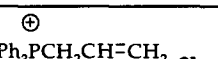
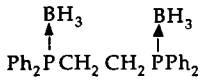
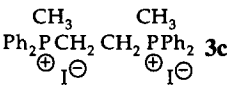
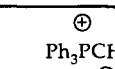
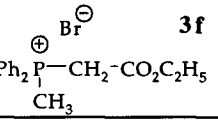
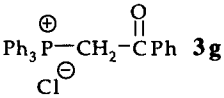
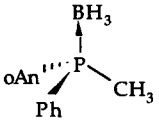
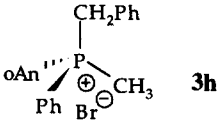
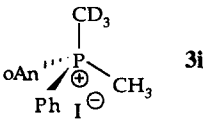
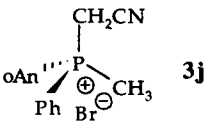
Since triphenylphosphine borane **1a** has been described as a mild reducing agent for olefins,[4] we have envisaged to adopt this route to release the phosphines under neutral and non-nucleophilic conditions. In addition, it was expected that the alkyl borane formed would be poorer complexing agent. Therefore, we have envisaged here the direct use of phosphine boranes for the preparation of phosphonium salts by a decomplexation-quaternization tandem reaction. Although the synthesis of quaternary phosphonium salts is well known [5], it is of particular interest to access optically active compounds which are usually prepared by resolution of the racemic form [6]. On another hand, it is also interesting to have access to cyclic phosphonium salts such as **3e**, which are versatile reagents useful for the synthesis of unconjugated dienes.[7]

We describe herein a convenient procedure which allows to prepare phosphonium salts **3a-j**, by heating the phosphine borane complexes **1a-e** with an alkyl (or aryl) halide **2a-h** in a mixture of 1-octene/THF (Scheme 1), [8] and which are recovered in high yield by a simple filtration.



Scheme 1

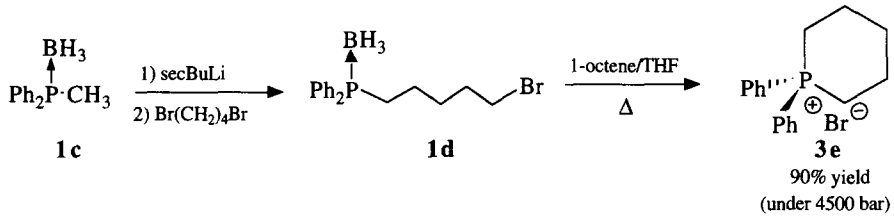
Table

Entry	Phosphine borane complexes	Halides	Phosphonium salts [a]	Yield [e] (%)
1	$Ph_3P.BH_3$ **1a**	CH_3I **2a**	 **3a**	85
2	$Ph_3P.BH_3$ **1a**	CH_2=CH-CH_2Br **2b**	 **3b**	90
3	 **1b**	CH_3I **2a**	 **3c**	87
4	$Ph_2PCH_3.BH_3$ **1c**	PhBr **2c** [b]	 **3d**	56
5	**1d**	------	**3e**	25 90 [d]
6	**1c**	$BrCH_2CO_2C_2H_5$ **2d**	 **3f**	60
7	**1a**	$ClCH_2COPh$ **2e**	 **3g**	50
8	 (*R*) - PAMP [c]. BH_3 **1e**	$PhCH_2Br$ **2f**	 **3h**	75
9	**1e**	CD_3I **2g**	 **3i**	92
10	**1e**	$BrCH_2CN$ **2h**	 **3j**	50

[a] All products present satisfactory analytical data . [b] In presence of 10% $NiBr_2$.[9]

[c] PAMP : o-Anisyl methyl phenyl phosphine. [d] Under high pressure (4500 bar). [e] Isolated yields.

Under the above conditions triphenylphosphine borane **1a** reacted with methyl iodide or allyl bromide to give the corresponding phosphonium salts **3a, 3b** in 85 and 90% yield respectively (entries 1, 2). When DPPE borane complex **1b** was used, the quaternization with methyl iodide led to the diphosphonium salt **3c** in 87% yield (entry 3). This tandem reaction can be also applied to the methyl diphenylphosphine borane **1c** with bromobenzene in the presence of a catalytic amount of $NiBr_2$,[9] to lead to the methyl triphenyl phosphonium bromide **3d** in 56% yield (entry 4). The synthesis of the cyclic phosphonium salt **3e** was performed with 5-bromopentyl diphenyl phosphine borane **1d**, prepared by alkylation of the methyl diphenyl phosphine borane **1c** with 1,4-dibromobutane (Scheme 2).



1c **1d** **3e**

90% yield
(under 4500 bar)

Scheme 2

When compound **1d** was heated in 1-octene/THF, the cyclic phosphonium salt **3e** was obtained in 25% yield by an intramolecular cyclization, whereas under high pressure (4500 bar), 90% yield was obtained (entry 5). The pressure influence in this case is not surprising, since it is well known that cyclization reactions, caracterized by a negative activation volume, are favored under such conditions.[10] More interestingly, the enantiomerically pure (*R*)-(+)- PAMP borane **1e** was quaternized with benzyl bromide to give stereospecifically the (*S*)-(-)-phosphonium salt **3h** with retention of the configuration (75% yield).[11a] Using CD_3I, (*R*)-(+)- PAMP borane **1e** gave the first example of a phosphonium salt **3i** with a P chiral center, due to the isotopic substituent (92% yield, entry 7). Unfortunately, ^2H NMR spectroscopy in a chiral liquid crystal [11b] of the compound **3i** revealed an enantiomeric excess of only 54% indicating a partial racemization, which has been already observed during another quaternization step with CH_3I.[12] We have also verified that these experimental conditions were compatible with functional groups such as esters (entry 6), ketones (entry 7) or nitriles (entry 10).

In conclusion, we have found a short and convenient "one pot" procedure to prepare mono and diphosphonium salts in 50-92% overall yield, starting from easily handled phosphine borane complexes. We have shown that a high pressure increases the chemical yield during the formation of the cyclic phosphonium salt **3e**. Finally, we have shown also that this tandem decomplexation-quaternization reaction proceeds with retention of the configuration at the P center. This method could be used as an alternative for the synthesis of optically active quaternary phosphonium salts in a preparative scale.

Acknowledgement: We thank M.Stephan for helpful discussion and the Ministry of Research for financial support to our team.

References and notes

1. (a) Schmidbaur H. *J. Organomet. Chem.* **1980**, 200, 287-306. (b) Imamoto T. *Yuki Gosei Kagaku* **1987**, *45*, 592-602.

2. (a) Jugé, S.; Stephan, M.; Laffitte, J.A.; Genêt, J.P. *Tetrahedron Lett.* **1990**, *31*, 6357-6360. (b) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244-5252. (c) Kaloun, E.B.; Merdes, R.; Genêt, J.P.; Uziel J.; Jugé, S. *J. Organomet. Chem.*,. in press.

3. (a) Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301-5303. (b) Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993**, *34*, 4523-4526. (c) McKinstry, L.; Livinghouse, T. *Tetrahedron* **1995**, *51*, 7655-7666.

4. Pelter, A.; Rosser, R.; Milles, S. *J.Chem.Soc. Chem. Comm.* **1981**, 1014-1015.

5. Smith, D. J. H. in *Comprehensive Organic Chemistry*, Barton, D.; Ollis, W. D., Eds. **1982**, *2*, 1160-1163, Pergamon Press, Oxford.

6. Kumli, K.F.; Mc Ewen W.E.; Vander Werf, C.A. *J. Am. Chem. Soc.* **1959**, *81*, 248-249.

7. (a) Muchowski J.M.; Venuti M.C. *J. Org. Chem.* **1981**, *46*, 459-461. (b) Yamamoto I.; Fujimoto T.; Ohta K.; Matsuzaki K. *J. Chem. Soc. Perkin. Trans. I* **1987**, 1537-1539.

8. **Typical procedure** : A solution of 1 mmol of phosphine borane complex, 4 mmol of olefin and 2 mmol of halide in 3 mL of dry THF is refluxed until consumption of the starting material (TLC in toluene). The precipitate salt is filtered and washed with 5 mL of ether. **3a** : mp= 186-187°C (litt.[13] mp= 183-185°C). **3b** : mp= 222-223°C (litt.[14] mp= 216-219°C) ; ^{1}H NMR($CDCl_3$) : 4.75 (2, dd,$^3J_{HH}$= 6.6, $^2J_{PH}$= 15.4), 5.4 (1, m), 5.5-5.9 (2, m), 7.6-7.9 (15, m). ^{31}P NMR ($CDCl_3$) : + 22. **3c** : mp= 297-298°C (litt.[15]mp= 290-298°C) ; Anal. Calcd. for $C_{28}H_{30}I_2P_2$ (682) : C, 49.27; H, 4.40; P, 9.09. Found : C, 48.95; H, 4.76; P, 9.12. **3d** : mp= 227-228°C (litt.[13] mp= 229-232 °C). **3e** : mp= 254°C (litt.[16] mp= 261-262°C) ; ^{1}H NMR ($CDCl_3$) : 2.0 (2, s), 2.1(4, s), 3.4 (4, dd), 7.6-7.9 (6, m), 8.0-8.2 (4, m) ; ^{13}C NMR ($CDCl_3$) : 19.6 (d, $^1J_{PC}$= 48), 21.8 (d, $^2J_{PC}$= 6), 23.7 (d, $^3J_{PC}$ = 6), 118.6 (d, $^1J_{PC}$ = 83), 130.4 (d, $^2J_{PC}$ = 13), 132.6, 134.7. ^{31}P NMR ($CDCl_3$) : +19.1. **3f** : ^{1}H NMR($CDCl_3$) : 1.0 (3, t, $^3J_{HH}$= 6), 3.0 (3, d, $^2J_{PH}$= 17), 4.0 (2, q, $^3J_{HH}$= 6), 5.0 (2, d, $^2J_{PH}$= 17), 7.5 (6, m), 7.9 (4, m). ^{31}P NMR ($CDCl_3$) : +22. **3g** : mp= 256-8°C. ^{1}H NMR ($CDCl_3$) : 6.5 (2, d, $^2J_{PH}$= 13), 7.4-8.6 (15, m). ^{31}P NMR ($CDCl_3$) : +22.5 (litt.[18] 22.3). **3h** : mp= 202-203°C ; $[\alpha]_D$= -36 (c 1.3, $CHCl_3$) (litt.[17] $[\alpha]_D$= -43) ; ^{1}H NMR($CDCl_3$) : 2.6 (3, d, $^2J_{PH}$ = 13.5), 3.85 (3, s), 4.5 (1, dd, $^2J_{HH}$ = 14.5, $^2J_{PH}$ = 16.6), 5.1 (1, t, $^2J_{HH}$ = $^2J_{PH}$ = 14.7), 7.2-7.8 (14, m). ^{31}P NMR ($CDCl_3$) : + 21.2. **3i**: mp= 202-203°C ; $[\alpha]_D$= -3 (c 1.2, $CHCl_3$) ; Anal. Calcd. for $C_{15}H_{15}IPOD_3$ (375) : C, 48; H, 4; P, 8.26; O, 4.26. Found : C, 47.8; H, 4.22; P, 8.18; O, 4.12. ^{1}H NMR($CDCl_3$) : 2.75 (3, d, $^2J_{PH}$ = 14), 3.9 (1, s), 7.2 (2, m), 7.75 (7, m); ^{31}P NMR ($CDCl_3$): + 18.05. **3j** : $[\alpha]_D$= +3 (c 0.87, $CHCl_3$); ^{1}H NMR($CDCl_3$) : 3.0 (3, d, $^2J_{PH}$= 13), 3.8 (3, s), 5.2 (1, t, $^2J_{PH}$= 18), 5.45 (1, t, $^2J_{PH}$= 18), 7.2 (2, m), 7.5-8.1 (7,m); ^{31}P NMR ($CDCl_3$): + 22.5.

9. Lückenbach, R. *Phosphorus and Sulfur* **1972**, *1*, 229-236.

10. Jurczak, J. in *Organic High Pressure Chemistry* , Vol.37, LeNoble, W.J. Ed., Elsevier, Amsterdam, **1988**.

11. The enantiomeric excess has been determined by ^{13}C or ^{2}H NMR in a chiral liquid crystal : (a) Lesot, P. ; Merlet, D.; Meddour, A.; Courtieu, J.; Lowenstein, A. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1371-1375. (b) Canet, I.; Courtieu, J.; Loewenstein, A.; Meddour, A.; Péchiné, J.M. *J. Am. Chem. Soc.* **1995**, *117*, 6520-6526.

12. Jugé, S.; Wakselman, M.; Stephan, M.; Genêt, J.P. *Tetrahedron Lett.* **1990**, *31*, 4443-4444.

13. Wittig G.; Geissler, G. *Ann.* **1953**, *580*, 44-68.

14. Swan, J.M.; Wright, S.H.B. *Aust. J. Chem.*, **1971**, *24*, 777-783.

15. Schindlauer, H.; Golser, L.; Hilzensauer, V. *Chem. Ber.* **1964**, *97*, 1150-1154.

16. Märkl, G. *Angew. Chem. Int. Ed.* **1963**, *2*, 620.

17. Coumbe, T.; Lawrence, N.J.; Muhammad, F. *Tetrahedron Lett.* **1994**, *35*, 625-628.

18. Brittain, J.M. ; Jones, R.A. *Tetrahedron* **1979**, 1139-1144.

(*Received in France* 4 *March* 1997; *accepted* 2 *April* 1997)