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$B(C_6F_5)_3$-catalyzed silylation versus reduction of phosphonic and phosphinic esters with hydrosilanes

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Abstract—$HSiR_3$/cat-$B(C_6F)_3$ induced dealkylation or reduction of esters of phosphorus at 20°C. A specific conversion to P-silylesters occurred by reaction with tertiary silanes. In contrast, free phosphines were observed in the reaction with mono- or disubstituted silanes. A mechanism was proposed to rationalize these results. © 2002 Elsevier Science Ltd. All rights reserved.

Tris(pentafluorophenyl)borane is a commercially available Lewis acid of comparable strength to BF_3, but without the problems resulting from the B-F reactivity. Application of this water-tolerant reagent in organic synthesis is rapidly growing.[1] The most comprehensive results concerned the use of the anhydrous $B(C_6F_5)_3$ as a catalyst associated with various $HSiR_3$ reagents. The $B(C_6F_5)_3/HSiR_3$ reagent combination was used in the selective hydrosilation of the carbon–oxygen double bond,[2] in the synthesis of silylethers from the corresponding alcohol,[3] during the cleavage of aryl and alkyl ethers[4] and in the course of direct reduction of aliphatic- aldehyde-, ester- and carboxylic functions into a methyl group.[5] Also stable organophosphoryl adducts of $B(C_6F_5)_3$ with ligands such as phosphine-oxides, phosphonate and phosphinate esters[6] and organophosphine adducts[7,8] have been recently synthesized and characterized.

To our knowledge, chemical transformations of organophosphorus derivatives involving $B(C_6F_5)_3$ have never been described previously. We decided to evaluate the potential of this Lewis acid as a catalyst in organophosphorus chemistry. This paper shows the preparation of some primary and secondary free phosphines from the corresponding phosphonic and phosphinic esters. Free phosphines are very sensitive towards oxidation. They are usually stored as air-stable phosphine/borane complexes which are useful reagents in organophosphorus chemistry.[9] Unfunctionalized phosphines have been obtained by reduction of the corresponding acids or esters by silanes,[10,11] or by $LiAlH_4$. When a functional group was present in position α to the phosphorus, alane and dichloroalane were found to be the most selective reducing agents.[12] The protocol involving hydrosilanes remained the most simple method to deoxygenate the P–O bond. However, the elevated temperature required (>120°C) limited their application to the preparation of stable and non-volatile phosphines. We assumed that the strong Si–H bond activation induced by $B(C_6F_5)_3$[2,4] should decrease the reduction temperature thus allowing access to volatile and unstabilized phosphines. In this paper, it is shown that the chemoselectivity of the reduction process involving the $HSiR_3$/cat.-$B(C_6F_5)_3$ system[†] was strongly dependent on the structure of hydrosilane: dealkylation of phosphonic and phosphinic esters was observed with trisubstituted silanes while reduction to free phosphines was observed with mono- or disubstituted silanes.[‡] A mechanism was proposed to explain these results.

Dealkylation process. A stable $CH_3PO(OMe)_2/B(C_6F_5)_3$ complex[8] was formed by the addition of 2 mol% of $B(C_6F_5)_3$ in solution to methylphosphonate **1a** in tolu-

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[†] The use of anhydrous grade $B(C_6F_5)_3$ was critical (sublimation at 105°C under vacuum (0.02 mbar). All the manipulations should be carried out under a neutral gas in dry solvents and reagents.

[‡] Esters **1**, **3** or **6** were added dropwise at ambient temperature to a mixture containing 1–5 mol% B(C6F5)3 and the corresponding silane (1–4 equiv.) in toluene solution. Reaction time (1–3 days) was monitored by ^{31}P NMR.

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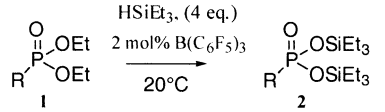
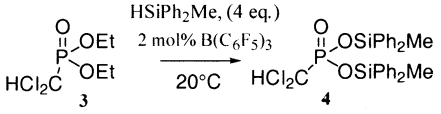
ene containing 4 equiv. of $HSiEt_3$ at 20°C. No further reaction was observed even after heating this solution at 100°C for several days. The situation dramatically changed when **1a** was slowly added to a toluene solution of $HSiEt_3$/cat.-$B(C_6F_5)_3$; the silylester **2a** was the only product observed (Eq. (1)).



(1)

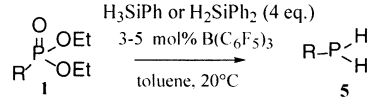
1a, R = Me ; **1b**, R = $ClCH_2$; **1c**, R = HCl_2C ; **1d**, R = H



(2)

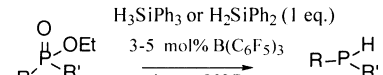
This reaction was extended to the preparation of silyl phosphonates **2b**–**2d**[§] at room temperature bearing various functional groups (Eq. (1)). A similar process was observed with diphenylmethylsilane. Thus phosphonate **3** was converted to the corresponding silylester **4** in a nearly quantitative yield (Eq. (2)). All these compounds were fully stable in the crude mixture at 100°C for a few days. No traces of the free phosphine could be observed. Silylesters are versatile intermediates in organophosphorus chemistry and their preparation and synthetic applications are well documented.[13] This methodology is an interesting alternative to previous methods since the yields are excellent and the protocol is very easy to perform.

Reduction.[¶] The reduction of phosphonates **1a**–**c** to free phosphines **5a**–**c** was performed with $PhSiH_3$ or Ph_2SiH_2 (4 equiv.) in the presence of 3–5 mol% $B(C_6F_5)_3$ (Eq. (3)). The reaction was generally slow at 20°C (2–4 days). No change could be observed by increasing the temperature. Yields were generally better with $PhSiH_3$. The formation of unidentified by-products could not, however, be avoided. Yields fell in the range of ca. 25% (for **5a**,**c**) to 95% (for **5b**,**d**). On the other hand, the reduction of phosphinates **6a**–**c** and H-phosphinate **6d** occurred with only 1 equiv. of phenylsilane (Eq. (4)). Phosphines **7a**,**b**[16]and **7d** were formed in an efficient way (85% yields) but the reaction involving **6a** was incomplete (40% conversion). This methodology is easy to perform as compared to that involving alane derivatives as the reducing agent.[12]



(3)

1a, R = Me ; **1b**, R = $ClCH_2$; **1c**, R = HCl_2C; **1d**, R = H

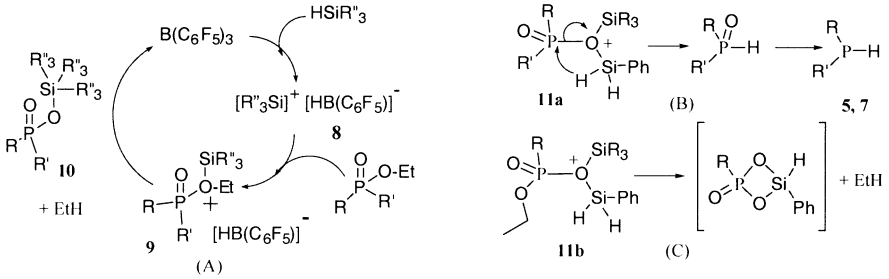


(4)

6a R = Me, R' = Et **6b**, R = $EtCl_2C$, R' = menthyl

6c, R = $PhCH_2$, R' = vinyl **6d**, R = Ph, R' = H

Mechanism. Crossover experiments provided solid supports for an unusual mechanism involving Si–H bond activation through the ate-complex $[R''_3Si]^+$ $[HB(C_6F_5)]^-$ **8** as the intermediate.[2,4] In our experiments, the silylester **10** was formed by coordination of the silicenium ion to the oxygen atom of POEt via the oxonium ion **9**, followed by hydrid transfer and evolution of ethane (Scheme 1, part A). Ester **10** should be considered as the common primary product. Silylesters **2** and **4** were only observed in the absence of an additional Si–H bond. In contrast, formation of free phosphines **5** and **7** was consistent with an internal hydrid transfer from the activated Si–H bond to the phosphorus (intermediate **11a**) followed by reduction of the phosphine oxide (Scheme 1, part B).[18] The by-products observed during the reduction of phosphonates **1** can result from a competitive reduction involving the adjacent P-OEt group (intermediate **11b**). A transient cyclic silylester formed by hydride transfer and evolution of ethane was proposed tentatively[18] (Scheme 1, part C). Selectivity can be expected in the absence of another POEt group. Free phosphines **7** were the main products in the reduction of phosphinates **6a**–**c** and *H*-phosphinate **6d**. The incomplete reduction of ester **6c** was attributed to a competitive formation of the $B(C_6F_5)_3$/**6c** complex occurring when the reduction was too sluggish. The above mechanism was in good agreement with the experimental data observed.



Scheme 1.

[§] All the new products were fully characterized by ^{31}P, ^{13}C, and ^{1}H NMR data, as well as HRMS.

[¶] Phosphines **5** and **7** or their borane complexes were characterized on the basis of their ^{1}H and ^{31}P NMR data as compared with those of authentic samples.[14–17] Yields of free phosphines were evaluated from NMR data. The reaction involving the inflammable PH_3 **1d** was performed in a sealed NMR tube.

In summary, these preliminary results demonstrate well the potential of the $HSiR_3$/cat-$B(C_6F)_3$ system in silylation reactions and in the reduction of esters of phosphorus to free phosphines. The efficiency and the simplicity of the protocol for the silylation of P-esters make this method a useful alternative to the previously described approaches. On the other hand, the practical and simple reduction of phosphonates and phosphinates to free phosphines is also of synthetic value. In some instances, no work-up is necessary. This process remains, however, mainly reserved to the structures bearing no other reducible group in proximity of the target P-OR function. The proposed mechanism is in good agreement with the experimental data.

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