

New examples of the hydride transfer reaction in three-component reaction systems

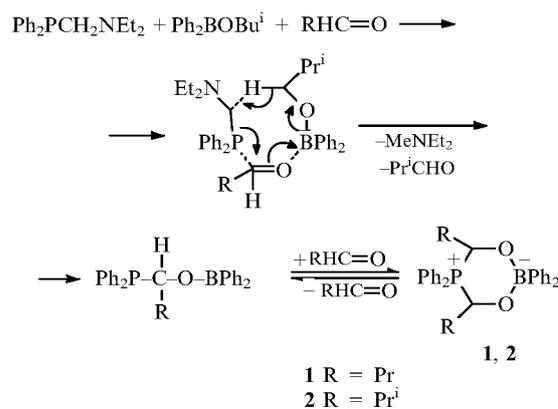
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Heterocyclic zwitterions, namely, 1,3,2,5-dioxaborataphosphoniarinanes and 5-aza-2-borata-1,3-dioxanes are obtained by hydride transfer in three-component reaction mixtures: aminomethylphosphine or diaminomethane–aldehyde–isobutyl diphenylborinate.

It has previously been shown that some compounds of the interesting class of 1,4-heterocyclic zwitterions, namely 1,3,2,5-dioxaborataphosphoniarinanes, may be obtained by hydride transfer in the three-component reaction system: aminomethylphosphine–formaldehyde–isobutyl diphenylborinate.¹ Furthermore, 1,3,2,5-dioxaborataphosphoniarinanes and 5-aza-2-borata-1,3-dioxanes can be synthesized by [2+4]-cycloaddition of aldehydes to 1,2-diheteroatomic compounds.² Here we show that the hydride transfer reaction, resulting in the formation of heterocyclic zwitterions, can be carried out in three-component reaction systems, including various compounds containing two heteroatoms with lone electron pairs in the gem-position, a compound with an aldehyde group and diphenylborinate, and is probably general.

The interaction of aminomethylphosphine and isobutyl diphenylborinate is possible not only with formaldehyde but also with some other aliphatic aldehydes, such as butyric and



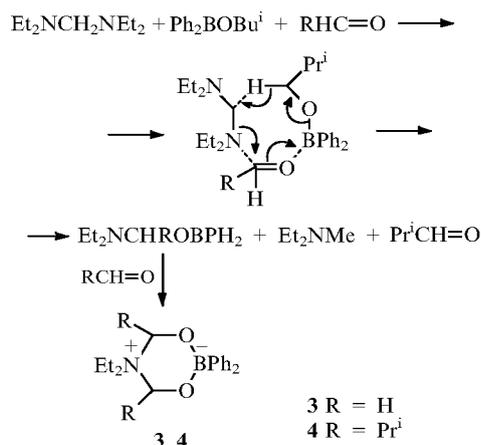
Scheme 1

isobutyric aldehydes. Unlike the previous case,¹ the reaction proceeds under mild conditions with a slight exothermic effect and in a solvent.

The spectral and analytical data of compounds **1** and **2** coincide with reported data for these compounds obtained from diphenylphosphine, aldehyde and the ester of diphenylboric acid.³ These compounds dissociate to a great extent in solution with the release of aldehyde.^{3†}

We continued this investigation and showed that this reaction can also proceed in another three-component reaction system: diaminomethane–aldehyde–isobutyl diphenylborinate, Scheme 2.

The reaction is accomplished under mild conditions and is



Scheme 2

accompanied by a small exothermic effect and probably begins with the activation of three-coordinated nitrogen and boron atoms by the aldehyde carbonyl group. The hydride ion originates from the α -carbon atom of the isobutyl fragment and attacks the carbon atom bonded to two nitrogen atoms. In the course of the reaction the tertiary amine, isobutyric

aldehyde and unstable α -boryloxyalkyl amine are formed; the latter is stabilized by the addition of a second molecule of aldehyde with the formation of a betaine 5-aza-2-borata-1,3-dioxane.

The synthesis of compound **3** was carried out as follows: 2 equiv. of paraformaldehyde were dissolved in bis(diethylamino)methane with careful heating and isobutyl diphenylborinate was added to the cooled mixture. The crystalline product formed was recrystallized from acetone. The use of an equimolar quantity of paraformaldehyde decreased the yield of betaine **3**. The synthesis of betaine **4** was carried out by subsequent mixing of the reagents and recrystallization of the resulting compound **4** from acetone.

The structure of compounds **3** and **4** was verified by elemental analysis, ¹H NMR and IR spectroscopy and also by the counter-synthesis of the previously described compound **3** from diethylamine, paraformaldehyde and isobutyl diphenylborinate.^{2‡} The formation of diethylmethylamine was proved by its isolation as triethylmethylammonium iodide.[§] The formation of isobutyric aldehyde in the reaction with formaldehyde was proved by GLC.^{||}

Thus the hydride transfer reaction takes place in both three-component reaction systems: aldehyde–isobutyl diphenylborinate–aminomethylphosphine and aldehyde–isobutylborinate–diaminomethane; this reaction is probably of a general nature.

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† All new compounds synthesized had satisfactory elemental analysis data.

[‡] *Spectroscopic data for 1*: (39%); mp 96 °C (acetone); ¹H NMR (²H₆DMSO): δ 0.53–2.03 (m, 14 H, Pr), 6.77–8.12 (m, 20 H, Ph) and 9.57 (s, 1 H, CH=O); ³¹P NMR (C₆H₆): δ -7.1; IR (KBr, Nujol): ν/cm^{-1} 705, 720, 785, 855, 895, 915, 935, 995, 1040, 1050, 1090, 1145, 1190 and 3070.

2: (77%); mp 95 °C (acetone); ¹H NMR (²H₆DMSO): δ 1.08 (d, 12 H, Me, ³J_{H-H} 7 Hz), 7.01–8.00 (m, 20 H, Ph) and 9.53 (s, 1 H, CH=O); ³¹P NMR (C₆H₆): δ -11.56; IR (KBr, Nujol): ν/cm^{-1} 700, 720, 750, 770, 880, 900, 957, 1005, 1037, 1095, 1110 (sh), 1130, 1155 (sh), 1230, 1590 and 3065.

[§] *Spectroscopic data for 4*: (30%); mp 84 °C (acetone); ¹H NMR (CDCl₃): δ 1.07–1.70 (m, 18 H, Me), 2.91–3.34 (m, 6 H, CH₂+CH), 5.78 (brs, N-CH-O), 9.51 (s, CH=O) (total intensity 2 H) and 7.29–7.89 (m, 10 H, Ph); IR (KBr, Nujol): ν/cm^{-1} 720, 750, 770, 853, 913, 940, 1012, 1045, 1090, 1120, 1145, 1185 and 3048. **4** dissociates in solutions similar to **1** and **2**.

^{||} The reaction mixture was heated to 80 °C without the isolation of **3** and volatile products were collected in the trap charged with ethyl iodide at 10 °C. The excess ethyl iodide was removed and triethylmethylammonium iodide was recrystallized from benzene–acetonitrile (2:1), mp 306 °C; its IR-spectrum coincides with the spectrum of the sample obtained by direct synthesis from triethylamine and methyl iodide.

[¶] The reaction mixture was heated to 100 °C without isolation of compound **3** and the volatile products were collected in the trap cooled by liquid nitrogen. The presence of isobutyric aldehyde in the fraction obtained was proved by GLC.

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