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Preliminary Communication

A new type of stabilized carbonucleophiles with a carboranyl group

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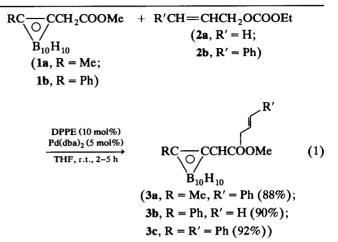
Abstract

Palladium-catalyzed allylation of carboranylacetic esters gives C-allyl derivatives in high yield. Thus, a new type of stabilized carbonucle-ophiles with the electron-withdrawing *o*-carboranyl group has been made.

The strong electron-withdrawing effect of 1-ocarboranyl group $(1-o-C_2B_{10}H_{11})$ results in an essentially increasing acidity of functionally connected acids, hydroxy-, amino-, and mercapto substituents [1-3]. The thermodynamic acidity of CH₂-protons in 1-methyl-2benzyl-o-carborane has been shown to be 19.5, whereas the acidity of the C-H bond of carborane is with 21.0 of the same order scale [4].

We thought that the exchange of the phenyl group in 1-methyl-2-benzyl-o-carborane with a more electronwithdrawing group like, for example, carbomethoxy would promote an increasing acidity of CH_2 -protons. In order to test the ability of carboranylacetic esters to form stabilized carbanions of type $MeO_2C-C^-H-CB_{10}H_{10}CH$, the palladium-catalyzed allylation of carbonucleophiles was carried out under neutral conditions using allyl carbonates [5].

Carboranylacetic methylesters 1 have been found to react readily with allyl carbonates 2 in THF in the presence of Pd⁰ catalyst at room temperature to form allyl derivatives 3 on the CH₂-group in high yields (eqn. (1)).



The reactions occur rather fast and 1 disappears after 2-5 h. In the cases of the reaction of 1b with 2a the formation of a little amount of diallyl derivative (MS-data) was observed. However, the reactions of 1a or 1b with 2b for 120 h at room temperature or 10-20h at 65°C did not produce any diallyl derivatives.

This Pd-catalyzed reaction under such conditions, is very sensitive to the CH-acidity of carbonucleophiles, and we could not obtain the C-allylated products when 1-phenyl-2-benzyl-, 1-methyl-2-benzyl-, and 1,2-dibenzyl-o-carboranes were reacted with **2a**, **2b** under the same conditions. This is due to a lower acidity of CH₂-group in the above mentioned compounds, compared with that in carboranylacetic esters. It should be noted that some carborane derivatives with a free CH-bond react with allyl carbonate to form C-allylcarboranes when catalyzed by palladium [6].

We have also found that carboranylacetic esters are able to undergo an alkylation reaction, under phasetransfer conditions to produce C-alkyl derivatives. For example, the reaction of 1b with allyl bromide in a mixture of benzene-NaOH (2:1) in the presence of benzyltriethylammonium chloride gives 3b (eqn. (2)).

$$\mathbf{1b} + \mathbf{CH}_2 = \mathbf{CHCH}_2 \mathbf{Br} \xrightarrow[10-15^{\circ}\mathbf{C}]{}^{\mathbf{C}_6\mathbf{H}_6, 50\% \text{ NaOH}}_{\mathbf{10}-15^{\circ}\mathbf{C}} \mathbf{3b} (85\%)$$
(2)

The latter reaction suggests the high acidity of CH_2 -protons in carboranyl acetic esters. Thus, our preliminary experiments have showed that carborany-lacetic esters can act as soft nucleophiles with two

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electron-withdrawing groups like malonates and β -ke-toesters.

We think that the new synthetic method can be used in the preparation of ${}^{10}B$ carriers for neutron capture therapy. Work on this is in progress.

1. Experimental details

The solution of 10 mg Pd(dba)₂, 6.6 mg dppe, 1 mmol **1a** or **1b**, and 2 mmol of **2a** or **2b** in 3 ml of dry THF was stirred for 2–5 h (TLC controlled). Ether (10 ml) and water (10 ml) were added, the organic layer separated and the aqueous layer extracted with three portions of ether (5 ml), dried (MgSO₄), and concentrated. The resulting product was crystallized.

All new compounds were fully characterized by spectroscopic methods (¹H NMR, IR, MS) and their molecular formulas established by microanalyses. M.p., ¹H NMR, IR-data, and mass spectra of the products are as follows:

3a. M.p.: 78–79°C. MS: m/e 346. IR (KBr): 1734 cm⁻¹ (C=O), 2580–2590 cm⁻¹ (B–H). ¹H-NMR (200 MHz) (CDCl₃): δ 1.50 (s, 1H), 2.08 (s, 3H), 2.60–3.12 (m, 2H), 3.65 (s, 3H), 5.67–5.97 (m, 1H), 6.39–6.47 (d, 1H), 7.19–7.30 (m, 5H).

3b. M.p.: 51°C. MS: *m/e* 332. IR (KBr): 1750 cm⁻¹ (C=O), 2580-2590 cm⁻¹ (B-H). ¹H-NMR (200 MHz) (CDCl₃): δ 1.56 (s, 1H), 2.10–2.64 (m, 2H), 3.63 (s, 3H), 4.78–4.91 (m, 2H), 5.21–5.34 (m, 1H), 7.37–7.68 (m, 5H).

3c. M.p.: 130–131°C. MS: m/e 409. IR (KBr): 1744 cm⁻¹ (C=O), 2550–2560 cm⁻¹ (B–H). ¹H-NMR (200 MHz) (CDCl₃): δ 1.55 (s, 1H), 2.26–2.77 (m, 2H), 3.59 (s, 3H), 5.54–5.69 (m, 1H), 6.10–6.18 (d, 1H), 7.12–7.24 (m, 5H), 7.41–7.68 (m, 5H).

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