

Some Specific Features of Conjugate Addition Reactions with Lithium and Magnesium *o*-Carborane Derivatives

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Abstract—Reactions of lithium and magnesium *o*-carborane derivatives with ethyl α -nitrocinnamate, ethyl β -(3-indolyl)- α -nitroacrylate, and diethyl *m*-nitrobenzylidenemalonate were studied. Some specific features of these reactions were established, and preparative methods for the synthesis of previously unknown *o*-carborane derivatives were developed.

We previously showed [1, 2] that lithium and magnesium derivatives of *o*-carboranes react with β -nitrostyrene and ethyl α -nitrocinnamate according to the 1,4-addition scheme to give, respectively, carboranyl-substituted nitroalkanes and α -nitrodihydrocinnamic acid esters. The present work continues studies on these reactions. We have found that lithium and magnesium *o*-carborane derivatives **I** and **II** react with ethyl α -nitrocinnamate (**III**) in a selective fashion, regardless of the solvent nature and order of mixing of the reactants, yielding ambident resonance-stabilized adducts **A**; treatment of the latter with dilute hydrochloric acid quantitatively gives carboranyl-containing nitro ester **IV**, while *aci*-nitro ester **V** was obtained by the action of water (Scheme 1). The yield of products **IV** and **V** attained 94% when M = Li, and it did not exceed 70% for M = MgBr.

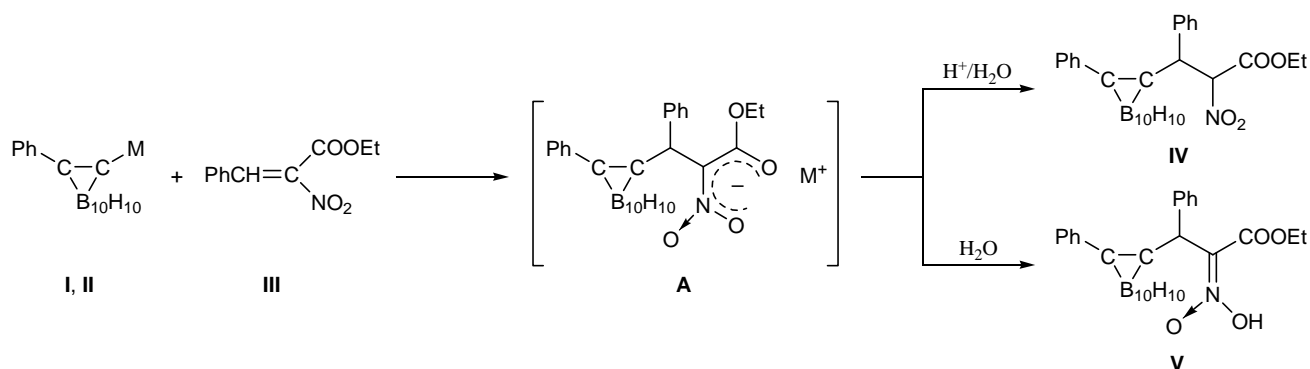
Analogous reactions occurred between lithium and magnesium *o*-carborane derivatives **I** and **II** with ethyl

β -(3-indolyl)- α -nitroacrylate (**VI**) at a reactant molar ratio of 2 (and more):1; the products were nitro ester **VII** and *aci*-nitro ester **VIII** (Scheme 2). The structure of compounds **IV**, **V**, **VII**, and **VIII** was confirmed by their IR and ^1H NMR spectra and chemical transformations shown in Scheme 3.

Undoubtedly, ready interconversions in the series of carboranyl-containing nitro and *aci*-nitro esters are favored by formation of ambident resonance-stabilized adducts **V**. Due to nonuniform electron density distribution over the oxygen atoms, adducts **V** exhibit a high selectivity for protolytic reagents, which agrees well with the concept of hard and soft acids and bases.

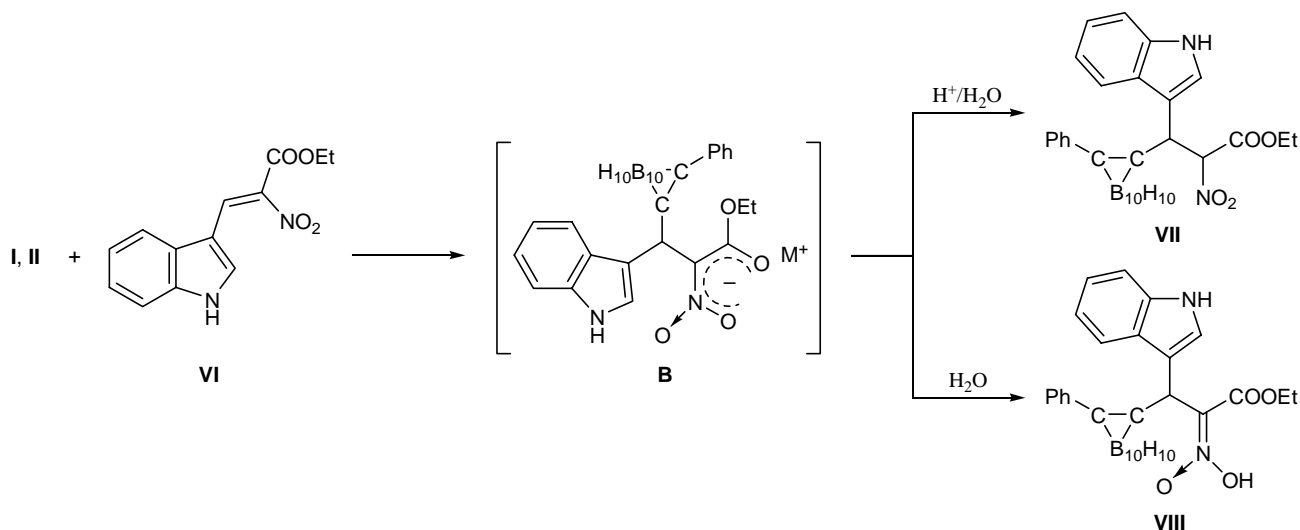
Lithium *o*-carborane derivatives **I** and **IX** reacted with diethyl *m*-nitrobenzylidenemalonate (**X**) following the 1,4-addition pattern and yielding α -carboranyl-*m*-nitrobenzyl-substituted diethyl malonates **X** and **XI** (Scheme 4). Primary adducts **D** turned out to be inactive toward organometallic compounds, and they

Scheme 1.



I, M = Li; **II**, M = MgBr.

Scheme 2.



M = Li, MgBr.

did not change even on prolonged heating of the reaction mixtures containing a large excess of lithium derivative **I** or **IX**. The structure of esters **XI** and **XII** was confirmed by their elemental composition and IR spectra (see Experimental).

EXPERIMENTAL

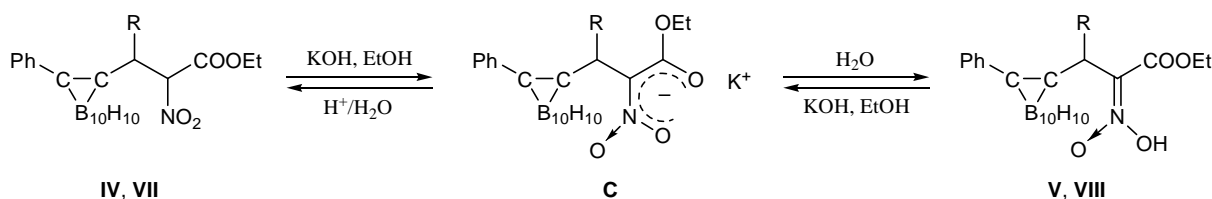
The IR spectra were recorded in KBr on a UR-20 instrument. The ¹H NMR spectra were obtained on a Tesla BS-587 spectrometer (80 MHz) using acetone-*d*₆ as solvent and tetramethylsilane as internal reference. All reactions with lithium and magnesium *o*-carborane derivatives were carried out under nitrogen.

Ethyl α-nitro-β-phenyl-β-(phenyl-*o*-carboranyl) propionate (IV). *a.* A solution of 10 mmol of nitro ester **III** in 10 ml of diethyl ether was added at 10–20°C to 20 ml of a benzene–diethyl ether solution of 10 mmol of 1-lithio-2-phenyl-*o*-carborane (**I**) which was prepared from 10 mmol of phenyl-*o*-carborane and a benzene solution of 12 mmol of BuLi. The

mixture was stirred for 6 h at 20°C, treated with dilute hydrochloric acid, and extracted with diethyl ether. The extract was dried over Na₂SO₄ and evaporated, and the residue was recrystallized from hexane. Yield 89%, mp 125–126°C (from benzene–heptane, 1:5). IR spectrum, ν , cm⁻¹: 2600 (B–H); 1760 (C=O); 1560, 1370 (NO₂). ¹H NMR spectrum, δ , ppm: 0.59 t (3H, CH₃CH₂, *J* = 3.2 Hz), 3.70 q (2H, CH₃CH₂, *J* = 8 Hz), 5.01 d (1H, CHPh, *J* = 10 Hz), 6.83 d (1H, CHNO₂, *J* = 10 Hz), 7.19 m and 7.5–7.7 m (H_{arom}). Found, %: C 51.46; H 6.27; B 24.67; N 2.96. C₁₉H₂₇B₁₀NO₄. Calculated, %: C 51.70; H 6.12; B 24.49; N 3.18.

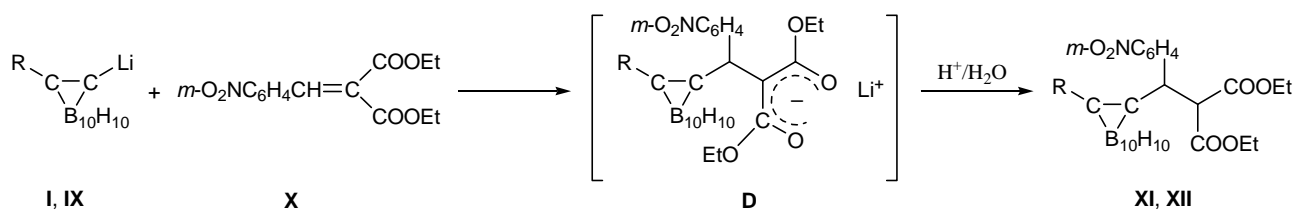
b. A solution of 10 mmol of compound **III** in 10 ml of THF was added at 10–20°C to 20 ml of a THF solution containing 10 mmol of 1-bromomagnesio-2-phenyl-*o*-carborane (**II**) which was prepared from 10 mmol of phenyl-*o*-carborane and 13 mmol of EtMgBr. The mixture was stirred for 10 h at 20°C, treated with dilute hydrochloric acid, and extracted with diethyl ether. The extract was dried over Na₂SO₄ and evaporated to isolate ester **IV** in 60% yield; mp 125–126°C.

Scheme 3.



IV, V, R = Ph; VII, VIII, R = 3-indolyl.

Scheme 4.



I, XI, R = Ph; **IX, XII**, R = *i*-Pr.

Ethyl α -*aci*-nitro- β -phenyl- β -(phenyl-*o*-carboranyl)propionate (V). *a.* A solution of 10 mmol of ester **III** in 10 ml of diethyl ether was added at 10–20°C to 20 ml of a benzene–diethyl ether solution containing 10 mmol of compound **I**. The mixture was stirred for 6 h at 20°C, treated with distilled water, and extracted with diethyl ether. The extract was dried over Na_2SO_4 and evaporated to obtain 76% of ester **V**, mp 133–134°C (from benzene–heptane, 1:5). IR spectrum, ν , cm^{-1} : 3250–3240 (O–H), 2600 (B–H), 1750 (C=O), 1640 (C=N). Found, %: C 51.78; H 6.61; B 24.66; N 2.85. $C_{19}H_{27}B_{10}NO_4$. Calculated, %: C 51.70; H 6.12; B 24.49; N 3.18.

b. A solution of 10 mmol of ester **III** in 10 ml of THF was added at 10–20°C to 20 ml of a THF solution containing 10 mmol of compound **II**. The mixture was stirred for 10 h at 20°C and was treated as described above. Yield of ester **V** 57%, mp 133–134°C.

Ethyl β -(3-indolyl)- α -nitro- β -(phenyl-*o*-carboranyl)propionate (VII). *a.* A solution of 5 mmol of ester **VI** in 10 ml of diethyl ether was added at 0°C to 20 ml of a benzene solution containing 10 mmol of lithium derivative **I**. The mixture was stirred for 4 h at 20°C, treated with dilute hydrochloric acid, and extracted with benzene. The extract was dried over Na_2SO_4 and evaporated, and the residue was recrystallized from hexane. Yield 93%, mp 159–161°C (from benzene–hexane, 1:5). IR spectrum, ν , cm^{-1} : 3000 (C–H); 2600 (B–H); 1735 (C=O); 1560, 1350 (NO_2); 3400, 1620, 1450 (indolyl). Found, %: C 52.12; H 5.48; B 22.73; N 5.38. $C_{21}H_{28}B_{10}N_2O_4$. Calculated, %: C 52.50; H 5.83; B 22.50; N 5.83.

b. A solution of 5 mmol of ester **VI** in 5 ml of THF was added at 0°C to 20 ml of a solution of 10 mmol of compound **II** in THF. The mixture was stirred for 6 h at 20°C and was then treated as described above. Yield of **VII** 67%, mp 159–161°C.

Ethyl β -(3-indolyl)- α -*aci*-nitro- β -(phenyl-*o*-carboranyl)propionate (VIII). *a.* A solution of 5 mmol of ester **VI** in 5 ml of diethyl ether was added at 0°C

to 20 ml of a benzene solution containing 10 mmol of compound **I**. The mixture was stirred for 4 h at 20°C, treated with distilled water, and extracted with diethyl ether. The extract was dried over Na_2SO_4 and evaporated, and the residue was recrystallized from hexane. Yield 94%, mp 223°C (decomp., from benzene–hexane, 1:5). IR spectrum, ν , cm^{-1} : 3300–3100 (O–H); 3000 (C–H); 2600 (B–H); 1740 (C=O); 1660 (C=N); 3400, 1620, 1450 (indolyl). Found, %: C 52.23; H 5.56; B 22.88; N 5.41. $C_{21}H_{28}B_{10}N_2O_4$. Calculated, %: C 52.50; H 5.83; B 22.50; N 5.83.

b. A solution of 5 mmol of ester **VI** in 5 ml of THF was added at 0°C to 20 ml of a THF solution containing 10 mmol of compound **II**. The mixture was stirred for 6 h at 20°C and was then treated as described above in *a.* Yield of ester **VIII** 59%, mp 223°C (decomp.).

Interconversions of nitro and *aci*-nitro esters IV, VII and V, VIII in the presence of potassium hydroxide. *a.* A solution of 3 mmol of nitro ester **IV** in ethanol was added at 20°C to a solution of 6 mmol of potassium hydroxide in 10 ml of ethanol. The mixture was stirred for 1 h at 20°C, treated with distilled water, and extracted with diethyl ether. The extract was dried over Na_2SO_4 and evaporated, and the residue was recrystallized from hexane to obtain 98% of *aci*-nitro ester **V**, mp 133–134°C. Following an analogous procedure, from nitro ester **VII** we obtained 97% of *aci*-nitro ester **VIII**, mp 223°C (decomp.).

b. An ethanolic solution of 3 mmol of *aci*-nitro ester **V** was added at 20°C to a solution of 6 mmol of KOH in 10 ml of ethanol. The mixture was stirred for 1 h at 20°C, treated with dilute hydrochloric acid, and extracted with diethyl ether. The extract was dried over Na_2SO_4 and evaporated, and the residue was recrystallized from hexane to isolate 99% of nitro ester **IV**, mp 125–126°C. Likewise, from *aci*-nitro ester **VIII** we obtained 98% of nitro ester **VII**, mp 159–161°C.

Diethyl α -(phenyl-*o*-carboranyl)-*m*-nitrobenzylmalonate (XI). A solution of 10 mmol of diethyl

m-nitrobenzylidenemalonate (**X**) in 10 ml of benzene was added at 20°C to a solution of 10 mmol of compound **I** in 20 ml of benzene. The mixture was stirred for 5 h at 20°C, treated with dilute hydrochloric acid, and extracted with diethyl ether. The extract was dried over Na₂SO₄ and evaporated, and the residue was recrystallized from hexane. Yield 70%, mp 132–133°C (from benzene–hexane, 1:5). IR spectrum, ν , cm⁻¹: 3000 (C–H); 2600 (B–H); 1730 (C=O); 1520, 1370 (NO₂). Found, %: C 51.12; H 5.84; B 21.42; N 2.48. C₂₂H₃₁B₁₀NO₆. Calculated, %: C 51.46; H 6.04; B 21.05; N 2.73.

Diethyl α -(isopropyl-*o*-carboranyl)-*m*-nitrobenzylmalonate (XII). Following the above procedure,

from 20 ml of a solution of 10 mmol of 1-isopropyl-2-lithio-*o*-carborane **IX** in benzene–diethyl ether and 10 mmol of ester **X** we obtained 51% of ester **XII**, mp 127–128°C (from benzene–hexane, 1:5). IR spectrum, ν , cm⁻¹: 2990 (C–H); 2595 (B–H); 1740 (C=O); 1520, 1350 (NO₂). Found, %: C 47.37; H 6.53; B 22.78; N 2.66. C₁₉H₃₃B₁₀NO₆. Calculated, %: C 47.60; H 6.89; B 22.55; N 2.92.

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