

## Reactions of Lithium and Magnesium Derivatives of Substituted *o*- and *m*-Carboranes with 3-Ethoxycoumarin and Coumarin

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**Abstract**—Reactions of lithium and magnesium derivatives of substituted *o*- and *m*-carboranes with 3-ethoxycarbonylcoumarin and coumarin were investigated. The main directions and the laws of the processes were revealed.

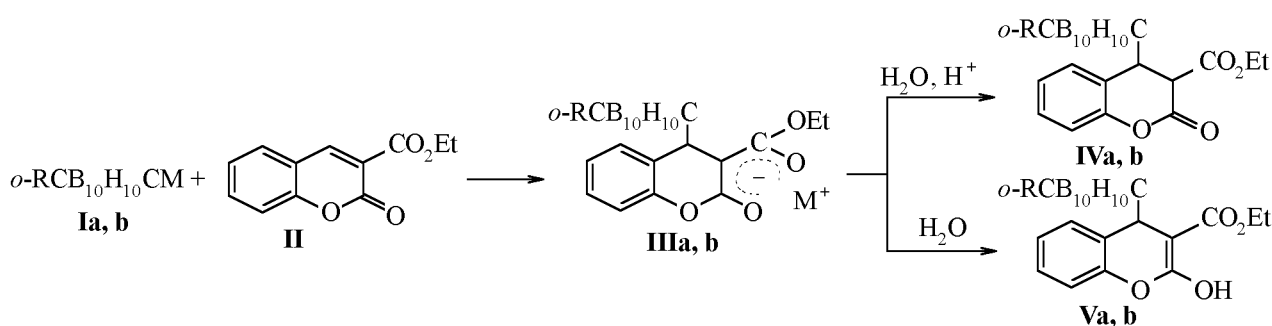
We showed formerly [1–3] that reactions of lithium and magnesium derivatives of substituted *o*-carboranes with 3-ethoxycarbonylcoumarin proceeded regioselectively providing products of conjugate addition, 3-ethoxycarbonyl-4-(*R*-*o*-carboranyl)-3,4-dihydrocoumarins.

In extension of our investigation of conjugate addition in the series of C-metal carborane derivatives we studied in detail reactions between lithium and magnesium derivatives of *o*- and *m*-carboranes and 3-ethoxycarbonylcoumarin and coumarin. Such reactions with the other organometallic compounds gave rise to mixtures of products.

The interest attracted by these reactions originates from insufficiently systematized and conflicting

results of previous studies, from the opportunity to get new understanding of the conjugate addition in the series of  $\alpha,\beta$ -unsaturated carbonyl compounds, and from a number of other no less important factors.

The study revealed that lithium and magnesium derivatives of substituted *o*-carboranes (**Ia, b**) reacted with 3-ethoxycarbonylcoumarin (**II**) along one pattern irrespective of solvent character, reagents ratio and their mixing order to furnish ambident resonance-stabilized adducts **IIIa, b** that at treatment with water solutions of mineral acids or NH<sub>4</sub>Cl without isolation from the reaction mixture formed quantitatively 3-ethoxycarbonyl-4-(*R*-*o*-carboranyl)-3,4-dihydrocoumarins (**IVa, b**), and with water provided 2-hydroxy-3-ethoxycarbonyl-4-(*R*-*o*-carboranyl)benzo-4*H*-pyrans (**Va, b**):

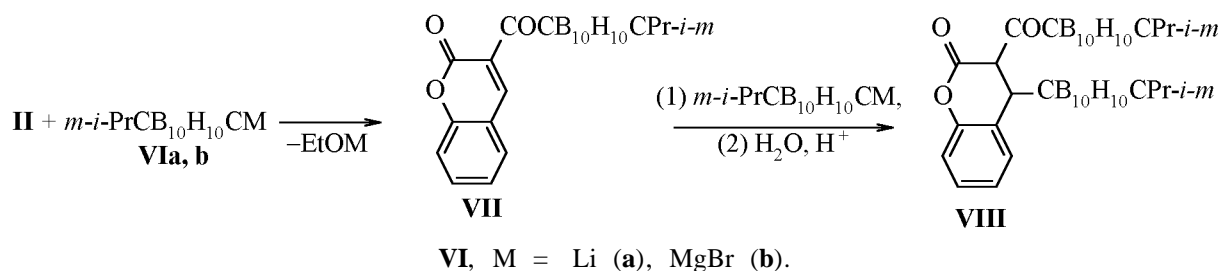


**III–V**, R = Ph (**a**), M = Li (**a**); R = *i*-Pr, M = MgBr (**b**).

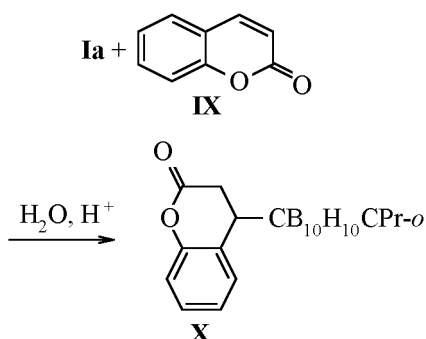
Reactions of lithium and magnesium derivatives of isopropyl-*m*-carborane (**VIa, b**) with 3-ethoxycarbonylcoumarin under the above conditions fol-

low first 1,2- and then 1,4-addition pattern and result in dicarborane coumarin derivative **VIII** (Scheme 1).

Scheme 1.



Scheme 2.



At equimolar ratio of compounds **II** and **VIa, b** the yield of compound **VIII** did not exceed 25%, and at increased molar fraction of metal derivatives **VIa, b** to double excess the yield attained 47%. The low yield of the target products and the presence of isopropyl-*m*-carborane in the reaction mixture is apparently due to enolization of the arising di-

carborane derivative **VIII** and hydrogenation of the initial organometallic compounds.

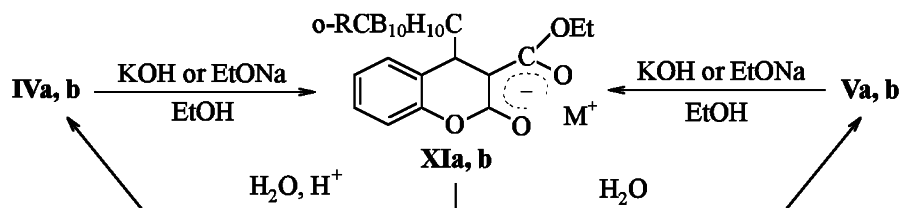
Lithium and magnesium derivatives of *o*-carboranes (**Ia, b**) reacted with coumarin (**IX**) regioselectively to afford products of conjugate addition **X** (Scheme 2).

Compounds **IVa, b** and **Va, b** treated with KOH and  $\text{C}_2\text{H}_5\text{Na}$  in ethanol readily transform into enolate anions **XIa, b** identical by the structure to enolate anions **IIIa, b**. These enolate anions with dilute HCl or acetic acid quantitatively yield esters **IVa, b**, and with water benzo-4*H*-pyrans **Va, b** (Scheme 3).

Coumarin derivative **IVa** at heating with  $\text{H}_4\text{P}_{207}$  or with mixtures HCl-AcOH, HBr-AcOH gave rise to 4-(phenyl-*o*-carboranyl)-3,4-dihydrocoumarin (**X**) identical to that described above, and at boiling in the glacial acetic acid it turned to acid **XII** that decomposed at melting (Scheme 3).

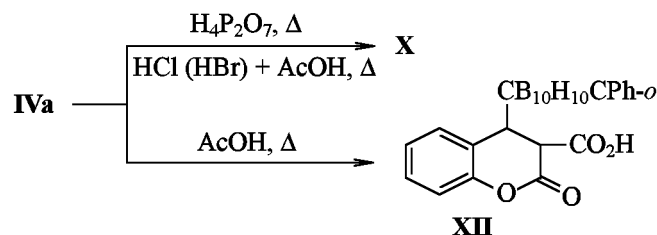
The composition and structure of compounds synthesized were confirmed with elemental analysis, IR

Scheme 3.



**XI, R = Ph, *i*-Pr; M = K (a), Na (b).**

Scheme 4.



and  $^1\text{H}$  NMR spectroscopy, and by chemical transformations. For molecule of ester **IVa** the spatial structure was also established by X-ray diffraction analysis (Scheme 4).

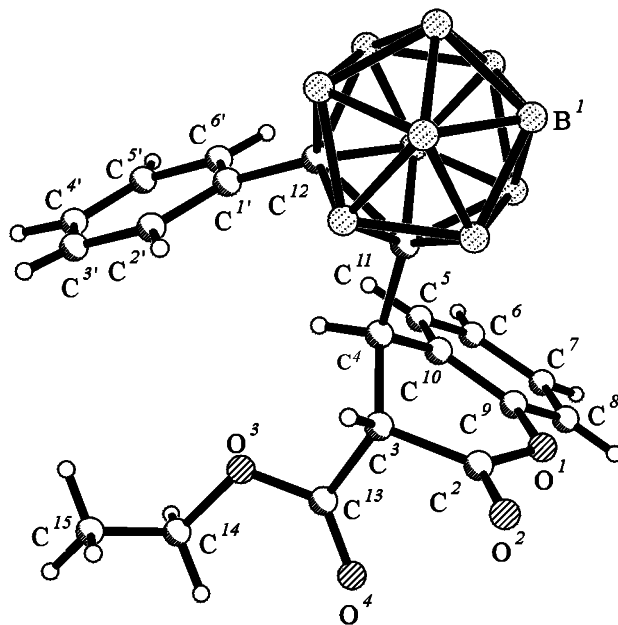
The structure of the molecule of compound **IVa** is seen on the figure. The atoms of the six-membered ring  $\text{C}^5\text{C}^6\text{C}^7\text{C}^8\text{C}^9\text{C}^{10}$  are coplanar within  $\pm 0.008$  Å. The heterocycle  $\text{O}^1\text{C}^2\text{C}^3\text{C}^4\text{C}^{10}\text{C}^9$  takes the conformation of considerably twisted *boat* ( $\Delta\text{C}^{3,4}$   $3.8^\circ$ ). Atoms  $\text{O}^1$ ,  $\text{C}^9$ ,  $\text{C}^3$ ,  $\text{C}^2$  are coplanar within  $\pm 0.02$  Å. The deviation of atoms  $\text{C}^4$ ,  $\text{C}^{10}$  from the plane where are located the other atoms is 0.84 and 0.38 Å respectively.

The ethoxycarbonyl group takes the axial  $\beta$ -orientation, the dihedral angle between the mean plane of the coumarin fragment and the mean plane of the ethoxycarbonyl group equals to  $78.4^\circ$ . The  $\text{C}^{13}$ ,  $\text{O}^4$ ,  $\text{O}^3$ ,  $\text{C}^{14}$  atoms of the ethoxycarbonyl group are coplanar within  $\pm 0.03$  Å. The position of  $\text{C}^{15}$  deviates from this plane by 0.98 Å. The bond length of  $\text{C}^{14}-\text{C}^{15}$  is significantly shortened and equals to 1.395(5) Å due to statistical disordering of  $\text{C}^{14}$  position in the crystal.

The phenyl-*o*-carboranyl group has axial  $\alpha$ -orientation with torsion angle  $\text{C}^{13}\text{C}^3\text{C}^4\text{C}^{11}$  equal to  $160.2(2)^\circ$ .

The lengths of C-C, C-B, B-B bonds in the icosahedron have values expected for carborane structures and vary from 1.694(3) ( $\text{C}^{11}-\text{B}^5$ ) to 1.786(4) Å ( $\text{B}^9-\text{B}^{10}$ ). The mean values for B-B, C-C, and C-B bonds were 1.7689, 1.722, and 1.712 Å respectively. This difference in the bond lengths results in some disparity of the bond angles in the icosahedron. For instance, the angles BBB, CBC, and BCC in the triangular facets acquire values from  $59.4$  to  $60.72^\circ$  with mean values 60.002, 59.98, and 60.01 respectively; the BBC angles are somewhat smaller (mean value  $59.79^\circ$ ), and BCB values a little larger (mean value  $62.42^\circ$ ).

The deviations of atoms in the planes  $\text{B}^1\text{C}^{12}\text{C}^{11}\text{C}^4$ , and also in the plane of the phenyl ring are insignificant and equal to  $\pm 0.003$ ,  $\pm 0.002$ ,  $\pm 0.003$  Å respectively. The dihedral angle between the plane through the atoms  $\text{C}^1\text{C}^{12}\text{C}^{11}\text{C}^4$  and the phenyl ring plane is  $87.1^\circ$ , and the angle between the mean plane of the coumarin fragment and that of the phenyl ring is  $51.2^\circ$ . The bond lengths of  $\text{C}^1-\text{C}^{12}$  and  $\text{C}^{11}-\text{C}^4$  are equal respectively to 1.501(3) and 1.547(3) Å and are within the acceptable limits.



Structure of **IVa** molecule according to X-ray diffraction analysis.

## EXPERIMENTAL

IR spectra were taken on UR-20 instrument from KBr pellets,  $^1\text{H}$  NMR spectra were registered on spectrometer Tesla BS-587 (80 MHz) in  $\text{C}_6\text{H}_6$ , internal reference HMDS.

All reactions were carried out under nitrogen atmosphere.

**X-ray diffraction study of 4-(phenyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydrocoumarin (IVa).** The cell parameters and intensities of 4211 independent reflections were measured on diffractometer Bruker ( $\text{MoK}_\alpha$ , graphite monochromator,  $\theta/2\theta$ -scanning to  $2\theta \leq 50^\circ$ ). Monoclinic crystals,  $a$  15.374(1),  $b$  10.638(1),  $c$  16.408(2),  $\beta$   $117.02(1)^\circ$ ,  $V$  2390.6 (4) Å<sup>3</sup>,  $\rho_{\text{calc}}$  1.218 g/cm<sup>3</sup>,  $Z$  4 ( $\text{C}_{20}\text{H}_{26}\text{O}_4\text{B}_{10}$ ), space group  $P2_1/n$ . The structure was solved by the direct method and refined in a full-matrix least-squares procedure in anisotropic approximation for nonhydrogen atoms. Hydrogen atoms parameters were obtained from difference synthesis save five of them ( $\text{H}^{14A}$ ,  $\text{H}^{14B}$ ,  $\text{H}^{15A}$ ,  $\text{H}^{15B}$ ,  $\text{H}^{15C}$ ) that were fixed from geometrical assumptions with the use of "rider" procedure. Into account were taken 2942 reflections with  $I > 2\sigma(I)$ . The final divergence factors were  $R$  0.053 and  $R_w$  0.137. The coordinates of atoms are listed in a table. All calculations were performed applying the software package SHELX-97.

Coordinates of atoms in the structure of compound **IVa** in fractions of unit cell axes ( $\text{\AA} \times 10^4$ , for H  $\text{\AA} \times 10^3$ )

Atom	x	y	z
O <sup>1</sup>	5948(1)	1773(1)	10168(1)
O <sup>2</sup>	5676(1)	3399(1)	10836(1)
O <sup>3</sup>	3511(1)	3774(1)	8005(1)
O <sup>4</sup>	3619(1)	2637(1)	9183(1)
C <sup>2</sup>	5578(1)	2937(2)	10136(1)
C <sup>3</sup>	5061(1)	3559(2)	9212(1)
C <sup>4</sup>	5485(1)	3197(1)	8556(1)
C <sup>5</sup>	5372(1)	1081(2)	7785(1)
C <sup>6</sup>	5458(2)	-213(3)	7835(2)
C <sup>7</sup>	5706(2)	-815(3)	8651(3)
C <sup>8</sup>	5661(1)	-149(2)	9417(2)
C <sup>9</sup>	5776(1)	1141(2)	9359(1)
C <sup>10</sup>	5553(1)	1787(2)	8557(1)
C <sup>11</sup>	6450(1)	3881(1)	8761(1)
C <sup>12</sup>	6406(1)	4558(2)	7906(1)
C <sup>13</sup>	3980(1)	3245(2)	8808(1)
C <sup>14</sup>	2443(2)	3715(4)	7548(3)
C <sup>15</sup>	2042(2)	4905(4)	7551(3)
C <sup>1</sup>	5461(1)	4983(2)	7048(1)
C <sup>2</sup>	4759(2)	5857(3)	6978(1)
C <sup>3</sup>	3890(3)	5948(5)	6180(4)
C <sup>4</sup>	3709(3)	5189(6)	5453(3)
C <sup>5</sup>	4381(3)	4346(5)	5498(2)
C <sup>6</sup>	5265(2)	4227(3)	6995(1)
B <sup>1</sup>	8396(2)	4466(4)	9811(2)
B <sup>2</sup>	8355(2)	5464(3)	8939(2)
B <sup>3</sup>	7713(2)	5883(4)	9569(2)
B <sup>4</sup>	7238(2)	4482(3)	9793(2)
B <sup>5</sup>	7570(2)	3211(3)	9306(2)
B <sup>6</sup>	8257(2)	3816(3)	8766(2)
B <sup>7</sup>	7015(2)	3440(3)	8107(2)
B <sup>8</sup>	7504(2)	4835(3)	7880(2)
B <sup>9</sup>	7168(2)	6112(3)	8373(2)
B <sup>10</sup>	6472(2)	5483(3)	8902(2)
H <sup>3</sup>	510(1)	442(2)	331(1)
H <sup>4</sup>	503(1)	347(1)	798(1)
H <sup>5</sup>	518(1)	152(2)	722(1)
H <sup>6</sup>	534(2)	-70(3)	728(2)
H <sup>7</sup>	575(1)	-174(3)	870(1)
H <sup>8</sup>	602(1)	-51(3)	998(1)
H <sup>2</sup>	492(2)	635(3)	755(2)
H <sup>3</sup>	350(4)	656(5)	616(3)
H <sup>4</sup>	305(3)	528(4)	482(3)
H <sup>5</sup>	436(3)	370(4)	504(3)
H <sup>6</sup>	572(1)	363(3)	635(1)
H <sup>1B</sup>	901(3)	438(3)	1044(2)
H <sup>2B</sup>	900(1)	602(2)	900(1)
H <sup>3B</sup>	787(2)	672(3)	1002(1)
H <sup>4B</sup>	707(1)	433(2)	1033(1)
H <sup>5B</sup>	758(1)	229(2)	955(1)
H <sup>6B</sup>	879(1)	323(3)	872(1)
H <sup>7B</sup>	668(1)	266(2)	762(1)
H <sup>8B</sup>	746(1)	494(2)	719(1)
H <sup>9B</sup>	696(1)	702(3)	805(1)
H <sup>10B</sup>	582(1)	593(2)	888(1)

**4-(Phenyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydrocoumarin (IVa).** (a) To a solution of 10 mmol of lithium derivative **Ia** in 15 ml of benzene prepared from 10 mmol of phenyl-*o*-carborane and 12 mmol of BuLi was added at room temperature a solution of 10 mmol of 3-ethoxycarbonylcoumarin (**II**) in 10 ml of benzene. The reaction mixture was stirred for 3 h at 20°C, treated with dilute HCl and then extracted with benzene. The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. The residue was crystallized from hexane to give compound **IVa** in 85% yield, mp 198–199°C (from benzene–hexane mixture, 1:1). (b) To a solution of 10 mmol of magnesium derivative **Ib** in 15 ml of THF prepared from 10 mmol of phenyl-*o*-carborane and 13 mmol of EtMgBr was added at room temperature a solution of 10 mmol of 3-ethoxycarbonylcoumarin (**II**) in 19 ml of benzene. The reaction mixture was stirred for at least 3 h at 20°C, treated with dilute HCl and then extracted with benzene. The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. The residue was crystallized from hexane to give compound **IVa** in 64% yield, mp 198–199°C (from benzene–hexane mixture, 1:1). IR spectrum in KBr,  $\nu$ , cm<sup>-1</sup>: 2980 (C–H), 2595 (B–H), 1760, 1720 (C=O). <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>),  $\delta$ , ppm: 0.30 t (3H, CH<sub>2</sub>CH<sub>3</sub>, *J* 7.1 Hz), 3.28 q (2H, CH<sub>2</sub>CH<sub>3</sub>, *J* 7.1 Hz), 3.59 d (1H, CHCB, *J* 1.0 Hz), 3.94 d (1H, CHCH, *J* 1.0 Hz), 7.1–7.5 m (9H, Ar–H). Found, %: C 54.62; H 7.21; B 24.92. C<sub>20</sub>H<sub>26</sub>B<sub>10</sub>O<sub>4</sub>. Calculated, %: C 54.92; H 7.43; B 24.71.

**4-(Isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydrocoumarin (IVb).** (a) In the same way as in above described procedure (a) from 10 mmol of the corresponding lithium derivative **Ia** and 10 mmol of compound **II** we obtained compound **IVb** in 79% yield, mp 188–189°C (from benzene–hexane mixture, 1:1). (b) Likewise by procedure (b) for preparation of compound **IVa** from 10 mmol of the corresponding magnesium derivative **Ib** and 10 mmol of compound **II** we obtained compound **IVb** in 56% yield, mp 188–189°C (from benzene–hexane mixture, 1:1). IR spectrum in KBr,  $\nu$ , cm<sup>-1</sup>: 2982 (C–H), 2600 (B–H), 1760, 1720 (C=O). <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>),  $\delta$ , ppm: 0.45 t (3H, CH<sub>2</sub>CH<sub>3</sub>, *J* 7.1 Hz), 0.87 d [6H, CH(CH<sub>3</sub>)<sub>2</sub>, *J* 7.0 Hz], 2.21 m [1H, CH(CH<sub>3</sub>)<sub>2</sub>, *J* 7.0 Hz], 3.22 d (1H, CHCB, *J* 1.0 Hz), 3.57 q (2H, CH<sub>2</sub>CH<sub>3</sub>, *J* 7.1 Hz), 4.07 d (1H, CHCH, *J* 1.0 Hz), 6.4–6.8 m (4H, Ar–H). Found, %: C 50.21; H 6.77; B 26.39. C<sub>17</sub>H<sub>28</sub>B<sub>10</sub>O<sub>4</sub>. Calculated, %: C 50.47; H 6.93; B 26.73.

**2-Hydroxy-4-(phenyl-*o*-carboranyl)-3-ethoxycarbonylbenzo-4*H*-pyran (Va).** (a) To a solution of

10 mmol of lithium derivative **Ia** in 15 ml of benzene was added at room temperature a solution of 10 mmol of 3-ethoxycarbonylcoumarin (**II**) in 10 ml of benzene. The reaction mixture was stirred for 3 h at 20°C, treated with distilled water and extracted with ethyl acetate. The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. The residue was crystallized from hexane to give benzo-4*H*-pyran derivative **Va** in 94% yield, mp 186°C (with decomp., from a mixture ethanol–water, 2:1). (b) To a solution of 10 mmol of magnesium derivative **Ib** in 15 ml of THF was added at room temperature a solution of 10 mmol of 3-ethoxycarbonylcoumarin (**II**) in 10 ml of benzene. The reaction mixture was stirred for 3 h at 20°C, treated with distilled water and extracted with ethyl acetate. The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. The residue was crystallized from hexane to give benzo-4*H*-pyran derivative **Va** in 82% yield, mp 186°C (decomp.). IR spectrum in KBr,  $\nu$ , cm<sup>-1</sup>: 3130–3600 (O–H), 2900–3000 (C–H), 2590 (B–H), 1700 (C=O), 1600 (C=C). Found, %: C 54.56; H 7.68; B 24.88. C<sub>20</sub>H<sub>26</sub>B<sub>10</sub>O<sub>4</sub>. Calculated, %: C 54.92; H 7.43; B 24.71.

**2-Hydroxy-4-(isopropyl-*o*-carboranyl)-3-ethoxycarbonylbenzo-4*H*-pyran (Vb).** (a) Similarly to the procedure (a) for preparation of compound **Va** from 10 mmol of an appropriate lithium derivative **Ia** and 10 mmol of compound **II** was obtained compound **Vb** in 84% yield, mp 179°C (with decomp., from a mixture ethanol–water, 2:1).

(b) Similarly to the procedure (b) for preparation of compound **Va** from 10 mmol of an appropriate magnesium derivative **Ib** and 10 mmol of compound **II** was obtained compound **Vb** in 72% yield, mp 179°C (decomp.). IR spectrum in KBr,  $\nu$ , cm<sup>-1</sup>: 3140–3600 (O–H), 2970 (C–H), 2600 (B–H), 1690 (C=O), 1600 (C=C). Found, %: C 50.08; H 6.72; B 26.97. C<sub>17</sub>H<sub>28</sub>B<sub>10</sub>O<sub>4</sub>. Calculated, %: C 50.49; H 6.93; B 26.73.

**3-Isopropyl-*m*-carboranoyl-4-(isopropyl-*m*-carboranyl)-3,4-dicoumarin (VIII).** (a) To a solution of 20 mmol of lithium derivative **VIa** in 25 ml of benzene was added at room temperature 10 mmol of 3-ethoxycarbonylcoumarin (**II**) in 10 ml of benzene. The reaction mixture was stirred at 20°C for 4 h, then treated with dilute HCl, extracted with benzene, the extract was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated. The residue was crystallized from hexane to afford compound **VIII** in 47% yield, mp 158–159°C (from isooctane). (b) To a solution of 20 mmol of magnesium derivative **VIb** in 25 ml of THF was added at room temperature 10 mmol of 3-ethoxy-

carbonylcoumarin (**II**) in 10 ml of benzene. The reaction mixture was stirred at 20°C for 5 h, then treated with dilute HCl, extracted with benzene, the extract was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated. The residue was crystallized from hexane to afford compound **VIII** in 47% yield, mp 158–159°C (from isooctane). IR spectrum in KBr,  $\nu$ , cm<sup>-1</sup>: 2980 (C–H), 2605 (B–H), 1750, 1700 (C=O). <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>),  $\delta$ , ppm: 0.55 d [12H, CH(CH<sub>3</sub>)<sub>2</sub>, *J* 6.7 Hz], 1.45–1.70 m [2H, CH(CH<sub>3</sub>)<sub>2</sub>, *J* 6.7 Hz], 3.7 d (1H, *J* 1.0 Hz), 4.82 d (1H, *J* 1.0 Hz), 6.65–6.75 m (4H, Ar–H). Found, %: C 44.32; H 7.05; B 39.46. C<sub>20</sub>H<sub>40</sub>B<sub>20</sub>O<sub>3</sub>. Calculated, %: C 44.11; H 7.35; B 39.70.

**4-(Phenyl-*o*-carboranyl)-3,4-dihydrocoumarin (X).** (a) To a solution of 10 mmol of lithium derivative **Ia** in 15 ml of benzene was added at room temperature a solution of 10 ml of coumarin **IX** in 10 ml of benzene. The reaction mixture was stirred for 3 h at 20°C, treated with dilute HCl and then extracted with benzene. The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. The residue was subjected to column chromatography on silica gel, eluent benzene–hexane, 1:1. We obtained compound **X** in 61% yield, mp 192–193°C (from benzene–hexane mixture, 1:1). (b) To a solution of 10 mmol of magnesium derivative **Ib** in 15 ml of THF was added at 20°C a solution of 10 ml of coumarin **IX** in 10 ml of benzene. The reaction mixture was stirred for 3 h, kept for 12 h at room temperature, then treated with dilute HCl and extracted with benzene. The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. The residue was subjected to column chromatography on silica gel, eluent benzene–hexane, 1:1. We obtained compound **X** in 82% yield, mp 192–193°C (from benzene–hexane mixture, 1:1). IR spectrum in KBr,  $\nu$ , cm<sup>-1</sup>: 2940–3000 (C–H), 2590 (B–H), 1750 (C=O). <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>),  $\delta$ , ppm: 1.51 d.d (1H, H<sup>4</sup>), 2.54 d.d (1H, H<sup>3</sup>, *J*<sub>3B,4</sub> 10.4 Hz), 2.59 d.d (1H, H<sup>3</sup>, *J*<sub>3A,4</sub> 13.0, *J*<sub>3A,3B</sub> 1.47 Hz), 6.6–7.2 m (9H, Ar–H). Found, %: C 55.41; H 5.28; B 29.38. C<sub>17</sub>H<sub>21</sub>B<sub>10</sub>O<sub>2</sub>. Calculated, %: C 55.89; H 5.75; B 29.58.

**Conversion of dihydrocoumarins IVa, b into benzo-4*H*-pyrans Va, b.** (a) To a solution of 3 mmol of dihydrocoumarin **IVa** in 10 ml of EtOH was added at room temperature a solution of 3.2 mmol of EtONa in 10 ml of EtOH, the reaction mixture was stirred for 1 h and treated with distilled water. The separated precipitate was filtered off. We obtained benzo-4*H*-pyran **Va** in 96% yield, mp 186°C (with decomp., from a mixture ethanol–water, 2:1). (b) To a solu-

tion of 2.2 mmol of KOH in 10 ml of anhydrous EtOH was added at room temperature 2 mmol of dihydrocoumarin **IVa** in 10 ml of EtOH. The reaction mixture was stirred for 1 h and then treated with distilled water. The separated precipitate was filtered off to obtain benzo-4*H*-pyran **Va** in 91% yield, mp 186°C (decomp.).

Similarly along procedure (b) from 2 mmol of compound **IVb** and 2.2 mmol of KOH was obtained benzo-4*H*-pyran **Vb** in 89% yield, mp 179°C (decomp.).

**Conversion of benzo-4*H*-pyrans Va, b into dihydrocoumarins IVa, b.** (a) To a solution of 4 mmol of benzo-6*H*-pyran **Va** in 10 ml of EtOH was added at room temperature a solution of 4.2 mmol of EtONa in 10 ml of EtOH. The reaction mixture was stirred for 0.5 h, treated with dilute HCl and extracted with benzene. The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. The residue was crystallized from hexane to give compound **IVa** in 94% yield, mp 198–199°C (from benzene–hexane mixture, 1:1). Likewise from 3 mmol of compound **Vb** and 3.2 mmol of EtONa was obtained dihydrocoumarin **IVb** in 92% yield, mp 188–189°C (from benzene–hexane mixture, 1:1).

(b) To a solution of 2.2 mmol of KOH in 10 ml of anhydrous EtOH was added at room temperature 2 mmol of benzo-4*H*-pyran **Va** in 6 ml of EtOH. The reaction mixture was stirred for 0.5 h and then treated with dilute HCl and extracted with benzene. The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. The residue was crystallized from hexane to give compound **IVa** in 89% yield, mp 198–199°C (from benzene–hexane mixture, 1:1). Likewise from 2 mmol of compound **Vb** and 2.2 mmol of KOH was obtained dihydrocoumarin **IVb** in 94% yield, mp 188–189°C.

**Reaction of dihydrocoumarin IVa with acids.**

(a) A mixture of 3 mol of compound **IVa** and 50 ml

of H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> was heated at 250–300°C for 6 h, then the reaction mixture was cooled, treated with distilled water and extracted with benzene. The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated, the residue was crystallized from hexane. We obtained compound **X** in 73% yield, mp 192–193°C (from benzene–hexane mixture, 1:1).

(b) A mixture of 2 mmol of dihydrocoumarin **IVa**, 6 ml of concn. HCl, and 20 ml of AcOH was boiled for 10 h, cooled, and the separated precipitate was filtered off. We obtained compound **X** in 82% yield, mp 192–103°C. (c) A mixture of 2 mmol of dihydrocoumarin **IVa**, 6 ml of concn. HBr, and 20 ml of AcOH was boiled for 5 h, cooled, and the separated precipitate was filtered off. We obtained compound **X** in 96% yield, mp 192–103°C. (d) A mixture of 2 mmol of dihydrocoumarin **IVa** and 30 ml of AcOH was boiled for 10 h, cooled, treated with distilled water and extracted with ethyl ether. The extract was dried on Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated, the residue was crystallized from hexane to furnish acid **XII** in 85% yield, mp 172°C (with decomposition, from THF–hexane mixture, 1:4). IR spectrum in KBr,  $\nu$ , cm<sup>-1</sup>: 3350–3600 (O–H), 2990 (C–H), 2590 (B–H), 1770 (C=O). Found, %: C 52.23; H 5.12; B 26.57. C<sub>18</sub>H<sub>22</sub>B<sub>10</sub>O<sub>4</sub>. Calculated, %: C 52.68; H 5.37; B 26.36.

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