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LETTERS TO THE EDITOR

Reactions of 4-(Isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydroxycoumarin with Metals and Their Derivatives

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Some natural and synthetic coumarin derivatives possess biological activity. Carboranyl-containing coumarin derivatives are of particular interest since they are the promising synthons for the synthesis of new pharmacologically active compounds with potentially a wide spectrum of biological activity.

Further developing our previous studies [1–4] on the chemistry of carboranyl-containing dihydrocoumarin **I**, we report here on the reaction of **I** with metals and their derivatives. Dihydrocoumarin **I** was prepared by reacting isopropyl-*o*-carboranyllithium with 3-(ethoxycarbonyl)coumarin.

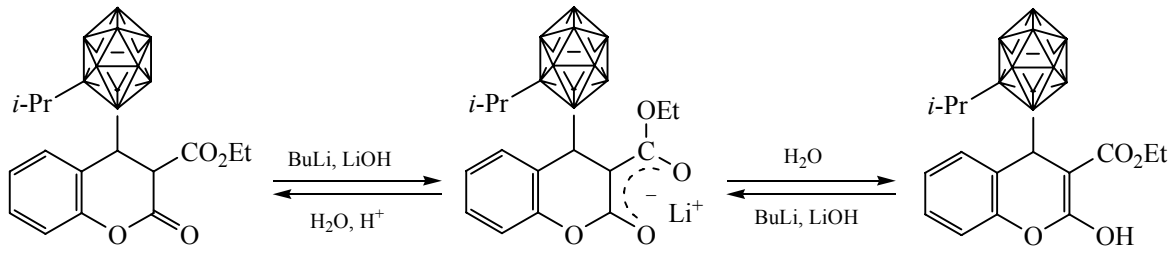
It was found that dihydrocoumarin **I** reacted with equimolar amount of BuLi in benzene as well as with LiOH in THF with the formation of enolate anion **II** in a high yield. Treating **II** with dilute HCl afforded quantitatively the starting dihydrocoumarin **I**. However, the interaction of **II** with water gave rise to benzo-4*H*-pyran **III**, which is able to further conversions (Scheme 1).

The reaction of dihydrocoumarin **I** with active metals (Li, Na, K, Mg) in THF provided quantitatively ambident resonance-stabilized adducts **IV–VII**, which differ from each other by their composition and structure according to the mass spectrometry data (Scheme 2).

The formation of different by composition and structure adducts **IV–VII** agreed with the coordination number of the involved metals and the tendency of the formed organometallic compounds to association.

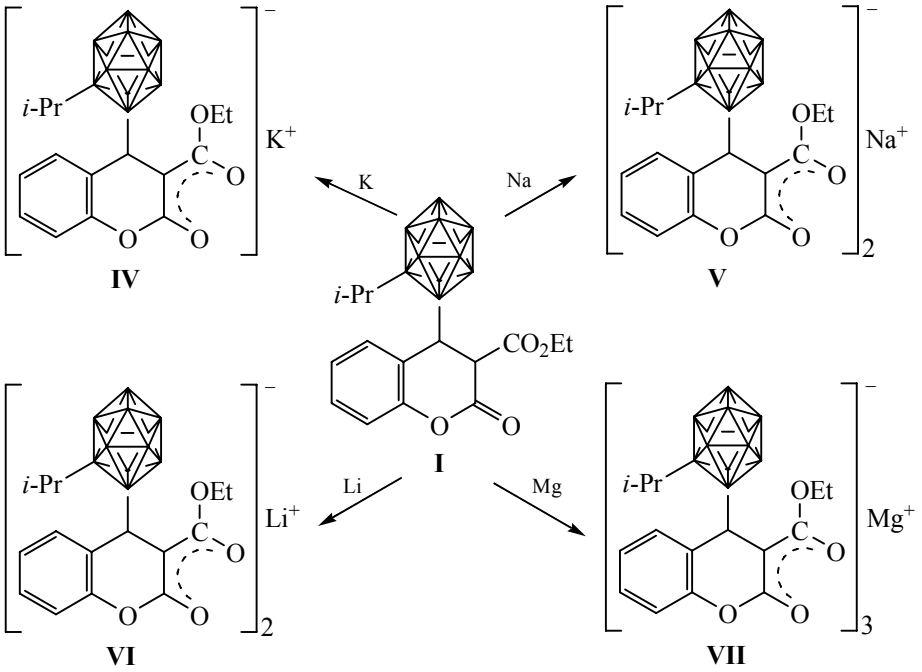
4-(Isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydroxycoumarin (I). To an ether–benzene solution of 10 mmol of isopropyl-*o*-carboranyllithium at 20°C was added at stirring 10 mmol of 3-(ethoxycarbonyl) coumarin. The reaction mixture was stirred for 3 h, treated with dilute HCl, and extracted with diethyl ether. The extract was dried over Na_2SO_4 and evaporated. The residue was crystallized from hexane. Yield 80%, mp 188–189°C (benzene–hexane, 1 : 1) (mp 188–189°C [4]).

Scheme 1.



I **II** **III**

Scheme 2.



4-(Isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-5,6-benzopyran-2-ol (III). *a.* A solution of 11 mmol of BuLi in 10 mL of benzene was added to a solution of 10 mmol of dihydrocoumarin **I** in benzene. The reaction mixture was stirred for 2 h under argon. The precipitate formed was filtered off, the filtrate was evaporated, and the residue was crystallized from hexane; the combined precipitates were recrystallized from benzene–hexane mixture (1 : 1) to give lithium enolate **II** in a 93% yield, mp 220–222°C (decomp.). After stirring compound **II** with water for 2 h, benzo-4*H*-pyran **III** was isolated in 84% yield, mp 179°C (ethanol–water, 2 : 1, decomp.) {mp 179°C (decomp.) [4]}.

b. To a solution of 10 mmol of dihydrocoumarin **I** in THF was added 10 mmol of LiOH. The reaction mixture was stirred at 20°C for 48 h followed by treatment with water. Yield 94%, mp 179°C (decomp.).

Potassium salt of 4-(isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydroxycoumarin (IV). To a solution of 10 mmol of dihydrocoumarin **I** in 15 mL of THF was added 0.4 g of potassium; the reaction mixture was stirred at 20°C for 2 h in argon. The precipitate formed was filtered off and washed with THF. Yield 98%, mp 148–150°C (decomp.). IR spectrum, ν, cm^{-1}: 2980, 2934 (C–H), 2615, 2572 (B–H), 1684 (C=O). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 7.03–7.04 m (4H, ArH, *J* 7.26 Hz), 4.12 t (2H, CH_2, *J* 1.37 Hz), 3.60 q [1H, $CH(CH_3)_2$, *J* 1.50 Hz], 1.30 d (3H, CH_3), 3.12–1.29 t [1H, $CH(CH_3)_2$, *J* 0.86 Hz]. ^{11}B NMR spectrum (CD_3OD), δ_B, ppm: –4.92 (2B), –8.94 (4B), –11.05 (4B). Mass spectrum (EI): *m*/*z* 440. Found, %: C 44.52; H 6.57; B 22.31. $C_{17}H_{27}B_{10}O_4K$. Calculated, %: C 44.63; H 6.74; B 22.41.

Sodium salt of 4-(isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydroxycoumarin V was prepared similarly from 10 mmol of compound **I** and 0.25 g of sodium. Yield 96%, mp 185–187°C (decomp.). IR spectrum, ν, cm^{-1}: 2981, 2943, 2878 (C–H); 2615, 2570 (B–H), 1682, 1613, 1596 (C=O), 1538 (C=C). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.23–1.90 m (10H, BH), 2.16 d [6H, $(CH_3)_2CH$, *J* 6.73 Hz], 3.70–4.13 m (8H, $CHCH_2$, *J* 6.15 Hz), 4.16 septet [1H, $CH(CH_3)_2$, *J* 6.93 Hz], 6.92–6.96 m (1H, Ar), 7.02–7.06 m (1H, Ar), 7.11–7.19 m (3H, Ar), 7.22–7.26 m (1H, Ar). ^{11}B NMR spectrum (CD_3OD), δ_B, ppm: 4.68 (2B), –8.76 (4B), –10.79 (4B). Mass spectrum (EI): *m*/*z* 829. Found, %: C 50.08; H 6.72; B 26.97. $C_{34}H_{54}B_{20}O_8Na$. Calculated, %: C 50.49; H 6.93; B 26.73.

Lithium salt of 4-(isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydroxycoumarin VI was prepared similarly from 10 mmol of compound **I** and

0.1 g of lithium. Yield 95%, mp 220–222°C (decomp.). IR spectrum, ν, cm^{-1}: 2979, 2880 (C–H), 2621, 2572 (B–H), 1678, 1611, 1594 (C=O), 1536 (C=C). ^1H NMR spectrum (CD_3OD), δ, ppm: 1.15–3.66 m (10H, BH), 4.50 d.d (1H, CHCH, *J* 1.54, 6.13 Hz), 6.85–6.90 m (1H, Ar), 6.96–7.06 m (3H, ArH), 7.12–7.16 m (1H, Ar). ^{11}B NMR spectrum (CD_3OD), δ_B, ppm: –4.68 (2B), –8.58 (4B), –11.11 (4B). Mass spectrum (EI): *m*/*z* 817. Found, %: C 55.41; H 7.28; B 24.38. $C_{34}H_{54}B_{20}O_8Li$. Calculated, %: C 55.82; H 7.03; B 24.05.

Magnesium salt of 4-(isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydroxycoumarin VI was prepared similarly from 10 mmol of compound **I** and 0.25 g of magnesium at stirring for 24 h. Yield 95%, mp 310°C (decomp.). IR spectrum, ν, cm^{-1}: 2983, 2943, 2879 (C–H), 2619, 2572 (B–H), 1667, 1612, 1595 (C=O), 1527 (C=C). ^1H NMR spectrum (CD_3OD), δ, ppm: 1.05–1.34 m (10H, BH), 1.74 d.d [6H, $(CH_3)_2CH$, *J* 14.8, 7.2 Hz], 1.99–2.04 septet [1H, CH $(CH_3)_2$, *J* 5.12 Hz], 4.24–4.35 d.d (1H, $CHCH_2$, *J* 1.8, 13.3 Hz), 5.13 d (2H, $CHCH_2$, *J* 1.7 Hz), 7.1–7.46 m (1H, Ar), 7.71–7.79 m (1H, Ar), 7.91–7.94 m (3H, ArH). ^{11}B NMR spectrum (CD_3OD), δ_B, ppm: 3.54 (2B), –5.45 (2B), –9.73 (2B), 11.01 (4B). Mass spectrum (EI): *m*/*z* 1239. Found, %: C 44.32; H 7.05; B 39.46. $C_{51}H_{81}B_{30}O_{12}Mg$. Calculated, %: C 44.11; H 7.35; B 39.70.

REFERENCES

1. Kazantsev, A.V., Aksartov, M.M., and Aksartova, L.M., *Metallorg. Khim*., 1990, vol. 3, no. 6, p. 1345.
2. Kazantsev, A.V., Kazantsev, Yu.A., and Butyaikin, V.V., *Metallorg. Khim*., 1992, vol. 5, no. 3, p. 570.
3. Kazantsev, A.V., Butyaikin, V.V., Otrashchenkov, E.A., and Muldakhmetov, Z.M., *Izv. Akad. Nauk*, 1995, no. 10, p. 2058.
4. Kazantsev, A.V., Otrashchenkov, E.A., Aksartov, M.M., Turdybekov, K.M., Yamovoi, V.I., and Adekenov, S.M., *Russ. J. Org. Chem*., 2002, vol. 38, no. 11, p. 1635. DOI: 10.1134/S0514749202110137.