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Synthesis and Reactions of Dehydracetic Acid Difluoroborane Complex

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Abstract—Dehydracetic acid difluoroborane complex, 3-acetyl-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate, was synthesized and characterized. The complex was involved into condensation reactions at the acetyl group with various aromatic and heterocyclic aldehydes, and with the 4-dimethylaminobenzaldehyde it reacted also at the methyl group in the position *6*.

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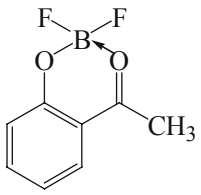
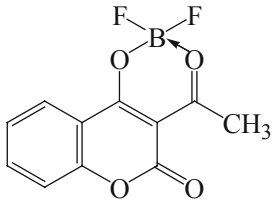
Dehydracetic acid (3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one) in the presence of bases is capable of condensation with various aldehydes both at the acetyl and methyl group in the position *6* [1, 2]. However the products of these reactions form in low yield and are difficult to isolate. We investigated a new promising condensation method of dehydracetic acid with aldehydes involving an intermediate preparation of its boron complex.

It was formerly established that 1,3-diketones and also the corresponding aromatic and heteroaromatic *vic*-hydroxyketones are capable of boron complexes formation. In particular, boron complexes were obtained from 2-hydroxyacetophenone (**I**) [3] and 3-acetyl-4-hydroxycoumarin (**II**) [4, 5].



I



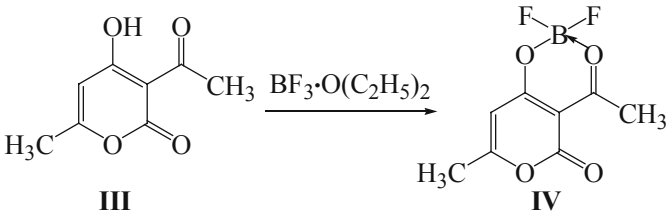
II

The introducing of a boron atom into the molecule results in a considerable increase in the reactivity of the methyl group in the acetyl moiety compared to the initial hydroxy compounds providing a possibility to perform condensation with carbonyl compounds and their derivatives, in particular, with acetals and anils [4, 6].

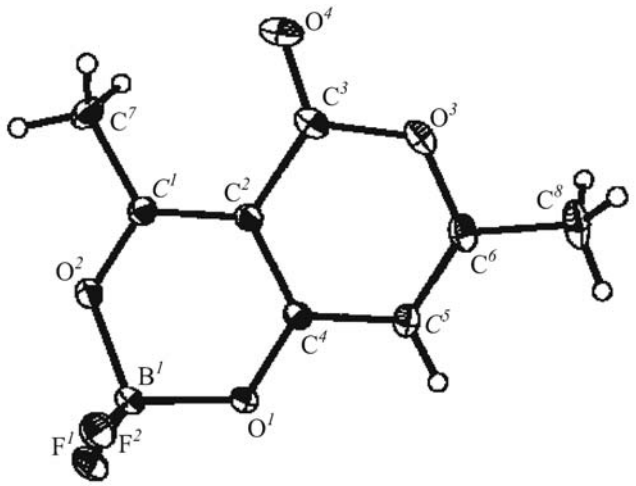
By a reaction of dehydracetic acid (**III**) with boron trifluoride etherate we obtained its boron complex, 3-acetyl-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (**IV**) (Scheme 1).

In the ^{1}H NMR spectrum of complex **IV** the proton signals of the methyl groups are shifted downfield: the proton signal of the acetyl group is shifted by 0.20 ppm, and that of the methyl in the position *6*, by 0.14 ppm. This shift reveals the enhanced CH-acidity of both methyl groups due to the complex formation. The structure of compound **IV** was also proved by XRD analysis (see the figure). According to the XRD data the atoms of the molecule are located in the same plane. The bond distances in the six-membered heterocycle involving the boron atom indicate an efficient electron density delocalization in the fragment $F_2BOC{=}CC{=}O$ (see the table). The observed leveling-off of bond distances in this moiety is caused by the formation of the donor-acceptor B–O bond and by a significant degree of π-delocalization. For instance, the bond lengths B^1–O^1 and

Scheme 1.



III **IV**



Structure of compound **IV** from XRD data

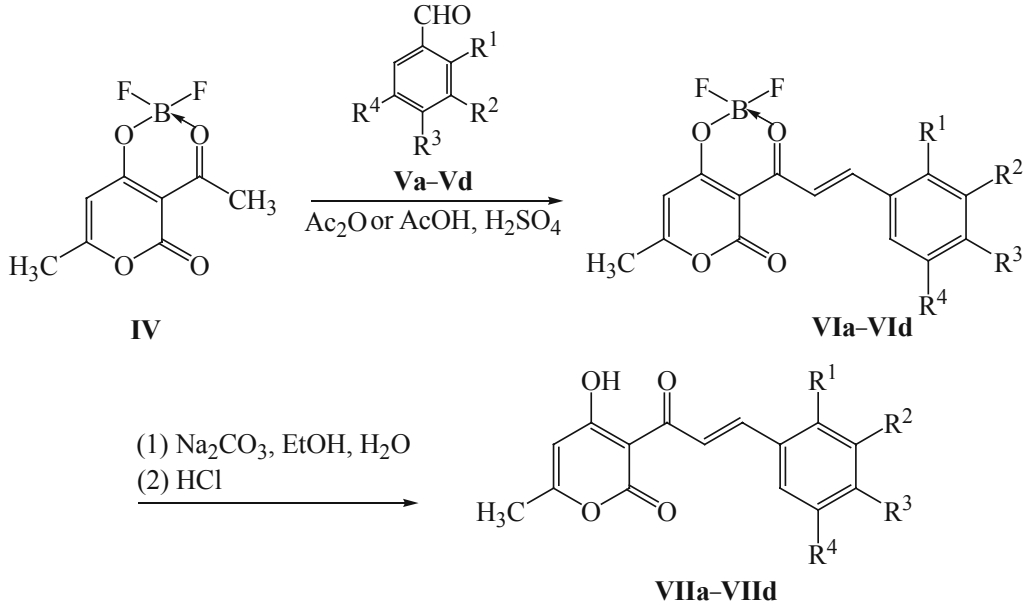
Geometric parameters of boron complex **IV** from XRD data

Bond	*d*, Å	Bond angle	ω, deg
F^1–B^1	1.3673(12)	$C^4O^1B^1$	119.57(7)
F^2–B^1	1.3764(12)	$C^1O^2B^1$	121.02(7)
O^1–C^4	1.3022(11)	$F^1B^1F^2$	112.82(8)
O^1–B^1	1.4829(11)	$F^1B^1O^1$	109.32(8)
O^2–C^1	1.2913(11)	$O^1B^1O^2$	109.81(7)
O^2–B^1	1.5082(12)	$O^2C^1C^2$	120.12(8)
C^1–C^2	1.4044(12)	$C^1C^2C^4$	118.40(8)
C^2–C^4	1.4115(12)	$O^1C^4C^2$	121.73(8)

B^1–O^2 equal respectrively 1.4829 and 1.5082 Å. The bond lengths C^1–O^2 and C^4–O^1 in the formed boron complex also become materially equal: 1.29 and 1.30 Å respectively. In general the structure of the six-membered boron ring in complex **IV** possesses the same bond distances and angles as in boron complex **II** [5].

Complex **IV** readily underwent crotonic condensation with aldehydes in the absence of bases. These reactions proceed especially cleanly with aromatic and heterocyclic aldehydes containing electron-donor substituents. We failed to carry out reactions in the absence of bases with aromatic aldehydes possessing electron-withdrawing substituents, for instance, with 4-nitrobenzaldehyde, and also with aliphatic aldehydes. From condensation of compound **IV** with aromatic aldehydes **Va–Vd** difluoridoborates **VIa–VId** were obtained (Scheme 2). The structure of the obtained complexes was confirmed by ^{1}H NMR and mass spectra. In the ^{1}H NMR spectra alongside the signals of the aromatic protons in the downfield region (6.10–9.00 ppm) two doublet signals were observed from methine protons with coupling constants of ~12–15 Hz. These values of the coupling constants indicate the mutual *trans*-location of the methine protons. The signal of methyl protons of acetyl group is lacking in these ^{1}H NMR spectra.

Scheme 2.



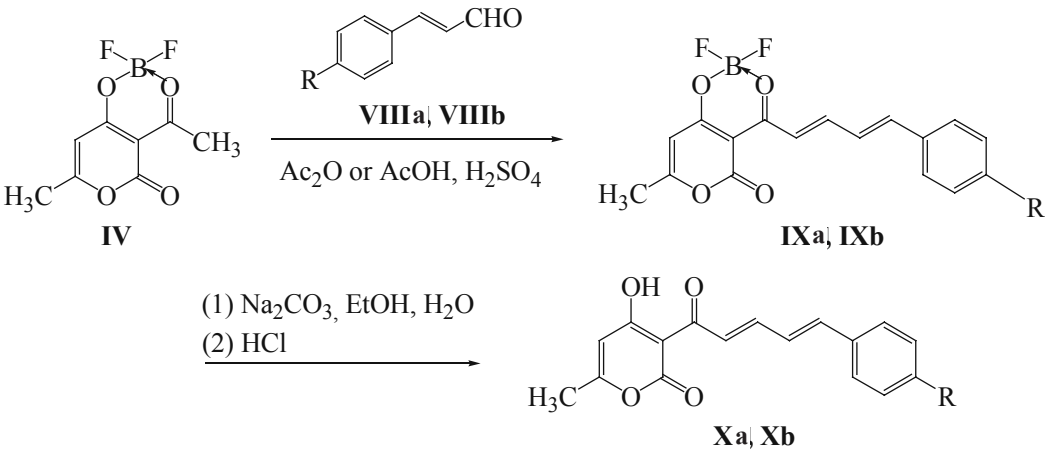
$R^1 = R^2 = R^4 = H$, $R^3 = N(CH_3)_2$ (**a**), OCH_3 (**b**); $R^1 = H$, $R^2 = R^3 = R^4 = OCH_3$ (**c**); $R^1 = OCH_3$, $R^2 = R^3 = H$, R^4 =Br (**d**).

Under the same conditions compound **IV** reacted also with the derivatives of cinnamaldehyde, 4-dimethylaminocinnamaldehyde (**VIIIa**) and 4-methoxycinnamaldehyde (**VIIIb**) (Scheme 3). Therewith compounds **IXa** and **IXb** formed whose structure was unambiguously proved by ^{1}H NMR and mass spectra. In the downfeld region of ^{1}H NMR spectra alongside the signals of aromatic protons appeared signals from four methine protons as two triplets and two doublets at 7.10–8.20 ppm.

3-Acetyl-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (**IV**) was also brought into condensation with heterocyclic aldehydes (Scheme 4). In this reaction boron complexes **XII** and **XV** were obtained. The structure of the compounds prepared was confirmed by ^{1}H NMR and mass spectra. In the ^{1}H NMR spectra of boron complexes alongside the proton signals of the thiophene ring two doublets in the downfield region (7.00–8.40 ppm, coupling constants ~12–15) Hz were observed belonging to methine protons.

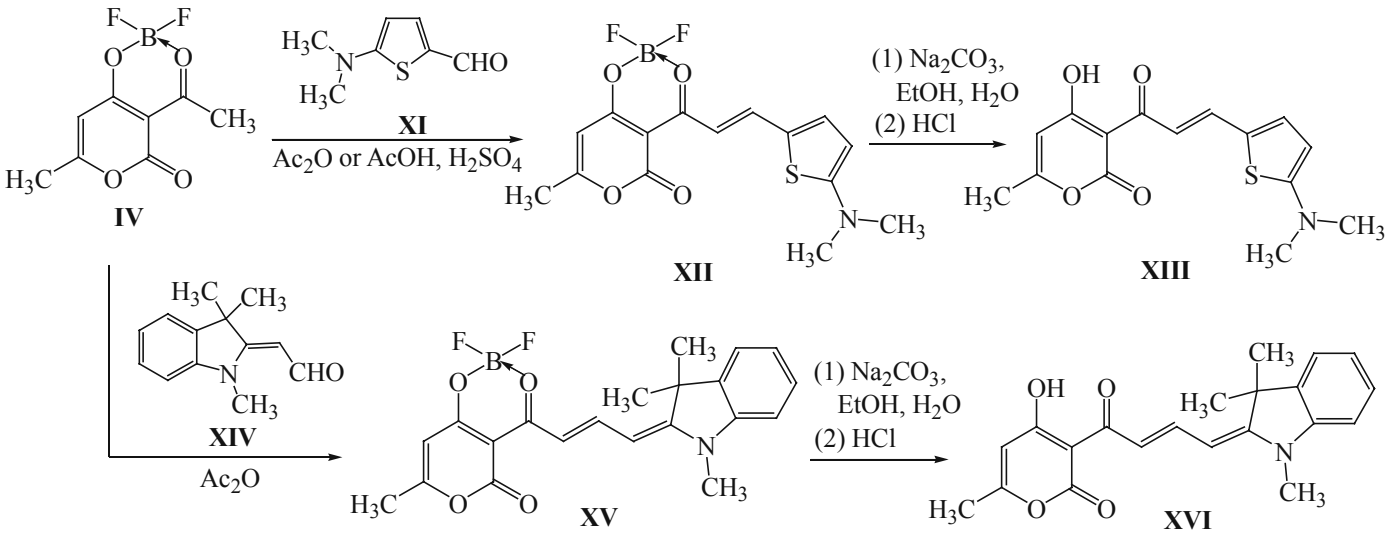
By reaction of boron complex **IV** with Fischer's aldehyde compound **XV** belonging to trimethine dyes was successfully synthesized. The structure of the compound was confirmed by ^{1}H NMR spectrum that alongside the signals of aromatic protons and those of methyl groups contained the resonances of three methine protons: a one-proton doublet at 6.10 ppm, a one-proton triplet at 8.73 ppm, and the doublet of the third

Scheme 3.



R = $N(CH_3)_2$ (**a**), OCH_3 (**b**).

Scheme 4.



proton from the trimethine chain superimposed on the multiplet of aromatic protons at 7.04–7.47 ppm.

It was formerly reported on the condensation with benzaldehyde of dihydracetic acid at the position *6* in the presence of a base *N*-benzylidenecyclohexylamine [7]. We found that boron complexes **IV, VIa, VIb**, and **VId** were capable of reacting at the methyl group in the position *6* even in the absence of a base (Scheme 5). However due to the longer distance from the acceptor boron atom the methyl group in the position *6* is less activated than the methyl from the acetyl moiety (the shift of these protons on complexing is 0.14 and 0.20 ppm respectively). Among the other aldehydes only 4-dimethylaminobenzaldehyde readily reacted. In the ^{1}H NMR spectrum of compound **XVIIa** in the downfield region (6.90–8.52 ppm) four signals of methine protons appeared as four doublets with coupling constants of ~12–15 Hz. The singlet from methyl group in the position *6* disappeared. We failed to register the ^{1}H NMR spectra of compounds **XVIIb** and **XVIId** because of their poor solubility.

Compound **XVIIa** was also synthesized by condensation of boron complex **IV** with two equiv of the corresponding aldehyde. The reaction proceeded simultaneously at both reaction sites.

The treatment of boron complexes obtained **VIa–VId, IXa, IXb, XII, XV, XVIIa, XVIIb**, and **XVIId** with sodium carbonate in aqueous-alcoholic medium followed by acidification resulted in the formation of the corresponding hydroxyketones **VIIa–VIId, Xa, Xb, XIII, XVI, XVIIIa, XVIIIb**, and **XVIIId**. In the ^{1}H NMR spectra of these ketones as distinct from the spectra of the boron complexes appeared the proton signal of the hydroxy group as a singlet in the downfield region (17.00–18.00 ppm). Besides the proton signals of the double bonds are shifted upfield on the average by 0.30 ppm. This shift is due to the elimination of the acceptor effect of the chelate ring after the hydrolysis of the boron complexes.

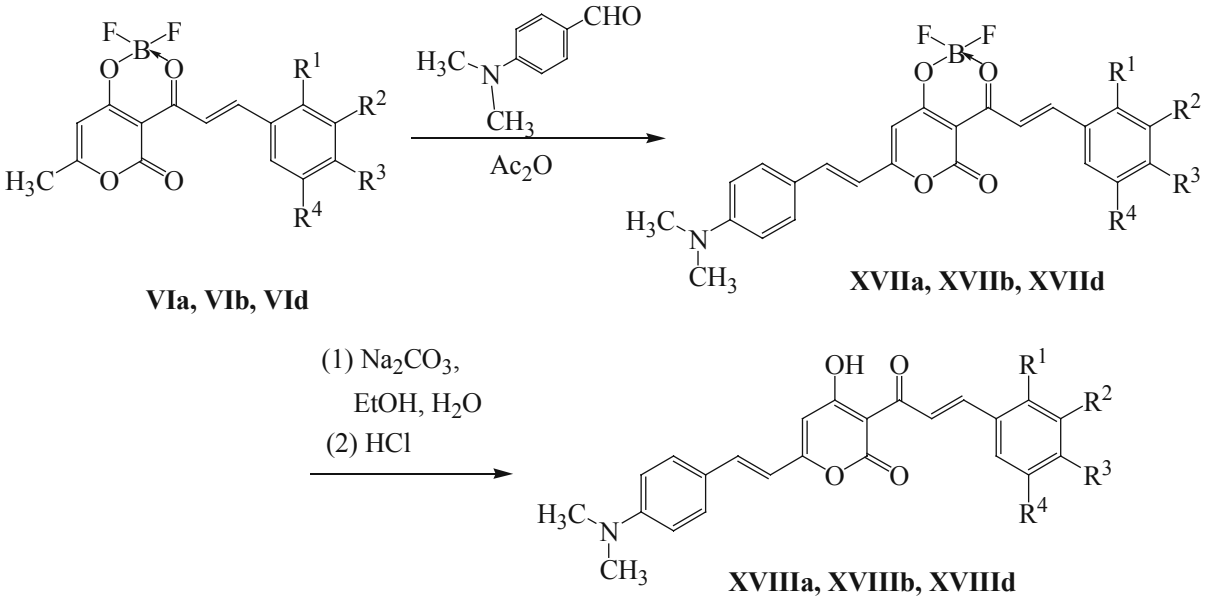
The structure of all compounds obtained was confirmed by mass spectra and elemental analyses.

Thus by the reaction of the boron complex of hydracetic acid with various aromatic and heterocyclic aldehydes boron complexes of the corresponding chalcones analogs were obtained. The complexes are deeply colored and exhibit fluorescence. Their hydrolysis led to the formation of new heterocyclic α,β-unsaturated ketones also characterized by fluorescence.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Bruker WP-200-SY, internal reference Me_4Si. Mass spectra were measured on MAT-112 instrument at ionizing electrons energy 80 eV, ion source temperature 250°C, vaporizer temperature 240°C.

Scheme 5.



$R^1 = R^2 = R^4 = H$, $R^3 = N(CH_3)_2$ (**a**), OCH_3 (**b**); $R^1 = OCH_3$, $R^2 = R^3 = H$, $R^4 = Br$ (**d**).

XRD experiment for compound **VI** was performed on an automatic five-circle diffractometer CAD-4 at 298 K. $C_8H_7BF_2O_4$. Crystals monoclinic, space group $P2(1)/c$, a 9.486(7), b 5.157(4), c 18.449(14) Å, β 104.02(10)°, V 875.54(11) Å^3, Z 4, d_{calc} 1.638 mg/m^3, μ(MoK_α) 0.153 mm^{-1}, F(000) 440.0. Intensities of 8800 reflections were measured at 298 K (λMoK_α, graphite monochromator, θ/2θ-scanning, 2θ < 50°), among them 2538 independent reflections with $I > 2\sigma$. The structure was solved by the direct method and by successive syntheses of the electron density. All hydrogen atoms localized from the difference synthesis of the electron density. The refinement by F^2_{hkl} was carried out in an anisotropic approximation for all nonhydrogen atoms and in isotropic approximation for hydrogen atoms. The final divergence factors are as follows: R 0.0324 for 2356 independent reflections with $I > 2\sigma(I)$, R_w 0.0913 for all measured reflections. All calculations were performed applying software package SHELXTL 5.10 [8].

Atomic coordinates and complete tables of bond distances and bond angles were deposited to Cambridge Structural Database.

3-Acetyl-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (IV). To a solution of 10 g (0.06 mol) of compound **III** in 17 ml of anhydrous benzene was added dropwise at boiling 10 g (0.07 mol) of boron trifluoride etherate. The reaction mixture was heated for 1 h, and then the separated precipitate was filtered off, washed with benzene, dried in air, and recrystallized from benzene. Yield 80%. Yellow needle crystals, mp 135–136°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.39 s (3H, 6-CH_3), 2.86 s (3H, 3-CH_3), 6.13 s (1H, H^5). Found, %: C 44.45; H 3.21. $C_8H_7BF_2O_4$. Calculated, %: C 44.50; H 3.27.

Difluoridoborates VIa, IXa, XII, and XV. General procedure. To a solution of 0.5 g (0.002 mol) of boron complex **IV** in 6 ml of acetic acid at 60°C was added a solution of 0.002 mol of an appropriate aldehyde in 2 ml of acetic anhydride. The mixture was heated at 90°C for 30 min. On cooling the settled precipitate was filtered off, washed on the filter with acetic acid, and recrystallized from acetic acid.

3-{(2*E*)-3-[4-(Dimethylamimino)phenyl]prop-2-enoyl}-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (VIa). Yield 84%, dark-red crystals, mp 238–239°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 s (3H, CH_3), 3.17 s [6H, N(CH_3)$_2$], 6.07 s (1H, H^5), 6.70 d (2H, H_{arom}, J 8.8 Hz), 7.68 d (2H, H_{arom}, J 8.8 Hz), 8.08 d (1H, CH, J 14.9 Hz), 8.42 d (1H, CH, J 14.9 Hz). Mass spectrum: m/z 348 [M]$^+$. Found, %: C 58.79; H 4.60; N 4.00. $C_{17}H_{16}BF_2NO_4$. Calculated, %: C 58.82; H 4.65; N 4.04.

3-{(2*E*,4*E*)-5-[4-(Dimethylamino)phenyl]penta-2,4-dienoyl}-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (IXa). Yield 64%, dark-green crystals, mp 242–243°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (3H, CH_3), 3.31 s [6H, N(CH_3)$_2$], 6.41 s (1H, H^5), 6.79 d (2H, H_{arom}, J 8.7 Hz), 7.28 t (1H, CH), 7.57 d (1H, CH, J 14.3 Hz), 7.65 d (2H, H_{arom}, J 8.7 Hz), 7.68 d (1H, CH, J 14.3 Hz), 8.17 t (1H, CH). Mass spectrum: m/z 374 [M]$^+$. Found, %: C 61.19; H 4.89; N 3.65. $C_{19}H_{18}BF_2NO_4$. Calculated, %: C 61.16; H 4.86; N 3.75.

3-{(2*E*)-3-[5-(Dimethylamino)-2-thienyl]prop-2-enoyl}-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (XII). Yield 88%, dark-blue crystals, mp 223–224°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.26 s (3H, CH_3), 3.38 s [6H, N(CH_3)$_2$], 6.22 s (1H, H^5), 6.86 d (1H, H_{Ht}, J 5.1 Hz), 7.06 d (1H, CH, J 12.9 Hz), 8.01 d (1H, H_{Ht}, J 5.1 Hz), 8.21 d (1H, CH, J 12.9 Hz). Mass spectrum: m/z 354 [M]$^+$. Found, %: C 51.04; H 4.09; N 3.96; S 9.10. $C_{15}H_{14}BF_2NO_4S$. Calculated, %: C 51.02; H 4.00; N 3.97; S 9.08.

6-Methyl-2-oxo-3-[(2*E*,4*E*)-4-(1,3,3-trimethyl-1,3-dihydro-2*H*-indol-2-ylidene)but-2-enoyl]-2*H*-pyran-4-yl difluoridoborate (XV). Yield 76%, violet crystals, mp 250–251°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.68 s [6H, (CH_3)$_2$], 2.29 s (3H, CH_3), 3.54 s [3H, N(CH_3)], 6.01 s (1H, H^5), 6.10 d (1H, CH, J 14 Hz), 7.04–7.47 m (5H, 4H_{arom}), 8.73 t (1H, CH). Mass spectrum: m/z 400 [M]$^+$. Found, %: C 63.15; H 5.10; N 3.49 $C_{21}H_{20}BF_2NO_4$. Calculated, %: C 63.18; H 5.05; N 3.51.

Difluoridoborates (VIb–VId, and IXb). *General procedure.* To a solution of 0.5 g (0.002 mol) of boron complex **IV** in 6 ml of acetic acid at 60°C was added a solution of 0.002 mol of an appropriate aldehyde in 2 ml of acetic acid and 0.13 ml of concn. sulfuric acid. The mixture was heated at 90°C for 30 min. On cooling the settled precipitate was filtered off, washed on the filter with acetic acid, and recrystallized from acetic acid.

3-[(2*E*)-3-(4-Methoxyphenyl)prop-2-enoyl]-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (VIb). Yield 80%, red crystals, mp 220–221°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.38 s (3H, CH_3), 3.88 s (3H, OCH_3), 6.55 s (1H, H^5), 7.11 d (2H, H_{arom}, J 8.8 Hz), 7.90 d (2H, H_{arom}, J 8.8 Hz), 8.13 d (1H, CH, J 15.2 Hz), 8.40 d (1H, CH, J 15.2 Hz). Mass spectrum: m/z 335

[*M*]$^+$. Found, %: C 57.56; H 3.98. $C_{16}H_{13}BF_2O_5$. Calculated, %: C 57.72; H 3.92.

3-[(2*E*)-3-(3,4,5-Trimethoxyphenyl)prop-2-enoyl]-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (VIc). Yield 65%, red crystals, mp 192–193°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.39 s (3H, CH_3), 3.98 s (9H, 3OCH_3), 6.14 s (1H, H^5), 6.99 s (2H, H_{arom}), 8.21 d (1H, CH, *J* 15.4 Hz), 8.34 d (1H, CH, *J* 15.4 Hz). Mass spectrum: *m/z* 395 [*M*]$^+$. Found, %: C 54.98; H 4.26. $C_{18}H_{17}BF_2O_7$. Calculated, %: C 54.85; H 4.35.

3-[(2*E*)-3-(5-Bromo-2-methoxyphenyl)prop-2-enoyl]-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (VId). Yield 80%, orange crystals, mp 198–199°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.39 s (3H, CH_3), 3.95 s (3H, OCH_3), 6.14 s (1H, H^5), 6.84 d (1H, H_{arom}, *J* 9.2 Hz), 7.54 d (1H, H_{arom}, *J* 9.2 Hz), 7.83 s (1H, H_{arom}), 8.39 d (1H, CH, *J* 15.4 Hz), 8.63 d (1H, CH, *J* 15.4 Hz). Mass spectrum: *m/z* 414 [*M*]$^+$. Found, %: C 46.49; H 2.90. $C_{16}H_{12}BBrF_2O_5$. Calculated, %: C 46.53; H 2.93.

3-[(2*E*,4*E*)-5-(4-Methoxyphenyl)penta-2,4-dienoyl]-6-methyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (IXb). Yield 74%, dark-blue crystals, mp 198–199°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s (3H, CH_3), 3.87 s (3H, OCH_3), 6.11 s (1H, H^5), 6.92 d (2H, H_{arom}, *J* 8.7 Hz), 7.02 t (1H, CH), 7.20 d (1H, CH, *J* 14.3 Hz), 7.53 d (2H, H_{arom}, *J* 8.7 Hz), 7.80 d (1H, CH, *J* 14.3 Hz), 8.19 t (1H, CH). Mass spectrum: *m/z* 361 [*M*]$^+$. Found, %: C 60.08; H 4.16. $C_{18}H_{15}BF_2O_5$. Calculated, %: C 60.03; H 4.20.

Difluoridoborates XVIIa, XVIIb, and XVIId. *General procedure.* To a solution of 0.4 mmol of an appropriate boron complex in 2 ml of acetic anhydride at 60°C was added a solution of 0.05 g (0.4 mmol) of aldehyde **Va** in 2 ml of acetic anhydride. The mixture was boiled for 30 min. On cooling the settled precipitate was filtered off, washed on the filter with acetic acid, and recrystallized from acetic acid.

3-{(2*E*)-3-[4-(Dimethylamino)phenyl]prop-2-enoyl}-6-{(*E*)-2-[4-(dimethylamino)phenyl]vinyl}-2-oxo-2*H*-pyran-4-yl difluoridoborate (XVIIa). Yield 47%, dark-green crystals, mp 330–331°C. Mass spectrum: *m/z* 479 [*M*]$^+$. Found, %: C 65.24; H 5.23; N 5.86. $C_{26}H_{25}BF_2N_2O_4$. Calculated, %: C 65.29; H 5.27; N 5.86.

6-{(*E*)-2-[4-(Dimethylamino)phenyl]vinyl}-3-[(2*E*)-3-(4-methoxyphenyl)prop-2-enoyl]-2-oxo-2*H*-pyran-4-yl difluoridoborate (XVIIb). Yield 42%, dark-red crystals, mp 295–296°C. Mass spectrum: *m/z* 466 [*M*]$^+$. Found, %: C 64.50; H 4.73; N 3.01. $C_{25}H_{22}BF_2NO_5$. Calculated, %: C 64.54; H 4.77; N 3.01.

3-[(2*E*)-3-(5-Bromo-2-methoxyphenyl)prop-2-enoyl]-6-{(*E*)-2-[4-(dimethylamino)phenyl]vinyl-2-oxo-2*H*-pyran-4-yl difluoridoborate (XVIId). Yield 38%, dark-red crystals, mp 345–346°C. Mass spectrum: *m/z* 546 [*M*]$^+$. Found, %: C 55.21; H 3.92; N 2.58. $C_{25}H_{21}BBrF_2NO_5$. Calculated, %: C 55.18; H 3.89; N 2.57.

Hydroxycompounds VIIa–VIId, Xa, Xb, XIII, XVI, XVIIIa, XVIIIb, and XVIIId. *General procedure.* In 10 ml of 60% aqueous ethanol was dissolved 3 mmol of an appropriate boron complex, and 1.59 g (15 mmol) of Na_2CO_3 was added to the solution. The reaction mixture was heated at reflux for 1–5 h (TLC monitoring, the reaction was carried out till total disappearance of the initial boron complex). On cooling the solution obtained was filtered and acidified with dilute hydrochloric acid till pH 6.5–7. The separated precipitate was filtered off, washed with water, and recrystallized from 2-propanol.

3-{(2*E*)-3-[4-(Dimethylamino)phenyl]prop-2-enoyl}-4-hydroxy-6-methyl-2*H*-pyran-2-one (VIIa). Yield 83%, red crystals, mp 218–219°C (220°C [9]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.23 s (3H, CH_3), 3.04 s [6H, $N(CH_3)_2$], 6.16 s (1H, H^5), 6.76 d (2H, H_{arom}, *J* 7.9 Hz), 7.55 d (2H, H_{arom}, *J* 7.9 Hz), 7.93 s (2H, 2CH, degenerate, 14.69 s (1H, OH). Mass spectrum: *m/z* 300 [*M*]$^+$. Found, %: C 68.19; H 5.68; N 4.61. $C_{17}H_{17}NO_4$. Calculated, %: C 68.22; H 5.72; N 4.68.

3-[(2*E*)-3-(4-Methoxyphenyl)prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (VIIb). Yield 80%, yellow crystals, mp 208–209°C (208°C [9]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.27 s (3H, CH_3), 3.85 s (3H, OCH_3), 5.93 s (1H, H^5), 6.90 d (2H, H_{arom}, *J* 8.7 Hz), 7.63 d (2H, H_{arom}, *J* 8.7 Hz), 7.91 d (1H, CH, *J* 15.9 Hz), 8.16 d (1H, CH, *J* 15.9 Hz), 18.15 s (1H, OH). Mass spectrum: *m/z* 287 [*M*]$^+$. Found, %: C 67.08; H 4.98. $C_{16}H_{14}O_5$. Calculated, %: C 67.13; H 4.93.

3-[(2*E*)-3-(3,4,5-Trimethoxyphenyl)prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (VIIc). Yield 78%, yellow crystals, mp 124–125°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.27 s (3H, CH_3), 3.91 s (9H, 3OCH_3), 5.95 s (1H, H^5), 6.90 s (2H, H_{arom}, degenerate), 7.84 d (1H, CH, *J* 15.9 Hz), 8.17 d (1H, CH, *J* 15.9 Hz), 17.94 C (1H, OH). Mass spectrum: *m/z* 347 [*M*]$^+$. Found, %: C 62.39; H 5.27. $C_{18}H_{18}O_7$. Calculated, %: C 62.42; H 5.24.

3-[(2*E*)-3-(5-Bromo-2-methoxyphenyl)prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (VIId). Yield 90%, yellow crystals, mp 157–158°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.28 s (3H, CH_3), 3.90 s (3H, OCH_3), 5.95 s (1H, H^5), 6.78 d (1H, H_{arom}, *J* 8.7Hz), 7.43 d (1H, H_{arom}, *J* 8.7 Hz), 7.79 s (1H, H_{arom}), 8.15 d (1H, CH, *J* 15.9 Hz), 8.28 d (1H, CH, *J* 15.9 Hz), 17.89 s (1H, OH). Mass spectrum: *m/z* 366 $[M]^+$. Found, %: C 52.58; H 3.63. $C_{16}H_{13}BrO_5$. Calculated, %: C 52.63; H 3.59.

3-{(2*E*,4*E*)-5-[4-(Dimethylamino)phenyl]penta-2,4-dienoyl}-4-hydroxy-6-methyl-2*H*-pyran-2-one (Xa). Yield 72%, dark-green crystals, mp 204–205°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.23 s (3H, CH_3), 2.30 s [6H, $N(CH_3)_2$], 6.19 s (1H, H^5), 6.72 d (2H, H_{arom}, *J* 8.7 Hz), 7.07–7.71 m (6H, $2H_{arom}$, 4CH). Mass spectrum: *m/z* 326 $[M]^+$. Found, %: C 70.10; H 5.92; N 4.31. $C_{19}H_{19}NO_4$. Calculated, %: C 70.14; H 5.89; N 4.30.

3-[(2*E*,4*E*)-5-(4-Methoxyphenyl)penta-2,4-dienoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (Xb). Yield 74%, dark-blue crystals, mp 156–157°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.28 s (3H, CH_3), 3.84 s (3H, OCH_3), 5.92 s (1H, H^5), 6.88–7.79 m (8H, $4H_{arom}$, 4CH), 18.18 C (1H, OH). Mass spectrum: *m/z* 313 $[M]^+$. Found, %: C 69.20; H 5.11. $C_{18}H_{16}O_5$. Calculated, %: C 69.22; H 5.16.

3-{(2*E*)-3-[5-(Dimethylamino)-2-thienyl]prop-2-enoyl}-4-hydroxy-6-methyl-2*H*-pyran-2-one (XIII). Yield 88%, dark-red crystals, mp 190–191°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.17 s (3H, CH_3), 3.16 s [6H, $N(CH_3)_2$], 6.04 s (1H, H^5), 6.25 d (1H, H_{Ht}, *J* 4.1 Hz), 7.26 d (1H, CH, *J* 14.3 Hz), 7.57 d (1H, H_{Ht}, *J* 4.1 Hz), 8.04 d (1H, CH, *J* 14.3 Hz), 14.00 s (1H, OH). Mass spectrum: *m/z* 306 $[M]^+$. Found, %: C 59.03; H 4.98; N 4.63; S 10.56. $C_{15}H_{15}NO_4S$. Calculated, %: C 59.00; H 4.95; N 4.59; S 10.50.

4-Hydroxy-6-methyl-3-[(2*E*,4*E*)-4-(1,3,3-trimethyl-1,3-dihydro-2*H*-indol-2-ylidene)but-2-enoyl]-2*H*-pyran-2-one (XVI). Yield 76%, red crystals, mp 250–251°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.66 s [6H, $(CH_3)_2$], 2.20 s (3H, CH_3), 3.32 s [3H, $N(CH_3)$], 5.85 s (1H, H^5), 6.17 d (1H, CH, *J* 14 Hz), 6.78–7.48 m (5H, $4H_{arom}$), 8.39 t (1H, CH), 18.82 s (1H, OH). Mass spectrum: *m/z* 352 $[M]^+$. Found, %: C 71.75; H 6.08; N 4.02. $C_{21}H_{21}NO_4$. Calculated, %: C 71.78; H 6.02; N 3.99.

3-{(2*E*)-3-[4-(Dimethylamino)phenyl]prop-2-enoyl}-6-{(*E*)-2-[4-(dimethylamino)phenyl]vinyl}-4-hydroxy-2*H*-pyran-2-one (XVIIIa). Yield 72%, dark-red crystals, mp 256–257°C. ^{1}H NMR spectrum (DMSO-d_6 + TFA), δ, ppm: 3.51 s [12H, $2N(CH_3)_2$], 6.52 s (1H, H^5), 6.92 d (1H, CH, *J* 15.8 Hz), 7.67 d (2H, H_{arom}, *J* 8.8 Hz), 7.71 d (2H, H_{arom}, *J* 8.7 Hz), 7.75 d (1H, CH, *J* 15.8 Hz), 7.87 d (2H, H_{arom}, *J* 8.8 Hz), 7.99 d (2H, H_{arom}, *J* 8.7 Hz), 8.03 d (1H, CH, *J* 16.2 Hz), 8.44 d (1H, CH, *J* 16.2 Hz). Mass spectrum: *m/z* 431 $[M]^+$. Found, %: C 72.50; H 6.01; N 6.50. $C_{26}H_{26}N_2O_4$. Calculated, %: C 72.54; H 6.09; N 6.51.

6-{(*E*)-2-[4-(Dimethylamino)phenyl]vinyl}-4-hydroxy-3-[(2*E*)-3-(4-methoxyphenyl)prop-2-enoyl]-2*H*-pyran-2-one (XVIIIb). Yield 64%, red crystals, mp 240–241°C. Mass spectrum: *m/z* 418 $[M]^+$. Found, %: C 71.85; H 5.59; N 3.32. $C_{25}H_{23}NO_5$. Calculated, %: C 71.93; H 5.55; N 3.36.

3-[(2*E*)-3-(5-Bromo-2-methoxyphenyl)prop-2-enoyl]-6-{(*E*)-2-[4-(dimethylamino)phenyl]vinyl-4-hydroxy-2*H*-pyran-2-one (XVIIId). Yield 65%, dark-red crystals, mp 263–264°C. Mass spectrum: *m/z* 497 $[M]^+$. Found, %: C 60.52; H 4.50; N 2.80. $C_{25}H_{22}BrNO_5$. Calculated, %: C 60.50; H 4.47; N 2.82.

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