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Synthesis of Benzimidazolone Derivatives Based on 2-Acylcyclohexane-1,3-diones Alkoximes

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Abstract—2-(1-Alkoxyiminoalkyl)cyclohexane-1,3-diones undergo at heating Beckmann rearrangement to give 6,7-dihydro-1,3-benzoxazol-4(5*H*)-one derivatives that under treatment with amines in acid medium are converted into 1,5,6,7-tetrahydro-4*H*-benzimidazol-4-ones. In reaction of 6,7-dihydro-1,3-benzoxazol-4(5*H*)-ones with *O*-ethylhydroxylamine 4-ethoxyimino derivatives were obtained that treated with hydrochloric acid formed the corresponding *N*-ethoxybenzimidazolones.

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Ethers of oxime derivatives (alkoximes) of cyclohexane β-triketones **I** are the active reagents of the present-day graminicide herbicides of cyclohexoximes series like alloxidim (**Ia**), sethoxydim (**Ib**), traloxydim (**Ic**) etc. [1–3]. Owing to the structural likeness to natural substances containing some kind of β-tricarbonyl system [4, 5] this pesticide group possesses a valuable complex of properties: They are characterized by low consumption, selectivity of action, they are nontoxic, do not possess oncogenic, mutagenic, teratogenic, and other undesirable properties [6]. Unlike graminicides from the series of alkoxyphenoxypropionic acids derivatives [3] the cyclohexoximes suffer very fast degradation in soil giving nontoxic decomposition products that after several weeks are no more detectable in soil, and their residual content in the cultivated plants is many factors of ten smaller than those of the other classes of herbicides.

In the course of storage and natural metabolism of oximes **I** form benzoxazolones **II** [7] that also are obtained as side products in the synthesis of oximes [8]. The benzoxazole moiety proper is also a biophore and is included into a considerable number of insecticide, fungicidal, and other pesticide preparations [1, 2], and also in drugs [9]. Benzoxazoles are often found alongside benzimidazoles in naturally occurring substances [10, 11], therefore both classes of compounds are the subject of an extensive research by synthetic chemists [12, 13] and pharmacologists [14, 15].

The above aspects arose our interest to the synthesis and the study of properties of new benzoxazolones derivatives with a goal of their conversion into benzimidazoles in order to obtain new substances with a potential biological, in particular, pesticide, action.

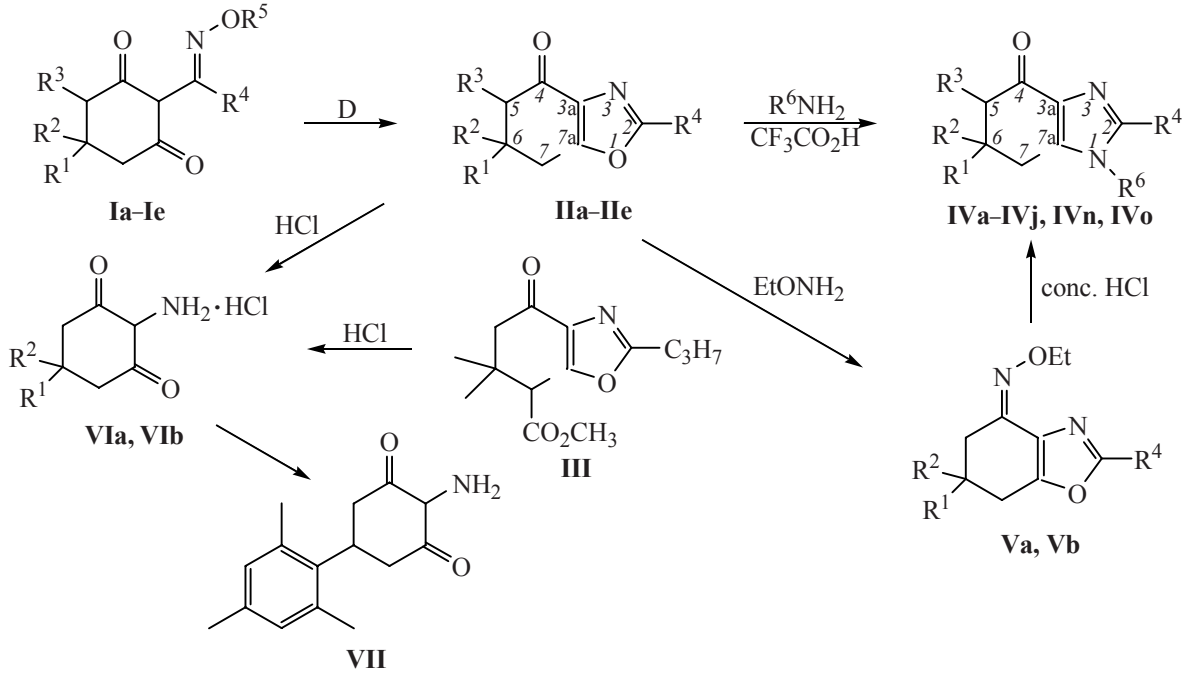
We showed formerly [8] that alkoxyiminodiketones easily underwent Beckmann rearrangement providing benzoxazolones. In this study the reaction was investigated by an example of oximes **Ia–Ie**. On boiling these compounds for 24 h in ethanol substances **Ib–Ie** were converted into the corresponding benzoxazolones **IIa–IId**, and the unsymmetrical alkoximine **Ia** yielded a mixture of isomers **Ie** and **III** in a ratio 2:1 (see the scheme).

Spectral characteristics and elemental composition of compounds obtained were consistent with the assumed structures. In the ^{1}H and ^{13}C NMR spectra of 5-ethylthiopropyl-substituted benzoxazolone **IIa** containing chiral centers at C^{6} and $C^{2''}$ most atoms gave rise to a double set of signals proving the presence of a diastereomers mixture.

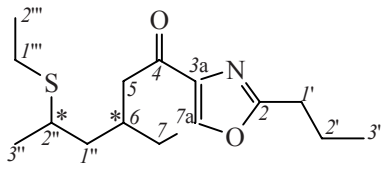
By reaction of benzoxazolones **IIa–IId** with amines (*p*-anisidine, benzylamine, phenethylamine or methylamine) in the presence of trifluoroacetic acid we obtained 60–80% yields the corresponding benzimidazolones **IVa–IVj**.

The reaction of 5-methoxycarbonyl-substituted benzoxazolone **IIe** and its isomer 7-methoxycarbonyl-substituted derivative **III** with benzylamine in both cases

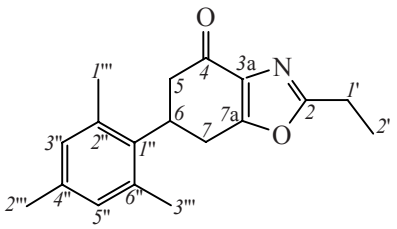
Scheme.



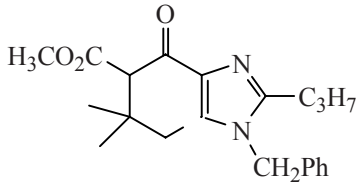
I, $R^1 = R^2 = CH_3$, $R^3 = CO_2CH_3$, $R^4 = C_3H_7$, $R^5 = CH_2CH{=}CH_2$ (**a**); $R^1 = R^3 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = R^5 = C_3H_7$ (**b**); $R^1 = R^3 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3Ph$, $R^4 = R^5 = C_2H_5$ (**c**); $R^1 = R^2 = CH_3$, $R^3 = H$, $R^4 = R^5 = C_2H_5$ (**d**); $R^1 = R^3 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = R^5 = C_2H_5$ (**e**); **II**, $R^1 = R^3 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = C_2H_5$ (**a**); $R^1 = R^3 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3Ph$, $R^4 = C_2H_5$ (**b**); $R^1 = R^2 = CH_3$, $R^3 = H$, $R^4 = C_2H_5$ (**c**); $R^1 = R^3 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = C_3H_7$ (**d**); $R^1 = R^2 = CH_3$, $R^3 = CO_2CH_3$, $R^4 = C_3H_7$ (**e**); **IV**, $R^1 = R^3 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = C_3H_7$, $R^6 = CH_2Ph$ (**a**); $R^1 = R^3 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = C_3H_7$, $R^6 = 4\text{-}CH_3OPh$ (**b**); $R^1 = R^3 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = C_2H_5$, $R^6 = CH_2Ph$ (**c**); $R^1 = R^3 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = C_2H_5$, $R^6 = 4\text{-}CH_3OPh$ (**d**); $R^1 = R^2 = CH_3$, $R^3 = H$, $R^4 = C_2H_5$, $R^6 = CH_2Ph$ (**e**); $R^1 = R^2 = CH_3$, $R^3 = H$, $R^4 = C_2H_5$, $R^6 = 4\text{-}CH_3OPh$ (**f**); $R^1 = R^3 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3Ph$, $R^4 = C_2H_5$, $R^6 = CH_2Ph$ (**g**); $R^1 = R^3 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3Ph$, $R^4 = C_2H_5$, $R^6 = 4\text{-}CH_3OPh$ (**h**); $R^1 = R^3 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3Ph$, $R^4 = C_2H_5$, $R^6 = CH_2CH_2Ph$ (**i**); $R^1 = R^3 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3Ph$, $R^4 = C_2H_5$, $R^6 = CH_3$ (**j**); $R^1 = R^3 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3Ph$, $R^4 = C_2H_5$, $R^6 = OC_2H_5$ (**n**); $R^1 = R^3 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = C_3H_7$, $R^6 = OC_2H_5$ (**o**); **V**, $R^1 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3Ph$, $R^4 = C_2H_5$ (**a**); $R^1 = H$, $R^2 = CH_2CH(SC_2H_5)CH_3$, $R^4 = C_3H_7$ (**b**); **VI**, $R^1 = R^2 = CH_3$ (**a**); $R^1 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3Ph$ (**b**).



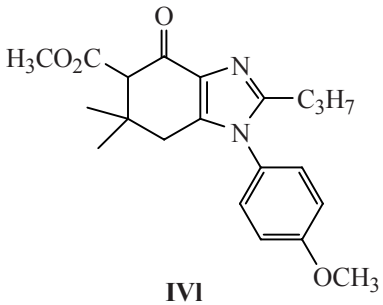
IIa



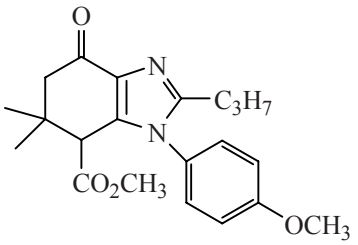
IIb



IVk



IVl

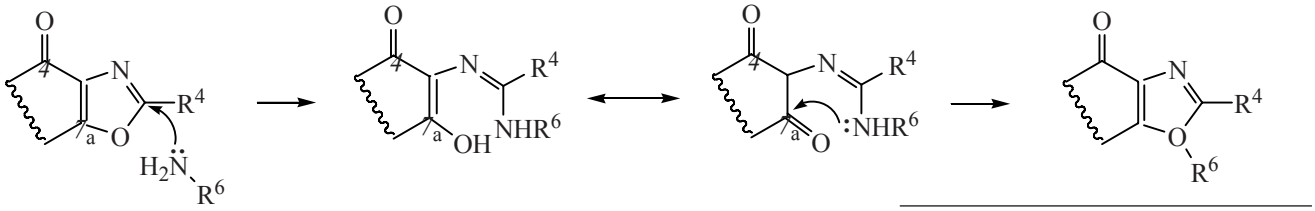


IVm

resulted in the formation of the same benzimidazolone **IVk**, and the reaction of compounds **IIe** and **III** with *p*-anisidine gave the same mixture of regioisomeric products **IVl** and **IVm** in a ratio ~2:1. These facts show that at the opening of the oxazole ring first a nucleophilic attack occurs at C^2 atom of the benzoxazole followed by a cyclization both at atoms C^4 and C^{7a}. The structure of obtained benzimidazolones **IV** was unambiguously confirmed by the sum of data of IR, ^{1}H NMR, mass spectra, and elemental analyses reported in EXPERIMENTAL.

Boiling benzoxazolones **IIa–IId** with an ethanol solution of O-ethylhydroxylamine resulted in the oximation of the carbonyl group of the ring leading to the formation of the corresponding *O*-ethyloximes **Va–Vc**. At heating with concn. hydrochloric acid compounds **Va** and **Vb** converted in N-ethoxy-substituted benzimidazolones **IVn** and **IVo**. N-Ethoxy-substituted benzimidazolones **IVn** and **IVo** were also obtained directly from benzoxazolones **IIb** and **IIc** in one stage process by prolonged boiling in toluene in the presence of trifluoroacetic or concn. hydrochloric acid without isolation of intermediately formed derivatives **Va** and **Vb**.

On treating benzoxazolone **IIc** with concn. hydrochloric acid the opening of the oxazole ring occurred with the formation of aminodiketone hydrochloride **VIa** identical in physicochemical and spectral characteristics to the previously described compound [16]. Under the same conditions 7-methoxycarbonyl-substituted benzoxazolone **III** alongside the opening the oxazole ring suffered decarboxylation; as a result the isolated product was identical to salt **VIa**. Same as mentioned in [16] we failed to isolate from salt **VIa** the compound with a free amino group due to its instability. However from 6-mesityl-substituted benzoxazolone **IIb** after the opening of the oxazole ring by concn. hydrochloric acid and treating obtained salt **VIb** with sodium hydroxide we prepared aminodiketone **VII** that unlike such compounds described in the literature proved to be relatively stable and was characterized by IR and ^{1}H NMR spectra.



The described reaction of benzoxazolones with amines can serve an efficient and simple procedure for preparation of N-substituted benzimidazolones.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-20 from samples of solid compounds pelletized with KBr, from oily substances, in thin film. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance 500 at operating frequencies 500 (^{1}H) and 125 MHz (^{13}C) from solutions in deuterochloroform (or, if indicated, in DMSO-d_6), reference TMS. Mass spectra were measured on MKh-1320 instrument. Melting points were determined on a Boëtius heating block. The reaction progress was monitored and the homogeneity of compounds was checked by TLC on Kieselgel 60 F_{254} plates (Merck), the spots were visualized under UV irradiation followed by spraying with iron(III) chloride solution. For column chromatography silica gel Kieselgel 60 (Fluka) was used.

Benzoxazolones IIa–IIe. A solution of 10 mmol of alkoxyiminodiketone **Ia–Ie** in 50 ml of ethanol was boiled for 24 h (TLC monitoring). The reaction mixture was evaporated in a vacuum, the residue was subjected to chromatography on silica gel, eluent petroleum ether–ethyl acetate.

2-Ethyl-6-[2-(ethylsulfanyl)propyl]-6,7-dihydro-1,3-benzoxazol-4(5*H*)-one (IIa). Yield 1.91 g (68%). Oily substance. IR spectrum, cm^{-1}: 1700, 1620, 1590. ^{1}H NMR spectrum, δ, ppm (diastereomers mixture 1:1): 0.99 t and 1.00 t (3H, $CH_3CH_2CH_2$, *J* 7.4 Hz), 1.25 t and 1.26 t (3H, CH_3CH_2S, *J* 7.4 Hz), 1.31 d and 1.32 d (3H, CH_3CHS, *J* 6.6 Hz), 1.61–1.74 m (2H, CH_2CHS), 1.82 m (2H, $CH_3CH_2CH_2$), 2.33 m (1H, 6-CH_A), 2.55 q and 2.56 q (2H, CH_3CHS, *J* 7.4 Hz), 2.61 m,(1H, C^4H_A), 2.65 m (1H, C^6H_B), 2.68 m (1H, C^5H), 2.76 t (2H, $CH_3CH_2CH_2$, *J* 7.4 Hz), 2.83 m (1H, SCH), 3.07 m (1H, C^4H_B). ^{13}C NMR spectrum, δ, ppm: 13.67 ($C^{3'}$), 14.81 and 14.83 ($C^{2'''}$), 20.15 ($C^{2'}$), 21.98 and 22.20 ($C^{3''}$), 23.73 and 24.18 ($C^{1'''}$), 27.98 and 28.67 (C^7), 29.95 ($C^{1'}$), 33.16 and 33.26 (C^6), 36.60 and 36.94 ($C^{2''}$), 42.39 and 42.68 ($C^{1''}$), 43.89 and 44.46 (C^5), 134.13 (C^{3a}), 163.28 (C^{7a}), 165.35 (C^2), 190.55 (C^4). Mass spectrum, *m/z*: $[M]^+$ 281, $[M+1]^+$ 282, $[M+2]^+$ 283. Found, %: C 64.15; H 8.11;

N 4.97; S 11.56. $C_{15}H_{23}NO_2S$. Calculated, %: C 64.02; H 8.24; N 4.98; S 11.39. *M* 281.42.

6-(Mesityl)-2-ethyl-6,7-dihydro-1,3-benzoxazol-4(5*H*)-one (IIb). Yield 2.69 g (95%), mp 117–119°C (from petroleum ether). IR spectrum, cm^{-1}: 1700, 1615, 1595. ^1H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3CH_2, *J* 7.6 Hz), 2.27 s (3H, 4'-CH_3Ph), 2.33 br.s and 2.44 br.s [6H, 2',6'-$(CH_3)_2$Ph], 2.66 d.d (1H, C^6H_A, J_1 17.0, J_2 4.3 Hz), 2.84 q (2H, CH_3CH_2, *J* 7.6 Hz), 2.97 d.d (1H, C^4H_A, J_1 17.8, J_2 5.7 Hz), 3.22 d.d (1H, C^6H_B, J_1 17.0, J_2 14.1 Hz), 3.44 d.d (1H, C^4H_B, J_1 17.8, J_2 12.1 Hz), 4.06 m (1H, C^5H), 6.89 s ($2H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.96 ($C^{2'}$), 20.65 ($C^{2'''}$), 21.35 br ($C^{1'''}$), 21.69 ($C^{1'}$), 22.22 br ($C^{3'''}$), 26.33 (C^7), 35.84 (C^5), 41.70 (C^6), 129.84 br ($C^{3''}$), 131.57 br ($C^{5'''}$), 134.02 (C^{3a}), 134.24 ($C^{1''}$), 136.22 br ($C^{2''}$), 136.73 ($C^{4'''}$), 163.48 (C^{7a}), 166.39 (C^2), 191.00 (C^4). Found, %: C 76.51; H 7.33; N 4.87. $[M]^+$ 283. $C_{18}H_{21}NO_2$. Calculated, %: C 76.29; H 7.47; N 4.94. *M* 283.37.

6,6-Dimethyl-2-ethyl-6,7-dihydro-1,3-benzoxazol-4(5*H*)-one (IIc). Yield 1.56 g (81%). Oily substance. IR spectrum, cm^{-1}: 1695, 1615, 1590. ^1H NMR spectrum, δ, ppm: 1.15 s (6H, CH_3CCH_3), 1.34 t (3H, CH_3CH_2, *J* 7.7 Hz), 2.34 s (2H, CH_2), 2.76–2.82 m (4H, $2CH_2$), 2.98 s (2H, CH_2). Found, %: C 68.53; H 7.91; N 7.17. $[M]^+$ 193. $C_{11}H_{15}NO_2$. Calculated, %: C 68.37; H 7.82; N 7.25. *M* 193.25.

2-Ethyl-6-[2-(ethylsulfanyl)propyl]-6,7-dihydro-1,3-benzoxazol-4(5*H*)-one (IId). Yield 1.74 g (65%). Oily substance. IR spectrum, cm^{-1}: 1695, 1616, 1588. ^1H NMR spectrum, δ, ppm: 1.23 t and 1.25 t (3H, CH_3CH_2S, *J* 7.4 Hz), 1.30 and 1.31 d (3H, CH_3CHS, *J* 6.6 Hz), 1.35 t (3H, CH_3CH_2C, *J* 7.6 Hz), 1.60–1.70 m (2H, CH_2CHS), 2.31 m (1H, C^6H_A), 2.54 q and 2.55 q (2H, CH_3CHS, *J* 7.4 Hz), 2.60 m (1H, C^4H_A), 2.63 m (1H, C^6H_B), 2.68 m (1H, C^5H), 2.72 m (2H, CH_3CH_2C), 2.83 m (1H, SCH), 3.06 m (1H, C^4H_B). Mass spectrum, *m/z*: $[M]^+$ 267, $[M + 1]^+$ 268, $[M + 2]^+$ 269. Found, %: C 62.73; H 8.01; N 5.07; S 11.76. $C_{14}H_{21}NO_2S$. Calculated, %: C 62.89; H 7.92; N 5.24; S 11.99. *M* 267.39.

From allyloxyiminodiketone **Ia** was obtained a mixture of **methyl 6,6-dimethyl-2-propyl-4-oxo-4,5,6,7-tetrahydro-1,3-benzoxazole-5-carboxylate (IIe)** and its regioisomer, **methyl 6,6-dimethyl-2-propyl-4-oxo-4,5,6,7-tetrahydro-1,3-benzoxazole-7-carboxylate (III)** in a ratio 2:1. Overall yield 1.90 g (72%). The compounds were isolated in individual state by column chromatography; they were identical by physicochemical characteristics to substances described in [8] .

Benzimidazolones IVa–IVe. To a solution of 1.0–1.5 mmol of benzoxazolone **IIa–IIe**, or **III** in 20 ml of toluene was added 1.1 equiv of amine and 1.1 equiv of trifluoroacetic acid. The reaction mixture was boiled for 2–3 h (with benzylamine and *O*-ethyloxime for 24 h); the reaction completion was monitored by TLC. On completion of the reaction toluene was removed on a rotary evaporator. The residue was dissolved in 20 ml chloro-form, washed with 20 ml of water, the water layer was separated, and products were extracted into chloroform (3×10 ml). Combined extracts were dried with anhydrous sodium sulfate, the solvent was removed on a rotary evaporator. The residue was subjected to column chromatography on silica gel, eluent chloroform–ethanol.

1-Benzyl-2-propyl-6-[2-(ethylsulfanyl)propyl]-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVa). Yield 61%. Oily substance. IR spectrum, cm^{-1}: 1675, 1540. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.94 t and 0.95 t (3H, $CH_3CH_2CH_2$, *J* 7.4 Hz), 1.14–1.27 m (6H, CH_3CH_2CHS, CH_3CH_2S), 1.52–1.66 m (2H, $CHCH_2S$), 1.76 m (2H, $CH_3CH_2CH_2$), 2.27–2.36 m (2H, C^5H_A, C^7H_A), 2.46 q and 2.51 q (CH_3CH_2S), 2.56–2.82 m (6H, C^5H_B, C^6H, C^7H_B, SCH, $CH_3CH_2CH_2$), 5.03–5.14 m (2H, CH_2Ph), 6.96 d ($2H_{arom}$, *J* 7.4 Hz), 7.30–7.40 m ($3H_{arom}$). Mass spectrum, *m/z*: $[M]^+$ 370, $[M + 1]^+$ 371. Found, %: C 71.48; H 8.21; N 7.67; S 8.55. $C_{22}H_{30}N_2OS$. Calculated, %: C 71.31; H 8.16; N 7.56; S 8.65. *M* 370.56.

1-[4-(Methoxy)phenyl]-2-propyl-6-[2-(ethylsulfanyl)propyl]-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVb). Yield 68%. Oily substance. IR spectrum, cm^{-1}: 1675, 1525. ^1H NMR spectrum, δ, ppm: 0.90 t (3H, $CH_3CH_2CH_2$, *J* 7.4 Hz), 1.17 t and 1.20 t (3H, CH_3CH_2S, *J* 7.4 Hz), 1.22 d and 1.23 d (CH_3CHS, *J* 6.6 Hz), 1.50–1.66 m (4H, $CH_3CH_2CH_2$, $CHCH_2S$), 2.18–2.26 m (1H, C^5H_A), 2.30–2.38 m (1H, C^7H_A), 2.40–2.58 m (7H, C^5H_B, C^6H, C^7H_B, CH_3CH_2S, $CH_3CH_2CH_2$), 2.74 m (1H, CHS), 3.87 C (3H, OCH_3), 7.04 d ($2H_{arom}$, *J* 8.5 Hz), 7.24 d ($3H_{arom}$, *J* 8.5 Hz). Mass spectrum, *m/z*: $[M]^+$ 386, $[M + 1]^+$ 387. Found, %: C 68.47; H 7.71; N 7.35; S 8.25. $C_{22}H_{30}N_2O_2S$. Calculated, %: C 68.36; H 7.82; N 7.25; S 8.30. *M* 386.56.

1-Benzyl-2-ethyl-6-[2-(ethylsulfanyl)propyl]-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVc). Yield 58%. Oily substance. IR spectrum, cm^{-1}: 1680, 1545. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.14–1.25 m (9H, CH_3CH_2, CH_3CH_2S, CH_3CH), 1.51–1.60 m (2H, $CHCH_2S$), 2.16–2.24 m (1H, C^5H_A), 2.31–2.53 m

(5H, C^5H_B, C^6H, C^7H_A, CH_3CH_2S), 2.60 m (2H, CCH_2CH_3), 2.72 m and 2.80 m (1H, SCH), 2.87 m (1H, C^7H_B), 5.16 C (2H, CH_2Ph), 7.01 d ($2H_{arom}$, *J* 7.4 Hz), 7.24–7.35 m ($3H_{arom}$). Mass spectrum, *m/z*: $[M]^+$ 356, $[M+1]^+$ 357. Found, %: C 71.81; H 8.05; N 7.77; S 8.85. $C_{21}H_{28}N_2OS$. Calculated, %: C 70.75; H 7.92; N 7.86; S 8.99. *M* 356.53.

1-[4-(Methoxy)phenyl]-2-ethyl-6-[2-(ethylsulfanyl)propyl]-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVd). Yield 63%, mp 90–91°C (from a mixture ether–hexane). IR spectrum, cm^{-1}: 1700, 1525. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.15–1.25 m (9H, CH_3CH_2, CH_3CH_2S, CH_3CH), 1.56 m (2H, $CHCH_2S$), 2.20–2.28 m (1H, C^5H_A), 2.32–2.42 m (1H, C^7H_A), 2.42–2.58 m (7H, C^5H_B, C^6H, C^7H_B, CH_3CH_2S, CH_3CH_2C), 2.75 m (1H, CHS), 3.87 s (3H, OCH_3), 7.05 d ($2H_{arom}$, *J* 8.9 Hz), 7.29 d ($3H_{arom}$, *J* 8.9 Hz). Mass spectrum, *m/z*: $[M]^+$ 372, $[M+1]^+$ 373. Found, %: C 67.66; H 7.65; N 7.57; S 8.65. $C_{21}H_{28}N_2O_2S$. Calculated, %: C 67.71; H 7.58; N 7.52; S 8.61. *M* 372.53.

1-Benzyl-6,6-dimethyl-2-ethyl-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVe). Yield 60%. Oily substance. IR spectrum, cm^{-1}: 1680, 1540. ^1H NMR spectrum, δ, ppm: 1.09 s (6H, CH_3CCH_3), 1.24 t (3H, CH_3CH_2, *J* 7.4 Hz), 2.27 s (2H, C^5H_2), 2.56 s (2H, C^7H_2), 2.59 q (2H, CH_3CH_2, *J* 7.4 Hz), 5.14 s (2H, CH_2Ph), 6.97 d ($2H_{arom}$, *J* 7.4 Hz), 7.23–7.34 m ($3H_{arom}$). Found, %: C 76.68; H 7.91; N 9.97. $[M]^+$ 282. $C_{18}H_{22}N_2O$. Calculated, %: C 76.56; H 7.85; N 9.92. *M* 282.39.

6,6-Dimethyl-1-[(4-methoxy)phenyl]-2-ethyl-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVf). Yield 72%, mp 142–143°C (from toluene). IR spectrum, cm^{-1}: 1680, 1520. ^1H NMR spectrum, δ, ppm: 1.09 s (6H, CH_3CCH_3), 1.19 t (3H, CH_3CH_2, *J* 7.5 Hz), 2.29 s (2H, C^5H_2), 2.42 s (2H, C^7H_2), 2.52 q (2H, CH_3CH_2, *J* 7.5 Hz), 3.87 s (3H, CH_3O), 7.05 d and 7.23 d ($4H_{arom}$, *J* 8.8 Hz). Found, %: C 72.64; H 7.57; N 9.29. $[M]^+$ 298. $C_{18}H_{22}N_2O_2$. Calculated, %: C 72.46; H 7.43; N 9.39. *M* 298.39.

1-Benzyl-6-mesityl-2-ethyl-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVg). Yield 66%. Oily substance. IR spectrum, cm^{-1}: 1680, 1540. ^1H NMR spectrum, δ, ppm: 1.35 s (3H, CH_3CH_2, *J* 7.5 Hz), 2.22 br.s and 2.23 s (6H, $2CH_3Ph$), 2.36 br.s (3H, CH_3Ph), 2.58–2.68 m (2H, C^5H_A, C^7H_A), 2.71 q (2H, CH_3CH_2, *J* 7.5 Hz), 3.12 d.d (1H, C^5H_B, J_1 16.7, J_2 12.2 Hz), 3.24 d.d (1H, C^7H_B, J_1 16.8, J_2 14.1 Hz), 3.99 m (1H, C^6H), 5.04 d and 5.09 d (2H, CH_2Ph, *J* 16.7 Hz), 6.83 s ($2H_{arom}$), 6.95 d ($2H_{arom}$, *J* 7.0 Hz), 7.29–7.36 m ($3H_{arom}$). Found, %: C 80.81; H 7.61; N 7.67. $[M]^+$ 372. $C_{25}H_{28}N_2O$. Calculated, %: C 80.61; H 7.58; N 7.52. *M* 372.51.

1-[(4-Methoxy)phenyl]-6-mesityl-2-ethyl-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVh). Yield 78%, mp 218–220°C (from ethyl acetate). IR spectrum, cm^{-1}: 1700, 1525. ^1H NMR spectrum, δ, ppm: 1.26 s (3H, CH_3CH_2, *J* 7.6 Hz), 2.22 s (3H, CH_3Ph), 2.23 br.s (3H, CH_3), 2.41 br.s (3H, CH_3), 2.51 d.d (1H, C^7H_A, J_1 17.4, J_2 5.3 Hz), 2.66 d.d (1H, C^7H_A, J_1 17.0, J_2 4.2 Hz), 2.81 m (2H, CH_3CH_2), 3.15 d.d (1H, C^5H_B, J_1 17.4, J_2 12.2 Hz), 3.29 d.d (1H, C^7H_B, J_1 17.0, J_2 14.3 Hz), 3.87 s (1H, OCH_3), 4.03 s (1H, C^6H), 6.83 s ($2H_{arom}$), 7.04 d ($2H_{arom}$, *J* 8.9 Hz), 7.23 d ($2H_{arom}$, *J* 8.9 Hz). Found, %: C 77.38; H 7.31; N 7.17. $[M]^+$ 388. $C_{25}H_{28}N_2O_2$. Calculated, %: C 77.29; H 7.26; N 7.21. *M* 388.51.

6-Mesityl-1-phenethyl-2-ethyl-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVi). Yield 70%, mp 201–203°C (from ethyl acetate). IR spectrum, cm^{-1}: 1680, 1545. ^1H NMR spectrum, δ, ppm: 1.27 t (3H, CH_3CH_2, *J* 7.5 Hz), 2.16 s (3H, CH_3Ph), 2.17 d.d (1H, C^5H_A, J_1 16.6, J_2 4.2 Hz), 2.20 br.s and 2.24 C (6H, $2CH_3Ph$), 2.43 d.d (1H, C^7H_A, J_1 16.6, J_2 5.4 Hz), 2.56 q (2H, CH_3CH_2, *J* 7.5 Hz), 2.64 d.d (1H, C^5H_B, J_1 16.6, J_2 12.3 Hz), 2.86–2.94 m (3H, C^7H_B, $PhCH_2CH_2N$), 3.66 m (1H, C^6H), 4.05 m ($PhCH_2CH_2N$), 6.69 s ($2H_{arom}$), 6.96 d ($2H_{arom}$, *J* 6.5 Hz), 7.15–7.21 m ($3H_{arom}$). Found, %: C 80.88; H 7.83; N 7.47. $[M]^+$ 386. $C_{26}H_{30}N_2O$. Calculated, %: C 80.79; H 7.82; N 7.25. *M* 386.54.

1-Methyl-2-ethyl-6-[2-(ethylsulfanyl)propyl]-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVj). Yield 48%, mp 232–236°C (from ethyl acetate). IR spectrum, cm^{-1}: 1665, 1550. ^1H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3CH_2, *J* 7.5 Hz), 2.27 C (3H, CH_3), 2.31 br.s and 2.46 br.s (6H, $2CH_3$), 2.58 d.d (1H, C^5H_A, J_1 16.6, J_2 4.2 Hz), 2.75 q (2H, CH_3CH_2, *J* 7.5 Hz), 2.78 d.d (1H, C^7H_A, J_1 16.6, J_2 5.5 Hz), 3.20–3.32 m (2H, C^5H_B, C^7H_B), 3.49 C (3H, CH_3N), 4.04 m (1H, C^6H), 6.88 C ($2H_{arom}$). Mass spectrum, *m/z*: $[M]^+$ 296, $[M+1]^+$ 297, $[M+2]^+$ 298. Found, %: C 77.09; H 8.30; N 9.37. $C_{19}H_{24}N_2O$. Calculated, %: C 76.99; H 8.16; N 9.45. *M* 296.41.

Methyl 1-benzyl-6,6-dimethyl-4-oxo-2-propyl-4,5,6,7-tetrahydro-1*H*-benzimidazole-5-carboxylate (IVk). Yield 64%, mp 181–183°C (from toluene). IR spectrum, cm^{-1}: 1740, 1685, 1535. ^1H NMR spectrum, δ, ppm: 0.94 t (3H, CH_3CH_2, *J* 7.4 Hz), 1.09 s and 1.11 s (6H, CH_3CCH_3), 1.80 m (2H, CH_3CH_2), 2.23 d (1H, C^7H_A, *J* 16.7 Hz), 2.58 m (2H, $CH_3CH_2CH_2$), 3.09 d (1H, C^7H_B, *J* 16.7 Hz), 3.38 s (1H, C^5H), 3.43 s (3H, OCH_3),

5.08 d and 5.13 d (2H, $PhCH_2N$, *J* 17.1 Hz), 6.87 d ($2H_{arom}$, *J* 7.1 Hz), 7.29–7.36 m ($3H_{arom}$). Mass spectrum, *m/z*: $[M]^+$ 354, $[M+1]^+$ 355. Found, %: C 71.08; H 7.56; N 8.08. $C_{21}H_{26}N_2O_3$. Calculated, %: C 71.16; H 7.39; N 7.90. *M* 354.45.

Methyl 6,6-dimethyl-1-[4-(methoxy)-phenyl]-4-oxo-2-propyl-4,5,6,7-tetrahydro-1*H*-benzimidazole-5-carboxylate (IVl). Yield 54%, mp 200–202°C (from toluene). IR spectrum, cm^{-1}: 1745, 1690, 1525. ^1H NMR spectrum, δ, ppm: 0.87 t (3H, CH_3CH_2, *J* 7.4 Hz), 1.13 s and 1.16 s (6H, CH_3CCH_3), 1.64–1.72 m (2H, CH_3CH_2), 2.19 d (1H, C^7H_A, *J* 16.7 Hz), 2.51 m (2H, $CH_3CH_2CH_2$), 2.99 d (1H, C^7H_B, *J* 16.7 Hz), 3.32 s (1H, C^5H), 3.70 s (3H, OCH_3), 3.89 s (3H, $PhOCH_3$), 7.03 d ($2H_{arom}$, *J* 8.9 Hz), 7.16 d ($2H_{arom}$, *J* 8.9 Hz). Found, %: C 68.22; H 7.06; N 7.40. $[M]^+$ 370. $C_{21}H_{26}N_2O_4$. Calculated, %: C 68.09; H 7.07; N 7.56. *M* 370.45.

Methyl 6,6-dimethyl-1-[4-(methoxy)-phenyl]-4-oxo-2-propyl-4,5,6,7-tetrahydro-1*H*-benzimidazole-7-carboxylate (IVm). Yield 28%. Oily substance. IR spectrum, cm^{-1}: 1745, 1700, 1525. ^1H NMR spectrum, δ, ppm: 0.87 t (3H, CH_3CH_2, *J* 7.4 Hz), 1.10 s and 1.17 s (6H, CH_3CCH_3), 1.64–1.72 m (2H, CH_3CH_2), 2.27 d (1H, C^5H_A, *J* 16.5 Hz), 2.43 m (2H, $CH_3CH_2CH_2$), 2.93 d (1H, C^5H_B, *J* 16.5 Hz), 3.28 s (1H, C^7H), 3.55 s (3H, OCH_3), 3.88 s (3H, $PhOCH_3$), 7.00 br.s and 7.13 br.s ($4H_{arom}$). Found, %: C 68.02; H 7.19; N 7.65. $[M]^+$ 370. $C_{21}H_{26}N_2O_4$. Calculated, %: C 68.09; H 7.07; N 7.56. *M* 370.45.

6-Mesityl-2-ethyl-6,7-dihydro-1,3-benzoxazol-4(5*H*)-one O-ethyloxime (Va). In 20 ml of ethanol was dissolved 1 g (3.6 mmol)of benzoxazolone **IIb**, and 0.27 g (4.4 mmol) of O-ethylhydroxylamine was added. The mixture was heated at reflux for 24 h. The solvent was removed on a rotary evaporator, and the residue was crystallized from toluene. Yield 1 g (90%), crystalline substance, mp 112–114°C. IR spectrum, cm^{-1}: 1660, 1630, 1590. ^1H NMR spectrum, δ, ppm: 1.30 t (3H, CH_3CH_2O, *J* 7.0 Hz), 1.40 t (3H, CH_3CH_2C, *J* 7.6 Hz), 2.31 s [3H, 4'-(CH_3)Ph], 2.36 br.s and 2.47 br.s [6H, 2',6'-$(CH_3)_2$Ph], 2.80–2.90 m (2H, C^4H_A, C^6H_A), 2.87 q (2H, CH_3CH_2C, *J* 7.6 Hz), 3.25–3.33 m (2H, C^4H_B, C^6H_B), 3.77 m (1H, C^5H), 4.25–4.31 m (2H, CH_3CH_2O), 6.92 s ($2H_{arom}$). Found, %: C 73.47; H 8.14; N 8.69. $[M]^+$ 326. $C_{20}H_{26}N_2O_2$. Calculated, %: C 73.59; H 8.03; N 8.58. *M* 326.44.

2-Propyl-6-[2-(ethylsulfanyl)propyl]-6,7-dihydro-1,3-benzoxazol-4(5*H*)-one O-ethyloxime (Vb) was obtained like compound **Va** and purified by column chromatography on silica gel, eluent petroleum ether–ethyl acetate. Yield 0.49 g (42%), oily substance. IR spectrum, cm^{-1}: 1740, 1660, 1590. ^1H NMR spectrum (DMSO-d_6), δ, ppm (diastereomers mixture 1:1): 1.01 t and 1.02 t (3H, $CH_3CH_2CH_2$, *J* 7.4 Hz), 1.23 t and 1.24 t (3H, CH_3CH_2S, *J* 7.4 Hz), 1.26–1.31 m (6H, CH_3CHS, CH_3CH_2O), 1.51–1.67 m (2H, CH_2CHS), 1.78 m (2H, $CH_3CH_2CH_2$), 2.01 m (1H, C^6H_A), 2.26 m (1H, C^5H), 2.38 m (1H, C^4H_A), 2.51 q and 2.52 q (2H, CH_3CH_2S, *J* 7.4 Hz), 2.68 t (2H, $CH_3CH_2CH_2$, *J* 7.4 Hz), 2.82 m (1H, SCH), 2.86 m (1H, C^6H_B), 3.01 m (1H, C^4H_B), 4.09 m and 4.20 m (2H, CH_3CH_2O). Mass spectrum, *m/z*: $[M]^+$ 324, $[M+1]^+$ 325, $[M+2]^+$ 326. Found, %: C 63.11; H 8.73; N 8.59, S 9.99. $C_{17}H_{28}N_2O_2S$. Calculated, %: C 62.93; H 8.70; N 8.63, S 9.88. *M* 324.48.

6-Mesityl-2-ethyl-1-ethoxy-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVn). A mixture of 0.2 g (0.63 mmol) of benzoxazole **Va** and 3 ml of concn. HCl was heated for 30 min hill the disappearance of the initial compound (TLC monitoring). The mixture was diluted with 10 ml of water and extracted with chloroform (2×10 ml). The combined extracts were washed with water, dried with sodium sulfate, and evaporated on a rotary evaporator. The residue was crystallized from ethyl acetate. Yield 0.17 g (86%), crystalline substance, mp 136–138°C. IR spectrum, cm^{-1}: 1690, 1550. ^1H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3CH_2, *J* 7.5 Hz), 1.40 t (3H, CH_3CH_2O, *J* 7.0 Hz), 2.27 s (3H, CH_3), 2.32 s (3H, CH_3), 2.47 s (3H, CH_3), 2.60 d.d (1H, C^7H_A, J_1 16.9, J_2 4.1 Hz), 2.80 q (2H, CH_3CH_2, *J* 7.5 Hz), 2.92 d.d (1H, C^5H_A, J_1 16.6, J_2 5.4 Hz), 3.20–3.38 m (2H, C^5H_B, C^7H_B), 4.03 m (1H, C^6H), 4.21 q (2H, CH_3CH_2O, *J* 7.05 Hz), 6.90 s ($2H_{arom}$). Found, %: C 73.48; H 7.98; N 8.47. $[M]^+$ 326. $C_{20}H_{26}N_2O_2$. Calculated, %: C 73.59; H 8.03; N 8.58. *M* 326.44.

2-Ethyl-1-ethoxy-6-[2-(ethylsulfanyl)propyl]-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (IVo) was similarly obtained from benzoxazole **Vb** and purified by column chromatography on silica gel, eluent chloroform–ethanol. Yield 59%. Oily substance. IR spectrum, cm^{-1}: 1685, 1550. ^1H NMR spectrum, δ, ppm: 1.00 m (3H, $CH_3CH_2CH_2$, *J* 7.4 Hz), 1.25 t and 1.26 t (3H, CH_3CH_2S, *J* 7.4 Hz), 1.30 d and 1.31 d (3H, CH_3CHS, *J* 6.7 Hz), 1.37 t (3H, CH_3CH_2O, *J* 7.0 Hz), 1.57 m and 1.70 m (2H, CH_2CHS), 1.78 m (2H, $CH_3CH_2CH_2$), 2.20–2.29 m (1H, C^7H_A), 2.38–2.48 m (2H, C^5H_A, C^6H), 2.56 m (2H, CH_3CH_2S), 2.56–2.64 m (1H, C^7H_B), 2.78 t (2H, $CH_3CH_2CH_2$, *J* 7.4 Hz), 2.84–2.97 m (2H, C^5H_B, SCH), 4.23 q (2H, CH_3CH_2O, *J* 7.0 Hz). Mass spectrum, *m/z*:

$[M]^+$ 324, $[M+1]^+$ 325, $[M+2]^+$ 326. Found, %: C 63.09; H 8.82; S 9.80. $C_{17}H_{28}N_2O_2S$. Calculated, %: C 62.93; H 8.70; S 9.88. *M* 324.49.

2-Amino-5,5-dimethylcyclohexane-1,3-dione hydrochloride (VIa). In 5 ml of concn. HCl was boiled 1 g (5.18 mmol) of benzoxazolone **IIc** for 30 min, the reaction mixture was evaporated on a rotary evaporator till syrup-like residue, 15 ml of water was added thereto, the separated crystals were filtered off, washed with water on the filter, then with chloroform, and dried in a vacuum. Yield 0.87 g (88%), yellowish-brown crystals, mp 125°C (decomp.). IR spectrum, cm^{-1}: 1680, 1630, 1570. ^1H NMR spectrum, δ, ppm: 1.08 s (6H, CH_3CCH_3), 2.44 br.s (4H, $2CH_2$), 9.15 br.s (1H, OH enol). Salt **VIa** was also obtained by this procedure from benzoxazolone **III** (yield 85%).

2-Amino-5-mesitylcyclohexane-1,3-dione hydrochloride (VIb) was obtained likewise from benzoxazolone **IIb**. Yield 0.85 g (85%), mp 240°C (decomp.). IR spectrum, cm^{-1}: 1650, 1570, 1500. ^1H NMR spectrum, δ, ppm: 2.18 s (3H, CH_3), 2.33 s (6H, $2CH_3$), 2.54 br.d (2H, CH_2, *J* 17.0 Hz), 3.10 d.d (2H, CH_2, J_1 17.0, J_1 13.6 Hz), 3.74 m (1H, C^5H), 6.83 s (2H, C_6H_2), 9.10 br.s (1H, OH enol).

2-Amino-5-mesitylcyclohexane-1,3-dione (VII). To a solution of 0.28 g (1 mmol) of salt **VIb** in 10 ml of methanol was added an equimolar quantity of NaOH in water, methanol was distilled off in a vacuum, the residue was diluted with water, the reaction product was extracted into ethyl acetate, the organic extracts were dried with sodium sulfate, evaporated on a rotary evaporator, and the residue was dried in a vacuum. Yield 0.23 g (92%). Colorless crystals, mp 150°C (decomp.). IR spectrum, cm^{-1}: 1620, 1510. ^1H NMR spectrum, δ, ppm: 2.04 d.d (1H, C^6H_A, J_1 16.7, J_1 4.5 Hz), 2.14 s (3H, CH_3), 2.17 m (1H, C^6H_B), 2.27 br.s (6H, $2CH_3$), 2.34 m (1H, C^4H_A), 2.79 d.d (1H, C^4H_B, J_1 15.9, J_1 13.8 Hz), 3.62 m (1H, C^5H), 6.76 s (2H, C_6H_2). Found, %: C 73.58; H 7.71; N 5.68. $[M]^+$ 245. $C_{15}H_{19}NO_2$. Calculated, %: C 73.44; H 7.81; N 5.71. *M* 245.32.

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