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Mukaiyama Reagents in the Synthesis of (*E*)-2-(1*H*-Benzo[*d*]imidazol-2-yl)-2-[1-alkylpyridin-2(1*H*)-ylidene]acetonitriles and Their Further Electronic Rearrangements Effected by the Action of Acids and Alkylating Agents

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Abstract—Reactions of *N*-alkyl-2-chloropyridinium salts with benzimidazolylacetonitriles result in (*E*)-2-(1*H*-benzo[*d*]imidazol-2-yl)-2-[1-alkylpyridin-2(1*H*)-ylidene]acetonitriles. The alkylation of the latter with ω-bromoacetophenones in boiling acetone may gives rise to the *N*-alkylated salts, which are stabilized in two configurations, *Z* and *E*. The heating of the salts in acetonitrile causes their transformation into 2-({1*H*-benzo[*d*]-imidazol-2(3*H*)-ylidene}(cyano)methyl)-1-methylpyridinium bromide due to the dearoylmethylation. The structure of the latter was proved by the XRD analysis.

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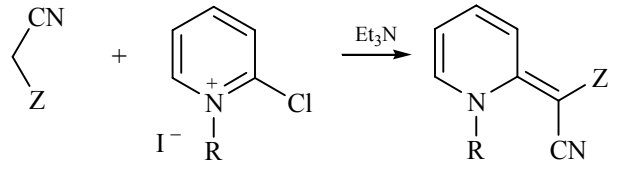
We have shown previously [1] that CH-acids, malonodinitrile derivatives **Ia–Ig**, react with 2-halopyridinium salts **IIa** and **IIb**, known as Mukaiyama reagents [2, 3], to substitute α-halogen atom by the nucleophilic mechanism. The end products are 2-[1-methylpyridin-2(1*H*)-ylidene]malononitrile derivatives **IIIa–IIIk**.



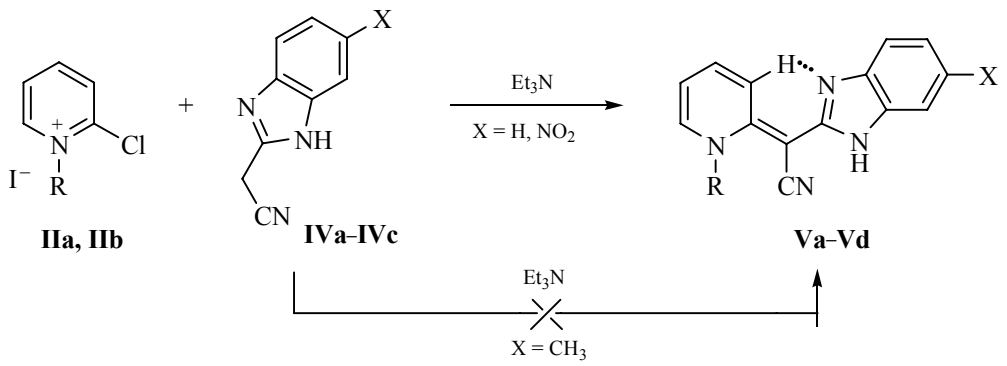
Ia–Ig **IIa, IIb** **IIIa–IIIj**

I, Z = CN (**a**), $CO_2CH_2CH_3$ (**b**), $C(NH_2)C(CN)_2$ (**c**), 3-phenylthiazolyl (**d**), 3-(4-chloro)phenylthiazolyl (**e**), 3-(2-methoxy)phenylthiazolyl (**f**), 3-(3-nitro)phenylthiazolyl (**g**); **II**, R = CH_3 (**a**), CH_2CH_3 (**b**); **III**, Z = CN, R = CH_3 (**a**); Z = CN, R = CH_2CH_3 (**b**); Z = $CO_2CH_2CH_3$, R = CH_3 (**c**); Z = $C(NH_2)C(CN)_2$, R = CH_3 (**d**); Z = $C(NH_2)C(CN)_2$, R = CH_2CH_3 (**e**); Z = 3-phenylthiazolyl, R = CH_3 (**f**); Z = 3-(4-chloro)phenylthiazolyl, R = CH_3 (**g**); Z = 3-(2-methoxy)phenylthiazolyl, R = CH_3 (**h**); Z = 3-(3-nitro)phenylthiazolyl, R = CH_3 (**i**); Z = 3-(4-chloro)phenylthiazolyl, R = CH_2CH_3 (**k**).

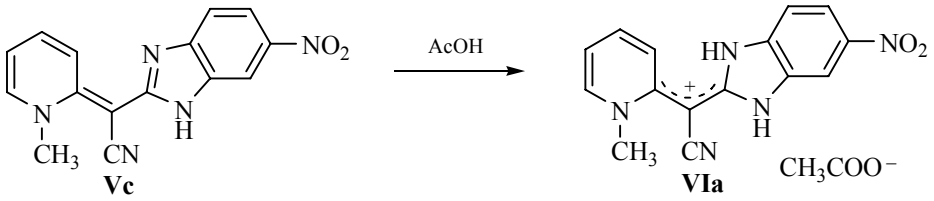
Continuing the study, we introduced 2-benzoimidazolylacetonitriles **IVa–IVc** into this reaction as the CH-acids. The reactions of unsubstituted (**IVa**) and 6-nitrosubstituted (**IVb**) 2-benzimidazolylacetonitriles were found to give only (*E*)-2-(1*H*-benzo[*d*]imidazol-2-yl)-2-[1-alkylpyridin-2(1*H*)-ylidene]acetonitriles **Va–Vd** that well correlates with the previous results [1]. However, 6-methylsubstituted 2-benzimidazolylacetonitrile **IVc** does not react with the Mukaiyama reagents **II** under similar conditions probably due to lower CH-acidity of the initial acetonitrile.

In the ^{1}H NMR spectra of acetonitriles **Va–Vd** the signals of pyridine C^3H-protons (*J* 8.73–9.43 Hz) are shifted downfield to δ 8.38–8.69 ppm as compared to *N*-alkyl-2(1*H*)-dicyanomethylene pyridines (δ 7.16–7.22 ppm) [1], indicating the probability of the intramolecular hydrogen bonding between the protons and nitrogen atom of the imidazole ring. A similar shift we observed previously by an example of compounds **III**, where Z = 2-thiazolyl and ethoxycarbonyl [1].

The recrystallization of compound **Vc** from acetic acid results in a salt **VIa**.



II, R = CH_3 (a), R = CH_2CH_3 (**b**); **IV**, X = H (**a**), NO_2 (**b**), CH_3 (**c**); **V**, R = CH_3, X = H (**a**); R = CH_2CH_3, X = H (**b**); R = CH_3, X = NO_2 (**c**); R = CH_2CH_3,



In the ^{1}H NMR spectrum of **VIa** the signal of C^3H-pyridine proton is shifted upfield (δ 7.44 ppm) compared with the initial acetonitrile (δ 8.53 ppm) and appears as a doublet of doublets with constants *J* 9.40 and 6.82 Hz. This can be due to the fact that in the salt **VIa** C^3H-proton is not involved into the formation of an intramolecular hydrogen bond with the nitrogen atom of the benzimidazole fragment.

The alkylation of compound **Va** with ω-bromoacetophenones **VIIa–VIIc** (X = H, Cl, OCH_3) results in salts **VIb** (X = H) and **VIIIa, VIIIb** (X = Cl, OCH_3) as a mixture of two stable *Z*- and *E*-conformers (1:1). In the ^{1}H NMR spectra of the salts **VIIIa** and **VIIIb** the signals of pyridine and *N*-methyl protons appear in different regions. Thus, the signals of the protons of Z-conformer are shifted upfield in comparison with those of *E*-conformer. Probably, in the *Z*-isomers of **VIIIa** and **VIIIb** the pyridine protons are shielded with the aromatic ring of *N*-aroylmethyl fragment. In the case of *E*-configuration the shielding effect is absent, and the pyridine signals appear roughly in the same region as the signals of this fragment in the salts **VIa** and **VIb**. Compounds **VIIIa** and **VIIIb** are very labile and transform easily into bromide **VIb** on heating in acetonitrile. Its structure was proved by the XRD analysis (Figs 1, 2, Tables 1, 2).

According to the XRD data, in crystalline state compound **VIb** is a monohydrate salt of an organic

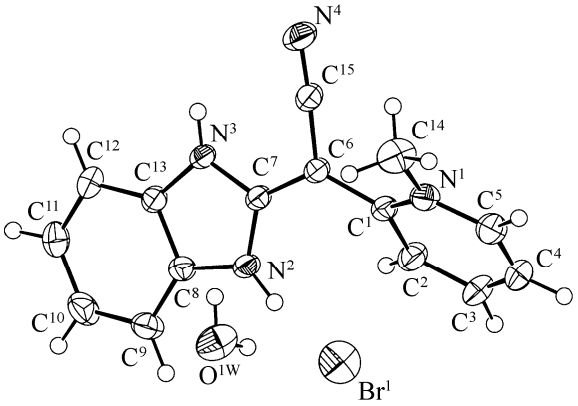


Fig. 1. General view of the molecule of **VIb** according to the X-ray data.

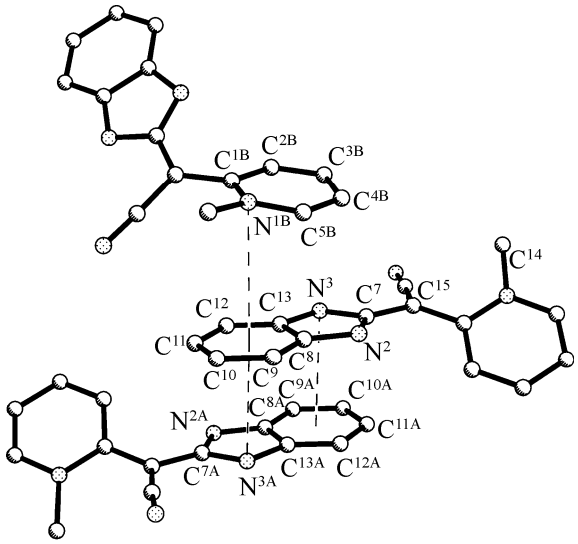


Fig. 2. Stacking interactions in **VIb** structure.

Table 1. Bonds lengths (*d*, Å) in **VIb** structure

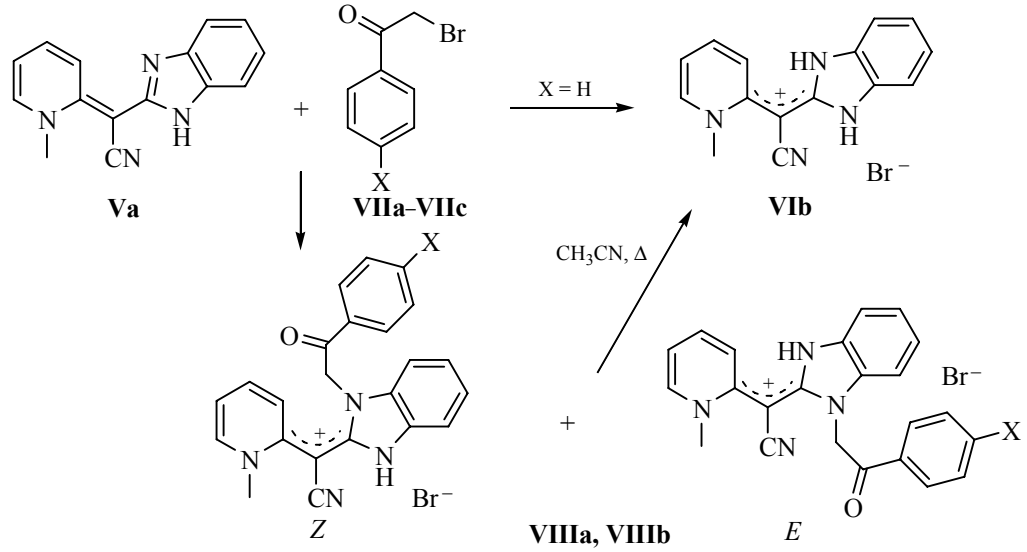
Bond	*d*	Bond	*d*
N^1–C^1	1.369(3)	C^3–C^4	1.378(4)
N^1–C^5	1.365(3)	C^4–C^5	1.364(5)
N^1–C^{14}	1.473(4)	C^6–C^7	1.421(3)
N^2–C^7	1.346(3)	C^6–C^{15}	1.405(3)
N^2–C^8	1.392(3)	C^8–C^9	1.389(3)
N^3–C^7	1.350(3)	C^8–C^{13}	1.389(3)
N^3–C^{13}	1.385(3)	C^9–C^{10}	1.387(4)
N^4–C^{15}	1.148(3)	C^{10}–C^{11}	1.386(4)
C^1–C^2	1.403(3)	C^{11}–C^{12}	1.384(4)
C^1–C^6	1.443(3)	C^{12}–C^{13}	1.390(3)
C^2–C^3	1.373(3)		

Table 2. Bonds angles (ω, deg) in **VIb** structure

Angle	ω	Angle	ω
$N^1C^1C^2$	117.2(2)	$C^5C^4C^3$	118.6(2)
$N^1C^1C^6$	120.4(2)	$C^7N^2C^8$	109.27(17)
$N^2C^7N^3$	107.95(19)	$C^7N^3C^{13}$	109.64(18)
$N^2C^7C^6$	128.54(19)	$C^7C^6C^1$	123.5(2)
$N^3C^7C^6$	123.5(2)	$C^8C^{13}C^{12}$	121.7(2)
$N^3C^{13}C^8$	106.44(18)	$C^9C^8N^2$	131.4(2)
$N^3C^{13}C^{12}$	131.9(2)	$C^9C^8C^{13}$	121.9(2)
$N^4C^{15}C^6$	175.7(3)	$C^{10}C^9C^8$	116.1(2)
$C^1N^1C^{14}$	121.8(2)	$C^{11}C^{10}C^9$	122.0(2)
$C^2C^1C^6$	122.4(2)	$C^{11}C^{12}C^{13}$	116.4(2)
$C^2C^3C^4$	119.8(3)	$C^{12}C^{11}C^{10}$	121.9(2)
$C^3C^2C^1$	121.4(2)	$C^{13}C^8N^2$	106.69(19)
$C^4C^5N^1$	121.8(3)	$C^{15}C^6C^1$	121.8(2)
$C^5N^1C^1$	121.0(2)	$C^{15}C^6C^7$	113.42(19)
$C^5N^1C^{14}$	117.0(2)		

cation with bromide anion. The nitrile group lies almost in the plane of benzimidazole ring [torsion angle $C^{15}C^6C^7N^2$ –175.4(2)°]. The pyridine ring is turned out relative to this fragment [torsion angle $N^1C^1C^6C^{15}$ 41.0(3)°] due to the steric repulsion between the nitrile and methyl groups (shortened intramolecular contact $C^{14}\cdots C^{15}$ 2.89 Å at the van der Waals radii sum of 3.42 Å [4]). The positive charge of the cation is probably localized mainly on the C^6 carbon atom as evidenced by the close values of the bond lengths C^6–C^1 1.443(3) Å and C^6–C^7 1.421(3) Å, which are intermediate between the average values for the double and single bonds (1.32 and 1.46 Å, respectively [5]), as well as shortening of the C^6–C^{15} bond to 1.405(3) Å compared with an average value (1.43 Å).

In the crystal, the cations are bound into centrosymmetric dimers by hydrogen bonds N^3–$H^3\cdots N^{4(i)}$ [i: –*x*, –*y*, –*z*] (H···N 2.12 Å, N–H···N 157°). The bromide anions and water molecules form chains along the crystallographic *b* axis by the hydrogen bonds O^{1W}–$H^{1WB}\cdots Br^1$ (H···Br 2.39 Å, O–H···Br 176°) and O^{1W}–$H^{1WA}\cdots Br^{1(ii)}$ [ii: 1 – *x*, –1/2 + *y*, 1/2 – *z*] (H···Br 2.37 Å, O–H···Br 175°). These chains are bound with the cations by the hydrogen bonds N^2–$H^2\cdots O^{1W(iii)}$ [iii: 1 – *x*, 1/2 + *y*, 1/2 – *z*] (H···O 1.86 Å, N–H···O 163°) и C^5–$H^5\cdots Br^{1(iv)}$ [iv: 1 – *x*, –*y*, 1 – *z*] (H···Br 2.79 Å, C–H···Br 170°). Also in the crystal each cation is linked through the stacking interactions with two neighboring cations (A and B) located above and below the benzimidazole fragment of the base molecule. The benzimidazole fragment of the molecule A is oriented strictly parallel to the corresponding



VII, X = H (**a**), Cl (**b**), OCH_3 (**c**); **VIII**, X = Cl (**a**), OCH_3 (**b**).

fragment of the base molecule, and the pyridine fragment of the molecule B at a 13° angle; the shortest distances C···C (Å) are: $C^{13}\cdots C^{13A}$ 3.32, $C^{7}\cdots C^{11A}$ 3.34 [A: $-x$, $1-y$, $-z$] and $C^{8}\cdots C^{5B}$ 3.36 [B: x, $0.5-y$, $-0.5+z$].

EXPERIMENTAL

The IR spectra were recorded on an IKS-40 instrument for the samples in mineral oil (**Va, Vb**) and Spectrum One (Perkin-Elmer) spectrometer from KBr pellets (**Vc, Vd, VIb, VIIb**). The ^{1}H NMR spectra were registered on a Varian VRX-200 (200 MHz) (**Va, Vb, VIa**) and Bruker Avance II-400 (400 MHz) spectrometers in DMSO-d_6 (**Vc, Vd, VIb, VIIa, VIIb**) and F_3CCOOH (**VIIIa, VIIIb**) relative to internal TMS. The mass spectra were recorded on a MKh-1321 (**Vb, Vc, Vd, VIb**) and Varian 1200 L spectrometers (**Va, VIa, VIIa**) (70 eV) with direct sample admission into the ion source. The melting points were determined on a Koeffler block. The reaction progress and the purity of compounds obtained were monitored by TLC on Silufol UV 254 plates eluting with acetone–hexane mixture (3:5) and detecting with iodine vapors or UV irradiation.

The crystals of compound **VIb** at 298 K are monoclinic, $C_{15}H_{13}N_4^+\cdot Br^-\cdot H_2O$: a 14.1653(8), b 8.4549(3), c 14.0844(7) Å; V 1498.07(12) Å^3; M 347.22; Z 4; space group $P21/c$, d_{calc} 1.54 g cm^{-3}, μ(MoK_α) 2.75 mm^{-1}; F(000) 704. The unit cell parameters and intensities of 23557 reflections (4904 independent, R_{int} 0.026) were measured on a Xcalibur 3 automatic four-circle diffractometer (MoK_α, graphite monochromator, CCD detector, ω-scanning, $2\theta_{max}$ 32.17°). The extinction was accounted for non-empirically (T_{min} 0.41, T_{max} 0.56). The structure was solved by the direct method using a SHELX-97 software [6]. The positions of the hydrogen atoms were calculated geometrically and refined in a *rider* model with $U_{iso} = nU_{eq}$ of the carrier atom (n = 1.5 for methyl groups and water molecules, n = 1.2 for the remaining hydrogen atoms). The structure was refined with respect to F_2 using a least-squares full-matrix method in anisotropic approximation for the non-hydrogen atoms to wR_2 0.181 for 4904 reflections (R_1 0.055 for 3743 reflections with $F > 4\sigma(F)$, S = 1.03). The bond lengths and angles are given in Tables 1 and 2, respectively. The crystallographic parameters, atomic coordinates, as well as complete tables of the bond lengths and bond angles are deposited in the Cambridge Structural Database (CCDC 806094). (*E*)-2-[1-Alkylpyridin-2(1*H*)-ylidene]-2-(1*H*-benzo[*d*]imidazol-2-yl)acetonitriles **Va–Vd** were obtained by the procedure [1].

(*E*)-2-(1*H*-Benzo[*d*]imidazol-2-yl)-2-[1-methylpyridin-2(1*H*)-ylidene]acetonitrile (Va). Yield 0.322 g (52%), orange powder, mp 285–286°C (EtOH). IR spectrum, ν, cm^{-1}: 3404 (N–H), 2171 (C≡N). ^{1}H NMR spectrum, δ, ppm: 3.82 s (3H, CH_3), 6.66 d.d (1H, C^5H, J 6.71, 5.38 Hz), 7.00 d.d (2H, $CH_{benzimidazole}$, J 5.95, 3.17 Hz), 7.34 d.d (2H, $CH_{benzimidazole}$, J 5.95, 3.17 Hz), 7.42–7.55 m (1H, C^4H), 7.88 d (1H, C^6H, J 6.40 Hz), 8.38 d (1H, C^3H, J 9.43 Hz), 11.71 s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 248 (100) $[M]^+$, 158 (13), 208 (15), 220 (25), 232 (16), 247 (35), 249 (18). Found, %: C 72.50; H 4.92; N 22.51. $C_{15}H_{12}N_4$. Calculated, %: C 72.56; H 4.87; N 22.57.

(*E*)-2-(1*H*-Benzo[*d*]imidazol-2-yl)-2-[1-ethylpyridin-2(1*H*)-ylidene]acetonitrile (Vb). Yield 0.452 g (69%), red crystals, mp 252°C (EtOH). IR spectrum, ν, cm^{-1}: 3403 (N–H), 2170 (C≡N). ^{1}H NMR spectrum, δ, ppm: 1.40 t (3H, CH_3, J 7.05 Hz), 4.40 q (2H, CH_2, J 7.05 Hz), 6.65 t (1H, C^5H, J 6.67 Hz), 7.01 d.d (2H, $CH_{benzimidazole}$, J 5.77, 3.08 Hz), 7.21–7.55 m (3H, H_{Ar}), 7.87 d (1H, C^6H, J 6.67 Hz), 8.53 d (1H, C^3H, J 9.25 Hz), 11.71 s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 262 (100) $[M]^+$, 145 (36), 208 (13). Found, %: C 73.20; H 5.45; N 21.31. $C_{16}H_{14}N_4$. Calculated, %: C 73.26; H 5.38; N 21.36.

(*E*)-2-[1-Methylpyridin-2(1*H*)-ylidene]-2-(6-nitro-1*H*-benzo[*d*]imidazol-2-yl)acetonitrile (Vc). Yield 0.453 g (62%), red powder, mp 280–282°C (EtOH). IR spectrum, ν, cm^{-1}: 3435 (N–H), 2177 (C≡N). ^{1}H NMR spectrum, δ, ppm: 3.98 s (3H, CH_3), 6.94 t (1H, C^5H, J 5.73 Hz), 7.42 d (1H, $C^4H_{benzimidazole}$, J 8.40 Hz), 7.72 t (1H, C^4H, J 8.73 Hz), 7.97 d (1H, $C^5H_{benzimidazole}$, J 8.40 Hz), 8.13 s (2H, C^6H, $C^7H_{benzimidazole}$), 8.53 d (1H, C^3H, J 8.73 Hz), 12.23 s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 294 (75) $[M+1]^+$, 154 (100). Found, %: C 61.49; H 3.72; N 23.82. $C_{15}H_{11}N_5O_2$. Calculated, %: C 61.43; H 3.78; N 23.88.

(*E*)-2-(6-Nitro-1*H*-benzo[*d*]imidazol-2-yl)-2-[1-ethylpyridin-2(1*H*)-ylidene]acetonitrile (Vd). Yield 0.498 g (65%), red powder, mp >300°C (decomp., EtOH). IR spectrum, ν, cm^{-1}: 3435 (N–H), 2168 (C≡N). ^{1}H NMR spectrum, δ, ppm: 1.47 t (3H, CH_3, J 7.08 Hz), 4.50 q (2H, CH_2, J 7.08 Hz), 6.94 br. s (1H, C^5H), 7.43 d [1H, $C^4H(C^7H)_{benzimidazole}$, J 8.78 Hz], 7.68 br.s (1H, C^4H), 7.97 d.d [1H, $C^5H(C^6H)_{benzimidazole}$, J 8.78, 2.19 Hz], 8.14 br.s [2H, C^6H, $C^7H(C^4H)_{benzimidazole}$], 8.69 d (1H, C^3H, J 9.03 Hz), 12.24 br. s and 12.09 br.s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 307 (100) $[M]^+$, 78 (8), 144 (21), 190 (22), 233 (16). Found, %: C 62.58; H 4.22; N 22.73. $C_{16}H_{13}N_5O_2$. Calculated, %: C 62.53; H 4.26; N 22.79.

2-{Cyano(5-nitro-1*H*-benzo[*d*]imidazol-2(3*H*)-ylidene)methyl}-1-methylpyridinium acetate (VIa). Acetonitrile **Vc** (0.5 mmol) was heated in 10 ml of acetic acid to full dissolution and filtered. After 24 h the formed precipitate was filtered off and washed sequentially with acetic acid and acetone. Yield 0.159 g (90%), red powder, mp 199–202°C (CH_3COOH). ^1H NMR spectrum, δ, ppm: 1.88 s (3H, CH_3COO), 4.06 s (3H, CH_3), 7.32 t (1H, C^5H, *J* 6.82 Hz), 7.44 d.d (1H, C^3H, *J* 9.40, 6.82 Hz), 7.21–7.55 m (3H, H_{Ar}), 7.92–8.20 m [3H, C^4H, $C^4H(C^7H)_{benzimidazole}$, $C^7H(C^4H)_{benzimidazole}$], 8.33 d [1H, $C^5H(C^6H)_{benzimidazole}$, *J* 8.50 Hz], 8.46 d (1H, C^6H, *J* 6.82 Hz), NH-proton exchanges with water. Mass spectrum, *m*/*z* (I_{rel}, %): 293 (100) $[M - 1]^+$, 118 (7), 157 (8), 176 (8), 246 (11), 294 (17), 295 (2). Found, %: C 57.72; H 4.23; N 19.88. $C_{17}H_{15}N_5O_4$. Calculated, %: C 57.79; H 4.28; N 19.82.

2-({1*H*-Benzo[*d*]imidazol-2(3*H*)-ylidene}(cyano)-methyl)-1-methylpyridinium bromide (VIb). *a*. To a suspension of 1.0 mmol of acetonitrile **Va** in 10 ml of acetone was added 1.0 mmol of bromoacetophenone **VIIa**. The reaction mixture was refluxed for 4–6 h. After 24 h acetone was evaporated, the residue was triturated with 10 ml of acetonitrile. The formed precipitate was filtered off and washed with acetonitrile. Yield 0.226 g (69%, bromoacetophenone), yellow crystals, mp 252°C (CH_3CN).

b. The salts **VIIa** and **VIIb** (1.0 mmol) were heated in 20 ml of acetonitrile to full dissolution and filtered. After 24 h the formed precipitate was filtered off and washed with acetonitrile. Yield 0.243 g (70%, *p*-chlorobromoacetophenone), yellow crystals, mp 170°C (CH_3CN) (monohydrate **VIb**); 0.249 g (76%, *p*-methoxybromoacetophenone), mp 252°C (CH_3CN). IR spectrum, ν, cm^{-1}: 3128, 3187, 3295 (N–H), 2180 (C≡N). ^1H NMR spectrum, δ, ppm: 4.08 s (3H, CH_3), 7.26 d.d (2H, $CH_{benzimidazole}$, *J* 3.50, 5.06 Hz), 7.41 d.d (2H, $CH_{benzimidazole}$, *J* 3.50, 5.06 Hz), 7.49 t (1H, C^5H, *J* 6.80 Hz), 8.05 d (1H, C^3H, *J* 8.44 Hz), 8.13 t (1H, C^4H, *J* 8.44 Hz), 8.63 d (1H, C^6H, *J* 6.80 Hz), 13.03 s (2H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 249 (100) $[M]^+$. Found, %: C 54.78; H 3.91; N 17.09. $C_{15}H_{13}N_4Br$. Calculated, %: C 54.73; H 3.98; N 17.02. Found, %: C 51.80; H 4.41; N 16.09. $C_{15}H_{15}N_4BrO$ (monohydrate). Calculated, %: C 51.89; H 4.35; N 16.14.

General procedure of preparation of compounds VIIIa and VIIIb. To a suspension of 1.0 mmol of acetonitrile **Va** in 10 ml of acetone was added 1.0 mmol of the corresponding ω-bromoacetophenones **VIIb** and **VIIc**. The reaction mixture was refluxed for 4–6 h. After 24 h the precipitate was filtered off and washed with acetone.

(*E*,*Z*)-2-({1-[2-(4-Chlorophenyl)-2-oxoethyl]-1*H*-benzo[*d*]imidazol-2(3*H*)-ylidene}(cyano)methyl)-1-methylpyridinium bromide (VIIIa). Yield 0.295 g (61%), yellow powder, mp 228°C (CH_3COCH_3). ^1H NMR spectrum, δ, ppm: 4.02 s (3H, CH_3, *Z*), 4.14 s (3H, CH_3, *E*), 6.11 br. s (2H, CH_2), 6.98 t (1H, C^5H, *J* 6.55 Hz, *Z*), 7.14 d (1H, C^3H, *J* 8.58 Hz, *Z*), 7.23 d.d (1H, $CH_{benzimidazole}$, *J* 5.88, 3.17 Hz), 7.42–7.46 m [1H, C^5H (*E*), 1H, $CH_{benzimidazole}$], 7.53 d.d (1H, $CH_{benzimidazole}$, *J* 6.13, 3.09 Hz), 7.58 d (2H, CH_{Ar}, *J* 8.51 Hz), 7.66 t (1H, C^4H, *J* 8.58 Hz, *Z*), 7.81 d.d (1H, $CH_{benzimidazole}$, *J* 6.13, 3.09 Hz), 7.98 d (1H, C^3H, *J* 8.58 Hz, *E*), 8.07–8.14 m [1H, C^4H (*E*), 2H, CH_{Ar}], 8.32 d (1H, C^6H, *J* 6.55 Hz, *Z*), 8.67 d (1H, C^6H, *J* 6.51 Hz, *E*); NH-proton was not detected in DMSO-d_6 due to the deuterium exchange; in F_3CCOOH 13.01 br. s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 248 (100) [*M* – aroylmethyl]$^+$, 78 (10), 111 (10), 131 (39), 149 (23), 170 (14), 208 (19), 247 (47), 249 (16). Found, %: C 57.40; H 3.72; N 11.69. $C_{23}H_{18}N_4BrOCl$. Calculated, %: C 57.34; H 3.77; N 11.63.

(*E*,*Z*)-2-(Cyano-{1-[2-(4-methoxyphenyl)-2-oxo-ethyl]-1*H*-benzo[*d*]imidazol-2(3*H*)-ylidene}methyl)-1-methylpyridinium bromide (VIIIb). Yield 0.300 g (63%), yellow powder, mp 188–191°C (CH_3COCH_3). IR spectrum, ν, cm^{-1}: 3421 (N–H), 2179 (C≡N), 1679 (C=O). ^1H NMR spectrum, δ, ppm: 3.89 s (3H, OCH_3), 3.98 s (3H, CH_3, *Z*), 4.10 s (3H, CH_3, *E*), 6.03 br.s (2H, CH_2), 6.92 t (1H, C^5H, *J* 6.24 Hz, *Z*), 7.03 d (2H, CH_{Ar}, *J* 8.61 Hz), 7.12 d (1H, C^3H, *J* 8.53 Hz, *Z*), 7.19 d.d (1H, $CH_{benzimidazole}$, *J* 5.66, 3.09 Hz), 7.33 t (1H, C^5H, *J* 6.26 Hz, *E*), 7.40 d.d (1H, $CH_{benzimidazole}$, *J* 5.66, 3.09 Hz), 7.50 d.d (1H, $CH_{benzimidazole}$, *J* 5.95, 3.03 Hz), 7.62 t (1H, C^4H, *J* 8.53 Hz, *Z*), 7.79 d.d (1H, $CH_{benzimidazole}$, *J* 5.95, 3.03 Hz), 7.98–8.03 m [1H, C^4H (*E*), 1H, C^3H (*E*), 2H, H_{Ar}], 8.28 d (1H, C^6H, *J* 6.24 Hz, *Z*), 8.60 d (1H, C^6H, *J* 6.26 Hz, *E*); NH-proton was not detected in DMSO-d_6 due to the deuterium exchange; in F_3CCOOH 13.01 br. s (1H, NH). Found, %: C 60.45; H 4.38; N 11.79. $C_{24}H_{21}N_4BrO_2$. Calculated, %: C 60.39; H 4.43; N 11.74.

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