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Synthesis of Methyl 2-Aryl-5-chlorosulfonyl-1,3-oxazole-4-carboxylates and Their Reactions with Amines and Amidines

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Abstract—Previously unknown methyl 2-aryl-5-chlorosulfonyl-1,3-oxazole-4-carboxylates have been synthesized. Their reactions with amines and amidines have yielded the corresponding sulfonamides and 6*H*,7*H*-[1,3]oxazolo-[5,4-*d*]pyrimidin-7-ones.

Keywords: esters of 1,3-oxazole-4-carboxylic acids, 6*H*,7*H*-[1,3]oxazolo[5,4-*d*]pyrimidin-7-one, elimination, Smiles rearrangement

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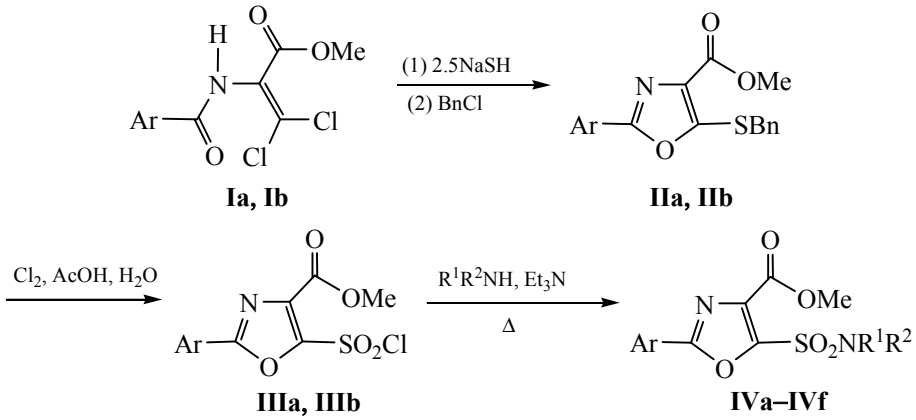
Chemistry of functionalized derivatives of 1,3-oxazole has been rapidly developed over recent decades due to their wide use in preparation of heterocyclic compounds [1–5]. Furthermore, many of synthetic and natural representatives of this class exhibit biological activity [1, 6, 7]. Sulfonylamide moiety of 1,3-oxazole derivatives is a part of some bioactive agents [8–11]. However, sulfonyl chloride derivatives of 1,3-oxazole has been poorly known so far.

Recently, we have developed method of 2-aryl-4-cyano-1,3-oxazole-5-sulfonylchlorides preparation and studied their reactions with amines, amidines, and aminoazoles yielding the corresponding sulfonamides, bi- and tricyclic compounds [12–14]. This work focuses on the synthesis of methyl esters of 2-aryl-5-chlorosulfonyl-1,3-oxazole-4-carboxylic acids **IIIa** and **IIIb** as well as on the study of their reactions with amines and amidines.

Scheme 1.



Ia, Ib **IIa, IIb** **IIIa, IIIb** **IVa–IVf**

Ar = Ph (**I–IIIa**, **IVa–IVc**), 4-MeC_6H_4 (**I–IIIb**, **IVd–IVf**); R^1R^2N = $PhCH_2$ (**IVa**, **IVd**), $(CH_2)_5N$ (**IVb**, **IVe**), $O(CH_2)_4N$ (**IVc**, **IVf**).

Table 1. Yields, melting points, and elemental analysis data of compounds **III–VI**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N (S)		C	H	N (S)
IIa[a]	70	102–104 (EtOH)	66.38	4.69	4.21 (9.86)	$C_{18}H_{15}NO_3S$	66.44	4.65	4.30 (9.85)
IIb	74	96–97 (EtOH)	67.20	5.12	4.20 (9.40)	$C_{19}H_{17}NO_3S$	67.24	5.05	4.13 (9.45)
IIIa[b]	62	89–91 (hexan)	43.80	2.61	4.55 (10.52)	$C_{11}H_8ClNO_5S$	43.79	2.67	4.64 (10.63)
IIIb[c]	65	94–95 (hexan)	45.75	3.23	4.51 (10.11)	$C_{12}H_{10}ClNO_5S$	45.65	3.19	4.44 (10.16)
IVa	78	105–106 (EtOH)	58.02	4.37	7.44 (8.59)	$C_{18}H_{16}N_2O_5S$	58.06	4.33	7.52 (8.61)
IVb	74	99–100 (EtOH)	54.84	5.23	8.11 (9.17)	$C_{16}H_{18}N_2O_5S$	54.85	5.18	7.99 (9.15)
IVc	84	161–162 (EtOH)	51.05	4.50	7.88 (9.01)	$C_{15}H_{16}N_2O_6S$	51.13	4.58	7.95 (9.10)
IVd	75	104–105 (EtOH)	59.06	4.72	7.35 (8.22)	$C_{19}H_{18}N_2O_5S$	59.06	4.70	7.25 (8.30)
IVe	82	121–122 (EtOH)	55.95	5.49	7.77 (8.89)	$C_{17}H_{20}N_2O_5S$	56.03	5.53	7.69 (8.80)
IVf	80	133–134 (EtOH)	52.48	4.96	7.51 (8.70)	$C_{16}H_{18}N_2O_6S$	52.45	4.95	7.65 (8.75)
Va[d]	52	>300 (MeCN–DMF, 3 : 1)	63.41	4.05	18.52	$C_{12}H_9N_3O_2$	63.43	3.99	18.49
Vb[e]	63	>300 (MeCN–DMF, 3 : 1)	70.49	3.85	14.67	$C_{17}H_{11}N_3O_2$	70.58	3.83	14.52
Vc	67	>300 (MeCN–DMF, 3 : 1)	71.90	4.72	13.31	$C_{19}H_{15}N_3O_2$	71.91	4.76	13.24
Vd	65	>300 (MeCN–DMF, 1 : 1)	67.76	4.12	13.22	$C_{18}H_{13}N_3O_3$	67.71	4.10	13.16
Ve	58	>300 (MeCN–DMF, 1 : 1)	66.41	3.30	13.54	$C_{17}H_{10}FN_3O_2$	66.45	3.28	13.67
Vf[f]	53	>300 (MeCN–DMF, 1 : 1)	63.12	3.15	12.86	$C_{17}H_{10}ClN_3O_2$	63.07	3.11	12.98
Vg	55	>300 (MeCN–DMF, 3 : 1)	64.65	4.65	17.50	$C_{13}H_{11}N_3O_2$	64.72	4.60	17.42
Vh	60	>300 (MeCN–DMF, 3 : 1)	71.34	4.32	13.86	$C_{18}H_{13}N_3O_2$	71.28	4.32	13.85
Vi	68	>300 (MeCN–DMF, 3 : 1)	72.51	5.13	12.78	$C_{20}H_{17}N_3O_2$	72.49	5.17	12.68
Vj	70	>300 (MeCN–DMF, 1 : 1)	68.40	4.59	12.69	$C_{19}H_{15}N_3O_3$	68.46	4.54	12.61
Vk	54	>300 (MeCN–DMF, 1 : 1)	67.30	3.77	13.12	$C_{18}H_{12}FN_3O_2$	67.29	3.76	13.08
Vl[g]	52	>300 (MeCN–DMF, 1 : 1)	64.05	3.62	12.52	$C_{18}H_{12}ClN_3O_2$	64.01	3.58	12.44

[a] mp 103–105°C [15]. [b] Found Cl, %: 11.84. Calculated Cl, %: 11.75. [c] Found Cl, %: 11.33. Calculated Cl, %: 11.23. [d] Mp 306–308°C [27]. [e] mp 374–376°C [26, 27]. [f] Found Cl, %: 10.88. Calculated Cl, %: 10.95. [g] Found Cl, %: 10.43. Calculated Cl, %: 10.50.

Readily available methyl 2-acylamino-3,3-dichloroacrylates **Ia** and **Ib** [15] were used as starting materials. As shown in Scheme 1, **Ia** and **Ib** were converted into methyl 2-aryl-5-benzylsulfanyl-1,3-oxazole-4-carboxylates **IIa** and **IIb** with yields of 70–74%. Interaction of **IIa** and **IIb** with chlorine in aqueous acetic acid at 0°C gave the target methyl 5-chloro-sulfonyl-1,3-oxazole-4-carboxylates **IIIa** and **IIIb**, stable crystalline solids, with yields of 62–65%. The latter products were treated with benzylamine, piperidine, or morpholine in the presence of triethylamine in dioxane to obtain the corresponding sulfonamides **IVa**–**IVf** with 74–84% yields.

Composition and structure of the prepared compounds were confirmed by elemental analysis (Table 1), IR, ^{1}H and ^{13}C NMR spectroscopy, and gas chromatography–mass spectrometry (Table 2). The IR spectra contained absorption bands assigned to carbonyl (1708–1755 cm^{-1}) and sulfonyl (1142–1158 and 1353–1402 cm^{-1}) groups. In ^{1}H NMR spectra of **III** and **IV** no signal of the $PhCH_2$ fragment, characteristic of 5-benzylsulfanyl oxazole derivatives **IIa** and **IIb,** was found. In the spectra of sulfonamides **IVa**–**IVf,** the signals of benzylamine, piperidine, and morpholine fragments were identified.

Methyl 5-chlorosulfonyl-1,3-oxazole-4-carboxylates **III** contained two electrophilic centers and were expected to form seven-membered thiadiazepine cycles via reaction with 1,3-binucleophiles (see [16, 17]). Attempting to obtain the condensed oxazolothia-

Table 2. Spectral data of compounds **III–VI**

Comp. no.	IR spectrum (KBr), ν, cm^{-1}	^1H NMR spectrum (DMSO-d_6), δ, ppm	Mass spectrum, m/z, $[M + 1]^+$
IIa	1067, 1150, 1201, 1351, 1437, 1513; 1720 (CO)	3.81 s (3H, OCH_3), 4.55 s (2H, SCH_2), 7.25–7.98 m (10H, $2C_6H_5$)	326
IIb[a]	1080, 1159, 1232, 1341, 1540; 1698 (CO)	2.38 s (3H, CH_3), 3.80 s (3H, OCH_3), 4.52 s (2H, SCH_2), 7.25–7.86 m (9H, C_6H_4, C_6H_5)	340
IIIa	1057; 1158, 1402 (SO_2); 1226, 1449, 1482, 1545; 1747 (CO)	4.07 s (3H, OCH_3), 7.53–8.20 m (10H, $2C_6H_5$)	302
IIIb	1059; 1156, 1397 (SO_2); 1224, 1493, 1551, 1612; 1755 (CO)	2.44 s (3H, CH_3), 4.05 s (3H, OCH_3), 7.34 d (2H, C_6H_4, $^3J_{HH}$ 8.4 Hz), 8.07 d (2H, C_6H_4, $^3J_{HH}$ 8.4 Hz)	316
IVa	1057, 1086; 1149, 1353 (SO_2); 1176, 1245, 1335, 1450, 1556; 1708 (CO); 3291 (NH)	3.90 s (3H, OCH_3), 4.32 s (2H, CH_2), 7.11–7.68 m (10H, $2C_6H_5$), 9.09 s (1H, NH)	373
IVb	1051; 1142, 1377 (SO_2); 1181, 1223, 1451, 1554; 1742 (CO)	1.45 br.s, 1.68 br.s (6H, $3CH_2$, piperidine), 3.35 br.s (4H, CH_2, piperidine), 3.93 s (3H, OCH_3), 7.61–8.05 m (5H, C_6H_5)	351
IVc	1073, 1113; 1148, 1371 (SO_2); 1182, 1223, 1450, 1545; 1746 (CO)	3.33 br.s (4H, $2CH_2$, morpholine), 3.70 br.s (4H, $2CH_2$, morpholine), 3.92 s (3H, OCH_3), 7.65–8.08 m (5H, C_6H_5)	353
IVd	1055; 1149, 1367 (SO_2); 1184, 1225, 1435, 1498, 1726 (CO); 3256 (NH)	2.40 s (3H, CH_3), 3.88 s (3H, OCH_3), 4.30 s (2H, CH_2), 7.12–7.25 m (5H, C_6H_5), 7.40 d (2H, C_6H_4, $^3J_{HH}$ 8.0 Hz), 7.82 d (2H, C_6H_4, $^3J_{HH}$ 8.0 Hz), 9.11 s (1H, NH)	387
IVe	1050; 1143, 1373 (SO_2); 1160, 1183, 1296, 1330, 1495; 1746 (CO)	1.55 br.s, 1.65 br.s (6H, $3CH_2$ + 4H, $2CH_2$, piperidine), 2.42 s (3H, CH_3), 3.38 br.s (4H, CH_2, piperidine), 3.98 s (3H, OCH_3), 7.30 d (2H, C_6H_4, $^3J_{HH}$ 8.4 Hz), 8.01 d (2H, C_6H_4, $^3J_{HH}$ 8.4 Hz)	365
IVf	1078, 1111; 1149, 1367 (SO_2); 1182, 1223, 1298, 1332, 1494, 1551, 1613; 1744 (CO)	2.39 s (3H, CH_3), 3.40 br.s (4H, CH_2, morpholine), 3.77 br.s (4H, $2CH_2$ + 4H, $2CH_2$, morpholine), 3.99 s (3H, OCH_3), 7.31 d (2H, C_6H_4, $^3J_{HH}$ 8.0 Hz), 8.00 d (2H, C_6H_4, $^3J_{HH}$ 8.0 Hz)	367
Va	1195, 1262, 1573; 1704 (CO); 3050 (NH)	2.44 s (3H, CH_3), 7.61–8.08 m (5H, C_6H_5), 12.84 br.s (1H, NH)	228
Vb	1195, 1269, 1532, 1557; 1692 (CO); 3054 (NH)	7.59–8.20 m (10H, $2C_6H_5$), 13.03 br.s (1H, NH)	290
Vc[b]	1195, 1272, 1345, 1515, 1556, 1573; 1700 (CO); 3120 (NH)	1.25 br.s (3H, CH_3), 2.73 br.s (2H, CH_2), 7.41–8.13 m (9H, C_6H_4, C_6H_5), 12.86 br.s (1H, NH)	318
Vd	1184, 1261, 1515, 1556, 1590; 1693 (CO); 3061 (NH)	3.88 s (3H, OCH_3), 7.11–8.21 m (9H, C_6H_4, C_6H_5), 12.83 br.s (1H, NH)	320
Ve	1167, 1238, 1350, 1516; 1688 (CO); 3086 (NH)	7.42–8.25 m (9H, C_6H_4, C_6H_5), 13.15 br.s (1H, NH)	308
Vf	1184, 1265, 1344, 1530; 1688 (CO); 3097 (NH)	7.63–8.20 m (9H, C_6H_4, C_6H_5), 13.17 br.s (1H, NH)	324
Vg	1195, 1264, 1499, 1576; 1695 (CO); 3040 (NH)	2.40 s (3H, CH_3), 2.43 s (3H, CH_3), 7.40 d (2H, C_6H_4, $^3J_{HH}$ 8.0 Hz), 7.96 d (2H, C_6H_4, $^3J_{HH}$ 8.0 Hz), 12.80 br.s (1H, NH)	242
Vh	1180, 1342, 1509, 1536; 1696 (CO); 3060 (NH)	2.42 s (3H, CH_3), 7.42–8.19 m (9H, C_6H_4, C_6H_5), 12.95 br.s (1H, NH)	304
Vi	1182, 1344, 1516; 1694 (CO); 3115 (NH)	1.23 t (3H, CH_3), 2.42 s (3H, CH_3), 2.71 k (2H, CH_2, $^3J_{HH}$ 8.0 Hz), 7.41–8.12 m (8H, $2C_6H_4$), 13.00 br.s (1H, NH)	332

Table 2. (Contd.)

Comp. no.	IR spectrum (KBr), ν, cm^{-1}	^1H NMR spectrum (DMSO-d_6), δ, ppm	Mass spectrum, m/z, $[M+1]^+$
Vj	1179, 1261, 1515, 1613; 1692 (CO); 3095 (NH)	2.41 s (3H, CH_3), 3.87 s (3H, OCH_3), 7.11 d (2H, C_6H_4, $^3J_{HH}$ 8.0 Hz), 7.42 d (2H, C_6H_4, $^3J_{HH}$ 7.5 Hz), 8.00 d (2H, C_6H_4, $^3J_{HH}$ 8.0 Hz), 8.18 d (2H, C_6H_4, $^3J_{HH}$ 7.5 Hz), 12.90 br.s (1H, NH)	334
Vk	1165, 1236, 1348, 1516; 1692 (CO); 3095 (NH)	2.42 s (3H, CH_3), 7.42–8.24 m (8H, $2C_6H_4$), 13.11 br.s (1H, NH)	322
Vl	1197, 1267, 1347, 1507, 1534, 1558; 1694 (CO); 3080 (NH)	2.42 s (3H, CH_3), 7.42 d (2H, C_6H_4, $^3J_{HH}$ 7.5 Hz), 7.66 d (2H, C_6H_4, $^3J_{HH}$ 8.5 Hz), 8.01 d (2H, C_6H_4, $^3J_{HH}$ 7.5 Hz), 8.18 d (2H, C_6H_4, $^3J_{HH}$ 8.5 Hz), 13.17 br.s (1H, NH)	338

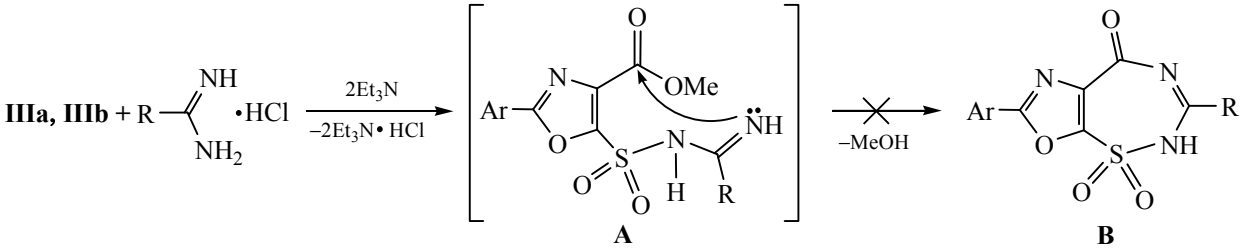
[a] ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 21.15 (CH_3), 36.05 (CH_2), 51.84 (OCH_3), 123.13 ($C^4_{oxazole}$), 126.07, 127.61, 128.64, 128.97, 129.01, 129.86, 137.13, 141.39, 152.93 (SO), 160.59 ($C^5_{oxazole}$), 161.29 ($C^2_{oxazole}$). [b] ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 15.25 (CH_3), 28.14 (CH_2), 120.48, 126.05, 126.75, 128.23, 128.33, 128.88, 129.46, 131.85, 148.56, 155.58, 157.20, 158.50, 164.00.

diazepines **B**, we carried out the reaction of compounds **III** with amidines (Scheme 2).

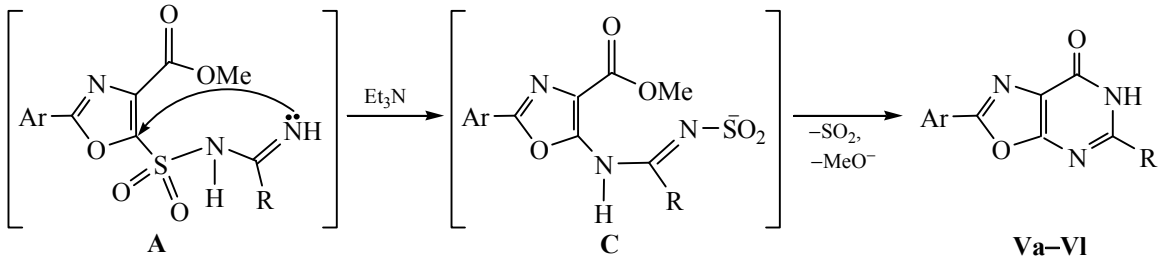
However, according to elemental analysis as well as IR, ^1H NMR, ^{13}C NMR, and GC–MS spectral data, that interaction was accompanied with elimination of sulfur dioxide to form oxazolopyrimidines **Va–Vl** (Scheme 3). The formation of 6*H*,7*H*-[1,3]oxazolo-[5,4-*d*]pyrimidin-7-ones could be rationalized as a result of transformation of the seven-membered ring **B** into a six-membered cycle through elimination of sulfur dioxide. Generally, such transformation occurs under severe conditions [18, 19]. Therefore, in the studied case the more likely opportunity was the intramolecular rearrangement of the products **A** of amidines *N*-sulfonylation into the intermediates **C** via attack at the C^5 atom of oxazole ring with nucleophilic nitrogen atom. Subsequent release of sulfur dioxide and methanol resulted in the target compounds **Va–Vl**.

The **A** → **C** conversion was similar to the Smiles rearrangement accompanied by elimination of sulfur dioxide [20–25] followed by the intramolecular cyclization **C** → **V**. It should also be noted that a

Scheme 2.



Scheme 3.



Ar = Ph (**Va–Vf**), 4-MeC_6H_4 (**Vg–Vl**); R = Me (**Va**, **Vg**), Ph (**Vb**, **Vh**), 4-EtC_6H_4 (**Vc**, **Vi**), 4-$MeOC_6H_4$ (**Vg**, **Vj**), 4-FC_6H_4 (**Ve**, **Vk**), 4-ClC_6H_4 (**Vf**, **Vl**).

similar reaction pathway was observed in the case of interaction of 2-aryl-4-cyano-1,3-oxazole-5-sulfonyl chlorides with 5-amino-1*H*-pyrazoles and 5-amino-1*H*-1,2,4-triazoles to form tricyclic structures [14].

Structure of 6*H*,7*H*-[1,3]oxazolo[5,4-*d*]pyrimidin-7-ones **Va–Vl** was confirmed by IR, ^{1}H NMR spectroscopy and chromatography–mass spectrometry. The IR spectra contained no absorption bands of SO_2 group at 1156–1158 and 1397–1402 cm^{-1}. The absorption band of C=O group was shifted to lower frequency ($\nu_{C=O}$ 1688–1704 cm^{-1}) as compared to that in the spectrum of the starting sulfonyl chlorides **III** ($\nu_{C=O}$ 1747–1755 cm^{-1}). Absorbance band at 3050–3120 cm^{-1} was assigned to the NH group stretching. The ^{1}H NMR spectra lacked signal of the CH_3O moiety. The proton of NH group resonated as broad singlet in the range of 12.80–13.17 ppm. Furthermore, the spectral data of **Vb** synthesized by procedure [26] were identical to those of **Vb** prepared from **IIIa**.

In summary, chlorination of methyl 2-aryl-5-benzylsulfanyl-1,3-oxazole-4-carboxylates (aq. AcOH, 0°C) afforded methyl 5-chlorosulfonyl-1,3-oxazole-4-carboxylates in yields of 62–65%. The latter were converted into the corresponding sulfonamides and substituted 6*H*,7*H*-[1,3]oxazolo[5,4-*d*]pyrimidin-7-ones.

EXPERIMENTAL

IR spectra (KBr) were recorded with the Vertex 70 instrument. ^{1}H NMR spectra were obtained with the Bruker AVANCE DRX-500 spectrometer (500 MHz) relative to internal TMS reference. GC-MS spectra were registered with the Agilent 1100 Series HPLC device equipped with a mass selective UV diode array detector. Conditions of the GC–MS analysis were as follows: Zorbax SB-C18 column (1.18 μm, 4.6 × 15 mm, PN 821975-932); acetonitrile–water (95 : 5), 0.1% aqueous trifluoroacetic acid; eluent flow rate 3 mL/min; injection volume 1 μL; UV detector (215, 254, 285 nm); chemical ionization at atmospheric pressure (APCI), scanning range *m*/*z* 80–1000. Elemental analysis was performed at the analytical laboratory of the Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine. Carbon and hydrogen contents were determined by the gravimetric Pregl method; nitrogen and sulfur contents were quantified by the volumetric Dumas micro method and the Shoniger titration method, respectively [28]. Melting points were measured using the Fisher-Johns apparatus. The reaction progress was monitored by TLC on Silufol UV-254 plates eluting with the 9 : 1 chloroform–methanol mixture and developing with UV irradiation.

Methyl 2-aryl-5-benzylsulfanyl-1,3-oxazole-4-carboxylates (IIa, IIb). 0.025 mol of sodium hydrosulfide was added to a solution of 0.01 mol of the corresponding methyl dichloroacrylate **Ia** or **Ib** in 50 mL of methanol. The mixture was stirred at 20–25°C during 24 h, and the volatile fraction was removed in vacuum. The residue was refluxed in a mixture of 30 mL of methanol and 0.011 mol of benzyl chloride during 2–3 h. Next, the mixture was incubated at 20–25°C during 12 h. After the solvent removal, the residue was treated with water; the precipitate was filtered off and recrystallized.

Methyl 2-aryl-5-chlorosulfonyl-1,3-oxazole-4-carboxylates (IIIa, IIIb). A solution of 0.01 mol of **IIa** or **IIb** in 30 mL of 95% acetic acid was bubbled with Cl_2 upon stirring and cooling (0°C) during 0.5 h. Then the mixture was incubated at 4–5°C during 12 h and poured onto ice. The precipitate was filtered off, dried over phosphorus(V) oxide, and recrystallized.

Methyl 2-aryl-5-(benzylamino-1-sulfonyl)-1,3-oxazole-4-carboxylates (IVa, d), methyl 2-aryl-5-(piperidino-1-sulfonyl)-1,3-oxazole-4-carboxylates (IVb, IVe), methyl 2-aryl-5-(morpholino-1-sulfonyl)-1,3-oxazole-4-carboxylates (IVc, IVf). A mixture of a solution of 0.001 mol of **IIIa** or **IIIb** in 15 mL of anhydrous dioxane, 0.001 mol of the corresponding amine (benzylamine, piperidine, or morpholine), and 0.001 mol of Et_3N was refluxed during 2 h. Then the mixture was incubated at 20–25°C during 12 h; the precipitate was filtered off, and the solvent was removed in vacuum. The residue was treated with water, filtered off, dried, and recrystallized.

5-Aryl(methyl)-2-aryl[1,3]oxazolo[5,4-*d*]pyrimidine-7(6*H*)-ones (Va–Vl). A mixture of 0.001 mol of **IIIa** or **IIIb**, 0.001 mol of the corresponding amidine hydrochloride, and 0.002 mol of triethylamine in 10 mL of anhydrous tetrahydrofuran was stirred at 20–25°C during 24 h and then at 65°C during 1 h. After cooling, 20 mL of water was added. The precipitate was filtered off, dried, and recrystallized.

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