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SHORT COMMUNICATIONS

Recyclization of 4-Oxo-1,3-benzoxazinium Salts by Treating with Guanidinobenzimidazole

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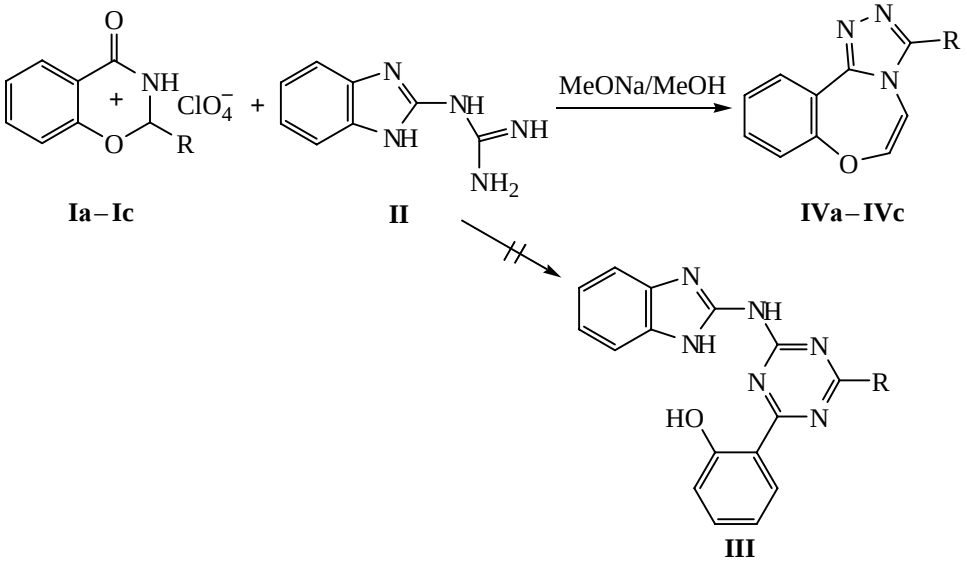
In previous studies we established that 4-oxo-1,3-benzoxazinium perchlorates easily underwent recyclization when treated with guanidine to afford 1,3,5-triazines [1, 2]. At treating 4-oxo-1,3-benzoxazinium salts **Ia–Ic** with guanidinobenzimidazole (**II**) [3] we obtained instead of expected benzimidazole-substituted 1,3,5-triazines **III** triazolebenzoxazepines **IVa–IVc**, previously unknown heterocyclic systems (see Scheme).

Triazolebenzoxazepines **IVa–IVc** presumably form as a result of recyclization of perchlorates **I** by fragments of guanidinobenzimidazole arising through decomposition of the latter under the action of sodium methylate.

The composition and structure of obtained heterocycles **IVa–IVc** was proved by elemental analysis, IR and ^{1}H spectra. The composition and structure of triazolebenzoxazepine **IVa** was also confirmed by mass spectrum.

3-Methyl-4*H*-1,2,4-triazolo[4,5-*d*]benzoxazepine (IVa). To sodium methylate prepared from 0.14 g of sodium and 6 ml of methanol was added 0.37 g (5 mmol) of guanidinobenzimidazole and 1.31 g (5 mmol) of perchlorate **Ia**. The mixture was boiled for 15 min, cooled, the precipitated product was filtered off and recrystallized from DMF. Yield 0.25 g (25%), colorless crystals, mp 292–294°C. IR spectrum, ν, cm^{-1}: 1640 (C=N), 1600 (C=N), 1540 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.91 s (3H, CH_3), 7.18 t (1H, H^9), 7.35 t (1H, H^{10}), 7.31 m (3H, H^5, H^8 H^{11}), 7.87 d (1H, H^6). Mass spectrum, *m/z* (I_{rel}, %): 199 (96) $[M]^+$, 158(99), 131 (10), 104 (9), 90 (20), 77 (7), 63 (10), 53 (8), 42 (34). Found,

Scheme.



Ia–Ic **II** **IVa–IVc** **III**

R = CH_3 (**a**), 4-ClC_6H_4CH=CH (**b**), 4-$HOOCCH_2OC_6H_4CH$=CH (**c**).

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%: C 66.03; H 4.22; N 21.51. $C_{11}H_9N_3O$. Calculated, %: C 66.33; H 4.52; N 21.11.

3-(4-Chlorophenyl)vinyl-4*H*-1,2,4-triazolo[4,5-*d*]-benzoxazepine (IVb) was prepared in the same way as **IVa**. Yield 28%, red crystals, mp 280–282°C. IR spectrum, ν, cm^{-1}: 1660 (C=N), 1650 (C=N), 1630 (C=C), 1600 (C=C). ^1H NMR spectrum, δ, ppm: 7.22 t (1H, H_{arom}), 7.44 t (1H, H_{arom}), 7.45–7.61 m (5H, H_{arom}), 7.82 d (1H, H_{arom}), 7.91–8.09 m (4H, H_{arom}). Found, %: C 67.45; H 3.96; C1 10.99; N 13.63. $C_{18}H_{12}ClN_3O$. Calculated, %: C 67.19; H 3.73; Cl 11.04; N 13.06.

3-(4-Carboxymethyloxyphenyl)vinyl-4*H*-1,2,4-triazolo[4,5-*d*]benzoxazepine (IVc) was prepared in the same way as **IVa**. Yield 31%, yellow crystals, mp 220–222°C. IR spectrum, ν, cm^{-1}: 1650 (C=N), 1630 (C=N), 1610 (C=C), 1600 (C=C). ^1H NMR spectrum, δ, ppm: 4.75 s (2H, CH_2), 7.02 d (2H, H_{arom}), 7.21 m (1H, H_{arom}), 7.38 m (1H, H_{arom}), 7.51 m (3H, H_{arom}), 7.68 d (1H, H_{arom}), 7.87 m (2H, H_{arom}), 8.01 (2H, H_{arom}). Found, %: C 66.23; H 4.27; N 11.5. $C_{20}H_{15}N_3O_4$. Calculated, %: C 66.48; H 4.16; N 11.63.

IR spectra of compounds **IVa–IVc** were registered on a spectrophotometer Specord 75IR from mulls in mineral oil, ^1H NMR spectra were recorded on spectrometer Varian Unity-300 (300 MHz) from solutions in DMSO-d_6 at 20°C, mass spectrum was measured on VG 7070E instrument (electron impact, 70 eV).

REFERENCES

1. Vikrishchuk, N.I., Suzdalev, K.F., Korol'chenko, G.A., and Ryabukhin, Yu.I., *Khim.-Farm. Zh.*, 1995, vol. 29, p. 30.
2. Vikrishchuk, I.I., Suzdalev, K.F., Ryabukhin, Yu.I., and Zhdanov, Yu.A., *Zh. Org. Khim*., 1998, vol. 34, p. 599.
3. King, F.E., *J. Chem. Soc*., 1948, vol. 9, p. 1366.