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SHORT COMMUNICATIONS

Reaction of 5-Aryl-3*H*-furan-2-ones and Their 3-Arylmethylidene Derivatives with Thiosemicarbazide

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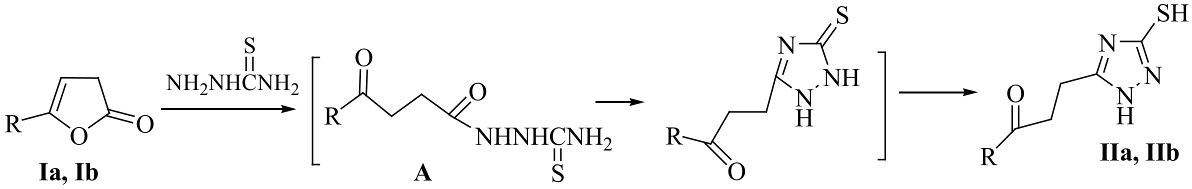
The interest to 3*H*-furan-2—ones and their arylmethylidene derivatives is due to the structural features. The presence of several electrophilic sites, the reciprocal position of groups makes these compounds valuable substrates for the synthesis of versatile heterocyclic systems [1].

The goal of this study was obtaining substituted triazole structures by the reactions of 5-aryl-3*H*-furan-2-ones and their 3-arylmethylidene derivatives with thiosemicarbazide under the conditions of basic catalysis.

Reactions of 5-aryl-3*H*-furan-2-ones **Ia, Ib** with thiosemicarbazide were carried out in ethanol solution in the presence of a catalytic quantity of triethylamine.



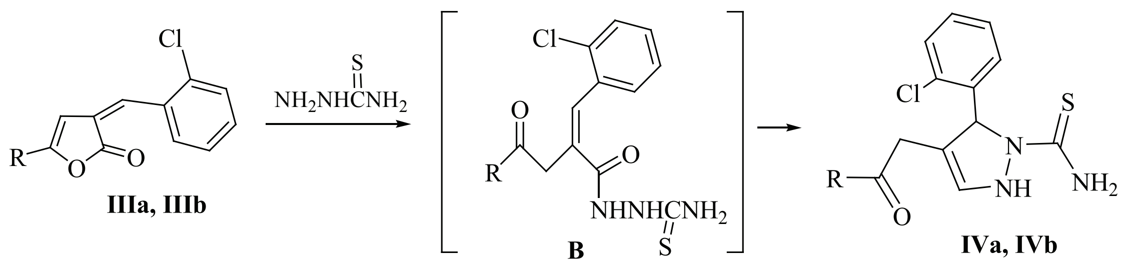
R = Tol (**a**), Ph (**b**).

IR and ^{1}H NMR spectra confirm the fact of heterocyclization and the formatiom of products which we have identified as 3-(5-mercapto-2*H*-1,2,4-triazol-3-yl)-1-arylpropan-1-ones **IIa, IIb**. IR spectra contain the absorption bands of carbonyl group (1672–1666 cm^{-1}), methylene groups (818–815 cm^{-1}), NH group (2928–2922 cm^{-1}). In the ^{1}H NMR spectra of compounds **IIa, IIb** the following signals were observed: triplets of methylene groups (2.73–2.74, 3.29 ppm), singlets of protons of NH groups (7.87– 7.89 ppm), proton signals of mercapto groups (2.17– 2.29 ppm).

The attack of the NH_2 group of the thiosemicarbazide is directed to the electron-deficient carbon atom of the furanone ring causing the ring opening with the formation of thiosemicarbazones of 4-oxoacids **A**, which in the reaction conditions undergo the cyclization into triazoles derivatives **IIa, IIb**. Compounds **IIa, IIb** exist in diverse tautomeric forms due to the lability of proton in their structures. The presence in the ^{1}H NMR spectra of proton signals from groups SH, NH, and CH_2 and the lack in the IR spectra of the absorption band belonging to the C=S bond prove the formation of mercaptotriazoles **IIa, IIb**.

Beside 3*H*-furan-2-ones **Ia, Ib** we used as initial compounds 5-aryl-3-(2-chlorophenylmethylidene)-3*H*-furan-2-ones **IIIa, IIIb**. The reaction was carried out under the same conditions but at longer heating.

We characterized compounds obtained as 5-(2-chlorophenyl)-4-(2-oxo-2-arylethyl)-2,5-dihydro-1*H*-pyrazole-1-carbothioamides **IVa, IVb**. Their spectral characteristics confirm the cyclic structure.



R = Tol (**a**), Ph (**b**).

IR spectra of compounds **IVa, IVb** contain absorption bands of the bond C=S (1282–1262 cm$^{–1}$), amino group (3200–3400 cm$^{–1}$), C=O group (1684–1678 cm$^{–1}$), CH bond of the heteroring (762–758 cm$^{–1}$). In the ^{1}H NMR spectra singlets appear of the protons of NH (8.03 ppm) and NH_2 (2.02–2.17 ppm) groups, of the protons at the tertiary carnon atom (4.22–4.28 ppm), at the vinyl carbon atom (7.18–7.19 ppm) and of the methylene group (4.04–4.09 ppm). The reaction apparently proceeds analogously involving the carbonyl fragment of the substrate leading primarily to the opening of the ring and the formation of the thiosemicarbazone of 4-oxoacid **B**, which further undergoes heterocyclization involving the methylidene fragment.

Thus we studied the reactions of 5-aryl-3*H*-furan-2-one and its arylmethylidene derivatives with thiosemicarbazide. The reaction did nt stop at the stage of the formation of a linear product but underwent a heterocyclization providing substituted pyrazoles and triazoles.

Compounds IIa, IIb. General procedure. In 30 ml of ethanol 6 mmol of 5-aryl-3*H*-furan-2-one **Ia, Ib** and 9 mmol of thiosemicarbazide was heated for 10 h in the presence of 0.1 ml of triethylamine. The reaction mixture was poured into cold water, neutralized and left standing for 24 h, then it was extracted with chloroform, and the solvent was distilled off. The obtained crystals were recrystallized from 2-propanol.

3-(5-Mercapto-2*H*-1,2,4-triazole-3-yl)-1-(4-methylphenyl)propan-1-one (IIa). Yield 0.97 g (65%), mp 73–75°C. IR spectrum, ν, cm$^{–1}$: 2922 (NH), 1666 (C=O), 815 (CH_2). ^{1}H NMR spectrum, δ, ppm: 2.17 s (1H, SH), 2.55 s (3H, CH_3), 2.74 t (2H, $COCH_2\underline{CH_2}$, *J* 8 Hz), 3.29 t (2 H, $CO\underline{CH_2}CH_2$, *J* 8 Hz), 7.00–7.31 m (4H, Ar), 7.87 s (1H, NH). Found, %: C 58.56; H 5.63; N 16.16; S 13.57. $C_{12}H_{13}N_3OS$. Calculated, %: C 58.28; H 5.30; N 16.99; S 12.97.

3-(5-Mercapto-2*H*-1,2,4-triazole-3-yl)-1-phenylpropan-1-one (IIb). Yield 0.96 g (71%), mp 69–70°C. IR spectrum, ν, cm$^{–1}$: 2928 (NH), 1672 (C=O), 818 (CH_2). ^{1}H NMR spectrum, δ, ppm: 2.29 s (1H, SH), 2.73 t (2H, $COCH_2\underline{CH_2}$, *J* 8 Hz), 3.29 t (2H, $CO\underline{CH_2}CH_2$, *J* 8 Hz), 7.13–7.42 m (4H, Ar), 7.89 s (1H, NH). Found, %: C 57.46; H 4.93; N 17.16; S 12.57. $C_{11}H_{11}N_3OS$. Calculated, %: C 56.63; H 4.75; N 18.01; S 13.74.

Compounds (IVa, IVb). General procedure. In 30 ml of ethanol 3 mmol of aryl-3-(2-chlorophenylmethylidene)-3*H*-furan-2-one **IIIa**, **IIIb** and 4.5 mmol of thiosemicarbazide was heated for 18 h in the presence of 0.1 ml of triethylamine. The reaction mixture was poured into cold water, neutralized and left standing for 24 h, then it was extracted with chloroform, and the solvent was distilled off. The obtained crystals were recrystallized from 2-propanol.

5-(2-Chlorophenyl)-4-[2-oxo-2-(4-methylphenyl)ethyl]-2,5-dihydro-1*H*-pyrazole-1-carbothioamide (IVa). Yield 0.81 g (73%), mp 103–104°C. IR spectrum, ν, cm$^{–1}$: 3400–3200 [ν_{as} and ν_s (NH_2)], 1684 (ArCOR), 1262 (=S), 815 (CH_2), 758 (CH of heterocycle). ^{1}H NMR spectrum, δ, ppm: 2.02 s (2H, NH_2), 2.41 s (3H, CH_3), 4.04 s (2H, CH_2), 4.22 s (1H, CH), 7.18 s (1H, =CH), 7.16–7.88 m (8H, Ar), 8.03 s (1H, NH). Found, %: C 61.04; H 4.86; Cl 9.52; N 11.30; S 7.70. $C_{19}H_{18}ClN_3SO$. Calculated, %: C 61.36; H 4.33; Cl 9.61; N 11.37; S 8.66.

5-(2-Chlorophenyl)-4-(2-oxo-2-phenylethyl)-2,5-dihydro-1*H*-pyrazole-1-carbothioamide (IVb). Yield 0.72 g (67%), mp 103–104°C. IR spectrum, ν, cm$^{–1}$: 3400–3200 [ν_{as} and ν_s(NH_2)], 1678 (ArCOR), 1282 (=S), 815 (CH_2), 762 (CH of heterocycle). ^{1}H NMR spectrum, δ, ppm: 2.17 s (2H, NH_2), 4.09 s (2H, CH_2), 4.28 s (1H, CH), 7.19 s (1H, =CH), 7.18–7.69 m (8H, Ar), 8.03 s (1H, NH). Found, %: C 61.01; H 4.72; Cl 9.52; N 11.02; S 10.34. $C_{18}H_{16}ClN_3SO$. Calculated, %: C 60.41; H 4.51; Cl 9.91; N 11.74; S 8.96.

IR spectra were recorded on an IR Fourier spectrometer FSM 1201 from pellets with KBr, ^{1}H NMR spectra, on a spectrometer Bruker MSL-400 (operating frequency 400 MHz) in $CDCl_3$, internal reference TMS. The purity of compounds was checked by TLC on Silufol plates, eluent ethyl acetate–hexane–chloroform, 2 : 2 : 1, development in iodine vapor.

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REFERENCES

1. Grinev, V.S., Amal'chieva, O.A., Egorova, A.Yu., and Lyubun', E.V., *Zh. Org. Khim.*, 2010, vol. 46, p. 1376.