

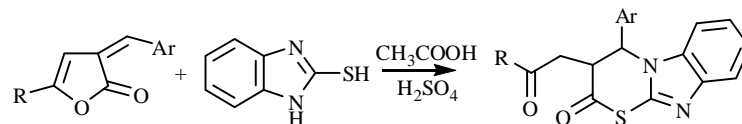
REACTIONS OF 3-ARYLMETHYLIDENE-3H-PYRROL-2-ONES WITH 2-MERCAPTOBENZYMIDAZOLE

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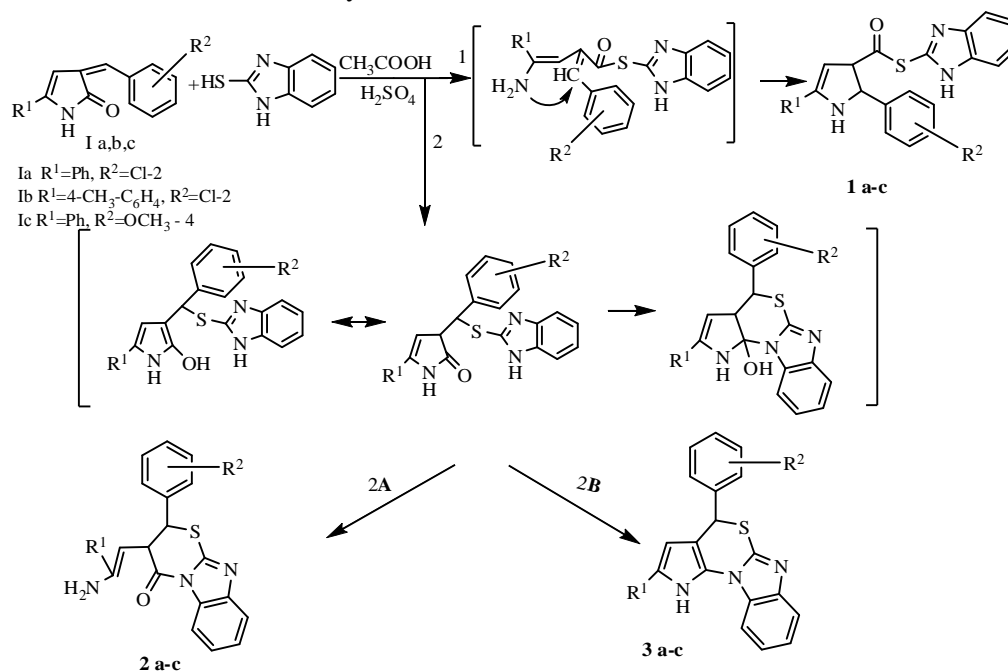
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Interest to the arylmethylidene derivatives of 3H-pyrrol-2-ones is due to a wide spectrum of their useful properties, many of which find application in medicine, industry, and agriculture, their analogues are parts of alkaloids and drugs. Of special interest is modification of the pyrrolonic cycle under the action of nucleophilic reagents. We studied the reaction of 3-arylmethylidene-3H-furan-2-ones with binucleophilic - 2-mercaptobenzimidazole. The interaction under study can proceed by several reaction centers, which enables the substrate's structure to be modified by means of regioselective chemical transformations.

5-R-3-arylmethylidene-3H-furan-2-ones are known to react with 2-mercaptobenzimidazole at heating, in a solution of icy acetic acid, in the presence of catalytic amounts of concentrated sulfuric acid and do not interact at boiling in an ethanol solution, in the presence of catalytic amounts of triethylamine (potassium carbonate, sodium alcoholate) /1/.



We studied the interaction of 5-R-3-(2-chlorobenzylidene)-3H-pyrrol-2-ones **Ia,b** and 5-phenyl-3-(4-methoxybenzylidene)-3H-pyrrol-2-one **Ic** with 2-mercaptobenzimidazole at heating during 30 hours in a solution of icy acetic acid and catalytic amounts of sulfuric acid. In the structure of the arylmethylidene derivatives of pyrrol-2-ones there are several reaction centers liable to nucleophilic attack, namely, an exocyclic double C-C bond, a carbonylic group, labile bonds in the cycle (C-N and C-H); besides, the presence of a second nucleophilic center in the reagent promotes its attack by the carbonylic carbon atom and closing the corresponding five-membered or six-membered cycles.



The data of elementary analysis and spectral characteristics, in combination with quantum mechanical computations, suggest the compounds formed to be 3-(2-amino-2-R¹-vinyl)-2-R²-2H-benzo[4,5]imidazo[2,1-b][1,3]thiazine-4(3H)-ones **2a-c**, whilst the possibility of forming products **1a-c** and **3a-c** is excluded.

Reaction products **2a-c** were isolated with a yield up to 73%. The IR spectra of compounds **2a-c** have the absorption bands of a carbonylic group 1698-1707 cm⁻¹, NH₂ 3183-3201, 3426-3520 cm⁻¹, vibrations of aromatic rings 1600-1620 cm⁻¹. In the ¹H NMR spectra of compounds **2a-c** we note the signals of a vinyl proton within 5.68-5.71 ppm, the signals of the protons at tertiary carbon atoms within 5.72-5.74 and 6.82-6.92 ppm, the signal of a NH₂ group's protons at 9.97-9.99 ppm, the multiplet of aromatic rings within 7.17-7.69 ppm, the signal of the methyl group protons of an aromatic substituent (for compound **2b**) around 2.35 ppm, and that of a methoxylic group (for compound **2c**) at 3.82 ppm.

We also tried to implement reaction of 5-R¹-3-R²-3H-pyrrol-2-ones with 2-mercaptobenzimidazole under microwave radiation. Only the source compounds were detected in the reaction mixture, which means this reaction not proceeding under microwave radiation.

EXPERIMENTAL

IR spectra were recorded on an FSM-1201 Fourier spectrometer in KBr tablets, the spectral range being 400-4000 cm⁻¹. ¹H NMR spectra were obtained on a Varian-400 spectrometer within 20-25°C in CDCl₃, TMS being the internal reference. The working frequency was 400 MHz.

3-(2-amino-2-R¹-vinyl)-2-R²-2H-benzo[4,5]imidazo[2,1-b][1,3]thiazine-4(3H)-ones (2a-c). A mixture of 5-R-3-arylmethylidene-3H-furan-2-one (Ia,b,c) (0.01 mol) and 2-mercaptobenzimidazole (0.015 mol) was boiled in icy acetic acid with a catalytic amount of sulfuric acid during 30 hours, poured into cold water, and neutralized by a sodium carbonate solution. The crystals precipitated were filtered on a Schott filter and recrystallized from ethanol. For **2a**: yield 73%; mp 263-265⁰C; ¹H NMR, δ: 5.70-5.71 (1H, d), 5.72-5.73 (1H,d), 6.86-6.90 (1H, t), 9.97 (2H, NH₂), 7.19-7.66 (13H, m, Ar). Found (%) C, 66.74; H, 3.94; N, 6.69; S, 7.65. Calc. for C₂₄H₁₈N₃SOCl (%) C, 66.74; H, 4.17; N, 7.73; S, 7.42. For **2b**: yield 71%; mp 249-251⁰C; ¹H NMR, δ: 5.70-5.71 (1H, d), 5.73-5.74 (1H,d), 6.89-6.92 (1H, t), 9.97 (2H, NH₂), 7.17-7.63 (13H, m, Ar), 2.23 (3H, s). Found (%) C, 67.92; H, 4.60; N, 4.05; S, 7.50. Calc. for C₂₅H₂₀N₃SOCl (%) C, 67.33; H, 4.52; N, 9.42; S, 7.19. For **2c**: yield 68%; mp 141-142⁰C; ¹H NMR, δ: 5.68-5.69 (1H, d), 5.72-5.73 (1H,d), 6.82-6.86 (1H, t), 9.99 (2H, NH₂), 7.20-7.69 (13H, m, Ar), 3.82 (3H, s). Found (%) C, 68.75; H, 4.33; N, 8.10; S, 7.44. Calc. for C₂₅H₂₁O₂N₃S (%) C, 69.40; H, 4.95; N, 9.83; S, 7.50.

References

1. Anis'kova T.V., Yegorova A.Yu., and Chadina V.V. The synthetic capabilities of 3-arylmethylene-3H-furan-2-ones in the reaction with N,-C,-S-nucleophilic reagents// 5th International Conference on Organic Chemistry for Young Scientists (Abstract of Reports.), 2009. Saint-Petersburg: 2009. P.92

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