Materials of Conferences

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

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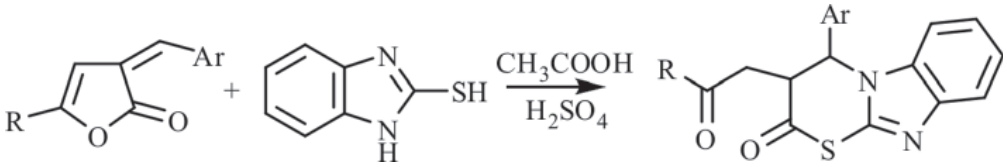
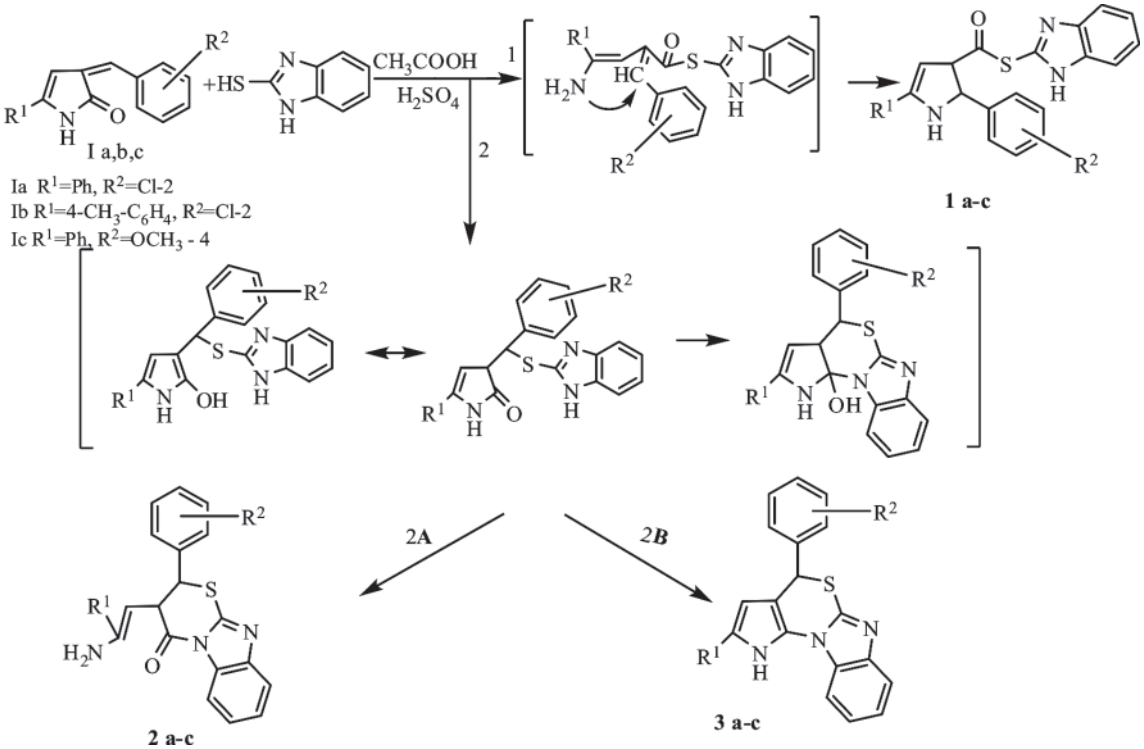
Interest to the arylmethylidene derivatives of 3H-pyrrol-2-ones is due to a wide spectrum of their useful properties, many of which find application in medicine, industry, and agriculture, their analogues are parts of alkaloids and drugs. Of special interest is modification of the pyrrolonic cycle under the action of nucleophilic reagents. We studied the reaction of 3-arylmethylidene-3H-furan-2-ones with binucleophilic – 2-mercaptobenzymidazole. 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-mercaptobenzymidazole 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-mercaptobenzymidazole 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-R^1-vinyl)-2-R^2-2H-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}, NH_2 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-R^1-3-R^2-3H-pyrrol-2-ones with 2-mercaptobenzymidazole 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 $CDCl_3$, 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-mercaptobenzymidazole (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 263–265 °C; ^1H NMR, δ: 5,70–5,71 (1H, d), 5,72–5,73 (1H,d), 6,86–6,90 (1H, t), 9,97 (2H, NH_2), 7,19–7,66 (13H, m, Ar). Found (%) C, 66,74; H, 3,94; N, 6,69; S, 7,65. Calc. for $C_{24}H_{18}N_3SOCl$ (%) C, 66,74; H, 4,17; N, 7,73; S, 7,42.

For **2b**: yield 71%; mp 249–251 °C; ^1H NMR, δ: 5,70–5,71 (1H, d), 5,73–5,74 (1H,d), 6,89–6,92 (1H, t), 9,97 (2H, NH_2), 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 $C_{25}H_{20}N_3SOCl$ (%) C, 67,33; H, 4,52; N, 9,42; S, 7,19

For **2c**: yield 68%; mp 141–142 °C; ^1H NMR, δ: 5,68–5,69 (1H, d), 5,72–5,73 (1H,d), 6,82–6,86 (1H, t), 9,99 (2H, NH_2), 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 $C_{25}H_{21}O_2N_3S$ (%) C, 69,40; H, 4,95; N, 9,83; S, 7,50.

References

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FUNDAMENTALS OF CHEMOMETRICS IN DIFFERENT BRANCHES OF CHEMICAL SCIENCE

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The article shows the possibility of applying the method of multilevel modeling in evaluating the physical and chemical variables.

In Nature, as well as in the natural sciences, everything is interconnected. This regular occurrence is usually not seen, if we bear in mind two functional parameters. But multiparameter functional relationship is observed when we apply not less than three characteristics to the sought-for parameter [1, 2, 3].

In the study of the method of multilevel modeling (MMLM), which permits to carry out mathematical modeling of certain chemical processes in different environments, and also to estimate absent (scarce) characteristics in physical-chemical methods of analysis, let's limit with the assumption that regression is linear and is determined by the following dependence:

$$Y = a + b_1X_1 + b_2X_2 + ... + b_nX_n. \quad (1)$$

If we accept that a number of arguments is equal to two, then in terms of geometry, this equation defines the plane in the space of variables X_1, X_2 and Y.

To determine parameters a, b_1, ... b_n in equation (1) let's apply the method of least squares. After differentiation according to the variable parameters this method leads to the system:

$$\Sigma y = na + b_1\Sigma X_1 + ... + b_n\Sigma X_n; \quad (2\text{-a})$$

$$\Sigma yX_1 = a\Sigma X_1 + b_1\Sigma X_1^2 + ... + b_n\Sigma X_1X_2...X_n; (2\text{-b})$$

. . . . . .

$$\Sigma yX_n = a\Sigma X_n + b_1\Sigma X_1X_2 + ... + b_n\Sigma X_n^2. (2\text{-c})$$

To solve this system we divide equation (2-a) to n, then we obtain:

$$a = y_{av} - b_1X_{1(av)} - b_2X_{2(av)} - ... - b_nX_{n(av)}.$$

Substituting this value for a in formula (1) and equation (2-b) and (2-c), we find out that the formula MMLM with n variables has the following form:

$$Y\text{-}y_{av} = b_1(X_1\text{-}X_{1(av)}) + b_2(X_2 - X_{2(av)}) + ... + b_n(X_n - X_{n(av)}), \quad (3)$$

the coefficients b_1, b_2, ..., b_n are found from the following system of linear equations:

$$b_1\Sigma x_1^2 + b_2\Sigma x_1x_2 + ... + b_n\Sigma x_1x_n = \Sigma x_1y_1;$$

$$b_1\Sigma x_1x_2 + b_2\Sigma x_2^2 + ... + b_n\Sigma x_2x_n = \Sigma x_2y_2;$$

. . . . . .

$$b_1\Sigma x_1x_n + b_2\Sigma x_2x_n + ... + b_n\Sigma x_n^2 = \Sigma x_ny_n,$$

where the following conventional signs are adopted: