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LETTERS TO THE EDITOR

REACTION OF 2-HYDRAZINO-BENZIMIDAZOLES WITH ACETOACETIC ESTER AND TRIFLUOROMETHYL-ACETOACETIC ESTER

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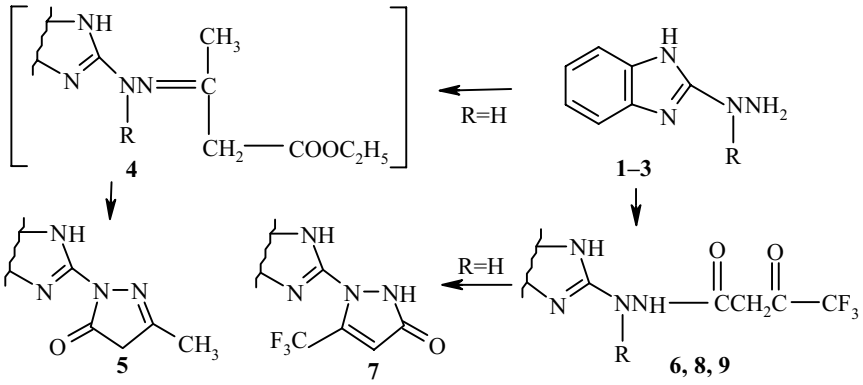
Keywords: 1-(2-benzimidazolyl)-1-ethyl-2-hydrazide of trifluoromethylacetoacetic acid, 2-hydrazinobenzimidazole, 2-(3-methyl-5-oxopyrazol-1-yl)benzimidazole, trifluoromethylacetoacetic ester, 2-(2H-3-oxo-5-trifluoromethylpyrazol-1-yl)benzimidazole.

Condensation of 2-hydrazino(alkylhydrazino)benzimidazoles **1-3** with β-dicarbonyl compounds occurs ambiguously. Depending on the nature of the dinucleophilic reagent either 2-substituted benzimidazoles [1] are obtained or ring closure occurs to give 1,2,4-triazepino- [2] and 1,2,4-triazinobenzimidazoles [3].

Condensation of 2-hydrazinobenzimidazole (**1**) with acetoacetic ester in boiling methanol (0.5 h) with a catalytic amount of hydrochloric acid occurs *via* initial formation of hydrazone **4** which cyclizes in the reaction conditions to 2-(3-methyl-5-oxopyrazol-1-yl)benzimidazole (**5**). Under analogous conditions hydrazine **1** reacts with trifluoromethylacetoacetic ester to give trifluoromethylacetoacetic acid 2-benzimidazoylhydrazide (**6**) and the product of its cyclization, isomeric 2-(2H-3-oxo-5-trifluoromethylpyrazol-1-yl)benzimidazole (**7**).



1, **4**, **6** R = H, **2**, **8** R = C_2H_5, **3**, **9** R = $CH_2C_6H_5$

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Condensation of alkylhydrazinobenzimidazoles **2** and **3** with trifluoromethylacetoacetic ester in boiling acetic acid (3 h) or toluene (5 h) stopped at the stage of synthesis of the substituted hydrazides **8** and **9**; attempts of cyclization of these compounds were unsuccessful.

2-(3-Methyl-5-oxopyrazol-1-yl)benzimidazole (5). Yield 60%; mp 249-250°C (acetonitrile). R_f 0.71. IR spectrum (KBr), ν, cm^{-1}: 1660 (C=O), 3330 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.28 (3H, s, CH_3); 2.19 (2H, s, CH_2); 7.17-7.52 (4H, m, H_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 215 (10), M^+ 214 (100), $[(M + H) - C_4H_5N_2O]^+$ 118 (28), $[M - C_7H_5N_2]^+$ 97 (18). Found, %: C 61.83; H 4.65; N 26.45. $C_{11}H_{10}N_4O$. Calculated, %: C 61.71; H 4.74; N 26.15.

Hydrazide 6. Yield 10%; mp 264-266°C (DMF). IR spectrum (KBr), ν, cm^{-1}: 1670, 1710 (C=O), 3250 (NH). Found, %: C 45.99; H 3.21; N 19.60. $C_{11}H_9N_4F_3O_2$. Calculated, %: C 46.15; H 3.17; N 19.57.

2-(2H-3-Oxo-5-trifluoromethylpyrazol-1-yl)benzimidazole (7). Yield 80%; mp 241-242°C (aqueous methanol). R_f 0.84. IR spectrum (KBr), ν, cm^{-1}: 1670 (C=O), 3260 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.31 (1H, s, NH); 7.30-7.60 (4H, m, H_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 269 (14), M^+ 268 (100), $[M - F]^+$ 249 (3), $[M - CF_3]^+$ 199 (27), $[(M + H) - NHCOCHCCF_3]^+$ 132 (12), $[(M + H) - C_4H_2N_2F_3O]^+$ 118 (24). Found, %: C 49.26; H 2.63; N 20.89. $C_{11}H_7N_4F_3O$. Calculated, %: C 49.26; H 2.63; N 20.89.

Trifluoromethylacetoacetic Acid 1-(2-Benzimidazolyl)-1-ethyl-2-hydrazide (8). Yield 80%; mp 230-231°C (aqueous methanol). IR spectrum (KBr), ν, cm^{-1}: 1660, 1720 (C=O), 3190 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.20 (3H, t, CH_2CH_3); 3.37 (2H, s, CH_2); 3.78 (2H, q, CH_2N); 6.90-7.40 (4H, m, H_{arom}). Found, %: C 49.41; H 4.43; N 17.85. $C_{13}H_{13}N_4F_3O$. Calculated, %: C 49.69; H 4.13; N 17.83.

Trifluoromethylacetoacetic Acid 1-(2-Benzimidazolyl)-1-benzyl-2-hydrazide (9). Yield 88%; mp 220-221°C (acetonitrile). IR spectrum (KBr), ν, cm^{-1}: 1650, 1680 (C=O), 3180 (NH). ^1H NMR spectrum (CD_3OD), δ, ppm: 3.20 (2H, s, CH_2); 4.82 (2H, s, CH_2N); 6.88-7.25 (4H, m, H_{arom}). Found, %: C 57.32; H 3.95; N 14.95. $C_{18}H_{15}N_4F_3O$. Calculated, %: C 57.44; H 4.01; N 14.88.

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