NOVEL SYNTHESIS OF CONDENSED 2H-1,4-THIAZINE SYSTEMS

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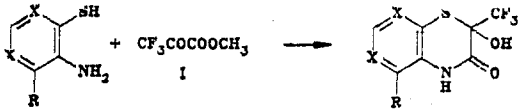
Annelated 1,4-thiazines are usually obtained from 1,2-aminothiols and α-haloketones [1], nitromethyl ketones, α-haloacids, or related compounds [2]. We have shown that methyl trifluoropyruvate (I) undergoes heterocyclization with aromatic and heteroaromatic 1,2-aminothiols to give the annelated 2-hydroxy-2-trifluoromethyl-2H-1,4-thiazin-3-ones (II, III).



II X=CH, R=H; III X=N, R=OCH$_3$ II, III

For example, o-aminothiophenol reacts with an equimolar amount of the ester (I) in benzene at 25°C to give after seven days (and boiling for five hours) approximately 90% of (II). 5-Amino-6-methoxypyrimidine-4-thiol reacts with the ester (I) under similar conditions.

The orientation of addition of (I) to the aminothiols was shown by comparing the ^{13}C NMR spectrum of (II) with that of its oxygen analog [3].

2-Hydroxy-2-trifluoromethyl-2H-1,4-benzo[b]thiazin-3-one (II). Yield 88%, mp 186-188°C; R_f 0.45 (acetone–CCl_4, 1:2). ^{13}C NMR spectrum (acetone): 161.31 ($C_{(3)}$); 136.93 ($C_{(4a)}$); 128.88, 128.57 ($C_{(6)}$, $C_{(7)}$); 125.22, 118.41 ($C_{(5)}$, $C_{(8)}$); 124.86 (CF_3, J_{CF} = 284.00 Hz); 117.59 ($C_{(8a)}$; 77.41 ($C_{(2)}$, J_{CF} = 31.00 Hz. ^1H NMR spectrum (acetone-D_6): 7.40-7.00 (4H, m, 5–8-H, ABCD-system). ^{19}F NMR spectrum (acetone-D_6): −0.88 (3F, s, CF_3), m/z 249 (M^+).

2-Hydroxy-2-trifluoromethyl-5-methoxy-2H-pyrimido[6,5-b][1,4]thiazin-3-one (III). Yield 71%, mp 206-208°C (from nitromethane); R_f 0.35 (acetone–CCl_4, 1:2). ^{13}C NMR spectrum (DMSO): 160.85 ($C_{(3)}$); 158.92 ($C_{(5)}$); 153.56 ($C_{(4a)}$); 148.57 ($C_{(8a)}$); 125.51 (CF_3, J_{CF} = 283.00 Hz); 120.57 ($C_{(7)}$); 80.44 ($C_{(2)}$, $^2J_{CF}$ = 30.00 Hz); 56.83 (OCH_3), m/z 283 (M^+).

LITERATURE CITED

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