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SYNTHESIS OF 4-IMINO-2-TRIFLUOROMETHYL-3,4-DIHYDRO-2H-BENZO-[1,3]THIAZINES

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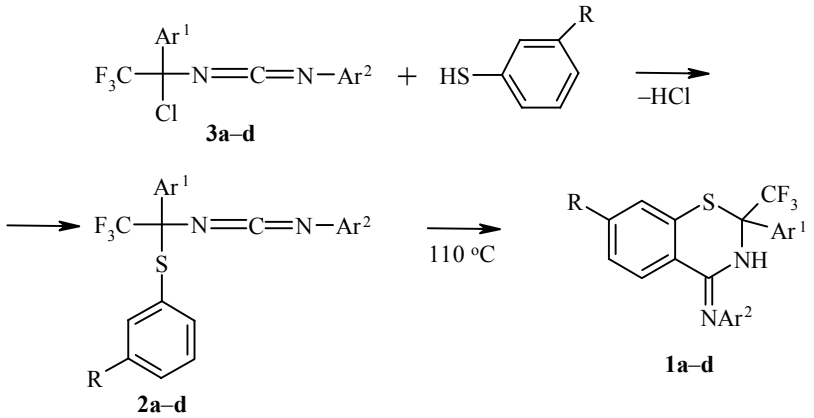
4-Imino-2-oxo-3,4-dihydro-1,3-benzothiazines are obtained by condensation of 3-chlorobenzisothiazolium chloride with formamides [1]. Their analogs containing a trifluoromethyl group in the 2 position of the thiazine ring have not been studied.

We have synthesized 4-arylimino-2-trifluoromethyl-3,4-dihydro-2H-benzo[1,3]thiazines (**1a-d**), based on the use of N-(1-aryl-1-arylthio-1-trifluoromethyl)-N'-arylcarbodiimides (**2a-d**) obtained by reaction of 1-chloroalkylcarbodiimides (**3a-d**) [2] with thiophenols (**4a,b**). The method essentially consists of noncatalytic intramolecular cyclization of heterocumulenes **2** as a result of electrophilic attack by the carbodiimide moiety at the activated substituent R in the *ortho* position of the arylthio group. Most likely, the proposed approach is a general one, as is evidenced by the synthesis [3, 4] of other types of benzazine systems.



1, 2, 3 a $Ar^1 = Ar^2 = Ph$; **b** $Ar^1 = Ph$, $Ar^2 = 4\text{-}MeC_6H_4$; **c** $Ar^1 = 4\text{-}MeC_6H_4$, $Ar^2 = Ph$, **d** $Ar^1 = Ar^2 = 4\text{-}MeC_6H_4$; **1, 2 a** R = Me, **b-d** R = MeO, **4 a** R = Me, **b** R = MeO

The ^1H and ^{19}F NMR spectra were measured in DMSO-d_6 on a Varian Gemini 300 spectrometer (internal standard TMS and $CFCl_3$, respectively). The IR spectra were taken on a UR-20; in toluene for compounds **2a-d**, in pressed KBR disks for compounds **1a-d**.

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A solution of thiophenol **4a,b** (0.005 mol) and triethylamine (0.005 mol) in toluene (5 ml) was added with stirring to a solution of 1-chloroalkylcarbodiimide **3a-d** (0.005 mol) in toluene (30 ml). The mixture was stirred for 2 h and the precipitate of triethylamine hydrochloride was filtered off. 1-(Arylthio)alkylcarbodiimides **2** contained in the filtrate (IR spectrum, ν, cm^{-1}: 2150-2165 (N=C=N); ^{19}F NMR spectrum, δ_F, ppm: 73-74 [5]) were boiled without separation for 16 h. The solvent was removed under vacuum, and the residue was recrystallized from a 1:1 hexane–benzene mixture.

7-Methyl-2-phenyl-4-phenylimino-2-trifluoromethyl-3,4-dihydro-2H-benzo[1,3]oxazine (1a). Yield 24%; mp 179-180°C. IR spectrum, ν, cm^{-1}: 1645 (C=N), 3435 (N–H). ^1H NMR spectrum, δ, ppm: 2.33 (3H, s, CH_3); 7.80 (1H, d, 5-H); 7.06 (1H, d, 8-H); 6.91 (1H, dd, 6-H); 7.66-7.08 (10H, m, two C_6H_5 groups); 9.11 (1H, s, NH). ^{19}F NMR spectrum: 81.37 (s, CF_3). Found, %: C 66.54; H 4.02; N 7.38. $C_{23}H_{17}F_3N_2S$. Calculated, %: C 66.32; H 4.30; N 7.03.

7-Methoxy-2-phenyl-4-(4-tolylimino)-2-trifluoromethyl-3,4-dihydro-2H-benzo[1,3]oxazine (1b). Yield 48%; mp 195-196°C. IR spectrum, ν, cm^{-1}: 1640 (C=N), 3440 (N–H). ^1H NMR spectrum, δ, ppm: 2.29 (3H, s, CH_3); 3.81 (3H, s, CH_3O); 7.83 (1H, d, 5-H); 6.81 (1H, d, 8-H); 6.63 (1H, dd, 6-H); 7.66-7.17 (9H, m, C_6H_5, C_6H_4); 8.99 (1H, s, NH). ^{19}F NMR spectrum: 81.37 (s, CF_3). Found, %: C 64.82; H 4.30; N 6.48. $C_{23}H_{19}F_3N_2OS$. Calculated, %: C 64.47; H 4.47; N 6.54.

7-Methoxy-4-phenyliminino-2-(4-tolyl)-2-trifluoromethyl-3,4-dihydro-2H-benzo[1,3]oxazine (1c). Yield 51%; mp 190-191°C. IR spectrum, ν, cm^{-1}: 1650 (C=N), 3465 (N–H). ^1H NMR spectrum, δ, ppm: 2.25 (3H, s, CH_3); 3.82 (3H, s, CH_3O); 7.83 (1H, d, 5-H); 6.81 (1H, d, 8-H); 6.64 (1H, dd, 6-H); 7.54-7.06 (9H, m, C_6H_5, C_6H_4); 9.01 (1H, s, NH). ^{19}F NMR spectrum: 81.42 (s, CF_3). Found, %: C 64.74; H 4.42; N 6.69. $C_{23}H_{19}F_3N_2OS$. Calculated, %: C 64.47; H 4.47; N 6.54.

7-Methoxy-2-(4-tolyl)-4-(4-tolylimino)-2-trifluoromethyl-3,4-dihydro-2H-benzo[1,3]oxazine (1d). Yield 54%; mp 172-173°C. IR spectrum, ν, cm^{-1}: 1645 (C=N), 3450 (N–H). ^1H NMR spectrum, δ, ppm: 2.25 (3H, s, CH_3); 2.29 (3H, s, CH_3); 3.81 (3H, s, CH_3O); 7.84 (1H, d, 5-H); 6.81 (1H, d, 8-H); 6.63 (1H, dd, 6-H); 7.52-7.17 (8H, m, two C_6H_4 groups); 9.00 (1H, s, NH). ^{19}F NMR spectrum: 81.46 (s, CF_3). Found, %: C 64.82; H 5.01; N 6.20. $C_{24}H_{21}F_3N_2OS$. Calculated, %: C 65.14; H 4.78; N 6.33.

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