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USE OF THE TETRACHLOROSILANE–SODIUM AZIDE SYSTEM FOR SYNTHESIS OF TETRAZOLES FROM CARBOXYLIC ACID AMIDES

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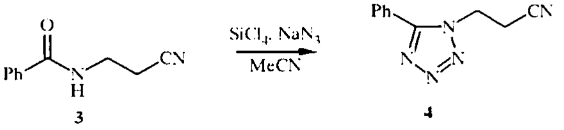
A promising aziding system, tetrachlorosilane–sodium azide, has been proposed for synthesis of tetrazoles. This system has been used successfully to obtain NH-unsubstituted tetrazoles from primary carboxylic acid amides in 76-94% yield [1]. The use of this system for azidation of (5-phenyltetrazol-2-yl)acetamide (**1**) made it possible to obtain the corresponding ditetrazole **2**.

Based on the reaction mechanism proposed in [1] and assuming that secondary amides can be used as the substrate, we have demonstrated the possibility of formation of 1,5-disubstituted tetrazoles when secondary amides react with the system tetrachlorosilane–sodium azide. N-(2-Cyanoethyl)benzamide (**3**) reacts with the indicated system with formation of 1-(2-cyanoethyl)-5-phenyltetrazole (**4**).



Probably secondary amides are less reactive with respect to the given aziding system than primary amides, since a significantly longer time was required for the process to go to completion.

5-(5-Phenyltetrazol-2-yl)methyltetrazole (2). A solution of amide **1** (2.03 g, 0.01 mol), tetrachlorosilane (1.70 g, 0.01 mol), and sodium azide (1.95 g, 0.03 mol) in of dry acetonitrile (20 ml) was boiled with stirring and protection from moisture in the air for 3 h (monitored by TLC). The reaction mass was poured into a cold aqueous solution of sodium carbonate. The silicic acid precipitate was filtered off; sodium nitrite (2.07 g, 0.01 mol) was added to the filtrate and the solution was slowly acidified with conc. HCl to pH 2. The precipitate formed was filtered off and recrystallized from aqueous ethanol. Obtained 1.70 g (71%) of ditetrazole **2**; mp 145°C. According to data in [2], mp 147.5-148°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 6.52 (2H, s, CH_2); 7.54-8.12 (5H, m, Ph); 14.71 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 46.1 (CH_2), 126.2, 126.8, 128.7, 130.3 (Ph), 153.5 (CN_4), 165.0 ($Ph\underline{C}N_4$). Found, %: C 47.43; H 3.67; N 49.41. $C_9H_8N_8$. Calculated, %: C 47.37; H 3.53; N 49.10.

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1-(2-Cyanoethyl)-5-phenyltetrazole (4). A solution of amide **3** (1.74 g, 0.01 mol), tetrachlorosilane (2.55 g, 0.015 mol), and sodium azide (2.60 g, 0.04 mol) in dry acetonitrile (50 ml) was boiled with stirring while protecting it from moisture in the air for 15 h (monitored by TLC). The reaction mass was poured into a cold aqueous solution of sodium carbonate. The precipitate was filtered off, washed with acetone (2×50 ml), and the acetone filtrate was evaporated. The residue was recrystallized from aqueous acetone. Obtained 0.70 g (35%) of tetrazole **4**; mp 79-80°C. ^{1}H NMR spectrum (acetone-d$_6$), δ, ppm: 3.32 (2H, t, *J* = 6.6 Hz, CH_2CN); 4.93 (2H, t, *J* = 6.6 Hz, $C\underline{H}_2CH_2CN$); 7.66-7.87 (5H, m, Ph). ^{13}C NMR spectrum: 18.3 ($\underline{C}H_2CN$); 44.1 ($\underline{C}H_2CH_2CN$); 117.3 (CN); 124.5, 129.5, 129.7, 131.7 (Ph); 155.1 (CN_4). Found, %: C 60.87; H 4.10; N 35.84. $C_{10}H_9N_5$. Calculated, %: C 60.29; H 4.55; N 35.15.

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