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SHORT COMMUNICATIONS

Cycloaddition of Chloral *N*-Alkoxycarbonylimines to Substituted 1,2,4-Thiadiazol-5(2*H*)-imines

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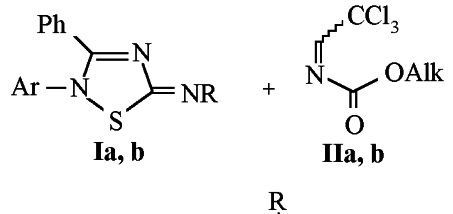
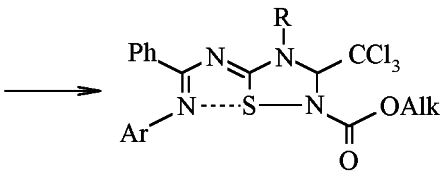
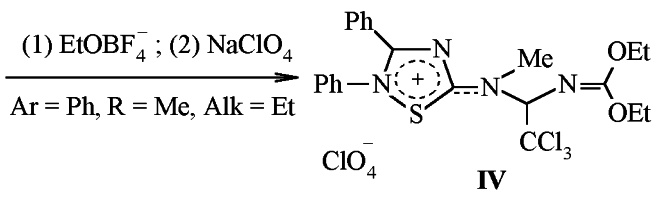
Recently was found that the avalabbe multycenter nucleophilic reagents, substituted 1,2,4-thiadiazol-5(2*H*)-imines (**I**) are capable of [3+2]-cycloaddition to nitriles and heterocumulenes [1]. In this publication we report on the fact that the similar process easily proceeds in the reaction of **I** with chloral *N*-alkoxycarbonylimines (**II**), possessing emphasized electrophilicity of their C=N bond. Structure of the formed cycloaddition compounds **III** was established by spectral and x-ray structural investigations which prove formation of 1,2,4-thiadiazolidine ring with the sulfur atom coordinated additionally with the terminal nitrogen in the side chain of 1,3- diaza-1,3-diene group. Such coordination is obviously significant not only for stabilization of structure of compounds **III** but also in the process of **IIIa** → **IV** ethylation:



Ia, b **IIa, b**



IIIa, b



IV

I, III, Ar = Ph, R = Me (**a**), Ar = 4-MeC_6H_4, R = 4-$MeOC_6H_4$ (**b**); **II, III**, Alk = Et (**a**), Me (**b**).

The cycloaddition of other chloral *N*-acylimines to **I** and reactivity of compounds **III** will be considered in details in future publications.

Ethyl 4-methyl-3-trichloromethyl-5-[(*E*)-*N*-phenylbenzimidoyl-(*Z*)-imino]-1,2,4-thiadiazolidyne 2-carboxylate (IIIa). To a solution of 4.55 g (15 mmol) of base Ia hydrochloride [2] in 15 ml of CH_2Cl_2 was added with stirring in 0.5 h a solution of 3.28 g (15 mmol) of *N*-ethoxycarbonylchloralimine [3] and 1.52 g (15 mmol) of triethylamine in 10 ml of CH_2Cl_2. The mixture was stirred for 5 h at room temperature, 30 ml of water, was added, the organic layer was separated, the solvent was removed in vacuo. To the residue 15 ml of ethanol was added, the crystalline precipitate was filtered off and recrystallized from ethyl acetate. Yield of compound **IIIa** 5.1 g (70%), colorless crystals, mp 146–147°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 t (3H, $\underline{C}\underline{H}_3CH_2$), 3.69 s (3H, CH_3N), 4.19 q (2H, $CH_3\underline{C}\underline{H}_2$), 5.90 s (1H, CCl_3CH), 7.03–7.57 m (10H, H arom.). Found, %: Cl 21.65; N 11.29. $C_{20}H_{19}Cl_3N_4O_2S$. Calculated, %: Cl 21.89; N 11.53.

Methyl-4-*n*-methoxyphenyl-5-[(*E*)-*N*-*n*-tolyl-benzimidoyl-(*Z*)-imino]-3-trichloromethyl-1,2,4-thiadiazolidine 2-carboxylate (IIIb). To a suspension of 2.24 g (6 mmol) of compound Ib obtained by the general procedure for the synthesis of base **I** [1] in 15 ml anhydrous dioxane was added 1.23 g (6 mmol) of *N*-methoxycarbonylchloralimine. The mixture was stirred for 5 h at 20–25°C, the precipitate formed was filtered off and recrystallized from benzene. Yield of compound **IIIb** 2.29 g (66%), colorless crystals, mp 179°C (decomp.) ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H, $\underline{C}\underline{H}_3C_6H_4$), 3.80 s (3H, CH_3O), 6.45 s (1H, CCl_3CH), 6.93–7.56 m (13H, H arom.). Found, %: Cl 18.25; S 5.51. $C_{26}H_{23}Cl_3N_4O_3S$. Calculated, %: Cl 18.40; S 5.55. According to X-ray structural analysis, the bond

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lengths (*d*, Å) are: S^1–N^2 1.916 (2); S^1N_{exo} 1.960 (2); N^2–C^3 1.421 (3); C^3–N^4 1.466 (3); N^4–C^5 1.351 (3); C^5–S^1 1.733 (3). **5-[*N*-Methyl-*N*-(1-diethoxymethylenamino-2,2,2-trichloro)ethyl]amino-2,3-diphenyl-1,2,4-thiadiazolium perchlorate (IV).** To a solution of 1.46 g (3 mmol) of compound **IIIa** in 10 ml of CH_2Cl_2 was added 0.57 g (3 mmol) of triethyloxonium tetrafluoroborate. The mixture was stirred for 0.5 h and left for 48 h at 20–25°C. Volatile components were removed in vacuo and to the residue was added 5 ml of ethyl acetate, the precipitate was filtered off and then dissolved in 10 ml of methanol. To the solution was added 3 ml of 3N solution of sodium perchlorate in methanol and after 24 h the precipitate was filtered off. Yield of compound **IV** was 1.03 g (55%), mp 167°C (decomp.) (MeOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 m (6H, $C\underline{H}_3CH_2$), 3.85 s (3H, CH_3N), 4.42 m (2H, $CH_3C\underline{H}_2$), 4.64 m (2H, $CH_3C\underline{H}_2$), 5.79 c (1H, CCl_3CH), 7.30–7.58 m (10H, H arom.). Found, %: Cl 2.50; S 5.14. $C_{22}H_{24}Cl_4N_4O_6S$. Calculated, %: Cl 23.08; S 5.22. The ^{1}H NMR spectra were registered on Varian VXR-300 (compounds **IIIa** and **IV**) and Bruker WP-100 (**IIIb**) instruments with internal TMS. H-ray structural investigation of compound **IIIb** was performed in cooperation with dr. Nernega on an Enraf–Nonius CAD-4 difractometer (MoK_α irradiation, λ 0.71069 Å).

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