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An Efficient Method for the Synthesis of Aliphatic α-Organothio Aldoximes

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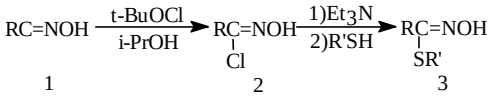
Abstract: A new and simple procedure for the synthesis of aliphatic α-organothio aldoximes was reported. The aliphatic aldoxime was chlorinated by t-BuOCl, the resulting hydroxime acid chloride was treated with triethylamine and alkyl mercaptan in a one pot procedure to get the target compounds. The method is very efficient with high yield and good purity.

Keywords: Aliphatic α-organothio aldoximes; α-chlorination; t-butyl hypochlorite.

The importance of the aliphatic α-organothio aldoxime compounds **3** in the preparation of various pesticides is well established. Molecules comprising the α-organothio oxime moiety have been reported to exhibit wide range of biological activities, such as insecticidal, nematocidal, miticidal activity [1, 2]. In the synthesis of the compounds **3**, the α-chlorination of the corresponding aliphatic aldoxime **1** is the key step. In conventional methods, the aliphatic aldoxime **1** is α-chlorinated by chlorine (Cl_2), then the resulting hydroxime acid chloride **2** is treated with sodium alkyl mercaptide to obtain the desired compounds **3** [3]. Although free Cl_2 is the most common chlorinating agent, it is laborious to determine the accurate amount that has been absorbed, and the high reactivity of Cl_2 always leads to side reactions. In connection with an ongoing research project, we require an efficient and simple method for the synthesis of the compound **3**. An improved synthesis process according to the following scheme is reported in this paper.



3a: R'=CH_3,	R''=CH_3	3d: R=CH $(CH_3)_2$	R''=CH_3
3b: R'=CH_3,	R''=$CH_3CH_3CH_2$	3b: R=CH $(CH_3)_2$	R''=$CH_3CH_3CH_2$
3a: R'=CH_3,	R''=CH_2Ph	3c: R=CH $(CH_3)_2$	R''=CH_2Ph

In the process, the aliphatic aldoxime **1** is chlorinated by t-butyl hypochlorite (t-BuOCl). t-Butyl hypochlorite is milder and more safe than chlorine, and it is readily prepared and stored. It has been widely used as chlorinating agent in other fields[4], but its utilization to this compound has been seldom reported. Our experiments, which show

satisfactory results, indicate that t-BuOCl is useful chlorinating agent for aliphatic aldoxime. The reaction is fast, just for about 15 minutes, and almost in quantitative yield without side products. After chlorination, the reaction mixture is treated with triethylamine and alkyl mercaptan to give compound **3** in a one pot procedure. The overall yield of the reaction can reach up to 85-93% .

General Procedure for Preparation of α-Organothio aldoxime 3

t-Butyl hypochlorite (0.042mol) was added in portions to a mixture of aldoxime (0.04mol), 15 mL isopropanol and 30 mL dichloromethane at -12°C with rapid stirring. After stirring for 15 minutes, triethylamine (0.04 mol) was added, the reaction mixture was stirred for a few minutes, and alkyl mercaptan (0.04 mol) was added to. The reaction remained at -12°C for 1 hr, then 20 mL cool water was added to the mixture to dissolve the solid. The organic phase was seperated and the water layer was extracted with 2×10 mL CH_2Cl_2, the combined organic layer was dried over $MgSO_4$, and the solvent was removed *in vacuo* to give the compound **3** as white solid.
Compound **3a**: yield 85.2%; mp: 88-92℃. ^{1}HNMR ($CDCl_3$): δ 2.16 (s, CH_3), 2.36 (s, SCH_3), 9.38 (br s, NOH). Compound **3b**: yield 89.1%; mp: 43-47℃. ^{1}HNMR ($CDCl_3$): δ 0.99 (t, CH_3), 1.64 (q, CH_2), 2.13 (s, CH_3C=), 2.79 (t, SCH_2), 9.79 (br s, NOH). Anal.Calcd for $C_5H_{11}NOS$: C, 45.08; H, 8.32; N, 10.51. Found: C, 45.17; H, 8.43; N, 10.42 Compound **3c**: yield 88.1%; mp: 140-143℃. ^{1}HNMR ($CDCl_3$): δ 2.10 (s, CH_3), 4.08 (s, SCH_2), 7.34 (s, C_6H_5), 8.4 (br s, NOH). Anal.Calcd for $C_9H_{11}NOS$: C, 59.64; H, 6.11; N, 7.70 . Found: C, 59.67; H, 6.24; N, 7.37. Compound **3d**: yield 86%; mp: 61-62℃. ^{1}HNMR ($CDCl_3$): δ 1.25 (d, $(CH_3)_2$), 1.60 (m, CH_2), 2.6 (t, SCH_3), 3.06-3.10 (m, CH). 2.40 (s, SCH_3), 2.65-2.98 (m, CH), 9.64 (br s, NOH). Anal.Calcd for $C_5H_{11}NOS$: C, 45.08; H, 8.32; N, 10.51. Found: C, 45.08; H, 7.98; N, 10.66. Compound **3e**: yield 93.2%; mp: 39-43℃. ^{1}HNMR ($CDCl_3$): δ 0.95 (t, CH_3), 1.13-1.16 (d, $(CH_3)_2$), 2.40 (s, SCH_3), 2.65-2.98 (m, CH), 9.64 (br s, NOH). Anal.Calcd for $C_7H_{15}NOS$: C, 52.14; H, 9.37; N, 8.68. Found: C, 51.95; H, 8.88; N, 8.63. Compound **3f**: yield 93.3%; mp: 100-103℃. ^{1}HNMR ($CDCl_3$): δ 1.11 (d, $(CH_3)_2$), 3.15 (m, CH), 4.18 (s, CH_2), 7.29-7.31 (m, C_6H_5), 8.4 (br s, NOH). Anal.Calcd for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.69. Found: C, 63.41; H, 7.13; N, 6.87.

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