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ORIGINAL PAPER

A synthesis of *N*-alkyl and *N,N*-dialkyl *O*-ethyl thiocarbamates from diethyl dixanthogenate using different oxidants

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Abstract A novel synthesis of *N*-alkyl and *N,N*-dialkyl *O*-ethyl thiocarbamates from diethyl dixanthogenate and primary and secondary amines, using three oxidizing systems, has been developed on the laboratory scale, and the method using sodium hypochlorite has been applied on a semi-industrial scale. The effect of the oxidizing agents, sodium hypochlorite, in-situ-generated peracetic acid, and the manganese(II) acetate/oxygen system on product purity and yield was studied. The results obtained by use of these three methods were compared with those obtained by reaction of sodium ethyl xanthogenacetate and amines, and of sodium ethyl xanthate with amines in the presence of sulfated nickel zeolite catalyst. The reaction mechanism of sodium hypochlorite oxidation has been established on the basis of isolation of reaction intermediates and determination of their structure by use of Fourier-transform infrared, ^{1}H and ^{13}C NMR, and mass spectrometric methods. The suggested sodium hypochlorite and manganese(II) acetate/oxygen systems have many advantages in comparison with commercial and catalytically promoted synthetic methods, because they are new ecologically friendly syntheses.

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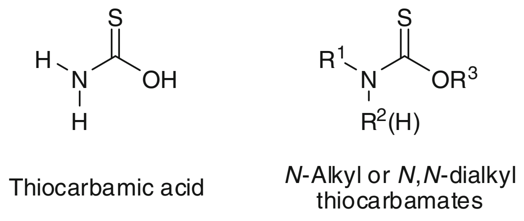
Introduction

The synthesis and properties of *N*-alkyl and *N,N*-dialkyl *O*-ethyl thiocarbamates have been of interest for many years because of their structural characteristics, for example the direct connection of the thiocarbonyl group to nitrogen, which contributes to their significant biological activity [1, 2].

Thiocarbamates are derivatives of thiocarbamic acid, thus *N*-alkyl and *N,N*-dialkyl thiocarbamates are *N*-alkyl and *N,N*-dialkyl *O*-alkyl esters of thiocarbamic acid (Scheme 1).

Wide application of these selective collectors in flotation of copper and zinc ores is well known [2]. They are also fungicidal [3], bactericidal [4], herbicidal [5], pesticidal [6], and pharmaceutically active [7] compounds. A general method for their preparation is the reaction of dithiocarbonic acid *O*,*S*-diesters in aqueous or alcoholic solution with primary or secondary amines, and reaction of monothiocarbonic acid *O*-ester chloride with the corresponding amines [8]. Thiocarbonic esters are obtained in a single-stage reaction of an alkaline xanthogenate, an amine, and an oxidizing agent [9]. Also, synthesis of thiocarbamates from thiols and isocyanates under catalyst-free and solvent-free conditions has been performed [10].

Besides other procedures reported in the literature [11–15], alkyl thiocarbamates can be obtained by reaction of sodium or potassium alkyl xanthates in aqueous solution with primary or secondary aliphatic amines and elemental sulfur [16]. Thiocarbamates can also be prepared by



Scheme 1

reaction of xanthogenates and amines in the presence of nickel(II) sulfate hexahydrate as catalyst [17].

However, reported methods for thiocarbamate synthesis have specific disadvantages which necessitate development of a more efficient and convenient method applicable on an industrial scale. Nowadays, the most striking criterion for choice of a production process is environmental friendliness. Development of a process which could use raw materials either from a commercial source or waste material could be an optimum alternative for selection of new production technology. One such idea is developed in this work focused on the possibility of using the waste material diethyl dixanthogenate (3,8-dioxa-5,6-dithiadecane-4,7-dithione) for synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates. Diethyl dixanthogenate is an inevitably generated oxidizing by-product from xanthate flotation collector production plants, or it could be available as commercial material. The main objective of this study was to develop a novel optimum synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates from waste diethyl dixanthogenate using different oxidizing agents.

Results and discussion

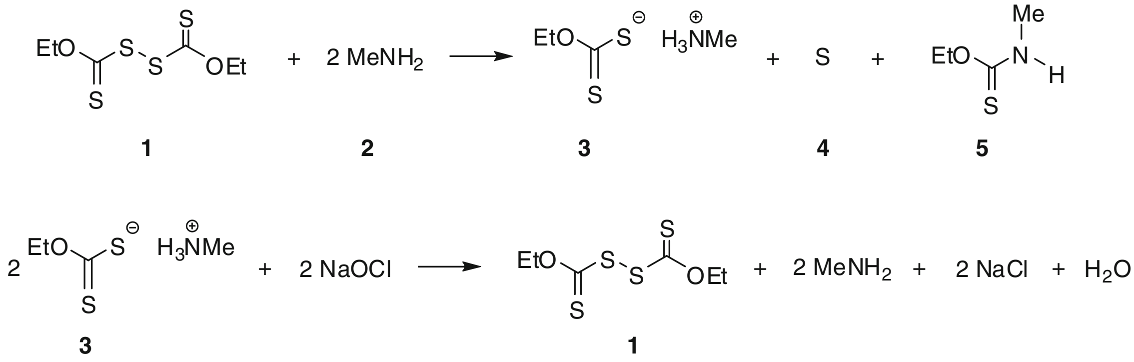
In this work, a novel synthesis of eight *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates was developed, starting from diethyl dixanthogenates and primary and secondary mono and disubstituted alkyl amines in the presence of oxidizing agents. Synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates from diethyl dixanthogenates and amines without an oxidizing agent gave only a minor quantity of product which was difficult to isolate from the crude reaction product. That result indicates that oxidizing species are crucially important in successful thiocarbamate synthesis. Three oxidizing agents were used: sodium hypochlorite, in-situ-generated peracetic acid, and the manganese(II) acetate/oxygen system [18].

The alkyl amines used were: methylamine, dimethylamine, ethylamine, diethylamine, *n*-propylamine, di-*n*-propylamine, isopropylamine, and diisopropylamine. Study of the reaction mechanism indicates nucleophilic attack of the amine on the S–S bond, assisted by the oxidizing species present, probably causes heterolytic cleavage of that bond, producing *O*-ethyl thiocarbamic acid methylammonium salt (**3**), elemental sulfur (**4**), and *N*-methyl *O*-ethyl thiocarbamate (**5**). In addition, the oxidizing species in the reaction media oxidizes the intermediate product **3** to the starting diethyl dixanthogenate (**1**) (Scheme 2).

Moreover, the results of the innovative synthesis have been compared with those obtained by reaction of sodium ethyl xanthogenacetate and mono and dialkyl amines [19], an industrial method widely used for thiocarbamate production. Catalytically promoted synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates using sulfated nickel zeolite catalyst [20] was performed for evaluation of the success of the developed innovative methods.

According to the established optimum synthetic methods 1, 2, and 3 described in the Experimental section, a series of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates were obtained; the results are given in Table 1.

From the results presented in Table 1 it is apparent that satisfactory yields and purities of the *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates were achieved by use of the optimum methods 1–3 developed in this work. The best results were obtained by use of the manganese(II) acetate/oxygen system, somewhat lower with sodium



Scheme 2

Table 1 Yields and purities of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates obtained according to methods 1, 2, and 3

No.	Compound	Method 1		Method 2		Method 3	
		Yield (%)	GC[a] (%)	Yield (%)	GC (%)	Yield (%)	GC (%)
5	EtOC(S)NHMe	87.2	97.9	82.8	98.6	95.8	98.7
6	EtOC(S)NMe$_2$	87.0	97.8	81.3	97.4	94.6	97.6
7	EtOC(S)NHEt	86.0	97.0	80.0	97.5	94.6	97.9
8	EtOC(S)NEt$_2$	86.8	97.6	79.4	97.8	93.0	98.2
9	EtOC(S)NHPr	86.2	98.0	77.7	98.3	94.8	98.4
10	EtOC(S)NPr$_2$	82.5	98.4	75.3	98.0	94.7	98.8
11	EtOC(S)NH(*i*-Pr)	80.1	99.6	73.1	99.1	92.0	99.0
12	EtOC(S)N(*i*-Pr)$_2$	74.0	98.9	64.9	98.6	90.2	98.6

[a] GC purity

hypochlorite, and lowest using in-situ-generated peracetic acid oxidant.

Product yield is highly dependent on the structure of the amine. Somewhat lower yields were achieved in the synthesis of *N*,*N*-di-*n*-propyl *O*-ethyl thiocarbamate (82.5% by method 1 and 75.3% by method 2), *N*-isopropyl *O*-ethyl thiocarbamate (80.1% by method 1 and 73.1% method 2), and the lowest yield was achieved with *N*,*N*-diisopropyl *O*-ethyl thiocarbamate (74.0% by method 1 and 64.9% by method 2). Satisfactory yields of both *N*,*N*-di-*n*-propyl *O*-ethyl and *N*,*N*-diisopropyl *O*-ethyl thiocarbamates were obtained by use of method 3. The voluminous di-*n*-propyl, isopropyl, and diisopropyl groups contribute to significant steric repulsion with diethyl dixanthogenate, which prevents approach of the amine to effect nucleophilic heterolysis of the S–S bond in the first reaction step. The structures of amines is of vital importance in their nucleophilic reactivity [21], and further kinetic studies could provide more information about the reaction mechanism and the rate-determining step.

The success of the optimum innovative synthetic methods 1–3 was compared with results obtained by use of the well known literature method [19] (method 4), and sulfated nickel zeolite catalyst-promoted synthesis (method 5) (Table 2).

Table 2 Yields and GC purities of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates obtained by use of methods 4 and 5

No.	Method 4		Method 5	
	Yield (%)	GC[a] (%)	Yield (%)	GC (%)
5	82.4	98.4	86.0	98.6
6	80.9	97.2	85.4	97.4
7	79.6	97.2	84.6	97.5
8	78.2	97.8	84.9	77.8
9	76.8	98.1	85.7	98.3
10	73.9	98.0	82.0	98.0
11	72.0	99.2	79.5	99.1
12	62.8	98.8	73.6	98.6

[a] GC purity

It is apparent from Tables 1 and 2 that somewhat lower yields of the *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates were obtained by use of methods 4 and 5. The results indicate that all synthetic methods using an amine for heterolytic S–S cleavage in the presence of different oxidizing agents are the methods of choice for synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates. On that basis, future studies will be focused on synthetic and mechanistic studies of thiocarbamate synthesis in the presence of new oxidants or new oxygen/catalyst system combinations. Results from MS and from Fourier-transform infrared (FT-IR), and ^{1}H, and ^{13}C NMR spectroscopy of the *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates are in agreement with literature data and undoubtedly corroborate the structures of all the *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates synthesized by use of methods 1–5. Also, considering method 1, definite experimental data have been presented for establishment of the proposed reaction mechanism. A mechanistic study of the synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates by use of different oxidizing agents is of utmost significance for optimization of laboratory synthesis and technological development and application.

It was stated that the reaction mechanism of the thiocarbamate synthesis, according to method 1, probably proceeds via nucleophilic heterolysis of the S–S bond of diethyl dixanthogenate (**1**) by an amine (**2**), producing ethyl xanthic acid methylammonium salt (**3**), elemental sulfur (**4**) finely suspended in the reaction media, and *N*-methyl *O*-ethyl thiocarbamate (**5**). Subsequent oxidation of amine salt **3** by hypochlorite ion produces diethyl dixanthogenate (**1**). The proposed reaction steps are consecutively repeated, i.e., the amine present performs heterolysis of the S–S bond of the oxidatively obtained diethyl dixanthogenate (Scheme 2).

The quantity of sulfur obtained after filtration of the reaction mixture is almost equal to the stoichiometric quantity expected according to calculation on the basis of the reaction yield obtained.

In the second reaction step, oxidation of the ammonium salt of ethyl xanthic acid by hypochlorite ion gives solely diethyl dixanthogenate, even in reactions with different amines. It is also proved that in the reaction of diisopropyl dixanthogenate with ethylamine and isopropylamine according to method 1 only diisopropyl dixanthogenate is isolated, which is a crucial proof of the second reaction step.

Study of the reaction mechanism of thiocarbamate synthesis performed according to method 3 was not possible by these experimental techniques. The catalytic activity of manganese(II) ion is high enough to promote the oxidizing power of oxygen, and the reaction probably follows a radical mechanism, which is confirmed by scavenging of the generated oxygen radical using 1,1-diphenyl-2-picrylhydrazyl (DPPH).

Satisfactory reaction yields obtained by method 1 and simple work-up on synthesis of the thiocarbamate enabled implementation of the optimized laboratory technique on a semi-industrial scale. Before the start of production based on the invented procedure, the method has been the object of a patent application [22]. Techno-economical aspects of the implemented innovative method 1 indicate extraordinary economic benefit. It was confirmed that the reaction product was not present in water, and concentrations of dixanthogenates have been determined to be under the maximum contamination limit [23]. The necessary waste water purification process is also very simple. Innovative method 1 could be widely used for thiocarbamate synthesis starting from different raw materials: ammonium salt [24] and alkaline salt of *O*-alkyl xanthic acid [9], and waste or commercial diethyl dixanthogenate.

Semi-industrial application of process 3 is however strongly determined by the need to introduce oxygen at increased pressure, use of triethylamine, and, therefore, far lower financial gain; this does not justify application of this method on an industrial scale.

Conclusion

The presented work describes the optimum synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates from diethyl dixanthogenates and amine in the presence of different oxidants: sodium hypochlorite, in-situ-generated peracetic acid, or the manganese(II) acetate/oxygen system. High conversion of starting materials into products (74.0–87.2%) was achieved by use of sodium hypochlorite; in-situ-generated peracetic acid results in lower yields (64.9–82.8%), and the highest yields (90.2–95.8%) were obtained by using the manganese(II) acetate/oxygen system. Method 1 using sodium hypochlorite oxidant has been developed on the laboratory scale and applied on a semi-industrial scale. Techno-economic aspects of innovative method 1 are extraordinary whereas, despite the high yield, method 3 does not offer the possibility of commercial application because it requires use of high-cost equipment. Results from the synthesis applying the commercially well known method 4, and synthesis performed in the presence of sulfated nickel zeolite catalyst do not offer comparable alternatives to methods 1 and 3. In conclusion, the innovative method presented is a powerful and versatile method for preparation of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates. This method has several unique merits, namely simple operation, mild reaction conditions, avoidance of hazardous organic solvents, use of moderately toxic and inexpensive reagents, short reaction times, and high product yields. This new environmentally benign process is a suitable alternative to existing methods, and a significant contribution to protection of the human environment.

Experimental

General method for the purification of diethyl dixanthogenate on laboratory and semi-industrial scales

Purification of waste oxidized product from xanthate production to obtain diethyl dixanthogenate was achieved by two successive extractions with hot distilled water and filtration. The xanthate alkaline salt is extracted into the aqueous solution which could be used for thiocarbamate production according to method 1. Two filtration cakes were collected and dried giving 55% yield of 99% pure diethyl dixanthogenate.

Alternatively, for comparison, commercial diethyl dixanthogenate was used for synthesis of all the compounds, and similar yields and purities were obtained (data not presented). These results strongly indicate the usefulness of the presented methods for synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates from commercial and purified industrial waste material.

Method 1: Optimum reaction conditions for synthesis of N-alkyl and N,N-dialkyl O-ethyl thiocarbamates using sodium hypochlorite

In a three-necked flask (250 cm^3), equipped with magnetic stirrer, dropping funnel, condenser, and thermometer, 100 cm^3 water and 18.5 g (0.075 mol) 98% diethyl dixanthogenate were placed. During 1 h 11.4 cm^3 (0.15 mol)

40% methylamine solution was added with vigorous stirring, and an increase of temperature to 30 °C occurred. After that period 20.5 g (0.075 mol) sodium hypochlorite (130 g active chlorine/1,000 cm^3) was added dropwise. The temperature of the reaction mixture gradually rose to 45 °C during the course of reaction of 1.5 h, after which the reaction was complete. In the course of the reaction sulfur particles precipitated in a quantity corresponding almost stoichiometrically to the reaction yield.

The reaction mixture was filtered on a Büchner funnel, and the precipitated sulfur was separated as filtration cake from an aqueous emulsion phase of *N*-ethyl *O*-ethyl thiocarbamate. The product was separated from the aqueous phase by two ethereal extractions, the organic phase was dried with sodium sulfate, and the ether was removed by distillation at atmospheric pressure. Pure product was obtained by fractional vacuum distillation at 105 °C/2 kPa (Ref. [25] 93 °C/1 kPa). *N*-methyl *O*-ethyl thiocarbamate (15.6 g) was obtained, representing a yield of 87.2% (gas chromatographic (GC) purity 97.9%).

All other *N*-alkyl and *N,N*-dialkyl *O*-ethyl thiocarbamates were synthesized in an analogous manner to the above procedure, using the appropriate amines under reaction conditions as presented in Table 3; results of the syntheses are given in Table 1.

Experimental procedures for isolation of reaction intermediates according to method 1

In a 250 cm^3 three-necked flask equipped with magnetic mixer, dropping funnel, condenser, and thermometer, 100 cm^3 water and 18.5 g (0.075 mol) 98% diethyl dixanthogenate were placed. Under gentle stirring 5.7 cm^3 (0.075 mol) 40% methylamine was added during half an hour, causing the temperature to increase to 35 °C. After that period, 20.5 g (0.075 mol) sodium hypochlorite (130 g active chlorine/1,000 cm^3) was added dropwise. After half an hour, the reaction mixture was filtered, to give filtration cake consisting mainly of sulfur (1.9 g determined analytically, precipitating as barium sulfate). The filtrate was then transferred to a separation funnel, and the organic phase separated as upper layer (*N*-methyl *O*-ethyl thiocarbamate, confirmed by FT-IR, ^{1}H and ^{13}C NMR, GC MS–MS spectroscopic data; 4.9 g crude product). The aqueous solution was transferred into a beaker and hydrochloric acid (1:1) was added with continuous stirring until the pH of the solution became slightly acidic (pH $\approx$ 5). At the bottom of the beaker a light yellow substance insoluble in water was deposited, which was extracted with diethyl ether. The solution was dried with sodium sulfate and ether was removed by distillation. The structure was confirmed as ethyl xanthic acid (7.0 g) by MS, FT-IR, ^{1}H, and ^{13}C NMR data, and its purity was determined potentiometrically to be 98%.

In the second experiment, repeated as described above, the isolated amine salt of ethyl xanthic acid (the lower aqueous solution) was filtered to remove sulfur, and then treated with 20.5 g (0.075 mol) sodium hypochlorite (150 g active chlorine/1,000 cm^3). The temperature was maintained at 45 °C for 1 h. After completion of the reaction, the reaction mixture was filtered. The filtration cake contained pure diethyl dixanthogenate (structure confirmed by FT-IR, ^{1}H, and ^{13}C NMR data). A parallel experiment was performed with diisopropyl dixanthogenate in reaction with ethylamine and isopropylamine, and analogously with the former experiment, diisopropyl dixanthogenate was isolated as reaction product (structure confirmed by FT-IR, ^{1}H, and ^{13}C NMR data).

In the third experiment, the aqueous phase containing the alkyl ammonium salt of ethyl xanthic acid was treated with zinc(II) sulfate to precipitate the corresponding salt of ethyl xanthic acid. The dried zinc salt was characterized using FT-IR, ^{1}H, and ^{13}C NMR techniques, and atomic absorption spectroscopy. In that way it was proved beyond doubt that the alkyl ammonium salt of ethyl xanthic acid was the intermediate product in the proposed reaction mechanism presented in Scheme 2.

Table 3 Reaction conditions for synthesis of *N*-alkyl and *N,N*-dialkyl *O*-ethyl thiocarbamates by method 1

No.	Diethyl dixanthogenate (mol)	Amine (mol)	Sodium hypochlorite (mol)	Reaction time (h)	Temperature (°C)
5	0.075	0.15	0.075	2.0	30–45
6	0.075	0.15	0.075	2.0	30–45
7	0.075	0.15	0.075	2.0	30–45
8	0.075	0.15	0.080	2.0	30–45
9	0.075	0.15	0.075	2.0	30–45
10	0.075	0.15	0.100	3.0	40–50
11	0.075	0.15	0.100	3.5	40–55
12	0.075	0.15	0.130	4.5	40–55

Method 2: Synthesis of N-alkyl and N,N-dialkyl O-ethyl thiocarbamates analogously to method 1 using in-situ-generated peracetic acid

The synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates using in-situ-generated peracetic acid was performed analogously to method 1. Ethylenediamine tetraacetic acid (EDTA), obtained from tetrasodium EDTA and hydrochloric acid, was used as source of acetic acid, and sodium perborate and sodium percarbonate were used as oxygen sources. Decomposition of sodium perborate and percarbonate was catalyzed by addition of 100 ppm Fe(III). The results obtained using these two oxidizing agents were similar and only the results for the EDTA/perborate system are presented in Table 1.

Method 3: Synthesis of N-alkyl and N,N-dialkyl O-ethyl thiocarbamates using manganese(II) acetate/oxygen system

In a 250 cm^3 three-necked flask equipped with magnetic mixer, dropping funnel, condenser, thermometer, and oxygen bubbling device 100 cm^3 water and 18.5 g (0.075 mol) 98% diethyl dixanthogenate were placed. During 1 h, 11.4 cm^3 (0.15 mol) of 40% methylamine solution was added dropwise with vigorous stirring, causing the temperature to increase to 30 °C. At this point, 15.2 g (0.15 mol) triethylamine and 30.0 mg (1.2×10^{-4} mol) manganese(II) acetate tetrahydrate were added, and oxygen bubbling was started immediately. The reaction mixture was maintained at constant temperature of 50 °C while providing an oxygen pressure of 2×10^5 Pa for 1.0 h, after which the reaction was complete. In the course of the reaction sulfur particles precipitated in a quantity less than expected for the reaction yield. Some elemental sulfur was probably oxidized to sulfur oxides.

The reaction mixture was filtered on a Büchner funnel, separating sulfur from an aqueous emulsion phase of *N*-methyl *O*-ethyl thiocarbamate. The product was isolated from the aqueous phase by two ethereal extractions, the organic phase was dried with sodium sulfate, and ether was removed by distillation at atmospheric pressure. Pure product was obtained by fractional vacuum distillation at 105 °C/2 kPa, giving 18.7 g *N*-methyl *O*-ethyl thiocarbamate (yield 95.8%, GC purity 98.7%).

All other *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates were synthesized in an analogous manner to the above procedure, using the appropriate amines; results of the syntheses are given in Table 1.

Method 4: Synthesis of N-alkyl and N,N-dialkyl O-ethyl thiocarbamates by reaction of sodium ethyl xanthogenacetate and mono and dialkyl amines

For comparison, synthesis of *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates was performed by the well known literature method [19]; results of the syntheses are presented in Table 2.

Method 5: Synthesis of N-alkyl and N,N-dialkyl O-ethyl thiocarbamates by reaction of sodium ethyl xanthate and mono and dialkyl amines in the presence of sulfated nickel zeolite catalyst

Catalyst preparation [20]

Sulfated nickel/Y-zeolite catalyst was prepared by the impregnation technique. A determined amount of the prepared nickel sulfate aqueous solution was slowly added to a known amount of Na–Y zeolite support at room temperature. The concentration of the solution was adjusted to obtain a catalyst of approximately 7% nickel loading (Ni content determined by atomic absorption spectroscopy). The catalyst was then dried at 120 °C for 4 h and calcined from 350 to 450 °C with controlled heating rate (5 °/min). The catalyst was activated by heating at 450 °C for 2 h and under a hydrogen atmosphere at the same conditions. No differences in catalytic activity were observed, and only results from use of the heat-activated catalyst are presented.

Synthesis of N-alkyl and N,N-dialkyl O-ethyl thiocarbamates using sulfated nickel zeolite catalyst

To a 250 cm^3 round bottom flask containing 120 cm^3 deionized water, 60.4 g 81% active commercial sodium ethyl xanthate (0.34 mol) was added, with stirring. After the xanthate was completely dissolved, 23.2 g sulfated nickel/Y-zeolite catalyst was added to the reactor. Subsequent to addition of the catalyst, 28.9 cm^3 40% methylamine solution (0.38 mol) was added. The reactor was then heated to 80 °C and maintained at this temperature for 16 h, followed by cooling to room temperature. Pure *N*-methyl *O*-ethyl thiocarbamate (34.8 g, yield 86.0%, GC purity 98.6%) was obtained by fractional vacuum distillation at 105 °C/2 kPa. The results of the syntheses of other *N*-alkyl and *N*,*N*-dialkyl *O*-ethyl thiocarbamates according to method 5 are given in Table 2.

For all *N*-alkyl and *N*,*N*-dialkyl-*O*-ethyl thiocarbamates synthesized by the methods presented above, boiling point, MS, FT-IR, ^{1}H, and ^{13}C NMR data agree with the literature values [25–31].

Instrumental techniques used for determination of the structures of the synthesized compounds and reaction intermediates

The ^{1}H and ^{13}C NMR spectral measurements were performed on a Bruker AC 250 spectrometer at 250 MHz for ^{1}H NMR and 62.89 MHz for ^{13}C NMR spectra. The spectra were recorded at room temperature in deuterated solvent in 5 mm tubes. The chemical shifts are expressed in ppm (δ) values referenced to the tetramethylsilane standard signal.

All mass spectra were recorded on a Thermo Finnigan Polaris Q ion-trap mass spectrometer, including TraceGC 2000 (ThermoFinnigan, Austin, TX, USA) integrated GC–MS–MS system. DIP (direct insertion probe) mode was used to introduce the sample and EIMS–MS to acquire the spectra. Ionization conditions were: ion source temperature 200 °C, maximum energy of electron excitation 70 eV, corona current 150 μA. GC analysis was performed with a Perkin–Elmer 8700 equipped with FID detector and a column packed with 5% OV-210 on Gas-Chrom Q (length 2 m, diameter 0.3175 cm (1/8″)); conditions were: injector temperature 250 °C, detector temperature 270 °C, column program mode: 50 °C (5 min) → 10 °/min → 130 °C (15 min), carrier gas nitrogen (purity 99.99%, flow 1 cm^3/min), air flow 250 cm^3/min (purity 99.99%), hydrogen flow 25 cm^3/min (purity 99.99%). Atomic absorption spectroscopy with an AAS-306 Perkin Elmer spectrometer was used for determination of zinc and nickel content. FT-IR spectra were recorded in transmission mode using a BOMEM (Hartmann and Braun) spectrometer. Elemental analysis was performed using a VARIO EL III Elemental analyzer, and results were found to be in good agreement (±0.2%) with calculated values.

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