

Synthesis of *N,N*-dialkylnitramines from secondary ammonium nitrates in liquid or supercritical carbon dioxide

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An efficient explosion-proof method was developed for the preparation of *N,N*-dialkylnitramines by treatment of dialkylammonium nitrates with a mixture of nitric acid and acetic anhydride in the presence of $ZnCl_2$ in liquid or supercritical carbon dioxide.

Key words: nitration, nitramines, carbon dioxide, green chemistry.

Nitramines are one of the most important class of organic energetic compounds, which are produced industrially and have application as components of energetic military- or industry-oriented compositions,¹ herbicides,² plant growth stimulants,³ biologically active nucleosides.^{4,5} They are generally prepared by nitration of secondary amines or their derivatives with various nitrating agents, such as acetyl nitrate,^{6,7} N_2O_5 ,^{8–11} acetone cyanohydrin nitrate,¹² 2-(trifluoromethyl)propan-2-yl nitrate,¹³ nitronium triflate.¹⁴ The nitration is carried out using nitrating agents that are pre-formed^{4,6,9,11–14} or generated *in situ*, for example, from HNO_3 ^{7,15} or its salts¹⁶ and acid anhydrides.^{6,7} The process is usually performed in a large excess of the nitrating agent in an organic solvent, such as acetonitrile,¹² CCl_4 ,⁹ CH_2Cl_2 ,^{11,13} dichloroethane,¹⁷ acetic acid,^{7,15,18} acetic anhydride,¹⁸ which makes the process explosive and fire hazardous. In addition, the reaction not always proceeds selectively in said systems containing oxidizing and reducing agents.

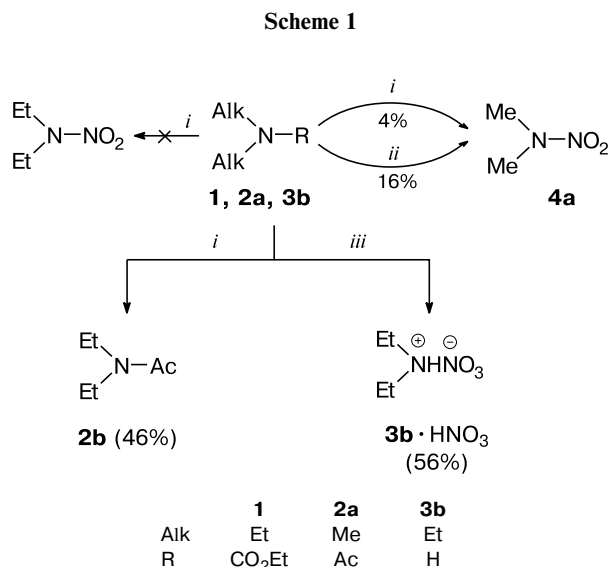
In our opinion, one of the methods for decreasing the risk of non-controlled side reactions is performing the nitration reaction in liquid or supercritical carbon dioxide (*sc*- CO_2), wherein the carbon atom is in the highest oxidation state and, consequently, cannot undergo oxidative transformations under the action of a nitrating agent. Having high heat capacity (C_p 6.35 J g⁻¹ K⁻¹ at 25 °C and 64 bar¹⁹ (for toluene C_p 1.70 J g⁻¹ K⁻¹ at 25 °C)²⁰), CO_2 is capable of efficiently remove heat from the reaction zone, which additionally decreases explosion and fire hazards of the process. Carbon dioxide is a non-toxic, non-flammable, thermally stable substance and an ideal solvent in terms of green chemistry.^{21–24} Finally, it is exclusively cheap and available compound, whose resources are virtually inexhaustible.

In recent years, *sc*- CO_2 has extensively been studied as a solvent for organic reactions, including hydrogenation,²⁵

hydroformylation²⁶, and polymerization²⁷. There is evidence for the possibility of performing the nitration reactions of organic compounds in the carbon dioxide medium,^{28,29} however, we failed to find the detailed description of experimental conditions.

First of all, we studied the reaction of a series of model amino compounds with nitrating agents in liquid CO_2 and *sc*- CO_2 . We chose ethyl *N,N*-diethylcarbamate (**1**), *N,N*-dimethylacetamide (**2a**), and diethylamine (**3b**) as the subjects of research. Compounds **1** and **2a** contain the tertiary nitrogen atom linked with the ethoxycarbonyl and acetyl groups, respectively, which can act as leaving groups in the nitration process, compound **3b** is a representative of secondary amines. Acyl nitrates obtained *in situ* from HNO_3 and acid anhydrides were the nitrating agents. The reaction was performed at 100 bar at 40 °C. It turned out that ethyl *N,N*-diethylcarbamate (**1**) did not react with acetyl nitrate under the studied conditions, and *N,N*-dimethylacetamide (**2a**) afforded dimethylnitramine (**4a**) in a yield of 4%. The use of a mixture of HNO_3 and $(CF_3CO)_2O$ as a nitrating agent made it possible to slightly increase the yield of nitration product **4a**, although, in this case, it did not exceed 16%. Secondary amine **3b** exhibited higher reactivity in the reaction with the system $HNO_3 - Ac_2O$ in *sc*- CO_2 compared to compounds **1** and **2a**, however, the products containing no nitramine group formed. The reaction pathway depended on the order of mixing the reagents. Upon addition of HNO_3 to a mixture of **3b**, Ac_2O , and *sc*- CO_2 , *N,N*-diethylacetamide (**2b**) was isolated in a yield of 46%, while upon successive treatment of a solution of amine **3b** in supercritical carbon dioxide with nitric acid and acetic anhydride, diethylammonium nitrate **3b**· HNO_3 formed, which did not undergo further transformations under the reaction conditions (Scheme 1).

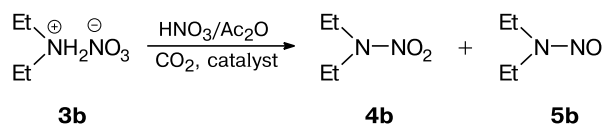
One could assume that performing the reaction in the presence of the Cl^- anions, which are known to be cata-



Reagents and conditions: *i.* Ac₂O, HNO₃, 100 bar, 40 °C, 4 h; *ii.* (CF₃CO)₂O, HNO₃, 100 bar, 40 °C, 4 h; *iii.* HNO₃, Ac₂O, 100 bar, 40 °C, 6 h.

ylsts of nitration of amines in organic solvents,^{17,18} would favor the formation of nitramine **4b**. To check this assumption, we studied the reaction of amine **3b** with a mixture of HNO₃ and Ac₂O in liquid CO₂ and *sc*-CO₂ in the presence of various chlorides, including ZnCl₂, NH₄Cl, MeNH₃Cl, NEt₄Cl, and NBu₄Cl. For suppression of the side N-acylation reaction, amine **3b** was introduced into the reaction mixture in the form of nitrate **3b**·HNO₃, which is in equilibrium with the free amine in the presence of Ac₂O (see Ref. 17). The catalyst concentration was 1–10 mol.% and the amount of HNO₃ was 0.1–0.2 equiv. based on the amount of starting salt **3b**·HNO₃. In all cases, the reaction afforded a mixture of nitration product **4b** and nitrosation product **5b**, the major component being diethylnitramine **4b** (Table 1, Scheme 2).

Scheme 2



The yields of products **4b** and **5b** depend on the content of the Cl[−] ions in the system, the nature of the cation and the reaction conditions. The best efficiency was achieved in the presence of ZnCl₂, the yield of nitramine **4b** under comparable conditions (0.1 equiv. of the Cl[−] ions in reference to nitrate **3b**·HNO₃) being maximal (55%) (Runs 1–5). The decrease in the amount of the Cl[−] ions (0.05 equiv. for NEt₄Cl, 0.02 equiv. for ZnCl₂) made the process inefficient (Runs 6 and 7). The increase in the

Table 1. Nitration of diethylammonium nitrate (**3b**·HNO₃) with a mixture of HNO₃ and Ac₂O in carbon dioxide catalyzed by chlorides

Run	T/°C	p/bar	t/h	Catalyst (equiv. of Cl [−])	HNO ₃ equiv.	Ac ₂ O	Yield (%)	
							4b	5b
1	40	100	8	NH ₄ Cl (0.1)	0.1	2	36	19
2	40	100	8	MeNH ₃ Cl (0.1)	0.1	2	7	6
3	40	100	8	Et ₄ NCl (0.1)	0.1	2	40	9
4	40	100	8	Bu ₄ NCl (0.1)	0.1	2	26	8
5	40	100	8	ZnCl ₂ (0.1)	0.1	2	55	12
6	40	100	8	Et ₄ NCl (0.05)	0.1	2	22	10
7	40	100	8	ZnCl ₂ (0.02)	0.1	2	13	5
8	40	100	8	ZnCl ₂ (0.2)	0.1	2	42	21
9	40	100	8	ZnCl ₂ (0.1)	0.1	1.5	59	15
10	40	100	8	ZnCl ₂ (0.1)	0.2	2	63	17
11	40	100	8	ZnCl ₂ (0.1)	0.2	1.5	55	15
12	40	100	4	ZnCl ₂ (0.1)	0.2	2	54	12
13	40	100	2	ZnCl ₂ (0.1)	0.2	2	50	9
14	50	100	2	ZnCl ₂ (0.1)	0.2	2	53	15
15	40	150	2	ZnCl ₂ (0.1)	0.2	2	50	11
16	40	80	8	ZnCl ₂ (0.1)	0.2	2	57	18
17	20	80	8	ZnCl ₂ (0.1)	0.2	2	40	11
18	20	80	24	ZnCl ₂ (0.1)	0.2	2	67	15

amount of the Cl[−] ions up to 0.2 equiv. adversely affected the yield of nitro compound **4b**, the fraction of nitrosation product **5b** being increased (Run 8). The further experiments on optimization of the amount and composition of the nitrating mixture and on the reaction conditions were performed in the presence of 5 mol.% ZnCl₂ (0.1 equiv. of the Cl[−] ions). It was found that the molar ratio Ac₂O : HNO₃ plays an important role. The decrease in this ratio from 20 : 1 (Run 5) to 15 : 1 (Run 9) and to 10 : 1 (Run 10) led to the increase in the yield of nitration product **4b** to 59% and 63%, respectively. However, upon further decrease in the molar ratio Ac₂O : HNO₃ (to 7.5 : 1), the yield of nitramine **4b** decreased to 55% (Run 11). The reduction of the reaction time at the same (Runs 12, 13) or elevated temperature and pressure (Run 14) also reduced the productivity of the process. At the same time, the transition of CO₂ from the supercritical state to liquid by decreasing the pressure (to 80 bar) and temperature (to 20 °C) with simultaneous increase in the process time from 8 to 24 h allowed us to increase the yield of nitramine **4b** to 67% (Run 18).

The conditions of Runs 10 and 18 (see Table 1) where the model reaction product **4b** formed in the highest yield were then used for the synthesis of dialkylnitramines **4a,c–i**. It was found that linear and cyclic (heterocyclic) secondary amine nitrates **3** react with acetyl nitrate in supercritical (method A) or liquid carbon dioxide (method B) in the presence of ZnCl₂ to form the corresponding nitration products. The reaction selectivity and the product yields

Table 2. Synthesis of secondary *N*-nitramines in supercritical (method *A*) and liquid CO₂ (method *B*)

Com- pound	The product yields ^a (%)				
	4			5	
	<i>A</i>	<i>B</i>	Lit.	<i>A</i>	<i>B</i>
a	76	45	65 ^{18, b}	— ^c	— ^c
b	63	67	40 ^{17, d} , 60 ^{18, b}	17	15
c	65	75	76 ^{17, d}	16	17
d	65	75	72 ^{17, d} , 58 ^{18, b}	20	19
e	36	8	17 ^{18, b}	22	31
f	83	78	92 ^{18, b}	— ^c	— ^c
g	78	70	65 ^{18, e}	— ^c	— ^c
h	63	76	58 ^{18, b}	28	13
i	57	—	91 ^{11, f}	— ^c	— ^c

^a The yields are given for compounds **4b–e, h** and **5b–e, h** according to the ¹H NMR spectral data of the reaction mixture and for compounds **4a, f, g, i** according to the ¹H NMR spectral data after recrystallization.

^b HNO₃ – Ac₂O – ZnCl₂ without solvent.

^c Produced in trace amounts (<1%).

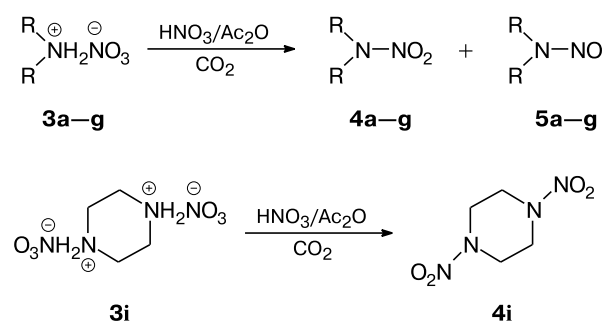
^d HNO₃ – Ac₂O – ZnCl₂ in dichloroethane.

^e HNO₃ – Ac₂O – ZnCl₂ in AcOH.

^f Prepared from 1,4-bis(trimethylsilyl)piperazine and N₂O₅ in CH₂Cl₂.

depend on the structure of the starting compounds. In the reactions involving dimethylamine **3a** and amines **3f, g, i** containing the heteroatoms and functional groups in the

substituents R, the corresponding nitramines **4a, f, g, i** were isolated as single products, while upon nitration of dialkylamines **3b–e, h** the corresponding nitroso compounds **5b–e, h** formed along with nitro compounds **4b–e, h**. The maximum amount of the side nitrosation product was noted in the case of compound **3e** containing the branched alkyl groups (Table 2). Nitramines **4** were isolated in pure state from the obtained mixtures by distillation under reduced pressure or by crystallization from EtOH (Table 3).

Scheme 3

3–5: R = Me (**a**), Et (**b**), Prⁿ (**c**), Buⁿ (**d**), Buⁱ (**e**), O₂NCH₂CH₂ (**f**); R, R = –CH₂CH₂OCH₂CH₂– (**g**), –(CH₂)₅– (**h**);

Reagents and conditions: ZnCl₂ (5 mol.%), method *A*: 100 bar, 40 °C, 8 h; method *B*: 80 bar, 20 °C, 24 h.

Thus, an efficient method for the synthesis of *N,N*-dialkyl nitramines by the ZnCl₂-catalyzed reaction of sec-

Table 3. Physicochemical properties of nitramines **4**

Com- pound	M.p./°C or B.p./°C (<i>p</i> /Torr) ^a	IR spectrum, v/cm ⁻¹		¹ H NMR spectrum (CDCl ₃ , δ, <i>J</i> /Hz)
		NO ₂ ^{as}	NO ₂ ^s	
4a	57–58 [54–56] ¹⁵	1448, 1500	1280, 1336	3.42 (s, 6 H, NCH ₃)
4b	99–100 (18) [90–91 (14)] ¹⁵	1452, 1500	1276, 1376	1.29 (t, 6 H, CH ₃ , <i>J</i> = 6.9); 3.82 (q, 4 H, NCH ₂ , <i>J</i> = 6.9)
4c	120–121 (20) [105–106 (10)] ¹⁵	1460, 1512	1268, 1380	0.92 (t, 6 H, CH ₃ , <i>J</i> = 7.3); 1.68 (m, 4 H, CH ₂); 3.66 (t, 4 H, NCH ₂ , <i>J</i> = 7.7)
4d	142–143 (18) [123–124(9)] ⁷	1464, 1512	1284, 1384	0.94 (t, 6 H, CH ₃ , <i>J</i> = 7.0); 1.33 (m, 4 H, CH ₂); 1.64 (m, 4 H, CH ₂); 3.70 (t, 4 H, NCH ₂ , <i>J</i> = 7.3)
4e	80–81 [81.5–82.5] ⁷	1472, 1492	1272, 1328	0.95 (d, 6 H, CH ₃ , <i>J</i> = 7.3); 2.22 (m, 2 H, CH); 3.58 (d, 4 H, NCH ₂ , <i>J</i> = 7.3)
4f	50–51 [51–52] ¹⁸	1512, 1640 (ONO ₂)	1276	4.12 (t, 4 H, OCH ₂ , <i>J</i> = 5.0); 4.75 (t, 4 H, NCH ₂ , <i>J</i> = 5.0)
4g	50–51 [52–53] ⁷	1512	1256, 1312	3.82 (s, 8 H, CH ₂)
4h	121–122 (18) [116–117(17)] ¹⁵	1512	1244, 1276, 1328	1.52 (q, 2 H, CH ₂ , <i>J</i> = 6.0); 1.68 (m, 4 H, CH ₂); 3.82 (t, 4 H, NCH ₂ , <i>J</i> = 6.0)
4i	214–215 [215–216] ⁷	1556	1244, 1332	4.06 (s, 8 H, NCH ₂) ^b

^a Presented in square brackets are literature data.

^b The ¹H NMR spectrum was recorded in DMSO-d₆.

ondary amines with a mixture of nitric acid and acetic anhydride in liquid or supercritical CO₂ was developed. The yields of nitramines **4** under the suggested conditions are comparable with those obtained by the known methods.^{17,18} The advantages of the proposed procedure are the absence of the toxic organic solvents, particularly CH₂Cl₂ and dichloroethane, and enhancement of the process safety due to the dilution of the explosive mixture HNO₃–Ac₂O by inert carbon dioxide. The nitroso compounds formed in some cases can then be oxidized to the corresponding nitro compounds in the same reactor,³⁰ which will increase the efficiency of the process and minimize its negative environmental impact. Finally, in contrast to the known methods, no by-products, such as acetamides **2**, are produced in the reaction in CO₂.

Experimental

IR spectra were obtained on a Specord M-80 spectrometer in thin film on NaCl plates or in KBr pellets. ¹H NMR spectra were recorded on a Bruker AM-300 (300 MHz) spectrometer in CDCl₃ or DMSO-*d*₆ using Me₄Si as the internal standard. Dichloromethane, dimethylacetamide were predistilled. Compound **1** was obtained according to a known procedure.³¹

Nitration of ethyl *N,N*-diethylcarbamate (1**).** A steel autoclave (*V* = 35 mL) containing Ac₂O (2.04 g, 20 mmol) was filled with CO₂ (60 bar) and cooled to 0–5 °C. Then 95% HNO₃ (0.94 g, 15 mmol) was added through a feeding capillary, the temperature was raised to 20 °C in 30 min and carbamate **1** (1.00 g, 7 mmol) was added. The mixture was heated to 40 °C and the pressure of CO₂ was increased to 100 bar. The reaction mixture was stirred for 4 h under these conditions. CO₂ was removed and the residue was poured into ice water (50 mL) and extracted with CH₂Cl₂ (4 × 10 mL), the organic layer was successively washed with a saturated solution of NaHCO₃ and water and dried with Na₂SO₄. After evaporation of the solvent, compound **1** (0.54 g, 54%) was isolated. ¹H NMR (CDCl₃), δ: 1.08 (t, 6 H, CH₃); 1.22 (t, 3 H, CH₃); 3.24 (q, 4 H, NCH₂); 4.10 (q, 2 H, OCH₂).

Nitration of *N,N*-dimethylacetamide **2a with a mixture of Ac₂O and HNO₃.** A steel autoclave (*V* = 35 mL) containing Ac₂O (1.62 g, 16 mmol) was filled with CO₂ (60 bar) and cooled to 0–5 °C. Then 95% HNO₃ (0.73 g, 12 mmol) was added through a feeding capillary, the temperature was raised to 20 °C in 30 min and amide **2a** (0.96 g, 11 mmol) was added. The reaction was carried out, and the reaction mixture worked up, as described above. The product was crystallized from EtOH. Compound **4a** was obtained in a yield of 0.03 g (4%), its physicochemical characteristics and spectral data are given in Table 3.

Nitration of *N,N*-dimethylacetamide **2a with a mixture of (CF₃CO)₂O and HNO₃.** A steel autoclave (*V* = 35 mL) containing trifluoroacetic anhydride (1.68 g, 8 mmol) was filled with CO₂ (60 bar) and cooled to –5–0 °C. Then 95% HNO₃ (0.63 g, 10 mmol) was added through a feeding capillary and the temperature was raised to 20 °C in 30 min. Then *N,N*-dimethylacetamide **2a** (0.44 g, 5 mmol) was added. The mixture was heated to 40 °C and the pressure of CO₂ was increased to 100 bar. The reaction was carried out, and the product was isolated, as described above. Compound **4a**, which is identical to the com-

pound obtained upon nitration of **2a** in Ac₂O, was obtained in a yield of 0.07 g (16%).

Nitration of diethylamine (3b**) with a mixture of Ac₂O and HNO₃.** **A.** A steel autoclave (*V* = 35 mL) containing amine **3b** (0.73 g, 10 mmol) was filled with CO₂ (60 bar), cooled to 0–5 °C and Ac₂O (2.04 g, 20 mmol) was added through a feeding capillary. Upon cooling with ice water, 95% HNO₃ (0.63 g, 10 mmol) was added in 3 portions with 10 min intervals. The mixture was kept for 30 min and then heated to 40 °C. The pressure of CO₂ in the reactor was increased to 100 bar and the reaction mass was stirred for 6 h under these conditions. Work-up of the reaction mixture as described above afforded *N,N*-diethylacetamide **2b** (0.53 g, 46%). IR (NaCl), ν/cm⁻¹: 2976, 2936, 1724, 1640, 1608, 1432, 1384, 1364, 1280, 1100. ¹H NMR (CDCl₃), δ: 1.08 (t, 3 H, CH₃); 1.14 (t, 3 H, CH₃); 2.04 (s, 3 H, CH₃); 3.26 (q, 2 H, NCH₂); 3.34 (q, 2 H, NCH₂).

B. A steel autoclave (*V* = 35 mL) containing amine **3b** (0.73 g, 10 mmol) was filled with CO₂ (60 bar), cooled to 0–5 °C and 95% HNO₃ (0.63 g, 10 mmol) was added through a feeding capillary. The temperature was raised to 20 °C for 30 min and then Ac₂O (2.04 g, 20 mmol) was added. The mixture was heated to 40 °C and the pressure of CO₂ was increased to 100 bar. The reaction mass was stirred for 6 h under these conditions. CO₂ was removed and the residue was filtered off, washed with hexane and dried for 1 h at 20 °C and 2 Torr. Compound **3b**·HNO₃ was obtained in a yield of 0.76 g (56%). M.p. 101–102 °C (*cf.* Ref. 32: m.p. 103–104 °C).

Reactions of dialkylammonium nitrates **3 with a mixture of Ac₂O and HNO₃ in the presence of ZnCl₂ in supercritical (method **A**) and liquid (method **B**) CO₂.** **Method A.** A steel autoclave (*V* = 35 mL) containing nitrate **3**·HNO₃ (20 mmol) and a solution of ZnCl₂ (0.14 g, 1 mmol) in Ac₂O (2.04 g, 20 mmol) was filled with CO₂ (60 bar) and a mixture of 95% HNO₃ (0.27 g, 4 mmol) and Ac₂O (2.04 g, 20 mmol) prepared beforehand was added through a feeding capillary. The reaction mixture was heated to 40 °C and the pressure of CO₂ was increased to 100 bar and stirred for 8 h under these conditions. The reaction mixture was worked up as described in the nitration of **1** and the residue was distilled *in vacuo* or crystallized from EtOH. The yields of products **4** and **5** are given in Table 2, the physicochemical properties, ¹H NMR and IR spectral data of nitramines **4** are given in Table 3.

Method B. A steel autoclave (*V* = 35 mL) containing nitrate **3**·HNO₃ (20 mmol) and a solution of ZnCl₂ (0.14 g, 1 mmol) in Ac₂O (2.04 g, 20 mmol) was filled with CO₂ (60 bar) and a mixture of 95% HNO₃ (0.27 g, 4 mmol) and Ac₂O (2.04 g, 20 mmol) prepared beforehand was added through a feeding capillary. The pressure of CO₂ was increased to 80 bar and the reaction mass was stirred for 24 h at 20 °C. CO₂ was removed and the products were isolated as described in method **A**.

Nitration of diethylammonium nitrate **3b·HNO₃ with a mixture of Ac₂O and HNO₃ in the presence of chlorides.** The reactions were performed analogously to methods **A** and **B** under the conditions presented in Table 1.

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