Monatsh Chem (2010) 141:205–211
DOI 10.1007/s00706-009-0248-x

ORIGINAL PAPER

Condensation of aromatic aldehydes with *N*,*N*-dimethylacetamide in presence of dialkyl carbonates as dehydrating agents

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Received: 14 August 2009 / Accepted: 23 December 2009 / Published online: 27 January 2010

Abstract Reactions of benzaldehydes with excess *N*,*N*-dimethylacetamide at 140 °C in the presence of diethyl carbonate as dehydrating agent and a base gave (*E*)-*N*,*N*-dimethylcinnamamides in good yields. If hydroxybenzaldehydes are used as substrates the reaction is accompanied by alkylation.

Keywords C–C bond formation · Aldol-type reaction · Alkylation · AOX removal · Al–Ni alloy

Introduction

β-Arylacrylamides (cinnamamides) are common in synthetic chemistry. The cinnamamides have been used as building blocks for cyclopentanone [1], for synthesis of chiral 3-substituted-4-ketoamides [2], α,β-epoxy amides [3], alcohols [4, 5], and as monomers for special polymeric materials [6]. Some derivatives of cinnamamides have antiestrogenic activity [7]. *N*,*N*-dimethylcinnamamides serve as intermediates for ligand synthesis [8]. Alkoxycinnamamides **2** have been patented as UV absorbers for cosmetics [9] and as anti-allergic agents [10].

N,*N*-Dimethylcinnamamides are generally available via the reactions of cinnamic acids [11], benzaldehydes [12–18], halogenobenzenes [19, 20], styrenes [21], arylacetylenes [22], benzylalcohols [23], and 2-chloro-3-hydroxyamides [24]. However, each of the published syntheses of *N*,*N*-dimethylcinnamamides [11–24] has some disadvantages. Sometimes mixtures of (*E*) and (*Z*) stereoisomers of cinnamamides have been formed [17, 19, 21]. Stoichiometric amounts of by-products [11, 13, 18, 20–24] were produced in some of the above mentioned synthetic procedures. Palladium catalysts are well known for their high activity for the coupling reaction of arylhalides with unsaturated compounds, for example acrylamides [19, 20]. However, application of homogeneous catalysis causes major problems in purification of products and separation of the expensive heavy metal catalyst, and leads to toxic waste. These problems are of environmental and economic concern in large-scale synthesis.

Formation of **2** by condensation of aldehydes **1** with *N*,*N*-dimethylacetamide (DMA) was described as an undesirable reaction during Suzuki coupling of phenylboronic acid with 4-chlorobenzaldehyde dissolved in DMA at 130–150 °C in the presence of $Pd(OAc)_2$, *n*-Bu_4NBr, and K_3PO_4 [25].

Dialkylcarbonates $(RO)_2CO$ are well known as solvents and alkylating compounds with low toxicity (similar to the corresponding alcohols) [26], which could be produced from renewable sources [26]. To the best of our knowledge, application of $(RO)_2CO$ as dehydrating agents has been mentioned in a few cases of ring-closure reactions only [27, 28] although $(RO)_2CO$ are ideal for use at high temperatures because of their ability to react smoothly with water in the presence of base or acid [29].

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Herein we wish to report, for the first time, efficient and straightforward methodology for synthesis of (*E*)-*N*,*N*-dimethylcinnamamides using condensation of benzaldehydes with DMA in the presence of $(RO)_2CO$ as dehydrating agents.

Results and discussion

We discovered that the alkylation of vanillin (**1a**) with diethyl carbonate (DEC) dissolved in excess DMA in the presence of K_2CO_3 led to the formation of (*E*)-4-ethoxy-3-methoxy-*N*,*N*-dimethylcinnamamide (**2a**) in nearly quantitative yield (Table 1, entry 1). This reaction was tested on a series of hydroxybenzaldehydes **1a**–**1f** using DEC, dimethyl carbonate (DMC), and dibutyl carbonate (DBC) as alkylating agents (Table 1, entries 1–9). Isolation of the products from the evaporated reaction mixture was achieved by simple crystallization from alkanes.

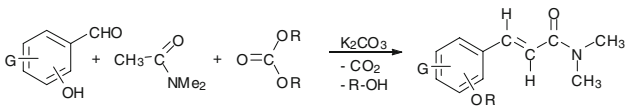
Moreover, we demonstrated that the mixtures of unreacted DMA with $(RO)_2CO$ are simply recyclable without loss of yield after refilling of spent DMA and $(RO)_2CO$. The structure of **2b** was proved by X-ray crystallography (Fig. 1).

Interestingly, the condensation reaction of vanillin (**1a**) with DMA and base without addition of $(RO)_2CO$ does not proceed (Table 1, entry 10). To evaluate the effect of $(RO)_2CO$, the reaction of 4-methoxybenzaldehyde (**1g**) with DMA was selected as model reaction; the results are presented in Table 2. The reaction was monitored by ^1H NMR spectroscopy of $CDCl_3$ extracts of evaporated reaction mixtures. It could be seen that addition of excess DEC or DMC to the mixture of **1g**, DMA, and K_2CO_3 provides better results, whereas in the absence of $(RO)_2CO$ under the same reaction conditions the conversion to **2g** was low. Formation of the appropriate alcohols was proved in distillates obtained during the condensation reaction of **1g** with DMA when DEC or DMC were added to the reaction mixture (Table 2, entries 2–7).

Replacement of K_2CO_3 with K_3PO_4, which is known as a simple substitute for strong bases in polar aprotic solvents [30], enables complete conversion of **1g** to **2g** (Table 2, entries 3, 5–7). It was proved that application of excess of DEC enables direct reuse of solvent distilled from the reaction mixture (Table 2, entries 6–7) without the need for additional dehydration.

In order to study the scope of the condensation reaction between ArCHO and DMA, a series of cinnamamides **2g**–**2p** were synthesized and isolated simply by crystallization of the evaporated reaction mixture (Table 3, entries 1–8). DEC was used as more suitable $(RO)_2CO$ despite its boiling point (126 °C). When we tried to expand the series of benzaldehydes to *ortho*-nitro or *para*-nitrobenzaldehyde, we found that these compounds were decomposed to an unseparable mixture of products, probably because of parallel S_NAr reactions (Table 3, entries 9, 10).

Table 1 Synthesis of (*E*)-alkoxy-*N*,*N*-dimethylcinnamamides **2** by reaction of hydroxybenzaldehydes **1** with $(RO)_2CO$ and DMA



1a-1f **2a-2i**

Entry	Substituted hydroxybenzaldehyde as substrate	*t* (h)	Used $(RO)_2CO$	Yield of **2** (%)[a]	Yield of purified **2** (%)[b]
1	4-Hydroxy-3-methoxy- (**1a**)	48	DEC	97 (**2a**)	72 (**2a**)
2	2-Hydroxynaphthalene-1-carbaldehyde (**1b**)	48	DEC	90 (**2b**)	67 (**2b**)
3	3-Hydroxy- (**1c**)	73	DEC	93 (**2c**)	67 (**2c**)
4	2-Hydroxy- (**1d**)	44	DMC	91 (**2d**)	62 (**2d**)
5	3-Hydroxy- (**1c**)	47	DMC	97 (**2e**)	53 (**2e**)
6	3,4-Dihydroxy- (**1e**)	44	DMC	93 (**2f**)	69 (**2f**)
7	4-Hydroxy- (**1f**)	62	DMC	90 (**2g**)	67 (**2g**)
8	3-Hydroxy- (**1c**)	21	DBC	92 (**2h**)	65 (**2h**)
9	3,4-Dihydroxy- (**1e**)	67	DBC	94 (**2i**)	56 (**2i**)
10	4-Hydroxy-3-methoxy- (**1a**)	48	None	Unreacted **1a**	–

10 mmol **1** at 145-150 °C in air using 15 mmol base, 100 mmol DEC, and 50 cm^3 DMA, each reaction proceeds with 100% conversion of starting ArCHO

[a] Based on ^1H NMR

[b] After crystallization

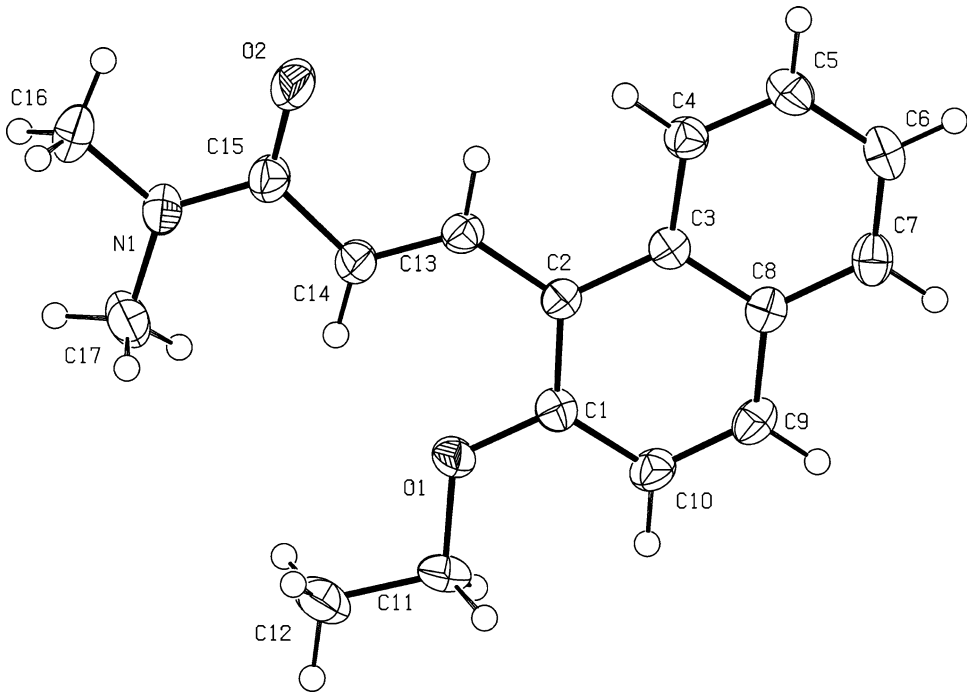


Fig. 1 The molecular structure of **2b** (CCDC No. 723820), an ORTEP view showing the thermal ellipsoids at 50% probability (arbitrary spheres for H atoms); selected bond lengths (Å) and angles (°): O1 C1 1.360(2), O1 C11 1.441(2), N1 C15 1.351(3), N1 C17 1.450(3), N1 C16 1.450(3), C2 C13 1.460(3), C14 C13 1.328(3), C14 C15 1.475(3), C15 O2 1.229(3), C1 O1 C11 119.28(17), C15 N1 C17 124.1(2), C15 N1 C16 120.0(2), C17 N1 C16 115.69(19), O1 C1 C2 116.95(18), O1 C1 C10 121.49(19)

Table 2 Optimization of reaction conditions for condensation of 4-methoxybenzaldehyde (**1g**) with DMA

Entry	*t* (h)	Base	Addition of $(RO)_2CO$	Conversion of **1g**, by ^{1}H NMR (%)	Yield of **2g**, by ^{1}H NMR (%)
1	44	1.1 eq. K_2CO_3	None	4	4
2	42	1.1 eq. K_2CO_3	7.5 eq. DMC	82	71
3	43	1.1 eq. K_3PO_4	7.5 eq. DMC	100	93
4	42	1.1 eq. K_2CO_3	7.5 eq. DEC	83.5	74
5	44	1.1 eq. K_3PO_4	7.5 eq. DEC	100	94
6[a]	46	1.1 eq. K_3PO_4	1 eq. DEC	100	92
7[b]	46	1.1 eq. K_3PO_4	1.2 eq. DEC	100	95

[a] Recycled solvents from entry 5 (mixture of DMA and DEC) were used

[b] Recycled solvents from entry 6 (mixture of DMA and DEC) were used

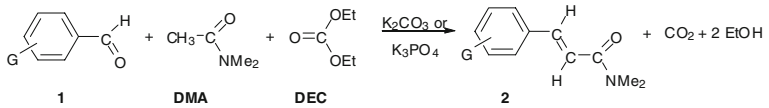
Upscaling of **2n** preparation (X-ray structure of **2n** is shown in Fig. 2) was performed using two-times recycled DMA and DEC which were distilled from the reaction mixture during the work-up. Consumption of DEC and DMA (less than 10% during each reaction cycle) was supplemented with fresh DEC and DMA (compared with the first reaction using commercial 99%+ DEC and DMA) without significant drop of the yield of **2n**. During repeated syntheses of **2n** aqueous mother liquor from the reaction work-up was collected, and contained undesirable quantities of 2-bromoaromatic compounds, mainly **2n**.

Experiments were performed to reduce the quantity of brominated aromatic compounds (adsorbable organic halogens, AOX) in this mother liquor by reductive pretreatment [31]. The modified dehalogenation method published by Lunn [31], based on addition of Raney aluminum–nickel alloy to the alkaline aqueous solution of halogenated aromatic compounds, has been tested satisfactorily for pretreatment of aqueous mother liquor contaminated with **2n**. The essentially quantitative dehalogenation of **2n** is supported by the ^{1}H NMR spectral pattern typical of a monosubstituted phenyl ring with a CH_2–CH_2–G group. Subsequent GC–MS analysis verified the formation of *N*,*N*-dimethyl-3-phenylpropionamide **3** ($C_{11}H_{15}NO$, $M = 177$) (Scheme 1).

Conclusions

The reaction of hydroxybenzaldehydes in DMA using dialkyl carbonates as inexpensive and non-toxic alkylating agents serves as a simple and selective method for preparation of (*E*)-*N*,*N*-dimethylalkoxycinnamides. In addition, the condensation reaction of aromatic aldehydes with DMA was developed using DEC as dehydrating agent. All the prepared cinnamamides were obtained exclusively in

Table 3 Synthesis of (*E*)-*N*,*N*-dimethylcinnamamides **2** by condensation reaction of ArCHO **1** and DMA



Entry	Ar-CHO **1**	*t* (h)	Base	Yield of **2** (%)[a]	Yield of purified **2** (%)[b]
1	*p*-MeO–C_6H_4– (**1g**)	44	K_3PO_4	94 (**2g**)	74 (**2g**)
2	Ph– (**1h**)	48	K_2CO_3	90 (**2j**)	63 (**2j**)
3	*p*-Me–C_6H_4– (**1i**)	42	K_3PO_4	92 (**2k**)	56 (**2k**)
4	*p*-Cl–C_6H_4– (**1j**)	45	K_2CO_3	91 (**2l**)	71 (**2l**)
5	*o*-Cl–C_6H_4– (**1k**)	64	K_2CO_3	92 (**2m**)	62 (**2m**)
6	*o*-Br–C_6H_4– (**1l**)	47	K_2CO_3	91 (**2n**)	73 (**2n**)
7	*m*-NO_2–C_6H_4– (**1m**)	21	K_2CO_3	93 (**2o**)	75 (**2o**)
8	terephthaldehyde (**1n**)	72	K_3PO_4	89 (**2p**)	61 (**2p**) (G = 4-CH=CH–$CONMe_2$
9	*o*-NO_2–C_6H_4– (**1o**)	40	K_2CO_3 or K_3PO_4	–[c]	–
10	*p*-NO_2–C_6H_4– (**1p**)	40	K_2CO_3 or K_3PO_4	–[c]	–

10 mmol **1** at 145–150 °C in air using 15 mmol base, 100 mmol DEC, and 50 cm^3 DMA

[a] Based on ^1H NMR spectra

[b] After crystallization

[c] Formation of complex mixture of compounds

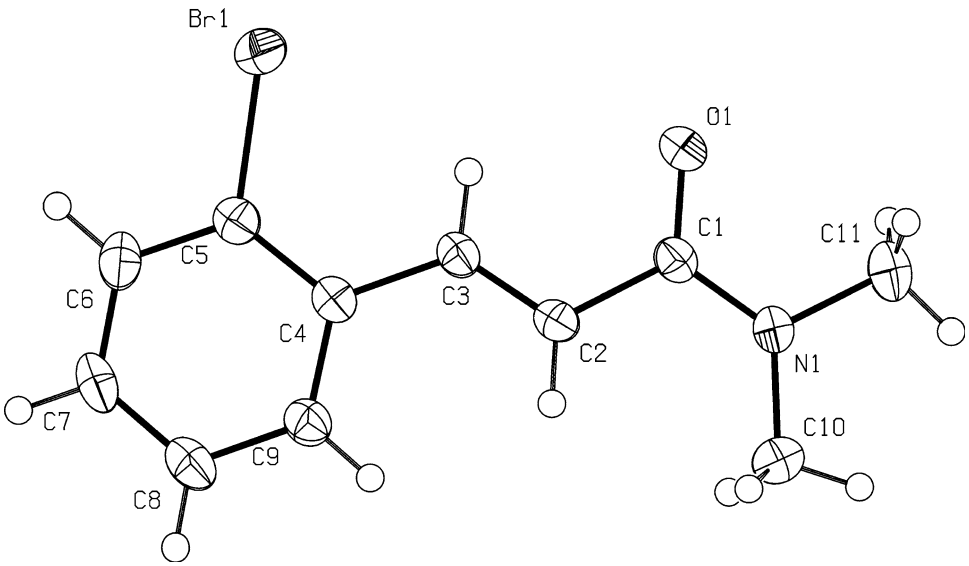
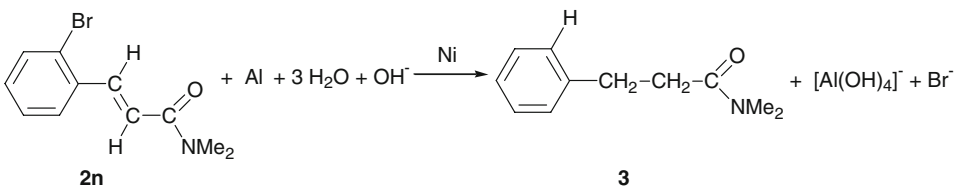


Fig. 2 The molecular structure of **2n** (CCDC No. 691110), an ORTEP view showing the thermal ellipsoids at 50% probability (arbitrary spheres for H atoms); selected bond lengths (Å) and angles (°): O1 C1 1.236(4), C2 C3 1.316(5), C2 C1 1.491(4), N1 C1 1.341(4), N1 C11 1.454(4), N1 C10 1.455(5), C3 C4 1.469(4), C3 C2 C1 118.9(3)

Scheme 1



(*E*) configuration in good yields. It was demonstrated that unreacted DEC and DMA could be simply recycled without significant change of the yield of cinnamamides. The advanced method for AOX minimization was tested successfully using dehalogenation of bromoaromatic compound **2n**, which contaminated the aqueous mother

liquor. Samples of the reported compounds are available from the authors.

Experimental

All reactions were carried out in air. All chemicals were purchased as reagent grade from commercial suppliers (Across, Sigma–Aldrich) and used without further purification. IR spectra were measured on a Mattson ATI Genesis FT-IR spectrometer. Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra of all products were recorded at 25 °C on a Bruker 360 at 360.14 and 90.57 MHz, respectively. The chemical shifts are given in ppm on the delta scale (δ). The ^{1}H NMR spectra are referenced to tetramethylsilane ($\delta = 0$ ppm) in $CDCl_3$ or to the signal of the solvent peak (DMSO-d_6, $\delta = 2.55$ ppm). Chemical shifts of ^{13}C NMR spectra are reported in ppm ($CDCl_3$: $\delta = 77.0$ ppm, DMSO-d_6: $\delta = 39.6$ ppm). Detailed ^{1}H and ^{13}C NMR spectra are available from the authors. The elemental analyses (C, H, N) were conducted using Elemental Analyzer EA 1108 (Fisons) and results agreed favorably with calculated values. Melting points were determined on a Boetius (Carl Zeiss Jena) apparatus. Low-resolution mass spectra were recorded on a Shimadzu GCMS QP 2010 GC–MS instrument equipped with a DB-XLB capillary column (30 m × 0.25 mm, 0.25 μm) and operating at an ionization energy of 70 eV. The oven temperature (GC) was 250 °C. The X-ray data for colorless crystals of **2b** (CCDC No. 723820) and **2n** (CCDC No. 691110) were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode (Table 4). Data reductions were performed with DENZO-SMN [32]. The absorption was corrected by integration methods [33]. Structures were solved by direct methods (Sir92) [34] and refined by full matrix least-square based on F^2 (SHELXL97) [35]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of the crystal, all hydrogens were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or 1.5 U_{eq} for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene, and hydrogen atoms in the aromatic ring, respectively, 0.86 and 0.82 Å for N–H and O–H groups, respectively. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or url: http://www.ccdc.cam.ac.uk).

Table 4 Crystallographic data for **2b** and **2n**

Compound	**2b**	**2n**
Empirical formula	$C_{17}H_{19}NO_2$	$C_{11}H_{12}BrNO$
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1/c$
a (Å)	8.0232(9)	8.8470(6)
b (Å)	8.1688(11)	11.9740(7)
c (Å)	22.9021(12)	10.7030(6)
β (°)	102.284(7)	108.946(5)
Z	4	4
V (Å^3)	1466.6(3)	1072.39(11)
D_c (g cm^{-3})	1.301	1.574
Crystal size (mm^3)	0.47 × 0.24 × 0.16	0.19 × 0.17 × 0.11
Crystal shape	Colorless needle	Colorless needle
μ (mm^{-1})	0.089	3.799
F (000)	616	512
h; k; l range	−10, 10; −10, 10; −28, 29	−11, 10; −15, 15; −13, 13
θ range (°)	1; 27.5	3.40; 27.5
Reflections measured	16,875	10,530
Independent R_{int}^a	3,324 (0.0482)	2,450 (0.0408)
Observed $I > 2\sigma(I)$	2,314	1,924
Parameters refined	191	127
Max/min $\Delta\rho$ (eÅ^{-3})	0.275/−0.381	0.519/−0.582
GOF^b	1.088	1.135
R^c/wR	0.0632/0.1406	0.0434/0.0866
CCDC No.	723820	691110

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$

[b] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data

[c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for observed data, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data

*General preparation of **2g–2p** exemplified by **2n** (this procedure enables the recycling of solvent without decrease of yield)*

To 3.9 g 2-bromobenzaldehyde (**1l**, 0.02 mol) dissolved in 12 cm^3 DEC (12.3 g, 0.104 mol) and 160 cm^3 DMA (153.5 g, 1.744 mol) 4.4 g anhydrous K_3PO_4 (0.02 mol) was added. The reaction flask was fitted to a condenser equipped with a $CaCl_2$ tube. The reaction mixture was stirred at 145 °C for 62 h, cooled, and the distillate was weighed and analyzed by ^{1}H NMR (5.2 g, contains 74.1 mol% EtOH and 25.9 mol% DEC). The cooled reaction mixture was evaporated at max. 135 °C to dryness under reduced pressure (1.33 kPa at the end of distillation), cooled, the distillate (149.9 g) was analyzed by ^{1}H NMR (it contained 4.5 mol% DEC, 93.8 mol% DMA, and 1.7 mol% EtOH). This means that recovery of solvents was 91.8% (90.6%) for DMA (DEC). The distillation residue was diluted with 200 cm^3 water, heated under reflux for

5 min, and cooled. The insoluble residue was crystallized from diethoxymethane leading to pure **2n** (3.3 g, 65%). The next quantity (0.4 g, 8% of theory) of pure **2n** crystallized as yellowish needles after a few days of standing of the aqueous mother liquor at room temperature.

(E)-3-(2-Bromophenyl)-N,N-dimethyl-2-propenamide (**2n**, $C_{11}H_{12}BrNO$)
M.p.: 85–86 °C (from cyclohexane); IR (KBr): $\overline{\nu} = 1{,}645$ (C=O, amide), 1,619 (C=C), 1,144 (C–N), 748 (C–H arom.) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): $\delta = 2.96$ and 3.06 (s, 6H, 2× CH_3), 6.73 (d, 1H, $^3J = 15.4$ Hz, CH=), 7.10–7.15 (m, 1H, H-arom.), 7.20–7.25 (m, 1H, H-arom.), 7.49–7.53 (m, 2H, H-arom.), 7.88 (d, 1H, $^3J = 15.4$ Hz, CH=) ppm; ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 35.6$ (CH_3), 37.2 (CH_3), 120.6 (CH), 124.6 (C_q), 127.3 (CH), 127.4 (CH), 130.2 (CH), 133.0 (CH), 135.2 (C_q), 140.3 (CH), 165.9 (C=O) ppm; MS (70 eV): *m/z* (%) = 253 (M^+, 6), 255 (M^++2, 6), 209 (31), 211 (30), 174 (100), 102 (69), 98 (33).

*Reductive treatment of aqueous mother liquor from preparation of **2n***

The alkaline mother liquor from **2n** was saturated with bromo derivative **2n** and contained DMA, as was confirmed by ^1H NMR spectroscopy of the $CDCl_3$ extract. Al–Ni alloy (0.54 g, 50% Ni + 50% Al, 0.01 mol of Al) was added to 100 cm^3 waste water (pH 11.2) from the synthesis of **2n** and vigorously stirred overnight by magnetic stirring at room temperature. After filtration of the metal slurry the filtrate was extracted with $CDCl_3$ and analyzed by GC–MS which indicated formation of *N,N*-dimethyl-3-phenylpropionamide; MS (70 eV): *m/z* (%) = 177 (M^+, 79), 105 (Ph–CH_2CH_2–, 59), 91 ($PhCH_2$–, 98), 72 ($CONMe_2$, 82), 58 (23), 45 (100).

(E,E)-3,3′-(1,4-phenylene)bis(N,N-dimethyl-2-propenamide) (**2p**, $C_{16}H_{20}N_2O_2$)
M.p.: 242–244 °C (from diethoxymethane–ethanol); IR (KBr): $\overline{\nu} = 1{,}645$ (C=O, amide), 1,603 (C=C), 1,139 (C–N) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): $\delta = 3.05$ (bs, 6H, 2× CH_3), 6.84 (d, 2H, $^3J = 15.3$ Hz, 2× CH=), 7.45 (s, 4H, H-arom.), 7.58 (d, $^3J = 15.3$ Hz, 2H, 2× CH=) ppm; ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 36.6$ (2× CH_3), 117.9 (2× CH=), 128.1 (4× CH), 136.4 (C_q), 141.4 (2× CH=), 143.4 (CH), 166.4 (2× C=O) ppm; MS (70 eV): *m/z* (%) = 272 (M^+, 36), 228 (63), 229 (74), 201 (19), 183 (56), 155 (35), 128 (41), 127 (49), 72 (100).

Compounds **2j** [21, 36], **2k** [37, 38], **2l** [37, 39], **2m** [40], and **2o** [37] were characterized by comparison of their spectral data (^1H, ^{13}C NMR) and melting points with data found in literature.

*General preparation of **2a–2i** exemplified with **2a***

To 1.52 g vanillin (**1a**, 0.01 mol) dissolved in 11.8 g DEC (0.1 mol) and 90 cm^3 DMA (82.5 g, 0.947 mol) 2.77 g anhydrous K_2CO_3 (0.02 mol) was added. The reaction mixture was heated at 145 °C with magnetic stirring for 48 h. The collected reaction distillate was weighed and analyzed by ^1H NMR (1.4 g, contained 86.5 mol% EtOH, 10.38 mol% DEC, and 3.11 mol% DMA). The hot reaction mixture was filtered, and the filtrates were evaporated to dryness at max. 130 °C under reduced pressure (1.33 kPa). The distillate (88.9 g) was analyzed by ^1H NMR and contained 7.9 mol% DEC and 92.1 mol% DMA (recovery 97.6% of DMA and 80.5% of DEC). The distillation residue was crystallized from cyclohexane to afford 1.8 g (72%) **2a**.

(E)-3-(4-Ethoxy-3-methoxyphenyl)-N,N-dimethyl-2-propenamide (**2a**, $C_{14}H_{19}NO_3$)
M.p.: 125–127 °C; IR (KBr): $\overline{\nu} = 1{,}653$ (C=O, amide), 1,606 (C=C), 1,267 (R–O–Ar), 1,138 (C–N), 793 (C–H arom.) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): $\delta = 1.32$ (t, 3H, CH_3), 2.92 (s, 3H, CH_3), 3.04 (s, 3H, CH_3), 3.71 (s, 3H, CH_3O), 4.00 (q, 2H, CH_2), 6.67 (d, 1H, $^3J = 15.5$ Hz, CH=), 6.77 (d, 1H, $^3J = 8.2$ Hz, H-arom.), 6.96 (d, 1H, $^4J = 1.8$ Hz, H-arom.), 7.01 (dd, 1H, $^3J = 8.2$ Hz, $^4J = 1.8$ Hz, H-arom.), 7.52 (d, 1H, $^3J = 15.5$ Hz, CH=) ppm; ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 14.6$ (CH_3), 35.8 (CH_3), 37.3 (CH_3), 55.9 (CH_3), 64.2 (CH_2), 110.2 (CH), 112.2 (CH), 114.9 (CH), 121.6 (CH), 128.1 (C_q), 142.2 (CH), 149.2 (C_q), 149.7 (C_q), 166.8 (C_q) ppm; MS (70 eV): *m/z* (%) = 249 (M^+, 67), 205 (100), 177 (28), 145 (59), 117 (18), 89 (16).

(E)-3-(2-Ethoxy-1-naphthyl)-N,N-dimethyl-2-propenamide (**2b**, $C_{17}H_{19}NO_2$)
M.p.: 98–99 °C (from cyclohexane); IR (KBr): $\overline{\nu} = 1{,}639$ (C=O, amide), 1,589 (C=C), 1,294 (R–O–Ar), 808 (C–H arom.) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$): $\delta = 1.43$ (t, 3H, CH_3), 3.08 (s, 6H, 2× CH_3), 4.14 (q, 2H, CH_2), 7.17–7.34 (m, 3H, CH= and 2× H-arom.), 7.43–7.47 (m, 1H, H-arom.), 7.70–7.75 (m, 2H, H-arom.), 8.20–8.22 (d, 2H, H-arom.), 8.28 (d, 1H, $^3J = 15.5$ Hz, CH=) ppm; ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 15.1$ (CH_3), 35.8 (CH_3), 37.2 (CH_3), 64.6 (CH_2), 113.8 (CH), 117.5 (C_q), 122.6 (CH), 123.4 (CH), 123.6 (CH), 126.9 (CH), 128.3 (CH), 128.8 (C_q), 130.6 (CH), 132.9 (C_q), 134.9 (CH), 155.5 (C_q), 167.7 (C_q) ppm; MS (70 eV): *m/z* (%) = 269 (M^+, 12), 224 (100), 197 (61), 168 (16), 141 (25), 139 (19), 72 (24).

(E)-3-(3-Ethoxyphenyl)-N,N-dimethyl-2-propenamide (**2c**, $C_{13}H_{17}NO_2$)
M.p.: 72–73 °C (from cyclohexane); IR (KBr): $\overline{\nu} = 1{,}653$ (C=O, amide), 1,614 (C=C), 1,261 (R–O–Ar), 777 (C–H

arom.) cm^{-1}; ^1H NMR (DMSO-d_6): $\delta = 1.36–1.40$ (t, 3H, CH_3), 2.97 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 4.11 (q, 2H, CH_2), 6.96–6.99 (m, 1H, H-arom.), 7.21–7.37 (m, 4H, H-arom. and CH=), 7.44–7.49 (d, 1H, $^3J = 15.4$ Hz, CH=) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 14.7$ (CH_3), 35.4 (CH_3), 37.0 (CH_3), 63.2 (CH_2), 113.5 (CH), 115.7 (CH), 118.9 (CH), 120.6 (CH), 129.8 (CH), 136.7 (C_q), 141.0 (CH), 158.9 (C_q), 165.6 (C=O) ppm; MS (70 eV): *m/z* (%) = 219 (M^+, 50), 176 (34), 175 (57), 147 (100), 119 (27), 91 (34).

(E)-3-(3-Butoxyphenyl)-N,N-dimethyl-2-propenamide (**2h**, $C_{15}H_{23}NO_2$)

M.p.: 79–80 °C (from cyclohexane); IR (KBr): $\bar{\nu} = 2{,}596$, 2,939 (C–H), 1,655 (C=O, amide), 1,614 (C=C), 1,236 (R–O–Ar), 806 (C–H arom.) cm^{-1}; ^1H NMR (DMSO-d_6): $\delta = 0.95–1.00$ (t, 3H, CH_3), 1.44–1.55 (m, 2H, CH_2), 1.73–1.81 (m, 2H, CH_2), 3.08 (bs, 3H, NCH_3), 3.13 (bs, 3H, NCH_3), 3.95–3.99 (t, 2H, CH_2), 6.84–6.89 (m, 2H, H-arom., CH=), 7.04–7.11 (m, 2H, H-arom.), 7.24–7.29 (m, 1H, H-arom.), 7.60–7.65 (d, 1H, $^3J = 15.4$ Hz, CH=) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 13.7$ (CH_3), 19.1 (CH_2), 31.2 (CH_2), 35.8 (CH_3), 37.3 (CH_3), 67.6 (CH_2), 113.6 (CH), 115.4 (CH), 117.5 (CH), 120.1 (CH), 129.6 (CH), 136.6 (C_q), 142.1 (CH), 159.3 (C_q), 166.5 (C=O) ppm; MS (70 eV): *m/z* (%) = 247 (30), 204 (18), 147 (100), 119 (16), 91 (18).

(E)-3-(3,4-Dibutoxyphenyl)-N,N-dimethyl-2-propenamide (**2i**, $C_{19}H_{29}NO_3$)

M.p.: 77 °C (from hexane); IR (KBr): $\bar{\nu} = 2{,}958$, 2,872 (C–H), 1,647 (C=O, amide), 1,595 (C=C), 1,259 (R–O–Ar), 1,136 (C–N), 802 (C–H, arom.) cm^1; ^1H NMR ($CDCl_3$): $\delta = 0.89–0.94$ (m, 6H, 2× CH3), 1.42–1.46 (m, 4H, 2× CH_2), 1.70–1.76 (m, 4H, 2× CH_2), 3.04 (bd, 6H, 2× CH_3), 3.92–3.98 (m, 4H, 2× CH_2O), 6.67 (d, 1H, $^3J = 15.3$ Hz, CH=), 6.78 (d, 1H, $^3J = 7.3$ Hz, H-arom.), 6.98 (d, 1H, $^4J = 1.7$ Hz, H-arom.), 7.01 (dd, 1H, $^3J = 7.3$ Hz, $^4J = 1.7$ Hz), 7.53 (d, 1H, $^3J = 15.3$ Hz, CH=) ppm;^{13}C NMR ($CDCl_3$): $\delta = 13.6$ (CH_3), 13.7 (CH_3), 18.9 (CH_2), 19.0 (CH_2), 31.0 (CH_2), 31.1 (CH_2), 35.7 (CH_3), 37.2 (CH_3), 68.5 (CH_2), 68.9 (CH_2), 112.6 (CH), 113.0 (CH), 114.7 (CH), 121.7 (CH), 128.0 (C_q), 142.2 (CH), 148.9 (C_q), 150.6 (C_q), 166.7 (C=O) ppm; MS (70 eV): *m/z* (%) = 319 (M^+, 80), 275 (53), 219 (60), 163 (100), 145 (23).

Compounds **2d** [39], **2e** [37], **2f** [37, 41], and **2g** [42] were characterized by comparison of their spectral data (^1H, ^{13}C NMR) and melting points with data provided in literature.

Acknowledgments We are grateful to the Grant Agency of the Czech Republic, projects No. 203/07/P248, 104/09/0829 and Ministry of Education, Youth and Sports of the Czech Republic MSM 0021627501 and MSM 0021627502 for financial support.

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