Solid-phase oxidative halodecarboxylation of β-arylacrylic acids with the ceric ammonium nitrate—alkali halide system

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The solid-phase oxidation of cinnamic, 4-methoxy- and 3,4-dimethoxycinnamic acids with $Ce(NH_4)_2(NO_3)_6$—MHal system leads to β-halostyrenes. Similar procedure in the absence of a metal halide results in a cleavage of the C=C bond giving the corresponding benzaldehydes.

Key words: cinnamic acids, benzaldehydes, ceric ammonium nitrate, β-halostyrenes, halodecarboxylation, nitrodecarboxylation, solid-phase reactions, mechanochemical activation.

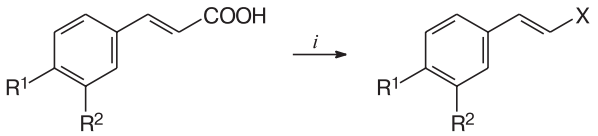
Ceric ammonium nitrate (CAN), one of the popular oxidants in organic chemistry, is used as the mediator in the formation of a carbon—heteroatom bond, as the initiator in the radical addition of functionalized compounds with activated C—H bond to olefins, as the reagent, capable of cleavage of a C—C bond in alcohols and carboxylic acids, and as the catalyst of certain reactions. In the last years, the CAN—alkali metal salt systems found their wide application in processes of oxidative functionalization of organic compounds of various classes. Achievements in the development of this trend are reviewed.[1,2] All the reactions of CAN with organic compounds were carried out with the use of solvents. Thus, the reaction of olefins with CAN—KBr in the two-phase dichloromethane—water system afforded vicinal dibromoalkanes.[3] Acetylenes under these conditions are converted into vicinal dibromoalkenes.[3] Bromination of aromatic compounds bearing electron-donating substituents (for example, anisole) with CAN—LiBr system in acetonitrile occurs at the aromatic core,[4] whereas bromination of alkylarenes with CAN—NaBr in MeCN—AcOH takes place at the side chain.[5] The addition of NO_2, ONO_2, N_3, SCN, SeCN, and SO_2Ar groups at a C=C bond with participation of CAN as the mediator is represented by numerous examples.[1]

Recently, we have shown that the oxidation of carboxylic acids and alcohols upon treatment with $Pb(OAc)_4$[6—8] and CAN[9] can be carried out as the solvent-free solid-phase process, which opens new prospectives in the application of these compounds in organic synthesis. Alkan-1-ols in the reaction with CAN—LiBr are converted into esters, the co-oxidation of alkanals and alkanols predominantly leads to α-bromocarboxylic acid esters.[9]

In order to broaden the scope of the solvent-free reactions of CAN, in the present work we accomplished a solid-phase oxidative chloro- and bromodecarboxylation of cinnamic (**1a**), 4-methoxycinnamic (**1b**), 3,4-dimethoxycinnamic (**1c**), and furan-2-carboxylic (**2**) acids with CAN—MX (M = Li, Na; X = Cl, Br) system.

It was found that the keeping of a thoroughly intermixed solid mixture of acid **1**, CAN, and MX in a closed vessel led to β-halostyrenes (Scheme 1, Tables 1 and 2).

Scheme 1



1a—c **3a—c, 4a,b**

i. CAN—MX, 20 or 65 °C, solvent-free.

Starting compound	R^1	R^2	X	Product
1a	H	H	Br	**3a**
			Cl	**4a**
1b	MeO	H	Br	**3b**
			Cl	**4b**
1c	MeO	MeO	Br	**3c**

When the molar ratio **1b,c** : CAN : LiBr is 1 : 2 : 2, temperature is 20 °C, and the reaction time is 24 h, the yield of bromides **3b** and **3c** is ~65%; when the temperature is raised to 65 °C, almost complete conversion of

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Table 1. The solid-phase oxidative decarboxylation of cinnamic acid **1a** (1.0 mmol) under the action of CAN—MX system

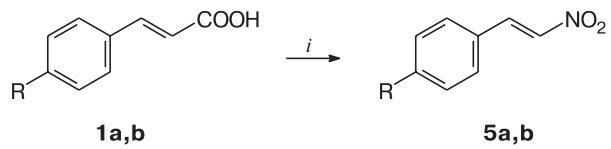
MX	Molar ratio **1a** : CAN : MX	Reaction conditions			Yield[c] (%)
		T/°C	Additional treatment[a]	τ[b]	
LiBr	1 : 2 : 2	20	—	72 h	**3a**, 46
	1 : 3 : 3	20	—	72 h	**3a**, 56
	1 : 2 : 2	65	—	6 h	**3a**, 68
	1 : 3 : 3	65	—	6 h	**3a**, 78
	1 : 2 : 2	20	MA	4 h	**3a**, 66
	1 : 3 : 3	20	MA	4 h	**3a**, 80
	1 : 3 : 3		MW (450 W)	20 min	**3a**, 40
KBr	1 : 2 : 2	65	—	6 h	**3a**, 57
		20	MA	4 h	**3a**, 49
LiCl	1 : 2 : 2	20	—	72 h	**4a**, 45
	1 : 2 : 2	65	—	6 h	**4a**, 71
	1 : 2 : 2	20	MA	4 h	**4a**, 59
	1 : 3 : 3	20	—	4 h	**4a**, 75
	1 : 3 : 3		MW (450 W)	2 min	**4a**, 36
$NaNO_2$	1 : 2 : 2	20	—	72 h	—[d]
	1 : 2 : 2	65	—	12 h	—[d]
	1 : 2 : 2	20	—	4 h	—[d]
	1 : 2 : 2		MW (450 W)	4 min×5[e]	**5a**, 31
	1 : 3 : 3		MW (450 W)	4 min×5[e]	**5a**, 55
	1 : 3 : 3		MW (600 W)	4 min×2[e]	**5a**, 57

[a] Mechanical activation (MA) or keeping in a microwave oven (MW).
[b] The reaction time.
[c] From the starting acid **1a**.
[d] Formation of products was not observed.
[e] The reaction mixture was subjected to the MW-activation during periods of 4 min, the interval between separate treatments was ~1 min.

acids **1b,c** is observed, and the yield of the products rises to >90% after 1 h. Mechanical activation of the reaction mixture in a vibrational mill at room temperature also decreases the conversion time of acids **1b,c**, the yield of the target products in this case is close to that obtained at 65 °C under stationary conditions.

Halodecarboxylation of unactivated acid **1a**, devoid of methoxy groups in the aromatic core, under stationary conditions proceeds slower than that of acids **1b** and **1c**, however, when amount of the oxidant was half increased (ratio of the reagents 1 : 3 : 3) or a mechanical activation was applied, bromo- and chlorostyrenes **3a** and **4a** were obtained in 75—80% yield (see Table 1).

Scheme 2



1a,b **5a,b**

i. CAN—$NaNO_2$, MW, solvent-free.

R = H (**5a**), MeO (**5b**)

Similar results were obtained by us[10] (see Table 2) in the bromodecarboxylation of acids **1b** and **1c** with CAN—LiBr system in MeCN—H_2O (10 : 1). The advantage of the solid-phase reaction of halodecarboxylation of cinnamic acids **1a—c** as compared with the reactions in solutions consists in the absence of additional experimental procedures dealing with preparation, handling, and utilization of the solvent.

A replacement of the carboxy group by the nitro group in acids **1a** and **1b** with CAN—$NaNO_2$ system was successful only under MW activation. β-Nitrostyrenes **5a,b** were the reaction products (Scheme 2, see Tables 1 and 2).

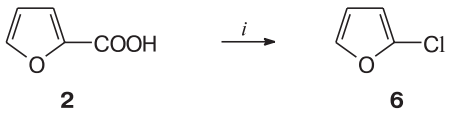
The β-substituted styrenes are formed as mixtures of *Z*- and *E*-isomers in ratio 1 : (4—5) (GLC). The assignment of signals in the ^1H NMR spectra was derived from the spin-spin coupling constant values in the isomers, as well as from comparison of the experimental spectrum with the calculated one. For PhCH(1)=CH(2)Br (**3a**), the experimental ^1H NMR spectrum of *E*-isomer: δ 7.07 H(1), 6.78 H(2); of *Z*-isomer: δ 6.94 H(1), 6.02 H(2); the calculated ^1H NMR spectrum of *E*-isomer: δ 6.94 H(1), 6.55 H(2); of *Z*-isomer: δ 6.84 H(1), 6.20 H(2).

Table 2. The solid-phase oxidative decarboxylation of 4-methoxycinnamic acid (**1b**), 3,4-dimethoxycinnamic acid (**1c**), and furan-2-carboxylic acid (**2**) under the action of CAN—MX system[a]

Starting acid	MX	Reaction conditions			Yield[c] (%)
		T/°C	Additional treatment[b]	τ[b]	
1b	LiBr	20	—	24 h	**3b**, 65
		65	—	1 h	**3b**, 94
		20	MA	4 h	**3b**, 91
		20	L.ph.	3 h	**3b**, 78
	KBr	20	MA	4 h	**3b**, 69
	LiCl	20	—	48 h	**4b**, 60
		65	—	3 h	**4b**, 74
		20	MA	4 h	**4b**, 80
	$NaNO_2$	20	—	48 h	—[d]
		65	—	3 h	—[d]
			MW (450 W)	10 min	**5b**, 32
			MW (450 W)	10 min	**5b**, 67
1c	LiBr	20	—	24	**3c**, 68
		65	—	1	**3c**, 79
		20	MA	4	**3c**, 71
		20	L.ph.	3	**3c**, 78
2	LiCl	20	—	30	**6**, 39
		65	—	2	**6**, 51
		20	MA	4	**6**, 43

[a] Molar ratio acid : CAN : MX = 1 : 2 : 2; the acid content was 1.0 mmol.
[b] Mechanical activation (MA) or keeping in a microwave oven (MW), liquid phase (L.ph.): MeCN—H_2O, 10 : 1.
[c] From the starting acid.
[d] Formation of products was not observed.
[e] Molar ratio **1b** : CAN : MX = 1 : 3 : 3; **1b** content was 1.0 mmol.

Scheme 3



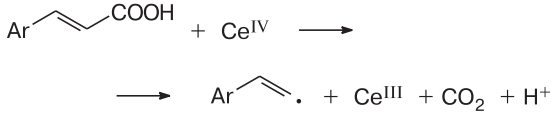
2 **6**

i. CAN—LiCl, 20 °C, solvent-free.

Like acids **1a,b**, though less efficient, furancarboxylic acid **2** undergoes decarboxylation in the solid-phase reaction with CAN—LiCl to form 2-chlorofuran (**6**) (Scheme 3, see Table 2). An increase in temperature and the use of mechanical activation also have a beneficial effect on the process of formation of compound **6**.

Mechanism of halodecarboxylation of acids **1a—c** is not clear enough. According to the available data, the oxidative decarboxylation of phenylacetic[11] and cinnamic[12,13] acids in aqueous acetonitrile, containing HNO_3 or H_2SO_4, can proceed through the formation of a complex between Ce^{IV} and the substrate and its subsequent decomposition with the generation of free radicals, in particular, β-phenylvinyl radicals.[12] We admit that in the solid-phase reaction of cinnamic acids **1a—c** with CAN—MX system, the formation of β-phenylvinyl radicals can also occur, which further are oxidized into the corresponding β-halostyrenes (Scheme 4).

Scheme 4



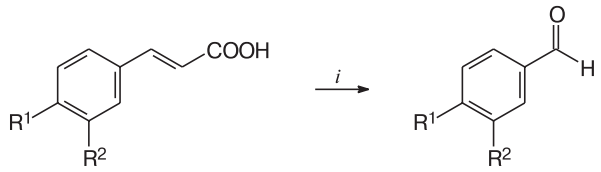
In this way, the oxidation of acids **1a—c** proceeds as the two-electron process, requiring 2 mol of CAN for the formation of one molecule of β-halostyrene **3a—c**, **4a,b**.

Another plausible mechanism of the halodecarboxylation of cinnamic acids **1a—c** can be proposed, which in the first step includes an addition of the halogen atom, generated by the oxidation of halide anion with CAN, at the C=C bond. β-Halo(carboxy)benzyl radicals thus formed undergo fragmentation according to the canoni-

cal scheme of β-cleavage to be converted into β-halostyrenes **3a—c**, **4a,b**.

The reaction of acids **1a—c** with CAN in the absence of MX salt follows a different pathway. In this case, both in the solid and in the liquid (in MeCN—H_2O solution) phases, a cleavage of the C=C bond occurs, resulting in the formation of the corresponding benzaldehydes **7a—c** (Scheme 5, Table 3).

Scheme 5



1a—c **7a—c**

i. CAN, in the solid phase or in MeCN—H_2O solution.

In all the experiments (see Table 3), aldehydes were isolated from the reaction mixture by the extraction with ether immediately after the reaction was over, *i.e.*, before the quenching with water and $NaHCO_3$. The results obtained allow one to suppose that the oxidation of acids **1a—c** with two equivalents of CAN proceeds through the intermediate formation of dinitrate $ArCH(ONO_2)CH(ONO_2)COOH$, which react with the third equivalent of CAN to generate $ArC^{\bullet}HONO_2$ radicals. From two possible directions of further transformations of the radicals, *i.e.*, an oxidation or β-cleavage at the O—N bond, the latter, leading to aldehydes, is most likely to be realized. Therefore, the nitrate group in CAN most likely serves as a source of oxygen atom in the aldehydes. A part of $^{\bullet}NO_2$ radicals, generated in the β-cleavage, probably, can bind to the double bond of acids **1a—c**, thus participating in their oxidation.

Table 3. The solid-phase reaction of cinnamic acid (**1a**), 4-methoxycinnamic acid (**1b**), and 3,4-dimethoxycinnamic acid (**1c**) with CAN[a]

Starting acid	Reaction conditions			Yield[b] (%)
	T/°C	AT[c]	τ/h	
1a	20	—	72	—[d]
	65	—	6	—[d]
	20	MA	4	**7a**, 20
	20	L.ph.	6	**7a**, 10
1b	20	—	72	**7b**, 44
	65	—	2	**7b**, 52
	20	MA	4	**7b**, 59
	20	L.ph.	3	**7b**, 65
1c	20	—	72	**7c**, 48
	65	—	2	**7c**, 52
	20	MA	4	**7c**, 60
	20	L.ph.	5	**7c**, 55

[a] Molar ratio **1** : CAN = 1 : 2; **1** content was 1.0 mmol.
[b] The yield of aldehydes calculated from the starting acid.
[c] Additional treatment: mechanical activation (MA), liquid phase (L.ph.): MeCN—H_2O, 10 : 1.
[d] Formation of products was not observed.

Esters of acids **1a—c** react with CAN similarly to the acids themselves. Thus, the solid-phase oxidation of methyl 4-methoxycinnamate (**8**) at 20 °C gave the corresponding aldehyde **7b**. When the molar ratio **8** : CAN was 1 : 2, the yield of aldehyde **7b** was ~20%, which was lower than in case of acid **1b**. Ester **8** under the action of CAN—LiBr system undergoes bromination at the C=C bond.

The structures β-substituted styrenes and benzaldehydes obtained were established by ^1H NMR spectroscopy and chromato-mass spectrometry. A molecular ion was observed in the mass spectra of the most β-substituted styrenes. The aldehydes were converted to the corresponding 2,4-dinitrophenylhydrazones.

In conclusion, we have shown that the oxidative halodecarboxylation of cinnamic acids with CAN—MX system can be easily accomplished in the solid phase and it can be used for the preparative synthesis of β-halostyrenes.

Experimental

Analysis of the reaction mixtures was performed by GLC on a LKhM-80 chromatograph with the flame-ionizing detector and analytical metal 2000×3 mm columns with 5% SE-30 and 5% FFAP on Chromaton N-AW-HMDS (0.16—0.20 mm). IR spectra were recorded on a Perkin—Elmer 577 spectrophotometer for neat samples. ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer under standard conditions for solutions in $CDCl_3$, the corresponding calculated spectra were obtained with the ACDLABS computer program; chromato-mass spectra were recorded on a Finigan MAT ITD-700 spectrometer (electron impact, 70 eV, temperature of the source of ions—ionic trap system was 220 °C), a Carlo Erba 4200 chromatograph, equipped with Ultra-1 25000×0.2 mm column (Hewlett-Packard), the film thickness of the stationary phase (polymethylsiloxane) was 0.33 μm, helium as the carrier gas. The starting cinnamic, 4-methoxycinnamic, 3,4-dimethoxycinnamic, and furan-2-carboxylic acids and ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$) (Acros) were used as purchased. Lithium chloride, lithium bromide, potassium bromide, and sodium nitrite (pure grade reagents) were pre-calcined before the reaction to remove the crystallization water. Acetonitrile (reagent of pure grade) was distilled before the reaction.

Solid-phase oxidative decarboxylation of acids 1 with CAN—MX system without mechanical activation (general procedure). A mixture of acid **1**, CAN and MX (ratios of reagents are given in Tables 1 and 2) was thoroughly triturated in air in a porcelain mortar for 5—10 min and kept in a tightly capped glass at 20 °C until the complete conversion of CAN. When the reaction was carried out at 65 °C, the triturated mixture was kept for 1—6 h (see Tables 1

and 2). After the reaction was over (a change of orange color of the reaction mixture to light yellow), water (10—15 mL) was added to the mixture and it was extracted with ether (3×20 mL). The combined extract was washed with saturated aq. $NaHCO_3$ (10—15 mL), water (10—15 mL), and dried with $MgSO_4$. After concentrating, the yields of the reaction products were determined by GLC with the use of an internal standard. The products were isolated by preparative GLC (2000×10 mm copper column with 5% SE-30 on Chromaton N-AW-HMDS 0.25-0.36 mm).

Mechanically activated oxidative decarboxylation of acids 1 and 2 with CAN—MX system. Mechanical activation of a mixture of acid **1** or **2**, CAN and MX (total amount, ~1—2 g, ratio of the reagents are given in Tables 1 and 2) was carried out at 20 °C on a vibrational mill with the frequency of 12 Hz and the amplitude of 11 mm in a sealed steel ~80-cm^3 reactor. Steel spheres 12.3 mm in diameter and total weight ~150 g were used as the activating packing. Duration of the mechanical activation was 4 h, then the mixture was treated as described above.

Oxidative decarboxylation acid 1 and 2 with CAN—LiBr system in MeCN—H_2O. A solution of acid **1** or **2**, CAN and LiBr in aq. MeCN (20 mL) (ratio MeCN : H_2O = 10 : 1) was vigorously stirred with a magnetic stirrer at ~20 °C until the complete conversion of the oxidant (a change of orange color to light yellow). Then it was extracted with ether (3×25 mL), the extract was washed with saturated aq. $NaHCO_3$, water, dried with $MgSO_4$, and the solvent was evaporated. The yield of the reaction products was determined by GLC (see Table 2).

Microwave-activated (MW) oxidative decarboxylation of acids 1a,b with CAN—$NaNO_2$ system. A mixture of **1a** or **1b**, CAN and $NaNO_2$ (ratios of the reagents are given in Tables 1 and 2) was thoroughly triturated in air in a porcelain mortar for 5—10 min, placed in a capped glass, and subjected to the irradiation (a Samsung consumer microwave oven). The power and the times of the irradiation are given in Tables 1 and 2. After the reaction was over (a change of orange color to light yellow), the reaction mixture was extracted with ether and treated as in the preceding procedures.

Oxidation of acids 1 and 2 with CAN. The reaction of cinnamic acids with CAN in the absence of a MX salt was carried out according to the procedures with participation of MX (see Table 3).

β-Bromostyrene (3a), b.p. 108 °C (20 Torr) (see Ref. 14a). ^{1}H NMR ($CDCl_3$), δ (*E*)-isomer: 6.77 (d, 1 H, CH, *J* = 14.0 Hz); 7.12 (d, 1 H, CH, *J* = 14.0 Hz); 7.29 (m, 2 H, H(3), H(5)); 7.38 (m, 1 H, H(4)); 7.59 (m, 2 H, H(2), H(6)); (*Z*)-isomer: 6.02 (d, 1 H, CH, *J* = 8.2 Hz); 6.94 (d, 1 H, CH, *J* = 8.2 Hz); 7.29 (m, 2 H, H(3), H(5)); 7.38 (m, 1 H, H(4)); 7.59 (m, 2 H, H(2), H(6)). MS, *m/z*: 184 $[M + H]^+$.

β-Chlorostyrene (4a), b.p. 90 °C (18 Torr) (see Ref. 14b). ^{1}H NMR ($CDCl_3$), δ (*E*)-isomer: 6.64 (d, 1 H, CH, *J* = 13.8 Hz); 6.84 (d, 1 H, CH, *J* = 13.8 Hz); 7.33 (m, 2 H, H(3), H(5)); 7.39 (m, 1 H, H(4)); 7.46 (m, 2 H, H(2), H(6)). (*Z*)-isomer: 5.83 (d, 1 H, CH, *J* = 8.1 Hz); 6.28 (d, 1 H, CH, *J* = 8.1 Hz); 7.33 (m, 2 H, H(3), H(5)); 7.39 (m, 1 H, H(4)); 7.46 (m, 2 H, H(2), H(6)). MS, *m/z*: 138 and 140 $[M]^+$.

1-Bromo-2-(4-methoxyphenyl)ethylene (3b), b.p. 160 °C (18 Torr) (see Ref. 15). ^{1}H NMR ($CDCl_3$), δ (*E*)-isomer: 3.82 (s, 3 H, OMe); 6.61 (d, 1 H, CH, *J* = 13.9 Hz); 6.87 (m, 2 H, H(2), H(6)); 7.05 (d, 1 H, CH, *J* = 13.9 Hz); 7.24 (m, H(3), H(5)); (*Z*)-isomer: 3.82 (s, 3 H, OMe); 6.32 (d, 1 H, CH, *J* = 8.1 Hz); 6.87 (m, 2 H, H(2), H(6)); 6.90 (d, 1 H, CH, *J* = 8.1 Hz); 7.24 (m, H(3), H(5)). MS, *m/z*: 214 $[M + H]^+$.

2-Chloro-1-(4-methoxyphenyl)ethylene (4b), b.p. 145 °C (20 Torr) (see Ref. 16). ^{1}H NMR ($CDCl_3$), δ (*E*)-isomer: 3.79 (s, 3 H, OMe); 6.50 (d, 1 H, CH, *J* = 13.9 Hz); 6.77 (d, 1 H, CH, *J* = 13.9 Hz); 6.86 (m, H(2), H(6)); 7.24 (m, 2 H, H(3), H(5)). MS, *m/z*: 179 $[M]^+$.

1-Bromo-2-(3,4-dimethoxyphenyl)ethylene (3c), m.p. 66 °C (see Ref. 17). ^{1}H NMR ($CDCl_3$), δ (*E*)-isomer: 3.82 (s, 3 H, OMe); 3.88 (s, 3 H, OMe); 6.62 (d, 1 H, CH, *J* = 14.0 Hz); 7.01 (d, 1 H, CH, *J* = 14.0 Hz); 6.98 (m, 1 H, H(3)); 7.12 (m, 1 H, H(4)); 7.22 (m, 1 H, H(6)); (*Z*)-isomer: 3.82 (s, 3 H, OMe); 3.88 (s, 3 H, OMe); 6.30 (d, 1 H, CH, *J* = 8.1 Hz); 6.90 (d, 1 H, CH, *J* = 8.1 Hz); 6.98 (m, 1 H, H(3)); 7.12 (m, 1 H, H(4)); 7.22 (m, 1 H, H(6)). MS, *m/z*: 244 $[M + H]^+$.

(*E*)-β-Nitrostyrene (5a), m.p. 58 °C (see Ref. 18). ^{1}H NMR ($CDCl_3$), δ: 7.42 (d, 1 H, CH, *J* = 14.0 Hz); 7.40 (m, 2 H, H(3), H(5)); 7.48 (m, 2 H, H(2), H(6)); 7.56 (m, 1 H, H(4)); 7.79 (d, 1 H, CH, *J* = 14.0 Hz). MS, *m/z*: 149 $[M]^+$.

(*E*)-1-(4-Methoxyphenyl)-2-nitroethylene (5b), m.p. 82 °C (see Ref. 19). ^{1}H NMR ($CDCl_3$), δ: 3.82 (s, 3 H, OMe); 6.32 (m, 2 H, H(2), H(6)); 7.19 (m, 2 H, H(3), H(5)); 7.72 (d, 1 H, CH, *J* = 10.8 Hz); 7.96 (d, 1 H, CH, *J* = 10.8 Hz). MS, *m/z*: 179 $[M]^+$.

2-Chlorofuran (6), b.p. 77 °C (see Ref. 20a). ^{1}H NMR ($CDCl_3$), δ: 6.28 (d, 1 H, H(3), *J* = 1.1 Hz); 6.54 (m, 1 H, H(4)); 7.48 (d, 1 H, H(5), *J* = 1.1 Hz). MS, *m/z*: 102 and 104 $[M]^+$.

Benzaldehyde (7a), b.p. 179 °C. IR, ν/cm^{-1}: 1696 (C=O). ^{1}H NMR ($CDCl_3$), δ: 7.53 (m, 2 H, H(3), H(5)); 7.64 (m, 1 H, H(4)); 7.89 (m, 2 H, H(2), H(6)); 10.03 (s, 1 H, CHO). MS, *m/z*: 105 $[M]^+$. Benzaldehyde **7a** 2,4-dinitrophenylhydrazone, m.p. 237 °C (see Ref. 20b).

4-Methoxybenzaldehyde (7b), b.p. 118 °C (10 Torr). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.88 (s, 3 H, OMe); 7.01 (m, 2 H, H(2), H(6)); 7.85 (m, 2 H, H(3), H(5)); 9.89 (s, 1 H, CHO). MS, *m/z*: 136 $[M]^+$. Benzaldehyde **7b** 2,4-dinitrophenylhydrazone, m.p. 254 °C (see Ref. 20c).

3,4-Dimethoxybenzaldehyde (7c), m.p. 44—45 °C. IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.88 (s, 3 H, OMe); 3.93 (s, 3 H, OMe); 6.97 (m, 1 H, H(3)); 7.43 (m, 1 H, H(6)); 7.47 (m, 1 H, H(4)); 9.86 (s, 1 H, CHO). MS, *m/z*: 166 $[M]^+$. Benzaldehyde **7c** 2,4-dinitrophenylhydrazone, m.p. 265 °C (see Ref. 20d).

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