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Synergism of metal and organocatalysis in condensation reactions of aromatic aldehydes with anilines affording imines: Effect of catalysts on the base of a supported Cerium (III) and proline

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Abstract: Condensation reactions between 4-X-benzaldehydes (X = NO_2, H, OCH_3) and 4-Y-anilines (X = NO_2, H, OCH_3) catalyzed by new catalyst, *i.e.* Ce (III) supported on weakly acidic cation-exchanger resin of polyacrylate type and/or by proline as organocatalyst giving 4-Y-*N*-[(*E*)-(4-X-phenyl)methylidene]anilines, were studied. It was found that the both of the used catalysts, *i.e.* metal and organocatalyst, shortened reaction time, thus contributing to higher yields of products. The synergism between catalytic action of polymer supported Ce (III) and proline was found. It was observed that simultaneous application of metal and organocatalyst led to shorter reaction times. On the other hand, it was found that the synergic efficiency of the both applied catalysts depends on electron influence of the substituents X, Y present in 4-X-benzaldehyde and 4-Y-aniline, as well. Imines were prepared under catalysis by Ce (III), proline or by simultaneous use of both catalysts in the yields 97-99% and identified. For comparison, the above mentioned condensation reactions were carried out under classical catalysis by mineral acid with different, usually poor, results.

Keywords: Imines, Metal Catalysis, Organocatalysis, Synergism, Polymer Supported Ce(III)

1. Introduction

As in recent years industrial production consumes increasing amount of chemical raw materials, for fine chemistry products especially, it is necessary to looking for new synthetic procedures that correspond to the principles of the Green Chemistry as one of the ways of the Sustainable Development of human population [1]. For this reason, there is an increasing interest for the use of metal and organocatalysis. In particular, the solid-support catalysis displayed an extensive progress recently. Solid supported catalysts combine namely the advantages of both heterogeneous and homogenous catalysts [2,3]. They have high activity, selectivity and stability, and they are easily separable and recyclable. Due to these properties they are useful for reactions carried out according to the principles of Green Chemistry [1].

Imines and their derivatives have been used for many years as one of the starting materials in the synthesis of nitrogen heterocycles, which are used in pharmacy, *etc.* [4-6]. Imine derivatives are very often used for the identification of organic compounds as well [7].

In last decade, lanthanide cations based Lewis acids, *e.g.* especially cerium(III) chloride in the heptahydrate form, attracted an attention in organic synthesis due to their stability, ease of handling, low toxicity, air tolerance, high reactivity and low cost [8-10]. Cerium(III) chloride heptahydrate or cerium(III) nitrate is currently used in reactions as a salt itself or supported on silica gel and eventually doped by sodium iodide – this type of supported catalyst was developed by Bartoli and Marcantoni [11,12]. The disadvantage of using these catalysts in the form of salts

is their difficult separation for reuse in the synthesis, which is also one of the goals of Green Chemistry. In our work [13] we showed that cerium (III) can be efficiently supported on weakly acidic cation-exchanger resin of polyacrylate type and as such easily separated and recycled for reuse in other syntheses.

Fortunately, proline, an inexpensive and readily available biomimetic, has become a promising catalyst in many reactions [14].

Current procedures for the direct synthesis of title 4-Y-*N*-[(*E*)-(4-X-phenyl) methylidene] anilines were published only for *N*-[(*E*)-(phenyl) methylidene] aniline and 4-methoxy-*N*-[(*E*)-(phenyl) methylidene] aniline. Both compounds can be generally prepared by the reaction of benzaldehyde with the corresponding aniline in solvents such as toluene, chloroform, ethanol, *etc.* under reflux [15-17]; in the presence of silica gel under ultrasound action [18]; by heating with anhydrous magnesium sulfate [19] or by heating with molecular sieve [20].

Further compounds from the studied set of 4-Y-*N*-[(*E*)-(4-X-phenyl) methylidene] anilines were prepared by other synthetic ways [21-28].

The goal of our research work was to carry out model condensation reactions between 4-X-benzaldehydes (X = NO_2, H, OCH_3) and 4-Y-anilines (Y = NO_2, H, OCH_3) leading to 4-Y-*N*-[(*E*)-(4-X-phenyl) methylidene] anilines in the presence of Ce(III) cation supported on a weakly acidic cation-exchanger resin of polyacrylate type and/or under action of proline as organocatalyst, and side by side for a comparison in the presence of catalytic hydrochloric acid (currently used catalytic method). Our elected set of substituents X, Y was chosen to include a methoxy group as a strong electron donor group (EDG), hydrogen substituent as an electron-neutral and nitro group as a strong electron withdrawing group (EWG). Nitro group should therefore activate the formyl group of 4-X-benzaldehyde for nucleophilic attack by aniline nitrogen, on the other hand a methoxy group should deactivate the formyl group. The reactivity of the amino group in the 4-Y-aniline should be influenced by both of the mentioned substituents in the reverse order.

2. Experimental

2.1. Chemicals

All reagents were purchased from commercial suppliers and used as received without further purification. L-proline was used as proline catalyst. Purolite C 104 Plus (Purolite® Worldwide), *i.e.* weakly acidic polyacrylic cation-exchanger resin of macroporous type, ionic form H^+, total volume capacity 4.5 mmol/ml, specific gravity 1.19 g/ml, was used as a solid support.

2.2. General

All of the reactions were monitored by TLC performed on precoated Silica gel 60 F^{254} plates (Merck). Dichloromethane was used as an eluent, UV light (254 and 356 nm) and iodine vapours were used for spots detection.

^{1}H NMR and ^{13}C NMR spectra were recorded on DRX 300 Avance (Bruker Biospin) spectrometer using tetramethyl silane as an internal standard.

Melting points are uncorrected and were recorded on Kofler's block Boetius Rapido PHMK 79/2106 (Wägetechnik), a temperature gradient 4°C/min.

2.3. Catalyst Preparation

The catalytic system containing Ce(III) cations supported on a weakly acidic macroporous cation exchanger of polyacrylate type was prepared according to patent [29]. Purolite C 104 Plus (75 g) was suspended in 200 ml of water and a saturated aqueous potassium carbonate solution was added under stirring until a pH of the solution remained at value of 12 for 10 min after the last addition. Aqueous solution was then decanted. The resin beads were washed 4 times by 200 ml of water. Cerium (III) chloride heptahydrate (122.7 g, 33 mmol) was dissolved in 500 ml of water and resin beads were put into the solution which was subsequently stirred overnight. Then the aqueous solution was decanted again. The resin beads were then washed 2 times by 200 ml of water and 2 times by methanol and finally dried in vacuum to constant weight.

The catalyst prepared in this way has cerium content about 2.3 mmol of Ce (III) per 1 g of catalytic system [29]. Catalyst is available from TauChem Ltd., Bratislava, Slovakia, http://www.tau-chem.sk/en/About/Company-description.alej.

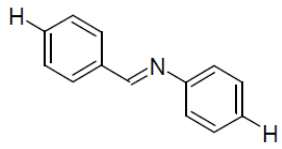
2.4. General Procedure for Preparation of 4-Y-N-[(E)-(4-X-Phenyl) Methylidene] Anilines

In a typical experimental procedure, mixture of 4-X-benzaldehyde (1 mmol), 4-Y-aniline (1 mmol) and appropriate catalytic system (10 mol%) in 10 ml of ethanol was stirred at a given temperature for a specified time, see Table 1, 2 below. After completion of the reaction (monitored by TLC) the mixture was concentrated on a rotary evaporator to 1/3 of a starting volume. The product precipitated by addition of water was filtered off and recrystallized from ethyl acetate.

Concentrated HCl (35%, 0.1 ml, 10 mol%) was the catalytic system A1, concentrated HCl (35%, 0.5 ml, 50mol%) was the catalytic system A2. Ce(III) cations supported on a weakly acidic cation exchanger was the catalytic system B (0.042 g, 10 mol%). Proline was catalytic system C (0.012 g, 10 mol%). Ce(III) cations supported on a weakly acidic cation exchanger (0.042 g, 10 mol%) combined with proline (0.012 g, 10 mol%) was catalytic system D.

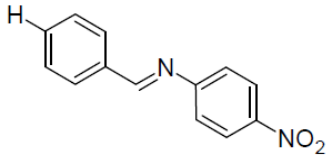
2.5. Characteristics of Products

Entry 1: (E)-N,1-Diphenylmethanimine



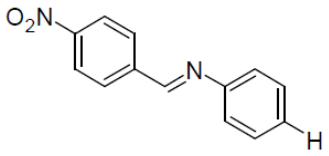
$C_{13}H_{11}N$ (m.w. 181.24), m.p. 54-55 °C (ethanol, Lit. [30] 54-55 °C). ^{1}H-NMR (δ / ppm): (Acetone-d_6) δ 8.37 (s, 1H, N=CH); 7.76 (m, 2H, Ar); 7.22-7.46 (m, 8H, Ar); 4.83 (s, 2H, Ar). ^{13}C-NMR (δ / ppm): (Acetone-d_6) δ 162.4; 139.1; 135.7; 131.4; 128.8; 128.7; 128.5; 128.2; 127.2; 65.1.

Entry 2: (E)-N-(4-Nitrophenyl)-1-phenylmethanimine



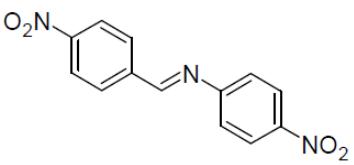
$C_{13}H_{10}N_2O_2$ (m.w. 226.23), m.p. 118-119 °C (ethanol, Lit. [31] 117-118 °C). ^{1}H-NMR (δ / ppm): (Acetone-d_6) δ 8.42 (s, 1H, N=CH); 8.26 (d, J = 9.0 Hz, 2H, Ar); 7.94-7.86 (m, 2H, Ar); 7.63-7.48 (m, 3H, Ar); 7.23 (d, J = 9.0 Hz, 2H, Ar). ^{13}C-NMR (δ / ppm): (Acetone-d_6) δ 163.3; 154.1; 145.9; 136.2; 132.8; 129.9; 129.6; 125.4; 121.6.

Entry 3: (E)-1-(4-Nitrophenyl)-N-phenylmethanimine



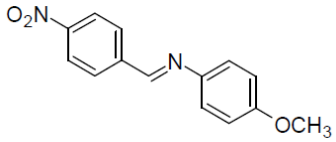
$C_{13}H_{10}N_2O_2$ (m.w. 226,23), m.p. 88-89 °C (ethanol, Lit. [32] 89-90 °C). ^{1}H-NMR (δ / ppm): (Acetone-d_6) δ 8.24 (s, 1H, N=CH); 8.16 (d, J = 8.4 Hz, 2H, Ar); 8.01-7.56 (m, 3H, Ar); 7.42-7.37 (m, 2H, Ar); 7.21 (d, J = 8.4 Hz, 2H, Ar). ^{13}C-NMR (δ / ppm): (Acetone-d_6) δ 157.2; 150.1; 149.3; 140.8; 129.1; 128.7; 125.4; 123.7; 120.1.

Entry 4: (E)-N,1-bis(4-Nitrophenyl)methanimine



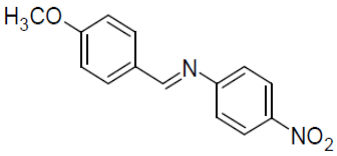
$C_{13}H_9N_3O_4$ (m.w. 271.23), m.p. 197-198 °C (ethanol, Lit. [33] 198-199 °C). ^{1}H-NMR (δ / ppm): (Acetone-d_6) δ 8.29 (s, 1H, N=CH); 8.17 (d, J = 8.4 Hz, 2H, Ar); 8.04-7.48 (m, 4H, Ar); 7.28 (d, J = 8.4 Hz, 2H, Ar). ^{13}C-NMR (δ / ppm): (Acetone-d_6) δ 159.4; 154.1; 148.7; 145.6; 142.2; 129.4; 124.8; 123.7; 121.6.

Entry 5: (E)-N-(4-Methoxyphenyl)-1-(4-nitrophenyl)-methanimine



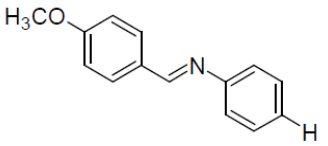
$C_{14}H_{12}N_2O_3$ (m.w. 256.26), m.p. 131-132 °C (ethanol, Lit. [34] 132 °C). ^{1}H-NMR (δ / ppm): (Acetone-d_6) δ 8.61 (s, 1H, N=CH); 8.29 (d, J = 8.2 Hz, 2H, Ar); 8.07 (d, J = 8.6 Hz, 2H, Ar); 7.32 (d, J = 8.6 Hz, 2H, Ar); 7.12 (d, J = 8.2 Hz, 2H, Ar); 3.91 (s, 3H, OCH_3).^{13}C-NMR (δ / ppm): (Acetone-d_6) δ 159.2; 155.6; 144.7; 142.2; 129.4; 123.9; 121.6; 114.6; 56.2.

Entry 6: (E)-1-(4-Methoxyphenyl)-N-(4-nitrophenyl)-methanimine



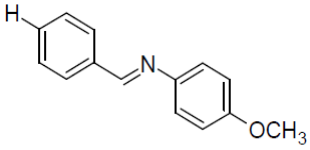
$C_{14}H_{12}N_2O_3$ (m.w. 256.26), m.p. 122-123 °C (ethanol, Lit. [35] 123-124 °C). ^{1}H-NMR (δ / ppm): (Acetone-d_6) δ 8.45 (s, 1H, N=CH); 8.12 (d, J = 8.2 Hz, 2H, Ar); 7.89 (d, J = 8.6 Hz, 2H, Ar); 7.29 (d, J = 8.6 Hz, 2H, Ar); 6.97 (d, J = 8.2 Hz, 2H, Ar); 3.87 (s, 3H, OCH_3). ^{13}C-NMR (δ / ppm): (Acetone-d_6) δ 161.4; 154.2; 145.7; 130.1; 128.7; 125.6; 121.8; 114.1; 55.2.

Entry 7: (E)-1-(4-Methoxyphenyl)-N-phenylmethanimine



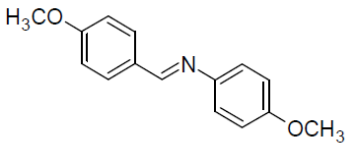
$C_{14}H_{13}NO$ (m.w. 211.26), m.p. 63-64 °C (ethanol, Lit. [39] 63 °C). ^{1}H-NMR (δ / ppm): (Acetone-d_6) δ 8.30 (s, 1H, N=CH); 7.81-7.76 (m, 2H, Ar); 7.42-7.32 (m, 3H, Ar); 7.18-6.96 (m, 2H, Ar); 6.87 (d, J = 8.8 Hz, 2H, Ar); 3.87 (s, 3H, OCH_3). ^{13}C-NMR (δ / ppm): (Acetone-d_6) δ 162.1; 159.2; 150.0; 130.8; 128.7; 125.1; 120.3; 114.1; 55.4.

Entry 8: (E)-N-(4-Methoxyphenyl)-1-phenylmethanimine



$C_{14}H_{13}NO$ (m.w. 211.26), m.p. 70-71 °C (ethanol, Lit. [40] 70.4-70.8 °C). ^{1}H-NMR (δ / ppm): (Acetone-d_6) δ 8.41 (s, 1H, N=CH); 7.87-7.79 (m, 2H, Ar); 7.45-7.42 (m, 3H, Ar); 7.28 (d, J = 8.8 Hz, 2H, Ar); 6.89 (d, J = 8.8 Hz, 2H, Ar); 3.82 (s, 3H, OCH_3). ^{13}C-NMR (δ / ppm): (Acetone-d_6) δ 158.6; 158.1; 144.2; 135.3; 131.4; 129.1; 121.4; 114.6; 56.3.

Entry 9: (E)-N,1-bis(4-Methoxyphenyl)methanimine

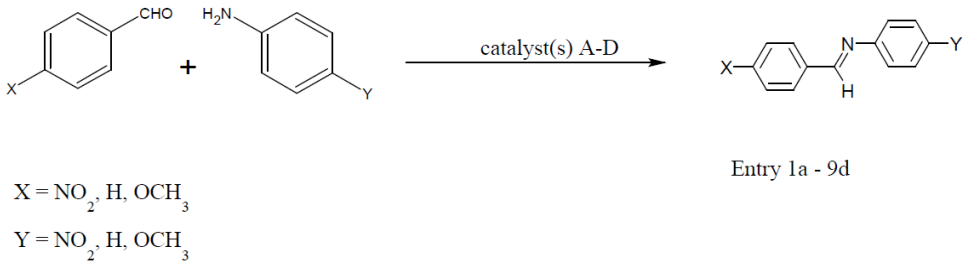


$C_{15}H_{15}NO_2$ (m.w. 241,29), m.p. 147-148 °C (ethanol, Lit. [41] 147-148 °C). ^{1}H-NMR (δ / ppm): (Acetone-d_6) δ 8.31 (s, 1H, N=CH); 7.82 (d, J = 8.6 Hz, 2H, Ar); 7.24 (d, J = 9.0 Hz, 2H, Ar); 6.92-6.83 (m, 4H, Ar); 3.91 (s, 3H, OCH_3); 3.82 (s, 3H, OCH_3). ^{13}C-NMR (δ / ppm): (Acetone-d_6) δ 162.3; 158.6; 142.3; 130.1; 129.2; 121.8; 114.5; 114.3; 56.3; 55.9.

3. Results and Discussion

As it was reported in the Introduction part, only *N*-[(*E*)-(phenyl) methylidene] aniline and 4-methoxy-*N*-[(*E*)-(phenyl)methylidene]aniline were prepared by direct condensation of benzaldehyde with aniline and 4-methoxyaniline, respectively. Condensation reaction was carried out under mineral acid catalysis and formed condensation water was taken out by different methods. Both sets of reagents represent relative well reacting molecules, because carbonyl carbon of benzaldehyde is either activated or deactivated by corresponding substituent X, on the other hand amino group of 4-methoxyaniline is activated by the presence of methoxy substituent. However, our sets of reagents, 4-X-benzaldehydes (X = NO_2, H, OCH_3) and 4-Y-anilines (Y = NO_2, H, OCH_3) leading to 4-Y-*N*-[(*E*)-(4-X-phenyl) methylidene] anilines, contain combination of reagents which are not favorable for easy course of condensation reaction, such as 4-methoxy-benzaldehyde and/or 4-nitro-aniline. Reactions of pairs of such poorly reacting substrates have not been described in the literature yet and that is why we tried to force them to react under the "classical" catalytic conditions, under catalysis by supported cerium cations, catalysis by proline or catalysis by combination of proline and supported cerium cation.

All of the syntheses were carried out according to the general procedure given in Section 2.4.



Scheme 1. *General scheme for synthesis of 4-Y-N-[(E)-(4-X-phenyl)methylidene]anilines*

First set of reactions was carried out at room temperature in order that we were able to monitor the progress of reactions (TLC) carefully throughout their duration and to determine the most accurate total time of reaction. Just shortening of reaction time eventually beside offered yields indicated efficiency of applied catalytic system.

As noted in section 2.4, concentrated HCl in a catalytic amount was the catalytic system A1, 50 mol% of concentrated HCl was the catalytic system A2. Ce (III) cations supported on a weakly acidic cation exchanger were used as a catalytic system B, and catalytic system C was represented by proline. Catalytic system D was formed by a combination of proline and Ce (III) cations supported on a weakly acidic cation exchanger.

Table 1 shows that the catalytic system A1 has proved to be inefficient. Acceptable results with this type of the catalytic system were achieved only for entries one and eight, *i.e.* for the reaction of benzaldehyde with aniline and for the reaction of benzaldehyde with 4-methoxyaniline. That corresponds with the results obtained from the literature, as demonstrated above [15-28]. Other entries were forcibly terminated after the referred time because only trace amounts of the product were found (TLC) in the reaction mixture after that time. Table 1 also shows that the greatest catalytic effect of the catalytic system B was achieved in reactions with 4-nitrobenzaldehyde containing EWG. This fact may be explained by the interaction of proline with 4-X-benzaldehyde in the reaction course. The activating action of nitro group to the aldehydic formyl group of benzaldehyde facilitates nucleophilic attack of aniline nitrogen. On the other hand, the coordination of 4-methoxybenzaldehyde to Ce(III) ions contained in the catalytic systems B and D proved to be catalytically more efficient than in the case of 4-nitrobenzaldehyde because of higher electron density on formyl oxygen in the case of 4-methoxybenzaldehyde.

Table 1. *Reaction of 4-X-benzaldehyde and 4-Y-aniline at room temperature.*

Entry		-X	-Y	Catalytic system	Time (h)	Yield (%)	Yield (g)
1	a	-H	-H	A1	336	62	0.117
	b			B	210	98	0.177
	c			C	252	98	0.176
	d			D	168	98	0.177
2	a	-H	$-NO_2$	A1	384	10	0.022
	b			B	358	97	0.219
	c			C	312	98	0.221
	d			D	264	97	0.220
3	a	$-NO_2$	-H	A1	120	5	0.013
	b			B	106	98	0.221
	c			C	72	98	0.222
	d			D	52	98	0.222
4	a	$-NO_2$	$-NO_2$	A1	648	3	0.008
	b			B	612	97	0.263
	c			C	564	98	0.266
	d			D	504	97	0.264
5	a	$-NO_2$	$-OCH_3$	A1	168	15	0.038
	b			B	94	98	0.251
	c			C	125	99	0.254
	d			D	22	99	0.253
6	a	$-OCH_3$	$-NO_2$	A1	940	5	0.013
	b			B	764	98	0.251
	c			C	868	98	0.251
	d			D	670	99	0.253
7	a	$-OCH_3$	-H	A1	264	3	0.006
	b			B	186	98	0.207
	c			C	232	98	0.207
	d			D	140	99	0.209
8	a	-H	$-OCH_3$	A1	288	58	0.122
	b			B	220	97	0.205
	c			C	262	98	0.207
	d			D	184	98	0.209
9	a	$-OCH_3$	$-OCH_3$	A1	312	4	0.009
	b			B	232	98	0.236
	c			C	278	99	0.238
	d			D	194	99	0.238

Used catalytic systems: A1 - Concentrated HCl (10 mol%). A2 - Concentrated HCl (50 mol%). B - Ce(III) cations supported on a weakly acidic cation exchanger (10 mol%). C – Proline (10 mol%). D - Ce(III) cations supported on a weakly acidic cation exchanger (10 mol%) combined with proline (10 mol%).

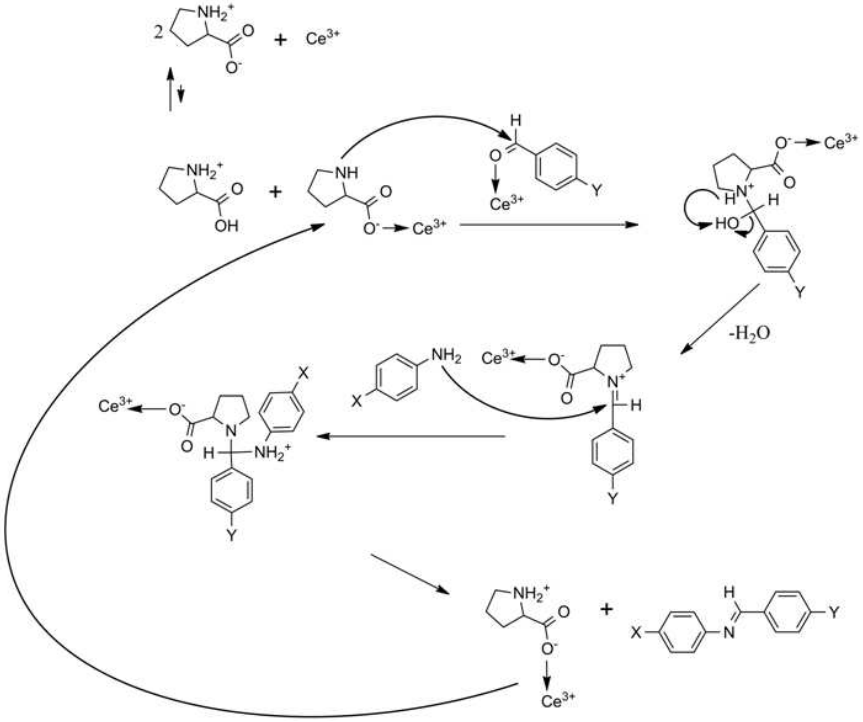
Table 2. *Reaction of 4-X-benzaldehyde and 4-Y-aniline under reflux.*

Entry		-X	-Y	Catalytic system	Time (h)	Yield (%)	Yield (g)
1	e	-H	-H	A2	23	87	0.157
	f			D	12	99	0.179
2	e	-H	$-NO_2$	A2	43	3	0.007
	f			D	21	98	0.221
3	e	$-NO_2$	-H	A2	14	4	0.009
	f			D	6	97	0.219
4	e	$-NO_2$	$-NO_2$	A2	98	2	0.005
	f			D	46	97	0.263
5	e	$-NO_2$	$-OCH_3$	A2	9	3	0.007
	f			D	2	98	0.251
6	e	$-OCH_3$	$-NO_2$	A2	116	4	0.010
	f			D	59	99	0.253
7	e	$-OCH_3$	-H	A2	28	4	0.008
	f			D	15	99	0.208
8	e	-H	$-OCH_3$	A2	37	83	0.175
	f			D	17	89	0.188
9	e	$-OCH_3$	$-OCH_3$	A2	41	5	0.012
	f			D	19	97	0.234

Used catalytic systems: A1 - Concentrated HCl (10 mol%). A2 - Concentrated HCl (50 mol%). B - Ce(III) cations supported on a weakly acidic cation exchanger (10 mol%). C – Proline (10 mol%). D - Ce(III) cations supported on a weakly acidic cation exchanger (10 mol%) combined with proline (10 mol%).

Furthermore, during this series of experiments the synergistic effect of the catalytic system of proline and Ce (III) cations supported on a weakly acidic cation exchanger (catalytic system D; see Table 1) was clearly demonstrated. The proposal of a probable reaction pathway for the used combined catalytic system D is shown in Scheme 2, which demonstrates interaction of Ce (III) cations and proline with the reagents. Scheme 2 states the intermediary complexes with the most important effect on the course of reaction.

We assume (Scheme 2) that betaine form of proline can be coordinated with Ce (III) by via carboxylate oxygen in reaction solution. This interaction then evokes the higher acidity on ammonium group of proline and two proline molecules form acid-base equilibrium system under formation of two intermediates, *i.e.* protonated proline and with Ce(III) ions coordinated by deprotonated proline. We suppose this assumption to be the primary explanation of the catalytic synergism of proline and Ce (III).



Scheme 2. *Probable mechanism of synthesis of 4-Y-N-[(E)-(4-X-phenyl)methylidene]anilines with indicated synergism of Ce(III) cation and proline.*

The coordinated proline anion is able to attack the formyl carbon of aldehyde via nitrogen. The formyl carbon has higher partial positive charge because of coordination with Ce(III). The nucleophilic attack of the coordinated proline to the coordinated aldehydic formyl is accompanied by elimination of water molecule and intermediary proline betaine is formed. Its higher stability (low energy) is determined by two factors, *i.e.* the positive charge on nitrogen is compensated by the presence of carboxylate group and, further, the negative charge of carboxylate group is enfeebled by the coordination of Ce(III). The resulting intermediate is attacked by the aniline nitrogen in the next step and proline as a good leaving group goes out under imine formation and the catalytic cycle can continue.

The best results, *i.e.* namely reaction times for the syntheses carried out at room temperature, were achieved with a catalytic system D, while the worst results were observed in reactions using the catalytic system A1. The 100% conversion of both of the starting compounds (TLC) was observed for all applied catalytic systems excluding A1.

Furthermore, we wanted to develop the optimal synthetic procedure for the title imines. Because syntheses realized at room temperature proceeded with too long times, we decided to carry out the same experiments once again under reflux temperature with combined catalytic system D. The synthesis under reflux was realized with hydrochloric acid as catalyst (A2 system) for comparison as well. In the case of A1 system application the reaction times were not satisfactory and the amount of catalyst was increased (catalytic system A2). As we expected, the observed reaction times were then shortened compared to syntheses carried out at room temperature. The results of this study are demonstrated in Table 2.

Trends concerning relationship among the structure of the used 4-X-aldehydes, 4-Y-anilines, applied catalytic system on the one hand, and reaction time and yield on the other hand, were the same as for the reactions carried out at room temperature (discussed above).

In the case of a reaction mixture containing catalytic system A2, about seven times higher acceleration of the reaction (based on the reaction time of entries one and the eight) was observed. Yields of the reactions in the case of entries one and eight were comparable with the yields obtained from reactions effected at room temperature. For

other entries, the products were again obtained in trace amounts only, despite the fact that 100% conversion of the substrate was achieved as it was in case of the reactions carried out at room temperature. This was caused by the formation of large amounts of side products during the reactions.

For reaction mixtures containing the catalytic system D, about 9-12 times higher acceleration of the reaction was observed in comparison to the reactions performed under room temperature. The conversion of substrates and the yields were comparable to the results of reaction carried out at room temperature as well.

4. Conclusion

Condensation reactions between 4-X-benzaldehydes (X = NO_2, H, OCH_3) and 4-Y-anilines (X = NO_2, H, OCH_3) catalyzed by Ce (III) supported on a weakly acidic cation-exchanger resin of polyacrylate type and/or by proline as organocatalyst giving 4-Y-*N*-[(*E*)- (4-X-phenyl) methylidene] anilines were studied. Optimal reaction conditions for effective realization of the condensation reaction between 4-X-benzaldehyde and 4-Y-aniline were found. Furthermore, it was found that all of the processes can be successfully catalyzed by both supported cerium cations and proline. The shortening of reaction times was the most significant indicator for the efficiency assessment of the used catalytic systems. It was shown that the efficiency of the used catalytic system depends on the character of the substituent X present in the starting 4-X-benzaldehyde, namely. Synergism in catalytic activity of Ce (III) cations and proline was found experimentally. Finally, the obtained results of study might be applied to similar syntheses involving the reaction of carbonyl compounds with (aza)-nucleophiles such as Mannich and similar reactions for their "greening".

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