

Kabachnik-Fields and Prins-Ritter Synthesis: Application of Ce(III) Supported on a Weakly Acidic Cation-exchanger Resin in Comparative Study

Keywords: α -Aminophosphonates; 4-Amidotetrahydropyranes; Metal catalysis; Polymer supported Ce(III); Solid support catalysis

Abstract

We described results of comparative studies of the application of Ce(III) cation supported on macroporous weakly acidic polyacrylate resin as catalyst in two model three-component domino syntheses, i.e. Kabachnik-Fields domino synthesis of α -aminophosphonates, and Prins-Ritter domino synthesis of 4-amidotetrahydropyran derivatives, respectively. It was discovered that cation Ce(III) supported on a weak acid macroporous cation-exchanger shown in the studied reactions at least the same or better catalytic activity as salt $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, eventually doped by NaI. Further, we found that reactivity of the low reactive 4-methoxybenzaldehyde as carbonyl compounds in the presence of Ce(III) catalyst increases, while the reactivity of the highly reactive 4-nitrobenzaldehyde in this case strongly decreases due to its low coordination with the catalyst. Finally, the presented synthetic protocols using cerium(III) supported on low-cost industrial resin further increases green impact of studied domino syntheses of α -aminophosphonates, and 4-amidotetrahydropyran derivatives.

Introduction

Molecule containing phosphonate structural motives are highly biologically potent. They can be used as inhibitors of synthase [1], HIV protease [2], PTPases [3,4], rennin [5], enzymes [6], antibiotics [7], herbicides [8], etc.

Generally α -aminophosphonates can be prepared by addition of phosphorous nucleophiles to imines in the presence of acids [9-11] or in three-component domino synthesis of amines, aldehydes and triethylphosphites with Lewis and Brønsted acids as catalysts. In this case, as catalysts can be used FeCl_3 [12], ZrCl_4 [13], $\text{SbCl}_3/\text{Al}_2\text{O}_3$ [14], Amberlyst-15 [15], sulfamic acid [16], $\text{BF}_3 \cdot \text{Et}_2\text{O}$ [17], etc.

4-Amidotetrahydropyran derivatives are often present in natural products as a glycamino acid [18,19], ambruticins VS [20,21] and others. 4-Amidotetrahydropyran derivatives can be generally prepared by the Prins-Ritter synthesis [22-24].

At the turn of the century lanthanide Lewis acids, as cerium(III) chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$), have attracted an attention in organic synthesis due to their high reactivity, stability, ease of handling, air tolerance, low toxicity and low cost [25,26]. Cerium(III) is the most commonly used as chloride or nitrate salt itself or supported on silica gel eventually doped by sodium iodide-this type of supported catalyst was developed by Bartoli and Marcantoni [27,28].



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Recently, we published two articles which dealt with the application Ce(III) cation supported on macroporous weakly acidic polyacrylate resin as catalyst for domino syntheses of some nitrogen containing heterocycles [29] and for synthesis of imines [30] in comparison with $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, eventually doped by sodium iodide. The obtained results showed that the polymer supported Ce(III) provides at least comparable or better catalytic activity in comparison with inorganic Ce(III) salts mentioned above.

Solid supported catalysts combine the advantages of both heterogeneous and homogenous catalysts [31,32]. They have high selectivity, reactivity, and stability. They are easily separable and recyclable. The one-pot and namely domino syntheses, by minimizing the number of intermediate synthetic steps and therefore minimizing the amount of waste, are very suitable type of syntheses for Green Chemistry [33].

Due to these characteristics they are suitable for reactions carried out in accordance with the goals and principles of Green Chemistry [33].

Experimental Section

Materials

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

All the reactions were monitored by TLC performed on precoated Silica gel 60 F254 plates (Merck). Synthesis of α -aminophosphonates: ethanol was used as eluent; UV light (254 and 356 nm) and ninhydrine reagent were used for detection of spots at 180 °C. Synthesis of 4-amidotetrahydropyranes: Et_2O was used as eluent; UV light (254 and 356 nm) was used for detection of spots.

All products were identified by use NMR and IR spectral methods, and by comparing of the measured melting points with literature values. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on DRX 300

Avance (Bruker Biospin) spectrometer using tetramethylsilane as an internal standard. Melting points are uncorrected and were recorded on Kofler's block Boetius Rapido PHMK 79/2106 (Wägetechnik), temperature gradient 4 °C min⁻¹.

Catalyst preparation

Ce(III) cations supported on cation exchanger: The catalytic system containing Ce(III) cations supported on a weakly acidic macroporous cation exchanger of polyacrylate type was prepared according to the patent [34]. 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 pH of the solution remained at value of 12 for 10 min after the last addition. Then was the aqueous solution was decanted and 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 modified resin beads were dropped into the solution which was then stirred overnight. Then was the aqueous solution was again decanted and the resin beads were washed 2 times by 200 mL of water and 2 times by methanol and finally dried in vacuum to constant weight. The prepared catalyst has cerium content about 2.3 mmol of Ce(III) per 1 g of modified resin beads [34]. This catalyst is also available from TauChem Ltd., Bratislava, Slovakia, <http://www.tau-chem.sk/en/About/Company-description.alej>.

Ce(III) cations and NaI supported on silica gel: The catalytic system containing Ce(III) cations and NaI supported on silica gel was prepared according to the article [28]. Silica gel was added to a mixture of CeCl₃·7H₂O and NaI in acetonitrile, and the mixture was stirred overnight at room temperature. The acetonitrile was removed by rotary evaporator and the resulting mixture was used as a catalyst. This catalytic system containing 0.65 mmol CeCl₃·7H₂O and 0.65 mmol NaI on 1.00 g of silica gel.

General synthetic procedures

General procedure for preparation of α-aminophosphonates [35]: A mixture of 2 mmol of amine, 2.2 mmol of diethyl phosphite, and 2 mmol of aldehyde with 0.06 mmol of appropriate catalytic system (Table 1) in 5 mL of ethanol as a solvent, was stirred at room temperature until disappearance of amine from the reaction mixture. The reaction was monitored by TLC. After the completion of reaction, the reaction mixture was heated until the precipitated crystals dissolved. Then the product was precipitated by adding ice water, filtrated off and washed with cold water. Obtained ¹H, ¹³C NMR and FT IR spectral data of all synthesized products were in agreement with published one [35].

General procedure for preparation of 4-amidotetrahydropyranes [36]: A mixture of 1.2 mmol of but-3-en-1-ol, 1 mmol of 4-X-benzaldehyde, and 1.5 mmol of acetyl chloride, in role of activator for Prins-Ritter domino synthesis [36], with 0.05 mmol of appropriate catalytic system (Table 2) in 5 mL of acetonitrile as a solvent and nucleophilic reagent, was stirred at room temperature until disappearance of carbonyl compound from the reaction mixture. The reaction was monitored by TLC. After the completion of reaction, the reaction mixture was quenched with water and extracted with 2x10 mL of ethyl acetate. The combined organic layers were dried with anhydrous Na₂SO₄ and purified with

silica gel. Acquired ¹H, ¹³C NMR and FT IR spectral data of obtained products were in accordance with published one [36].

Results and Discussion

To prove the efficiency of the catalytic system of Ce(III) cations supported on weakly acidic macroporous cation exchanger polyacrylate type, we performed a comparative study on two model domino syntheses.

The first of them was the preparation of α-aminophosphonates published previously in the article [35]. Catalytic system used in this case featured the 10 mol% of cerium trichloride heptahydrate CeCl₃·7H₂O. The second model synthesis was domino synthesis of 4-amidotetrahydropyran derivatives published previously in [36], where 5 mol% of CeCl₃·7H₂O was used as a catalyst.

We verified the both model synthetic procedures with published catalysts according to the general procedure published in the articles [35,36]. Syntheses were then carried out with Ce(III) supported on above described resin and the results were compared in terms of the reaction time and the yield relative to the used catalytic system.

Results of α-aminophosphonates study revealed that the Ce(III) cation supported on the resin provided at least as satisfying results as other catalytic systems, the results in Table 1 show the greatest shortening of reaction times and the maximal yields for the catalytic system Ce(III) supported on the weakly acidic cation exchanger in the comparison with the another used Ce(III) catalysts (Table 1). On the other hand, we observed that the electron effect of the present substituent on the used 4-X-benzaldehyde (X=OCH₃, H, NO₂) is under catalysis changed. In accord to results obtained and explained in article [29,30]. We found also that positive role of used catalyst is more significant for electron donating group in typically low reactive 4-methoxybenzaldehyde in contrast with very good reactive 4-nitrobenzaldehyde. The electron influence of substituents in the applied 4-Y-anilines (Y=OH, H, Cl) is not significant because of weak coordination/affinity between nitrogen atom of aniline amino group and Ce(III) – lower reactivity of 4-hydroxyaniline may be probably evoked by coordination of phenolic oxygen with Ce(III).

The role of Ce(III) cations as a catalyst in this procedure can be explained by formation of the some supposed key intermediates (Figure 1).

In the case of syntheses of 4-amidotetrahydropyran derivatives, the reactions catalyzed by Ce(III) ions in the presence of acetyl chloride as co-activator were in general much faster and yields were higher than in the case of uncatalyzed reactions, similarly as in the previous model syntheses. The highest yields and the shortest reaction times were again observed when procedures were catalyzed by catalytic system Ce(III) supported on the weakly acidic cation exchanger. Details are demonstrated in Table 2.

Acceleration of the reaction in the presence of Ce(III) cations can be explained by the supposed key intermediates formation in the course of reaction, as well (Figure 2). Coordination of Ce(III) cation to the carbonyl oxygen of the used 4-X-benzaldehydes (X=OCH₃, H, NO₂) and raises electron deficiency on this group and thus facilitates the bond formation between the oxygen of but-3-en-1-ol and the carbon of benzaldehyde group under hemiacetal formation (See

Table 1: Preparation of α -aminophosphonates derivatives – table of results.

Entry		Reactants	Catalytic system	Yield [%]	Time [min]
1	a	Benzaldehyde; Aniline; Diethyl phosphite	-	0	1440
	b		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}^2$	95	300
	c		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$	96	240
	d		Ce(III) supported on resin	98	220
	e		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$ supported on silica gel	93	330
2	a	4- CH_3O -Benzaldehyde; Aniline; Diethyl phosphite	-	0	1440
	b		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}^2$	91	270
	c		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$	93	240
	d		Ce(III) supported on resin	93	180
	e		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$ supported on silica gel	90	280
3	a	4- NO_2 -Benzaldehyde; Aniline; Diethyl phosphite	-	0	1440
	b		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}^2$	90	780
	c		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$	92	660
	d		Ce(III) supported on resin	94	600
	e		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$ supported on silica gel	90	780
4	a	Benzaldehyde; 4-Cl-Aniline; Diethyl phosphite	-	0	1440
	b		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}^2$	93	540
	c		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$	94	420
	d		Ce(III) supported on resin	97	360
	e		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$ supported on silica gel	91	560
5	a	Benzaldehyde; 4-Aminophenol; Diethyl phosphite	-	0	1440
	b		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}^2$	90	600
	c		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$	94	420
	d		Ce(III) supported on resin	96	350
	e		$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$ supported on silica gel	93	510

*At room temperature; ethanol as a solvent

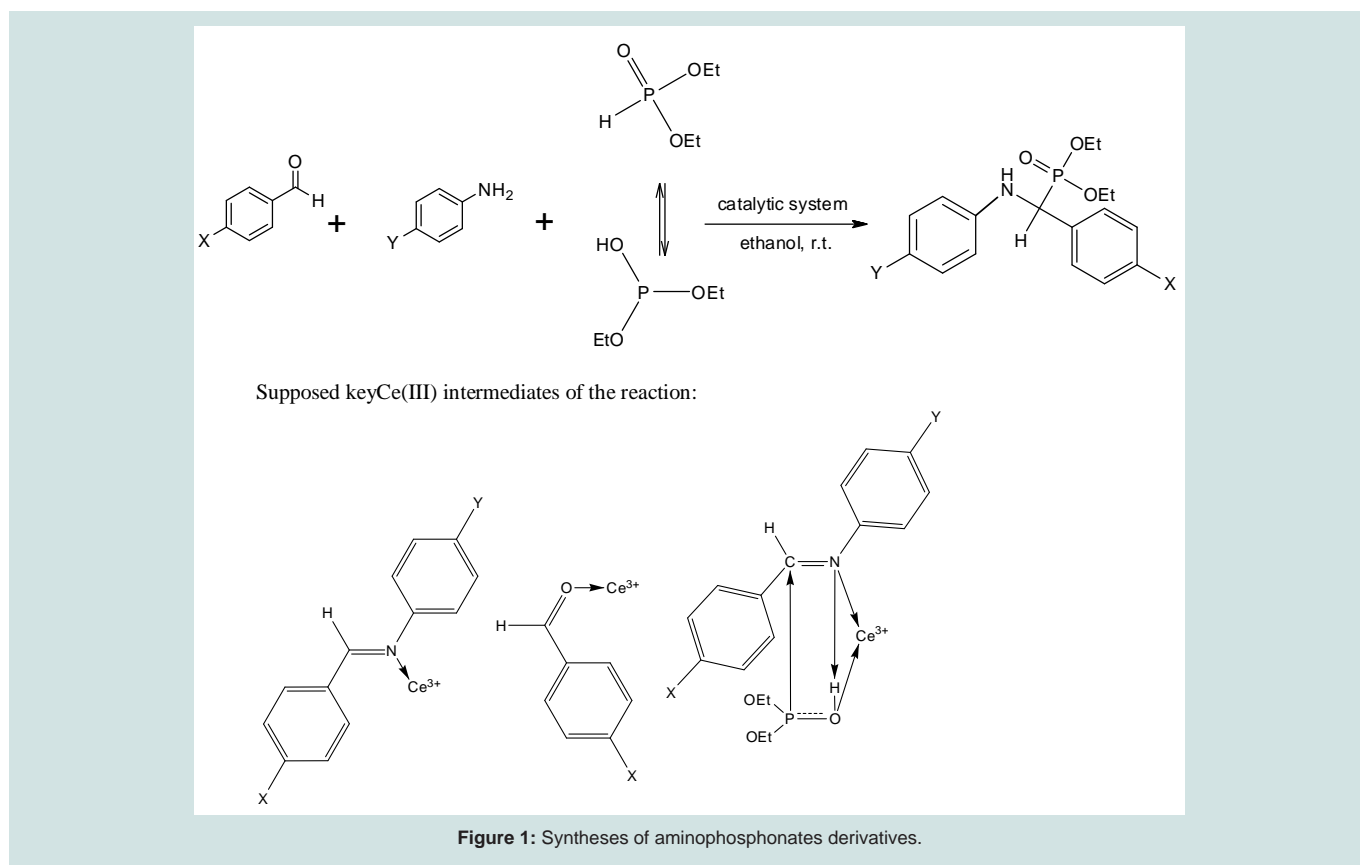


Figure 1: Syntheses of aminophosphonates derivatives.

Table 2: Preparation of 4-amidotetrahydropyran derivatives – table of results.

Entry		Reactants	Catalytic system	Yield [%]	Time [min]
1	a	Acetonitrile; But-3-en-1-ol; Benzaldehyde	-	31	1440
	c		CeCl ₃ ·7H ₂ O/NaI ³	84	420
	d		Ce(III) supported on resin	86	360
	e		CeCl ₃ ·7H ₂ O/NaI supported on silica gel	82	450
2	a	Acetonitrile; But-3-en-1-ol; 4-CH ₃ O-Benzaldehyde	-	45	1440
	c		CeCl ₃ ·7H ₂ O/NaI ³	93	360
	d		Ce(III) supported on resin	93	220
	e		CeCl ₃ ·7H ₂ O/NaI supported on silica gel	89	360
3	a	Acetonitrile; But-3-en-1-ol; 4-NO ₂ -Benzaldehyde	-	38	1440
	c		CeCl ₃ ·7H ₂ O/NaI ³	82	450
	d		Ce(III) supported on resin	84	340
	e		CeCl ₃ ·7H ₂ O/NaI supported on silica gel	80	480
4	a	Acetonitrile; But-3-en-1-ol; Cyclohexanone	-	35	1440
	c		CeCl ₃ ·7H ₂ O/NaI ³	90	480
	d		Ce(III) supported on resin	91	400
	e		CeCl ₃ ·7H ₂ O/NaI supported on silica gel	88	500

*At room temperature; acetonitrile as a solvent and nucleophilic reagent in excess

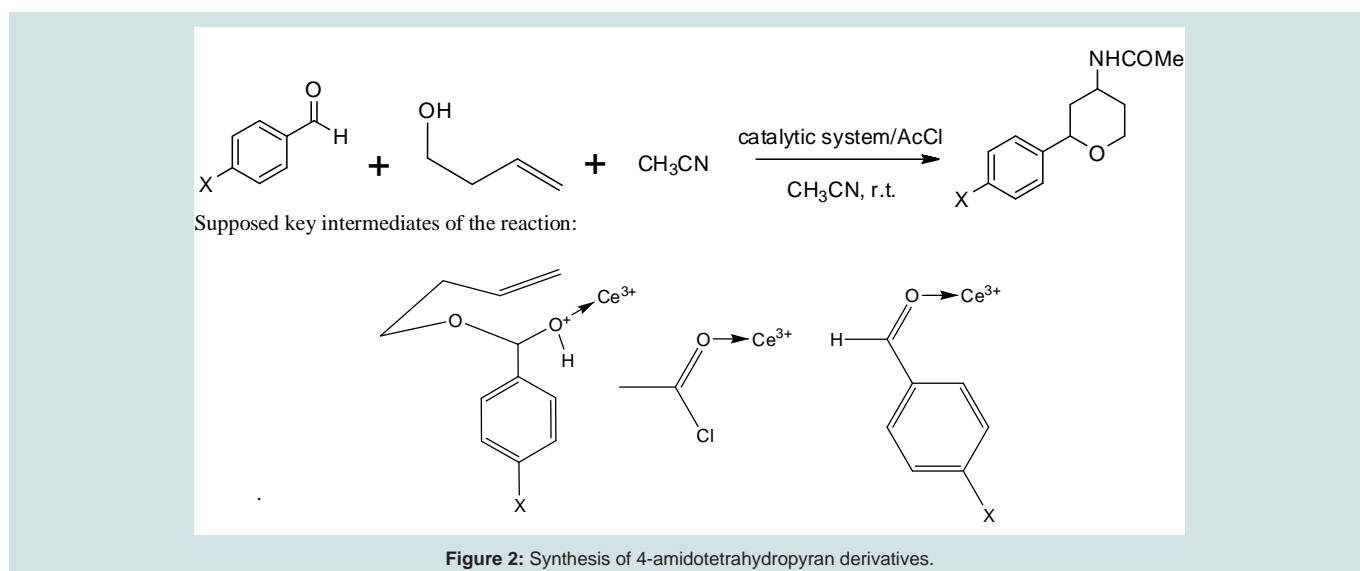


Figure 2: Synthesis of 4-amidotetrahydropyran derivatives.

Figure 2, for mechanism detail the ref. [36]). The electron effect of substituent X in the used 4-X-benzaldehydes on the reaction results was the same as described above for α -aminophosphonate formation.

Conclusions

In conclusion, a comparative studies of application a new catalyst - Ce(III) supported on weakly acidic cation exchanger resin and catalysts based on Ce(III) chloride, eventually doped by sodium iodide and/or supported on silica gel, were applied to one-pot syntheses of α -aminophosphonates, and 4-amidotetrahydropyran derivatives. The efficiency of all applied catalytic systems depends on the electron character of the present functional group in the starting 4-X-benzaldehydes, low reactive methoxy-substrate are activated very effectively. Further, it was found that the Ce(III) cation supported on the resin provided at least as effective as other catalytic systems used so far and moreover takes advantage in simple separation and reusing more than ten times without loss of

the catalytic efficiency. Solid support of Ce(III) cation was realized with low-cost industrial resin resulting in further savings. The used organic resin has not abrasive effect on surface of reaction vessels, in contradistinction to silica gel carrier. Finally, the advantages of the present protocol make the procedure an attractive alternative to the existing methods for the synthesis of α -aminophosphonates, and 4-amidotetrahydropyran derivatives.

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Graphical Abstract

