ONE-POT SYNTHESES USING CARBONYL COMPOUNDS CATALYZED BY CE(III) SUPPORTED ON A WEAKLY ACIDIC CATION-EXCHANGER RESIN

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Introduction

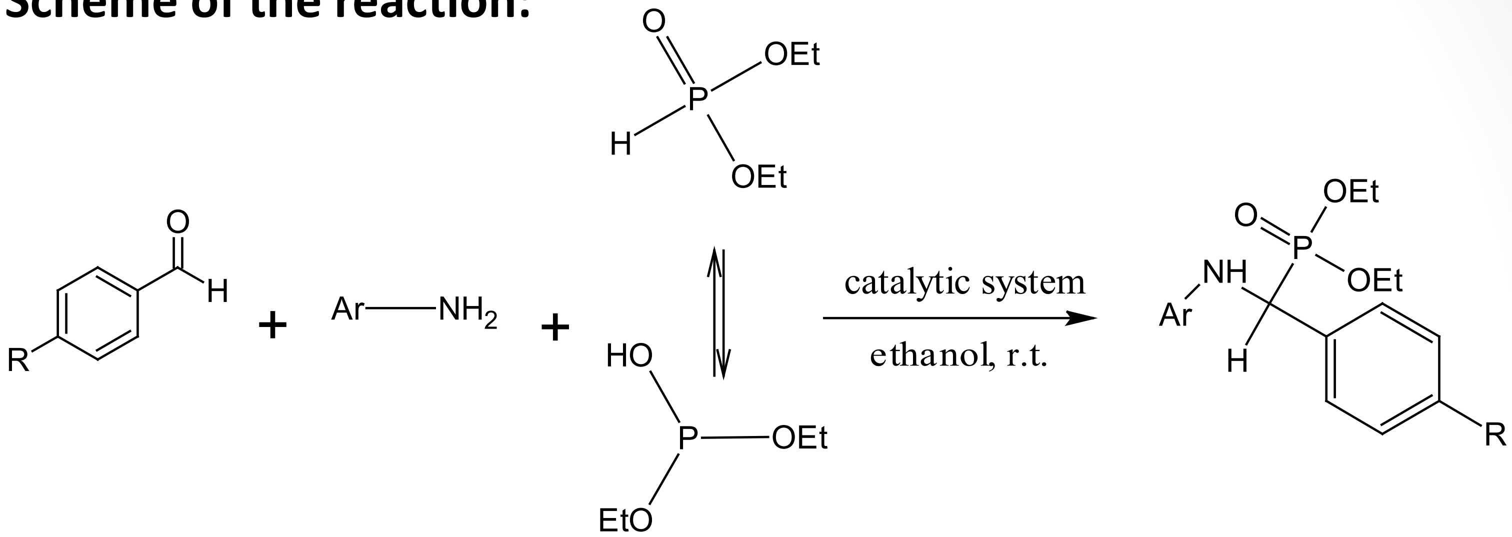
One of the possibilities to sophisticate compound syntheses is catalysis using supported catalyst which combines the advantages of both homogeneous and heterogeneous catalyst. An application of Ce(III) inorganic salts, first of all $CeCl_3.7H_2O$ doped by sodium iodide, not until has been described from start of 21st Century. Twenty communications has been present during this time only. Catalysis by Ce(III) salts has been used for an activation of carbonyl compounds and their derivatives in syntheses. Easily available, cheap and mechanically and thermally stable industrial cation-exchangers may be used as carriers[1]. These in connection with complex of cerium in oxidation state of 3^+ provide an effective, easily separable and recyclable catalytic system. This system has been studied with a view to its possible synthetic applications on model three-component domino syntheses, *i.e.* Kabachnik-Fields one-pot synthesis of α-aminophosphonates[2], and Prins-Ritter one-pot synthesis of 4-amidotetrahydropyran derivatives[3], respectively.

Preparation of catalysts

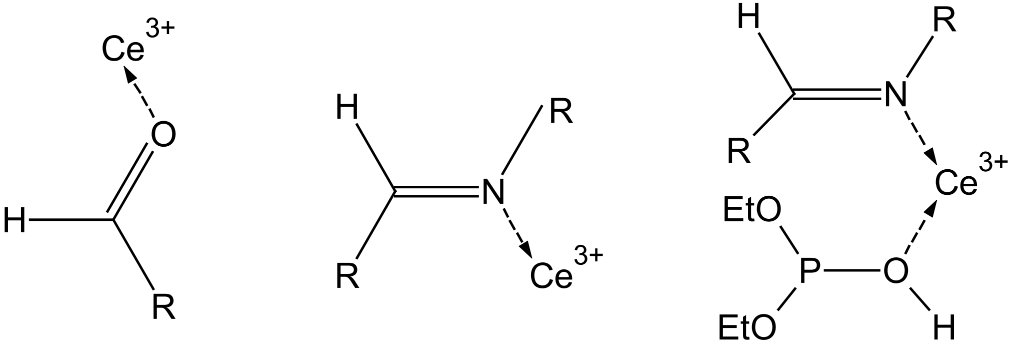
1) **Preparation of 30 mol% $CeCl_3.7H_2O$ and 30 mol% of NaI supported on silica gel [4]:** Silica gel was added to a mixture of $CeCl_3.7H_2O$ and NaI in acetonitrile, and the mixture was stirred overnight at room temperature. The acetonitrile was removed by rotary evaporator and the resulting mixture was used as a catalyst.
2) **Preparation of cation Ce(III) supported on a weak acid macroporous cation-exchanger resin (D113 Noromite; 4.5 mol/l) [1]:** Resin and water were stirred for 5 min. Than was slowly added a solution of sodium carbonate to pH cca 12. Subsequently, the aqueous phase was decanted and the solid phase was washed with of water. The solid phase was stirred with a solution of $CeCl_3.7H_2O$ in water overnight. The aqueous phase was again decanted and the solid phase washed with water and methanol, respectively. Finally, the thus prepared catalyst was dried under vacuum at room temperature to constant weight. The Ce(III) capacity in this resin was 2.3 mmol/g. An equivalent amount of NaI or eventual proline such as supported Ce(III) catalyst was added into a reaction mixture.

Preparation of α-aminophosphonates

- **Scheme of the reaction:**



- **Key cerium containing intermediate for Kabachnik-Fields synthesis:**



Preparation of α-aminophosphonates – table of results

Reactants	Catalyst	Molar Ratio [eqv]	Yield [%]	Time [min]
Benzaldehyde; Aniline; Diethyl phosphite	-	1 : 1,1	N.R.	1440
	$CeCl_3.7H_2O$ [2]	1 : 1,1 : 0,03	95	300
	$CeCl_3.7H_2O/NaI$	1 : 1,1 : 0,03	96	240
	$CeCl_3.7H_2O/NaI$ supported on resin	1 : 1,1 : 0,03	98	220
	$CeCl_3.7H_2O/NaI$ supported on silica gel	1 : 1,1 : 0,03	93	330
	Proline/$CeCl_3.7H_2O/NaI$ supported on resin	1 : 1,1 : 0,03	96	180
4-CH_3O-Benzaldehyde; Aniline; Diethyl phosphite	-	1 : 1,1	N.R.	1440
	$CeCl_3.7H_2O$ [2]	1 : 1,1 : 0,03	91	270
	$CeCl_3.7H_2O/NaI$	1 : 1,1 : 0,03	93	240
	$CeCl_3.7H_2O/NaI$ supported on resin	1 : 1,1 : 0,03	93	180
	$CeCl_3.7H_2O/NaI$ supported on silica gel	1 : 1,1 : 0,03	90	280
	Proline/$CeCl_3.7H_2O/NaI$ supported on resin	1 : 1,1 : 0,03	94	150

*At room temperature; ethanol as a solvent.

Preparation of α-aminophosphonates – table of results

Reactants	Catalyst	Molar Ratio [eqv]	Yield [%]	Time [min]
4-NO_2-Benzaldehyde; Aniline; Diethyl phosphite	-	1 : 1,1	N.R.	1440
	$CeCl_3.7H_2O$ [2]	1 : 1,1 : 0,03	90	780
	$CeCl_3.7H_2O$/NaI	1 : 1,1 : 0,03	92	660
	$CeCl_3.7H_2O$/NaI supported on resin	1 : 1,1 : 0,03	94	600
	$CeCl_3.7H_2O$/NaI supported on silica gel	1 : 1,1 : 0,03	90	780
	Proline/$CeCl_3.7H_2O$/NaI supported on resin	1 : 1,1 : 0,03	94	420
Benzaldehyde; 4-Cl-Aniline; Diethyl phosphite	-	1 : 1,1	N.R.	1440
	$CeCl_3.7H_2O$ [2]	1 : 1,1 : 0,03	93	540
	$CeCl_3.7H_2O$/NaI	1 : 1,1 : 0,03	94	420
	$CeCl_3.7H_2O$/NaI supported on resin	1 : 1,1 : 0,03	97	360
	$CeCl_3.7H_2O$/NaI supported on silica gel	1 : 1,1 : 0,03	91	560
	Proline/$CeCl_3.7H_2O$/NaI supported on resin	1 : 1,1 : 0,03	96	270

*At room temperature; ethanol as a solvent.

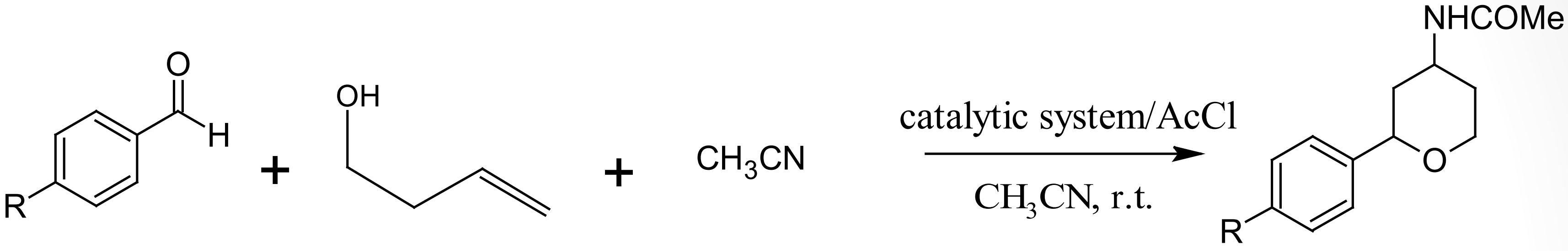
Preparation of α-aminophosphonates – table of results

Reactants	Catalyst	Molar Ratio [eqv]	Yield [%]	Time [min]
Benzaldehyde; 4-Aminophenol; Diethyl phosphite	-	1 : 1,1	N.R.	1440
	$CeCl_3.7H_2O$ [2]	1 : 1,1 : 0,03	90	600
	$CeCl_3.7H_2O$/NaI	1 : 1,1 : 0,03	94	420
	$CeCl_3.7H_2O$/NaI supported on resin	1 : 1,1 : 0,03	96	350
	$CeCl_3.7H_2O$/NaI supported on silica gel	1 : 1,1 : 0,03	93	510
	Proline/$CeCl_3.7H_2O$/NaI supported on resin	1 : 1,1 : 0,03	96	280

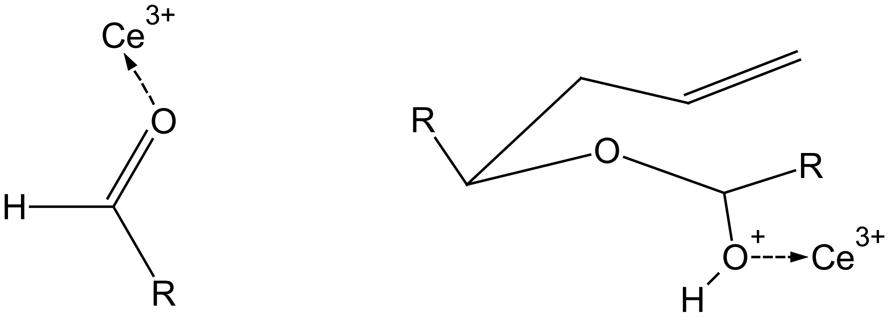
*At room temperature; ethanol as a solvent.

Preparation of 4-amidotetrahydropyranes

- **Scheme of the reaction:**



- **Key cerium containing intermediate for Prins-Ritter synthesis:**



Preparation of 4-amidotetrahydropyranes – table of results

Reactants	Catalyst	Molar Ratio [eqv]	Yield [%]	Time [min]
Acetyl chloride; But-3-en-1-ol; Benzaldehyde	-	1,5 : 1,2 : 1	31	1440
	$CeCl_3.7H_2O/NaI$ [3]	1,5 : 1,2 : 1 : 0,05	84	420
	$CeCl_3.7H_2O/NaI$ supported on resin	1,5 : 1,2 : 1 : 0,05	86	360
	$CeCl_3.7H_2O/NaI$ supported on silica gel	1,5 : 1,2 : 1 : 0,05	82	450
Acetyl chloride; But-3-en-1-ol; 4-CH_3O-Benzaldehyde	-	1,5 : 1,2 : 1	45	1440
	$CeCl_3.7H_2O/NaI$ [3]	1,5 : 1,2 : 1 : 0,05	93	360
	$CeCl_3.7H_2O/NaI$ supported on resin	1,5 : 1,2 : 1 : 0,05	93	220
	$CeCl_3.7H_2O/NaI$ supported on silica gel	1,5 : 1,2 : 1 : 0,05	89	360

*At room temperature; acetonitrile as a solvent.

Preparation of 4-amidotetrahydropyranes – table of results

Reactants	Catalyst	Molar Ratio [eqv]	Yield [%]	Time [min]
Acetyl chloride; But-3-en-1-ol; 4-NO_2-Benzaldehyde	-	1,5 : 1,2 : 1	38	1440
	$CeCl_3.7H_2O/NaI$ [3]	1,5 : 1,2 : 1 : 0,05	82	450
	$CeCl_3.7H_2O/NaI$ supported on resin	1,5 : 1,2 : 1 : 0,05	84	340
	$CeCl_3.7H_2O/NaI$ supported on silica gel	1,5 : 1,2 : 1 : 0,05	80	480
Acetyl chloride; But-3-en-1-ol; Cyclohexanone	-	1,5 : 1,2 : 1	35	1440
	$CeCl_3.7H_2O/NaI$ [3]	1,5 : 1,2 : 1 : 0,05	90	480
	$CeCl_3.7H_2O/NaI$ supported on resin	1,5 : 1,2 : 1 : 0,05	91	400
	$CeCl_3.7H_2O/NaI$ supported on silica gel	1,5 : 1,2 : 1 : 0,05	88	500

*At room temperature; acetonitrile as a solvent.

Conclusion

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 $CeCl_3.7H_2O$, eventually doped by NaI. In conclusion, we developed a novel and environmentally friendly catalyst, which can be used in a wide range of reactions of carbonyl and other compounds. The catalyst can be used repeatedly. The used organic resin has not abrasive effect on surface of reaction vessels, in contradistinction to silica gel carrier.

The advantages of the present protocol are mild, heterogeneous conditions, shorter reaction times, easy work-up, and low toxicity, inexpensive, ready availability, recoverability, recyclability of the catalyst that make the procedure an attractive alternative to the existing methods for the synthesis of α-aminophosphonates, and 4-amidotetrahydropyran derivatives.

References

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