Green Chemistry

Cite this: *Green Chem.*, 2011, **13**, 2130

www.rsc.org/greenchem

PAPER

Environmentally benign and energy efficient methodology for condensation: an interesting facet to the classical Perkin reaction†

Poonam Mahadev Pawar, Krishna Jagannath Jarag and Ganapati Subray Shankarling*

Received 19th October 2010, Accepted 13th May 2011
DOI: 10.1039/c0gc00712a

We have reported use of biodegradable deep eutectic solvent (DES) based on choline chloride and urea, for the synthesis of cinnamic acid and its derivatives *via* Perkin reaction. The reaction proceeds efficiently under mild condition without use of additional catalyst with better yields. Ease of recovery and reusability of solvent with consistent activity makes this method efficient and environmentally benign. This method is also energy efficient and easy to handle.

1. Introduction

Cinnamic acid and its derivatives are used in various fields such as medicines[1,2] perfumery, polymer, cosmetics[3,4] and agricultural fields.[5] They are also used as matrices for ultraviolet laser desorption mass spectrometry of protein,[6] and as useful intermediates for the synthesis of heterocyclic compounds.[7] Conventionally, cinnamic acid and its derivatives are prepared using benzaldehyde, acetic anhydride in presence of a base at 180 °C.[8] However, the conventional method has a lot of drawbacks such as use of strong and harmful base, organic solvents, higher reaction temperatures, longer reaction times and low yields.[9] In the literature various methods are reported to prepare cinnamic acid and its derivatives: Perkin reaction,[10–14] halo-benzene with acrylic acid,[15,16] benzaldehyde with acetone,[17] benzaldehyde with ketene or acetic acid,[18] from cinnamic aldehyde by air oxidation,[19] styrene with carbon monoxide or carbon dioxide,[20] and the hydrolyzation of 1,1,1,3-tetrachloro-3-phenylpropane from styrene and CCl_4.[21] Cinnamic acid synthesis using the Perkin condensation method involves use of different bases. The effects of various bases such as fused sodium acetate, sodium formate, sodium tartrate, sodium borate, sodium sulfite, sodium carbonate, and potassium carbonate on yield of Perkin reaction have been extensively studied.[22] John *et al.*[23] have reported calcium hydrate as a catalyst and Ping *et al.*[24] have reported solid base K_2O and Al_2O_3 as catalyst. NaF and K_2CO_3 are used as mixed catalyst for synthesis of cinnamic acid at 150 °C–170 °C.[25] Cinnamic acid and its derivatives are also synthesized from benzaldehyde and malonic acid by Knoevenagel condensation using pyridine as catalyst.[26]

Cinnamic acids have been synthesized by reacting aromatic aldehydes with aliphatic carboxylic acids in *N*-methyl-2-pyrrolidinone (NMP) at 180–190 °C in presence of either sodium borohydride[27] or boron tribromide as a reagent and 4-dimethylaminopyridine (4-DMAP) and pyridine as bases.[28] Reaction time required to complete such type of reactions is 8–10 h.

Microwave irradiation method is also used for Perkin reaction. Cesium salts (acetate, carbonate, and fluoride) with a small amount of pyridine[29] or sodium acetate trihydrate[30] were used as catalysts for synthesis of cinnamic acid and its derivatives from aromatic aldehydes and acetic anhydride under microwave irradiation. Cinnamic acids were also synthesized from aromatic aldehydes and malonic acid on the surface of graphite under a microwave irradiation.[31] Knoevenagel–Doebner synthesis used for preparation of cinnamic acid under microwave irradiation.[32] Hydroxystilbenes with *trans* selectivity was synthesized through modified Perkin reaction between benzaldehydes and phenylacetic acids in the presence of piperidine–methylimidazole and polyethylene glycol under microwave irradiation.[33]

In spite of great variety of well known and established methods for cinnamic acid and its derivatives, organic solvents and bases used in these transformations are high on the list of hazardous and harmful chemicals because of their volatile nature, considerable toxicity and their use in large quantities for the reaction. To overcome these drawbacks Jianyang Weng[34] and coworkers reported a process for synthesis of cinnamic acid in quaternary ammonium ionic liquids at 120 °C for 8 h. The process developed by Jianyang Weng and coworkers is environmentally benign, but higher reaction temperature (120 °C) and longer reaction time (8 h) makes this process more energy intensive. Therefore, development of new synthetic protocols for cinnamic acid derivatives, inexpensive reagents and environmentally benign conditions for such transformations is still an active field for researcher.

Department of Dyestuff Technology, Institute of Chemical Technology, N. P. Marg, Matunga, Mumbai, 400 019, India.
E-mail: gsshankarling@gmail.com, gs.shankarling@ictmumbai.edu.in; Fax: +91-22-33611020; Tel: +91-22-33612708

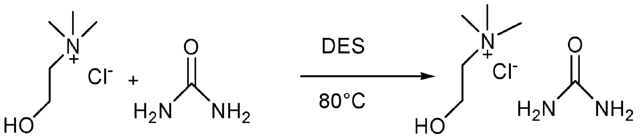
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c0gc00712a

In our previous attempt, deep eutectic solvent (DES) have been used for the synthesis of dye intermediates and novel dyes.[35] In the area of organic synthesis, energy efficiency calculation is recent phenomenon. Pandit and coworkers have made the systematic approach for calculating energy balance of the process.[36] We have also reported the energy balance for the chalcone synthesis process.[37]

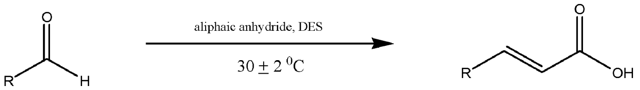
In the present work, we report the room temperature synthesis of cinnamic acid and its derivatives in DES based on choline chloride and urea. We have also made an attempt to compare energy balance for both the conventional as well as DES process.

2. Results and discussion

Recyclable DES is utilized as a catalyst and reaction media for Perkin condensation, avoiding the use of additional catalyst and organic solvent. All reactions are carried out at 30 ± 2 °C temperature. DES is a mixture of two compounds where there is a depression in the freezing point of the mixture compared with that of the separate components. It comprises mixtures of organic halide salts with hydrogen-bond donors, such as amides, amines, alcohols, and carboxylic acids.[38] Preparation of DES is easy and economically viable as it shows 100% atom economy. It is non-toxic and biodegradable.[39] Hence owing to these properties, we synthesized cinnamic acid and its derivatives *via* Perkin reaction using DES. The DES was prepared by reacting choline chloride with urea (1 : 2) at 80 °C by reported method[40] (Scheme 1). The feasibility of the Perkin reaction was examined using benzaldehyde as a model substrate. The experimental procedure is very simple. Benzaldehyde (1 mmol), acetic anhydride (1 mmol) and deep eutectic solvent (3 ml) were stirred at room temperature. The reaction was monitored by TLC. After completion, the reaction mass was diluted with water. The white solid mass was separated by filtration. (Scheme 2) The DES was recovered easily from filtrate by evaporating the water under vacuum. Product is purified from water followed by methanol. DES was re-used for three succession of the reaction without much loss of product yields.



Scheme 1 Schematic presentation of synthesis of DES based on choline chloride and urea.



Scheme 2 Schematic presentation of synthesis of cinnamic acid derivatives, where R = aryl, heteroaryl.

From the above results, the reaction was tested for different aromatic and heterocyclic aldehydes (results are summarized in Table 1). The yields of the product were found to vary from 60–92%. The reaction is also studied for various anhydrides. Benzaldehyde was reacted with symmetric and unsymmetric anhydrides in DES such as acetic anhydride, acetic propionic anhydride and propionic anhydride at 30 ± 2 °C. The reaction proceeds with the acetic and acetic propionic anhydride but not with the propionic anhydride. This may be because of the +I effect of the methyl group in propionic anhydride which reduces the acidity of the $-CH_2$ group (the results are summarized in Table 2). The results were compared with the conventional method for three compounds (**1a**–**3a**). In conventional method, the aldehydes (1 mmol), acetic anhydride (2 mmol) and sodium acetate (3 mmol) were refluxed at 140 °C for 9 h. Reaction was monitored on TLC. Reaction mass is then quenched in 50 ml ice cold water followed by acidification with 1 : 1 solution of concentrated hydrochloric acid and water. After being cooled to 20 °C, the acid is filtered over suction and washed with a ice cold water. Solid is filtered and dried in oven.

All the compounds are characterized by ^{1}H-NMR, FTIR, mass spectrometry. The probable reaction mechanism is provided in Appendix II of the ESI.†

Recycling of the choline chloride

Simple experimental procedures, ease of recovery and reuse of the reaction media contribute to the development of a green approach for synthesizing cinnamic acid derivatives. Experiments for testing the recyclability of DES were performed using benzaldehyde and acetic anhydride as reactants. The recovered DES was then successfully used for three runs showing no significant loss of yield (Table 3). It has been confirmed through NMR that structure of DES after reaction has been not changed.

Efficacy of energy utilization

Prasad *et al.*[36] and our earlier research paper have reported the procedure for the calculation of energy[37] Appendix I shows the comparison of the energy based performance of the two types of synthesis methods, *i.e.* conventional and using DES for synthesizing cinnamic acid (detailed information is provided in the ESI†). The energy utilized for the synthesis of cinnamic acid is the total energy supplied (kJ) per unit weight of the material processed (g). The reaction time to synthesize cinnamic acid was 4 h by DES method (**1**) and 9 h for conventional method (**1a**). Total energy required per unit weight of the material processed to synthesize cinnamic acid is 14.15 (kJ g^{-1}) for DES synthesis method and 37.85 (kJ g^{-1}) for conventional synthesis method.

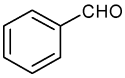
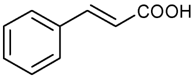
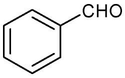
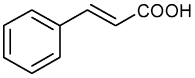
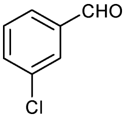
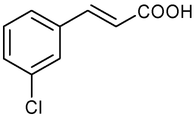
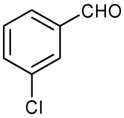
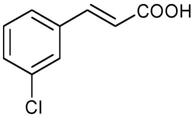
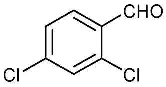
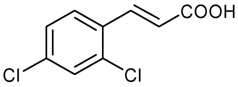
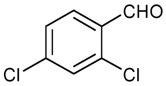
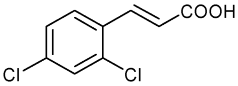
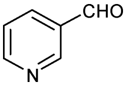
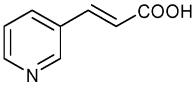
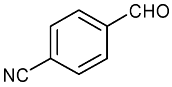
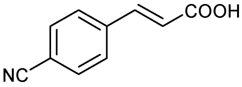
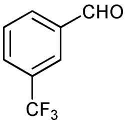
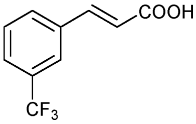
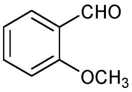
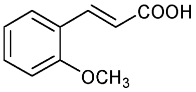
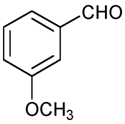
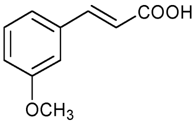
Thus, DES assisted method is proved to be energy efficient which saved more than 62% of energy utilized by conventional synthesis method and also a reduction in the reaction duration was observed as reported in Table 1.

3. Experimental

3.1. Materials and equipment

All melting points are uncorrected and are presented in °C. ^{1}H NMR spectrums were recorded on Varian 499.85 MHz mercury plus spectrometer, and chemical shifts are expressed in δ (ppm) using TMS as an internal standard.

Table 1 Synthesis of cinnamic acid derivatives using deep eutectic solvent[a] and conventional method[b]

Entry	Substrate	Product	$T/°C$	Reaction time (h)	Yield[c] (%)	Mp (°C), observed	Mp (°C), literature
1			30 ± 2	4	92	132–133	131–133[12]
1a			140	9	60	131–133	
2			30 ± 2	4	90	175–176	176–177[12]
2a			140	9	62	176–177	
3			30 ± 2	4	92	230–233	233–236[14]
3a			140	9	63	232–234	
4			30 ± 2	8	60	211–212	213–215
5			30 ± 2	8	75	254–255	255–256[41]
6			30 ± 2	9	62	133–135	135–137[38]
7			30 ± 2	6.5	68	184–185	185–186[14]
8			30 ± 2	7	65	115–116	116–119

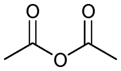
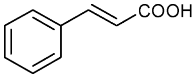
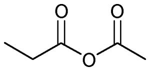
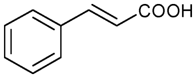
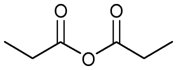
[a] Reaction condition: aromatic aldehydes: acetic anhydride, 1 : 1(mole ratio), DES, temp. 30± 2 °C. The reactions were monitored by thin layer chromatography (TLC) analysis. All products were characterized by FT-IR, Mass, ^{1}H NMR and their melting point matched previous literature. [b] Conventional method: benzaldehyde, acetic anhydride, sodium acetate trihydrate, 1 : 2 : 3 (mole ratio), temp. 140 °C. [c] Isolated yields.

Mass spectral data were obtained with a micromass - Q - TOF (YA105) spectrometer. FT-IR spectrum were recorded on Perkin Elmer 100 FT spectrometer. Common reagent grade chemicals were procured from SD Fine Chemical Ltd. (Mumbai, India) and were used without further purification. The reaction were monitored by TLC using 0.25 mm E-Merck silica gel 60 F_{254} precoated plates, which were visualized with UV light.

3.2 Synthesis of deep eutectic solvent

The synthesis of deep eutectic solvent has been carried out using method reported in the literature.[41] It is prepared by the mixing of choline chloride (100 g, 71 mmol) and urea (86 g, 140 mmol) in the ratio of 1 : 2. The two solids are then heated slowly and maintained at 80 °C for 30 min resulting in the formation of eutectic solvent with 100% atom economy. The liquid is allowed

Table 2 Reaction using deep eutectic solvent with different aliphatic anhydrides[a]

Entry	Substrate	Product	$T/°C$	Reaction time (h)	Yield (%)	Mp (°C), observed	Mp (°C), literature
1			30 ± 2	4	92	132–133	131–133[12]
2			30 ± 2	6	85	131–133	
3		—	30 ± 2		—	—	

[a] Reaction condition: benzaldehyde aldehydes: aliphatic anhydride, 1 : 1(mole ratio), DES, temp. 30± 2 °C. The reactions were monitored by thin layer chromatography (TLC) analysis. There is no reaction in case of entry 3.

Table 3 Recycling of deep eutectic solvent for cinnamic acid formation reaction using benzaldehyde[a]

Entry	Cycle	% Yield
1.	Fresh	92
2.	1st recycle	87
3.	2nd recycle	85
4.	3rd recycle	85

[a] Reaction condition: benzaldehyde: acetic anhydride, DES.

to cool till it attains room temperature and is used for synthesis of cinnamic acid and their derivatives without further purification.

3.3 Cinnamic acid formation reaction: a typical procedure (1–8)

In a typical reaction, benzaldehyde (0.5 g, 4.7 mmol), acetic anhydride (0.48 g, 4.7 mmol) and deep eutectic solvent (1.5 ml) were mixed and stirred at 30 ± 2 °C in a round bottom flask fitted with guard tube. The reaction was monitored by TLC. After completion of reaction, water was added. The DES being soluble in water comes in the water layer. The solid was separated by filtration. It was purified with water followed by methanol and dried in oven.

Cinnamic acid (1). White solid. m.p. 131–133 °C; ν_{max}/cm^{-1} 3000–2500 (O–H), 1678(C═O), 1630 (C═C); ^{1}H-NMR (499.85 MHz; DMSO; Me_4 Si) $\delta = 6.496–6.527$ (1H, d, $J = 15.9$ Hz, C–H), 7.392–7.397 (2H, d, $J = 2.5$ Hz), 7.557–7.589 (1H, d, $J = 15.9$ Hz), 7.657–7.667 (3H, t, $J = 2.5$ Hz), 12.384(1H, s); EIMS m/z 147. $C_9H_8O_2$ calculated m/z 148.05

3-Chloro cinnamic acid (2). White solid. m.p. 175–176 °C; ν_{max}/cm^{-1} 3000–2500 (O–H), 1652(C═O), 1602(C═C); ^{1}H-NMR (499.9 MHz; DMSO; Me_4 Si) $\delta = 6.983–6.998$ (1H, d, CH), 7.047–7.093 (3H, m), 7.095–7.110 (1H, s), 12.006 (1H, s);EIMS m/z 182. $C_9H_7ClO_2$ calculated m/z: 182.6

2,4-Dichloro cinnamic acid (3). White Solid. m.p. 230–233 °C; ν_{max}/cm^{-1} 3000–2500 (O–H), 1668(C═O), 1602 (C═C); ^{1}H-NMR (499.85 MHz; DMSO; Me_4 Si) $\delta = 6.779–6.796$ (1H, d), 7.246–7.340 (3H, m), 7.354–7.370 (1H, d), 12.482 (1H, s); EIMS m/z 216. $C_9H_6Cl_2O_2$ calculated m/z: 217.05

3-Pyridyl cinnamic acid (4). White Solid. m.p. 211–212 °C; ν_{max}/cm^{-1} 3000–2500 (O–H), 1678(C═O), 1630 (C═C); ^{1}H-NMR (499.85 MHz; DMSO; Me_4 Si) $\delta = 6.648–6.680$ (1H, d, $J = 15.9$ Hz), 7.591–7.623 (1H, d, $J = 15.9$ Hz), 8.121–8.144 (1H, tt, $J = 6.1$ Hz), 8.553–8.565 (1H, dd, $J = 4.9$ Hz), 12.540 (1H, s); EIMS m/z 149. $C_8H_7NO_2$ calculated m/z: 149.15

4-Cyano cinnamic acid (5). White Solid. m.p. 254–255 °C; ν_{max}/cm^{-1} 3000–2500 (O–H), 1693(C═O), 1627(C═C); ^{1}H-NMR (499.85 MHz; DMSO; Me_4 Si) $\delta = 6.675–6.707$ (1H, d, $J = 16.2$), 7.607–7.639 (1H, d, $J = 16.2$), 7.838–7.891(4H, m), 12.623(1H, s); mz (EI) 149. $C_8H_7NO_2$ calculated m/z: 149.15

3-Trifluoro methyl cinnamic acid (6). White Solid. m.p. 133–135 °C; ν_{max}/cm^{-1} 3000–2500 (O–H), 1684(C═O), 1630 (C═C); ^{1}H-NMR (499.85 MHz; DMSO; Me_4 Si) $\delta = 6.678–6.711$ (1H, d, $J = 16.5$ Hz), 7.613–7.645 (1H, t), 7.681–7.650 (1H, d, $J = 15.9$ Hz), 7.731–7.746 (1H, d) 7.996–8.012 (1H, d), 8.059 (1H,s), 12.522 (1H, s); EIMS m/z 216. $C_{10}H_7F_3O_2$ calculated m/z: 216.16

2-Methoxy cinnamic acid (7). White Solid. m.p. 180–182 °C; ν_{max}/cm^{-1} 3000–2500 (O–H), 1682(C═O), 1620 (C═C); ^{1}H-NMR (499.85 MHz; DMSO; Me_4 Si) $\delta = 3.836–3.978$ (3H, s), 6.481–6.513 (1H, d, $J = 15.9$ Hz), 6.940–6.971 (1H, t, $J = 6.7$ Hz), 7.040–7.056 (1H, d, $J = 7.9$ Hz), 7.359–7.387 (1H, t, $J = 6.7$ Hz), 7.641–7.653 (1H, d, $J = 6.1$ Hz), 7.816–7.847 (1H, d, $J = 15.9$ Hz); 12.315 (1H, s); EIMS m/z 178. $C_{10}H_{10}O_3$ calculated m/z: 178.18

3-Methoxy cinnamic acid (8). White solid. m.p. 115–116 °C; ν_{max}/cm^{-1} 3000–2500 (O–H), 1680(C═O), 1629 (C═C); ^{1}H-NMR (499.85 MHz; DMSO; Me_4 Si) $\delta = 3.764$ (3H, s), 6.524–6.556 (1H, d, $J = 15.8$ Hz), 6.939–6.960 (1H, dd, $J = 8.0$ Hz), 7.206–7.221 (1H, d, $J = 7.3$ Hz), 7.276–7.308 (1H, t, $J = 7.9$ Hz), 7.540–7.573 (1H, d, $J = 16.5$ Hz), 12.392 (1H, s) EIMS m/z 178. $C_{10}H_{10}O_3$ calculated m/z: 178.18

DES before reaction. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4 Si) $\delta = 3.187$ (9H), 3.505 (2H), 3.95 (2H), 4.424 (1H), 6.095 (8H).

^{13}C NMR (75 MHz, $CDCl_3$), $\delta = 161.945$, 67.804, 55.937, 54.006

DES after reaction. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4 Si) $\delta = 3.193$ (9H), 3.509 (2H), 3.978 (2H), 4.870(1H), 6.091 (8H).

^{13}C NMR (75 MHz, $CDCl_3$), $\delta = 162.003, 67.765, 55.937, 54.128$

3.4 Cinnamic acid formation reaction: a typical procedure: by conventional method (1a–3a)

In a typical reaction, benzaldehyde (0.5 g, 4.7 mmol), acetic anhydride (0.96 g, 9.4 mmol) and sodium acetate trihydrate (1.93 g, 14.1 mmol) were mixed and stirred at 140 °C for 9 h in round bottom flask fitted with reflux condenser. The reaction was monitored on TLC. The reaction mass quenched in 20 ml ice cold water and acidified with 1 : 1 aqueous hydrochloric acid. Precipitated solid was filtered, washed with cold water and dried at 40 °C.

3.5 Recycling study of choline chloride: urea (DES)

Benzaldehyde (10 g, 94 mmol), acetic anhydride (9.63 g, 94 mmol) and deep eutectic solvent (30 ml) were mixed and stirred at room temperature 30 ± 2 °C in a round bottom flask fitted with guard tube. After 4 h, the reaction mixture became viscous and solidified. The reaction was monitored by TLC. After completion of reaction, water was added. The DES being soluble in water comes in the water layer. The solid was separated by filtration, purified from water and methanol and dried in oven under vacuum (yield = 92%). The deep eutectic solvent was recovered from the filtrate by evaporating the water phase at 80 °C under vacuum. The recycled deep eutectic solvent was used for the next batch and recycled again. (Table 2)

4. Conclusion

Perkin condensation using biodegradable ammonium deep eutectic solvent based on choline chloride and urea provides an efficient and convenient method for the synthesis of cinnamic acid and their derivatives. This method offers marked improvements in terms of decreased reaction time, general applicability, good isolated product yields, energy efficient reaction and the use of environmentally benign procedures and solvents. This method also eliminates the use of hazardous organic solvents and toxic catalysts, and thus provides a better and practical alternative to existing methods. Deep eutectic solvents provide a good alternative for industrial synthesis as the reaction is readily scalable. The recyclability and biodegradability of deep eutectic solvent makes the process greener and economically more viable for the synthesis of cinnamic acid as compared to the reported protocols.

Acknowledgements

Authors are thankful to chemistry department, ICT, Mumbai, for recording FT-IR. One of the authors, Ms Poonam M. Pawar, is thankful to CAS-UGC for a fellowship.

References

1 Y. Aoyagi, N. Masuko, S. Ohkubo, M. Kitade, K. N. Shinji Okazaki Konstanty Wierzba, T. Terada, Y. Sugimoto and Y. Yamada, *Cancer Sci.*, 2005, **96**, 614.
2 J. Kanaani and H. Ginsburg, *Antimicrob. Agents Chemother.*, 1992, **2**, 1102–1108.
3 Y. Masashi, *EP pat.*, 0 450 892 A1, 1991.
4 E. Rogers, Harry-O'Kurn, Peoria, *US pat.*, 7 351 403 B2, 2008.
5 Y. Shi, Qing-Xi Chen, Q. Wang, K. Song and L. Qiu, *Food Chem.*, 2005, **92**, 707–712.
6 R. C. Beavis, B. T. Chait and H. M. Fales, *Rapid Commun. Mass Spectrom.*, 1989, **3**, 432–435.
7 (*a*) J. A. Joule, K. Mills, *Heterocyclic Chemistry.*, 4th ed., 2000, pp. 170–189; (*b*) W. F. Ringk, in *Kirk Othmer Encyclopedia of Chemical Technology.*, 3rd ed., 1981, vol. 6, pp.143–149.
8 (*a*) W. H. Perkin, *J. Chem. Soc.*, 1867, **20**, 586; (*b*) G. Bacharach and F. Brogan, *J. Am. Chem. Soc.*, 1928, **50**, 3333; (*c*) S. Kahn, N. J. Rutherford, *US pat.*, 3 813 414, 1974.
9 (*a*) E. Koepp, *Synthesis*, 1987, 177–179; (*b*) M. Aslam, W. F. Stansbury, R. J. Reiter and D. R. Larkin, *J. Org. Chem.*, 1997, **62**, 1550–1552.
10 (*a*) J. R. Johnson, *Org. React.*, 1942, **1**, 210; (*b*) J. R. Jhonson, *Org. Syn. Coll.*, 1955, **3**, 426.
11 R. E. Ruckles, *J. Chem. Educ.*, 1950, **27**, 210.
12 R. Kern, *DE Pat.*, 3 139 994, 1983.
13 M. G. Mihaiescu, N. Vasile, T. Sachelarie, *RO Pat.*, 90 224, 1986.
14 W. R. Peterson, *US Pat.*, 2 401 099, 1986.
15 (*a*) W. J. Houlihan, J. Nadelson, *US Pat.*, 3 870 751, 1975; (*b*) J. E. Telschow, *US Pat.*, 4 571 432, 1986.
16 N. A. Bumagin, N. P. Andryukhova and I. P. Beletskaga, *Metalloorg. Khim.*, 1989, **2**, 911.
17 J. H. Teles, N. Rieber, K. Breuer, D. Demuth, H. Hibst, H. Etzrodt, U. Rheude, *US Pat.*, 6 211 416, 1999.
18 (*a*) K. Karl, K. Thomas, S. Heinrich, *DE Pat.*, 3 437 624, 1986; (*b*) G. Ihl, G. Roscher, N. Mayer, *DE Pat.*, 3 743 616, 1988.
19 (*a*) B. Ramesh Babu and K. K. Balasubramaniam, *Org. Prep. Proced. Int.*, 1994, **26**, 123; (*b*) E. Dalacanale, G. Bottaccio, S. Compolmi, F. Montamari, *EP Pat.*, 0 146 373, 1985; (*c*) H. Harada, *EP Pat.*, 0 170 520, 1986.
20 H. Heinz, Y. Peres and A. Milchereit, *J. Organomet. Chem.*, 1986, **307**, C38.
21 (*a*) M. Hajek, J. Malek and P. Silhavy, *CS Pat.*, 217 518, 1983; (*b*) M. Hajek, P. Silhavy, *DE Pat.*, 3 524 475, 1986; (*c*) M. Hajek, J. Malek, P. Silhavy, *CS Pat.*, 209 347, 1981.
22 J. F. J. dippy and R. M. Evans, *J. Org. Chem.*, 1950, **15**, 451–456.
23 S. John and J. Sardella, *J. Am. Chem. Soc.*, 1950, **72**, 4322–4323.
24 C. Ping, G. Liangjun and T. Tao, *Huaxue Yu Shengwu Gongcheng*, 2008, **25**, 18–20.
25 Teng and Yefang, *Shiyou Huagong Yingyong*, 2008, **27**, 8–9.
26 L. Jianfen and C. Hongmei, *Jingxi Shiyou Huagong*, 2007, **24**, 34–37.
27 C. I. Chiriac, F. Tanasa and M. Onciu, *Tetrahedron Lett.*, 2003, **44**, 3579–3580.
28 C. I. Chiriac, F. Tanasa and M. Onciu, *Molecules*, 2005, **10**, 481–487.
29 E. Veverkova, E. Pacherova and S. Toma, *Chem. Pap.*, 1999, **53**, 257–259.
30 R. D. Pace and L. McWilliams, *J. Ark. Acad. Sci.*, 2006, **60**, 96–100.
31 H. Khabazzadeh, R. M. Nejad, H. Sheibani and K. Saidi, *Catal. Commun.*, 2007, **8**, 1411–1413.
32 K. H. M. Sampath, R. B. V. Subba and R. P. Thirupathi, *Org. Prep. Proced. Int.*, 2000, **32**, 81.
33 A. K. Sinha,*, V. Kumar, A. Sharma, A. Sharma and R. Kumar, *Tetrahedron*, 2007, **63**, 11070–11077.
34 J. Weng, C. Wang, H. Li and Y. Wang, *Green Chem.*, 2006, **8**, 96–99.
35 (*a*) S. B. Phadtare and G. S. Shankarling, *Green Chem.*, 2010, **12**, 458–465; (*b*) Y. A. Sonawane, S. B. Phadtare, B. N. Borse, A. R. Jagtap and G. S. Shankarling, *Org. Lett.*, 2010, **12**, 1456–1459.
36 (*a*) K. Prasad, D. V. Pinjari, A. B. Pandit and S. T. Mhaske, *Ultrason. Sonochem.*, 2010, **17**, 409–415; (*b*) K. Prasad, D. V. Pinjari, A. B. Pandit and S. T. Mhaske, *Ultrason. Sonochem.*, 2010, **17**, 697–703; (*c*) D. V. Pinjari and A. B. Pandit, *Ultrason. Sonochem.*, 2010, **17**, 845–852.
37 K. J. Jarag, D. V. Pinjari, A. B. Pandit and G. S. Shankarling, *Ultrason. Sonochem.*, 2011, **18**, 617–623.
38 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and P. Shikotra, *Inorg. Chem.*, 2005, **44**, 6497.
39 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003, 70.
40 T. Razzaq, J. M. Kremsner and C. O. Kappe, *J. Org. Chem.*, 2008, **73**, 6321–6329.
41 T. A. Wittstruck and E. N. Trachtenberg, *J. Am. Chem. Soc.*, 1967, **89**, 3803–3849.