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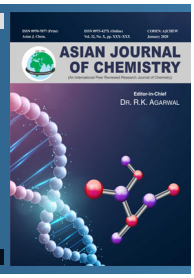

MINI REVIEW

Recent Advances in Catalysis of Hantzsch and Related Synthesis of 1,4-Dihydropyridines and Polyhydroquinolines: A Brief Overview

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Pharmacologically privileged 1,4-dihydropyridine (DHP) framework is a common playground of synthetic and medicinal chemists. Despite its widely general applicability popular Hantzsch methodology for the construction of this novel heterocyclic moiety suffers from limitations like long reaction time and poor yield of the product. Circumvention of these problems mainly relies on employment of a plethora of catalysis for improvement of the reaction. Objective of this mini review is to critically highlight the salient aspects of such catalysis during the past two decades.

Keywords: 1,4-Dihydropyridines, Polyhydroquinolines, Hantzsch synthesis, Catalysis.

INTRODUCTION

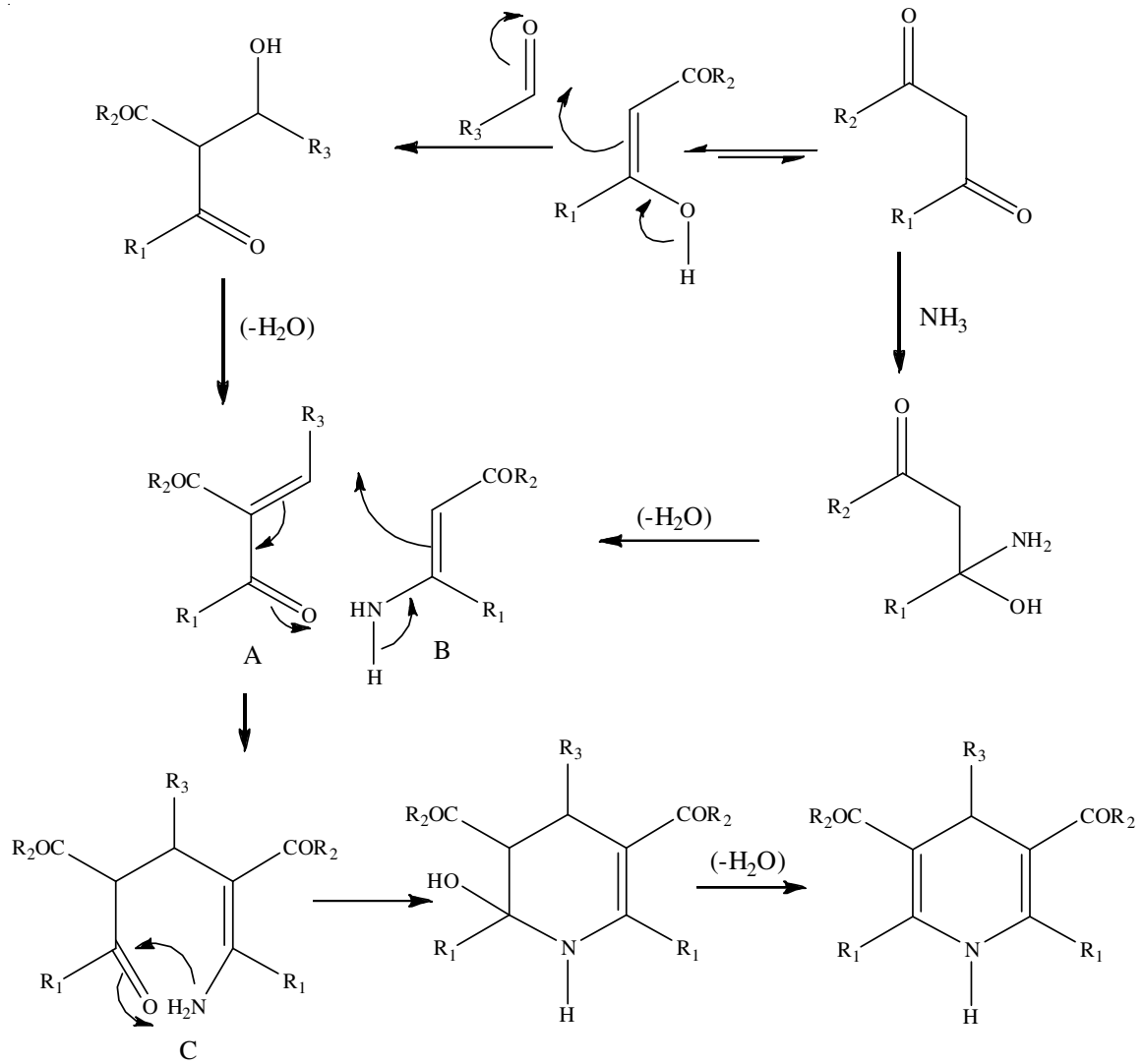
1,4-Dihydropyridine (DHP) derivatives are endowed with diverse pharmacological activities [1]. Huge number of clinically important molecules with DHP framework are available as over the counter drug throughout the world. Apart from stupendous pharmacological activities DHP′s also functionally mimic nicotinamide adenine dinucleotide (NADH)-the nature′s borohydride. Wide medicinal and chemical potentiality of DHP's demand relentless endeavour to be directed towards building up and modification of strategies for the synthesis of this novel heterocyclic scaffold.

Still today, the 139 year old Hantzsch reaction is considered as the most attractive avenue to DHP′s [2,3]. Conventionally this reaction involves cyclocondensation between a β-dicarbonyl compound (2 mol) and an aldehyde (1 mol) in the presence of ammonia. Usually the reaction occurs in refluxing alcohol and sometimes in the presence of acetic acid. Judicious modification of the skeletal units used in Hantzsch reaction has also been found to yield excellent results [4]. β-Dicarbonyl compound can be replaced by ω-cyanoacetophenone, ω-phenyl-thioacetophenone, other active methylene compounds like malononitrile, cycnoacetic ester, *etc*.

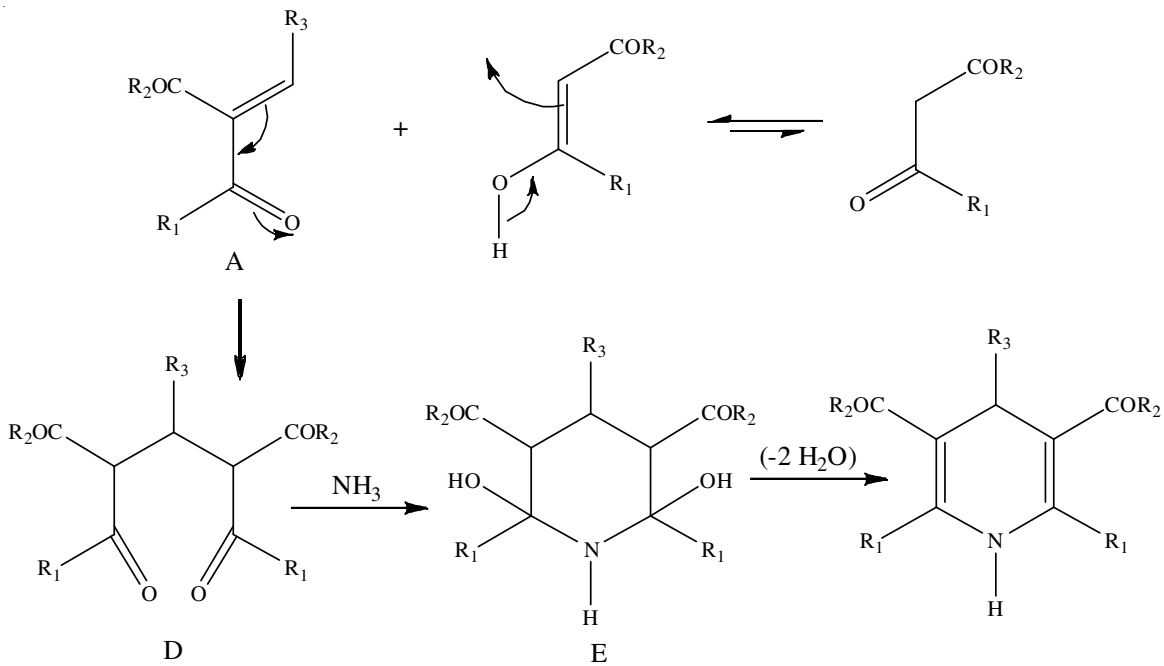
Mechanistic rationalization of Hantzsch reaction may be visualized in two ways. In one-way initial Knoevenagel condensation between the β-dicarbonyl compound and the aldehyde gives an α,β-unsaturated carbonyl compound (A)-the Knoevenagel condensation product. Compound A is an excellent Michael acceptor as the olefinic unit in it is activated by two carbonyl moieties. Reaction between ammonia and a second molecule of β-dicarbonyl compound yields enamino carbonyl compound (B). Nucleophilic attack of B to A through 1,4-conjugate addition furnishes compound C. Cyclization of compound C takes place *via* nucleophilic attack of nitrogen to the carbonyl carbon. Finally, dehydration leads to DHP (pathway A, **Scheme-I**).

In another way, the incipient Knoevenagel condensation product (A) may undergo Michael addition to a molecule of β-dicarbonyl compound to form a 1,5-dicarbonyl compound (D); the commonest precursor of pyridine derivatives. Reaction between compound D and ammonia followed by dehydration yields DHP (pathway B, **Scheme-II**).

Although spectroscopic studies strongly favour pathway A [5,6], involvement of pathway B is not inconsiderable specially when R_1 is a strongly electron withdrawing substituent [6]. Thus, for R_1 = -CF_3 compound (E) is the only product that



Scheme-I: Mechanism of Hantzsch reaction, pathway A



Scheme-II: Mechanism of Hantzsch reaction, pathway B

is isolated. Formation of compound (E) clearly demonstrates that pathway B is operative in this case. Failure of compound E to undergo dehydration must at least, in part, indicate the involvement of a carbocation-like transition state during the dehydration.

Although highly attractive, Hantzsch protocol often suffers from the disadvantages like lengthy reaction and sometimes notoriously poor yields of the desired product. Numerous attempts have, therefore, been made to circumvent these shortcomings. With the advancement of Green Chemistry, which mainly deals with minimisation of environmental hazards during operation of a chemical process, attempts to improvise Hantzsch and related methodologies have been increasingly envisaged in the perspective of green protocol. The most thoroughly investigated modification centres around the use of a variety of catalysts to promote the reaction. Performance of the reaction in aqueous and solvent-free medium, use of ionic liquids (IL) and exploitation of sophisticated techniques like sonication, ultraviolet, infrared and microwave irradiations also contribute towards improvisation of the reaction in green context.

Catalysis in the synthesis of 1,4-dihydropyridines (DHPs): Catalyzed Hantzsch or related reactions that appear in literature can be subdivided into the following categories (**Scheme-III**):

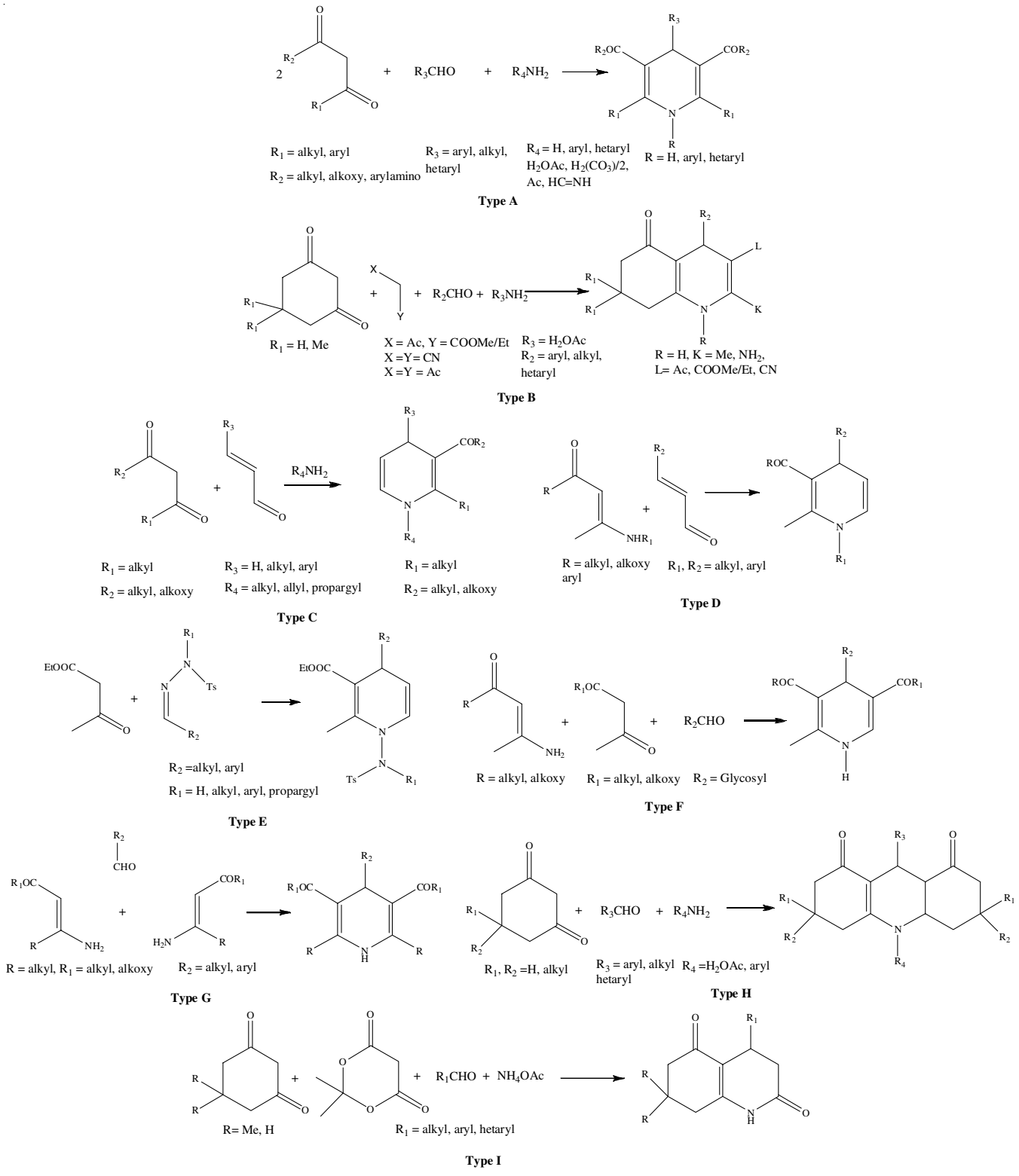
Type A: Multicomponent cyclocondensation involving β-diketone or β-ketoester, aldehyde and ammonia, ammonium salts, formamidine or acetamide leading to the formation of DHP derivatives. **Type B:** Multicomponent reaction among cyclohexane-1,3-dione or dimedone, β-diketone, malononitrile or β-ketoester, aldehyde and ammonia or ammonium salts giving rise to the generation of polyhydroquinolone (PHQ) derivatives. **Type C:** Reaction between β-diketone or β-ketoester and enal (α,β-unsaturated aldehyde) in the presence of alcohols and primary amines resulting in the formation of DHP derivatives. **Type D:** Reaction between enaminocarbonyl compound and α,β-unsaturated carbonyl compound. **Type E:** Reaction between ethyl acetoacetate and tosylhydrazone of aldehydes. **Type F:** Three component coupling of β-dicarbonyl compound, enaminocarbonyl compound and glycosyl aldehydes. **Type G:** Three component coupling of enaminocarbonyl compound and aldehydes. **Type H:** Three component coupling of cyclic β-diketone, aldehyde and ammonium acetate or aryl amine. **Type I:** Cyclocondensation involving cyclic 1,3-diketone, Meldrum′s acid, aldehyde and ammonium acetate.

As evident from the mechanism of Hantzsch reaction increase in electrophilicity of carbonyl carbon and acidity of β-dicarbonyl compound is expected to facilitate the reaction. Any compound capable of coordinating to carbonyl oxygen should achieve this feat and hasten the reaction. Thus, compounds with Lewis and Brønsted acidic character, other metal salts, neutral covalent molecules, nanostructured materials, bio and organoctalysists are reported to catalyze the reaction very effectively.

Catalysis by Lewis acids and other analogous compounds: Lewis acids and the cationic part of other related compounds effectively coordinate with the carbonyl oxygen of both β-dicarbonyl compound and the aldehyde. Electrophilicity of the corresponding carbonyl carbons is thus increased which facilitates the initial Knoevenagel condensation and the formation of enamino carbonyl compound. Finally, combination between the enamino carbonyl compound and the Michael acceptor is expected to be favoured by enhancement of electrophilicity of the α,β-unsaturated carbonyl compound through coordination with the Lewis acid or the cationic part of related compounds. Although great deal of work has been reported on such catalysis, related literature lacks investigation of the plausible mechanism of catalytic action. Choice of catalysts is also based purely on trial and error method. Ethanol, acetonitrile, chloroform, dichloromethane and in one case glycerine are used as solvents for these catalyzed reactions although employment of solvent-free conditions is also reported to produce excellent results in a number of occasions. Insolubility of the catalysts in reaction medium allows easy separation and purification of them for reuse. The catalysts are found to be reusable for several times without significant drop in their catalytic activity. Among the salts of iron(III), ferric fluoride is found to have the best catalytic activity presumably due to its water tolerance, high acidity and thermal stability. Bismuth nitrate pentahydrate and zinc (L) prolinate, in presence of neutral alumina, have been shown to produce excellent result under microwave irradiation than conventional heating. Potpourri of catalysis by Lewis acid and related compounds is summarized in Table-1.

Catalysis by Brønsted acids: Protonation of carbonyl oxygen of both the aldehyde and the β-dicarbonyl compound is the origin of catalysis by the Brønsted acids. Knoevenagel condensation between aldehyde and the active methylene compound and the reaction of active methylene compound with ammonia are thus favoured. Final dehydration step during the formation of DHP may also be facilitated by these catalysts. Strategic tethering of Brønsted acids to solid supports like silica [27-32], cellulose [33] or alumina [34] is found to increase the catalytic efficacy through allowance of easy separation, purification and reuse of the catalyst. Silica supported sulfuric acid can be conveniently prepared [35,36] by reaction between silica gel and chlorosulfonic acid at room temperature and is found to have better catalytic activity than sulfuric acid or chlorosulfonic acid. Sulfonic acid covalently anchored to silica gel (SiO_2-SO_3H) [28] is prepared by refluxing activated silica with trimethoxy (3-sulfanylpropyl)silane in toluene for 24 h and oxidation of the resulting 3-sulfanylpropyl substituted silica with 30% H_2O_2 in presence of conc. H_2SO_4.

Catalysis by cyanuric chloride (TCT) [37] is believed to occur by the hydrogen chloride released from TCT in presence of water. *p*-Toluenesulfonic acid (TsOH) [38,39] is reported to have better catalytic efficiency than other analogous Brønsted acids due to its non-oxidizing nature. In aqueous micelles TsOH catalyzed [40] reactions are found to proceed much better under ultrasonic irradiation. In thiamine hydrochloride [41] catalyzed reaction formamidine is reported to serve as the source of NH_3 and unexpectedly DHP derivatives are obtained instead of the normal Biginelli product dihydropyrimidinone. Catalysis by glycine hydrochloride [42] is somewhat interesting. Glycine hydrochloride is claimed to trap ammonia, released by thermal



Scheme-III

decomposition of ammonium carbonate in aqueous medium, in the form of the conjugate acid of ammonium glycinate. Loss of ammonia from the reaction medium is thereby prevented which boosts the reaction. Table-2 compositely delineates catalysis by Brønsted acids.

Catalysis by phase transfer catalysts (PTC) and aqueous hydrotopes: Phase transfer catalysts are known to transfer reagent from the aqueous medium to the organic phase where the substrate waits for the reagent. Cationic part of phase transfer catalysts are usually large organic moieties. Phase transfer catalysts appearing in literature for the catalysis of Hantzsch and related reactions are found to contain robustly substituted ammonium salts. In most of the cases, cyclocondensation between an aldehyde and a 1,3-dicarbonyl compound in presence

TABLE-1
CATALYSIS OF HANTZSCH AND ANALOGOUS REACTIONS FOR THE SYNTHESIS OF 1,4-DIHYDROPYRIDINE (DHP) AND POLYHYDROQUINOLONE (PHQ) BY LEWIS ACID AND RELATED COMPOUNDS

Entry	Catalyst	Type of reaction	Solvent	Reaction condition	Time	Yield (%)	Ref.
1	$Fe(O_2CCF_3)_3$ $Fe(CF_3SO_3)_3$	Type A	Solvent free	70 °C	20-60 min	85-98	[7]
2	$FeCl_3$	Type A	Solvent free	110 °C	1 h	85-95	[8]
3	$FePO_4$	Type A	Solvent free	70 °C	50-75 min	75-80	[9]
4	FeF_3	Type B	EtOH	75-80 °C	1-1.5 h	85-95	[10]
5	Anhd. $AlCl_3$	Type E	$CHCl_3$	Room temperature	1-10 h	24-96	[11]
6	$AlCl_3{\cdot}6H_2O$	Type A	Solvent free	60 °C	1-1.2h	73-80	[12]
7	$Ba(NO_3)_2$	Type A	Solvent free	Room temperature	10-25 min	83-96	[13]
8	$Bi(NO_3)_3{\cdot}5H_2O$	Type A	Solvent free	MW at 50 °C	2-3 min	84-99	[14]
9	LiBr	Type A	MeCN	Room temperature	3-6 h	81-93	[15]
10	$CdCl_2$	Type A	MeCN	Reflux	3-5 h	75-92	[16]
11	$Mg(ClO_4)_2 + MgSO_4$	Type C and D	CH_2Cl_2	Room temperature	70 h	32-94	[17]
12	$CeCl_3{\cdot}7H_2O$	Type A	MeCN	Room temperature	3-6 h	61-94	[18]
13	$Ce(SO_4)_2{\cdot}SiO_2$	Type A	Solvent free	80 °C	20-40 min	90-96	[19]
14	$Sc(OTf)_3$	Type B	EtOH	Room temperature	2-6 h	85-95	[20]
15	$Yb(OTf)_3$	Type B	EtOH	Room temperature	2-8 h	85-95	[21]
16	Glycerine-$CeCl_3{\cdot}7H_2O$	Type A	Glycerine	75-8 °C	3-5 h	85-93	[22]
17	$Zn(L\text{-}Prolin)_2$	Type A	Solid support (neutral Al_2O_3)	80 °C/MW	1-4 h/2-4 min	83-95	[23]
18	$K_7[PW_{11}CoO_4]$	Type B	MeCN	Reflux	25-35min	75-90	[24]
19	$ZrCl_4$	Type B	EtOH	Room temperature	2-4 h	84-94	[25]
20	$BiBr_3$	Type B	EtOH	Room temperature	1-3 h	79-93	[26]

TABLE-2
CATALYSIS OF HANTZSCH AND ANALOGOUS REACTIONS FOR THE SYNTHESIS OF 1,4-DIHYDROPYRIDINE (DHP) AND POLYHYDROQUINOLONE (PHQ) BY BRØNSTED ACIDS

Entry	Catalyst	Type of reaction	Solvent	Reaction condition	Time	Yield (%)	Ref.
1	Silica-H_2SO_4	Type A	Solvent free	Room temperature	15-45 min	90-97	[27]
2	SiO_2-SO_3H	Type A	Solvent free	60 °C	4.5-7h	83-95	[28]
3	SiO_2-$NaHSO_4$	Type A	MeCN	Room temperature	6-8 h	75-90	[29]
4	SiO_2-PPA	Type A	Solvent free	100 °C	15-35 min*	89-92	[30]
5	SiO_2-$HClO_4$	Type A and B	Solvent free	80 °C (A), 90 °C (B)	20-56 min (A) 8-20 min (B)	81-96	[31,32]
6	Cellulose-H_2SO_4	Type C	H_2O	100 °C	1-1.5 h	85-98	[33]
7	Al_2O_3-H_2SO_4	Type A and B	MeOH	70 °C	5 h (A), 2-2.5 h (B)	82-97	[34]
8	Cyanuric Chloride (TCT)	Type A	Solvent free	Room temperature	15-150 min	83-94	[37]
9	TsOH	Type A	Solvent free	80 °C	5-20 min	80-96	[38]
10	TsOH	Type B	EtOH	Room temperature	2-3 h	85-93	[39]
11	TsOH-SDS	Type A and B	H_2O-SDS**	Ultra sonication	1-3 h	72-97	[40]
12	Thiamine Hydrochloride	Type A	Solvent free/MeCN	Room temp/ reflux***	40 min	80-94	[41]
13	Glycine-HCl	Type A	H_2O	50-65 °C	10-30 min	75-97	[42]
14	Guanidine hydrochloride	Type A	EtOH	Room temperature	3 h	62-85	[43,44]
15	$PhB(OH)_2$	Type A	EtOH	Reflux	4-5 h	80-95	[45]
16	Trichlorocyanuric acid	Type A	EtOH-H_2O (1:1)	Reflux	1-4 h	53-92	[46]
17	Melamine trisulfonic acid	Type B	Solvent free	60 °C	2.5-3.5 h	88-95	[47,48]

*50-75 min (as evident from experimental section); **SDS = Sodium dodecyl sulfate; ***Reflux in MeCN when formamidine acetate is used as ammonia source

of ammonium acetate (Type A) is studied. Guo and Salah [49] reported the synthesis of 1,4-dihydropyridines in aqueous medium using tetrabutyl ammonium bromide as a phase-transfer catalyst under microwave irradiation. All the reactions are completed within 3-10 min with 77-99% yield. Khaskel and Barman [50] have used benzyltrimethylammonium fluoride hydrate (BTMAFH) under solvent-free conditions to accomplish an efficient synthesis of DHP through Hantzsch protocol (Type A). These authors have shown that catalytic efficiency of BTMAFH is better than the analogous halides presumably due to small size and high charge density on fluorine that facilitates deprotonation of the active methylene compound during the incipient Knoevenagel condensation. The proposed mechanism for catalytic activity of BTMAFH is based on coordination of carbonyl oxygens of aldehyde and the β-dicarbonyl compound to positive nitrogen of BTMAFH to facilitate Knoevenagel condensation and the reaction of ammonia with β-dicarbonyl compound to form enaminocarbonyl compound. The Michael

acceptor (Knoevenagel condensation product) is also activated by cationic nitrogen and attack of enaminocarbonyl compound to it is thereby favoured. Tetrabutylammonium hydrogen sulfate (TBAHS) has been employed by Goel *et al*. [51] to achieve the synthesis of DHP *via* Hantzsch methodology. Performance of the reaction under solvent-free conditions at 70 ºC for 55-90 min affords the desired products in 65-80% yield. Synthesis of glycosyl 1,4-dihydropyridines [52] is conveniently achieved by a three-component coupling of β-dicarbonyl compound, enaminocarbonyl compound and glycosyl aldehydes (Type F) in presence of TBAHS as catalyst in diethylene glycol. These reactions are completed in 1-2.5 h at 80 ºC with nearly quantitative yield (90-98%). In this case, TBAHS is also thought to facilitate the final dehydration step due to its acidic character. Gaikar *et al*. [53] demonstrated that aqueous hydrotropes can catalyze the synthesis of DHP through efficient solubilization of the substrates.

Catalysis by neutral covalent molecules: Oxophilicity of phosphorous and silicon allows their easy coordination to carbonyl oxygen of aldehyde and β-dicarbonyl compounds. Catalysis by triphenyl phosphine and trimethyl silyl iodide (TMSI) can therefore be rationalized in the same way as that of acid catalysed reactions. Debache *et al*. [54] reported the synthesis of DHP *via* a three component reaction of ethyl acetoacetate, aldehyde and ammonium acetate (Type A) in refluxing ethanol in the presence of triphenyl phosphine. Completion of the reactions needs 2-5 h with reasonably high yield (72-95%). However, these authors attributed the catalytic activity of triphenyl phosphine to its nucleophilic attack at the carbonyl carbon of aldehyde which lacks chemical tenability. Trimethyl silyl iodide (TMSI) is used by Sabitha *et al*. [55] for the synthesis of DHP with good result. These authors have synthesised DHP through a TMSI catalyzed three component coupling of ethyl/methyl acetoacetate, aldehyde and ammonium acetate in acetonitrile at room temperature in 6-8 h with 73-80% yield. They have also carried out the reaction between ethyl/methyl-3-amino crotonate and aldehyde (Type G) to furnish DHP derivatives under identical conditions in 2-3 h with reasonably high yield. Catalysis by molecular iodine has been reported by Yao *et al*. [56] in their synthesis of polyhydroquinolines from a four-component coupling of ethyl acetoacetate, 1,3-cyclohexane dione/dimedone, aldehyde and ammonium acetate (Type B) at room temperature in 0.5-6 h with almost quantitative yield.

Catalysis by clay materials and ion exchange resins: Montmorilonite K 10 [57,58] has been successfully employed in the synthesis of DHP through Hantzsch methodology. Catalysis by Na-norit and Cs-norit [59] has also been reported in the synthesis of the precursors of Hantzsch substrates under solvent free conditions. Basic nature of amberlite HRA 900 has been exploited for its use as a catalyst in the solvent free synthesis of dihydropyridines and polyhydroquinolines under mild conditions [60]. All these catalysts are easily separated from the reaction medium and reused after purification.

Catalysis by ceric ammonium nitrate (CAN): Menéndez *et al*. [61,62] have described a synthesis of 6-alkoxy-2-methyl-1,4,5,6-tetrahydropyridines through a CAN-mediated, four component reaction among primary aliphatic amines, β-keto esters or thioesters, α,β-unsaturated aldehydes and alcohols (Type C, R_2 = alkoxy, thioalkoxy). The reaction occurs under mild conditions at room temperature in acetonitrile. Products of this reaction are easily dehydrated to the corresponding 5,6-unsubstituted 1,4-dihydropyridines by treatment with neutral alumina (activity grade I) in refluxing acetonitrile. Syntheses of DHP and PHQ are achieved from 1,3-diones, 5-bromothiophene-2-carboxaldehyde and ammonium acetate at room temperature under solvent-free condition *via* CAN catalyzed Hantzsch reaction in 1-3 h [63]. Yao and Ko [64] accomplished a CAN catalyzed facile synthesis of PHQ *via* Hantzsch protocol. Mechanism of catalytic activity of CAN, however, is not investigated by researchers.

Catalysis by nanomaterials and hydrotalcites: Popularity of heterogeneous catalysts in organic synthesis stems from their easy isolation from the reaction medium by simple filtration and consequent reusability. Composite nanoparticles, because of their large surface to volume ratio, have increasingly gained importance in the realm of heterogeneous catalysts. Magnetic nanoparticles have attracted considerable interest in synthesis because of their simple separation by an external magnet and high degree of chemical immunity to various organic and inorganic solvents. Nanocatalyzed syntheses of DHP and PHQ are no exception. Maleki *et al*. [65] reported a facile synthesis of PHQ *via* TYPE B reaction catalyzed by magnetite/chitosan at room temperature under mild conditions. Magnesium oxide nanoparticles [66,67] has been used for the synthesis of DHP *via* TYPE A reaction in refluxing ethanol or acetonitrile. Catalytic activity of MgO nanoparticles is attributed to a synergic effect of the coordinating ability and basicity of magnesium and oxygen respectively.Synthesis of PHQ is developed involving a Type B condensation catalyzed by nano-γ-Fe_2O_3-SO_3H under solvent-free conditions [68]. Nickel nanoparticles is reported to catalyze the Type B reaction quite remarkably in solvent-free condition to form PHQ in only 1-1.5 min under microwave irradiation [69].

DHP and PHQ derivatives have been conveniently synthesized *via* Type A and B Hantzsch condensation using nanostructured TiO_2 in refluxing ethanol [70]. Zirconium dioxide nanopowder [71] has shown to catalyze the synthesis of DHP through a Type A reaction under microwave irradiation in a very short time. Pumice encapsulated in cellulose matrix [72] has been demonstrated as an efficient nanocatalyst in the synthesis of DHP under ultrasound irradiation. Here, also the catalytic activity of cellulose/pumice is ascribed to its coordination with carbonyl oxygen. Nano-magnetite [73,74] catalyzed Type B reaction has been found to produce PHQ in high yields under solvent free conditions. Catalysis by nanostructured bismuth tungstate [75] appears to be a convenient method for the synthesis of DHP and PHQ through Type A and B reactions, respectively. Hydrotalcites, which offer strong surface basicity, have also been successfully employed as catalyst in the synthesis of DHP. Good results are obtained with Mg-Al_2 [76] and Mg/Fe [77] hydrotalcites. Catalytic activity of hydrotalcites is believed to be due to their strong basicity. Catalytic efficacy of carbonaceous solid acid [78] has been explored in the synthesis of DHP through Type A reaction under solvent free conditions.

Catalysis by organo-, bio- and supramolecular catalysts: Catalysis by small organic molecules has become an integral and indispensible part in the context of green synthesis. Such molecules reported for the synthesis of DHP and PHQ are mainly of amino acid and alkaloid origins.

Kumar *et al*. [79] have studied the catalytic efficiency of L-proline, L-thiaproline, *trans*-4-hydroxy-L-proline, methyl L-prolinate, DL-2-phenyl glycine and (-) cinchonidine in the synthesis of PHQ through a Type B reaction. L-Proline has been reported to be the best catalyst presumably due to the presence of properly located imino and carboxyl functions in it. L-Proline has also been employed by the same group [80] to synthesize a series of *N*-aryl-1,4-dihydropyridines *via* a three component reaction involving 1,3-dicarbonyl compound, α,β-unsaturated aldehyde and aromatic amine (Type C) at room temperature under solvent free conditions. L-Proline mediated synthesis of PHQ has also been reported by Karade *et al*. [81] in refluxing ethanol. Chirality is intrinsically related to pharmacological activity of a molecule and organocatalysis has mainly been used for enantioselective synthesis [82] of configurationally pure DHP′s.

Biocatalysis of organic reactions is mainly carried out with enzymes which, due to their specific folding, offers a suitable pocket to accommodate the reactant molecules to bring them within reacting distance. Acidic and basic sites of the enzymes are also responsible for their functional specificity. In 2005, Lee [83] described an elegant synthesis of 4-methyl substituted 1,4-dihydropyridines from acetoacetic ester and ammonium acetate in phosphate buffer (pH 7) in the presence of glucose and fermenting Bakers′ yeast. Reaction between acetoacetic ester and 3-aminocrotononitrile under identical conditions also furnishes 4-methyl substituted 1,4-dihydropyridines. Glucose is thought to undergo glycolysis under the reactions conditions to produce acetaldehyde which acts as the aldehyde component to form the 4-methyl substituted DHP. Exactly identical reaction condition is used by Kumar and Maurya [84] in their synthesis of PHQ through a Type B reaction. In this case, added aryl alde-hydes are found to be incorporated in the product instead of the acetaldehyde generated from glucose. These results indicate higher reactivity of aryl aldehydes than aliphatic aldehydes in the Hantzsch or Hantzsch-type reactions. *Candida antarctica* lipase-B [85] catalyzed reaction is found to produce DHP through a Type A reaction using acetamide as the source of ammonia in methyl *tert*-butyl ether. Lipozyme® RM IM (triacyl glycerol acyl hydrolase, EC3.1.1.3) mediated multi-component mechano-chemical reactions of aromatic aldehyde, alkyl acetoacetate and alkyl 3-aminocrotonate are reported as a convenient route to DHP [86]. Ring nitrogen of histidine residue is speculated to promote deprotonation of alkyl aceto-acetate, which facilitates the initial Knoevenagel condensation.

Supramolecules have the unique ability to trap guest molecules in their inner cavity by non-covalent interactions and in this context they mimic enzymes. β-Cyclodextrin, a cyclic oligomer of D-glucose, has a toroidal cyclic structure with secondary hydroxyl groups at C-2 and C-3 of glucose on their more exposed face. Activation of carbonyl groups of aldehydes and β-ketoesters through hydrogen bonding with hydroxyl hydrogen has been reported to be the origin of catalytic efficiency of β-cyclodextrin in the solvent free Hantzsch synthesis (Type A) of DHP by Patil and Dalal *et al*. [87].

Synthesis of DHP and PHQ in ionic liquids: Existence of ionic liquids in the liquid form at or near room temperature is a result of inefficient packing of the constituent large (mostly delocalized heterocyclic) cations and large polyatomic anions in ionic crystals. Ionic liquids are endowed with some remarkable properties like high thermal stability, low inflammability, moderate conductivity, tuneable viscosity and negligible vapour pressure. These properties can be conveniently engineered by

TABLE-3
CATALYSIS OF HANTZSCH AND ANALOGOUS REACTIONS FOR THE SYNTHESIS OF 1,4-DIHYDROPYRIDINE (DHP) AND POLYHYDROQUINOLONE (PHQ) BY IONIC LIQUIDS

Entry	Ionic liquid	Type of reaction	Reaction condition	Time	Yield (%)	Ref.
1	TBA-AMPS	Type B	MeOH, 80 °C	8-18 min	90-97	[90]
2	Betainium salt	Type H	EtOH, 80 °C	1-8 h	75-96	[91]
3	[Bmim]OH	Type B	80 °C	10min	90-97	[94]
4	2-Hydroxyethyl ammonium carboxylates	Type A	30 °C	2h	45	[95]
5	4-[MBPY]	Type D and G	80 °C & reflux	8 h & 48 h	72 & 64	[96]
6	MSI_3PW	Type A & B	90 °C	4 h	84-99	[97]
7	$[MSI]HSO_4$	Type B	EtOH, reflux	20-120 min	75-93	[98]
8	[Hmim]Tfa	Type A	EtOH, MW	1-3 min	80-92	[99]
9	$[Hmim]BF_4$	Type B	90 °C	5-26	89-96	[100]
10	$[Bmim]BF_4$	Type I	80 °C	4-9 h	58-93	[101]
11	$[Bmim]BF_4$, $[Bmim]PF_6$,	Type F	Room temperature	4.5-8 h	80-93	[102]
12	[Dsim]Tfa	Type B	Room temperature ultrasonication	0.5-3 min	88-98	[103]
13	1-Methyl-3-(3-trimethoxysilylpropyl)imidazolium acnchored on Fe_3O_4, $NiCl_4^{2-}$	Type A	70 °C	10-40 min	90-99	[104]
14	[Bmim]saccharinate	Type A	100 °C	2-4 h	15-28	[105]
15	$[Dsim]HSO_4$	Type B	80 °C	25-40 min	88-96	[106]
16	1,3-di (3-trimethoxysilylpropyl) imidazolium chloride anchored on $Mn(OAc)_3$	Type B	80 °C	15-100 min	55-95	[107]

tailor-made designing of component ions and so ionic liquids are sometimes called "designer solvent" or "task-specific solvent". Although ionic liquids mostly provide a green reaction medium, catalytic activity [88] of them can't be ignored specially when the structures contain acidic and/or basic sites.

Catalytic activity of ionic liquids may be related to usual acid or base catalysis in the presence of acidic and basic sites in their structure. However, in absence of such structural features reason for catalytic activity remains uncertain. Somehow, they stabilise the transition state [89] to make the reaction kinetically favoured. Catalysis of Hantzsch and analogous reactions for the synthesis of DHP and PHQ by ionic liquids is summarized in Table-3.

Conclusion

Use of catalysts has contributed immensely to the improvement of Hantzsch and related methodologies for the synthesis of 1,4-dihydropyridines (DHPs) and polyhydroquinolines (PHQs). Both homogeneous and heterogeneous catalysts have been employed with excellent results. Despite the extensive work done on catalysis plausible mechanism of catalytic activity still remains mostly unexplored. Basis for the choice of catalysts also needs further consolidation. Absence of symmetrical products in the four component (Type B) reaction leading to PHQ is somewhat surprising although it is claimed that there is a difference in reactivity between the 1,3-dicarbonyl compounds employed in the reaction. α,β-Unsaturated aldehydes are dichotomously found to supply C-2, C-3 and C-4 for DHP in Type C and D reactions and C-4 in other cases. Thus, there is still ample scope to study the catalysis in detail with respect to these aspects.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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