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Ecofriendly microwave assisted synthesis of flavanones using Silica-HCl as a solid acid catalyst

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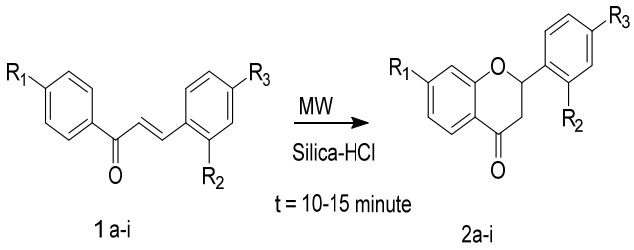
Abstract
We described herein, efficient, convenient and green chemistry approach for the synthesis of flavanones 2a-2i. We synthesized chalcones under basic condition using sonication. All synthesized chalcones were converted to corresponding flavanones by microwave irradiation. We used Silica-HCl catalyst for the conversion of chalcone into flavanones under microwave irradiation.

Keywords: Si-HCl, Microwave irradiation, 2-hydroxy chalcone, Flavanone, eco-friendly etc.

1. Introduction
Flavonoids are naturally occurring oxygen containing heterocyclic compounds and they are classified into flavanone, flavones, isoflavones, flavonols, anthocyanin. Flavanone is a key intermediate for synthesis of flavones or isoflavones and flavonols [1]. Naturally occurring flavanones are found in glycosylated or aglycone form and pyrano and furano form. Natural and synthetic flavanone shows various biological activities like antitumoral [2], anti-tyrosinase [3], anti-sindbis [4], anti-inflammatory [5], antileishmanial and antitrypanosomal [6], antioxidant properties [7], antimalarial [8], anti-atherosclerosis [9], Vasorelaxant agents [10] and oviposition stimulants [11]. Due to these wide ranges of biological activity of flavanones, they attract many researchers for their synthesis. Flavanones are generally synthesized by the treatment of 2'-hydroxy chalcones with acidic or basic reagent or oxidative cyclization of it. Cyclization of 2'-hydroxychalcone to flavanone is reported using methane sulphonic acid [12], amino acid [13], Celite supported potassium fluoride in Methanol [14], trifluoroacetic acid [15], sulfuric acid in methanol [16], polyphosphoric acid [17], Amberlyst A-21 [18], Basic reagent using triethly amine under reflux condition [19], NaOH [20], KOH in methanol [21], and Potassium carbonate in acetone under reflux condition [22]. This cyclization is also brought out using an oxidizing agent like Co (salpr) in methanol under oxygen [23], Potassium ferrocyanide using phase transfer catalyst [24] and photochemical irradiation [25]. However, these reported methods suffer from disadvantages like low yield; require longer reaction time, high temperature, and expensive catalyst, strongly acidic or basic conditions. Hence there is scope to develop a new method which should have advantageous such as eco-friendly, use of inexpensive and easily available catalyst, high yield and short reaction time.
In the last twenty years, microwave radiation has attracted many organic chemists to use its application in organic synthesis due to the rapid transformation of reactant into product, reaction time reduced from hours into minutes or seconds, generally high yield compared to conventional heating, solvent free reaction, use of unconventional heating and ecofriendly method. Recently Microwave radiation is used in the synthesis of 2, 4-disubstituted quinolines [26], homopropargylic alcohols [27], N-methylamide [28], α –amino Ketones [29], and synthesis of 1, 3-diphenylpropenones [30]. From literature, use of microwave radiation in the synthesis of flavonoids is very limited; it is used in the synthesis of flavones by a dehydrative cyclization of o-hydroxydibenzoyl methane using CuCl2 as a catalyst [31], synthesis of flavanones with TFA over silica gel [32], synthesis of functionalized flavones brought out by microwave irradiation condensation between phloroglucinol and β-keto esters [33]. Si-Hcl is inexpensive, non-toxic to the environment and easily available. Si-HCl is used as efficient solid acid in Knoevenagel condensation [34], the Ferrier reaction of per-O-acetylated/benzylated glycals with alcohols to give 2, 3-unsaturated α-glycosides in a few

minutes under microwave irradiation [35], an efficient heterogeneous catalyst for the tetrahydropyranylation of alcohols and phenols at ambient or near ambient temperature [36] and in synthesis of imines [37]. Here we report an efficient, practical environmentally benign and high yielding method for the synthesis of flavanones using Si-HCl as a catalyst under microwave irradiation. Catalyst is necessary for the cyclization reaction even under microwave conditions.

Next we explored the scope of reaction using various substituted 2'-hydroxychalcone by varying the substituted B ring of benzene from electron donating groups to withdrawing groups. The results are presented in Table 1. From table 1, it is clear that, the cyclization of chalcones proceeds healthy to give flavanones in good yield. As usual electron donating groups present on ring B, cyclization proceeds very smoothly to afford flavanones in good yield while electron drawing groups and steric effects generate cyclization slow leading to moderate yield of flavanone (Scheme 1).



2. Experimental

All reagents, chemicals and solvents were purchased from Loba, Merck and Sigma Aldrich. Microwave reactions were carried out using synthesized catalyst, India. TLC (pre-coated silica gel 60 F254, Merck) was used to monitor the progress of the reaction. Melting points were recorded by open capillary method and are uncorrected. IR spectra were recorded as KBr pellets using Shimazu FTIR. The 1H NMR spectra were obtained on a Bruker DRX-300 Avance instrument using CDCl3 as solvent and TMS as internal standard at 300MHz. All products are known compounds and their authenticity was ensured on the basis of spectroscopic data and on comparison with authentic samples.

General method for the synthesis of flavanone

Chalcone (1mmol) and silica pinch added in RBF. Then 2-3 drops of conc. HCl was added in RBF. Reaction mass was dissolved in 5 ml ethanol. Round bottom flask was kept in microwave oven for 10-15 minute on power level 4. Reaction was monitored by TLC. Reaction mass poured in ice under stirring and filtered out the solid. Recrystallized in ethanol and dried in oven under vacuum.

3. Results and Discussions

The First, we studied solvent free cyclization of 2'-hydroxychalcone to flavanone using Si-HCl under microwave radiation. 2'-Hydroxychalcone (1a) was adsorbed over Si-HCl with the help of ethanol, after evaporation of ethanol we got free flowing powder. The resulting powder was exposed to microwave irradiation at 245W at power level 3 and progress of the reaction was monitored by TLC using (1:9) ethyl acetate and pet ether for an interval of 2 min. and after 10 min. We observed that reaction proceed in the forward direction and formation of a new product that is flavanone (2a). After completion of the reaction, the product was separated from the catalyst by dissolving it in 10ml of ethyl acetate and filters it. The product was present in filtrate that is an ethyl acetate layer, after evaporation of ethyl acetate layer we got crude flavanone and purified by recrystallization from ethanol afforded pure flavanone. The structure of the product was confirmed by spectroscopic method and spectral data match with flavanone (2a). There was no reaction when cyclization was carried out without Silica-HCl which indicates that a catalyst is necessary for the cyclization reaction even under microwave conditions.

Entry	R_1	R_2	R_3	Time min.	Yield %	M.P. ^0C
2a	H	H	H	13	80	75
2b	H	H	Br	11	75	117
2c	H	H	Cl	13	70	93
2d	H	H	F	12	82	78
2e	H	H	OMe	12	88	88
2f	H	H	NO_2	12	60	161
2g	H	H	Me	11	67	65
2h	H	NO_2	H	13	80	143
2i	H	OMe	H	15	90	76

Next we explored the scope of reaction using various substituted 2'-hydroxychalcone by varying the substituted B ring of benzene from electron donating groups to withdrawing groups. The results are presented in Table 1. From table 1, it is clear that, the cyclization of chalcones proceeds healthy to give flavanones in good yield. As usual electron donating groups present on ring B, cyclization proceeds very smoothly to afford flavanones in good yield while electron withdrawing groups and steric effects generate cyclization slow leading to moderate yield of flavanone-**(Scheme1)**

4. Conclusion

In conclusion, here in we report an inexpensive, reproducible, eco-friendly synthesis of flavanones using Silica-HCl as a catalyst. This method has merits over other reported methods like inexpensive and easily available catalyst, high yield and short reaction time, and avoids use of toxic-solvent, reproducibility of catalyst.

5. Acknowledgement

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