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Silica Supported Acids ($HClO_4$-SiO_2, $KHSO_4$-SiO_2) as Eco-friendly Reusable Catalysts for Bromodecarboxylation of α,β-Unsaturated Carboxylic Acids using KBr under Solvothermal and Solvent-Free Conditions

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A mild procedure has been developed for the bromodecarboxylation of α,β-carboxylic acids using nano silica supported SiO_2-$HClO_4$, SiO_2-$KHSO_4$ as catalysts and KBr as a bromine source in conventional solvothermal, ultrasonic assisted and solvent-free microwave assisted conditions. The α,β-unsaturated cinnamic acids were converted to corresponding β-bromo styrenes with high regioselectivity, while aliphatic α,β-unsaturated carboxylic acids afforded related β-bromo alkenes.

Keywords: $HClO_4$-SiO_2, $KHSO_4$-SiO_2, Bromo decarboxylation, α,β-Unsaturated carboxylic acids.

INTRODUCTION

Bromo decarboxylation is one of the most widely used versatile reactions for the conversion of α,β-unsaturated acids into β-bromostyrenes [1-4]. Basically, the Hunsdiecker-Borodin reaction depicts the conversion of silver carboxylates into alkyl bromides in the presence of molecular bromine [1-4], while silver salts of α,β-unsaturated carboxylates are converted into β-bromo styrenes under similar conditions.

In due course, large number of publications appeared in literature on Hunsdiecker-Borodin reactions using molecular bromine and different metal salts like Hg(II), Tl(I), Pb(IV). But major limitations like toxicity of metal ions, hazards using molecular bromine and poor yields of reaction products. To overcome these issues, several research groups redesigned these reactions by replacing toxic metal ions and hazardous molecular bromine [5-14]. Certain metal-free protocols were also designed for successful conversion of α,β-unsaturated acids to β-halo styrenes by Kuang *et al*. [15,16] under microwave conditions using *N*-halocompounds. In the later years, Reddy *et al.* [17] developed a novel micellar mediated green Hunsdiecker-Borodin reaction using *N*-halocompounds. Reactions were catalyzed by cationic micelles like cetyl trimethyl ammonium bromide (CTAB), anionic micelles like sodium dodecyl sulfate (SDS) and non-ionic micelles like Triton X-100 (TX-100) in dichloroethane (DCE) under reflux conditions. Reactions occurred in 20-60 min, with the conversion of α,β-unsaturated acids into β-halo styrenes with high regioselectivity.

In due course, another land mark in the Hunsdiecker-Borodin reaction emerged out when Das *et al.* [18] successfully converted the α,β-unsaturated acids to β-nitrostyrenes using nitric acid and catalytic amounts of azobisisobutyronitrile (AIBN) in acetonitrile. Soon after, our research group has also accomplished the conversion of α, β-unsaturated carboxylic acids into β-nitrostyrenes using a set of metal nitrates under solvent-free conditions [19]. This protocol is a grindstone reaction grinding the reactants (α,β-unsaturated carboxylic acids) in a mortar with a pestle with a few drops of nitric acid together with metal nitrates like $Mg(NO_3)_2$, $Sr(NO_3)_2$, $Al(NO_3)_3$, $Ca(NO_3)_2$, $Ni(NO_3)_2$, $Cd(NO_3)_2$, $Zn(NO_3)_2$, $Hg(NO_3)_2$, $AgNO_3$, $ZrO(NO_3)_2$, $UO_2(NO_3)_2$, $Th(NO_3)_2$ and NH_4NO_3 under solvent-free conditions. Reactants (α,β-unsaturated carboxylic acids) underwent nitrodecarboxylation and provided corresponding β-nitrostyrenes in highly appreciable yields.

In the past two decades, silica (SiO_2) immobilized catalysts (like SiO_2-$KHSO_4$, SiO_2-$NaHSO_4$) have been explored as efficient and recyclable catalysts to synthesize tetrahydropyranylation [20] of alcohols and phenols, synthesis of heterocyclic pyrazoles and pyranyl pyridines [21], α-amino phosphonates [22], Biginelli condensation [23], Hantzsch condensation [24], synthesis of homoallylicamines [25], quinazolinones [26]. On the other hand, silica supported perchloric acid ($SiO_2/HClO_4$) has been described as a eco-friendly catalyst for wide varieties of organic transformations like *gem*-diacylation of aldehydes [27], xanthenes [28], Mannich reaction [29], synthesis of thioethers [30], polyhydroquinolines [31], glycosylation using sugar trichloroacetimidates [32] and ring opening of epoxide under microwave condition [33]. Recent literature reports also revealed that KBr could be used for bromination reactions in combination with different oxidizing agents such as H_2O_2/ sodium perborate [34-36], oxone [37,38], benzyltriphenylphosphonium peroxymonosulfate (BTPPMS) [39-43]. Recently, Siddiqui [44] synthesized coumaryl chalcones using SiO_2-$HClO_4$. In addition to these reports, recent literature reports also depicted that SiO_2-$HClO_4$ and SiO_2-$KHSO_4$ could be used for the thiocyanation [45] and sulfonation [46] of aromatic compounds

Encouraged by these features, herein, we wish to report a clean and environment friendly protocol comprising bromodecarboxylation α,β-unsaturated carboxylic acids into β-bromo styrene using nano-heterogeneous catalysts like SiO_2-$HClO_4$ and SiO_2-$KHSO_4$ and potassium bromide under reflux conditions. The same reactions under ultrasonically assisted solvothermal and microwave assisted solvent-free conditions were also explored.

EXPERIMENTAL

All chemicals used in this study were purchased either from Sigma-Aldrich (India), Avra (India) or SD (Fine Chemicals, India) and used without further purification.

Preparation of SiO_2-$HClO_4$ and SiO_2-$KHSO_4$ catalysts: To an aqueous solution of 20 mmol (25 mL) $HClO_4$, (4 g, 100-200 mesh) silica gel was added and stirred continuously for about 30 to 40 min a room temperature to ensure adsorption of $HClO_4$ on silica gel (SiO_2). Resultant powder was separated under vacuum and dried for about 3 h at 120 ºC to get crystalline powder, which was characterized by XRD and SEM adsorption methods. Procedure for the preparation of SiO_2-$KHSO_4$ catalyst is by and large, similar to that as described for the preparation of SiO_2-$HClO_4$ catalyst by replacing $HClO_4$ with (20 mmol) $KHSO_4$.

Scanning electron microscopy (SEM) analysis: The as-prepared catalyst was examined with SEM at different magnifications. Morphology recorded in the SEM images (Fig. 1 for SiO_2-$KHSO_4$ and (Fig. 2 for SiO_2-$HClO_4$) clearly depicted that no-uniform polynomial cubic crystals and flakes are spread over on the silica surface. Moreover, the under 50 µm (Figs. 1 and 2) magnification depicted non-uniform polynomial cubic

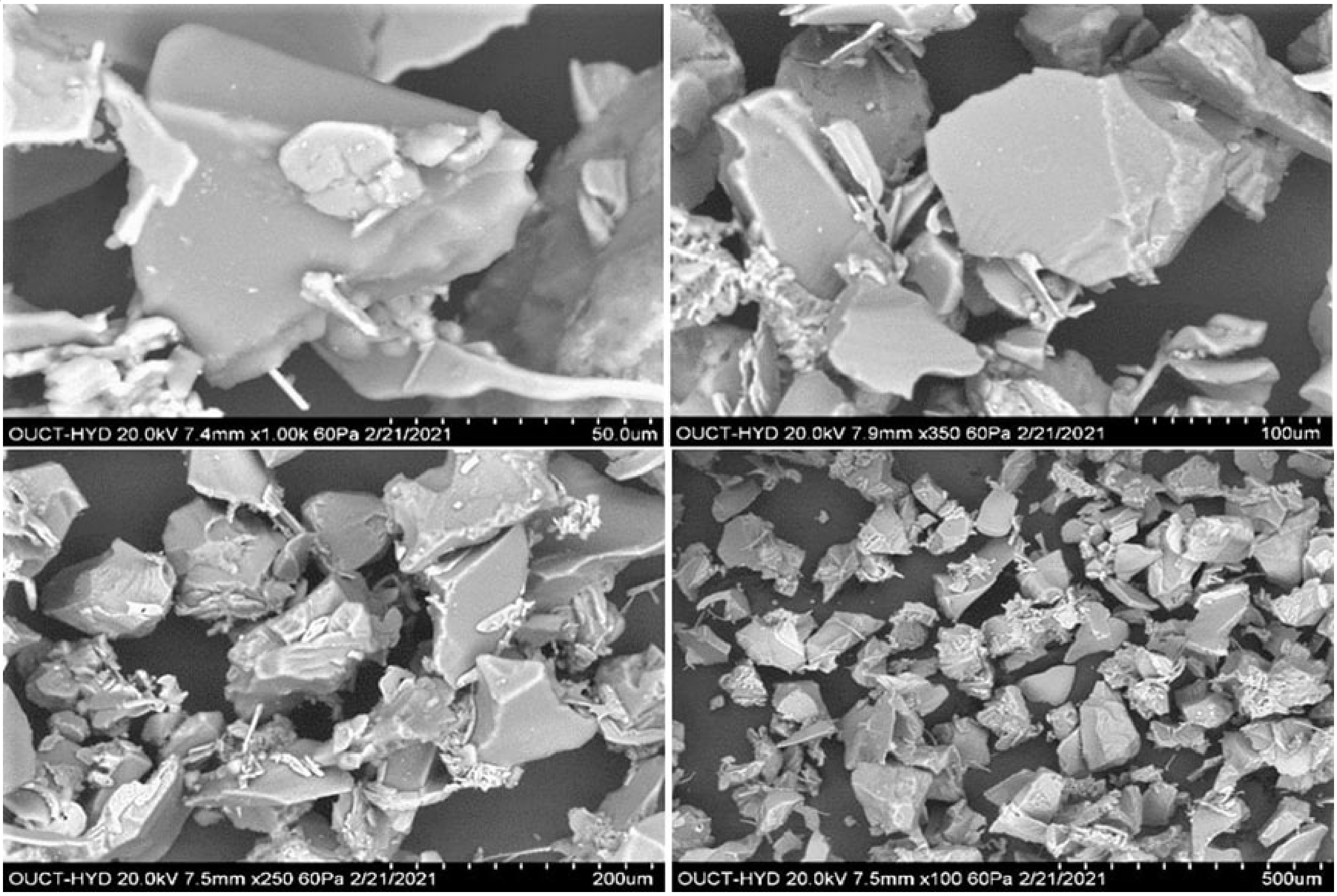


Fig. 1. SEM images and morphology of SiO_2-$KHSO_4$ catalyst under different magnifications

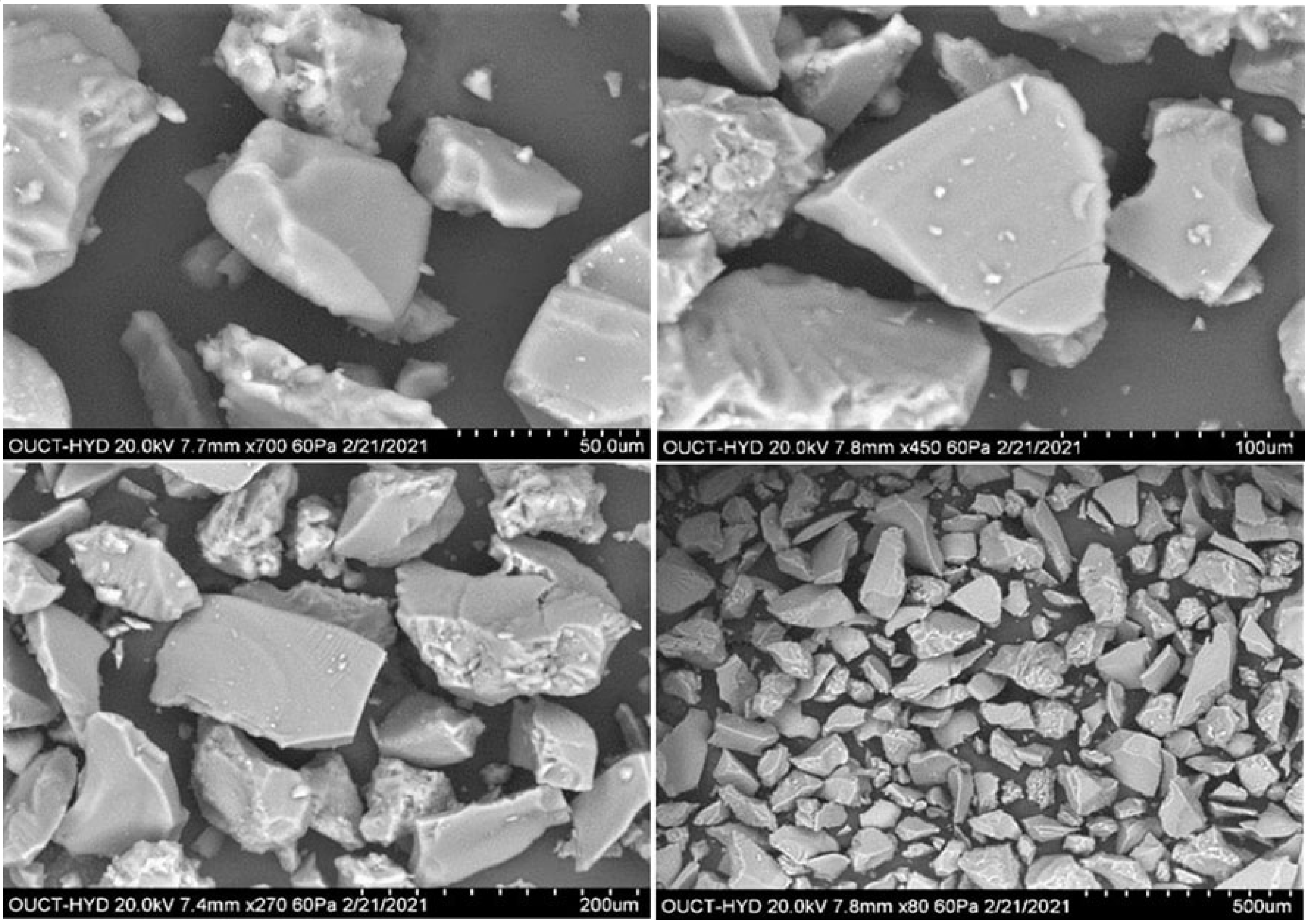
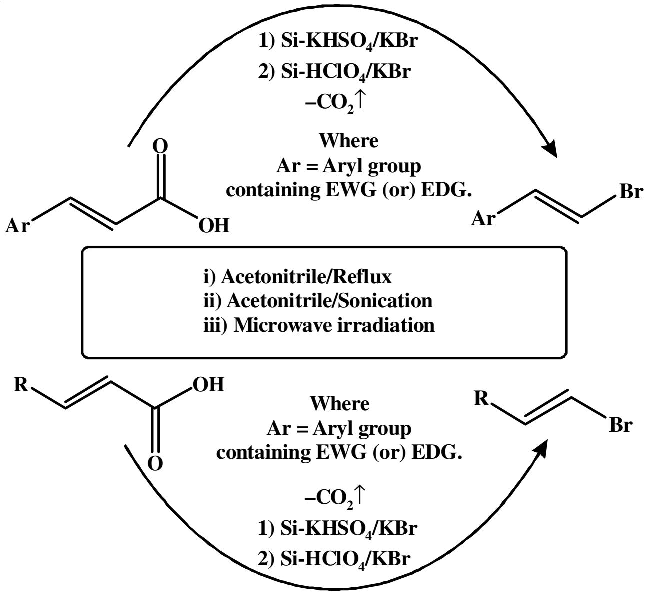


Fig. 2. SEM images and morphology of SiO_2-$HClO_4$ catalyst under different magnifications

crystals and flakes were spread over with nano grain acid species. These results are similar to the earlier findings of Siddiqui [44] and also by our research group [45,46].

Bromodecarboxylation of α,β-unsaturated carboxylic acids into β-bromo styrenes by conventional solvothermal conditions: In a typical solvothermal reaction mixture, 1.10 mmol silica immobilized nanocatalyst (SiO_2-$HClO_4$ or SiO_2-$KHSO_4$) and 1.0 mmol cinnamic acid (α,β-unsaturated carboxylic acid) and 1.0 mmol KBr (1 mmol) along with anhydrous acetonitrile or (dichloroethane-DCE) were suspended into a round bottomed flask and continuously stirred at room temperature till the reaction was completed, as confirmed by TLC. Reactions required about 3-6 h for completion, depending on the nature of the α,β-unsaturated carboxylic acid [47]. Afterwards, the reaction mixture was neutralized with aqueous sodium bicarbonate, followed by addition of ethyl acetate. The organic layer was separated, dried over Na_2SO_4 and purified with column chromatography and evaporated under vacuum to get final product (**Scheme-I**).

Ultrasonically assisted bromo decarboxylation of α,β-unsaturated carboxylic acids into β-bromostyrenes under solvothermal conditions: Reaction mixture was transferred into a clean reaction flask, which was clamped in an ultrasonically assisted benchtop laboratory sonicator bath [48]. Completion of the reaction was made out by TLC, followed by a similar



Schematic representation showing
Si-KHSO$_4$/KBr (and) Si-HClO$_4$/KBr triggered decarboxylative
bromination of aromatic and alephatic α,β-unsaturated carboxylic acids

Scheme-I: SiO_2-$KHSO_4$-KBr, SiO_2-$HClO_4$-KBr mediated bromo decarboxylation of α,β-unsaturated acids under solvothermal, ultrasonic assisted and solvent-free microwave assisted conditions work up procedure for isolation of the final products. Remarkable reduction in the reaction times from (3-6 h) in the solvothermal reactions to few minutes (15-25 min) under ultrasonic assisted sonication reactions, which revealed magnificent reaction rates, which could be attributed to the collapse of cavitation bubbles which were formed during sonication. Literature reports clearly revealed that the collapse of cavitation bubbles *in situ* release large amount of energy, which is responsible for the generation of a large fraction of reactive species than solvothermal reactions causing rate accelerations [49-51].

Solvent free microwave assisted bromodecarboxylation of α,β-unsaturated carboxylic acids into β-bromo styrenes under solvent-free conditions: After preparing the reaction mixture, small amount of silica gel was added in a cleaned beaker. Then, it was placed in a bench mate model, 300 W laboratory microwave oven, till the reaction was completed, as accomplished by TLC. The reaction mixture was then processed for obtaining final products. Highly notable reduction in the reaction times in solvothermal reactions from (3-6 h) to few minutes (3-5 min) in solvent-free microwave assisted reactions. These observations were explained due to the rate accelerations emerging from the selective absorption of microwave energy by polar molecules during microwave (MW) irradiation, while non-polar molecules become inert to the MW dielectric loss at the same time. Further, it is important to note that MW energy is able to heat the target molecules directly uniformly without heating the reaction vessel entire during MW irradiation, which saves time and energy. As a result, enormously higher fraction of molecules are activated causing extraordinary rate accelerations compared to either solvothermal or sonication reactions [51-55].

RESULTS AND DISCUSSION

This work was designed and presented SiO_2-$HClO_4$/KBr and SiO_2-$KHSO_4$/KBr, triggered bromodecarboxylation of α,β-unsaturated carboxylic acids. In first step, the optimized concentrations of both catalysts (SiO_2-$HClO_4$ or SiO_2-$KHSO_4$) in the range of (0.1 to 0.5g) using cinnamic acid as a specific α,β-unsaturated carboxylic acid. Reactions underwent smoothly when 0.5 g of Si-$KHSO_4$ and 0.4 g of Si-$HClO_4$ was used. Beyond these concentrations, reactions did not exhibit an increase in the product yield or reduction in the reaction time (Table-1). Observed results reflected that catalytic activity of SiO_2-$HClO_4$ better than SiO_2-$KHSO_4$ catalyst, which can be explained due to the fact that $HClO_4$ is stronger acid than $KHSO_4$. It is well established in literature that perchlorate ion (ClO_4^-) is a weaker ligand than sulphate (SO_4^{2-}) or bisulphate (HSO_4^-) and favours complete dissociation of $HClO_4$ into the release of proton [H^+]. The conversion yields of ultrasonically assisted decarboxylative bromination of cinnamic acid as presented in Table-1.

Purification and reusability of catalyst: It is of interest to note that both catalysts (SiO_2-$HClO_4$ and SiO_2-$KHSO_4$) could be recycled with a slight reduction in the yield of products. Once the first batch of reaction completed, catalyst was filtered from the reaction mixture, treated with ethylacetate to remove organic traces and dried in an oven at 120 °C for 2-3 h. The as-activated catalyst was reused for another batch of experiments. Similar procedure was adopted for four to five cycles to reusability of the catalyst and related observations are compiled in Table-2.

TABLE-1
CATALYST OPTIMIZATION FOR DECARBOXYLATIVE BROMINATION OF CINNAMIC ACID

Entry	SiO_2-$KHSO_4$		SiO_2-$HClO_4$	
	Amount of catalyst (g)	Yield (%)	Amount of catalyst (g)	Yield (%)
1	0.1	58	0.1	60
2	0.2	69	0.2	78
3	0.3	75	0.3	87
4	0.4	86	0.4	92
5	0.5	90	0.5	92
6	0.6	90	–	–

TABLE-2
REUSABILITY OF SiO_2-$HClO_4$, SiO_2-$KHSO_4$ CATALYSTS IN ULTRASONICALLY ASSISTED BROMO DECARBOXYLATION OF CINNAMIC ACID AT ROOM TEMPERATURE

Reused cycle	SiO_2-$HClO_4$		SiO_2-$KHSO_4$	
	RT (min)	Yield (%)	RT (min)	Yield (%)
Fresh (Ist run)	15	92	17	90
IInd run	17	91	18	88
IIIrd run	18	90	19	87
IVth run	19	89	19	86
Vth run	20	89	20	86

Successful recyclization of the catalysts became driving force for us to take up the study with a series substituted cinnamic acids and certain aliphatic α,β-unsaturated acids. The obtained results are summarized in Table-3. Cinnamic acid derivatives afforded corresponding β-bromo styrenes with high regioselectivity, while aliphatic α,β-unsaturated acids afforded corresponding β-bromo alkenes. The obtained products were detected by spectroscopic methods, such as ^{1}H NMR, IR. The products obtained are similar to those reported earlier in the literature, following Table-4 represents spectroscopic data for some of the products obtained.

Conclusion

In present study, the decarboxylative bromination of α,β-unsaturated carboxylic acids in both conventional (room temperature) and solvent free microwave conditions is demonstrated. KBr was employed as a bromine source and the reaction featuring heterogeneous, reusable catalysts SiO_2-$KHSO_4$/SiO_2-$HClO_4$ make this protocol significantly moderate than the previous reported method.

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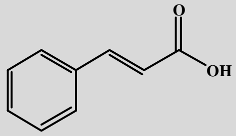
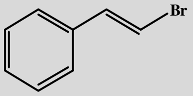
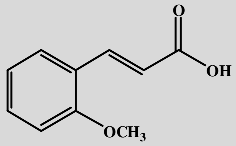
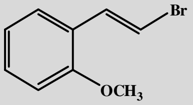
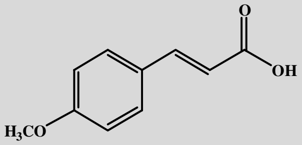
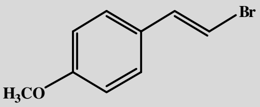
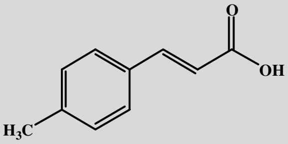
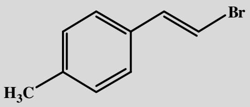
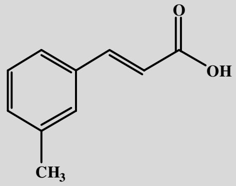
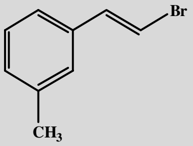
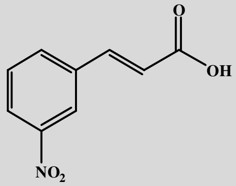
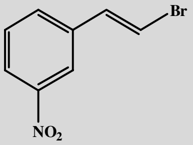
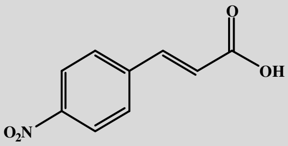
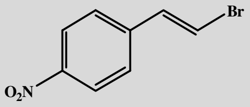
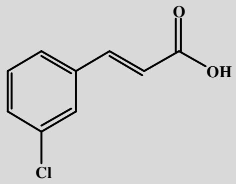
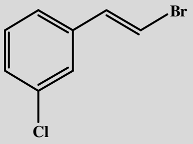
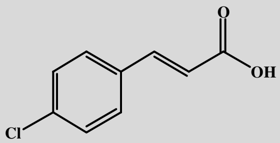
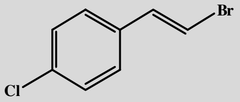
TABLE-3
BROMO DECARBOXYLATIVE OF α,β-UNSATURATED CARBOXYLIC ACIDS USING SiO_2-$HClO_4$ AND SiO_2-$KHSO_4$ CATALYSTS

Substrate	Product	SiO_2-$HClO_4$						SiO_2-$KHSO_4$					
		Solvo-thermal		Ultra-sonication		Micro-wave		Solvo-thermal		Ultras-onication		Micro-wave	
		RT (h)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (h)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)
		3	93	15	92	3	94	3	91	17	90	3	92
		4.5	88	20	85	3.5	89	5	86	21	83	4	88
		5	85	17	85	4	87	6	84	19	84	5	86
		3	91	15	87	3	93	4	90	17	85	3	91
		3.5	89	16	84	4	90	4.5	88	17	83	3	88
		5.5	84	13	82	4	85	6	83	15	81	5	87
		5	85	18	80	4	87	6	84	16	80	5	86
		4.5	84	19	80	4.5	87	5	83	21	80	5	85
		5	82	15	80	3.5	84	6	80	17	79	4	83

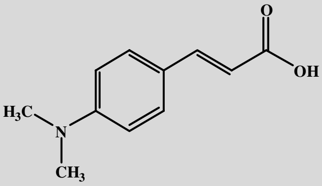
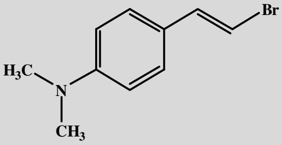
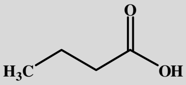
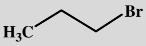
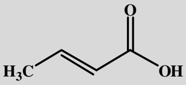
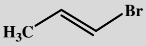
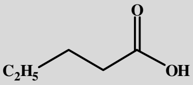
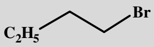
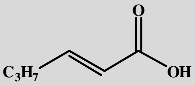
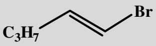
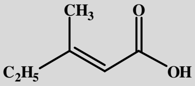
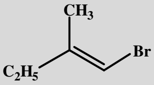
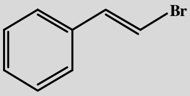
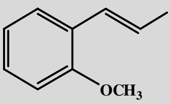
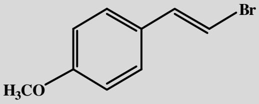
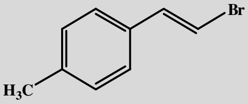
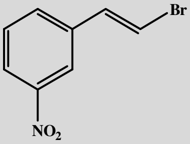
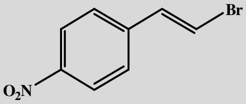
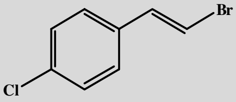
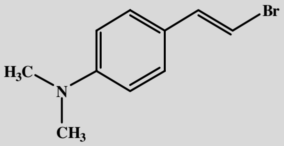
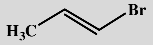
		5.5	84	25	82	4.5	86	6	82	25	80	5	84
		5	83	21	80	4	85	5	83	23	79	4	85
		6	85	14	82	4.5	87	6	85	18	81	5	87
		5	88	16	83	3.5	89	5	87	20	82	4	88
		5	85	14	84	3.5	88	6	83	19	84	3	87
		6	82	20	79	4	87	6	80	24	78	4	85

TABLE-4
SPECTROSCOPIC DATA OF SOME SYNTHESIZED PRODUCTS

Product	Spectroscopic data
 1-Bromo 2-phenyl alkene	^{1}H NMR ($CDCl_3$): δ (ppm) 6.77 (1H, d), 7.12 (1H, d), 7.32-7.74 (5H, m). IR (cm^{-1}): 1596, 1492, 3026, 750. MS (70eV, EI): *m/z* (%) = 182 [M$^+$], 107, 103, 91, 77, 51, 50. Yields: With SiO_2-$HClO_4$ = 92% (Ultra.), 93% (Micro.), With SiO_2-$KHSO_4$ = 90% (Ultra.), 92% (Micro.).
 1-Bromo 2-[2-methoxy phenyl]alkene	^{1}H NMR ($CDCl_3$): δ (ppm) 3.86 (3H, s), 6.87 (1H, d), 6.90 (1H, d), 6.91 (1H, d), 7.24-7.27 (2H, m), 7.31 (1H, d). IR (cm^{-1}): 1565, 1610, 1160, 785. Yields: With SiO_2- $HClO_4$ = 85% (Ultra.), 89% (Micro.), With SiO_2-$KHSO_4$= 83% (Ultra.), 88% (Micro.).
 1-Bromo 2-[4-methoxy phenyl]alkene	^{1}H NMR ($CDCl_3$): δ (ppm) 3.66 (3H, s), 6.54 (1H, d, J=8.1 Hz), 6.62 (1H, d), 6.79 (2H, d), 7.04-7.14 (2H, d). IR (cm^{-1}): 1606, 1533, 1215, 760. MS (70eV, EI): *m/z* (%) = 212 [M$^+$], 197, 169, 133, 118, 102, 90, 69, 63, 51. Yields: With SiO_2- $HClO_4$ = 85% (Ultra.), 87% (Micro.), With SiO_2-$KHSO_4$= 84% (Ultra.), 86% (Micro.).
 1-Bromo 2-[4-methyl phenyl]alkene	^{1}H NMR ($CDCl_3$): δ (ppm) 2.30 (3H, s), 6.70 (1H, d), 6.99 (1H, d), 7.16 (2H, d), 7.18 (2H, d). IR (cm^{-1}): 1600, 1520, 790. MS (70eV, EI): *m/z* (%) = 196 [M$^+$], 117, 91, 58, 39. Yields: With SiO_2- $HClO_4$ = 87% (Ultra.), 93% (Micro.), With SiO_2-$KHSO_4$= 85% (Ultra.), 91% (Micro.).
 1-Bromo 2-[3-nitro phenyl]alkene	^{1}H NMR ($CDCl_3$): δ (ppm) 6.64 (1H, d), 7.16 (1H, d) 7.55 (1H, t), 7.91 (1H, d), 8.11 (1H, m), 8.51 (1H, s). IR (cm^{-1}): 1606, 1512, 1265, 760. Yields: With SiO_2- $HClO_4$ = 82% (Ultra.), 85% (Micro.), With SiO_2-$KHSO_4$= 81% (Ultra.), 87% (Micro.).
 1-Bromo 2-[4-nitro phenyl]alkene	^{1}H NMR ($CDCl_3$): δ (ppm) 6.61-6.75 (1H, d), 7.11-7.25 (1H, d), 7.75-7.89 (2H, d), 8.20-8.35 (2H, d). IR (cm^{-1}): 1595, 1535, 1345, 780. Yields: With SiO_2- $HClO_4$ = 80% (Ultra.), 87% (Micro.), With SiO_2-$KHSO_4$= 80% (Ultra.), 86% (Micro.).
 1-Bromo 2-[4-chloro phenyl]alkene	^{1}H NMR ($CDCl_3$): δ (ppm) 6.38-6.65 (1H, d), 6.84-6.96 (1H, d), 7.26-7.39 (2H, d), 7.56-7.76 (2H, d). IR (cm^{-1}): 1610, 1590, 1015, 945, 785. Yields: With SiO_2- $HClO_4$ = 80% (Ultra.), 84% (Micro.), With SiO_2-$KHSO_4$= 79% (Ultra.), 83% (Micro.).

 1-Bromo 2-[4-*N,N*-dimethyl phenyl]alkene	^{1}H NMR ($CDCl_3$): δ (ppm) 6.42 (1H, d), 6.85 (1H, d), 7.20-7.35 (2H, d), 7.64-7.72 (2H, d). IR (cm^{-1}): 1610, 1335, 790. Yields: With SiO_2- $HClO_4$ = 82% (Ultra.), 86% (Micro.), With SiO_2-$KHSO_4$= 80% (Ultra.), 84% (Micro.).
 1-Bromo 2-methyl alkene	^{1}H NMR ($CDCl_3$): δ (ppm) 1.67 (3H, d), 5.85 (1H, d), 6.03 (1H, m). IR (cm^{-1}): 1596, 3025, 760. Yields: With SiO_2- $HClO_4$ = 80% (Ultra.), 85% (Micro.), With SiO_2-$KHSO_4$= 79% (Ultra.), 85% (Micro.).

CONFLICT OF INTEREST

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

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