SILTY CLAY-CONTAINING SOIL CATALYZED MICROWAVE ASSISTED MULTICOMPONENT SYNTHESIS OF OCTAHYDROQUINAZOLINONE DERIVATIVES

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Keywords: Octahydroquinazolinones; microwave-assisted synthesis; multicomponent synthesis; heterogeneous silt catalyst.

An efficient protocol was developed for the synthesis of octahydroquinazolinone derivatives in presence of silty clay-containing soil in solvent free conditions under microwave irradiation. The isolated products were characterized by FTIR, ^{1}HNMR and ^{13}C NMR spectroscopy. The catalyst was characterized by wet chemical analysis, SEM, EDS, XRD and IR spectroscopy.

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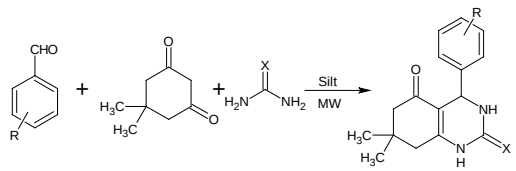
Introduction

Octahydroquinazolinone derivatives is an important class of organic compounds because of their pharmacological activities such as antihypertensive,[1] antibacterial,[2,3] antitumor,[4] anti-inflammatory etc.[5] Multicomponent reactions (MCRs) have apparently been a route to the synthesis of large number of complex molecules from readily available building blocks.[6]Octahydroquinazolinones synthesis is a modified Biginelli reaction.[1] Octahydroquinazolinone have been synthesized using aromatic aldehydes, dimedone and urea/thiourea in presence of various catalysts such as montmorillonite,[7] zeolites,[8] boron compounds,[9] $Zn(OTf)_2$,[3] conc. H_2SO_4,[10] ionic liquids,[11] ion exchange resins,[12] Trimethyl silyl chloride,[13] Nafion-H,[14] $VOSO_4$,[15] conc. HCl,[16] $Fe(NO_3).9H_2O$,[17] silica sulfuric acid,[18]t-BuOK,[19] TiO_2,[20] ammonium metavanadate,[21] $Cu(OTf)_2$,[22]phosphotungstic acid nanoclusters,[23] $BMI.InCl_4$,[24] SiO_2-$NaHSO_4$,[25] ZnO_2 nanoparticles,[26]phytic acid,[27] lanthanum oxide,[28] Naion-Ga,[29] CuS QDs,[30] $ZrOCl_2.8H_2O$,[31] Cu/SiO_2,[32] β-cyclodextrin, aqueous hydrotropic solution of Na-p-Toluene sulfonic acid under microwave irradiation (MW),[33] $BF_3.SiO_2$,[34] Aluminate Sulfonic Acid Nanoparticles,[35] Ion exchange resin Nafion[12] $H_4CuPW_{11}O_{39}$,[36] polyvinyl polyvinylpolypyrrolidine supported chlorosulfonic acid,[37]and molybdenum based heterogeneous catalysts ($MoO_2(acac)_2$ on zeolite)[38] under MW irradiation.[39]



Scheme1. Synthesis of Octahydroquinazolinones using silt catalyst

Experimental

All the chemicals used without further purification and were of AR grade. Microwave irradiation was done in RAGA'S Scientific Microwave system. Synthesized products were characterized by IR, ^{1}HNMR and ^{13}C NMR spectroscopy data and melting points. Melting points were recorded in an open capillary and were uncorrected. IR spectra were recorded using Perkin-Elmer spectrometer with ATR technology. ^{1}HNMR and ^{13}C NMR spectra were recorded on 500MHz Bruker FT-NMR spectrometer using $CDCl_3$ solvent.

Catalyst preparation

The silty soil collected from bed of Godavari River, Kopargaon, A.Nagar, India. The silt is naturally available granular brown colour material having particle size (0.05-0.002mm), it may occur as soil. Chemical composition of collected silty soil was calculated by wet chemical analysis method reported in Table1.

Table 1. Siltysoilcompositionbywetchemicalanalysis

Constituent	Silty clay-containing soil %
sand	41.93
clay	19.35
silt	38.70

Activation of silt

Received silty clay-containing soil was sieved through different mesh sizes to remove any coarse material and to get uniform particle. This silty clay containing soil was kept at temperature of 400°C in silica crucible for 1h in an electric oven for activation and used as siltyclay-containing soil catalyst for investigation. The average diameter of silty-clay-containing soil used is about 50 µm (Figure 1)

General procedure for the synthesis of octahydroquinazolinones under MW

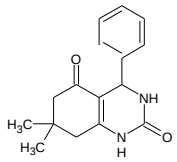
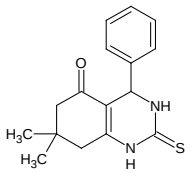
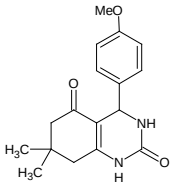
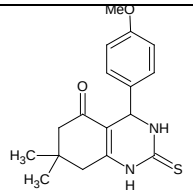
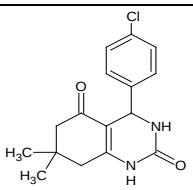
Synthesis of octahydroquinazolinones were done using a mixture of aromatic aldehyde (1.0 mmol), dimedone (1.0

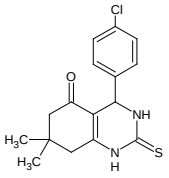
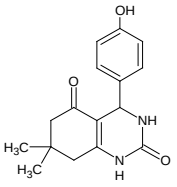
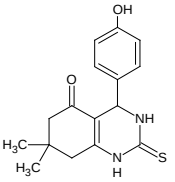
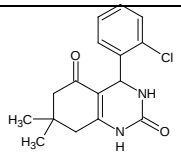
Table 2. Optimization of reaction conditions from 4-chlorobenzaldehyde, dimedone and urea

Entry	Catalyst / Solvent	Condition	Reaction time, min	[a]Yield, %
1	Nocatalyst/$CHCl_3$	R.T	180	NoReaction
2	Nocatalyst/$CHCl_3$	Reflux	180	22
3	Catalyst (20 wt%)/$CHCl_3$	Reflux	60	62
4	Catalyst (20 wt%)/EtOH	Reflux	60	73
5	Nocatalyst/---	MW 240 W	35	36
6	Nocatalyst/---	MW 300 W	30	48
7	Catalyst (20 wt%)/EtOH	MW 300 W	20	82
8	Catalyst (20 wt%)/---	MW 240 W	20	80
9	Catalyst (10 wt%)/---	MW 300 W	20	78
10	Catalyst (20 wt%)/---	MW 300 W	20	94

ReactionCondition: 4-chlorobenzaldehyde (1.0 mmol), dimedone (1.0 mmol), urea (1.2 mmol) and silty-soilcatalyst

Table 3. Synthesis ofoctahydroquinazolinonecatalyzedbysiltyclay-containingsoilfrombenzaldehydes, urea (thiourea) and dimedone

Entry	R in RC_6H_4CHO	X in $(H_2N)_2C=X$	Product	Reaction time, min	Yield, %[a]	M.P.	
						Found	Literature
4a	H	O		10	96	96	291
4b	H	S		15	86	218	218-219
4c	4-MeO	O		15	89	246	246-247
4d	4-MeO	S		20	80	275	273-275
4e	p-Cl	O		20	94	301	304-306

4f	p-Cl	S		15	87	290	288-290
4g	p-OH	O		15	90	301	300-302
4h	p-OH	S		20	86	280	--
4i	o-Cl	O		15	89	284	282-285

mmol) and urea/thiourea (1.5 mmol) and silt (20 wt %) taken in round bottom flask and kept in MW at 300 W for required time (Table 3). The progress of reaction was monitored by thin layer chromatography using ethyl acetate: hexane solvent system. On completion of reaction, the reaction mass was filtered and concentrated. Isolation of catalyst and purification of product was done by recrystallisation using ethanol (Scheme1).Results and discussion

Catalyst has been characterized using XRD, FTIR, SEM and EDS, techniques.

X-ray diffraction analysis

To determine various minerals present in silt soil, X-ray diffraction study was carried out on Philips, Holland X-ray diffractometer. The XRD of the silty clay-containing soil is given in the supplementary material. By correlating the results with JCPDS database, silt consists of components having SiO_2, Al_2O_3, Fe_2O_3, TiO_2, potassium, sodium, magnesium and calcium oxide building components (Figure 2).[40-45]

S. No.	Component	%
1	SiO_2	38
2	Al_2O_3	19
3	Fe_2O_3	9
4	TiO_2	5
5	K_2O	2
6	Na_2O	3
7	CaO	1

SEM and EDS analysis

The study of morphology and elemental composition was carried out by Scanning Electron Microscopy and Energy Dispersive Spectroscopy. The electron microphotographs were recorded on JEOL-JSM-6360A operating at 20KV. The catalyst sample is analyzed under SEM at different magnification. Figure 3 shows silty clay containing soil morphologies which contains oxygen, Na, Mg, Al, Si, Cl, K, Ca, Ti, Fe. The scanning electron microphotograph of silt shows the particle size to be around 50µm. The typical aggregate structure of material has been observed.

Infrared spectroscopy (FT-IR)

FT-IR study of catalyst was done to confirm presence of silica, iron and aluminum. The distinct band at 3612.7cm^{-1} and 3621cm^{-1} indicate existence of isolated OH group of Si and Al. The band at 462.02 cm^{-1} indicates O-Si-O bending mode whereas band at 1185.80 cm^{-1}, 992.06 cm^{-1}, 797.45 cm^{-1} signify occurrence of Si-O-Fe, Al-OH and Fe-OH vibrations, respectively. The bands at 536.84 cm^{-1}, and 451.85 cm^{-1} are due to Fe-O bond stretching.

Optimization of reaction conditions

Optimization of reaction conditions were done on model reaction of benzaldehyde (1mmol), dimedone (1mmol) and urea (1.2mmol), with silt catalyst under microwave irradiation. It is represented in Table 2.The generability of this method was studied by performing the reaction of several substituted aromatic aldehyde, dimedone and

urea/thiourea using silt as a catalyst under MWI without solvent. The results are summarized in Table 3.

Spectral data

4a:4-Phenyl-7,7-dimethyl-1,2,3,4,5,6,7,8-octahydroquinazoline-2,5-dione, M.p.: 291 ^{0}C, FT-IR (cm^{-1}): 3380, 3260, 3130, 2940, 1697, 1620, 1455, ^{1}H NMR (500 MHz, DMSO-d_6, TMS, ppm):0.89 (s, 3H, -CH_3), 1.02(s, 3H, -CH_3), 2.01-2.04 (d, 1H, CH, J=13HZ), 2.18-2.21 (d, 1H, CH, J=13 Hz), 2.25-2.29 (d, 1H, CH, J=13 Hz), 2.39-2.43(d, 1H, CH, J=13 Hz), 5.15(s, 1H, CH), 7.20-7.24 (m, 3H, ArH), 7.29-7.32 (m, 2H, ArH), 7.76 (bs, 1H, NH), 9.4 (bs, 1H, NH) ^{13}C NMR (DMSO-d_6, TMS, ppm): 27.30, 29.22, 32.76, 50.28, 52.43, 107.86, 126.69, 127.59, 128.77, 145.10, 152.39, 152.85, 193.33.

4e: 4-(4-Chlorophenyl)-7,7-dimethyl-4,6,7,8-tetrahydroquinazoline-2,5(1*H*,3*H*)-dione, M.p.:301 ^{0}C, FTIR (cm^{-1}): 3320, 3242, 2960, 1705, 1670, 1613, 1488, 1418 ^{1}H NMR (TMS, ppm): 0.88 (s,3H,-CH_3), 1.01 (s,3H,-CH_3), 2.01-2.04(d, 1H, CH, J=13 Hz), 2.17-2.21(d, 1H, CH, J=13 Hz), 2.25-2.28 (d, 1H, CH, J=13 Hz), 2.39-2.42 (d, 1H, CH, J=13 Hz), 5.15(s, 1H, CH), 7.24-7.25 (d, 2H, ArH, J=6.76 Hz), 7.37-7.39 (d, 2H, ArH, J=6.7 Hz), 7.80 (s, 1H, NH), 9.52 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, TMS, ppm): 27.31, 29.16, 32.75, 50.23, 51.94, 107.48, 128.59, 128.76, 132.07, 144.06, 152.21, 153.03, 193.35.

4i: 4-(2-Chlorophenyl)-7,7-dimethyl-4,6,7,8-tetrahydroquinazoline-2,5(1*H*,3*H*)-dione, M.P.:284 ^{0}C FTIR (cm^{-}1): 3253, 3090, 2953, 1698, 1640, 1430, 1372, ^{1}H NMR: 0.96 (s, 3H, -CH_3), 1.03 (s, 3H, -CH_3), 1.97-2.00 (d, 1H, CH, J=13 Hz), 2.15-2.18 (d, 1H, CH, J=13HZ), 2.31-2.34 (d, 1H, CH, J=13Hz), 5.56 (s, 1H, CH), 7.23-7.32 (m, 3H, ArH), 7.38-7.39 (m, 1H, ArH), 7.7 (s, 1H, NH), 9.5 (s, 1H, NH) ^{13}C NMR (DMSO-d_6, TMS, ppm): 27.52, 29.19, 32.71,50.26, 51.08, 106.29, 127.87, 129.42, 129.88, 129.99, 132.33, 141.68, 151.54, 153.50, 193.08.

Conclusion

The most important advantage of this method is use of naturally available, economical and competent silt catalyst. It works without solvent under microwave irradiation in short time. This implicates fruitful addition to the non-conventional methods for the synthesis of octahydroquinazolinone derivatives.

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