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ENVIRONMENTAL FRIENDLY SYNTHESIS OF 1-(2-AMINO-5-(2, 3, 4-SUBSTITUTEDPHENYL)THIAZOL-4-YL)ETHAN-1-ONE UNDER AQUEOUS CONDITION

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ABSTRACT:

Environmentally benign low cost synthesis of some biologically important derivatives of 1-(2-amino-5-(2,3,4-substitutedphenyl)thiazol-4-yl)ethan-1-one (4) by mechanochemical methods were carried out using the naturally obtained CaO as a base catalyst from 2-bromo-1-(2,4-dichlorophenyl)but-3-yn-1-one (1) and substituted Thioureas. The reactions were performed in the aqueous medium. The structures of all synthesized compounds were established on the basis of elemental analysis, IR, NMR and Mass spectral data.

KEYWORDS: *Environmentally benign, low cost, naturally obtained base catalyst, aqueous medium, CaO.*

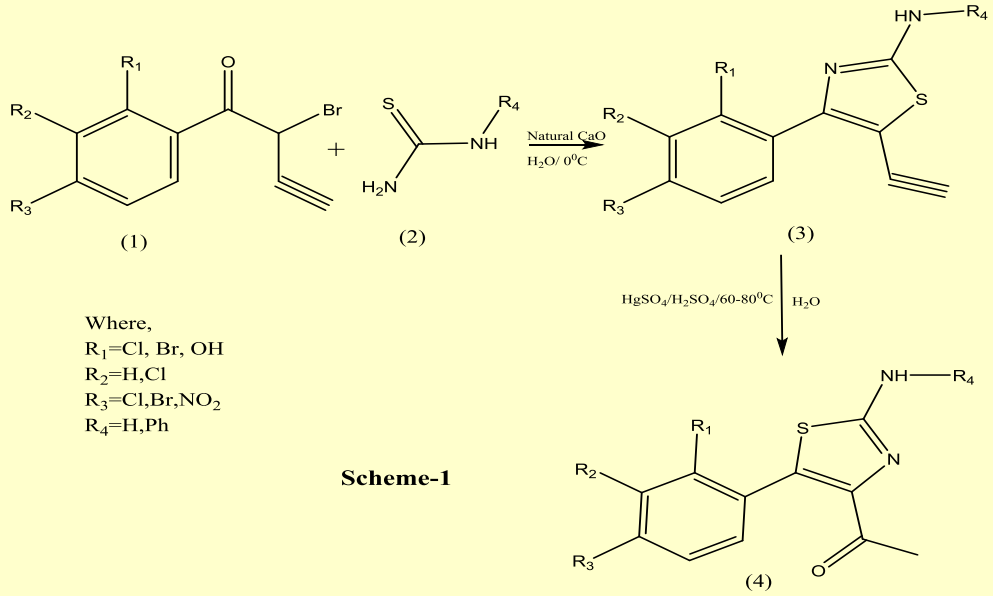
INTRODUCTION:

Thiazole is nitrogen and sulphur containing heterocyclic compound. The compounds co taining nitrogen and sulphur are pharmaceutical and biologically active. 1, 3-Thiazole is an important five membered heterocyclic compounds having nitrogen and sulphur as hetero atom present at 1 and 3 position. It is pale yellow liquid having molecular

formula C_3H_3NS. This ring is observed in most of the naturally occurring biochemicals like vitamins thiamine B_1. Thiazole comprises[1] the important class of heterocyclic compounds showing the potent biological activities. It was observed that this compound have remarkable role in drug development. It is the remedies for inflammation, hypertension, allergies, bacterial, HIV infections, schizophrenia, and hypnotics and for the treatment of various types of pain. Drug like properties of some compounds bearing thiazole ring includes Abafungin (antifungal drug) with trade name Abasol cream, Bleomycine, Sulfathiazol (antimicrobial drug), Ritonavir (antiretroviral drug), and Tiazofiirin (antineoplastic drug). In addition to this substituted derivative of thiazole posseses antimicrobial[2], antibacterial[3-4], antiviral[5], antidiuretic, antihelmintic, anti-inflammatory[6], antitubercular, analgesic[7], fibrinogen receptor antagonists with antithrombotic activity, fluorescent and luminescent activities, inhibitors of bacterial DNA gyrase B. some of the notable activities of thiazole[8] derivatives includes antihypertensive, anesthetic, sedative, anti-thrombotic bacteriostatic and fungistatic. Thiazole and its derivatives[9-12] also possess the properties of anticancer activities and some of the anticancer drug containing Thiazole ring is includes thiazofurine, sulfathiazole, bleomycin and dasatinib etc.

Knowing the importance of the thiazole derivatives in diverse field its synthesis becomes the prime importance. Huge methods of synthesis of these biologically important compounds are available in the literature. The thiazole molecule were first synthesize by Hantzsch[13]in 1887 from alpha haloketones and thiourea or thioamides this reaction regarded as Hantzsch thiazole synthesis. Later on numbers of alternative methods[14-15] were added in the synthesis of different thiazole derivatives. In spite of above methods some microwave assisted methods without using solvents were reported.[16-18] sulfuryl chloride, chlorosulfonic acid, thionyl chloride, sulfur monochloride, sulfur trioxide, sulfuric acid, nitric acid, and sulfur are the promising oxidizing agent for the preparations of 2-amino-4-phenylthiazole[19] derivatives from acetophenone and thioureas.

The synthesis of 1-(2-amino-5-(2,3,4-substitutedphenyl)thiazol-4-yl)ethan-1-one (4) were carried out by the treatment of 2-bromo-1-(2,4-dichlorophenyl)but-3-yn-1-one (1) and substituted Thioureas in aqueous condition using the calcinated egg cell as a basic catalyst. The intermediate obtained are further treatment with the $HgSO_4$ and H_2SO_4 the acetylene group converted into the carbonyl group gives the desired products **(Scheme-1)**.



Where,
R_1=Cl, Br, OH
R_2=H,Cl
R_3=Cl,Br,NO_2
R_4=H,Ph

Scheme-1

Figure 1. Scheme of synthesis of target compounds

METHODS:

All chemicals used were of AR grades. The chemical used for all these works were purchased from research lab fine chemical industry, Mumbai. The melting points of all the synthesized compounds were recorded using hot paraffin bath. The Carbon and Hydrogen analysis were carried out on Carlo-Ebra 1106 analyser. Nitrogen estimation was carried out on Colman-N-analyzer-29. IR spectra were recorded on Bruker neo. Ltd. spectrometer in the range 4000-400 cm^{-1} in KBr pellets. NMR spectra were recorded on Brucker AC-500F spectrometer with TMS as internal standard using $CDCl_3$ as solvent. Mass spectra were recorded on shimadzu 2010s Mass spectrometer. The purity of compound was checked on silica Gel-G plates by TLC with layer thickness of 0.3 mm.

PREPARATION OF CATALYST- CALCINATED EGG CELL NATURAL CaO

Approximately 94% of a dry eggshell is calcium carbonate and has a typical mass of 5.5 grams waste egg shells were collected and washed to remove the undesirable sticky material with plenty of water. Then place the cleaned egg shell in the oven to dry completely. Crush the dried egg shell in mortar and pestle to a fine powder. Then introduce the powder in muffle furnace to calcinate at 900^0C, after heating 2-3 hour thermal decomposition of Egg Shell (calcium carbonate) gives a white soft powder, calcinated egg cell (CES).

CHARACTERISATION OF CATALYST BY XRD: XRD of CES is compared with XRD of CaO, which shows the formation of CaO from calcinations of egg Shell.

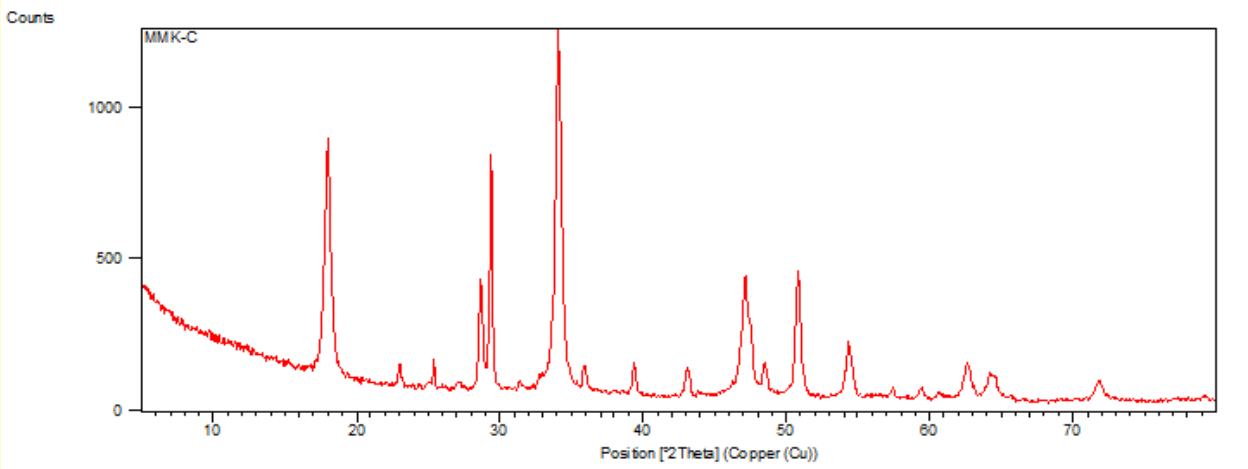


Figure 2.1 XRD of CaO

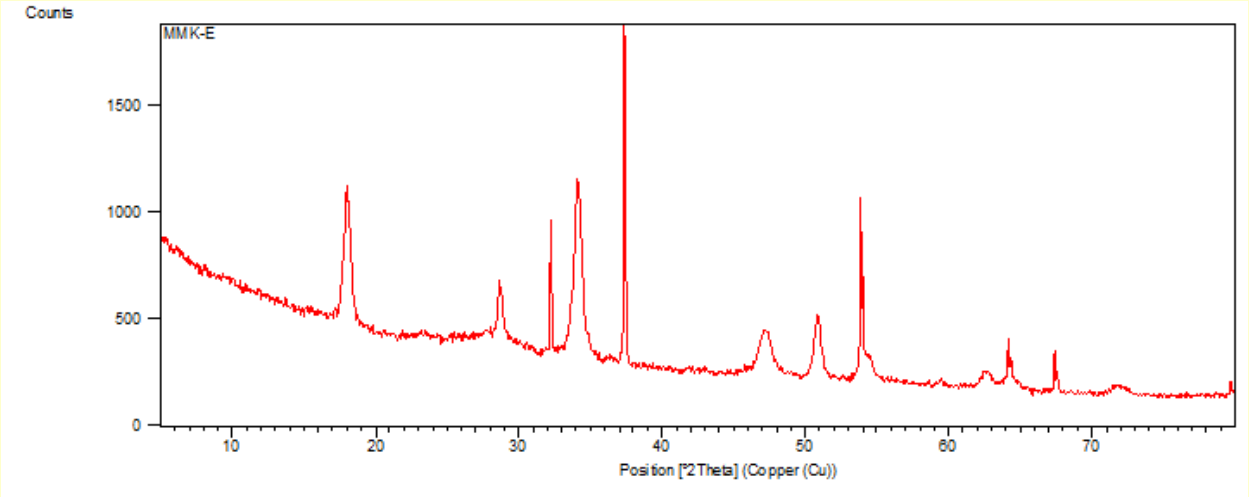


Figure 2.2 XRD of CES

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RESULT S:

Synthesis of 2-bromo-1-(2, 4-dichlorophenyl)but-3-yn-1-one (1a)

This compound was synthesized by known method of bromination from 1-(2,4-dichlorophenyl)but-3-yn-1-one 0.01 M 1-(2, 4-dichlorophenyl)but-3-yn-1-one was dissolved in 10 ml acetic acid in 100 mol Round bottom flask. Keep the Round bottom flask in ice containing water bath on magnetic stirrer. Prepare the mixture of 0.01M bromine in 0.5ml acetic acid and take in separating funnel. Add the above brominating mixture drop by drop with constant stirring. Keep the temperature near about 0^0C until complete addition of brominating mixture. After the addition of brominating mixture keep the reaction mixtures stirring for 1h. Dissolve

the reaction mixture ice cold water to get the product 2-bromo-1-(2,4-dichlorophenyl)but-3-yn-1-one (1) dried and used for further reaction.

Procedure for synthesis of 1-(2-amino-5-(2,4-dichlorophenyl)thiazol-4-yl)ethan-1-one (4a)

0.01M corresponding thiourea and 40 mol% of CaO obtained from calcinations of egg cell were taken in mortar and the mixture was mechanically cruses with help of pestle until the reaction mixture becomes homogeneous. This homogeneous reaction mixture was transferred into the round bottom flask. Add 10 ml of water and 0.01M 2-bromo-1-(2,4-dichlorophenyl)but-3-yn-1-one (1a) and mix with mechanical shaking. The mixture was stirred for two hour on water bath at 0^0C the completion for reaction was monitored by TLC (ethylaceate : N-hexane = 50:50) the brown yellow colored reaction mixture was poured into saturated solution of sodium thiosulphate, the separated solid product was filtered and washed with distilled water dried and recrastalised from ethyl alcohol.

0.01M 4-(2,4-dichlorophenyl)-5-ethynylthiazol-2-amine (3a), 1% $HgSO_4$ 1M and 40% H_2SO_4 Solution 1M were taken in 10 ml distilled water heated at 60-80^0C for 1h. the completion for reaction was monitored by TLC (ethylaceate : N-hexane = 70:50) the yellow brown yellow colored reaction mixture was poured into ice cold water, the separated solid product was filtered and washed with distilled water dried and recrystalized from ethyl alcohol.
The yield of the dried crude product was found to be 80%
Melting Point: - 118^{o}C
Colour of compound (4a) – Yellow brown Crystalline solid

Molecular Weight: 272.1
m/z: 270.9 (100.0%), 272.9 (63.9%), 272.0 (10.8%), 274.9 (10.2%), 274.0 (6.9%), 272.9 (4.5%), 274.9 (2.9%), 275.9 (1.1%) Analysis: C, 44.00%; H, 1.90%; Cl, 25.98%; N, 10.32; S, 11.80%.IR (KBr, cm^{-1}): 3333.32cm^{-1}, 3151.12 cm^{-1}, 1615.20 cm^{-1}, 1725 cm^{-1}, 1245.79 cm^{-1}, 3043.12 cm^{-1}, 1446.35 cm^{-1}, 723.71 cm^{-1}. 1H NMR (500 MHz, $CDCl_3$): δ 6.61(s, 2H,-NH_2), δ 2.17(s,3H,-CH_3), δ7.25 -7.76(s,3H,Ar-H)

Procedure for synthesis of 1-(2-amino-5-(3-bromo-2,4-dichlorophenyl)thiazol-4-yl)ethan-1-one (4b)

0.01M corresponding thiourea and 40 mol% of CaO obtained from calcinations of egg cell were taken in mortar and the mixture was mechanically cruses with help of pestle until the reaction

mixture becomes homogeneous. This homogeneous reaction mixture was transferred into the round bottom flask. Add 10 ml of water and 0.01M 2-bromo-1-(3-bromo-2,4-dichlorophenyl)but-3-yn-1-one (1b) and mix with mechanical shaking. The mixture was Stirred for 2.5 hour on water bath at 0^0C the completion for reaction was monitored by TLC (ethylaceate : N-hexane = 70:50) the dark yellow colored reaction mixture was poured into saturated solution of sodium thiosulphate, the separated solid product was filtered and washed with distilled water dried and recrastalised from ethyl alcohol.

0.01M 4-(3-bromo-2,4-dichlorophenyl)-5-ethynylthiazol-2-amine (3b) 0.01M, 1% $HgSO_4$ 1M and 40% H_2SO_4 Solution 1M were taken in 10 ml distilled water heated at 60-70^0C for 1h. the completion for reaction was monitored by TLC (ethylaceate : N-hexane = 70:50) the dark yellow colored reaction mixture was poured into ice cold water, the separated solid product was filtered and washed with distilled water dried and recrastalised from ethyl alcohol.

The yield of the dried crude product was found to be 71%
Melting Point: - 158^{o}C
Colour of compound (4b) – Dark Yellow Crystalline solid

Chemical Formula: $C_{11}H_7BrCl_2N_2OS$,Molecular Weight: 366.1, m/z: 363.9 (100.0%), 365.9 (97.3%), 365.9 (63.9%), 367.9 (62.2%), 364.9 (11.9%), 366.9 (11.6%), 367.9 (10.2%), 369.9 (9.9%), 366.9 (7.6%), 368.9 (7.4%), 365.9 (4.5%), 367.9 (4.4%), 367.9 (2.9%), 369.9 (2.8%), 368.9 (1.2%), 370.9 (1.2%),Analysis: C, 36.00%; H, 1.90%; Br, 21.84%; Cl, 18.98%; N, 7.50%; S, 8.79% IR (KBr, cm^{-1}): 3345 cm^{-1}, 1659.22 cm^{-1}, 1260.28 cm^{-1}, 2899.70 cm^{-1}, 1345.11 cm^{-1}, 737.31 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (s, 2H,-NH_2), δ 2.48(s,3H,-CH_3), δ7.49 - 7.70(s,3H,Ar-H).

Procedure for Synthesis of 1-(2-amino-5-(2,4-dichloro-3-nitrophenyl)thiazol-4-yl)ethan-1-one(4c)

0.01M corresponding thiourea and 40 mol% of Cao obtained from calcinations of egg cell were taken in mortar and the mixture was mechanically cruses with help of pestle until the reaction mixture becomes homogeneous. This homogeneous reaction mixture was transferred into the round bottom flask. Add 10 ml of water and 0.01M 2-bromo-1-(2,4-dichloro-3-nitrophenyl)but-3-yn-1-one (1c) and mix with mechanical shaking. The mixture was stirred 2 hour on water bath at 0^0C. the completion for reaction was monitored by TLC (ethylaceate : N-hexane = 70:50) the dark yellow colored reaction mixture was poured into saturated solution

of sodium thiosulphate, the separated solid product was filtered and washed with distilled water dried and recrastalised from ethyl alcohol.

0.01M 4-(2,4-dichloro-3-nitrophenyl)-5-ethynylthiazol-2-amine (3c) 0.01M, 1% $HgSO_4$ 1M and 40% H_2SO_4 Solution 1M were taken in 10 ml distilled water heated at 60-80^{0}C for 1h. the completion for reaction was monitored by TLC (ethylaceate : N-hexane = 70:50) the dark yellow colored reaction mixture was poured into ice cold water, the separated solid product was filtered and washed with distilled water dried and recrastalised from ethyl alcohol.

The yield of the dried crude product was found to be 85%

Melting Point: - 170^{o}C

Colour of compound (4c) – Lemmon Yellow Crystalline solid

Chemical Formula: $C_{11}H_7Cl_2N_3O_3S$, Molecular Weight: 332.2,m/z: 331.0 (100.0%), 333.0 (63.9%), 332.0 (11.9%), 335.0 (10.2%), 334.0 (7.6%), 333.0 (4.5%), 335.0 (2.9%), 336.0 (1.2%), 332.0 (1.1%),Analysis: C, 39.50; H, 2.15; Cl, 21.32; N, 12.70; S, 9.80, IR (KBr, cm^{-1}): 3345 cm^{-1}, 1667.88 cm^{-1}, 1273.06 cm^{-1}, 2987.55 cm^{-1}, 1359.84 cm^{-1}, 752.04 cm^{-1}, 1530 cm^{-1}, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (s, 2H,-NH_2), δ 2.70(s,3H,-CH_3), δ7.52 -7.44(s,3H,Ar-H).

Table 1: showing the synthesis of different substituted 1,3-Thiazole derivative

Sr No.	Expt. No.	Compound	Yield%	M.P ^{0}C	Colour
1	4	1-(2-amino-5-(2,4-dichloro-3-hydroxyphenyl)thiazol-4-yl)ethan-1-one(4d)	75	180	Yellow solid
2	5	1-(2-amino-5-(3-amino-2,4-dichlorophenyl)thiazol-4-yl)ethan-1-one(4e)	65	120	Yellow solid
3	6	1-(2-amino-5-(naphthalen-2-yl)thiazol-4-yl)ethan-1-one(4f)	75	140	Golden Yellow
4	7	1-(2-amino-5-(1-hydroxynaphthalen-2-yl)thiazol-4-yl)ethan-1-one(4g)	60	216	Brown
5	8	1-(2-amino-5-(1-hydroxy-5-nitronaphthalen-2-yl)thiazol-4-yl)ethan-1-one(4h)	78	135	Light brown
6	9	1-(2-amino-5-(5-bromo-1-hydroxynaphthalen-2-yl)thiazol-4-yl)ethan-1-one (4i)	72	165	Dark brown solid
7	10	1-(2-amino-5-(2-hydroxyphenyl)thiazol-4-yl)ethan-1-one(4j)	75	110	Lemmon yellow

DISCUSSION:

As we know that the egg cell contains the 94% of calcium carbonate ($CaCO_3$) the calcium carbonate converted into the CaO when powdered form of egg cell heated in muffle furnace above 900^0C. The process of conversion of calcium carbonate into calcium oxide is known as calcinations and the product obtain is said to be calcinated egg cell and abbreviated as CES. The calcium carbonate dissolved in water converted in to calcium hydroxide ($Ca(OH)_2$ known as milk of lime as shown below.

$$CaCO_3 \xrightarrow{900\ ^\circ C} CaO \xrightarrow{H_2O} Ca(OH)_2$$

Powder egg cell — Calcium oxide — Calcium Hydroxide

The calcium hydroxide is less soluble in water. The solubility of calcium hydroxide decreases with increase in temperature. It shows a retrograde solubility as it observed from the increase of solubility from 0.66 g/L at 100 °C to 1.89 g/L at 0 °C. The solubility product of lime of water (Calcium hydroxide) at 25 °C was found to be K_{sp} of 5.02×10^{-6}.

The calcium hydroxide when mixed with water it dissociate as follow.

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

The hydroxide ion produced in water make the milk of lime solution alkaline having pH 12.5. This basic character of calcium oxide obtained from natural source such as waste egg cell attracts to use in chemical transformation.

In the present research work synthesis of 1-(2-amino-5-(2,4-dichlorophenyl)thiazol-4-yl)ethan-1-one (4a) from 2-bromo-1-(2,4-dichlorophenyl)but-3-yn-1-one (1a) were carried out and the time required for completion of reaction were noted it was observed that the time required for completion of reactions was in between 2 to 3 hours. As well as the solvent medium water are easily available and cost effective. To reduce time duration required for completion of reaction and for maintaining green chemistry parameters and to develop new reaction conditions, the reactions were carried out in water mediums.

To study the exact concentration of catalyst required to complete the reaction in good yield the interaction of 1-(2-amino-5-(2,4-dichlorophenyl)thiazol-4-yl)ethan-1-one (4a) with 2-bromo-1-(2,4-dichlorophenyl)but-3-yn-1-one (1a) with different quantity of CES in water medium were carried out. It was observed that as the quantity of CES increases the yield also increased at sufficient level. With further increasing the quantity of catalyst the yield of the product does not

increases satisfactorily also the time required was long. So 40% mol of CES catalyst is the appreciable quantity for this reaction as shown in the above table.

CONCLUSION:

The waste egg cell contains 94% calcium carbonate after calcination calcium carbonate converted into calcium oxide. Partially soluble Calcium oxide in water gives calcium hydroxide, which acts as a base. The basicity increases with decrease in temperature. The reaction complete in ice cold condition and water medium. This work may increase interest among the researchers and inspire them about the use of CES as a base catalyst in organic transformations..

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