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Synthesis of Bisindole using Novel Clay catalyst

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ABSTRACT

The present paper represent the synthesis of bis-indole by using local clay material obtained from Bashir farm at Jatadevale, Tq Pathardi, Dist. Ahmednagar gives very clean and good product it is a fast reaction and within five minutes completes.

Keywords: Clay, EDS, FESEM, bis-indole, substituted aldehydes, nanomaterial.

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INTRODUCTION

Indole and its derivatives have wide range of applications in biological and medicinal activities [1] Bis-indole derivatives not only increase the natural metabolism of hormones in the body and also also used as anticancer drug [2]. Such as anti-bacterial antitumor. Bis-indole derivatives are members of promising new drug class these are diarylamidine derivatives that target DNA synthesis, providing a broad-spectrum antibacterial activity [4].For the synthesis of bisindole from indole different catalyst are reported such as Ln $(OTf)_3$,I_2, PCl_5, PPA/SiO_2, silica sulphuric acid, Lewis acid, protic acid [5].However , many of procedures have significant drawbacks such as required stoichiometric amount of catalyst, long reaction time, expensive catalyst, low yield and use of environmentally toxic reagents[6-7].Secondly, nowadays, research is focused on search of new, novel effective catalyst for various chemical synthesis[8-13] But in the present work, we replaced this catalyst by low cost cheaply available clay.

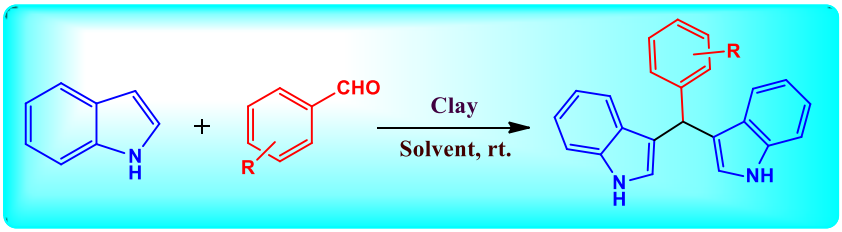
Preparation of catalyst-The clay is crushed as a fine powder in mortar and pestle wash with distilled water and soak this mixture in 0.1 M $H_2SO_4$to remove organic particles for 24 hour then filter with whatman filter paper then wash the catalyst distilled water for several times to remove adsorbed acid particles dry it at 110^{o}C in over then cool and use it as a catalyst. This catalyst is characterized by using XRD, EDS and FESEM.

EXPERIMENTAL

All chemicals were purchased from major chemical suppliers as high or highest purity grade and without further purification. The melting points are uncorrected TLC is run in N- hexaneandethylacetate in required amount. FT-IR is recorded in KBr, HNMR in $CDCl_3$ from CIF University of Pune. X-Ray Powder diffraction (XRD) is recorded from department of Physics, University of Pune. Energy-dispersive X-Ray Spectroscopy (EDS) and Field Emission Scanning Electron Microscope (FESEM) by using instrument Nova Nano SEM 450 UOP were recorded from CIF, University of Pune Maharashtra.

General procedure for the synthesis of bis-indole derivatives: The mixture of one mole of aldehydes of two mole of indole and 0.10 mg of catalyst in ethyl acetate in mortar and pestlegrindthis reaction mixture well for specific period. The reaction was monitored by TLC. Reactions checked by TLC then add 10ml dichloromethane then reaction mixture was filtered. Catalyst is separated by filtration. This catalyst reused. Then some amount of N-hexane is added in solvent. This mixture was kept in deep freezer pure crystals are separated. As a part of our study of the chemistry indole [biological active moiety] we have synthesized bis-indole by using novel Clay catalyst.

Reaction scheme: We have synthesized five bis-indole derivative syntheses by this method. The general scheme is given below we also compare this reaction with stone powder as catalyst but the reactive gives moderate yield and require longer duration of time(Scheme 1).



Scheme: Synthesis of bis-indole using clay catalyst

In Table 1, the indole and aldehydes along with product is given true yield, time period and melting point of product is also given. The reaction completes from 10 to 35 minutes with quite good yield 75 to 95 %. The catalyst is characterized using EDS, FESEM and X-ray Diffraction.

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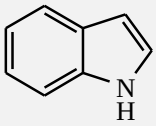
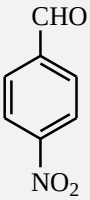
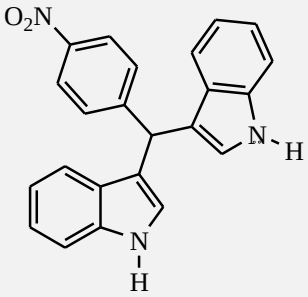
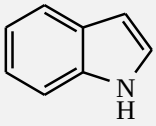
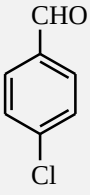
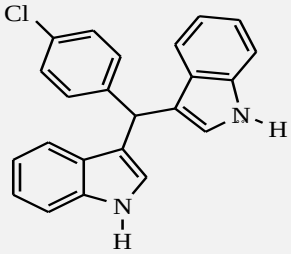
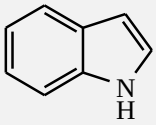
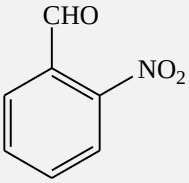
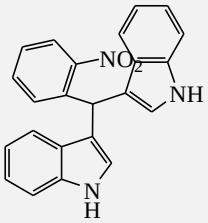
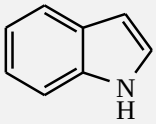
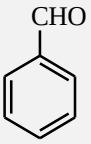
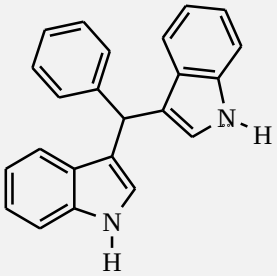
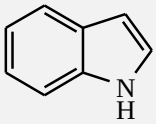
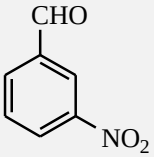
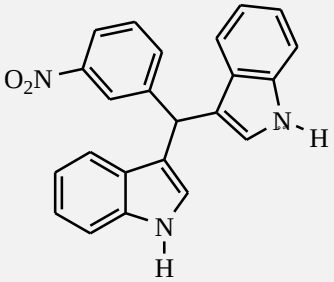
Table 1: Characterization of bis-indole derivatives.

Sr. No.	Indole	Aldehyde	Product	Times (Min)	Yield[b] (%)	Melting point ^0C
1				10	95	230
2				15	85	80
3				30	80	156
4				40	78	125
5				35	75	256

[b] Isolated yield

RESULT AND DISCUSSION

Spectral Data:1)IR: 3623, 3411, 3123, 3016, 2820, 2850, 1615, 1340, 1089, 733 cm^{-1};Mass: 368, 367, 366, 350, 252, 251, 116; HNMR**:** 6.1 (d,1H), 6.3(d,1H), 6.8(d, 2H), 7.0(m, 1H), 7.1(m,1H), 7.2(m, 1H), 7.3(m, 2H), 7.4(m, 2H), 7.4(m, 2H), 7.5(m, 1H), 7.8(m,1H), 8.0(S, 2H).

2)IR: 3419, 3213, 3113, 3019, 2922, 2849, 1615, 1339, 1078, 741 cm^{-1}; Mass: 356, 355, 354, 240, 241, 116; HNMR ($CDCl_3$): 5.8(S, 1H), 6.3(S, 1H), 6.8(m, 1H), 6 .9(m, 1H), 7.0(m, 2H), 7.2(m, 4H), 7.3(m, 4H), 7.5(d, 1H), 10.82(S 2H).
3)IR: 3529, 3413, 3113, 3019, 2922, 2849, 1615, 1339, 1078, 731 cm^{-1}; Mass: 368, 367, 366, 350, 252, 251, 116;HNMR: 6.0(S, 1H), 6.8(m, 2H), 7.0(m, 2H), 7.2(t, 2H), 7.3(dd, 2H), 7.5(d, 2H), 7.6(d, 2H), 8.1(d,2H), 10.9(S, 2H).

4)IR: 3425, 3113, 3019, 1599, 1499, 732; cm^{-1};Mass: 368, 367, 366, 350, 252, 251, 116; HNMR: 5.8(S, 1H), 6.3(S, 1H), 6.8(m, 1H), 6.9(m, 1H), 7.0(m, 2H), 7.2(m, 4H), 7.3(m, 6H), 10.82(S, 2H).

5) IR: 3625, 3413, 3113, 3019, 2920, 2850, 1615, 1340, 1088, 732; cm^{-1}; Mass: 368, 367, 366, 350, 252, 251,116 ; HNMR**:** 6.0(d,1H), 6.5(d,1H), 6.6(d, 2H), 7.0(m, 1H), 7.1(m,1H), 7.2(m, 1H), 7.3(m, 2H), 7.4(m, 2H), 7.5(m, 2H), 7.6(m, 1H), 7.7(m,1H), 8.0(S,1H), 8.1(S,1H).

Characterization of the clay by using Field emission scanning electron microscope (FESEM) by using Novananosem 450 instruments.(Fig 1)

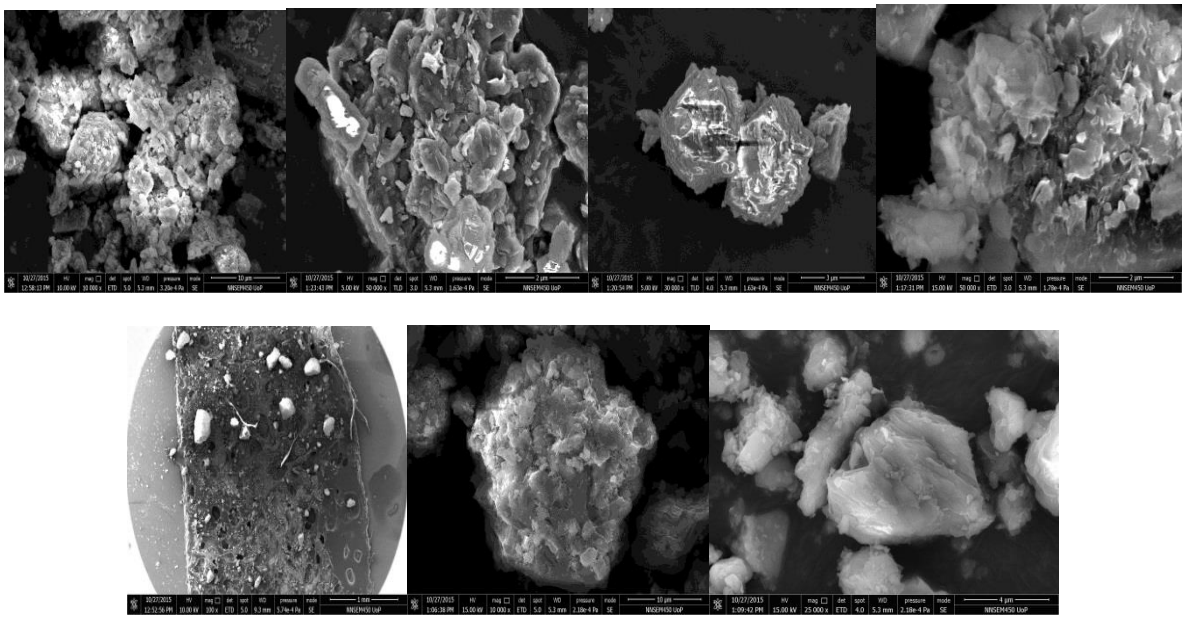


Fig : 1: SEM images of catalyst

First image is subjected to high voltage at 10.00 kV with magnification of 10000 X, detector used is ETD, Spot 5.0 is area covered by beam on detector, working difference is 5.3 mm, vacuum pressure is applied on sample it is $3.20e^{-4}$ pa, and mode of action is secondary electron. Second image Sample is subjected with 5.00kV high voltage with magnification of 50000 X , detector used is TLD, Spot 3.0 is area covered by beam on detector, working difference is 5.3 mm, pressure apply on sample is negative pressure is applied on sample it is $1.63e^{-4}$ pa, secondary electron mode of action. Third image is subjected high voltage at 5.00 kV with magnification of 30000 X, detector used is TLD, Spot 4.0 gives information about area covered by beam on detector, working difference is 5.3 mm, pressure apply on sample it is $1.63e^{-4}$ pa, mode of action is secondary electron. Image four is applied with high voltage at 15.00 kV with magnification of 50000 X, detector used is ETD, area covered by beam on detector is 0.3, working difference is 5.3 mm, vacuum pressure is applied on sample it is 1.78e-4 pa, and secondary electron is mode of action. Image fifth with spot 5.0 is area covered by beam on detector which is subjected with high voltage at 10.00 kV with magnification of 100 X , detector used is ETD, working difference is 9.3 mm, pressure apply on sample it is $5.74e^{-4}$ pa, mode of action is secondary electron .sixth image gives information that which is subjected high voltage at 15.00 kV with magnification of 10000 X , detector used is ETD, Spot 5.0 is area covered by beam on detector, working difference is 5.3 mm, pressure apply on sample is negative pressure at $2.18e^{-4}$ pa, mode of action is secondary electron .seventh image is subjected with high voltage at 15.00 kV with magnification of 25000 X , detector used is ETD, Spot 4.0 gives information about area covered by beam on detector, working difference is 5.3

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mm, pressure apply on sample is 2.18e^{-4} pa, mode of action is secondary electron . Characterization of clay by using Energy dispersive X-ray spectroscopy (Fig 2 a & b)

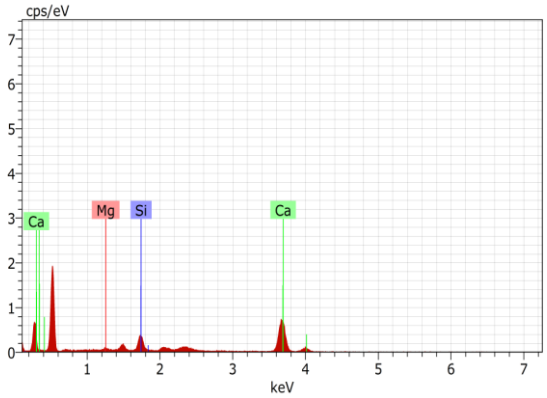

Fig 2(a): Energy dispersion X-ray spectra

Spectrum: BN2 403

El AN Series unn.C norm.C Atom. C Error (1 Sigma)
[wt.%] [wt.%] [at.%] [wt.%]

Ca 20 K-series 44.79 86.66 81.82 1.59
Si 14 K-series 6.39 12.36 16.65 0.32
Mg 12 K-series 0.51 0.99 1.54 0.07

Total: 51.69 100.00 100.00

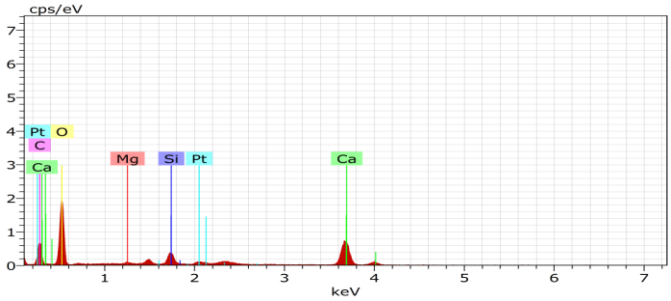

Fig 2(b); Energy disersion X-ray spectra with platinum metal

Spectrum: BN2 403

El AN Series unn.C norm.C Atom. C Error (1 Sigma)
[wt.%] [wt.%] [at.%] [wt.%]

O 8 K-series 46.03 50.50 62.25 6.09
Ca 20 K-series 30.65 33.63 16.55 1.09
C 6 K-series 9.71 10.66 17.50 1.57
Si 14 K-series 4.40 4.83 3.39 0.23
Mg 12 K-series 0.35 0.39 0.32 0.05
Pt 78 M-series 0.00 0.00 0.00 0.00

Total: 91.14 100.00 100.00

Catalytic activity: This catalyst can be recycle and use several times for reuse. This gives good yield for three times. Indole show electrophilic substitution reaction at beta or three positions. When aldehydes react with indole in presence of clay as a catalyst in ethyl acetate as solvent, bis-indole ware obtained in good yield. The reaction is illustrated in scheme 1 the proposed mechanism of the reaction is given in scheme 2Effect of catalyst. As this is ecofriendly catalyst that's why it is easily separated and use as catalyst in same reaction we

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have used this catalyst in same reaction scheme in several times we get better yield and better catalytic activity but as number of cycle increases more than four cycle yield is poor percent of yield and number of cycles of reaction given below chart (Fig 3)

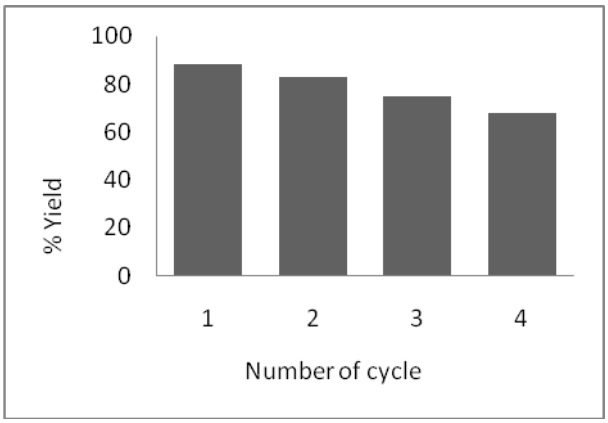
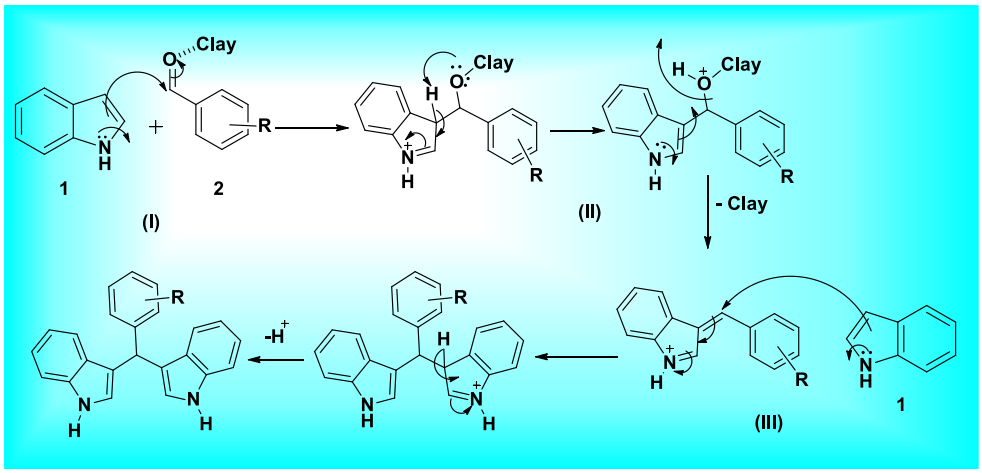


Fig 3: Catalytic activity of clay



Reaction mechanism: Synthesis of bis-indole in clay catalyst.

CONCLUSION

Indole is more reactive towards electrophilic substitution reaction at beta position the effect of substituents in the aromatic ring of aldehydes was investigated. The yield of bis-indole derivatives in the presence of clay as catalyst is summaries in the table 1. It is seen that Para nitro benzaldehyde gives very fast reaction a high yield within five minutes at room temperature.

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