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Synthesis and characterization of some new chlorosubstitured Δ^2- pyrazoles under microwave irradiation

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Abstract : Heterocyclic system containing pyrazole ring and its derivative have attracted the attention of chemists on account of the significant medicinal properties associated with them. The proposed study deals with the synthesis and characterization of newly synthesized chlorosubstituted Δ^2 -pyrazoles under the microwave irradiation on micro-scale quantity. The short reaction times and expanded reaction range was offered by themicrowave assisted synthesis to the chemists. The reaction of chromones and phenylhydrazine hydrochloride result in the formation of Pyrazoles.
The newly synthesize compounds were characterized on the basis of FTIR, H^1NMR, Uv and Massspectroscopic techniques.
Key Words : Chromanone,chromone,Pyrazole, H^1 NMR, FTIR, Uv and Mass spectra.

Introduction:

Heterocyclic chemistry is the branch of organic chemistry dealing with the synthesis, properties and applications of the heterocycles. Pyrazole is the five membered heterocyclic compound with two nitrogen atoms in the 1, 2-position.

Heterocyclic system containing pyrazolering and its derivative have attracted the attention of chemists on account of the significant medicinal properties associated with them. Pyazoles are reported to have properties such asantibacterial[1],hypoglycamic agent[2], anti-inflammatory[3], antitumour[4]analgesic agent and antipyretic property[5].

Ling[6]*et al* have investigated pyrazoles by the action of 2, 3-dihydropyridine 4, hydrazine hydrate and diethyl maleate. Brone[7]*et al* have synthesized a metal-free continuous flow method for the generation of a variety of N-arylatedpyrazoles.

The proposed study deals with the synthesis and characterization of newly synthesized chlorosubstituted Δ^2-pyrazolesby the reaction of chromones and phenylhydrazinehydrochloride by using the microwave irradiation.

Materials and Methods:-

There are various methods reported for the synthesis of pyrazoles. It is interesting to synthesize and characterized some new chlorosubstitutedΔ^2-pyrazoles from diketone on reactions with aldehydes in ethanolic medium via chromone. The present study deals with the synthesis of pyrazoles through microwave irradiation.The purity of synthesized compounds was tested by TLC. All melting points measured in open glass

capillary tube. All reactions were carried out in laboratory microwave oven (New microwave system model (R-210D, 800w 24L light-up Dial, SHARP TLABMA638). The structures of the newly synthesized compounds were confirmed by using spectroscopic technique via Uv, FTIR, H^1NMR and Mass. The spectral analysis was carried out at SAIF and CIL, Punjab University, Chandigarh, (India).General procedure for the synthesis of pyrazoles:-

(1) Synthesis of 2-hydroxy 3,5-dichloroacetophenone :- (A)

Substitutedphenylacetate (25ml) was mixed with anhydrous aluminiumtrichloride(60g) and heated at 120^0C for 45 minutes on oil bath.The reaction mixture was decomposed by ice cold water containing a little HCl to get the crude product. A greenish white solid of the compound (A) was obtained, yield: 57%,m.p: 59^0C.

Spectral data for compound (A):-

(a) FTIR :- (KBr, cm^{-1}): 3429(OH stretching), 3069 (Ar-CH stretching), 2974 (C-H stretching in CH_3), 1648 (C=O stretching), 643(C-Clstreching).
(b) H^1 NMR: - (400MHz, $CDCl_3$, δ ppm): 2.65 (S, 3H, $COCH_3$), 7.26-7.62 (m, 2H, Ar-H), 12.71 (s, 1H, OH).
(c) UV: - The UV-VIS spectrum of the compound (A) recorded in $CHCl_3$ showed λmax value 250nm corresponding to $n\rightarrow\Pi^*$ transition.
(d) Mass (Ab) **: -** (m/z) = 205.190, 162,134.

(2) Synthesis of 2-aroloxyacetophenone:-(Aband Af)

2-Hydroxy acetophenone(0.04M) and aromatic acid(0.05M) were suspended in dry pyridine (5ml) and to this $POCl_3$ (3 ml) was added dropwise with constant stirring and cooling. The reaction mixture was kept for overnightand then worked up by the dilution andacidification with ice cold HCl (10%) to neutralize pyridine. The solid productthus obtained crystallized from ethanol to get the compound (Af). Yield 71% m.p:76^0C.

2-Hydroxy acetophenone(0.04mol)and aromatic acid(0.05mol) were suspended in 10% NaOH (35 ml). The reaction mixture was shaken for about 25min then product was filtered. The solid productthus obtained crystallized from ethanol to get the compound (Ab). Yield: 67%,m.p: 72^0C.

Spectral data for compound (Af):-

(a) FTIR :-(KBr, cm^{-1}):3070 (Ar-CH stretching), 2974 (C-H stretching in CH_3), 1779, 1740 (C=O stretching), 1021 (C-O stretching), 740 (C-Clstreching).
(b) H^1 NMR: - (400MHz, $CDCl_3$, δ ppm): 2.65 (S, 3H, $COCH_3$), 7.26-7.64 (m, 5H, Ar-H).
(c) UV: - The UV-VIS spectrum of the compound (Af) recorded in $CHCl_3$ showed λmax value nm corresponding to $n\rightarrow\Pi^*$ transition.

Spectral data for compound (Ab):-

(a) FTIR :- (KBr, cm^{-1}): 3082 (Ar-CH stretching), 2925 (C-H stretching in CH_3), 1648, 1776 (C=O stretching), 1608 (benzene), 1114 (C-O stretching), 642 (C-Clstreching).
(b) H^1 NMR: - (400MHz, $CDCl_3$, δ ppm): 2.55 (s, 3H, $COCH_3$), 7.26-7.62 (m, 7H, Ar-H).
(c) UV: - The UV-VIS spectrum of the compound (Ab) recorded in $CHCl_3$ showed λmax value 280nm corresponding to $n\rightarrow\Pi^*$ transition.
(d) Mass: - (m/z) = 309,189, 161, 133.

(3) Synthesis of 1-(2-hydroxyaryl)-3-aryl-1, 3-propanediones :- (B and F)

2-Aroyloxy acetophenone (0.05mol)was dissolved in dry pyridine (40 ml). The solution warmed upto 60^0C and pulverized KOH (0.15 mol)was added slowly with constant stirring. The reaction mixture was kept for overnight and then worked up by the dilution and acidification with ice cold HCl (10%). The solid product thus obtained crystallized from ethanol to get the compounds (B and F). M.p: 99^0C and 120^0C.

Spectral data for compound (B):-

(a) FTIR :- (KBr, cm^{-1}): (B):- 3421 (Ar-OH – stretching), 3074 (Ar-CH-streching), 1768 (C=O stretching), 1680 (C=O stretching), 683 (C-Cl stretching).
(b) H^1 NMR: - (400MHz, $CDCl_3$, δ ppm): 2.22 (s, 2H, $-CH_2-$), 7.52-7.62 (m, 7H, Ar-H), 12.66 (s, 1H, OH).
(c) UV: - The UV-VIS spectrum of the compound (B) recorded in $CHCl_3$ showed λmax value 380nm corresponding to $n\rightarrow\Pi^*$ transition.
(d) Mass: - (m/z) = 309,204,190,162, 133, 132.

Spectral data for compound (F):-

(a) FTIR :- (KBr, cm^{-1}): 3376 (Ar-OH – stretching), 3070 (Ar-CH-streching), 1648 (C=O), 1609 (C=O stretching), 1648 (C=O stretching), 740 (C-Cl stretching).
(b) H^1 NMR: - (400MHz, $CDCl_3$, δ ppm): 2.65 (s, 3H, $COCH_3$), 7.26-7.74 (m, 7H, Ar-H), 12.71 (s, 1H, OH).
(c) UV: - The UV-VIS spectrum of the compound (F) recorded in $CHCl_3$ showed λmax value 320 nm corresponding to $n\rightarrow\Pi^*$ transition.

(4) Synthesis of3-aroylchromanones :(BC1 and FP1)

3-Aroylchromanone was prepared by using microwave irradiation. A mixture (0.01mol) propadiones (Band F), (0.01mol) of aromatic aldehyde dissolved separately in (25ml)ethanol with (0.5 ml)piperidine and irradiated for 2-3 min in microwave. The reaction mixtures on acidification with HCl (10%), followed by washing with water.The solid product thus obtained crystallized from ethanol to get the compounds (BC1 and FP1).

Spectral data for compound (BC1):-

(a) FTIR :- (KBr, cm^{-1}): (BC1):- 3073 (Ar-CH-streching), 2919, 2850 (C-H stretching in CH_3), 1778 (C=O), 1663 (C=O), 1174 (C-O stretching), 697 (C-Cl stretching).
(b) H^1 NMR: - (400MHz, $CDCl_3$, δ ppm): 1.77 (s, 3H,$-CH_3-$), 5.55 (s, 1H, -CH), 6.59-7.91 (m, 14H, Ar-H).
(c) UV: - The UV-VIS spectrum of the compound (BC1) recorded in $CHCl_3$ showed λmax value 350nm corresponding to $n\rightarrow\Pi^*$ transition.
(d) Mass: - (m/z) = 437,422, 320,243,215.

Spectral data for compound (FP1):-

(a) FTIR :- (KBr, cm^{-1}): (FC1): - 3069 (Ar-CH-streching), 1777 (C=O), 1738 (C=O), 1434 (C=N), 1022 (C-O stretching), 644 (C-Cl stretching).
(b) H^1 NMR: - (400MHz, $CDCl_3$, δ ppm): 5.35-6.98 (d, 2H, >C-C<), 6.98-7.64 (m, 8H, Ar-H).
(c) UV: - The UV-VIS spectrum of the compound (FP1) recorded in $CHCl_3$ showed λmax value nm corresponding to $n\rightarrow\Pi^*$ transition.

(5) Synthesis of3-aroychromones :- (BC2 and FP2)

The 3-aroylchromanone (BC1 and FP1)(0.01mol) treated separately with few crystals of iodine and (25ml) DMSO in microwave. After cooling the the reaction mixture was diluted with water. The solid product thus obtained crystallized from petroleum ether to get the compounds (BC2 and FP2).

Spectral data for compound (BC2):-

(a) FTIR :- (KBr, cm^{-1}): (BC2):- 2917 (Ar-CH-streching), 2849 (C-H stretching in CH_3),1632 (C=O), 1551 (C=O), 1088 (C-O stretching), 562 (C-Cl stretching).
(b) H^1 NMR: - (400MHz, $CDCl_3$, δ ppm):1.77 (s, 3H,$-CH_3$), 6.74 (s, 1H, -C=CH-), 7.04-7.82 (m, 12H, Ar-H).
(c) UV: - The UV-VIS spectrum of the compound (BC2) recorded in $CHCl_3$ showed λmax value 400nm corresponding to $n\rightarrow\Pi^*$ transition.
(d) Mass: - (m/z) = 435,420, 318, 213

Spectral data for compound (FP2):-

(a) **FTIR :-** (KBr, cm^{-1}): (FP2): - 3076, 1697 (C=O), 1649 (C=O), 1439 (C=N), 1088 (C-O stretching), 740 (C-Cl stretching).
(b) **H^1 NMR: -** (400MHz, $CDCl_3$, δ ppm): 6.99-7.77 (m, 7H, Ar-H).
(c) **UV: -** The UV-VIS spectrum of the compound (FP2) recorded in $CHCl_3$ showed λmax value nm corresponding to $n\rightarrow\Pi^*$ transition.

Synthesis of pyrazole: - :- (BC3 and FP3)

The 3-aroychromones (BC2 and FP2) (0.01M)separately treated with phenyl hydrazine hydrochloride in (7 ml) DMSO with few drops of piperidine under microwave condition for 4min. The reaction mixture on acidification with HCl (10%), followed by washing with sodium bicarbonate and water gave the compounds. The solid product thus obtained crystallized from ethanol to get the compounds (BC3 and FP3).

Spectral data for compound (BC3):-

(a) **FTIR :-** (KBr, cm^{-1}): (BC3):- 3376 (OH – stretching), 2922 (Ar-CH-stretching),2853 (C-H stretching in CH_3), 1665 (C=O stretching), 1449 (C=N stretching), 758 (C-Clstretching).
(b) **H^1 NMR: -** (400MHz, $CDCl_3$, δ ppm): 1.55 (s, 3H,-CH_3), 5.59 (s, 1H,-CH), 7.20-8.11 (m, 16H, Ar-H), 12.01(s, 1H, OH).
(c) **UV: -** The UV-VIS spectrum of the compound (BC3) recorded in $CHCl_3$ showed λmax value 310nm corresponding to $n\rightarrow\Pi^*$ transition.
(d) **Mass: -** (m/z) = 525,510, 433, 405, 303.

Spectral data for compound (FP3):-

a) **FTIR :-** (KBr, cm^{-1}): (FP3): - 3354 (OH – stretching), 3074 (Ar-CH-stretching), 1666 (C=O stretching), 1495 (C=N stretching), 754 (C-Cl stretching).
b) **(b)UV: -** The UV-VIS spectrum of the compound (FP3) recorded in $CHCl_3$ showed λmax value 390 nm corresponding to $n\rightarrow\Pi^*$ transition.
c) **(c)H^1 NMR: -** (400MHz, $CDCl_3$, δ ppm): 11.97 (s, 1H, OH), 6.96-7.21 (d, 2H, CH_2 in furyl), 7.25-8.26 (m, 14H, Ar-H).

Result and Discussion:-

The present work deals with a new series of (*Z*) - (3-(3, 5-dichloro-2-hydroxyphenyl)-1-phenyl-5-(1-phenylprop-1-en-2-yl)-1*H*-pyrazol-4-yl) (phenyl) methanone (BC3) and (3-(3, 5-dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1*H*-pyrazol-4-yl)(furan-2-yl) methanone (FP3) were synthesized by phenyl hydrazine hydrochloride and chromones. These reactions were carried out in micro quantity through microwave irradiation. The structures of the newly synthesized compounds were established on the basis of spectroscopic evidences and their synthesis by conventional methods. The title compounds (BC3 and FP3) were prepared according to the following scheme:

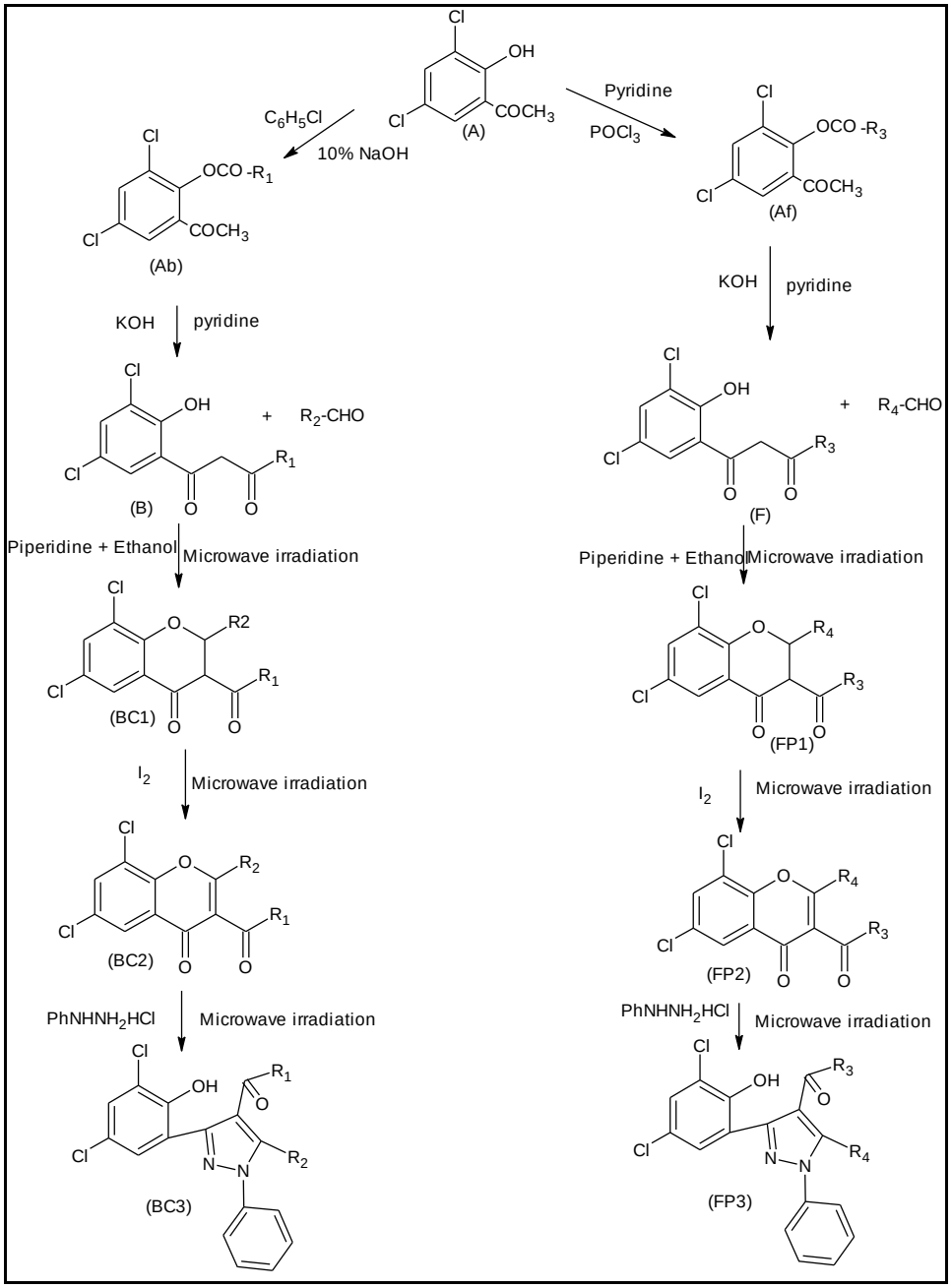
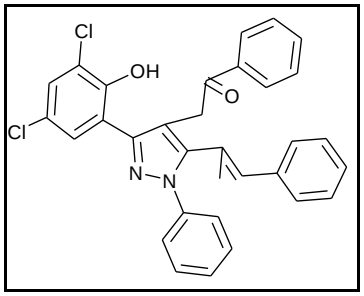
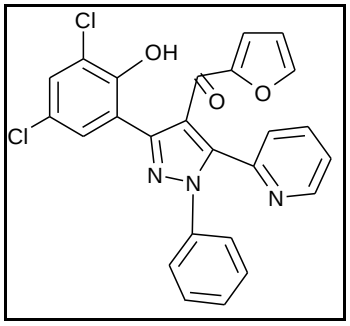


Fig: - The synthetic pathway for synthesis of pyrazole (BC3 and FP3) compound.
(R_3= C_5H_{10}, C_5H_8O. R_1= C_6H_6, C_7H_{14}, R_4= C_5H_8, C_5H_8N. R_2= $C_{10}H_{10}$, C_6H_6,).

The structure of (BC3 and FP3) Pyrazole:



(*Z*)-(3-(3,5-dichloro-2-hydroxyphenyl)-1-phenyl-5-(1-phenylprop-1-en-2-yl)-1*H*-pyrazol-4-yl)(phenyl) methanone (BC3)



(3-(3, 5-Dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1*H*-pyrazol-4-yl) (furan-2-yl) methanone (FP3)

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