INTRODUCTION

Pyrazoles and their derivatives are important on account of use in therapy in different disease\textsuperscript{1-6}. Antibacterial\textsuperscript{7}, fungicidal\textsuperscript{8}, antidiuretic\textsuperscript{9}, and anticancer\textsuperscript{10,11} properties of pyrazoles have been reported in the literature. Synthesis and interesting aspect of biological activity of arylazopyrazoles have been reported\textsuperscript{12,13}. In view of potential biological activities of pyrazoles and arylazopyrazoles we report herein the synthesis of new 1-(2,3-dichloroanilinomalonyl)-3,5-dimethyl-4-(unsubstituted/substituted phenylazo) pyrazoles. The present communication deals with the reaction of acetyl acetone with diazotised aromatic primary amine in presence of sodium acetate which furnished 2,4-diketo-3-(unsubstituted/substituted phenylazo) pentanes (I) which on treatment with (2,3-dichloroanilido) acetohydrazide (II) in acetic acid medium resulted in the formation of 1-(2,3-dichloroanilinomalonyl)-3,5-dimethyl-4-(unsubstituted/substituted phenylazo) pyrazoles (3a-k) in varying yield 30-60% (Table 1). Antibacterial and antifungal activities of new arylazopyrazoles were determined.

EXPERIMENTAL

All the chemicals were used for synthesis are of analytical reagent grade. Melting points are taken in open capillaries and are uncorrected. Purity of the compounds was checked by TLC. All the compounds gave satisfactory elemental analysis. IR Spectra were recorded on a Perkin-Elmer Spectrum RX1 FT IR Spectrophotometer using KBr palletisation technique and NMR Spectra were recorded on Bruker DRX-300 NMR Spectrophotometer. The NMR peaks were recorded on $\delta$ scale (ppm) against TMS. The solvent employed was DMSO (3.33-3.35 $\delta$). The elemental analysis of all the compounds done on Elementar vario EL III Carlo Erba 1108. 2,4-Diketo-3- (unsubstituted/
substituted phenylazo) pentane were synthesized by reported method\textsuperscript{14}. 2-(2,3-Dichloroanilido) acetonitrile was prepared by an adoption of the procedure given by Rathore and Ittner\textsuperscript{15}.

**Preparation of 2,4-diketo-3-(phenylazo) pentane (R = H)(1)**

Aniline (9.3 ml, 0.1 mol) was dissolved in aqueous hydrochloric acid (80 ml, 1:1). The contents were stirred, cooled (0-2°C) and cold solution of sodium nitrite (12.0 g in 30 ml water) was slowly added maintaining the temperature between 0-2°C.

The cold diazotized solution was added dropwise with stirring to a well cooled mixture of acetylacetone (0.1 mol, 10 ml) and sodium acetate (12 g dissolved in 10 ml of 50% aqueous ethanol). Stirring was further continued for forty five minutes, when yellow crystals separated. The product was filtered under suction, washed with water and recrystallised from aqueous ethanol. Yield; 56 %, M.P.; 63°C

Other 2,4-diketo-3 (unsubstituted/ substituted phenylazo) pentanes were prepared by above mentioned procedure.

**Preparation of 2-(2,3-dichloroanilido) acetonitrile (2)**

A mixture of 2,5-dichloroaniline (10 ml) and diethylmalonate (20 ml) was refluxed for forty five minutes in a round bottomed flask fitted with an air condenser of such a length (14") that ethanol formed escaped and diethylmalonate flowed back into the flask. Contents were cooled, ethanol (30 ml) was added, when malon-2,3-dichlorodianilide separated out. It was filtered under suction. The filtrate was poured on to crushed ice (ca 160 g) and stirred when ethyl-2-(2,3-dichloroanilido) ethanoate precipitated as green mass. On crystallization from aqueous ethanol (50%) ester was obtained as white crystals.

Ethyl 2-(2,3-dichloroanilido) ethanoate (2 g) was dissolved in ethanol (6 ml) in a small beaker kept in ice bath. Hydrazine hydrate (12 ml, 80%) was added and the contents were stirred for ten minutes. The solid obtained was filtered under suction and recrystallised from ethanol in white crystals.

Yield; 82 %, M.P.; 167°C

**Analysis (%)**

- Found; N 15.9, Cl 26.7, C\textsubscript{8}H\textsubscript{9}O\textsubscript{2}N\textsubscript{3}Cl\textsubscript{2}
- Calculated; N 16.0, Cl 27.0

\begin{center}
\textbf{Scheme 1: Arylazopyrazole}
\end{center}
IR (KBr) $\nu_{\text{max}}$ cm$^{-1}$

3220 (N—H --- (Sec. amide hydrogen bond), 3046 (C—H (aromatic), 1690 (C=O diketone), 1434 (C–Cl aromatic).

PMR (DMSO)

$\delta$ 4.45 (2H, s, CO-CH$_2$-CO), 4.3 (2H, s, NH$_2$), 7.1-8.6 (3H, m, Ar-H), 9.3 (1H, s, CO-NH D$_2$O exchangeable), 10.7 (1H, s, Ar-NH D$_2$O exchangeable).

1-(2,3-dichloroanilinomalonyl)-3,5-dimethyl-4-(phenylazo)pyrazole (3a)

2,4-Diketo-3-(phenylazo)pentane (0.204g, 0.001 mol) and 2-(2,3-dichloroanilido) acetohydrazide (0.262g, 0.001mol) were dissolved in glacial acetic acid (8 ml) and the solution was refluxed for 12 hrs. The resulting solid was purified by repeated washing with acetic acid and crystallized from acetic acid as yellow crystals. Yield: 56%, M.P.; 217°C

Analysis (%)

Found: N 16.5, Cl 16.3 C$_{20}$H$_{17}$O$_2$N$_5$Cl
Calculated: N 16.3, Cl 16.5

IR (KBr) $\nu_{\text{max}}$ cm$^{-1}$

3280-3070 (N-H Sec. amide hydrogen bond), 2970 (C-H Stretching Aromatic), 1640 (C=N Pyrazole), 1550 (C=C Aromatic), 1060 (C–Cl Aromatic).

PMR (DMSO):

$\delta$ 2.26 (2H, s, CH$_2$), 4.17 (1H, s, NH), 6.80-7.02 (7H, s, Ar-H).

Other 1-(2,3-dichloroanilinomalonyl)-3,5-dimethyl-4-((unsubstituted/substituted phenylazo)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>R</th>
<th>Colour</th>
<th>m.p. (°C)</th>
<th>Yield (%)</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a.</td>
<td>H</td>
<td>Yellow</td>
<td>284</td>
<td>56</td>
<td>C$<em>{20}$H$</em>{17}$O$_2$N$_5$Cl$_2$</td>
</tr>
<tr>
<td>3b.</td>
<td>CH$_3$(o)</td>
<td>Light Yellow</td>
<td>260</td>
<td>60</td>
<td>C$_2$H$_9$O$_2$N$_5$Cl$_2$</td>
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<tr>
<td>3c.</td>
<td>CH$_3$(m)</td>
<td>Yellow</td>
<td>216</td>
<td>52</td>
<td>C$_2$H$_9$O$_2$N$_5$Cl$_2$</td>
</tr>
<tr>
<td>3c.</td>
<td>CH$_3$(p)</td>
<td>Light Yellow</td>
<td>234</td>
<td>54.5</td>
<td>C$_2$H$_9$O$_2$N$_5$Cl$_2$</td>
</tr>
<tr>
<td>3d.</td>
<td>Cl(o)</td>
<td>Yellow</td>
<td>280</td>
<td>60</td>
<td>C$<em>{20}$H$</em>{17}$O$_2$N$_5$Cl$_2$</td>
</tr>
<tr>
<td>3e.</td>
<td>Cl(m)</td>
<td>Yellow</td>
<td>240</td>
<td>53.5</td>
<td>C$<em>{20}$H$</em>{17}$O$_2$N$_5$Cl$_2$</td>
</tr>
<tr>
<td>3f.</td>
<td>Cl(p)</td>
<td>Light Yellow</td>
<td>275</td>
<td>50</td>
<td>C$<em>{20}$H$</em>{17}$O$_2$N$_5$Cl$_2$</td>
</tr>
<tr>
<td>3g.</td>
<td>O-CH$_3$(o)</td>
<td>Light Yellow</td>
<td>260</td>
<td>58</td>
<td>C$<em>{20}$H$</em>{17}$O$_2$N$_5$Cl$_2$</td>
</tr>
<tr>
<td>3h.</td>
<td>O-CH$_3$(m)</td>
<td>Yellow</td>
<td>237</td>
<td>42</td>
<td>C$<em>{20}$H$</em>{17}$O$_2$N$_5$Cl$_2$</td>
</tr>
<tr>
<td>3i.</td>
<td>O-CH$_3$(p)</td>
<td>Light Yellow</td>
<td>275</td>
<td>47</td>
<td>C$<em>{20}$H$</em>{17}$O$_2$N$_5$Cl$_2$</td>
</tr>
<tr>
<td>3j.</td>
<td>F(p)</td>
<td>Yellow</td>
<td>226</td>
<td>30</td>
<td>C$<em>{20}$H$</em>{17}$O$_2$N$_5$Cl$_2$</td>
</tr>
</tbody>
</table>

* All compounds gave satisfactory elemental analysis.
pyrazoles were prepared by above mentioned procedure.

**Biological activities**

All the compounds were screened for antibacterial activities by agar plate disc diffusion method at 30 µg/mL concentration. Ampicillin and tetracycline were used as a reference compounds. *E. coli, S. aureus, Pseudomonas* species and *S. albus* used as the bacterial test organisms. The new compounds were also screened for antifungal activity against *Aspergillus niger*, *Alternaria alternata* and *Candida species* at concentration of 50 µg/mL using subroad and dextrose agar media. Amphotericin B discs were used as the standard drugs. Compound 3c, 3e, 3i and 3k have shown moderate activity against bacteria, whereas 3i has also shown moderate activity against *Aspergillus niger*.

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**REFERENCES**