CHAPTER V

NUCLEOPHILIC REACTIONS ON 2-CHLOROETHYL/2-MESYLETHYLINDOLES

INTRODUCTION
The importance of arylether and arylthioether linkages is evidenced from their presence in many antimycobacterials, analgesics, antibiotics and parasitic agents.

2-Phenoxy methyl-5-hydroxyindoles 399 have been prepared by Mazentseva et al. and they have shown very good antiviral activity.

\[
\begin{align*}
R &= H, Ac \\
R_1 &= H, CH_2N(Me)_2
\end{align*}
\]

Grinev et al. have synthesised the compound of the type 400 which displayed significant antiviral activity.
Panisheva and associates\textsuperscript{442} have synthesised the compound 401 which exhibited antiviral and antiarthritic activities.

\begin{center}
\includegraphics[width=0.3\textwidth]{401.png}
\end{center}

$R = \text{Et, Ph-CH}_2, \text{Ph, p-tolyl, p-anisyl, p-Br-C}_6\text{H}_4^-, p-\text{Cl-C}_6\text{H}_4^-$

Wieland and Ruehl\textsuperscript{443} have reported the synthesis of 2-methyl-3-phenylthioindole 402.

\begin{center}
\includegraphics[width=0.2\textwidth]{402.png}
\end{center}

Pandey and Raj\textsuperscript{444} have reported the synthesis of the compound 403.

\begin{center}
\includegraphics[width=0.5\textwidth]{403.png}
\end{center}

$R = \text{benzamido, phthalamido, nicotinamido;}$

$R^1 = \text{morpholino, piperidino}$
Gadaginamath and Patil\textsuperscript{445} have synthesised and reported the antimicrobial activity of 2-phenoxy-methylindole 404 and 2-phenylthiomethylindole derivatives 405.

\begin{center}
\begin{tikzpicture}
  \node (n1) at (0,0) {
    \begin{array}{c}
      \text{H}_3\text{CO} \\
      \text{Br} \\
      \text{CH}_2\text{O} - \text{R}
    \end{array}
  };
  \node (n2) at (1,0) {
    \begin{array}{c}
      \text{H}_3\text{CO} \\
      \text{Br} \\
      \text{CH}_2\text{S} - \text{R}
    \end{array}
  };

  \node (n3) at (0,0) {
    \begin{array}{c}
      \text{Br} \\
      \text{n-Bu}
    \end{array}
  };

  \node (n4) at (1,0) {
    \begin{array}{c}
      \text{n-Bu}
    \end{array}
  };

  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);

  \node (404) at (0.5,1) {404};
  \node (405) at (1.5,1) {405};

  \node (R) at (2,0) {R = \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{-Cl}(o), \text{C}_6\text{H}_4\text{-Cl}(p), \text{C}_6\text{H}_2\text{-Cl}_2 \ (2, \ 4) \ etc};
\end{tikzpicture}
\end{center}

Atkinson and coworkers\textsuperscript{446} have reported new method for the synthesis of 3-arylthioindole 406.

\begin{center}
\begin{tikzpicture}
  \node (n1) at (0,0) {
    \begin{array}{c}
      \text{R}^1 \\
      \text{R}^2
    \end{array}
  };

  \node (n2) at (1,0) {
    \begin{array}{c}
      \text{H} \\
      \text{N}
    \end{array}
  };

  \node (n3) at (0,0) {
    \begin{array}{c}
      \text{H}_3\text{CO} \\
      \text{Br}
    \end{array}
  };

  \node (n4) at (1,0) {
    \begin{array}{c}
      \text{CH}_2\text{-S} - \text{R}
    \end{array}
  };

  \draw (n1) -- (n2);
  \draw (n2) -- (n3);
  \draw (n3) -- (n4);

  \node (406) at (0.5,1) {406};
\end{tikzpicture}
\end{center}

R$^1$ = H, Me, Ph, CO$_2$Me, COOH ;

R$^2$ = Ph, C$_6$H$_4$-Cl(p), C$_6$H$_4$-CH$_3$(p), C$_6$H$_4$-OCH$_3$ (p) etc.
Present Work: Part A

Synthesis of 1-[2-phenoxyethyl] and 1-[2-phenylthioethyl]-5-methoxy-3-ethoxycarbonyl-2-methylindole/benz(g)indole derivatives
The 1-[2-hydroxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 371 and benz(g)indole 385 were reacted separately with triphenyl phosphine and carbon tetrachloride in refluxing acetonitrile to get the desired respective 1-[2-chloroethyl]-2-methylindole derivatives 407 and 410. The chloroethylindole derivatives 407 and 410 were further reacted separately with thiophenols and phenols to obtain the corresponding 1-[2-phenylthioethyl]indoles 408 and benz(g)indoles 411 and 1-[2-phenoxyethyl]-indoles 409 and benz(g)indoles 412 respectively [Scheme – 42 and 43].

The 1-[2-hydroxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 371 was reacted with triphenyl phosphine and CCl₄ in refluxing acetonitrile to secure the desired 1-[2-chloroethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 407. IR spectrum of 407 (Fig. 179) displayed a strong stretching band at 1680 cm⁻¹ due to C₃-ester carbonyl. Stretching band at 794 cm⁻¹ corresponded to C-Cl group. ¹H NMR spectrum of 407 (Fig. 180) exhibited triplet (J = 7.1 Hz) at 1.47 δ due to C₃-ester methyl protons. Singlet at 2.80 δ was accounted for C₂-methyl protons. Triplet (J = 7.1 Hz) at 3.74 δ was attributed to CH₂-Cl protons and singlet at 3.90 δ was assigned to C₅-methoxy protons. Multiplet ranging from 4.38-4.46 δ was ascribed to NCH₂ and C₃-ester methylene protons. Doublet of doublet (J = 8.5 Hz and 2.5 Hz) at 6.91 δ was assigned to C₆-proton while the doublet (J = 8.5 Hz) at 7.20 δ was accounted for C₇-proton. Doublet (J = 2.5 Hz) at 7.69 δ corresponded to C₄-proton.

This chloroethylindole 407 was reacted with thiophenol in refluxing dry ethanol in presence of K₂CO₃ to get the desired 1-[2-phenylthioethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 408a. IR spectrum of 408a (Fig. 181) exhibited a strong stretching band at 1684 cm⁻¹ due to C₃-ester carbonyl. ¹H NMR spectrum of 408a (Fig. 182) displayed a triplet (J = 7.1 Hz) at 1.46 δ corresponding to C₃-ester methyl protons. Singlet at 2.67 δ was accounted for C₂-methyl protons. Triplet (J = 7.1 Hz) at 3.19 δ corresponded to –CH₂–S protons and singlet at 3.89 δ belonged to C₅-methoxy protons.
Scheme-42

371

Ph3P / CC14
CH3CN, Δ

Phenol, K2CO3, KI, Dry ethanol Δ

371

407

Thiophenol, K2CO3, KI, Dry ethanol Δ

Phenol, K2CO3, KI, Dry DMF, Δ

(408 a-b)

408a - C6H5
408b - C6H4-Cl (4)

(409 a-b)

409a - C6H5
409b - C6H4-Cl (2)
409c - C6H4-Cl (4)
409d - C6H4-CH3 (4)

R

264
Scheme 43

Thiophenol, K$_2$CO$_3$, KI, Dry ethanol A
Phenol, K$_2$CO$_3$, KI, Dry DMF, A

R

411a - C$_6$H$_5$
411b - C$_6$H$_4$-Cl (4)

412a - C$_6$H$_5$
412b - C$_6$H$_4$-Cl (2)
412c - C$_6$H$_4$-Cl (4)
412d - C$_6$H$_4$-CH$_3$(4)

265
Triplet \((J = 7.1 \text{ Hz})\) at \(4.29 \delta\) was attributed to the N-CH\(_2\) protons while the quartet \((J = 7.1 \text{ Hz})\) at \(4.39 \delta\) was assigned to C\(_3\)-ester methylene protons. Doublet of doublet \((J = 8.5 \text{ Hz and } 2.5 \text{ Hz})\) at \(6.83 \delta\) was due to C\(_6\)-proton while the doublet \((J = 8.5 \text{ Hz})\) at \(6.99 \delta\) corresponded to C\(_7\)-proton. Multiplet ranging from 7.22 to 7.53 \(\delta\) belonged to protons of thiophenol and doublet \((J = 2.5 \text{ Hz})\) at \(7.65 \delta\) was attributed to C\(_4\)-proton.

Chloroethylindole 407 was also reacted with phenol in refluxing dry dimethyl formamide in presence of anhydrous K\(_2\)CO\(_3\) and KI to obtain the required 1-[2-phenoxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 409a. IR spectrum of this sample 409a (Fig. 183) displayed a strong stretching band at 1683 cm\(^{-1}\) due to C\(_3\)-ester carbonyl. \(^1\)H NMR spectrum of this sample 409a (Fig. 184) displayed a triplet \((J = 7.1 \text{ Hz})\) at 1.46 \(\delta\) due to C\(_3\)-ester methyl protons. Singlet at 2.81 \(\delta\) was accounted for C\(_2\)-methyl protons while another singlet at 3.89 \(\delta\) belonged to C\(_5\)-methoxy protons. Quartet \((J = 7.1 \text{ Hz})\) at 4.40 \(\delta\) was ascribed to CH\(_2\)-O- protons while another triplet \((J = 7.1 \text{ Hz})\) at 4.61 \(\delta\) was related to N-CH\(_2\) protons. Doublet of doublet \((J = 8.5 \text{ Hz and } 2.5 \text{ Hz})\) at 6.89 \(\delta\) belonged to C\(_6\)-proton while multiplet ranging from 7.39 - 7.93 \(\delta\) was attributed to C\(_7\), C\(_4\) and five protons of phenyl ring.

The 1-[2-hydroxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole 385 was reacted with triphenyl phosphine and CCl\(_4\) in refluxing acetonitrile to secure the desired 1-[2-chloroethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole 410. IR spectrum of 410 (Fig. 185) exhibited a strong stretching band at 1689 cm\(^{-1}\) due to C\(_3\)-ester carbonyl. The stretching band of C-Cl group was found at 758 cm\(^{-1}\). \(^1\)H NMR spectrum of the sample 410 (Fig. 186) displayed triplet \((J = 7.1 \text{ Hz})\) at 1.48 \(\delta\) due to C\(_3\)-ester methyl protons. Singlet at 2.87 \(\delta\) corresponded to C\(_2\)-methyl protons while triplet \((J = 7.1 \text{ Hz})\) at 3.90 \(\delta\) belonged to CH\(_2\)-Cl protons. A singlet at 4.09 \(\delta\) was accounted for C\(_3\)-methoxy protons. Quartet \((J = 7.1 \text{ Hz})\) at 4.45 \(\delta\) was attributed
to C₃-ester methylene protons and triplet (J = 7.1 Hz) at 4.86 δ was due to NCH₂ protons. Multiplet ranging from 7.49 to 7.65 δ was ascribed to C₆- and C₇- protons and singlet at 7.81 δ belonged to C₄-proton. Doublet (J = 8.5 Hz) at 8.13 δ was accounted for C₈-proton while another doublet (J = 8.5 Hz) at 8.45 δ corresponded to C₉-proton.

The chloroethylbenz(g)indole 410 was reacted with thiophenol in refluxing ethanol in presence of K₂CO₃ to secure the desired l-[2-phenylthioethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole 411a. IR spectrum of 411a (Fig. 187) displayed a strong stretching band at 1693 cm⁻¹ due to C₃-ester carbonyl. ¹H NMR spectrum of 411a (Fig. 188) exhibited a triplet (J = 7.1 Hz) at 1.49 δ due to C₃-ester methyl protons. Singlet at 2.74 δ belonged to C₂-methyl protons. Triplet (J = 7.1 Hz) at 3.30 δ was attributed to CH₂-S protons. Singlet at 4.07 δ was accounted for C₅-methoxy protons while the triplet (J = 7.1 Hz) at 4.71 δ was assigned to NCH₂ protons. Multiplet ranging from 7.28 – 7.56 δ belonged to C₆-, C₇- and five thiophenyl protons. Singlet at 7.77 δ corresponded to C₄-proton while the doublet (J = 8.5 Hz) at 7.90 δ belonged to C₈-proton. Doublet (J = 8.5 Hz) at 8.42 δ was due to C₉-proton.

The mass spectrum of 411a (Fig. 189) displayed molecular ion peak M⁺ at m/z (%) 419(100). The fragment F₁ displayed a peak at m/z (%) 296 (10) due to the loss of C₇H₇S from the molecular ion. The peak at m/z (%) 222(8) was assigned to fragment F₂ obtained by the loss of C₈H₉S, CH₃ and OC₂H₅ from the molecular ion. The fragment F₃ showed a peak at m/z(%) 180 (6) due to the loss of OCH₃, C₃H₄, CO₂ and C₈H₉S from the molecular ion. The peak at m/z (%) 137 (90) was attributed to the fragment F₄ secured from the molecular ion by the loss of C₁₇H₁₆NO₃. The peak at m/z (%) 109 (22) was accounted for fragment F₅ resulted by the loss of C₁₉H₂₀NO₃ from the molecular ion [Scheme - 44].
Scheme – 44

\[
\begin{align*}
& \text{F}_2 \\
& m/z \text{ (%)} \\
& 222(8) \\
& + \cdot \\
& c_{19}h_{20}n_{0}, \\
& 1M+ \cdot \\
& m/z \text{ (%)} \\
& 419(100) \\
& C,7H_{16}N_{03} \cdot i^* \\
& \text{SCH}_j CH_j \\
& \text{CH}_3 \\
& m/z \text{ (%)} \\
& 137(90) \\
& f_3 \cdot \\
& m/z \text{ (%)} \\
& 180(6) \\
& f_5 \\
& m/z \text{ (%)} \\
& 109(22) \\
& F_4 \\
& m/z \text{ (%)} \\
& 268
\end{align*}
\]
The chloroethylbenz(g)indole 410 was also reacted with phenol in refluxing dry dimethyl formamide in presence of anhydrous K$_2$CO$_3$ and KI to obtain the desired 1-[2-phenoxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole 412a. IR spectrum of 412a (Fig. 190) displayed a strong stretching band at 1685 cm$^{-1}$ due to C$_3$-ester carbonyl. $^1$H NMR spectrum of 412a (Fig. 191) exhibited triplet (J = 7.1 Hz) at 1.50 $\delta$ due to C$_3$-ester methyl protons. Singlets at 2.94 $\delta$ and 4.08 $\delta$ were attributed to C$_2$-methyl and C$_5$-methoxy protons. Quartet (J = 7.1 Hz) at 4.45 $\delta$ was accounted for C$_3$-ester CH$_2$ and NCH$_2$ protons while triplet (J = 7.1 Hz) at 5.00 $\delta$ corresponded to $-\text{CH}_2\text{-O}$-protons. Multiplets ranging from 6.84 to 7.27 $\delta$ was attributed to protons of phenyl function where as another multiplet from 7.44 to 7.61 $\delta$ was assigned to C$_6$- and C$_7$- protons. Singlet at 7.83 $\delta$ was due to C$_4$-proton. Doublet (J=8.5 Hz) at 8.25 $\delta$ belonged to C$_8$-proton while another doublet (J = 8.5 Hz) at 8.46 $\delta$ was ascribed to C$_9$-proton.
Present Work : Part  B

Cleavage of mesylethyl group at position-1 of 1-substituted indole/ benz(g)indole with sodium cyanide
In another investigation, the indole and benz(g)indole mesylates 372 and 385 were reacted separately with sodium cyanide in refluxing dimethyl sulfoxide with a desire to get the corresponding 1-[2-cyanoethyl]indole derivatives 413 and 415. However, the reaction did not yield the expected 1-[2-cyanoethyl]indole derivatives 413 and 415 but the reaction resulted in the cleavage at the N-CH₂ bond exclusively producing 2-methyl-3-ethoxycarbonyl-5-methoxyindole/benz(g) indole 414 and 416 where in the 1-position is free. [Scheme – 46].

The cyanide nucleophile has choice of attacking at the 1- and 2-positions of 2-mesylethyl group located at 1- position of 372a. However, under present experimental conditions, the nucleophilic attack of cyanide ion has taken place at position -1 of the 2-mesylethyl group of 372a leading to the cleavage of N-CH₂ bond as depicted in Scheme – 45.
Scheme – 46

Scheme – 46

372

H3CO

COOC2H5

NaCN/DMSO

Δ

385

H3CO

COOC2H5

NaCN/DMSO

Δ

413

H3CO

OC2H5

414

H3CO

OC2H5

415

H3CO

OC2H5

416

H3CO

OC2H5
The nucleophilic attack of cyanide ion via path 'a' seems to be more favourable due to the canonical structure 372b where in a lone pair of electrons on indole nitrogen are delocalised on C3-ester carbonyl oxygen which necessarily creates electron deficiency at position -1 of the 2-mesylethyl group of 372 leading to the cleavage of N-CH2 bond of indole/benz(g)indole. The reaction carried out with DMF/NaCN also yielded the same products 414 and 416 in good yields.

The IR spectrum of 2-methyl-3-ethoxycarbonyl-5-methoxyindole 414 (Fig. 192) exhibited a strong stretching band at 3262 cm⁻¹ due to NH function while strong stretching band at 1694 cm⁻¹ was attributed to C3-ester carbonyl. ¹H NMR spectrum of 414 (Fig. 193) displayed a triplet (J = 7.1 Hz) at 1.44 δ due to C3-ester methyl protons. Singlet at 2.70 δ was due to C2-methyl protons while another singlet at 3.87 δ was accounted for C5-methoxy protons. Quartet (J = 7.1 Hz) at 4.39 δ was assigned to C3-ester methylene protons. Doublet of doublet (J = 8.5 Hz and 2.5 Hz) at 6.82 δ was attributed to C6-proton while doublet (J = 8.5 Hz) at 7.17 δ was due to C7-proton. Doublet (J = 2.5 Hz) at 7.62 δ corresponded to C4-proton and broad singlet at 8.36 δ was assigned to NH proton which vanished on D₂O exchange.

IR spectrum of 416 (Fig. 194) displayed a strong stretching band at 3245 cm⁻¹ due NH function and another strong stretching band at 1699 cm⁻¹ was attributed to C3-ester carbonyl. ¹H NMR spectrum of 416 (Fig. 195) exhibited triplet (J = 7.1 Hz) at 1.44 δ due to C3-ester methyl protons. Two singlets at 2.76 δ and 4.05 δ were attributed to C2-methyl and C5-methoxy protons respectively. Quartet (J = 7.1 Hz) at 4.41 δ was assigned to C3-ester methylene protons. Multiplets ranging from 7.43 to 7.55 δ was accounted for C6- and C7- protons. Singlet at 7.63 δ was attributed to C4-proton. Doublet (J = 8.5 Hz) at 7.68 δ was ascribed to C5-proton while another doublet (J = 8.5 Hz) at 8.36 δ was attributed to C9-proton. Broad singlet at 8.96 δ was due to NH proton which vanished on D₂O exchange.
Fig. 183: IR Spectrum

Fig. 184: \textsuperscript{1}H NMR Spectrum 
CDCl\textsubscript{3}
Fig. 185: IR Spectrum

Fig. 186: $^1$H NMR Spectrum

CDCl$_3$
Fig. 187: IR Spectrum

Fig. 188: $^1$H NMR Spectrum
$CDCl_3$
Fig. 194: IR Spectrum

Fig. 195: $^1$H NMR Spectrum

CDCl$_3$
Experimental
1-[2-Chloroethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole: 407

To the solution of 371 (1g, 0.0036 mol) in acetonitrile (50 mL) was added carbon tetrachloride (1.09 g, 0.0072 mol) and triphenyl phosphine (1.89 g, 0.0072 mol). The reaction mixture was heated at reflux for 4 hours. The solvent was removed and the oil obtained was subjected to column chromatography on silica gel column (eluting system, benzene / ethylacetate 7:3). Evaporation of eluate afforded a solid which was recrystallised from ethanol as pale yellow needles, m.p. 138-9°C yield: 0.8 g, 75.4%.

Anal. Calcd for C_{15}H_{18}N_{03}C_{1}: C, 60.9; H, 6.13; N, 4.74. Found: C, 60.21; H, 6.32; N, 4.35.

1-[2-Phenylthioethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole: 408a.

To the solution of 1-[2-chloroethyl]indole derivative 407 (0.39, 0.001 mol) and thiophenol (0.11 g, 0.001 mol) in dry ethanol (50 mL), anhydrous K_{2}CO_{3} (1.38 g, 0.01 mol) was added. The reaction mixture was refluxed on water bath for 12 hours, cooled to room temperature and separated solid was filtered. The solid was triturated with dil. HCl (1:1) to pH 2, filtered, washed with water and recrystallised from suitable solvent (Table - 9).

1-[2-Phenoxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole: 409a.

To the solution of 1-[2-chloroethyl]indole derivative 407 (0.3 g, 0.001 mol) in dry dimethyl formamide (50 mL), anhydrous K_{2}CO_{3} (1g), KI (0.1 g) and phenol (0.001 mol) were added and the mixture was heated at reflux for 30 hours. It was then filtered hot and the solvent was distilled off under reduced pressure. The residue was treated with NaOH solution (1M, 10 mL) and extracted with chloroform (2 x 25 mL). Organic layer was dried over anhyd. Na_{2}SO_{4}. Chloroform was evaporated and the solid was recrystallised from suitable solvent (Table - 9).
1-[2-Chloroethyl]-3-ethoxycarbonyl-5-methoxy-2-methyIbenz(g)indole: 410

This compound 410 was prepared from 385 (1g, 0.003 mol) according to the procedure depicted for the compound 407 as brown granules, m.p. 140-1°C, yield : 0.89 g, 76%.

Anal. Calcd for C_{19}H_{20}NO_{3}Cl : C, 65.99; H, 5.83; N, 4.05. Found : C, 65.46; H, 5.64; N, 4.22.

1-[2-Phenylthioethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole: 411a

This compound 411a was prepared from 410 (0.35 g, 0.001 mol) according to the procedure given for the compound 408a and recrystallised from suitable solvent (Table – 10).

1-[2-Phenoxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole: 412a

This compound 412a was prepared from 410 (0.35 g, 0.001 mol) according to the procedure given for the compound 409a and recrystallised from suitable solvent (Table – 10).

3-Ethoxycarbonyl-5-methoxy-2-methylindole: 414

To the solution of indole mesylate 372 (0.4 g, 0.001 mol) in dimethyl sulphoxide (50 mL) was added sodium cyanide (0.245 g, 0.005 mol) in water (10 mL). The reaction mixture was heated at reflux for 3 hours and concentrated to half of its original volume and poured into crushed ice (50 g). The separated solid was filtered and washed with water, dried and recrystallised from ethanol as colourless granules, m.p. 159°C (lit. 161°C), yield : 0.25 g, (75.8%).

Anal. Calcd for C_{12}H_{13}NO_{3} : C, 65.14; H, 6.83; N, 6.33, Found : C, 65.26; H, 6.71; N, 6.48.
3-Ethoxycarbonyl-5-methoxy-2-methylbenz(g) indole : 416

This compound 416 was prepared from 385 (0.4 g, 0.00098 mol) as per the procedure given for the compound 415 and recrystallised from ethanol as colourless granules, m. p. 182-3°C, yield : 0.2 g, 71.5 %.

Anal. Calcd for C₁₆H₁₇N₅O₃ : C, 70.83; H, 6.31; N, 5.16. Found : C, 70.69; H, 6.48; N, 5.03.
### Table-9

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>m.p. °C</th>
<th>Yield(%)</th>
<th>Nature(Solvent)</th>
<th>Molecular Formula</th>
<th>Elemental Analysis</th>
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<td></td>
<td></td>
<td>C</td>
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<tr>
<td>408 a</td>
<td>C₆H₅</td>
<td>142-3</td>
<td>72</td>
<td>Colourless flakes (ethanol)</td>
<td>C₂₁H₂₃NO₃S</td>
<td>68.27</td>
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<td>408 b</td>
<td>C₆H₄-Cl(4)</td>
<td>155-6</td>
<td>68</td>
<td>Brown granules (ethanol)</td>
<td>C₂₁H₂₂NO₃SCl</td>
<td>62.44</td>
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<td>(3.61)</td>
</tr>
<tr>
<td>409 a</td>
<td>C₆H₅</td>
<td>182-3</td>
<td>65</td>
<td>Colourless powder (ethanol)</td>
<td>C₂₁H₂₂NO₄</td>
<td>71.37</td>
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Table-10

| Compound | R     | m.p. -C | Yield(|%) | Nature/Solvent | Elemental Analysis |
|----------|-------|---------|----------|----------------|-------------------|
| 411a     | C₆H₅  | 150-1   | 75       | Colourless needles (ethanol) | C₆H₅NO₂S (71.58, 71.39) C₂H₅N₂O₅S (66.28, 66.28) |
| 411b     | C₆H₄-Cl(2) | 163-4 | 70       | Brown granules (ethanol) | C₆H₅NO₂S (53.33, 53.33) C₂H₅N₂O₅S (53.33, 53.33) |
| 412a     | C₆H₅  | 171-2   | 68       | Pale brown flakes (ethanol) | C₆H₅NO₂S (6.24, 6.24) C₂H₅N₂O₅S (6.24, 6.24) |
| 412b     | C₆H₄-Cl(2) | 156-7 | 63.5     | Colourless granules (ethanol) | C₆H₅NO₂S (5.32, 5.32) C₂H₅N₂O₅S (5.32, 5.32) |
| 412c     | C₆H₄-Cl(4) | 166-7 | 73       | Colourless flakes (ethanol) | C₆H₅NO₂S (5.32, 5.32) C₂H₅N₂O₅S (5.32, 5.32) |
| 412d     | C₆H₄-Cl(4) | 178-9 | 69       | Colourless granules (ethanol) | C₆H₅NO₂S (6.24, 6.24) C₂H₅N₂O₅S (6.24, 6.24) |

Elemental Analysis:

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