CHAPTER VI
EFFECT OF pH ON THE DIAZO-COUPLING REACTION OF DIAMINOARYLSULPHIDES AND SULPHONES WITH INDOLE

(A reverse diazo-coupling reaction of indole)

In the previous chapters namely chapters III, IV and V, the diazo-coupling reactions of indole with the diazonium salts of several amines were carried out by following usual procedure of adding an alcoholic solution of indole to a solution of the diazonium salts at an appropriate pH. In this study, the diazo-coupling reactions were carried out by adopting a different procedure. The procedure adopted was the reverse of what had been done in the previous three cases. In the experiments carried out in this chapter, the diazonium salt solutions were added in aliquot proportions to an ethanolic solution of indole. The main idea behind the adoption of such a procedure was to study whether there appears any notable change in the pathway of the overall diazo-coupling reaction. It is assumed that any change in the pathway of the reaction can be found out by isolating and identifying the products of the reaction.

The primary aim of this study therefore, is to isolate the products of the reactions from the gross reaction yield and to see whether the products isolated resemble any of the products that were isolated earlier. If however, the reaction products differed, then the aim is to arrive at a possible pathway of the reaction which would be able to explain the formation of the products from the reactants used.
The second aim of this investigation is to find out whether the reaction products vary with the variation in pH of the reaction medium. In keeping with this aim, the 'reverse' diazo-coupling reactions were carried out at two different pH of the reaction medium namely at pH 2 and pH 5.

The amines that were used for subsequent conversion to the diazonium salts for carrying out the diazo-coupling reactions are the following

a) o-aminophenylmethylsulphide
b) o-aminophenylmethylsulphone

PROCEDURE FOR CARRYING OUT THE REACTION AT pH 5

The amines (0.05 mole) were dissolved in 200 ml. of water and 5 ml. of concentrated hydrochloric acid. To it was added a solution containing 0.05 mole of sodium nitrite in 10 ml. of water and allowed to stand for 15 minutes at 0-5°C. The diazonium salt solution so formed was added dropwise to a well stirred solution of indole (0.05 mole) in 250 ml. of water containing 50 ml. of ethanol, 0.5 gms of sodium hydroxide and 5 gms of sodium carbonate. The temperature of the reaction medium was maintained at 0-5°C and the addition of the diazonium salt solution was completed within 60 minutes. Stirring was continued till the reaction was complete. The completion of the reaction was tested with an alkaline solution of β-naphthol.
PROCEDURE FOR CARRYING OUT THE REACTION AT pH 2

The amines were dissolved in 30 ml of water containing 5 ml of concentrated hydrochloric acid and the solution was cooled to 0-5 °C. To this solution was added a solution containing 0.05 mole of sodium nitrite in 10 ml of water. The solution was allowed to stand for about 30 minutes. This diazonium salt solution was then added dropwise to an ethanolic solution (20 ml) of indole (0.05 mole) with constant stirring. The addition was completed in an hour's time. In this experiment the diazonium salt solution was added in slight excess so as to accelerate the rate of the reaction.

In both the above cases, the products obtained were in the form of a sticky mass which was subjected to thin layer chromatography with silica gel G as adsorbent and a mixture of benzene and ethyl acetate in the proportion 5:1 as the eluent. Several coloured zones were obtained which indicated the multiple nature of the reaction products. The gross yield of the reactions were then separated into the individual products by column chromatography using alumina (neutral) as the adsorbent and a mixture of benzene and ethyl acetate in the ratio of 5:1 as the eluent. Column chromatography was carried out several times so as to ensure a high state of purity of the individual compounds isolated.
NATURE OF THE PRODUCTS ISOLATED

a) At pH 5 of the reaction medium

From the gross yield of the reaction at pH 5, two major zones were isolated and identified by mainly interpreting the IR and UV spectra of the products. The major products obtained are given in scheme XXXI. The compounds are designated as compounds X (a,b) and compounds XI (a,b).

b) At pH 2 of the reaction medium

Similarly, from the gross yield of the reaction medium carried out at pH 2, four compounds were isolated, identified and characterized. These compounds are given in scheme XXXII and the physical characteristics are given in table XVII. Two compounds were identical to X(a,b) and XI(a,b) and the other two were XII(a,b) and the compound XIII.

It can be concluded from the above observation that at pH 2 of the medium the number of reaction products increases considerably. Another conclusion that can be drawn is that the reactions occurring at pH 2 and pH 5 may not always follow the same path. The outline of the reactions occurring at two different pH is shown in Scheme XXXIII.

MECHANISM OF THE REACTION AT pH 5

The products isolated from the reaction carried out at pH 5 are the 3-arylazoindole and the 2-aryl-3-arylazoindole. From the nature of the products isolated, it is possible to formulate a mechanism of the reaction and the pathway of the mechanism is given in scheme XXXIV.
COMPOUNDS ISOLATED FROM THE REACTION CARRIED OUT AT pH 5

\[ \text{SCHEME-XXXI} \]
COMPONENTS ISOLATED FROM THE REACTION CARRIED OUT AT pH 2

where \( A_r \) and \( A_r' \)

SCHEME - XXXII
THE REACTION PATHWAY AT $\text{pH} 2$ AND $\text{pH} 5$

\[ \text{X} \quad \text{Ar-N$_2$} \quad \text{pH 5} \quad \text{X} \]

\[ \text{XII} \quad \text{Ind-3'} \]

SCHEME-XXX III
PHYSICAL CHARACTERISTICS OF COMPOUNDS OBTAINED FROM THE REACTION AT pH 5
REF: SCHEME XXXI

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Yield (%)</th>
<th>Rf Value</th>
<th>M.p. °C</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xib</td>
<td>brown</td>
<td>12.25</td>
<td>0.63</td>
<td>242-245</td>
<td></td>
</tr>
<tr>
<td>Xia</td>
<td>brown</td>
<td>10.5</td>
<td>0.49</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>Xb</td>
<td>brown</td>
<td>41.5</td>
<td>0.74</td>
<td>181-183</td>
<td>(1c)</td>
</tr>
<tr>
<td>Xa</td>
<td>yellow</td>
<td>35.5</td>
<td>0.856</td>
<td>117-118</td>
<td>(1a)</td>
</tr>
</tbody>
</table>

TABLE XVI

REF: SCHEME XXXI

PHYSICAL CHARACTERISTICS OF COMPOUNDS OBTAINED FROM THE REACTION AT pH 5

TABLE XVI
TABLE XUII

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Yield</th>
<th>Boiling point C</th>
<th>Melting point C</th>
<th>%</th>
<th>ALI</th>
<th>AR</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>XIII</td>
<td>do</td>
<td>10%</td>
<td>2450</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>XIX</td>
<td>red</td>
<td>8%</td>
<td>2240</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>XIXb</td>
<td>dark</td>
<td>6%</td>
<td>2000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

PHYSICAL CHARACTERISTICS OF COMPOUNDS OBTAINED FROM THE REACTION AT pH 2

REF. SCHEME XXII

TAMALE XXII
The formation of the 3-aryiazindoie is a direct consequence of the electrophilic aromatic substitution of indole by the electrophile Ar-N₂. The yield of the 3-aryiazindoie is also found to be high which is in keeping with the observation arrived at in chapter V.

Here the main aim is to arrive at a mechanism which would explain the formation of the compound 2-aryl-3-arylazoindole. The mechanism arrived at is given in scheme XXXIV. The first step of the reaction is the formation of the 3-aryiazindoie which can act as a source for the formation of the compound 2-aryl-3-arylazoindole. The dizonium ions present in the reaction medium may decompose in solution eliminating N₂ gas and giving the aryl free radical. It had been observed earlier by Hey and Waters that the decomposition of the aryldiazonium ions give rise to the aryl free radical which subsequently undergoes rapid rearrangement or react with the substrate and also the solvent molecules present in the reaction medium. Under the conditions a free radical or a electron - transfer mechanism is possible for the formation of compounds of type XI. In the first step of the reaction the aromatic 3-aryiazindoie in a diffusion control step, transfers an electron to the aryldiazonium ion so that the encounter pair is composed of a radical and a radical cation (I). The radical then eliminated nitrogen (N₂) to give the aryl free radical (II). In the next step, the radical pair collapses to a 'σ-complex' intermediate. The
SCHEME - XXXIV

110A
aryl free radical being less selective will preferentially attack the C-2 position of the ion radical because of steric hindrance at C-3 position. The α-complex then eliminates a proton to give the final product.

MECHANISM OF THE FORMATION OF THE COMPOUNDS XII(a,b) AND COMPOUND XIII AT pH 2.

At pH 2 of the reaction medium two more products were isolated over and above the 3-arylazoindole (Xia,b) and the 2-aryl-3-arylazoindole (XIIa,b). These additional products have been identified as 2-(3'-indyl)-3-arylhydrazonoindolenine (compound XIIa and XIIb) and the other product 2,2-(3'-diindyl)-indoxyl (compound XIII). These are the products of the indole dimer. The mechanism of the formation of the compounds XIIa,b namely the 2-(3'-indyl)-3-arylazoindolenine and XIII are shown in scheme XXXV and scheme XXXVI respectively.

The formation of the compound XIIa,b (scheme XXXV) can be explained by taking the 3-arylazoindole as the starting compound which forms insitu. As has already been established, the 3-arylazoindole is formed by the electrophilic aromatic substitution of the indole molecule by the electrophile Ar-N₂. As a first step of this mechanism the 3-arylazoindole is assumed to undergo a tautomeric change leading to the formation of the 3-arylhydrazonoindolenine. Tautomerism is possible and it has been observed that 3-phenylazoindole appears in equilibrium with
MECHANISM OF THE FORMATION OF COMPOUND XII AT pH 2

\[
\begin{align*}
\text{Scheme XXXV}
\end{align*}
\]
3-phenylhydrazonoindolenine. The predominance of either of the two tautomers would however depend upon the reaction medium and their independent stability. This 3-arylhydrazonoindolenine undergoes protonation in the highly acidic condition of the reaction to give the N-protonated-3-arylhydrazonoindolenine. The protonated indolenine derivative contains the reactive \(-\text{C=N-}\) double bond where attack by the electrophiles can occur. Such an attack at the carbon end of the protonated \(-\text{C=N-}\) of the indolenine intermediate had been shown to occur by Fischer, Freund and Lebach, and Witkop. It is a well known fact that the C-3 position of the indole molecule has a high electron density and hence this position of the indole can act as a nucleophilic centre. The attack of the C-3 position of the second indole molecule in the carbon end of the protonated \(-\text{C=N-}\) group of the indolenine intermediate is therefore possible and the attack leads to the formation of the possible intermediate 'A' where the pyrrole ring of the indole molecule loses its aromaticity. This intermediate is assumed to be unstable because of the loss of aromaticity and regains aromatic character by eliminating a proton to give the 3-arylhydrazono-2-(3'-indyl)-indoline as another intermediate 'B'. This particular intermediate could not be isolated nor any evidence regarding its formation could be arrived at. Finally this intermediate probably undergoes oxidation by atmospheric oxygen leading to aromatization and the formation of the compound 3-arylhydrazono-2-(3'-indyl)-indolenine (compound XII a,b). The susceptibility of
TAUTOMERIC FORMS OF 3-ARYLAZO-INDOLES

SCHEME-XXXV

\[
\begin{align*}
&\text{N=N-} \quad \text{H} \\
&\text{N=N-} \quad \text{N-N-Ar}
\end{align*}
\]

\[\text{H}^+ \quad \text{H}^+\]

SCHEME-XXXV

\[\text{H} \quad \text{H} \]

\[\text{N-N-Ar} \quad \text{N-N-Ar}
\]
the intermediate 'b' towards oxidation by atmospheric oxygen is based on the observation that 2,3-disubstituted indolines or indoles are unstable in the presence of atmospheric oxygen.

The compound XII(a,b) is a tautomeric form of the corresponding azo compound. UV spectra of the compounds do not indicate the presence of the azo group. On the other hand, absorption pattern shows the presence of 2,3-disubstituted indolenine nucleus and the phenylhydrazone chromophore. The IR spectra of the compound shows the presence of a weak N-H stretching frequency however C=N- stretching frequency also appears. From the above observations it is assumed that both 3-azoindole structure and 3-hydrazonoindolenine structures are present but the equilibrium is probably more towards the formation of 3-hydrazonoindolenine structure. On this basis only the structure of the compound XII is written in the 3-hydrazonoindolenine form.

The second problem is to establish a pathway for the formation of the compound XIII. The compound XIII, which is dark red in colour and has a melting point of 245°C is identified as 2,2-(diindyl-3′)-indoxyl. The UV and IR spectra of this compound has been found to be exactly identical to the compound isolated by Siegel et al. and named as α-diindly-γ-indoxyl and which has also been synthesized by the
same authors and others. This compound is also known by an alternative name such as $\alpha$-diindylisatin.

The mechanism of the formation of compound XIII i.e. 2,2-(diindyl-3')-indoxyl is given in scheme XXXVI. It is assumed that the precursor of compound XIII is the 3-arylhydrazono-2-(3'-indyl)-indolenine which was also isolated from the gross reaction yield. The mechanism can be explained as follows:

In the highly acidic medium, the nitrogen atom (N) of the reactive C=N group of the indolenine residue is attacked by the H ions to give the protonated 3-arylhydrazono-2-(3'-indyl)-indolenine. The double bond (\(-C=NH-\)) of the protonated intermediate polarizes in such a way that a residual positive charge is present in the C-2 carbon centre. This electrophilic centre is susceptible to attack by another indole molecule present in excess in the reaction medium. The C-3 position of the second indole molecule therefore, attacks the C-2 carbon atom of the intermediate 'C' to give the intermediate 'D'. This intermediate then eliminates a proton to restore aromatic character of the attacking indole molecule to give the intermediate 'E'. Finally, the hydrazono group is hydrolyzed in acidic medium to give the final product 2,2-(diindyl-3')-indoxyl. The final step of hydrolysis is possible due to the steric strain in the molecule which comes into play due to the presence of two
MECHANISM OF THE FORMATION OF COMPOUND XIII AT pH²

SCHEME - XXXVI
bulky indolyl groups at the adjacent carbon atom. Elimination of steric strain, therefore, acts as a driving force for the process of hydrolysis which is possible under acidic conditions.

It may be mentioned at this point that the two products 2-(3'-indyl)-3-arylhydrazonoindolenine and 2,2-(diindyl-3')-indoxyl are formed due to the polymerization of the indole molecule. This polymerization is possible only because indole is always in excess in the reaction medium. It should be noted again that in these particular reactions the diazonium salt solutions were added in aliquot proportions to the indole solution such that indole was always in excess during the reaction. However these polymerization reactions and products are quite different from the polymerization products obtained when the reactions were carried out as in Chapter IV. The products in these experiments therefore, leads to the belief that in these particular reactions, polymerization of indole have taken place after the diazo-coupling reactions had occurred.

SPECTROSCOPIC IDENTIFICATION OF THE PRODUCTS OBTAINED

The products obtained were identified with the help of their UV and IR spectra. The UV spectra were taken in a Beckmann DK-2 recording spectrometer and the IR spectra were taken in an Elmer-Perkin 297 recording spectrometer.
1. Compound Xa: 3-(2'-thiamethyl)-phenylazoindole

The IR and UV spectra of this compound is found to be similar to the compound Ia (chapter III). The melting point, colour of zone in the chromatography column, R value and the micro-analytical data have also been found to correspond to the compound Ia. These similarities prove beyond doubt that the compound Xa is 3-(2'-thiamethyl)-phenylazoindole. The IR spectrum of this compound along with that of compound Ia is given in Plate XLIX.

2. Compound Xb: 3-(2'-methylsulphonyl)-phenylazoindole

The IR and UV spectra of this compound is found to be similar to that obtained for the compound Ic (chapter III). The melting point, colour of zone in the chromatography column, R value and the data obtained from micro analysis correspond to those obtained for the compound Ic. Hence the compound Xb is found to be identical to the compound Ic and has been identified as 3-(2'-methylsulphonyl)-phenylazoindole. The micro analysis data shows a molecular formula of \( \text{C}_{15} \text{H}_{13} \text{N}_3 \). The UV spectrum shows absorption at 260 nm (sulphonyl), 275 nm (3-substituted indole), 335 nm (azo group). The IR spectrum shows absorptions at the frequencies \( 3340 \text{ cm}^{-1} \), \( 810 \text{ cm}^{-1} \), \( 750 \text{ cm}^{-1} \), \( 1300 \text{ cm}^{-1} \) and \( 1090 \text{ cm}^{-1} \). The IR spectra of compound Xb and Ic are shown in Plate 50.
IR SPECTRA OF COMPOUNDS I (A) AND X (B)

PLATE XLIX

WAVENUMBER (Cm⁻¹)

A

B

600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800 3000 3200 3400 3600 3800 4000
Plate I

IR spectra of compounds Ic (a) and Xb (b)
4. **Compound XI:** 2-(2'-thiamethyl)phenyl-3-(2'-thiamethyl)-phenylazoindole

The micro analytical data of this compound along with its molecular formula is given in the following table:

<table>
<thead>
<tr>
<th>Element</th>
<th>Found</th>
<th>Calculated</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>67.82%</td>
<td>67.86%</td>
<td>C_{22}H_{19}N_{2}S_{2}</td>
</tr>
<tr>
<td>H</td>
<td>4.95%</td>
<td>4.89%</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>10.75%</td>
<td>10.8%</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>16.48%</td>
<td>16.45%</td>
<td></td>
</tr>
</tbody>
</table>

The molecular formula suggests the presence of two (2'-thiamethyl)-phenyl groups. The UV spectrum of this compound shows intense peak at 247 nm and 310 nm which are characteristic of the 2,3-disubstituted indole. Further absorption at 390-400 nm indicates the presence of the azo group in the molecule and finally a shoulder of low intensity at 210 nm indicates the presence of the sulfinide group. The IR spectrum gives absorption at 3450 cm\(^{-1}\) indicating the N-H stretching frequency of the indole, another absorption at 725 cm\(^{-1}\) is due to the presence of the o-disubstituted benzene ring. Absorption at 1430 cm\(^{-1}\) indicates the presence of the azo group, absorption at 3040-3060 cm\(^{-1}\) is because of the presence of the C-H stretching of the aromatic rings, absorption at 2560 cm\(^{-1}\) is due to the C-S stretching which is further indicated by the absorption occurring at 680 cm\(^{-1}\). The IR spectrum of this compound is given along with the IR spectra of the same compound obtained at pH 2.
IR SPECTRA OF COMPOUNDS X]A

PLATE II
3. Compound X: 2-(2'-methylsulphonyl)phenyl-3-(2'-methylsulphonyl)phenylazidonidole

The micro analysis data for this compound and its molecular formula are given in the table shown below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Found</th>
<th>Calculated</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>58.3 %</td>
<td>58.7 %</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>9.54%</td>
<td>9.27%</td>
<td>C H N S O</td>
</tr>
<tr>
<td>H</td>
<td>4.26%</td>
<td>4.2%</td>
<td>22 19 3 24</td>
</tr>
<tr>
<td>O</td>
<td>13.98%</td>
<td>14.12%</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>13.92%</td>
<td>14.12%</td>
<td></td>
</tr>
</tbody>
</table>

The molecular formula can be rationalized by assuming the presence of two phenyl-(2'-methylsulphonyl) groups. The UV spectrum shows absorptions at 240 and 300 nm which are characteristic of the 2,3-disubstituted indole. Absorption at 400 nm is due to the presence of the azo group and finally the absorption at 255 nm is due to the presence of the sulphonyl group. The IR spectrum of this compound shows absorptions at 3500 cm⁻¹ indicating the presence of the N-H stretching vibration of the indole molecule. 730 cm⁻¹ due to the out of plane bending vibration of the N-H group 1435 cm⁻¹ due to the azo group and the two absorptions at 1285 cm⁻¹ and 1140 cm⁻¹ both due to the sulphonyl group. The aromatic C-H stretching occurs in the region of 3000-3020 cm⁻¹. The presence of the methyl group is indicated by the absorption at 2520 cm⁻¹.
UV ABSORPTION SPECTRA OF COMPOUNDS XIa

PLATE LIII

UV ABSORPTION SPECTRA OF COMPOUNDS XIb
5. Compound XIIa: 3′-(2′-thiamethylphenylhydrazono)-2′-(3′-indyl)indolenine

In the UV region this compound shows an intense absorption at 260 nm which is characteristic of the indolenine chromophore. The absorption at 370 nm is due to the presence of the 2,3-disubstituted indolenine molecule. Further the absorption at 290 nm is due to the phenylhydrazone chromophore and finally the low intensity absorption at 205 nm is due to the sulphide linkage. The fact that this compound is in the form of a hydrazone is evident from the observation that the absorption due to the azo group is absent and in its place the absorption due to the phenylhydrazone is found.

The IR spectrum of this compound shows absorption at 3470 cm\(^{-1}\) due to the N-H stretching frequency of the indole nucleus which is supplemented by another absorption at 790 cm\(^{-1}\) due to the N-H bending vibration. The two absorptions found in the region 1540-1600 cm\(^{-1}\) may be due to the C=O stretching frequency of the phenylhydrazone group as well as the indolenine group. Absorption in the region 3060 cm\(^{-1}\) is due to C-H stretching frequency of the aromatic ring. The S-C stretching frequency appears at 2610 cm\(^{-1}\) and 690 cm\(^{-1}\) and finally the absorption at 2140 cm\(^{-1}\) shows the C=O stretching frequency of the phenylhydrazone group. The micro analytical data of this compound and its molecular formula is given in the following table:-
6. Compound XIII: 3-([4'-methylsulphonyl]phenylhydrazono)-2-([3'-
   indyl]-indolenine

   In the UV spectrum of this compound, an intense absorption at 255 nm is observed which is characteristic of the indolenine chromophore. The absorption at 348 nm is due to the 2,3-disubstituted indolenine group with extended conjugation. Further, the absorption at 305 nm indicates the presence of the phenylhydrazone chromophore and finally the absorption at 263 nm indicates the presence of the sulphonyl group. The IR spectrum of this compound shows absorption identical to those obtained for compound XIIa indicating the presence of similar groups in the molecule. Some of the important absorptions observed are the following:-

   -1

   i) 3150 cm⁻¹, N-H stretching frequency of indole
   -1
   ii) 780 cm⁻¹, N-H bending frequency
   -1
   iii) 1560 cm⁻¹, C=N stretching of the phenylhydrazone group
   -1
   iv) 1580 cm⁻¹ C=N stretching of the indolenine group
   v) 2110 cm⁻¹ due to the C=N group
vi) 1300 cm and 1090 cm both due to the sulphonyl group.

The micro analytical data of the compound XIIb and its molecular formula are given in the following table. The IR spectra of the compound XIIa and XIIb are shown together in plate LIV and the UV spectra of the compounds are shown in Plate LV.

<table>
<thead>
<tr>
<th>Element</th>
<th>Found</th>
<th>Calculated</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
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<td>67.12%</td>
<td>66.66%</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>4.4%</td>
<td>4.34%</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>12.98%</td>
<td>13.52%</td>
<td>C H N S O</td>
</tr>
<tr>
<td>O</td>
<td>7.88%</td>
<td>7.73%</td>
<td>23 18 4 2</td>
</tr>
<tr>
<td>S</td>
<td>7.62%</td>
<td>7.71%</td>
<td></td>
</tr>
</tbody>
</table>

In the compound XIIa and XIIb the absence of the absorptions due to the azo group in both the IR and UV spectra of the compounds lead to the fact that the azo group in the molecule is in the form of the phenylhydrazone group. Moreover the absorption in the IR and UV region indicate the presence of the phenylhydrazone group.

7. **Compound XIII: 2,2-(dinyl-3′)-indoxyl**

The micro analytical data and the molecular formula of this compound is given in the following table:
IR SPECTRA OF COMPOUNDS XII 3(a) AND XII b(b)
UV ABSORPTION SPECTRA OF COMPOUNDS XII a(A) AND XII b(B)

PLATE LV
The compound has been identified by comparing its physical properties such as melting points, colour and the UV and IR absorption characteristics with the compounds isolated by Witkop et al. Both the compounds are found to be identical hence it is established that the compound XIII is 2,2-(dindyl-3')-indoxyl. Such a compound was also isolated by Avramenko et al. by the diazo-coupling reaction of indole with diazonium salts. The details of the experiment carried out by these workers are not known because of the nonavailability of the full text of the paper published. The UV spectrum of this compound shows absorption at 385 - 400 nm typical of the indoxyl group another absorption at 280 nm is typical of the 3-substituted indoles.

In the IR spectrum absorptions are found in the region 3450 cm⁻¹ which is identified as the N-H stretching frequency. The absorption at 1600 cm⁻¹ is attributed to the N-C₆ group present in the molecule. Further, absorptions at 1755 cm⁻¹ and 1780 cm⁻¹ is due to the carbonyl stretching of the 3-oxo-indoles. Besides the above absorptions, there are also absorptions at 750 cm⁻¹ due to the o-disubstituted benzene ring and at 3080 cm⁻¹ due to the aromatic C-H stretching.
PLATE IV
IR SPECTRUM OF COMPOUND XIII