

stated, the use of the absorption band at  $0.16\mu$  appears to be ambiguous.

The Drude-type formula characterises the optical activity as arising due to an asymmetric structure of the molecule. The analysis carried out by Perekalina *et al*<sup>6</sup> shows that the crystal structure of  $\text{LiIO}_3$  does not possess a screw character but only an asymmetrization of  $\text{IO}_3^-$  which leads to its optical activity.

Since the same absorption wavelengths, viz.  $0.12$  and  $0.23\mu$ , account for the refractive dispersion (1) and (2) and also the rotatory dispersion (3) it can be concluded that the Drude-type formula is probably more appropriate for explaining the rotatory dispersion of this crystal.

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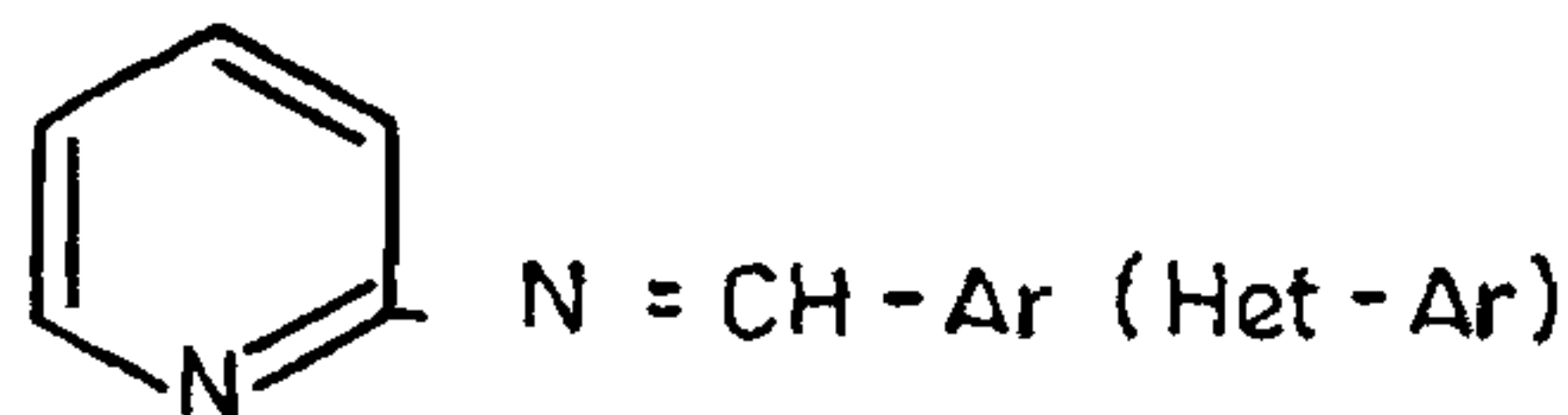
## SYNTHESIS OF SOME NEW N-OXIDOPYRIDYLTHIAZOLIDIN-4-ONES

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DIVERSE biological activities have been found to be associated with 4-thiazolidinone derivatives<sup>1</sup>. The

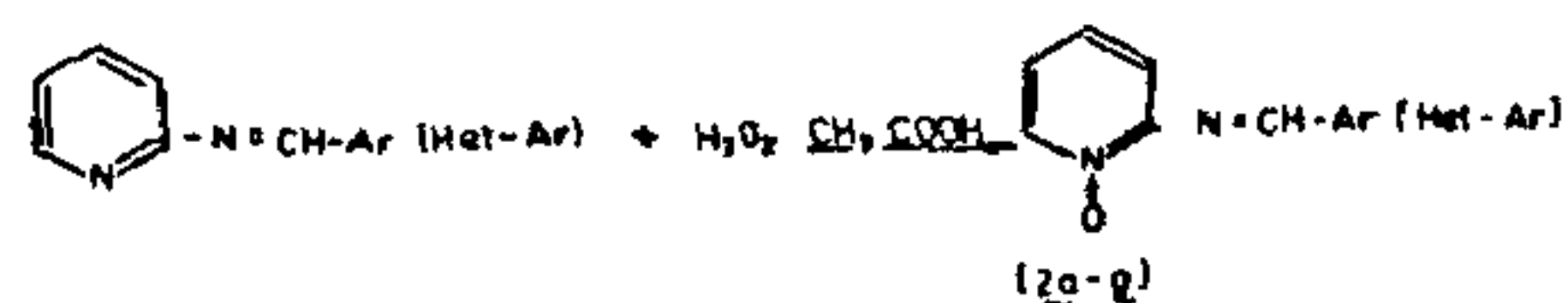
chemotherapeutic efficiency of these compounds as local anesthetic and anticonvulsant agents<sup>2,3</sup>, is of interest and justifies a detailed study of the toxicological properties of the most active compounds. As part of our studies on the chemistry of thiazolidinone heterocyclic systems<sup>4-9</sup> it is of interest to incorporate a polar function into the moiety of such molecules. Since it has been reported that N-oxide heterocyclic compounds are more polar and with much lower partition coefficient values which make them interesting for studying pharmacological properties<sup>10</sup> we describe here the synthesis of N-oxidopyridylthiazolidin-4-ones by (i) preparing the key intermediates, aryl-(heteroaryl)-idene-2-aminopyridine-N-oxides (2a-h) and (ii) cyclocondensation of the key intermediates on mercaptoacetic acid.

Aryl-(heteroaryl)-idene-2-aminopyridines were obtained by the condensation of 2-aminopyridine with different aldehydes in ethanol using piperidine or piperidine acetate as a basic catalyst.

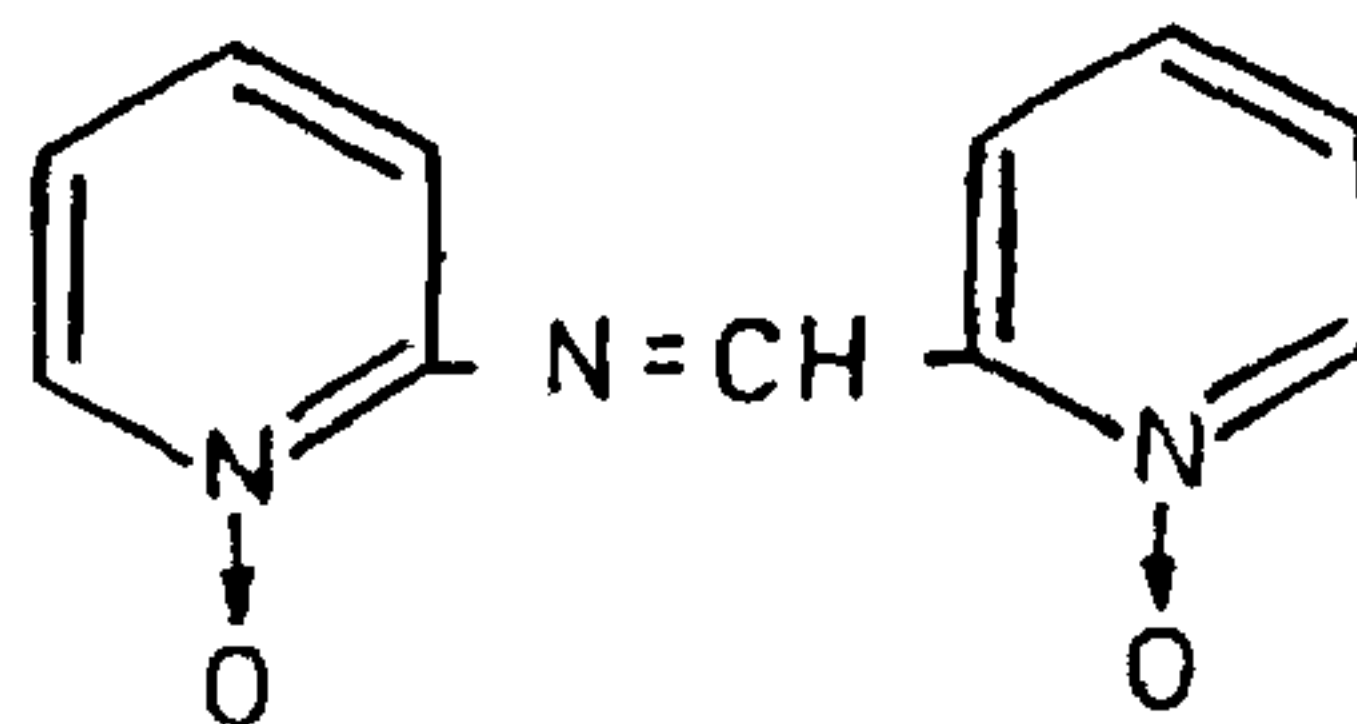


- lg - h
- |   |  |
|---|--|
| 1a, Ar $\text{C}_6\text{H}_5-$              | b, Ar $p\text{-Cl-C}_6\text{H}_4-$               |
| c, Ar $o\text{-OH-C}_6\text{H}_4-$          | d, Ar $p\text{-OH-C}_6\text{H}_4-$               |
| e, Ar $p\text{-NO}_2\text{-C}_6\text{H}_4-$ | f, Ar $p\text{-N(CH}_3)_2\text{-C}_6\text{H}_4-$ |
| g, Heteroaryl thienyl                       | h, Heteroaryl pyridyl                            |

N-oxidation of these derivatives was achieved by interaction with hydrogen peroxide in glacial acetic acid.



in the case of compound 1h the reaction afforded the corresponding dioxide (2h).



The structure of the compounds (2a-h) was established both by microanalytical as well as spectral data. Infrared spectra show strong absorption bands in  $1260\text{-}1320\text{ cm}^{-1}$  region due to  $\text{N} \rightarrow \text{O}$  as well as defined bands in the region  $1640\text{-}1580\text{ cm}^{-1}$  due to  $\nu\text{C}=\text{N}$ .

Cyclocondensation reaction of compounds (2a-h) on mercapto-acetic acid was carried out in refluxing benzene over periods of time ranging between 2 and 6 hr.

The structure of the 4-thiazolidinones was confirmed by a combination of elemental and spectral

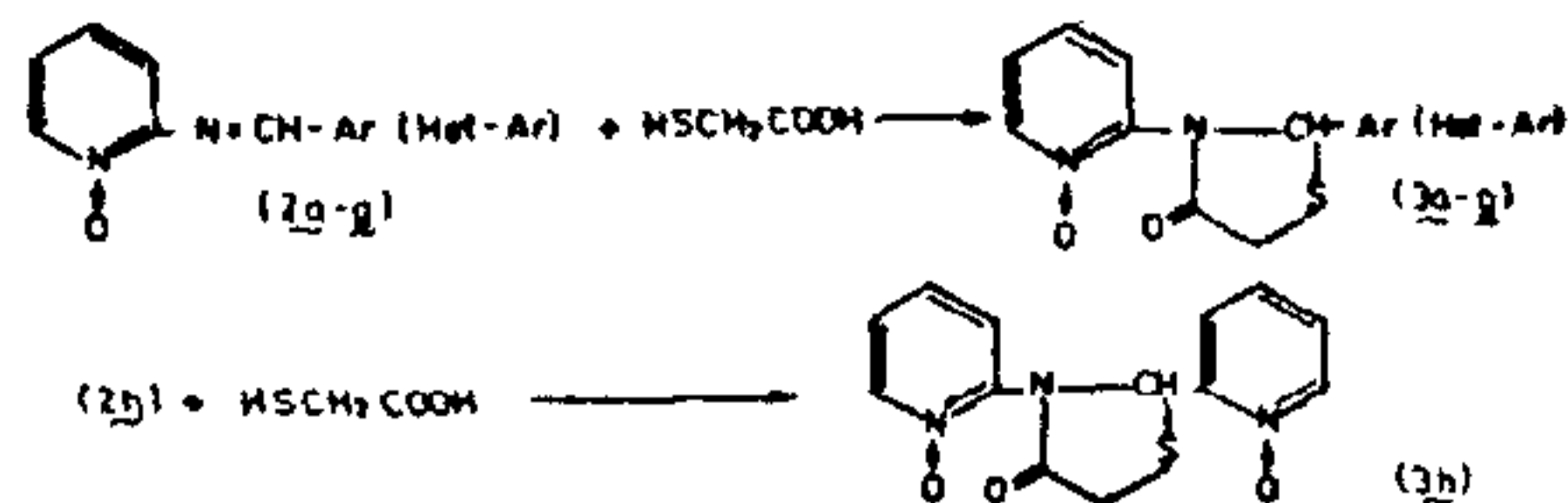


TABLE 1. *N*-oxidopyridine derivatives (2a-h)

|    | Ar(Het-Ar)   | m.p.<br>°C                     | Molecular formula*<br>(Mol. Weight)                                    |
|----|--|--------------------------------|--|
| 2a | phenyl   | 135 <sup>d</sup> (acetic acid) | C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O<br>(198)              |
| 2b | <i>p</i> -Cl-phenyl                                | 180 <sup>d</sup> (acetic acid) | C <sub>12</sub> H <sub>9</sub> ClN <sub>2</sub> O<br>(232.5)           |
| 2c | <i>o</i> -OH-phenyl                                | 205 (DMF)                      | C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub><br>(214) |
| 2d | <i>p</i> -OH-phenyl                                | 176 (acetic acid)              | C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub><br>(214) |
| 2e | <i>p</i> -NO <sub>2</sub> -phenyl                  | 217 (acetic acid)              | C <sub>12</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub><br>(243)  |
| 2f | <i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub> -phenyl | 195 (methanol)                 | C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O<br>(241)              |
| 2g | Thienyl  | 175 (acetic acid)              | C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> SO<br>(204)              |
| 2h | pyridyl  | 277 (DMF)                      | C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub><br>(215)  |

1\* All compounds gave satisfactory microanalysis (C ± 0.17, H ± 0.13, N ± 0.16).  
d with decomposition.

TABLE 2. *N*-oxidopyridylthiazolidin-4-ones (3a-h)

|    | Ar(Het-Ar)   | m.p.<br>°C       | Molecular formula*<br>(Mol. Weight)   |
|----|--|------------------|---|
| 3a | phenyl   | 189(acetic acid) | C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> SO <sub>2</sub><br>(272)               |
| 3b | <i>p</i> -Cl-phenyl                                | 225(acetic acid) | C <sub>14</sub> H <sub>11</sub> ClN <sub>2</sub> SO <sub>2</sub><br>(306.5)           |
| 3c | <i>o</i> -OH-phenyl                                | 238(DMF)         | C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> SO <sub>3</sub><br>(288)               |
| 3d | <i>p</i> -OH-phenyl                                | 215(ethanol)     | C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> SO <sub>3</sub><br>(288)               |
| 3e | <i>p</i> -NO <sub>2</sub> -phenyl                  | 248(acetic acid) | C <sub>14</sub> H <sub>11</sub> N <sub>3</sub> SO <sub>4</sub><br>(317)               |
| 3f | <i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub> -phenyl | 243(acetic acid) | C <sub>16</sub> H <sub>17</sub> N <sub>3</sub> SO <sub>2</sub><br>(315)               |
| 3g | Thienyl  | 295(DMSO)        | C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> S <sub>2</sub> O <sub>2</sub><br>(278) |
| 3h | pyridyl  | 295(DMSO)        | C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> SO <sub>3</sub><br>(289)               |

\* All compounds gave satisfactory microanalyses (C ± 0.11, H ± 0.13, N ± 0.12).



analysis. The infrared spectra are characterized by a band in the region  $1720-1690\text{ cm}^{-1}$  which is due to the  $\delta\text{C}=\text{O}$  group.

### Experimental

All melting points were uncorrected. The IR spectra were recorded on a spectrophotometer, (Pye Unicam SP 200 G), using KBr discs.

#### Synthesis of Schiff bases (1a-h)

These compounds were prepared according to standard procedure<sup>4</sup>.

#### Synthesis of N-oxidopyridines (2a-h)

The schiff base (1a-h) (0.02 mol) in glacial acetic acid (25 ml) was treated with hydrogen peroxide (10 ml). The reaction mixture was heated at reflux temperature for about 3 hr and left to stand at room temperature for 24 hr. On concentration and cooling the precipitated product was filtered off, washed with petroleum ether, then with dilute alcohol and dried. The results are given in table 1.

#### Synthesis of N-oxidopyridylthiazolidinones (3a-h)

A mixture of mercaptoacetic acid (0.015 mol) and the N-oxidopyridine derivatives (2a-h) (0.01 mol) in dry benzene (50 ml) was refluxed for 4 hr and stirred over periods of time ranging from 6 to 24 hr. The product which precipitated was filtered off and crystallized from the proper solvent. The results are shown in table 2.

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## PYRIDINE COMPLEXES OF NICKEL (II) AND COPPER (II) CONTAINING ORTHOPHOSPHATE ION/ ORTHOPHOSPHORIC ACID

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METAL complexes containing orthophosphate ion can be expected to show interesting coordination modes in view of the multivalent and multidentate nature of the orthophosphate ion. Very little work has been reported on such complexes so far<sup>1,2</sup>. When chlorides of Ni(II) and Co(II) were reacted with pyridine in the presence of orthophosphoric acid  $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$  and  $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot 0.5\text{H}_3\text{PO}_4$  (py = pyridine) were obtained. Some structural aspects of these complexes have been investigated.

All chemicals used were of A. R. grade. The reactions were carried out in dry alcohol to minimise the water content of the medium and thereby to possibly prevent coordination of water.  $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$  was prepared by adding solutions of pyridine (40 mmol in 20 ml) and  $\text{H}_3\text{PO}_4$  (20 mmol in 20 ml) to  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  solution (10 mmol in 20 ml) simultaneously. The green precipitate  $[\text{Ni}(\text{py})_2\text{Cl}_2]$  formed in the initial stages of addition of reactants was filtered off and to the filtrate the remaining pyridine and  $\text{H}_3\text{PO}_4$  were added. The pale blue compound precipitated out was filtered, washed and dried in vacuum ( $10^{-2}$  torr). Yield 1.6 g; Anal. found: Ni, 10.06; P, 10.47; N, 9.70; Calcd. for  $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ : Ni, 10.31; P, 10.87; N, 9.84.  $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot 0.5\text{H}_3\text{PO}_4$  was prepared by a similar method. The mixture of pale green and yellow compounds precipitated out initially was filtered off and on further addition of pyridine and  $\text{H}_3\text{PO}_4$  to the filtrate a blue precipitate was obtained, which was filtered, washed and dried in vacuo. Yield, 3.5 g; Anal. found: Cu, 18.79; P, 4.90; Cl, 20.50; N, 8.18; C, 35.10; H, 3.47; Calcd. for  $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot 0.5\text{H}_3\text{PO}_4$ : Cu, 18.61; P, 4.53; Cl, 20.76; N, 8.20; C, 35.15; H, 3.37. The above complexes were not soluble in common organic solvents. They were stable in air and melted with decomposition at  $190-225^\circ\text{C}$ .

The electronic absorption spectra of the complexes (nujol mulls) in the visible and near IR regions were recorded on a Cary-14 spectrophotometer. The magnetic susceptibilities were measured by the Gouy method using  $\text{HgCo}(\text{CNS})_4$  as standard.

The IR spectrum of  $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$  (nujol mulls) showed two bands at  $262\text{ cm}^{-1}(\text{m})$  and  $230\text{ cm}^{-1}(\text{s})$  in the region of  $200-300\text{ cm}^{-1}$  where metal-ligand stretching modes are expected. The IR active metal-