

## SYNTHESIS AND SPECTROSCOPIC STUDIES OF 2-ARYLIMINO-4, 6-DIPHENYLPYRANS AND THEIR ISOMERIC 2-PYRIDONES

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A number of 2-arylimino-4, 6-diphenylpyrans (III) have been prepared from 2-arylamino-pyrylium chlorides (II). 2-Arylimino-4, 6-diphenylpyrans (III) are smoothly rearranged by sodium ethoxide to the isomeric 1-aryl-4, 6-diphenyl-2-pyridones (IV). The isomeric compounds (III) and (IV) are readily distinguished by their UV and mass spectra.

### INTRODUCTION

Although 2-arylimino-4, 6-diphenylpyrans (III) and their isomeric 2-pyridones (IV) are potentially useful as synthetic intermediates, only a few compounds belonging to type (III and IV) have been reported. They include 2-anilino-4, 6-diphenylpyran (III, Ar=Ph) [1], 1,4,6-triphenyl-2-pyridone (IV, Ar=ph) [2], 1-amino-4, 6-diphenyl-2-pyridone (IV, Ar=NH<sub>2</sub>) [3], 1-pyridyl-2-pyridones (IV, Ar=pyridyl derivatives [2,4] and 1-(4-pyridonyl)-4,6-diphenyl-2-pyridones (IV, Ar=4-pyridones) [5].

Recently, we have reported the preparation of 1-aryl-4, 6-diphenyl-2-pyridones (IV) [4,5] using 4,6-diphenyl-2-pyrone (I) [6] or 4-pyrones [7,8] and aromatic amines (Scheme I). Although in our previous work we have described the preparation and rearrangements of the pyrylium salts (II) [4] but less attention has been paid to the isolation and rearrangement of the pyrans (III). In the present work the isolation of 2-iminopyrans (III), their rearrangement to the isomeric 2-pyridones (IV) and identification of the isomeric compounds (III) and (IV) by UV and mass spectra is described.

### MATERIALS AND METHODS

Unless otherwise stated, UV spectra were measured for solutions in ethanol and mass spectra were determined using Perkin-Elmer RMU-6E spectrometer (direct inlet system, source temperature 300°). Melting points were determined using Kofler hot-stage apparatus.

*General Method for Preparation of 2-Arylimino-4, 6-diphenylpyrans (IIIa-h) (Scheme I).* 4,6-Diphenyl-2-pyrone (I) (0.01 mol) and aromatic amines (0.01 mol) in phosphoryl chloride (15 ml) were heated under reflux (5-8 hr).

After cooling, ether (50 ml) was added and the solid product was collected. The residual sticky solid was washed over filter paper with ether-ethanol (50 %, 50 ml) to give 2-arylamino-4, 6-diphenylpyrylium chlorides (IIa-h). The chloride salts (IIa-h) on recrystallisation from pyridine-methanol (50 %) gave 2-arylimino-4, 6-diphenylpyrans (IIIa-h) in 30-50% yield. For pyrans (IIIa-h) the reaction time, yield and UV spectra are summarized in Table 1.

*Rearrangement of 2-Arylimino-4, 6-diphenylpyrans (IIIa-h) to 1-aryl-4, 6-diphenyl-2-pyridones (IVa-h) (Scheme I).* 2-Arylimino-4, 6-diphenylpyrans (IIIa-h) (0.01 mol) and freshly prepared sodium ethoxide (0.02 mol) in ethanol (20 ml) were heated under reflux (8-10 hr). After cooling, the solid product collected which on recrystallisation from ethanol gave 2-pyridones (IVa-h) in 40-50 % yield. The 2-pyridones (IVa-h) are identical with the authentic samples, already prepared from pyrylium salts (II). Experimental condition, m.p., yield and UV spectra is summarized in Table 1.

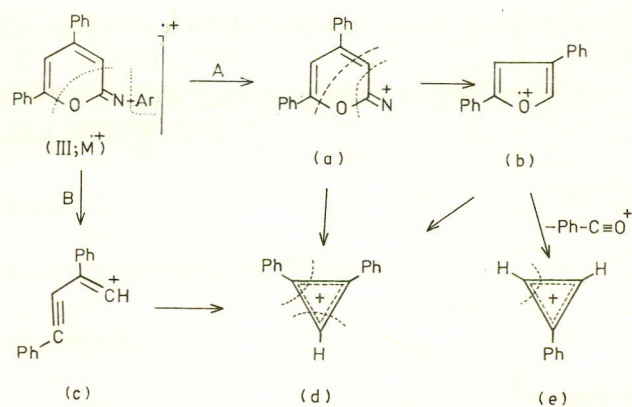
### RESULTS AND DISCUSSION

*2-Arylimino-4, 6-diphenylpyrans (IIIa-h).* 2-Pyrone (I) upon reaction with aromatic amines in boiling phosphoryl chloride gave 2-arylamino-4, 6-diphenylpyrylium chlorides (IIa-h) (Scheme I). The chlorides (II) were converted into 2-arylimino-4, 6-diphenylpyrans (IIIa-h) by recrystallisation from pyridine-methanol. Their structures are fully supported by UV, mass spectra and chemical transformations into isomeric 2-pyridones (IV). The isomeric structures (III) and (IV) might reasonably be expected to exhibit IR and NMR spectra similar to each other. The IR spectra show an absorption band in the region of 1650-1665 cm<sup>-1</sup>, which can be attributed to the C=N stretching

vibration, but 2-pyridones (IV) also absorb in this region (1650–1675  $\text{cm}^{-1}$ ). Similarly, the NMR spectra of the pyrans (III) support their structures, but cannot eliminate the isomeric 2-pyridone structures (IV). The UV and visible spectra characteristics of the 2-aryliminopyrans (III) are distinct from their isomeric 2-pyridones (IV) (Table 1). The yellow 2-aryliminopyrans (III) absorb at longer wavelength ( $\lambda_{\text{max}}$  390–410 nm) as compared to the colourless 2-pyridones (IV) ( $\lambda_{\text{max}}$  335 nm) (Fig. 1).

The mass spectra general fragmentation pattern which we have already discussed in our previous publication [2], is also applicable to the isomeric compounds of the type III and IV. Accurate mass measurements gave the elemental compositions of the ions, but the structures drawn for fragment ions are intended to represent constitutions rather than molecular geometries. Peaks of intensities less than 10% of that of the base peak have been neglected except in cases of special significance.

The fragmentation patterns of the 2-arylimino-4,6-diphenylpyrans (IIIa–h) (Scheme II) are simple. They show molecular ion  $M^{+\cdot}$  which apparently fragmented by two major pathways A and B. Pathway A gives the fragment ions (a)  $M^{+\cdot}-Ar^+$  and (b)  $M^{+\cdot}-Ar-N=C^+$  which undergo the usual further fragmentation giving the daughter ions (c), (d),  $PhC\equiv CH^+$  and  $PhC\equiv O^+$  (Scheme II). Pathway B is associated with the loss of  $H^+$  and  $Ar-N=C=O^+$  fragment



Scheme II

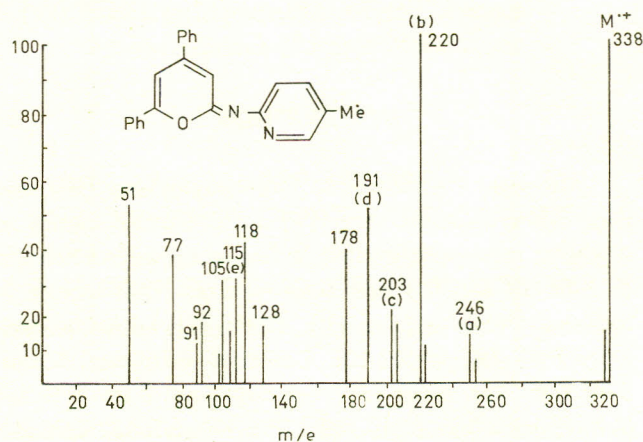
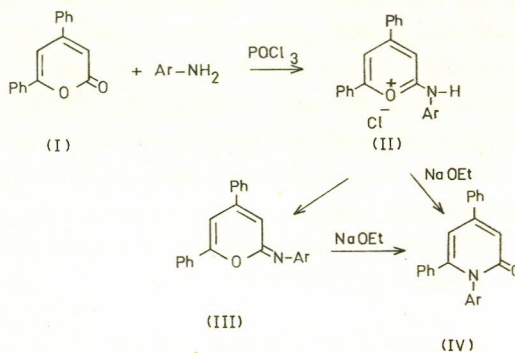


Fig. 2



Scheme I

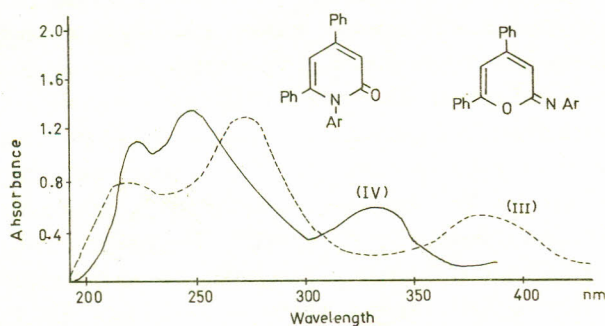


Fig. 1

giving ion of the type (c) which also give rise to the daughter ions (d), (e) and  $Ph-C\equiv CH^+$ . The observation of the 2,4-diphenylfuran fragment ion (b) at  $m/e$  220 and  $Ph-C\equiv O^+$  ( $m/e=105$ ) clearly identified the pyran type structures (III).

The mass spectra of the eight related 2-iminopyrans (IIIa–h) are recorded (Table 2) of which that of 2-(5-methyl-2-pyridylimino)-4,6-diphenylpyran (III f) is typical (Fig. 2).

**1-Aryl-4,6-diphenyl-2-pyridones (IV a–h).** 2-Arylimino-4,6-diphenylpyrans (III a–h) rearranged in hot ethanolic sodium ethoxide to the respective 2-pyridones (IV a–h) (Scheme I) in 30–50% yield. The identification of the isolated 2-pyridones (IV a–h) have been made through m.p. and direct comparison on TLC plate with those of our already prepared authentic samples of the 2-pyridones (IV a–h) from 2-arylamino-4,6-diphenylpyrylium chlorides (II a–h) (Scheme I).

The fragmentation pattern of 1-aryl-4,6-diphenyl-2-pyridones (IV a–h) (Scheme III) show a strong molecular ion peak ( $M^{+\cdot}$ ), which can be regarded as fragmenting by

Table 1. Reaction time, yield and UV spectra of 2-arylimino-4, 6-diphenylpyran.

| Compd. No. | Ar                     | Reaction time<br>(in hours) | m.p.<br>°C | Yield<br>% | $\lambda_{\max}$ nm |
|------------|------------------------|-----------------------------|------------|------------|---------------------|
| IIIa       | Phenyl                 | 4                           | 160        | 50         | 220, 275, 400       |
| IIIb       | <i>o</i> -Tolyl        | 4                           | 150        | 50         | 215, 275, 380       |
| IIIc       | <i>p</i> -Tolyl        | 4                           | 155        | 50         | 217, 280, 400       |
| III d      | <i>p</i> -Chlorophenyl | 5                           | 170        | 45         | 220, 280, 400       |
| IIIe       | 2-Pyridyl              | 8                           | 180        | 30         | 220, 280, 400       |
| III f      | 5-Methylpyridyl        | 6                           | 190        | 40         | 220, 282, 400       |
| III g      | 4-Methylpyridyl        | 6                           | 195        | 50         | 215, 280, 420       |
| III h      | 3-Methylpyridyl        | 6                           | 185        | 50         | 220, 280, 400       |
| IVa        | Phenyl                 | 6                           | 166        | 50         | 222, 250, 335       |
| IVb        | <i>o</i> -Tolyl        | 6                           | 200        | 50         | 225, 250, 337       |
| IVc        | <i>p</i> -Tolyl        | 6                           | 210        | 50         | 220, 250, 335       |
| IVd        | <i>p</i> -Chlorophenyl | 8                           | 220        | 40         | 225, 255, 335       |
| IVe        | 2-Pyridyl              | 8                           | 185        | 40         | 220, 250, 335       |
| IVf        | 5-Methylpyridyl        | 10                          | 218        | 50         | 220, 255, 335       |
| IVg        | 4-Methylpyridyl        | 10                          | 210        | 50         | 220, 255, 335       |
| IVh        | 3-Methylpyridyl        | 10                          | 205        | 50         | 222, 250, 335       |

Table 2. Relative abundance (%) of the principle ions in the mass spectra of the 2-arylimino-4, 6-diphenylpyrans (IIIa-h).

| Compd. No. | Ar.                    | $M^{+}$ | a  | b   | c  | d  | e  | $\text{Ph-C}\equiv\text{O}^{+}$ |
|------------|------------------------|---------|----|-----|----|----|----|---------------------------------|
| IIIa       | Phenyl                 | 100     | 15 | 100 | 15 | 75 | 60 | 40                              |
| IIIb       | <i>o</i> -Tolyl        | 100     | 20 | 100 | 30 | 80 | 80 | 50                              |
| IIIc       | <i>p</i> -Tolyl        | 100     | 15 | 100 | 10 | 70 | 50 | 30                              |
| III d      | <i>p</i> -Chlorophenyl | 50      | 80 | 100 | 30 | 60 | 50 | 40                              |
| IIIe       | 2-Pyridyl              | 100     | 50 | 60  | 30 | 50 | 20 | 20                              |
| III f      | 5-Methyl-2-pyridyl     | 100     | 10 | 50  | 20 | 50 | 30 | 30                              |
| III g      | 4-Methyl-2-pyridyl     | 50      | 40 | 100 | 25 | 20 | 10 | 20                              |
| III h      | 3-Methyl-2-pyridyl     | 100     | 20 | 100 | 30 | 50 | 40 | 30                              |

Table 3. Relative intensities (%) of the principle ions in the mass spectra of 1-aryl-4, 6-diphenyl-2-pyridones (IV a-h).

| Compd. No. | Ar.                    | $M^{+}$ | a  | b  | c  | d  | e  | f  | $\text{Ph-C}\equiv\text{N}^{+}$ |
|------------|------------------------|---------|----|----|----|----|----|----|---------------------------------|
| IVa        | Phenyl                 | 100     | 90 | 30 | 30 | 20 | 80 | 50 | 30                              |
| IVb        | <i>o</i> -Tolyl        | 100     | 30 | 15 | 40 | 20 | 60 | 65 | 40                              |
| IVc        | <i>p</i> -Tolyl        | 100     | 70 | 20 | 10 | 15 | 70 | 50 | 30                              |
| IVd        | <i>p</i> -Chlorophenyl | 100     | 90 | 15 | 15 | 20 | 80 | 50 | 20                              |
| IVe        | 2-Pyridyl              | 100     | 70 | 20 | 35 | 30 | 40 | 40 | 15                              |
| IVf        | 5-Methyl-2-pyridyl     | 100     | 50 | 15 | 20 | 30 | 40 | 50 | 15                              |
| IVg        | 4-Methyl-2-pyridyl     | 100     | 60 | 10 | 20 | 20 | 30 | 20 | 10                              |
| IVh        | 3-Methyl-2-pyridyl     | 100     | 70 | 20 | 35 | 30 | 30 | 20 | 20                              |

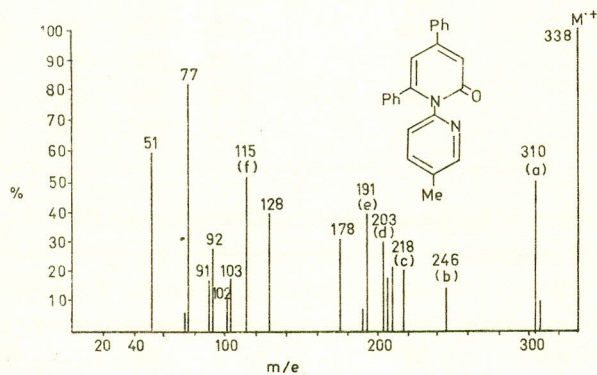
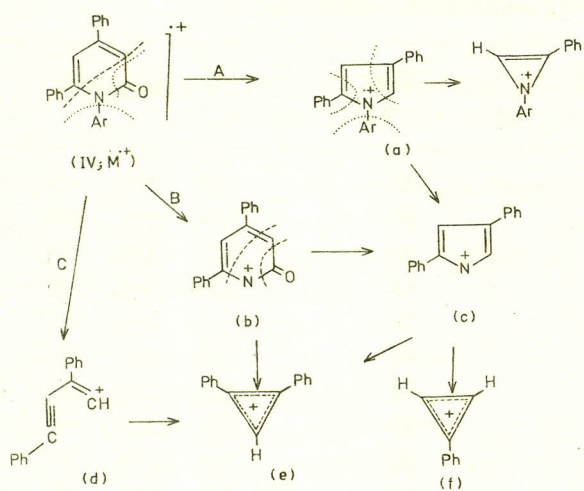


Fig. 3

three major pathways A, B, and C. Pathway A gives the fragment ion (a) due to the loss of CO, while pathway B is associated with the loss of  $\text{Ar}^+$  ion giving the fragment ion (b). Further fragmentation of the ions (a) and (b) account for the observation of the common pyrrole ion (c), (Scheme III). An additional pathway C is associated with the loss of  $\text{Ar-N=C=O}^+$  fragment giving the daughter ion (d). The fragment ions (c) and (d) undergo the usual further fragmentation giving ions (e), (f),  $\text{Ph-C}\equiv\text{CH}^+$  and  $\text{Ph-C}\equiv\text{N}^+$  ( $m/e = 103$ ).

The mass spectra of the eight related 1-aryl-4, 6-diphenyl-2-pyridones (IV a-h) (Scheme III) are recorded

(Table 3) of which that of the 1-(5-methyl-2-pyridyl)-4, 6-diphenyl-2-pyridone (IVf) is typical (Fig. 3).

It is observed that the mass spectra of the 2-arylimino-4, 6-diphenylpyrans (III a-h) (Scheme II) show 2,4-diphenylfuran fragment ion (b) at  $m/e$  220 and  $\text{Ph-C}\equiv\text{O}^+$  ( $m/e = 105$ ), whereas, their isomeric 2-pyridones (IV a-h) (Scheme III) are associated with the 2,4-diphenylpyrrole fragment ion (c) at  $m/e$  218 and  $\text{Ph-C}\equiv\text{N}^+$  ( $m/e = 103$ ) which is highly diagnostic of the heteroatom in the ring. This provides a valuable method of distinguishing between the isomeric structural type (III) and (IV) (Scheme I).

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