

## Effective Formation of Indole Imines and Enamines from Imidoyl Chlorides

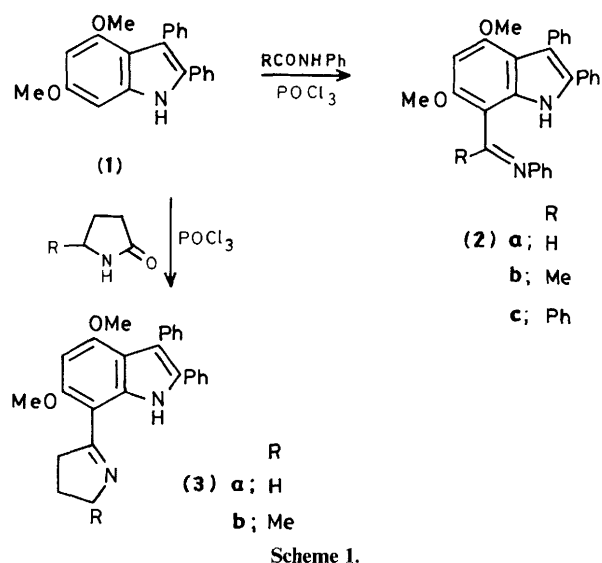
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Indoles can be converted into their related imine derivatives by imidoyl chloride reagents (derived from phosphoryl chloride and secondary amides), in a reaction superior to the combination of indole carbonyl compounds and primary amines; however, use of *N,N'*-diacetyl-*o*-phenylenediamine leads to the effective formation of enamines.

Recent work has focussed attention on the C-7 reactivity of 4,6-dimethoxy-2,3-diphenylindole (**1**)<sup>1</sup> towards electrophiles.<sup>2-4</sup> We now report that the indole (**1**) reacts readily with secondary amides (e.g. formanilide, acetanilide, and benzanilide) and lactams (e.g. pyrrolidin-2-one and 5-methylpyrrolidin-2-one) in the presence of phosphoryl chloride in chloroform, followed by mild neutralization with sodium carbonate to give high yields of the imines (**2a-c**) (64–92%)<sup>†</sup> and (**3a-b**) (78–86%) respectively (Scheme 1). The reactions presumably proceed *via* imidoyl chlorides.<sup>5,6</sup> Although the aldimine (**2a**) can be prepared in modest yield from the corresponding aldehyde and amine, the ketimines (**2b,c**) cannot be obtained by a similar process. Formation of the dihydropyrroles (**3a,b**) is especially effective by the imidoyl chloride route.

The nickel(II) complex of the dialdimine (**4a**) has been prepared by the metal template reaction<sup>3</sup> of the 7-formylindole

<sup>†</sup> All new compounds gave satisfactory spectroscopic and analytical data. For (**2b**): 79% yield; m.p. 179–180 °C;  $\delta$ (500 MHz, CDCl<sub>3</sub>) 2.43 (3 H, s, CH<sub>3</sub>), 3.78, 3.98 (each 3 H, s, OCH<sub>3</sub>), 6.29 (1 H, s, ArH), 7.10–7.44 (15 H, m, ArH), and 11.54 (1 H, br s, NH);  $m/z$  446 ( $M^+$ , 12.5%). For (**3b**): 78% yield; m.p. 195–196 °C;  $\delta$ (500 MHz, CDCl<sub>3</sub>) 1.39 (3 H, d, *J* 6.7 Hz, CH<sub>3</sub>), 1.45–1.59 (1 H, m, CH<sub>2</sub>), 2.13–2.24 (1 H, m, CH<sub>2</sub>), 3.76 and 3.94 (each 3 H, s, OCH<sub>3</sub>), 4.28 (1 H, br q, CH), 6.24 (1 H, s, ArH), 7.18–7.44 (10 H, m, ArH), and 12.28 (1 H, br s, NH);  $m/z$  410 ( $M^+$ , 71%). For (**5**): 70% yield; m.p. 201 °C;  $\delta$ (500 MHz, CDCl<sub>3</sub>) 2.49 (3 H, s, CH<sub>3</sub>), 3.60, 3.70 (each 3 H, s, OCH<sub>3</sub>), 5.77 and 5.97 (each 1 H, s, CH<sub>2</sub>), 6.19 (1 H, s, ArH), 6.94–7.77 (14 H, m, ArH), and 7.93 (1 H, br s, NH);  $m/z$  485 ( $M^+$ , 81%).



with *o*-phenylenediamine but related formation of the complex of the diketimine (**4b**) failed. Reaction of the indole (**1**) with *N,N'*-diacetyl-*o*-phenylenediamine in the presence of phosphoryl chloride in chloroform was therefore carried out, but also failed to yield the diketimine (**4b**); instead, the enamine (**5**) was produced cleanly in 70% yield. Such enamine formation was

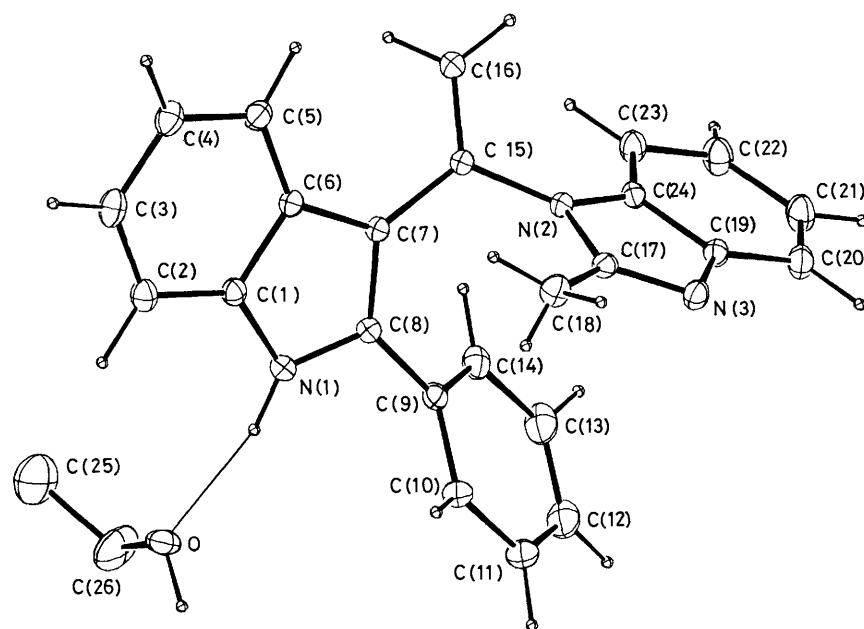
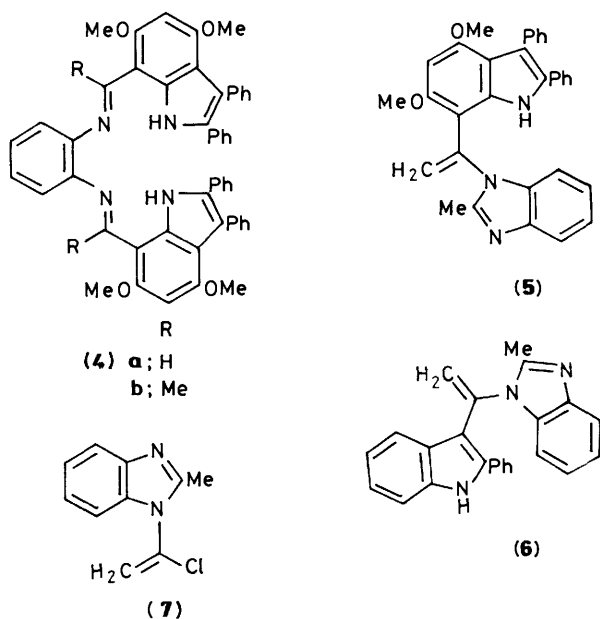


Figure.

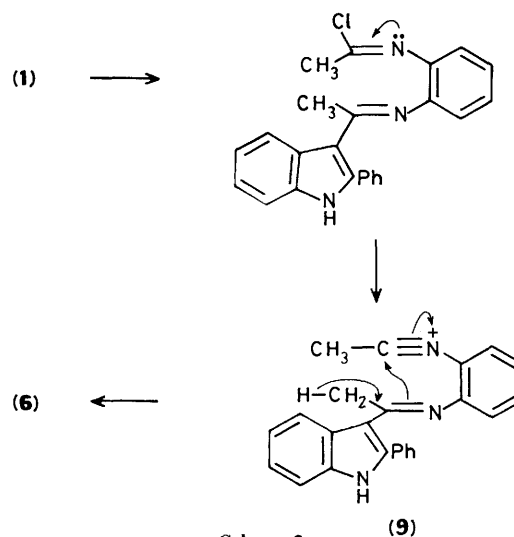


shown to be more general by the production of the enamine (6) from 2-phenylindole. In this case the product gave suitable crystals for an X-ray structure determination (Figure).<sup>\*</sup> Both compounds (5) and (6) showed single resonances in their <sup>1</sup>H n.m.r. spectra for the vinylic protons.

It has been shown<sup>7</sup> that *N,N'*-diacetyl-*o*-phenylenediamine undergoes reaction with phosphoryl chloride in dimethylformamide at 75 °C to give the chloro enamine (7). This compound is, however, not an intermediate in the formation of

<sup>\*</sup> Crystal data for (6). C<sub>24</sub>H<sub>19</sub>N<sub>3</sub>·C<sub>2</sub>H<sub>5</sub>OH, *M*, 395.5, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 8.139(1), *b* = 21.030(1), *c* = 14.048(2) Å, β = 113.91(1)°, *U* = 2 198.1(5) Å<sup>3</sup>, *D*<sub>c</sub> = 1.19 g cm<sup>-3</sup>, *Z* = 4, μ<sub>Cu</sub> = 5.45 cm<sup>-1</sup>. Crystal size 0.11 by 0.10 by 0.35 mm, min. and max. transmission factors 0.80 and 0.95, 2θ<sub>max</sub>, 140°, 4 152 measured reflexions, 2 766 observed (*I* > 3σ(*I*)), measured. Final residuals *R*, *R*<sub>w</sub> were 0.034, 0.047. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of this deposition system, see 'Instructions for Authors (1989)', *J. Chem. Soc., Perkin Trans. I*, 1989, Issue 1.

the products (5) and (6). These enamines could possibly be formed *via* intramolecular carbanion attack in the intermediate nitrilium cation (9) formed from the related imido-chloride (8) [e.g. formation of (6), Scheme 2].



Scheme 2.

### Acknowledgements

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