

CONFIGURATIONAL ISOMER MIXTURES AND C-PROTONATION  
IN SOME STERICALLY CROWDED ENAMINONES

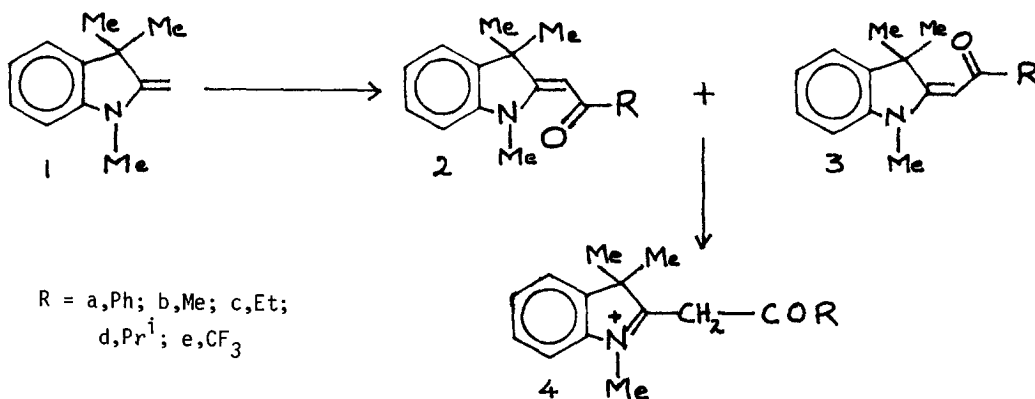
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Acylation of 1,3,3-trimethyl-2-methyleneindoline (Fischer's Base) gives enaminone derivatives which show unusual C-protonation and exist in solution as mixtures of the cis-s-cis and cis-s-trans configurations.

The enaminones are now recognised as a distinct class of organic compounds, of which the main sub-groups are vinylogous amides and vinylogous urethanes. Many reports have shown that simple vinylogous amides protonate on oxygen<sup>1</sup>. Such evidence as we have for vinylogous urethanes, however points to the not surprising suggestion that, like enamines, they protonate on carbon<sup>2</sup>.

Of the four theoretically possible configurations of the enaminone system<sup>1</sup>, the benzoyl derivative<sup>2,3</sup> (2a, 3a) is unlikely to adopt either the trans-s-trans or the cis-s-trans form because of steric interactions. The n.m.r. spectrum clearly shows both of the other two forms present in solution:-  $\tau$  4.18 (methine proton), 6.41 (N-Me), 8.60 (gem dimethyl) for the cis-s-cis form (2a) while  $\tau$  4.03, 6.80 and 8.16 are the corresponding resonances for the trans-s-cis form (3a). The ratio 3a:2a is  $4.0 \pm 0.5$ .



Irradiation (N.O.E.) of the N-CH<sub>3</sub> signal of 3a at 6.80  $\tau$  increased the intensity of the methine proton at 4.03  $\tau$  by 30  $\pm$  5%. Irradiation at 6.41  $\tau$  (for the N-CH<sub>3</sub> signal of 2a) increased the intensity of the methine proton at 4.18  $\tau$  by 13  $\pm$  3%. Four derivatives of aliphatic acids are included in the Table and in every case the trans-s-cis form predominates.

The u.v. spectra for neutral and protonated forms given in the Table confirm C-protonation for aqueous solution. O-protonation of enamines, is accompanied in most cases by a small hypsochromic shift (typically 10-18 nm)<sup>1</sup>. The much larger shifts for the present compounds, to give salts with spectra closely similar to that of Fischer's Base (1), are consistent only with C-protonation. These are the first vinylogous amides to show C-protonation, although vinylogous urethanes and simple enamines normally do so<sup>2</sup>.

Table: u.v. Spectra in Aqueous Solution

Compound	H <sub>2</sub> O		0.1N HCl	
	$\lambda_{\max}$	$\epsilon$	$\lambda_{\max}$	$\epsilon$
1	276 nm	4800	275	5300
2a, 3a	391	30500	285	9800
2b, 3b	360	26300	287	5300
2c, 3c	360	26500	285	6500
2d, 3d	361	28200	286	6800
2e, 3e	374	23600	374	18000

The trifluoroacetyl derivative<sup>5</sup> (2e, 3e) is too weakly basic to be fully protonated, it was the only compound to fail to give a sharp -CH<sub>2</sub>- signal in the n.m.r. in trifluoroacetic acid solution.

An X-ray analysis of the isobutyryl (3d) derivative showed it fully in the trans-s-cis form in the crystal<sup>6</sup>.

#### ACKNOWLEDGEMENT

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