

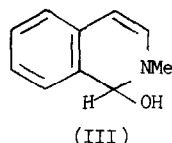
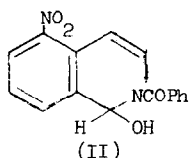
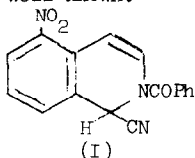
REISSERT COMPOUND CHEMISTRY: FORMATION OF A STABLE N-ACYL PSEUDO-BASE¹

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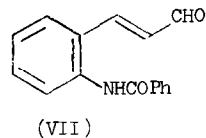
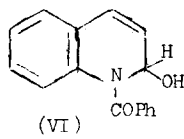
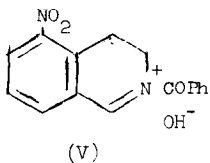
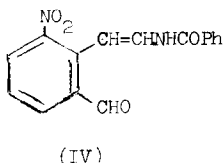
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In an attempt to prepare 5-nitroisoquinoline Reissert compound (I)² by the standard procedure³ the yellow pseudo-base (II), m.p. 188°, was precipitated in high yield. The same product was formed when the reaction was carried out in the absence of cyanide. This appears to be the first example of a stable N-acyl pseudo-base in this series although the N-alkyl pseudo-bases, e.g. (III) are well known.⁴

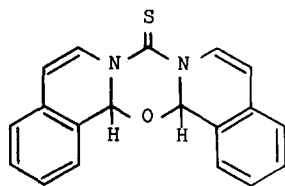


The structure (II) is supported by i.r. bands at 3385 (broad, OH), 1663 (amide carbonyl) and 1623 cm^{-1} ($\text{C}=\text{C}$), and by the close similarity of the u.v. spectrum with that of the authentic Reissert compound (I) (isolated in small yield from the mother liquors of the reaction after removal of (II)). Further support is afforded by the n.m.r. spectrum and the mass spectrum of (II). We could find no evidence for the presence of the possible tautomeric forms (IV) and (V).

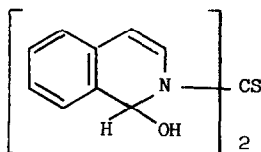
In 1905 Reissert claimed⁵ to have formed the analogous N-acyl pseudo-base (VI) from unsubstituted quinoline by treatment with benzoyl chloride and aqueous sodium hydroxide. However it has subsequently been shown^{6,7,8} that the compound was the aminoaldehyde (VII). The equivalent reaction does not take place with isoquinoline.



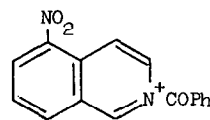
Although stable N-cyano pseudo-bases have been reported⁹ a nearer analogy is given in a recent observation of Hull¹⁰ that treatment of isoquinoline with thiophosgene in alkali gives products including (VIII). This is assumed to be formed by dehydration of (IX) (which was not isolated).



(VIII)



(IX)



(X)

It is of interest that the 5-nitro group causes such a complete change of behaviour from the normal Reissert reaction.³ Possibly the increased positive character of C-1 promotes solvation at this position in the intermediate (X), thus resulting in reaction with solvent. However such a tendency should be affected if cyanide concentration is increased at the expense of water. When this was done virtually no increase in yield of Reissert compound (I) resulted. Alternatively, the principle of soft and hard acids and bases¹¹ may be invoked in that the effect of the 5-nitro group is to enhance the hardness of the C-1 centre so favouring attack by the hard base, H₂O, rather than the soft base, CN⁻.

The chemistry of N-acyl pseudo-bases is being investigated further.

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