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## Unusually Stable O-Acylisoimides. Stereospecific Nucleophilic Attack on an Azacarbonium Ion Centre

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Summary The isoimide (5;  $R^2 = N$ -methyl-2,4-dinitroanilino) is formed by acetate attack on the azacarbonium ion (4); it undergoes intermolecular acyl transfer rather than isomerisation to the imide in aqueous solution. WE report the isolation of the O-acylisoimides (2) which are relatively stable towards rearrangement to the N-acylisomers (3). Thus treatment of the hydrazonyl bromides (1)  $[R^1 = Bu^t; R^2 = N(Me)C_6H_3(NO_2)_2-2,4]$  in 1:1 ace-

tone-water at 25 °C in the presence of 0.1M-sodium acetate gives the O-acyl compound (2), which is uncontaminated by the isomer (3). The structure of (2) is consistent with spectral evidence; in particular it has the characteristic ester carbonyl absorption at  $1770 \text{ cm}^{-1}$ . Other acetates of structure [2;  $R^1 = Ar$ ,  $R^2 = N(Me)C_6H_3(NO_2)_2$  or N(Me)-Ph] were similarly prepared.

The O-acyl compound  $[2; R^1 = Bu^t; R^2 = N(Me)C_sH_3$ - $(NO_2)_2$  could be recrystallised without difficulty from organic solvents below 60 °C, but on prolonged heating at temperatures higher than this rearrangement to the imide (3) occurred (e.g.,  $t_{t}$  for the rearrangement at 100 °C in chlorobenzene is 20 min). The isoimide structure (2) is rare in organic chemistry and is generally limited to cyclic materials in which the rearrangement to the imide is inhibited;<sup>1</sup> acyclic materials have been isolated previously but have a limited lifetime.<sup>2</sup>

We attribute the stability of the O-acyl structure in the present instance to its existence in the configuration (5) in which the nucleophilic lone-pair electrons on the neighbouring nitrogen and the acyl group are trans. In fact it appears that isomerisation of (5) about the C=N bond might be rate determining for the overall conversion of (2) into (3) since this shows acidic catalysis under anhydrous conditions. It has previously been demonstrated that the starting bromide (1) reacts via rate-determining azacarbonium ion (4) formation in aqueous acetone.<sup>3</sup> Nucleophilic attack by acetate ion on (4) must therefore be stereospecific, giving rise to just a single imine isomer (5). A key feature in the starting hydrazonyl bromide substrate (1) is that R<sup>2</sup> (attached to nitrogen) has an atom with lone-pair electrons. It is well established that this can slow the rate of isomerisation about the C=N bond (relative to, say, N-alkyl- or -aryl-imines),<sup>4</sup> which in turn permits the isolation of (5).



The O-acylisoimide (2) undergoes rapid acyl transfer in aqueous solution at room temperature, since under these conditions the isomerisation to (3) is slow. Intermolecular acylation is acid-catalysed and deacylation of  $[2; R^1 = Bu^t;$  $R^2 = N(Me)C_8H_3$ -(NO<sub>2</sub>)<sub>2</sub>-2,4] has a half life of 20 s at pH 2.0 in 25% dioxan at 25 °C.

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