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

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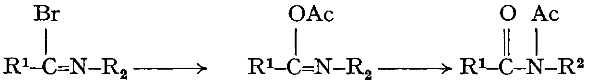
Summary The isoimide (**5**; $R^2 = N$-methyl-2,4-dinitroanilino) is formed by acetate attack on the azacarbonium ion (**4**); it undergoes intermolecular acyl transfer rather than isomerisation to the imide in aqueous solution.

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 acetone–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 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.

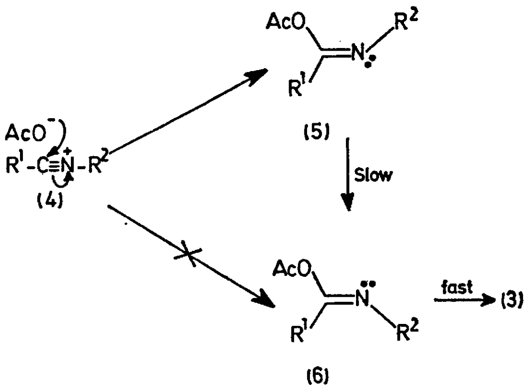


$$\mathrm{R^1{-}\overset{Br}{\overset{|}{C}}{=}N{-}R_2} \longrightarrow \mathrm{R^1{-}\overset{OAc}{\overset{|}{C}}{=}N{-}R_2} \longrightarrow \mathrm{R^1{-}\overset{O}{\overset{\|}{C}}{-}\overset{Ac}{\overset{|}{N}}{-}R^2}$$

(**1**) (**2**) (**3**)

The *O*-acyl compound [**2**; R^1 = Bu^t; R^2 = $N(Me)C_6H_3(NO_2)_2$] 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.*, $t_{\frac{1}{2}}$ 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;[1] acyclic materials have been isolated previously but have a limited lifetime.[2]

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.[3] 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^2 (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),[4] 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 = $N(Me)C_6H_3$-$(NO_2)_2$-2,4] has a half life of 20 s at pH 2·0 in 25% dioxan at 25 °C.

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