Methylation and Protonation Sites in Some *N*-Ammonioamidates

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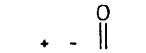
Summary Whereas methylation of *N*-ammonioamidates may occur on oxygen or nitrogen depending on whether the carbonyl group carries a methyl or methoxy substituent, n.m.r. spectroscopic evidence indicates that protonation occurs on nitrogen and in more acidic media dications are formed by further *N*- or *O*-protonation.

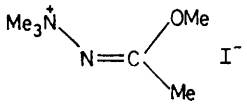
IN compounds (**1**)—(**3**) the nitrogen–nitrogen bond order is constrained to be unity, with the negative charge delocalised to form an 'enolate' unit which may act as an ambident nucleophile. We have therefore examined methylation and protonation of these charge-separated species.

With MeI in $CHCl_3$ compound (**1**) is methylated exclusively (n.m.r.) on oxygen and to the extent that the configuration of compound (**1**) resembles that of (**3**) in the solid state[1] the product has the configuration shown in (**4**); a similar result has been found previously.[2] However compound (**2**) is methylated exclusively on nitrogen under the same conditions to give compound (**5**) which was independently synthesised from trimethylhydrazine; compound (**3**) was not methylated even after prolonged reflux with MeI in $CHCl_3$. It is reasonable to suppose that compound (**4**) is the kinetic product; in solution in nitro[$^2H_5$]benzene compound (**4**) was stable in the probe of an n.m.r. spectrometer up to *ca.* 125 °C when extensive decomposition occurred to give a dark, coloured solution. Compound (**5**) is also probably the kinetic product from (**2**). Demethylation of an initially *O*-methylated salt by nucleophilic I^- to regenerate compound (**2**) which may then be *N*-methylated is unlikely since under similar conditions compound (**4**) is stable, and with methyl toluene-*p*-sulphonate in $CHCl_3$ *N*-methylation of compound (**2**) again occurs exclusively. It is also considered unlikely that O → N methyl migration

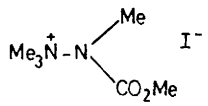
to give (**5**) *via* a Chapman rearrangement[3] occurs at the temperatures employed ($\leqslant$ 61 °C).



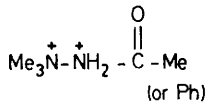
(1) R = Me
(2) R = OMe
(3) R = Ph
(and Ph-substituted derivatives)



(4)



(5)

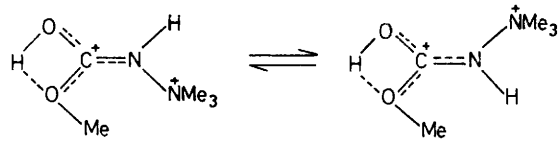


(or Ph)

(6)

It is well known that enolate anions may be alkylated on oxygen or carbon with different alkylating agents[4]; in the present work replacement of Me at the central atom of the heteroenolate 'anion' by OMe has caused a change to the formally 'softer' alkylation site as is typically observed in methylation of enolate anions with MeI.

N.m.r. spectra in pure CF_3CO_2H at −17 °C of the monocations of all the *N*-ammonioamidates except (**2**) do not reveal any signals additional to those of the NMe_3^+ and R groups owing to rapid proton exchange, but the spectrum of the most basic compound (**2**) does show an additional peak at low field (1H). In a more acidic medium, CF_3CO_2H –HSO_3F (35:65 v/v), in which all *N*-ammonioamidates are relatively stable, spectra of the dications are observed. An additional broad peak at δ *ca.* 9·2 integrates consistently as 2 additional protons for all the *N*-ammonioamidates except (**2**). As both additional protons appear to be equivalent, we believe the spectra to be due to the *N*-protonated dications (**6**). The n.m.r. spectra of compound (**2**) in the same solvent mixture below −10 °C show in the same spectral region two resonances (in the ratio 40:60), integrating as 1 additional proton, with the signal of the



OMe group also split into two resonances in the same ratio (the NMe_3^+ resonance is merely broadened). Under still more acidic conditions, in pure HSO_3F at −40 to −60 °C, compound (**2**) gives an additional signal at still lower field, in the same position as the OH resonance in *O*-protonated acetamide.[5] These facts are consistent with the presence of a *cis-trans* mixture of dications. Thus the first proton adds on to the nitrogen for this compound also. Hence, protonation studies lend support to the view that the *O*-methylated product (**4**) of compound (**1**) is thermodynamically unstable, whereas the *N*-methylated salt (**5**) of compound (**2**) is the thermodynamically stable product.

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