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AN ICR STUDY ON BENZOYLATION REACTIONS IN THE GAS PHASE

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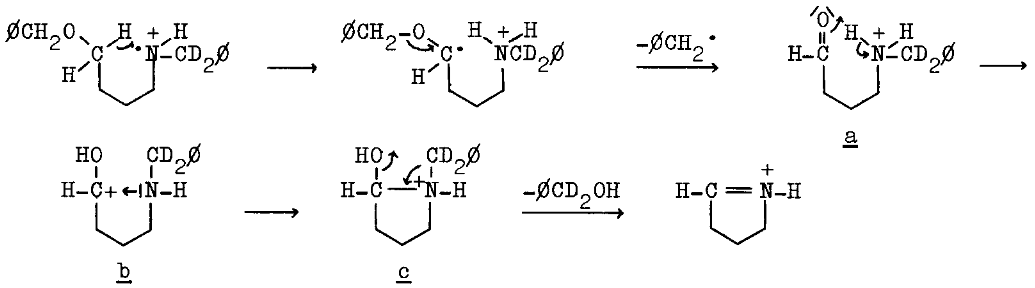
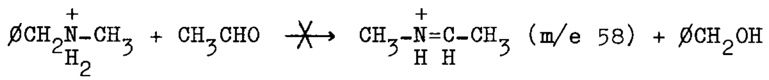
A most interesting reaction sequence among the mass spectral fragmentations of 1-benzylamino-4-benzyloxybutane is the successive loss of a benzyl radical and benzyl alcohol from the molecular ion[1]. Deuterium labelling in the benzylic position of the benzylamino group has revealed that the expelled benzyl alcohol fully contains the two deuterium atoms, a direct indication for a functional group interaction:



In order to investigate if the intramolecular reaction between a protonated amine and an aldehyde, leading to expulsion of benzyl alcohol after proton transfer and ring closure, has its analogous ion molecule reaction, a mixture of benzyl methyl amine and acetaldehyde[2] has been introduced into a standard Varian V 5903 Ion Cyclotron Resonance spectrometer. Unfortunately, no peak has been observed at m/e 58:



$$\text{Ø}CH_2\underset{H_2}{\overset{+}{N}}-CH_3 + CH_3CHO \not\longrightarrow CH_3-\underset{H}{\overset{+}{N}}=\underset{H}{C}-CH_3 \ (m/e\ 58) + \text{Ø}CH_2OH$$

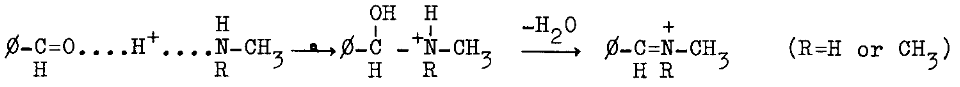
Using benzaldehyde instead of acetaldehyde more stable product ions might be expected due to resonance with the phenyl ring. A proton bound complex of benzaldehyde and benzyl methyl amine is observed indeed at m/e 228 but this ion has not been found to expel benzyl alcohol[2]. A more intense ion however appears at m/e 226, being the reaction product of the benzoyl cation and benzyl methyl amine (double resonance).

To observe this gas phase benzoylation reaction under more favourable conditions, mixtures of benzaldehyde and methyl amine, dimethyl amine or trimethyl amine respectively have been studied[2] giving product ions of lower mass that can be observed at higher marginal oscillator frequencies. The benzoylation reactions in Table 1 have been confirmed by double resonance.

Table 1. Reactions of the benzoyl cation with some simple aliphatic amines.

$\varnothing-\overset{+}{C}=O + H_2NCH_3$	$\longrightarrow$	$\varnothing-\overset{\overset{O}{\|}}{C}-\underset{H_2}{\overset{+}{N}}-CH_3$	(m/e 136)	(1)
$\varnothing-\overset{+}{C}=O + HN(CH_3)_2$	$\longrightarrow$	$\varnothing-\overset{\overset{O}{\|}}{C}-\underset{H}{\overset{+}{N}}(CH_3)_2$	(m/e 150)	(2)
$\varnothing-\overset{+}{C}=O + N(CH_3)_3$	$\longrightarrow$	$\varnothing-\overset{\overset{O}{\|}}{C}-\overset{+}{N}(CH_3)_3$	(m/e 164)	(3)

In a recent publication calculations on the benzoyl cation have shown that about 50% of the positive charge is located on the carbon atom of the carbonyl group, the remaining 50% being spread over the phenyl ring[3]. The reactions between the benzoyl cation and amines may thus find a reasonable explanation in a nucleophilic attack of the amino function on the carbonyl group, producing a protonated or methylated amide. Less powerful nucleophiles however, such as methanol and dimethyl ether do not appear to react with the benzoyl cation. Table 2 compiles the formation of products resulting from rearrangement and decomposition of proton bound complexes. Loss of water is only observed in the cases of a primary or secondary amine (reactions (5) and (8)). The data have been rationalised by assuming a rearrangement in the proton bound complex, followed by 1,2 elimination of water giving a protonated or methylated Schiff base:



$$\underset{H}{\varnothing-C}=O\ldots H^+\ldots\underset{R}{\overset{H}{N}}-CH_3 \longrightarrow \varnothing-\underset{H}{\overset{OH}{C}}-\underset{R}{\overset{H}{\overset{+}{N}}}-CH_3 \xrightarrow{-H_2O} \varnothing-\underset{H}{C}=\underset{R}{\overset{+}{N}}-CH_3 \qquad (R=H \text{ or } CH_3)$$

d e f

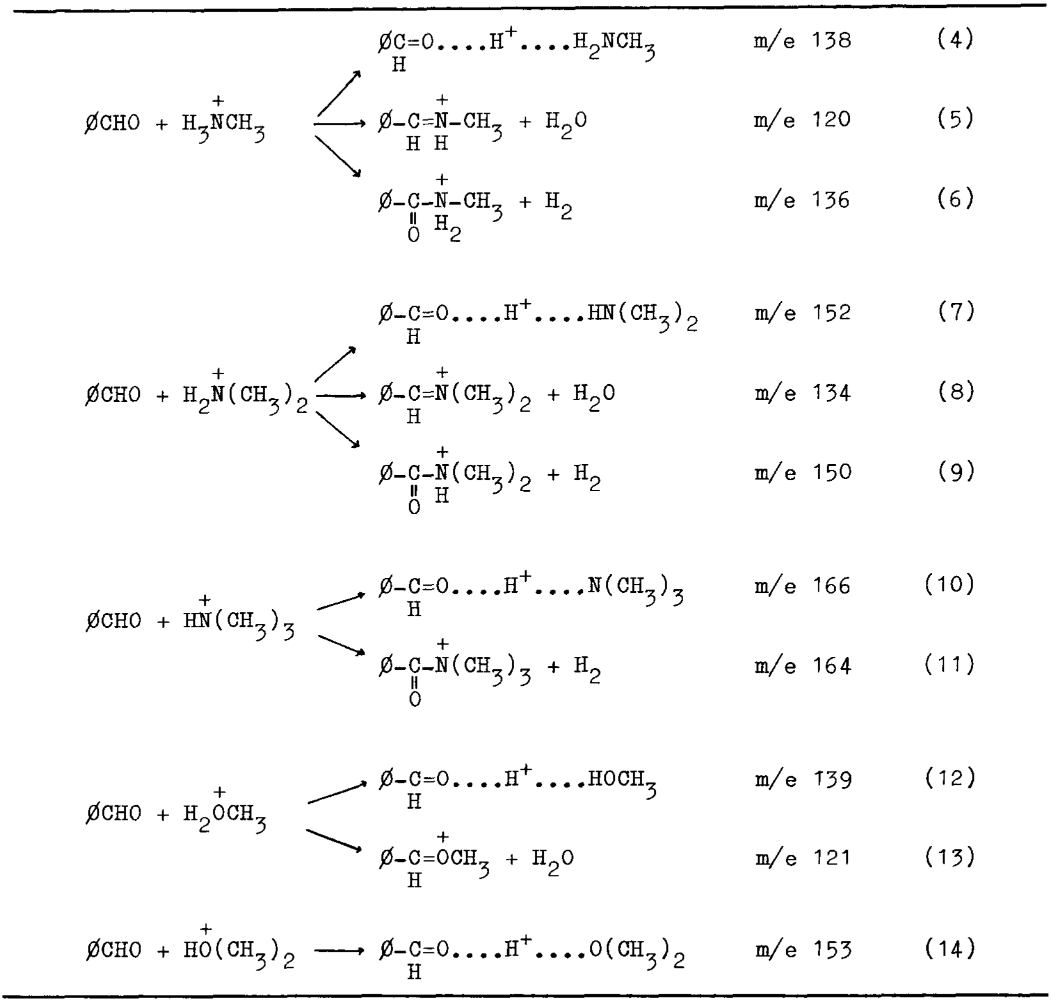
Double resonance experiments have revealed that the protonated amines are precursor ions of e and f, but no indication for a collision induced decomposition[4] of e, resulting in f, has been found.

The rearrangement of ion d to ion e is essentially analogous to the proton transfer followed by ring closure in the sequence a → b → c (vide supra).

It should be noted, that ion c has been observed to eliminate H_2O in addition to $\varnothing CH_2OH$, albeit to a minor extent[1].

In reactions (6), (9) and (11) ions are generated, having the same mass as the benzoylation products. Their structures, proposed to be identical to the ben-

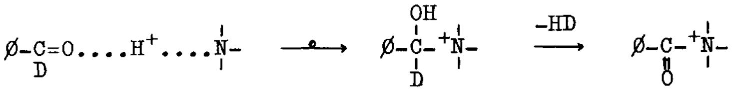
Table 2. Reactions involving proton bound complexes of benzaldehyde with some simple aliphatic amines, methanol and dimethyl ether.



$\text{ØCHO} + \overset{+}{H_3N}CH_3$	$\underset{H}{\text{ØC}}\text{=O}\cdots H^+\cdots H_2NCH_3$	m/e 138	(4)
	$\text{Ø-}\underset{H}{C}\text{=}\underset{H}{\overset{+}{N}}\text{-}CH_3 + H_2O$	m/e 120	(5)
	$\text{Ø-}\underset{O}{\underset{\Vert}{C}}\text{-}\underset{H_2}{\overset{+}{N}}\text{-}CH_3 + H_2$	m/e 136	(6)
$\text{ØCHO} + H_2\overset{+}{N}(CH_3)_2$	$\text{Ø-}\underset{H}{C}\text{=O}\cdots H^+\cdots HN(CH_3)_2$	m/e 152	(7)
	$\text{Ø-}\underset{H}{C}\text{=}\overset{+}{N}(CH_3)_2 + H_2O$	m/e 134	(8)
	$\text{Ø-}\underset{O}{\underset{\Vert}{C}}\text{-}\underset{H}{\overset{+}{N}}(CH_3)_2 + H_2$	m/e 150	(9)
$\text{ØCHO} + H\overset{+}{N}(CH_3)_3$	$\text{Ø-}\underset{H}{C}\text{=O}\cdots H^+\cdots N(CH_3)_3$	m/e 166	(10)
	$\text{Ø-}\underset{O}{\underset{\Vert}{C}}\text{-}\overset{+}{N}(CH_3)_3 + H_2$	m/e 164	(11)
$\text{ØCHO} + H_2\overset{+}{O}CH_3$	$\text{Ø-}\underset{H}{C}\text{=O}\cdots H^+\cdots HOCH_3$	m/e 139	(12)
	$\text{Ø-}\underset{H}{C}\text{=}\overset{+}{O}CH_3 + H_2O$	m/e 121	(13)
$\text{ØCHO} + H\overset{+}{O}(CH_3)_2$	$\text{Ø-}\underset{H}{C}\text{=O}\cdots H^+\cdots O(CH_3)_2$	m/e 153	(14)

zoylated ions (cf. Table 1 and 2), have been supported by experiments with ØCDO[5].

These have shown that again the protonated amines react with ØCDO to the benzoylation products at m/e 136, 150 and 164 as confirmed by double resonance. Apparently, HD is then eliminated from the collision complexes:



$$\text{Ø-}\underset{D}{C}\text{=O}\cdots H^+\cdots \overset{|}{\underset{|}{N}}\text{-} \longrightarrow \text{Ø-}\underset{D}{\overset{OH}{C}}\text{-}\overset{+}{\underset{|}{\overset{|}{N}}}\text{-} \xrightarrow{-HD} \text{Ø-}\underset{O}{\underset{\Vert}{C}}\text{-}\overset{+}{\underset{|}{\overset{|}{N}}}\text{-}$$

e'

Within the limits of observation no ions are found corresponding with loss of H_2 from the collision complexes.
Finally, it is found that the ions, generated in reactions (5) and (8), fully retain the deuterium atom.

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