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AN ICR STUDY ON BENZYL CATION TRANSFER REACTIONS AND THE NUCLEOPHILIC ATTACK OF AMINES ON THE $C_7H_7^+$ ION FROM BENZYL METHYL ETHER

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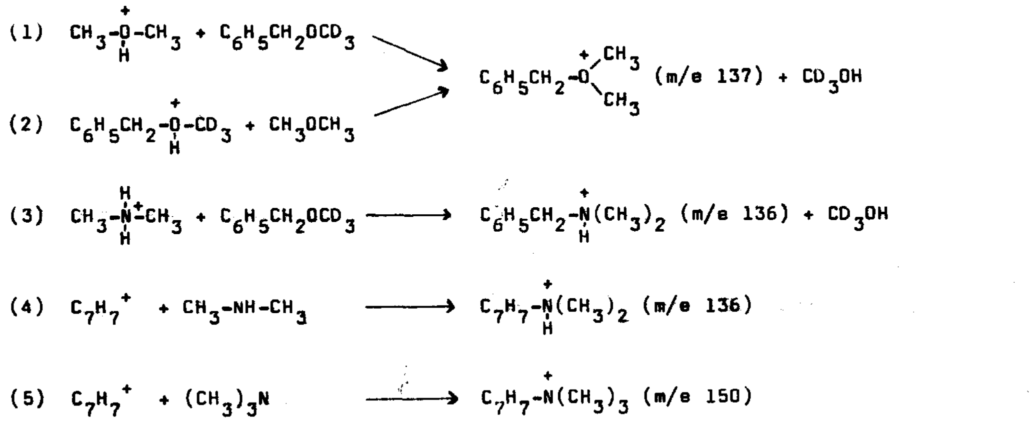
Previous D- and ^{18}O-labelling in 1,4-dibenzyloxybutane has shown the successive migration of a benzylic H atom to the opposite ether function in its molecular ion and transfer of the benzyl cation from this protonated O atom to the uncharged O atom in an S_Ni type reaction.[1]

In order to investigate a possible intermolecular benzyl cation transfer in an ion molecule reaction, benzyl trideuteromethyl ether was introduced into a Varian V 5903 ICR spectrometer together with dimethyl ether, dimethyl amine and trimethyl amine respectively. The reactions observed at total pressures of $\sim 5\times10^{-5}$ torr (ion pump) and low electron energy (15 eV for dimethyl ether, 20 eV for the amines) are listed in Table 1 and were confirmed by negative double resonance signals (only the signal for (3) is accompanied by a decrease in TIC). The benzyl dimethyl oxonium ion does not appear to be generated by a direct attack of dimethyl ether on the $C_7H_7^+$ ion, as one might expect from reactions (4) and (5). As either of the two protonated ethers gives rise to the formation of the oxonium ion, it is quite feasible that the reactions (1) and (2) proceed *via* a collision complex in which the two ether molecules are held together by a proton, a phenomenon frequently observed in gas phase ionic reactions of oxygen and nitrogen containing compounds.[2a-e] A pressure of 9×10^{-5} torr turned out to be too low for observing this complex at $\omega/2\pi=116$ kHz, but it could easily be identified upon raising the total pressure to $2\text{-}10\times10^{-4}$ torr (Penning III gauge, Leybold Hereaus, Germany).

Table 1. Relevant ion molecule reactions in mixtures of $C_6H_5CH_2OCD_3$ with CH_3OCH_3, CH_3NHCH_3 and $(CH_3)_3N$



(1) $CH_3-\underset{H}{\overset{+}{O}}-CH_3 + C_6H_5CH_2OCD_3 \longrightarrow C_6H_5CH_2-\overset{+}{O}{<}^{CH_3}_{CH_3}$ (m/e 137) + CD_3OH

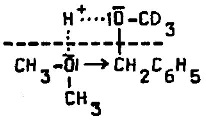
(2) $C_6H_5CH_2-\underset{H}{\overset{+}{O}}-CD_3 + CH_3OCH_3 \longrightarrow C_6H_5CH_2-\overset{+}{O}{<}^{CH_3}_{CH_3}$ (m/e 137) + CD_3OH

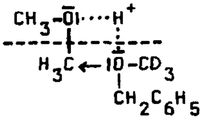
(3) $CH_3-\underset{H}{\overset{H}{N}}{}^{+}-CH_3 + C_6H_5CH_2OCD_3 \longrightarrow C_6H_5CH_2-\underset{H}{\overset{+}{N}}(CH_3)_2$ (m/e 136) + CD_3OH

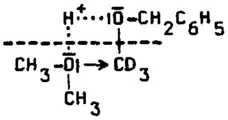
(4) $C_7H_7^+ + CH_3-NH-CH_3 \longrightarrow C_7H_7-\underset{H}{\overset{+}{N}}(CH_3)_2$ (m/e 136)

(5) $C_7H_7^+ + (CH_3)_3N \longrightarrow C_7H_7-\overset{+}{N}(CH_3)_3$ (m/e 150)

A careful inspection of the region m/e 135 to m/e 145 ($5x10^{-5}$ torr, sweep width 1 kGauss, tenfold amplification, response time 10 sec.) has shown the absence of the ions $C_6H_5CH_2-\overset{+}{O}{<}^{CH_3}_{CD_3}$ and $C_6H_5CH_2-\overset{+}{O}{<}^{CD_3}_{CD_3}$ (the latter by self-methylation of benzyl methyl ether) so that we have to deal with a <u>benzyl cation transfer</u> to dimethyl ether and not with any methyl cation transfer to benzyl methyl ether. Furthermore no peak is found at m/e 64 ($CD_3-\overset{+}{O}{<}^{CH_3}_{CH_3}$). We may therefore conclude that the collision complex decomposes <u>via</u> route A and not <u>via</u> routes B and C.

A


B


C


The same appears to be true for the decomposition of the collision complex in reaction (3).

The direct attack of an amine on a carbenium ion as in reactions (4) and (5) parrallels the formation of the tert-butyl ammonium ion from $C_4H_9^+$ and NH_3, reported by Su and Bowers,[3] although it is not clear whether the authors actually observed this ion or only proposed it as an intermediate.

From the exothermic reaction (1) and available literature data[4,5] the heat of formation of m/e 137 can be calculated to be $<$163 kcal/mole. This would imply, for the hypothetical reaction

$$(6)\quad C_7H_7^+ + CH_3OCH_3 \longrightarrow C_7H_7\text{-}\overset{+}{O}(CH_3)_2$$

$\Delta H^o < -9$ kcal/mole and $\Delta H^o < -2$ kcal/mole in the case of benzyl and tropylium structures for the $C_7H_7^+$ ion respectively.

Although the gas phase proton affinity of benzyl dimethyl amine is not yet known, it will exceed the proton affinity of trimethyl amine, because a benzyl group is expected to stabilise the positive charge better than a methyl group. With this in mind the calculated ΔH_f^o of the ammonium ion in reaction (3) would be $<$153 kcal/mole and ΔH^o(reaction 3) < -12 kcal/mole.

The ΔH^o of reaction (4) will be < -59 kcal/mole when the benzyl dimethyl ammonium structure is assumed for m/e 136. Reaction (5) will be even more exothermic than reaction (4) in view of the fact that a positive charge is generally better stabilised upon replacement of a hydrogen atom by a methyl group.

Acknowledgement

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