Tertiary Aminylium Radicals as Protic Acids†

By GIAN PIERO GARDINI
(*Istituto di Chimica Organica dell'Università, Via D'Azeglio* 85, 43100 *Parma, Italy*)
and JOACHIM BARGON
(*IBM Research Laboratory, San Jose, California* 95193)

Summary Evidence is presented from CIDNP experiments for a fast proton exchange between tertiary aliphatic aminylium radical cations and protic species.

WHILE it is reasonable to expect the acid character of aminylium radical cations such as $RNH_2^{+\cdot}$[1] or $PhNH_2^{+\cdot}$,[2] the behaviour of the tertiary aminylium radicals $R_3N^{+\cdot}$ as protic species is not so obvious and as far as we know it has neither been postulated nor observed.[3] However, their acidity becomes plausible on account of the resonance structures of their conjugate bases:

$$>\overset{\cdot+}{N}-CH_2- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} >\overset{\cdot+}{N}-\overset{-}{C}H- \longleftrightarrow >\overset{\cdot\cdot}{N}-\overset{\cdot}{C}H-$$

In order to provide evidence for this assumption, we have generated tertiary aliphatic aminylium radicals *via* photoinduced electron transfer from the corresponding amine to a suitable acceptor, ranging from acetonitrile to an aromatic hydrocarbon (naphthalene, biphenyl, *etc.*) with an appropriate reduction potential. In polar solvents the process shown in equation (1) takes place,[4] where A is the

$$A + D \longrightarrow A^{\cdot-} + D^{\cdot+} \qquad (1)$$

acceptor and D any tertiary aliphatic amine.

In a typical experiment, triethylamine and naphthalene‡ were irradiated directly, by $NiSO_4$-filtered light from a 1 kW mercury-xenon lamp, in a 100 MHz ^1H n.m.r. probe modified to admit light on the spinning sample. CIDNP signals arising from the radical ion pairs were interpreted on the basis of the amended Kaptein's rules.[5]

In the presence of added substrates bearing exchangeable protons, such as water, alcohols, terminal acetylenes, or β-dicarbonyl compounds, proton exchange with the protons bonded to the α-carbons of the amine did occur, as shown by the following observations. (i) In the system NEt_3–naphthalene in CD_3CN, the radical pairs $A^{-\cdot}D^{+\cdot}$ experience a fast 'in-cage' back electron-transfer, giving rise to a strongly enhanced absorption of the quartet due to the amine α-CH_2 only; this fact together with the lack of 'multiplet effect,' excludes the formation of α-carbon-centred radicals as intermediates, since they would cause CIDNP in the β-protons of the amine as well. (ii) Aminylium radicals escaping from the cage and carrying the complementary negative polarization at their α-protons, in the presence of H_2O or ROH, experience a fast proton exchange (together with the associated negative polarization) and the

$$>\overset{\cdot+}{N}-C\mathit{H}_2- + ROH \rightleftharpoons >\overset{\cdot+}{N}-C\mathit{H}H- + RO\mathit{H}$$

signal due to the OH protons then appears in the emission mode.[6] (iii) When using an α-perdeuteriated amine as a donor, no transfer of polarization to the exchangeable protons is observed. (iv) When using NMe_3 and D_2O or CD_3OD as the acidic species, the singlet in the absorption mode due to the amine methyl groups is split into a perturbed signal (approximately a doublet) owing to the formation of Me_2N–CH_2D, while a negative polarization due to an OH group appears in the appropriate range of the spectrum. (v) In the presence of an added strong base, such as MeO^-, the small amount of $^-CD_2CN$ produced by the equilibrium $CD_3CN + MeO^- \rightleftharpoons MeOD + CD_2CN$ also competes for the

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‡ 10^{-4} Mol of each reagent dissolved in 0·5 ml of CD_3CN, contained in a quartz n.m.r. tube.

polarized α-protons of the aminylium, giving rise to a strong emission in the quintet of the solvent, through the formation of polarized CD_2HCN (vi) On addition of trace amounts of dicyclohexyl-18-crown-6 to the system containing NEt_3–naphthalene–ROH in CD_3CN, while the enhanced absorption of the α-CH_2 due to the 'in cage' process remains unaffected, all the negative polarizations in the products arising from the escaped aminylium vanish Other crown compounds are much less effective We believe that this fact also may be rationalized by the 'acidity' of the six aminylium α-hydrogens, which can form six hydrogen bonds with the six oxygens of the crown, allowing the formation of a bridged complex similar to those of ammonium cations described by Izatt,[7] the complexation is probably diffusion-controlled and consequently the polarization vanishes through relaxation processes in the complex prior to the formation of the polarized products

Molecular models show a good complementary relationship from the geometric point of view

The acidity observed in the aminylium radicals may be employed in selective α-deuteriation or titration of tertiary aliphatic amines or eventually in the photochemical racemization of nitrogen derivatives bearing a chiral carbon to the nitrogen

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