

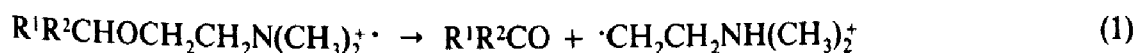
THE FORMATION AND REACTIONS OF DISTONIC AMINE ION ISOMERS

Thomas Bjørnholm^a, Steen Hammerum^a, and Dietmar Kuck^b

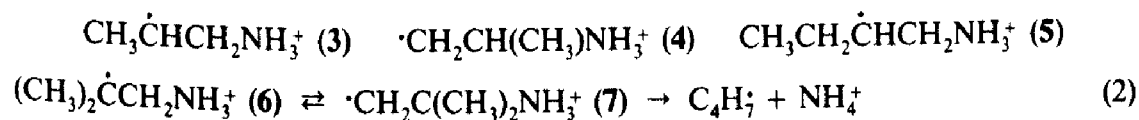
(a) University of Copenhagen, Denmark;¹ (b) Universität Bielefeld, FRG

Fifteen α - and β -distonic radical cations derived from $\cdot\text{CH}_2\text{NH}_3^+$ (1) and $\cdot\text{CH}_2\text{CH}_2\text{NH}_3^+$ (2) by introduction of alkyl substituents at C or N have been demonstrated to be stable species. The unimolecular reactions of β -distonic ions have been studied in detail. 1,2-Migration of NH_3 or NH_2R is a facile reaction, as is simple cleavage of the C-N bond in *N*-substituted ions (loss of alkene neutrals). Fragmentation *via* isomerization to amine molecular ions requires the presence of 'long' alkyl substituents, since it occurs by a relay mechanism involving abstraction of γ - or δ -hydrogen atoms. *N*-Substituted α -distonic ions undergo alkyl radical loss by direct C-N bond cleavage. It is difficult to distinguish between γ -distonic ions formed in fragmentation reactions and the corresponding amine molecular ions.

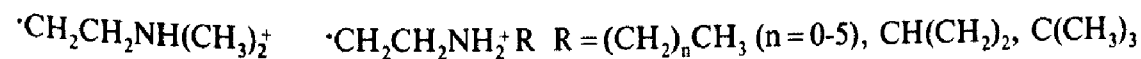
Distonic radical cations are formed by isomerization or dissociation of many organic ions. We have found that the fragmentation of alkoxyalkylamines, eq. (1), provides convenient access to a wide variety of distonic amine ions.^{2,3}



C-Alkylated distonic analogs of 2 are stable species. The methyl substituted ions do not even after collision isomerize to the corresponding amine molecular ions. However, the ions with two methyl groups at the same carbon atom, 6 and 7, interconvert by 1,2- NH_3 migration and cannot readily be distinguished. The only spontaneous unimolecular reaction observed for 3, 4, and 6 \rightleftharpoons 7 leads to NH_4^+ ions, while 5 reacts *via* isomerization to 2-butylamine.



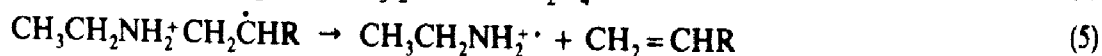
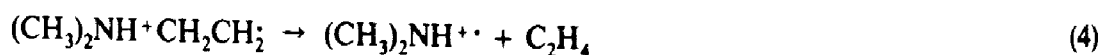
N-Alkyl analogs of 1 and 2 are likewise stable species, but isomerization frequently initiates the fragmentation reactions observed.



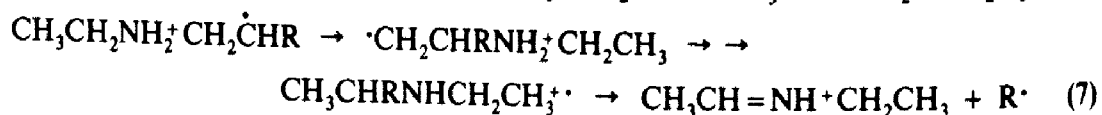
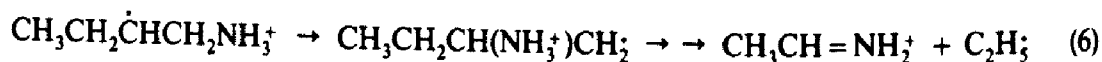
C-N Cleavage. *N*-Substituted α -distonic amine ions eliminate the *N*-alkyl group by simple cleavage of the C-N bond, eq. (3). This reaction gives rise to a dish-shaped peak in nearly all cases examined. Analogous reactions have been observed for other α -distonic ions.⁴



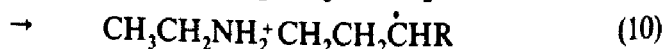
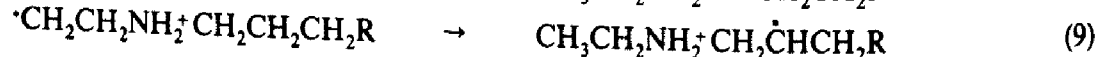
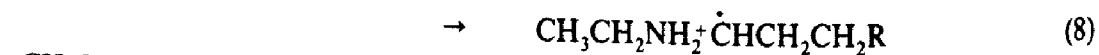
Simple fission of the C-N bond in *N*-substituted β -distonic ions leads to amine molecular ions by loss of alkene molecules, eq. (4) and (5). The reverse reaction, addition of amine molecular ions to alkenes, has been examined by ICR.⁵



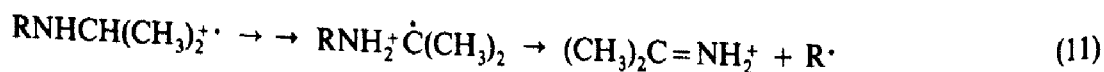
1,2-Migration of NH_3 or NH_2R occurs in β -distonic ions,³ eq. (6) and (7). The subsequent fragmentation occurs (after reciprocal hydrogen abstraction) by α -cleavage:



Intramolecular hydrogen abstraction in *N*-substituted β -distonic ions convert these to other distonic ions. Direct isomerization to the corresponding amine molecular ion does not occur. 1,4-Hydrogen transfer, eq. (8), leads to α -distonic ions (\Rightarrow alkyl radical loss); 1,5-transfer, eq. (9), leads to isomeric β -distonic ions (\Rightarrow amine migration and α -cleavage in the rearranged species, or alkene loss); 1,6- and 1,7-transfers, eq. (10), lead to distonic ions in which subsequent hydrogen abstraction from the $-\text{NH}_2-$ is possible, resulting in formation and α -cleavage of the corresponding amine molecular ion.



These results support that many fragmentation reactions of low-energy amine molecular ions take place *via* rearrangement of distonic intermediates. The often predominant loss of a β -alkyl group from primary and secondary amines occurs after N-migration in a β -distonic isomer, and C-N cleavage takes place after isomerization to an α -distonic ion:



References

- 1 Address for correspondence: Department of General and Organic Chemistry, The H.C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark
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