Intramolecular Rearrangements with Nuclear Magnetic Resonance Emission. Nuclear Polarization in 1,2-Shifts of Quaternary Nitrogen Intermediates

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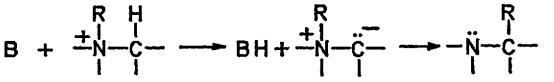
Summary ^{1}H n.m.r. emission at both α- and β-positions in Stevens rearrangement products, but not eliminated olefins, from quaternary ammonium intermediates is indicative of caged radical pairs in the migration process.

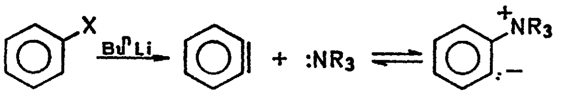
SINCE the intramolecularity of the Stevens rearrangement (equation 1) in quaternary ammonium salts has been



$$\mathrm{B} + \overset{+}{-}\underset{|}{\overset{\overset{\mathrm{R}}{|}}{\mathrm{N}}}-\underset{|}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}- \longrightarrow \mathrm{BH} + \overset{+}{-}\underset{|}{\overset{\overset{\mathrm{R}}{|}}{\mathrm{N}}}-\underset{|}{\overset{\overset{-}{\cdot\cdot}}{\mathrm{C}}}- \longrightarrow -\underset{|}{\overset{\cdot\cdot}{\mathrm{N}}}-\underset{|}{\overset{\overset{\mathrm{R}}{|}}{\mathrm{C}}}- \qquad (1)$$

demonstrated,[1] intermediates in the 1,2-migration process must be adequately characterized and compatible with the overall product results. Chemically-induced dynamic nuclear polarization was observed[2] for the α-protons in the amine product. However, both this position and the migrating group are now shown to be sources of ^{1}H n.m.r. emission and enhanced absorption multiplets (Figure).

The quaternary nitrogen intermediate in these studies was generated by the attack of n-butyl-lithium in hexane on a halogenobenzene in the presence of a tertiary amine. The initially formed aryne adds a nitrogen lone-pair to give an *o*-aniliniumide betaine (equation 2). Subsequent conversion into the α-ylide of the Stevens rearrangement or into elimination products is dependent on the structure of the tertiary amine.



(2)

Reaction conditions, as optimized, include temperature elevation to the point where solvent boiling does not yet

Characteristic ^{1}H *n.m.r. bands for products from the* Bu^{n}Li *aryne liberation in tertiary amines*

NR^{1}R^{2}R^3			C_6H_5X	Product n.m.r. bands δ (p.p.m.)[a]
R^1	R^2	R^3		
PhCH$_2$	Me	Me	F, Cl, *p*-F$_2$	5·02 q[b] (e/a)
PhCH$_2$	PhCH$_2$	Me	F,[c] Cl	5·12 t (e/a), 3·16 d (e/a)
PhCH$_2$	PhCH$_2$	Et	F	4·95 t (e/a), 4·44 s (n), 3·16 d (e/a)
Et	Et	Et	F	5·23 s (n)
Bu^n	Bu^n	Bu^n	F	5·78 m (n),[d] 4·82 m (n)[d]

[a] Normal (n), emission (e), enhanced absorption (a), or combinations (e/a) or (a/e) for multiplets.
[b] Relative absorption intensities in multiplet at maximum activity −0·9 : −4·9 : 5·6 : 1·1.
[c] *Cf.* Figure 1 for actual spectra.
[d] A B and C integral centres for vinyl protons in but-1-ene.

disturb measurements (60° for hexane solutions). These conditions minimize the amount of *NNN′N′*-tetramethylethylenediamine (TMEDA) necessary for RLi depolymerization[3] which results in fast reactions and intensification of the ^{1}H n.m.r. emission signals. The combinations of reagents studied under these conditions are indicated in the Table. Products are identical from fluoro- and chlorobenzene reactions. In addition, no shift in the methine hydrogen signal from *N*-α-phenethylaniline is evident on fluoro-substitution in the aniline ring.

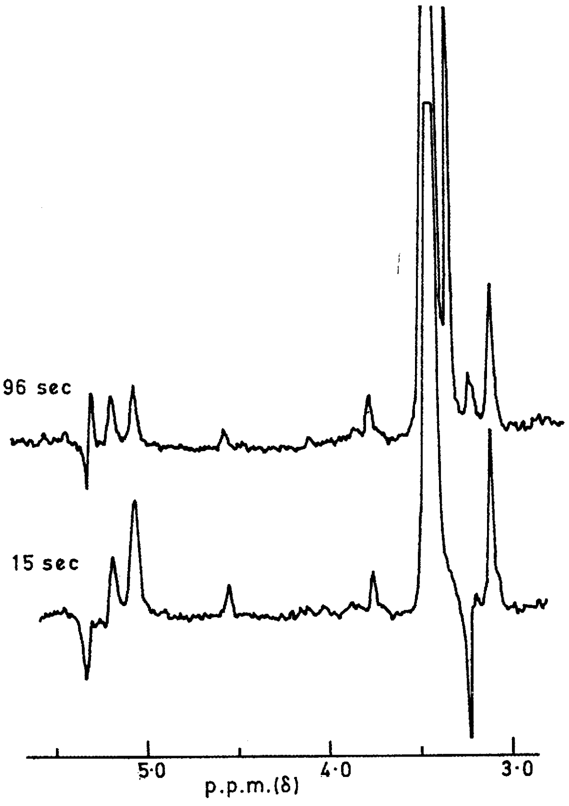
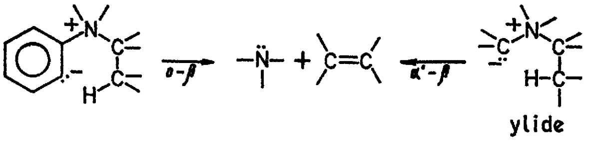


FIGURE. *Emission/absorption multiplet effect spectra for the benzylic methine and methylene protons of* N-*methyl*-N-*phenyl*-1,2-*diphenylethylamine produced during the tetramethylethylenediamine-catalysed reaction of n-butyl-lithium, fluorobenzene, and* N-*methyldibenzylamine.*

Both the amine and migrating benzyl portion have emission and absorption bands when the starting amine contains two benzyl groups. The β-position protons in the *N*-alkyl-1,2-diphenylethylamine products show no shift in location but some variation is evident for the α-methine signals. In all cases, the downfield bands of a multiplet are emission and the upfield bands absorption with the middle band of an odd multiplet (*cf.* triplet of Figure) disappearing or taking on derivative appearance as the intensity of emission increases.

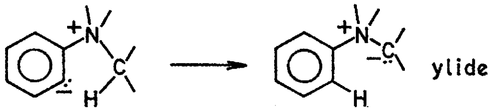
When triethyl- or tri-n-butyl-amines were used, products clearly identifiable by n.m.r. were the olefins, respectively, ethylene and but-1-ene. Neither of these showed any of the emission characteristics previously observed for alkyl halide–alkyl-lithium reactions.[4] Elimination may also occur in *N*-ethyldibenzylamine reactions and a signal for *NN*-dibenzylaniline obtains. However, no ethylene was evident in these reactions. Either an *o*–β or α′–β nucleophilic displacement route is possible with the benzylic



(3)

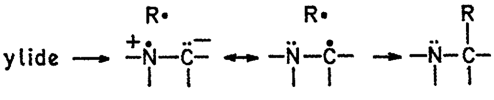
amine (equation 3), but *o*–β seems much more reasonable than either α′–β or α–β for the trialkylamines.

Transfer of a proton to give a benzyl ylide (equation 4)



(4)

is essential for the Stevens rearrangement process. The emission–absorption multiplets are indicative of unpaired electrons[5] in the process of group migration to the detected product. Thus, either the ylide must be excited to a triplet state during rearrangement, or a homolytic bond cleavage (equation 5) occurs (or both) during the shift of a group from nitrogen to carbon.



$$\text{ylide} \longrightarrow \overset{R\bullet}{\overset{+\bullet}{-N}-\overset{..-}{C}-} \longleftrightarrow \overset{R\bullet}{-\ddot{N}-\dot{C}-} \longrightarrow -\ddot{N}-\overset{R}{C}- \qquad (5)$$

If the reaction is so rapid that *very* few radicals leave the cage of formation, the necessary conditions for intramolecular transfer are met. This is compatible with the lifetimes of less than 10^{-5} but more than 10^{-9} sec. suggested as limits on the nuclear polarization process.[6] Radicals escaping the cage will readily abstract protons α to nitrogen in the substrate.[7] Such radicals will give products whose characteristic n.m.r. bands are for the most part nearly superimposable on those of the starting materials. Thus, these products would not be detected in the current experiments.

The immediate requirements of the current experiments are that one or more unpaired electron be involved in an intermediate which is converted directly into the observed product. This intermediate is capable of polarizing both the α- and β- protons on the carbon chain formed in the migration process. And, finally, the same relationship of upfield to downfield in emission and enhanced absorption is indicative of some correlation in the states for unpaired electron-adjacent proton spin interactions for the intermediate. These requirements for the intermediate are best met by a caged radical pair. Alternatives such as triplet carbenoid species[8] which might be postulated to undergo C–N or C–H insertion[9] would not produce nuclear spin polarization of the β-hydrogens. Although similar observations in other Stevens rearrangement systems would be desirable to confirm these conclusions, the generalization of these postulates should provide a new means of predicting the course of 1,2-shifts in quaternary nitrogen intermediates.

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