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THE STEVENS REARRANGEMENT IN AMINIMIDES‡

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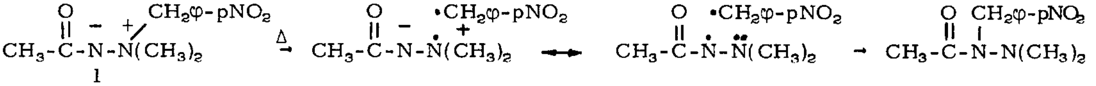
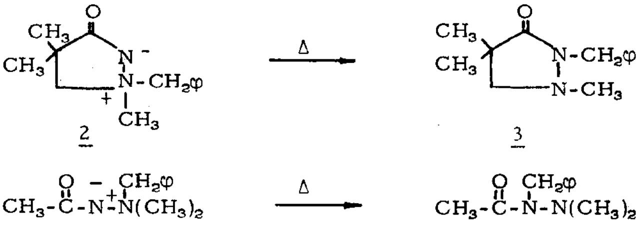
Recently, chemically induced dynamic nuclear polarization (CIDNP) was reported in the benzyl region of the Stevens product resulting from thermolysis of 1, 1-dimethyl-1-p-nitrobenzylamine-2-acetimide (1).[1] Therefore, a diradical mechanism was assumed to be the only reaction pathway. However, Jacobus has recently criticized the assumption that this type mechanism must be the major or only pathway operative when CIDNP is observed.[2]



$$CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\overset{-}{N}\text{-}\overset{+}{N}(CH_2\varphi\text{-}pNO_2)(CH_3)_2 \xrightarrow{\Delta} CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\overset{-}{N}\text{-}\overset{\bullet +}{N}(CH_3)_2\ \cdot CH_2\varphi\text{-}pNO_2 \longleftrightarrow CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\overset{\bullet}{N}\text{-}\overset{\bullet\bullet}{N}(CH_3)_2\ \cdot CH_2\varphi\text{-}pNO_2 \rightarrow CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}N(CH_2\varphi\text{-}pNO_2)\text{-}N(CH_3)_2$$

1

We have further investigated the mechanism of the Stevens rearrangement utilizing 1, 4, 4-trimethyl-1-benzyl-3-oxapyrazolidinium inner salt (2) and 1, 1-dimethyl-1-benzylamine-2-acetimide (4). Aminimide 2 produced 3 in 100% yield whereas aminimide 4 produced 5 in only 31% yield when decomposed in nitrobenzene. Kinetic data are shown in Table I.



2 → 3

4 → 5

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TABLE I

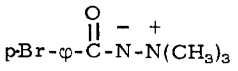
Rate Data from Aminimides 2 and 4 in Nitrobenzene[a]

Aminimide	k Stevens (min^{-1})[b]	Relative Rate Constants
2	1.7	240
4	0.007	1

(a) Decomposed at three temperatures in Varian A-60-A nmr spectrometer in purified nitrobenzene under vacuum (degassed).

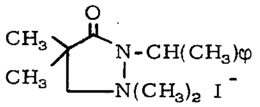
(b) Rates of formation of Stevens products extrapolated to 170°.

The 240 fold rate increase associated with 2 is probably caused by the relief of strain associated with the change in hybridization of the α-nitrogen atom (imide atom) between 2 and 3. An X-ray study has indicated that the imide nitrogen atom of trimethylamine p-bromobenzimide (6) is sp^2 hybridized.[3] However, nmr evidence indicates that the α-nitrogen atom of 1,1,4,4-tetramethyl-2-α-methylbenzyl-3-oxapyrazolidinium iodide (7) is sp^3 hybridized.[4]



$p\text{Br-}\varphi\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{-}{N}\text{-}\overset{+}{N}(CH_3)_3$

6



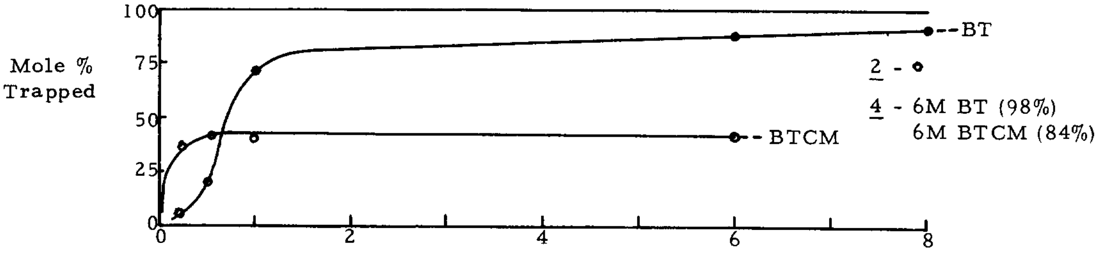
7 +

The α-nitrogen atoms of 3 and 5 are also assumed to be sp^3 hybridized. Since the angles of a regular pentagon are 108°, this change in hybridization from sp^2 to sp^3 would significantly decrease the angle strain of the ring system. If the transition state involved only formation of the radical pair and no germinant bonding of the benzyl radical to the α-nitrogen atom, with no concomitant rehybridization of that atom, then no rate acceleration due to relief of strain would be observed. However, if the transition state resembled the product in which the benzyl radical was partially bonded to the α-nitrogen atom and this atom had partially rehybridized, then the rate of 2 would be markedly enhanced. This explanation indicates that the migrating radical from 2 would also be more tightly bound to substrate than the migrating radical from 4 in order to relieve ring strain. This expectation is realized in trapping experiments described below.

The migrating radicals from 2 and 4 were trapped with benzyl thiol (BT) and bromotrichloromethane (BTCM) forming toluene and benzyl bromide respectively. Figure 1 indicates the mole % benzyl radicals trapped with varying concentrations of scavenger from 2 and 4.

FIGURE 1

Mole % Benzyl Radicals Trapped With Scavenger



Molar Concentration of Scavenger

The initial concentration of aminimide is 0.05 M in chloroform. Rearrangements were performed in sealed tubes and analyzed by vpc techniques using an internal standard. Each aminimide was decomposed for at least 5 half lives (150° for 2 and 185° for 4). An increase in temperature had no effect on the % radicals trapped at constant scavenger concentration. Products were stable at the reaction conditions.

The mole % benzyl radicals trapped from 2 by BTCM is higher than the amount trapped by BT at low concentrations of scavenger (up to 0.6M). The curve then levels out for BTCM but steadily increases with BT. The C-Br bond strength of BTCM is 54 k.cal./mole whereas the S-H bond strength of BT is approximately 75 k.cal./mole.[5] If bond strengths alone reflected the reactivity of each scavenger, the mole % trapped should be higher for BTCM at all concentrations of scavenger. The fact that the two curves cross can be explained in terms of increased ability of BT to intrude into the solvent cage as a result of the smaller Van der Waals radius of the hydrogen atom compared to the bromide atom.[6] The maximum % of radicals which would escape from the solvent cage of 2 in the absence of scavenger is approximately 43% since the curve from BTCM levels out at this value. Crossover experiments are currently being conducted to determine this value more accurately.

The mole % benzyl radicals from 4 by 6M BT and BTCM is 98% and 84% respectively (after correction for the 69% Curtius rearrangement). The corresponding values from 2 are 84% and 43% respectively. This increase in trapping efficiency can be attributed to two possible factors: (1) The benzyl radical from 2 forms a tighter radical pair due to increased germinant bonding with the α-nitrogen atom in order to relieve ring strain. (2) Since the terminal nitrogen atom of 4 is rapidly rotating about the C-N bond,[7] the solvation by chloroform at this point should be less than in 2. Due to the decreased ordering of solvent compared to 2, the scavenger would encounter less resistance in intruding into the radical cage.

The trapping experiments strongly suggest that the Stevens rearrangement in aminimides is entirely radical in nature. Benzyl radicals rather than anions are the abstracting species since hexachloroethane was detected in significant yields when BTCM was used. The % radicals trapped from 2 increased from 35% to 62% when 1M BTCM was used in nitrobenzene instead of chloroform. This is attributed to the formation of a π-complex of the benzyl radical with the aromatic solvent causing an increased radical lifetime.[8]

Further information concerning the Stevens rearrangement was obtained from the study of CIDNP. CIDNP was detected not only in the benzyl protons[1] of 3 but also in the N-methyl and ring methylene protons when 2 was decomposed at 130°, 140°, and 150°. The duration of emission from benzyl and N-methyl protons was three minutes at 150°. However, the ring methylene protons showed emission for four minutes and the relative intensity was three times larger than the other two signals. This indicates that the asymmetric environment about the quaternary nitrogen atom is maintained after initial bond dissociation so that the lone electron on that atom can preferentially couple with those protons with the longest lifetime in potential coupling states, i.e., those methylene protons held rigidly by the ring. Migration of the benzyl radical above the plane of the ring on the same side from which it dissociated is consistent with this explanation. Wadsworth has shown that the intramolecular Stevens rearrangement of alkyl groups also involves attack from the side of dissociation.[9]

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‡ The Stevens rearrangement is sometimes referred to as the Wawzonek rearrangement.

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