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MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS. CXCII.[1]

SKELETAL REARRANGEMENT IN THE FRAGMENTATION OF PHENYL AZIDE.[2]

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Following the demonstrations by Meyerson and co-workers[4] and Rinehart et al.[5] that the M-1 ion in the mass spectrum of toluene is best represented as a tropylium structure, analogous ring expansion pathways have been proposed to rationalize data from ^{13}C-labeled compounds in the quinoline, indole, and pyrrole series,[6] and from the even-electron $C_6H_6N^+$ fragment ion of aniline,[7,8] sulfanilamide[8] and p-nitroaniline.[8] The odd-electron $C_6H_7N^{+\cdot}$ ions from aniline (M^+) and acetanilide (M-42) are largely unrearranged[7,8] as is the molecular ion formed prior to loss of CO in phenol.[9] Hence the pattern appears to be emerging that even-electron aromatic ions are frequently rearranged whereas odd-electron ions are not. That such a generalization is not justified is shown by thiophenol which exhibits[9] considerable loss of ring-carbon identity in the formation of the odd-electron $C_5H_6^{+\cdot}$ ion by loss of CS from the molecular ion. We now report a second example of skeletal rearrangement in an odd-electron species.

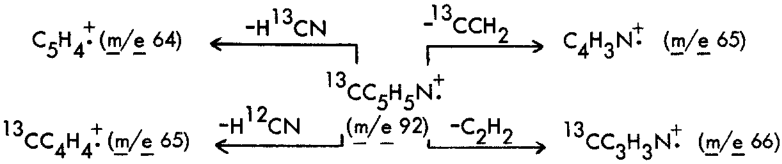
The observation by Crowe and Wentrup[10] that the M-28 (N_2) ion $C_6H_5N^{+\cdot}$ of mass 91 (formally ionized phenyl nitrene) in the spectrum of phenyl azide loses HCN in a qualitatively similar fashion to aniline prompted an investigation of the possibility of ring expansion in this odd-electron ion using 1-^{13}C-labeled material.

Labeled phenyl azide was synthesized from 42% enriched aniline-1-^{13}C[8] by reaction of the derived diazonium salt with sodium azide[11] followed by vacuum distillation. It was not possible to measure the mass spectrum on an A.E.I. MS-9 instrument using either the direct insertion or heated inlet techniques because of the volatility of the material and its susceptibility to decomposition to form aniline and azobenzene.[10] However, adsorption onto charcoal and direct insertion into an Atlas CH 4 spectrometer equipped with a "molecular beam" inlet system (initial ion source temperature ca. 100°) did not present these difficulties and the spectrum of an unlabeled sample at 70 ev was identical to that previously reported.[10] The 17 ev spectrum (Fig. 1) of the labeled material was used for calculation since fewer peaks are encountered as compared to 70 ev (when m/e 64 was the base peak). Four scans were run for each sample in the region m/e 63–m/e 66, the intensity values (measured relative to m/e 64 as 100) being highly reproducible (Table 1). Wide slit settings were used so that the signal heights were the sum of the isobaric components. The average values were corrected for the natural abundance of ^{13}C, and the figures then adjusted to Σ63–66 = 100 for calculation. It was assumed that there was no contribution (i) at m/e 64 of $^{13}CC_3HN$, C_4H_2N, or $^{13}CC_4H_3$ (ii) at m/e 65 of $^{13}CC_3H_2N$ or C_5H_5, and (iii) at m/e 66 of $^{13}CC_4H_5$ or $C_3H_2N_2$.

TABLE 1

m/e	Scans				Average	Corrected	Σ63–66 = 100
Unlabeled							
63	8	8	8	7.5	7.9	7.9	6.5
64	100	100	100	100	100	99.6	81.4
65	18	18	18	18	18	12.5	10.2
66	3	3	3	3	3	2.3	1.9
42% excess 1-^{13}C							
m/e	Scans				Average	Corrected	Σ63–66 = 100
63	7	7	7	7	7	7	5.0
64	100	100	100	100	100	99.6	71.8
65	32	32	32	32	32	26.5	19.1
66	7	7	7	7	7	5.7	4.1

The ion $^{13}CC_5H_5N^{+\cdot}$ of mass 92 may lose either C_2H_2 or HCN, giving rise to four possible fragments at m/e 64–66. In addition there is a contribution to m/e 64 from m/e 91 - $H^{12}CN$ and to m/e 65 from m/e 91 - C_2H_2. However, since the spectrum could not be determined on the MS-9 spectrometer it was not possible to obtain high resolution conditions necessary to separate isobaric ions of the same nominal mass, and the method of calculation had to be altered accordingly (cf. ref. 8).

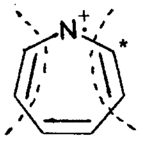


Consider first the loss of acetylene from m/e 92. The total loss can be expressed as the ratio of m/e 65/Σm/e 63–66 in the unlabeled spectrum. This ratio will also hold for total acetylene loss in the enriched spectrum (also measured relative to Σ63–66 as 100), in which m/e 66 (m/e 92 - C_2H_2) is a single fragment (a small unknown peak at m/e 66 in the unlabeled spectrum was subtracted). The total contribution from m/e 92 - $^{13}CCH_2$ and m/e 91 - C_2H_2 to m/e 65 can therefore be determined by subtraction of m/e 66 from the total acetylene loss; multiplication of the total acetylene loss by m/e 92/ m/e (91 + 92) then affords the value of labeled acetylene lost from m/e 92 at m/e 65. The percentage of labeled acetylene lost is then given by $^{13}CCH_2/^{13}CCH_2 + C_2H_2 = 52\%$.

The contribution of total acetylene loss to m/e 65 can now be subtracted from the labeled spectrum, leaving the value for m/e 92 - $H^{12}CN$. The contribution of (92 - $H^{13}CN$) to m/e 64 is given by m/e 64 x m/e 92 / m/e (91 + 92) and the percentage of $H^{13}CN$ expelled from m/e 92 is $H^{13}CN/ H^{13}CN + H^{12}CN$ = 66%. Therefore the percentage of $H^{12}CN$ lost (necessarily from a rearranged ion) is 34%.

Hence, in contrast to the odd-electron $C_6H_7N^{+\cdot}$ molecular ion of aniline, the odd-electron $C_6H_5N^{+\cdot}$ species from phenyl azide is rearranged to a considerable extent prior to loss of HCN. This result is not unreasonable since $C_6H_5N^{+\cdot}$ is formally ionized phenyl nitrene and might be expected to undergo an insertion reaction typical of carbenoid species prior to fragmentation.[12] The 34% represents one-half to five-sixths of the total rearrangement depending on the mechanism of ring expansion, i.e. insertion of nitrogen between the o-carbons to give the azepinium structure (I), or randomization throughout the ring as in toluene.[5]

Insofar as acetylene ejection is concerned (m/e 66 and m/e 65) the corresponding statistical figures are 20% loss of the label from azepinium-2-^{13}C (I, assuming expulsion of any two carbon atoms) and 33% loss from azepinium -γ-^{13}C. The value obtained (52%) suggests nearly specific insertion of nitrogen to give I and then loss of acetylene by cleavage of the N-o-carbon bonds (shown by dotted lines in I).



(I)

The difference in the values calculated for loss of $H^{13}CN$ (66%) and $^{13}CCH_2$ (52%) are not incompatible since the respective precursor $C_6H_5N^{+\cdot}$ ions need not have the same structure, and differential expulsion may occur.

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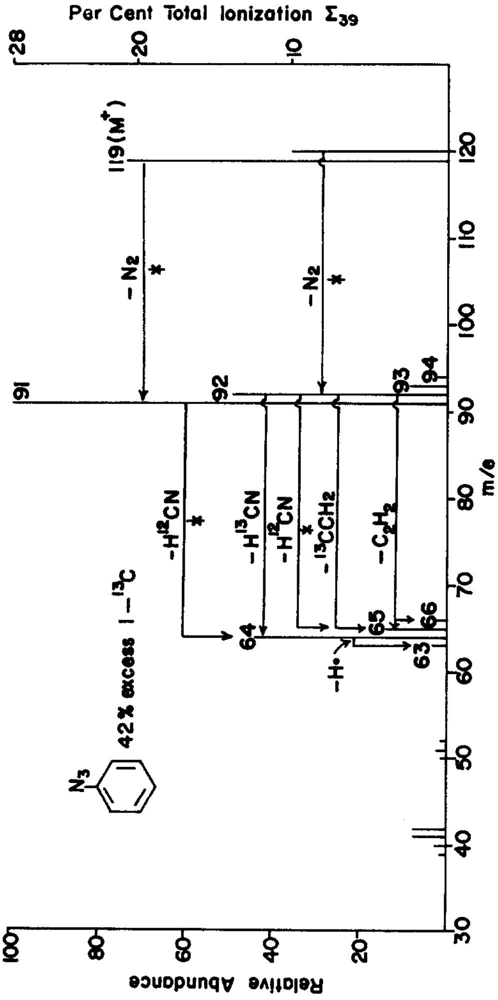

Fig.1 (17ev)