Carbon Scrambling in Azulene Molecular Ions

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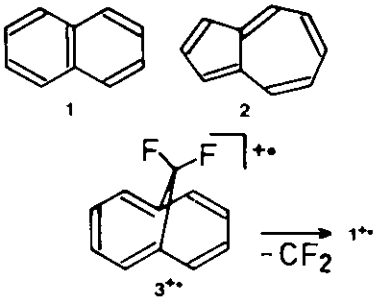
Molecular ions with low tendency for fragmentation often show rearrangement reactions. Benzene and other benzenoid hydrocarbons are well-established examples. For benzene it could be demonstrated by deuterium[1], carbon-13[2], and combined D/^{13}C[3] labelling experiments that prior to the elimination of C_2H_2 both, the hydrogen and carbon atoms suffer from a statistical distribution (complete scrambling). Both processes proceed independently from each other.[3] Dewar benzene, benzvalene, and prismane structures have been discussed as intermediates. Similar studies with deuterated[4] and ^{13}C-labelled[5] naphthalene (1) also indicate complete scrambling prior to the ejection of C_2H_2.



The mass spectrometric behaviour of azulene (2) is very similar to that of naphthalene (1)[5,6]. The non-decomposing molecular ions of naphthalene (1) and azulene (2) possess a common ion structure as proved by collisional activation (CA) measurements.[7] Furthermore, the $[M\text{-}CF_2]^+$. fragment from 11.11-difluoromethano [10] annulene (3) exhibit an identical CA spectrum.[7] This has been explained by a cheletropic reaction ($3^{+\cdot} \rightarrow 2^{+\cdot}$) accompanied by rearomatization leading to a naphthalene ionradical. This interpretation suggests that the $C_{10}H_8^+$ ions obtained from azulene (2), 11.11-difluoromethano [10]annulene (3), and naphthalene (1) are best described by a naphthalene structure. In accordance to the behaviour of naphthalene, this requires that the atoms of the azulene skeleton should lose their positional identity prior to fragmentation. In fact, deuterium labelling experiments[8] in an energy range of 17.1 eV have been interpreted with the assumption that 72% of the azulene molecular ions isomerize to a symmetric intermediate (H-scrambling) whereas the remaining part – supposed to consist of energy-rich ions – decomposes from the original azulene structure.

The successful synthesis of [4.7 –$^{13}C_2$] azulene[9] enabled us to study the behaviour of the azulene carbon skeleton after electron impact ionization. The results of low-voltage measurements (15 – 17 eV) demonstrate that molecular ions decomposing in the ion source undergo an extensive statistical distribution of the carbon atoms prior to fragmentation (scheme 1).

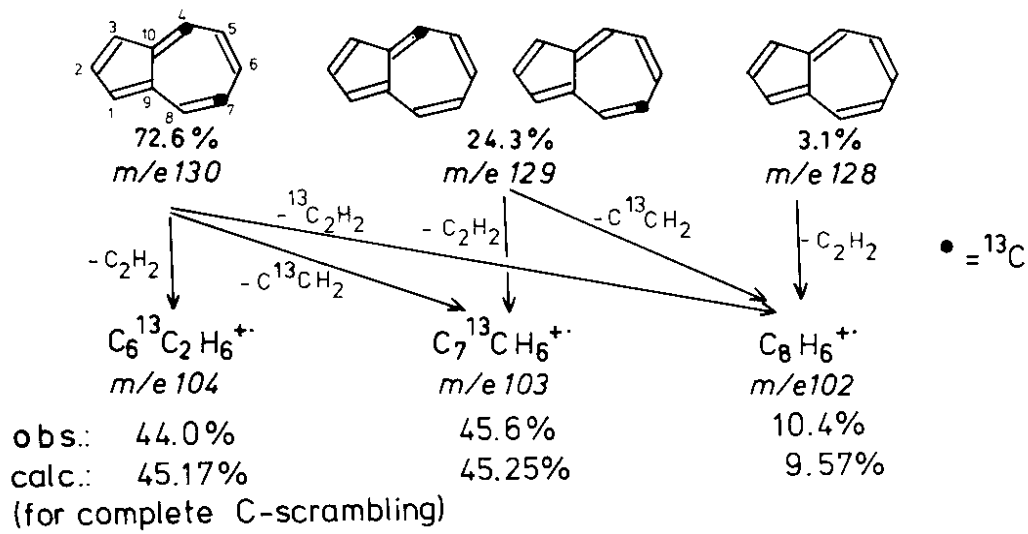
Due to uncomplete $^{13}C_2$-labelling[9] different precursors contribute to the fragment ions at 103 and 102. This weakness could be overcome with a technique which allows the selection of the doubly labelled molecular ion at m/e 130 and the detection of fragmentation processes originating exclusively from this defined species. The linked scan technique[10] meets this requirements.

The measurements have been performed using a Finnigan MAT 711 A instrument equipped with a metascan device. The metascan device enables the combined scan of the electric sector voltage U_A and the magnetic field B. Applying the scan function U_A/B = const., it becomes possible to register all daughter ions from a given parent ion decomposing in the first field free region.

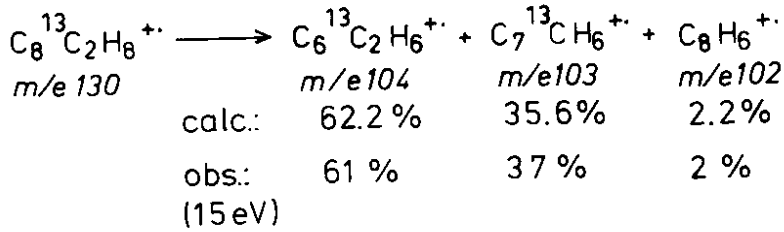
If both carbon atoms necessary for the elimination of C_2H_2 are taken statistically from the molecular ion $C_8{}^{13}C_2H_8^{+\cdot}$, the fragment ion distribution given in scheme 2 is calculated.

The experimental distribution* obtained from the linked scan spectrum at 15 eV is very close to the

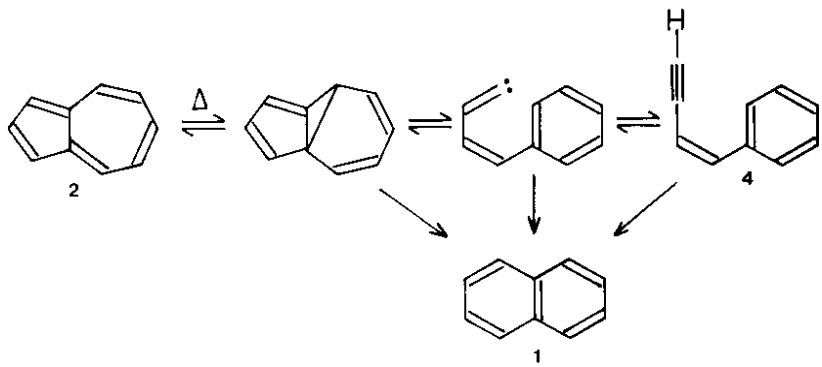
*Mean values from 12 independent measurements



Scheme 1



Scheme 2



Scheme 3

calculated values. The spectrum at 70 eV is identical within experimental errors. It should be emphasized that the loss of $^{13}C_2H_2$ from $C_8{}^{13}C_2H_8^{+\cdot}$ (m/e 130) is directly observed by the linked scan technique, whereas in the normal mass spectrum the occurrance of this fragmentation can only be deduced from the ^{13}C-distribution in the $[M-C_2H_2]^{+\cdot}$ fragment ions (scheme 1).

Thus, the linked scan measurements with [4.7-$^{13}C_2$] azulene undoubtedly demonstrate that the molecular ions of azulene predominantly decompose from an ion structure (or mixture of structures) characterized by the loss of positional identity of the carbon atoms. Finally, this renders possible to eliminate $^{13}C_2H_2$ from the doubly labelled molecular ion although there are no neighboured labelling positions in the original molecule. These results present further evidence that azulene molecular ions rearrange to identical ions as are obtained by electron impact ionization of naphthalene.

Recently, we have shown that the "norcaradiene-vinylidene" mechanism is of major importance in

the thermal rearrangement of azulene (2) into naphthalene (1). [11] This mechanism (scheme 3) includes the involvement of 1-phenylbut-1-en-3-yne (4). In this context, it is important to note that CA measurements indicate different structures for the molecular ions of 4 and the $C_{10}H_8^+$. ions obtained from 1, 2, and 3.[7] Thus, the participation of ionized 4 and consequently a mass spectrometric analogue of the "norcaradiene-vinylidene" mechanism can be excluded in the electron impact induced rearrangement of azulene.

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