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N-Isopropenylazoles: II.* Fragmentation of *N*-Isopropenylazoles under Electron Impact

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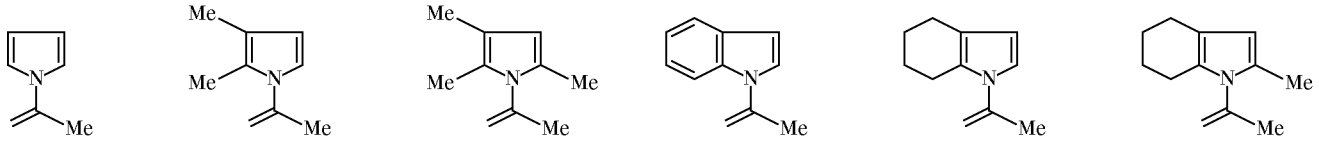
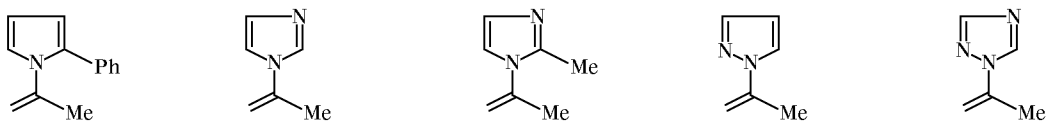
Abstract—Fragmentation under electron impact of all *N*-isopropenylazoles, except for *N*-isopropenyl-2-phenylpyrrole, involves elimination of propyne or allene with formation of the corresponding NH azoles. *N*-Isopropenylpyrrole, *N*-isopropenyl-4,5,6,7-tetrahydroindole, and *N*-isopropenylindole give rise to rearrangement of the molecular ion into azepine structure, while the fragmentation of *N*-isopropenyl-2-phenylpyrrole is accompanied by transfromation into 5-methyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline. Retrodiene decomposition is the main fragmentation pathway of the molecular ions derived from *N*-isopropenyl-4,5,6,7-tetrahydroindole and its 2-methyl-substituted analog. In the decomposition of 2,3-di- and 2,3,5-trimethyl-*N*-isopropenylpyrrole, the major fragment ions are formed from the $[M - H]^+$ ion having a pyridinium structure rather than from the molecular ion. *N*-Isopropenyldi- and -triazoles undergo fragmentation along competing pathways involving cleavage of the heteroring.

N-Isopropenylazoles are new highly reactive heterocyclic synthons which have recently been obtained by reactions of azoles with propyne and allene in the superbasic system KOH–DMSO [1].

The goal of the present work was to get primary information on the reactivity of *N*-isopropenylazoles on the basis of their mass spectra. For this purpose, we recorded the electron impact mass spectra of compounds **I**–**XI** at an energy of ionizing electrons of 60 eV (see table). It is seen that the molecular ions of **I**–**XI** are either the most abundant or second-abundance ions, which is typical of five-membered aromatic heterocycles [2]. The general fragmentation pathway of all compounds of this series, except for *N*-isopropenyl-2-phenylpyrrole (**VII**), is elimination of the isopropyl group as propyne or allene molecule with hydrogen migration to the nitrogen atom to give the corresponding NH-azoles; i.e., the process is the reverse to the synthesis of *N*-isopropenylazoles [1]. A large contribution of the decomposition pathway involving cleavage of the exocyclic N–C bond [which is shown in Scheme 1 with *N*-isopropenylpyrrole (**I**)



I **II** **III** **IV** **V** **VI**



VII **VIII** **IX** **X** **XI**

* For communication I, see [1].

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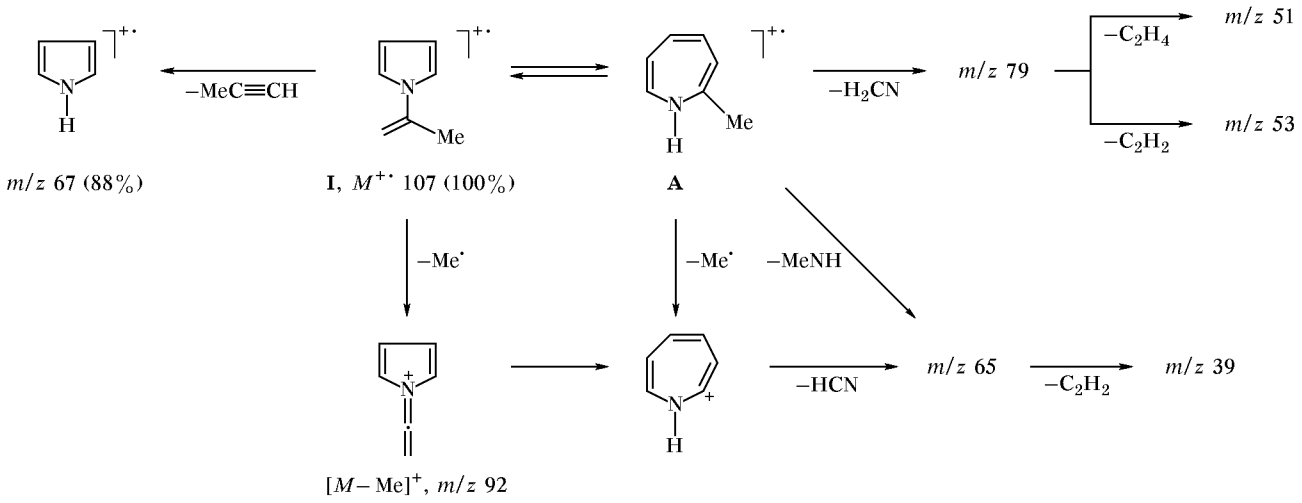
Scheme 1.

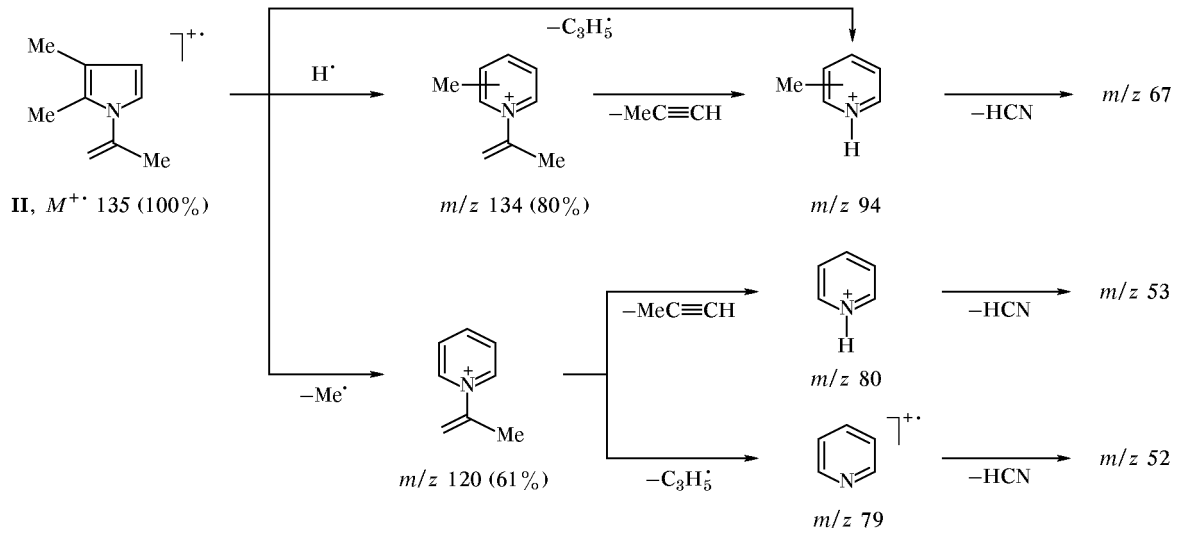


as an example] is likely to be favored by weakening of that bond due to conjugation of lone electron pair on the nitrogen atom with the ring π-system [3]. Further fragmentation of NH-azoles follows a conventional scheme [2].

In addition, the mass spectra of **I**–**XI** contain ion peaks indicating the occurrence of other concurrent fragmentation pathways. In the spectra of *N*-isopropenylpyrrole (**I**) and indoles **IV** and **V** we observed peaks from the $[M - Me]^+$ ion which successively loses hydrogen cyanide and acetylene to afford (from pyrrole **I**) ions with *m*/*z* 65 and 39. The $[M - Me]^+$ ion could be formed from both molecular ion and isomeric azepine structure **A** (Scheme 1). The latter pathway is supported by the presence of $[M - H_2CN]^+$ ion peak (*m*/*z* 79) in the spectrum of **I** (this ion cannot be formed from the molecular ion), as well as by the absence of $[M - Me]^+$ ion peak in the spectra of unsubstituted *N*-isopropenylazoles **VIII**, **X**, and **XI**. An analogous rearrangement to give an azepine structure was observed in the dissociative ionization of 1-phenylpyrrole [4]. The mass spectra of compounds **VI** and **IX** also lack $[M - Me]^+$ ion peaks. The presence of a methyl group in the α-position of the azole ring hampers expansion to seven-membered ring. In these cases, loss of the methyl group is strongly unfavorable [5].

Unlike compounds **I**, **IV**, and **V**, the mass spectrum of *N*-isopropenyl-2,3-dimethylpyrrole (**II**) is characterized by increased contribution of the $[M - H]^+$ and $[M - Me]^+$ ions, presumably due to their stabilization via expansion of the pyrrole ring to six-membered

Scheme 2.



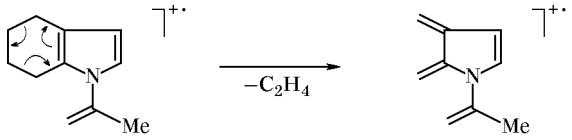
Mass spectra of *N*-isopropenylazoles **I**–**XI**

Compound no.	*m*/*z* (I_{rel}, %)
I	107 (100) $M^{+\cdot}$, 106 (6), 92 (10), 79 (7), 67 (88), 66 (13), 65 (12), 53 (2), 51 (8), 41 (27), 40 (9)
II	135 (100) $M^{+\cdot}$, 134 (77), 120 (61), 94 (73), 93 (16), 80 (27), 79 (23), 67 (9), 53 (14), 52 (9), 51 (9), 41 (18), 39 (35)
III	149 (100) $M^{+\cdot}$, 148 (61), 134 (51), 108 (42), 67 (8), 42 (13), 41 (19), 39 (16)
IV	157 (100) $M^{+\cdot}$, 156 (23), 142 (10), 117 (69), 116 (13), 115 (10), 90 (23), 89 (36), 63 (10), 30 (11)
V	161 (95) $M^{+\cdot}$, 160 (42), 146 (17), 133 (95), 132 (100), 131 (16), 121 (17), 119 (65), 118 (26), 105 (5), 93 (27), 91 (18), 77 (16), 65 (16), 53 (8), 52 (9), 51 (13), 41 (20), 39 (27)
VI	175 (70) $M^{+\cdot}$, 174 (22), 147 (100), 146 (65), 133 (35), 92 (6), 54 (6), 41 (7), 39 (6)
VII	183 (100) $M^{+\cdot}$, 182 (20), 168 (66), 156 (3), 115 (17), 41 (18), 39 (23)
VIII	108 (100) $M^{+\cdot}$, 107 (5), 81 (16), 80 (3), 68 (26), 67 (6), 54 (4), 42 (4), 41 (29), 40 (9), 39 (23)
IX	122 (100) $M^{+\cdot}$, 95 (5), 81 (44), 80 (15), 67 (5), 66 (6), 54 (27), 42 (21), 41 (25), 39 (28)
X	108 (100) $M^{+\cdot}$, 69 (56), 68 (77), 52 (4), 42 (11), 41 (32), 40 (6), 39 (31)
XI	109 (91) $M^{+\cdot}$, 82 (6), 69 (41), 55 (69), 54 (100), 41 (19), 40 (14), 39 (42)

pyridine (Scheme 2). Here, the structure of rearranged pyridinium ions is more favorable [5, 6]. Further decomposition of the pyridinium ions involves elimination of the isopropenyl group with or without hydrogen migration. A similar fragmentation pattern is typical of *N*-isopropenyl-2,3,5-trimethylpyrrole (**III**).

Presumably, the main process leading to the second-abundance ion in the fragmentation of *N*-isopropenyl-4,5,6,7-tetrahydroindole (**V**) (*m*/*z* 133) and to the base peak in the fragmentation of 2-methyl-substituted analog **VI** (*m*/*z* 147) is retrodiene-like decomposition [6] shown in Scheme 3. The presence of strong $[M - Et]^+$ ion peaks in the mass spectra of these compounds is typical of fragmentation of unsaturated rings [7].

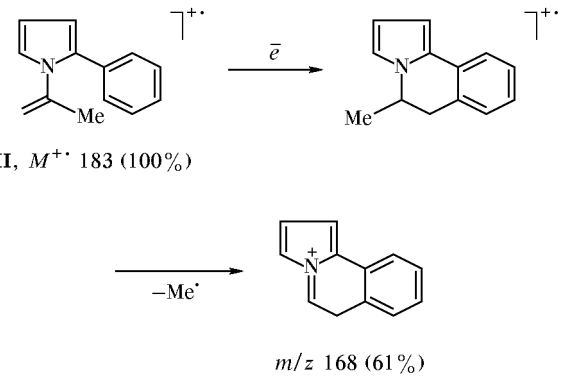
Scheme 3.



VI, $M^{+\cdot}$ 175 (70%) *m*/*z* 147 (100%)

A specific feature of the mass spectrum of *N*-isopropenyl-2-phenylpyrrole (**VII**) is the presence of ion peaks with *m*/*z* 168 (66%, $[M - Me]^+$) and 115 (17%). Abstraction of methyl radical from the isopropenyl group, which is observed for compounds **I**, **IV**, and **V** and is untypical of the other *N*-isopropenylazoles (compounds **VI** and **VIII**–**XI**), becomes possible due to rearrangement of the molecular ion of **VII** into 5-methyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline whose further decomposition gives no ions corresponding to elimination of isopropenyl group (Scheme 4).

Scheme 4.

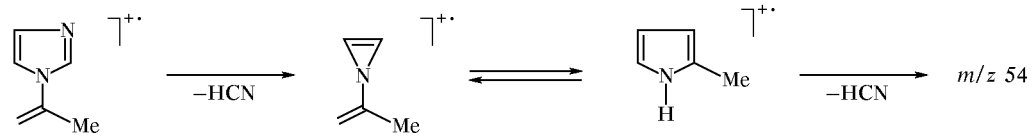


VII, $M^{+\cdot}$ 183 (100%) *m*/*z* 168 (61%)

Structurally related products were obtained by photochemical cyclization of pyrrole analogs of stilbene [8]. The formation of ion with *m*/*z* 115 can formally be interpreted as a synchronous expulsion of acetylene molecule and a species with *m*/*z* 42 from the molecular ion.

An alternative decomposition pathway of the molecular ions derived from *N*-isopropenylimidazoles **VIII** and **IX**, as in the fragmentation of unsubstituted imidazole [6], begins with elimination of HCN molecule with formation of ions with *m*/*z* 81 (16%) (**VIII**) and 95 (5%) (**IX**) (Scheme 5). Elimination of the second HCN molecule from the $[M - HCN]^{+\cdot}$ ion indicates its rearrangement into pyrrole.

Scheme 5.



VIII, $M^{+\cdot}$ 108 (100%) *m*/*z* 81

The mass spectrum of *N*-isopropenylpyrazole (**X**) contained the $[M - C_3H_3]^+$ ion peak, *m*/*z* 69 (56%), which is likely to arise from cleavage of the heteroring. In the fragmentation of *N*-isopropenyl-1,2,4-triazole (**XI**), elimination of propyne (allene) competes with decomposition of the heteroring, which includes successive elimination of two HCN molecules.

Thus, the general pathway of fragmentation of *N*-isopropenylazoles under electron impact is elimination of propyne or allene to give the corresponding NH azole; the process also involves skeletal rearrangements of both molecular ion and fragment ions, depending on the heteroring nature and substitution pattern.

EXPERIMENTAL

The mass spectra (electron impact, 60 eV) were recorded on an LKB-2091 GC–MS system; ion source temperature 240°C; SE-54 capillary column (30 m); injector temperature 250°C; oven temperature programming from 70 to 200°C at a rate of 10 deg/min.

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