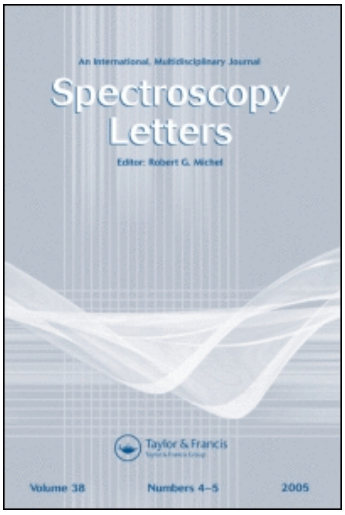

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

2-Halopyrroles. II. Mass Spectroscopic Studies

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To cite this Article Cordell, Geoffrey A.(1975) '2-Halopyrroles. II. Mass Spectroscopic Studies', Spectroscopy Letters, 8: 12, 983 — 991
To link to this Article: DOI: 10.1080/00387017508067401
URL: http://dx.doi.org/10.1080/00387017508067401

SPECTROSCOPY LETTERS, 8(12), 983-991 (1975)

2-HALOPYRROLES. II. MASS SPECTROSCOPIC STUDIES*

Keywords: 2-Halopyrroles, mass spectra.

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ABSTRACT:

The mass spectra of 11 pyrrole derivatives are discussed, with particular reference to the loss of any halogen atom present.

In simple derivatives such as 2-chloropyrrole (1), a loss of halogen is only as favorable as loss of HCN.

In more complex compounds, loss of halogen competes poorly with the other processes such as loss of carbon monoxide, the tropylium species, or methyl groups.

Substantial fragmentation of the pyrrole nucleus was observed before rearrangement of an alkyl pyrrole to a pyridinium species.

* For part I in this series see reference 1.

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INTRODUCTION

The synthesis and chemistry of a number of 2-halopyrrole derivatives has recently been described.[1] The present paper discusses the mass spectra of some of these compounds.

Many aspects of the mass spectral fragmentation of simple pyrroles have been elucidated and discussed elsewhere.[2-4] However, there are only limited reports of the mass spectra of 2-halopyrroles in the literature. It was of some interest therefore, to see how readily the halogen atom was lost in the small number of 2-halopyrroles which, because of their extreme instability[1], could be examined by this technique.

RESULTS AND DISCUSSION

The principal peaks in the mass spectra of the pyrroles studied (FIG. 1) are summarized in Table 1.

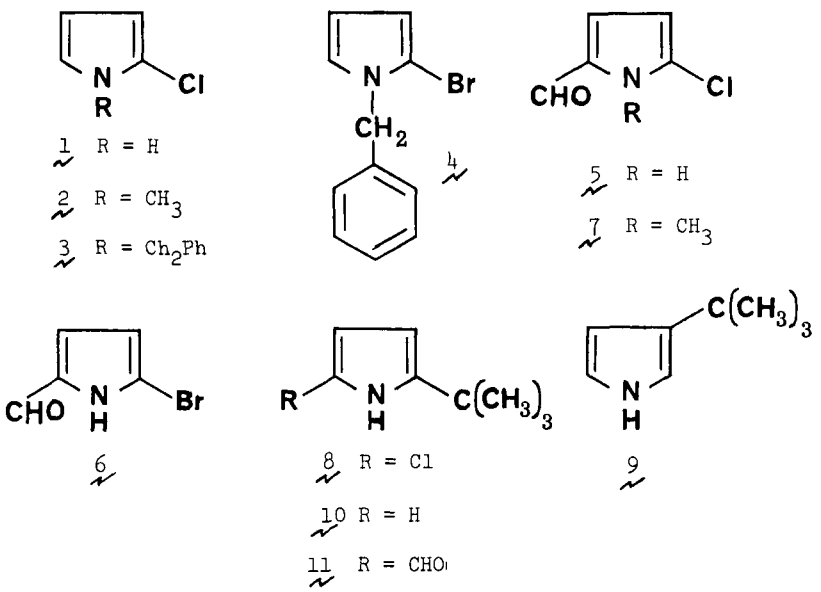


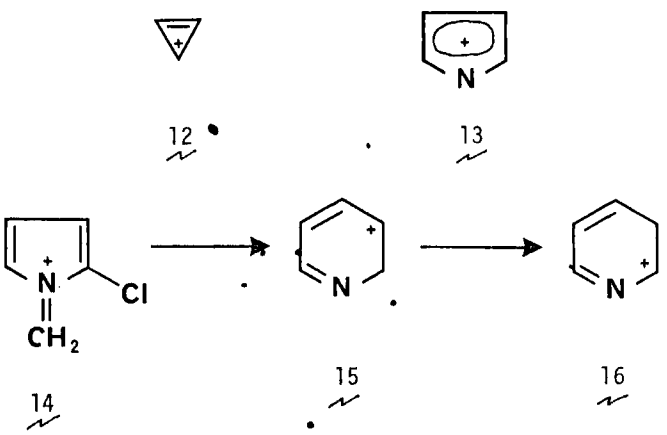
Fig. 1

TABLE 1
Summary of Mass Spectral Data for Pyrroles studied.

Compound	*m/e* (% of base peak)
1	103(34), 101(100), 74(15), 73(13), 66(15.6), 51(6.3), 41(13.7), 39(42.5).
2	117(33), 116(14), 115(100), 114(23.2), 100(11.25), 80(17.25), 78(28.5), 74(7), 73(14), 53(16), 51(11.5), 42(17.25), 39(23).
3	193(15.2), 192(6.1), 191(26.3), 92(8.2), 91(100), 65(11.5), 51(5), 39(5.5).
4	237(12.25), 235(13.25), 92(10), 91(100), 65(11), 51(5), 39(6).
5	131(38), 130(31), 129(100), 128(93), 102(14.5), 100(38), 75(15.5), 73(34.5), 66(12), 64(12), 41(17.5), 39(55).
6	175(95), 174(100), 173(100), 172(96), 146(22.5), 144(22.5), 119(13), 117(13), 66(8.25), 65(7.5), 24(9.4), 57(7.5), 55(6.7), 44(17.25), 43(7.1), 41(9.2), 40(8.25), 39(24.2) 38(19.25), 37(11.0).
7	145(22.5), 144(25), 143(95), 142(100), 114(14.5), 108(10.5), 80(8.05), 78(24.2) 73(31.3), 51(15.3), 39(23).
8	159(8), 157(19), 144(34), 142(100), 107(21), 79(14), 78(11), 73(9), 65(12), 53(12.5), 51(16), 41(34), 39(35).
9	123(66), 108(100), 107(6.2), 93(7.8), 80(13.0), 68(16.5), 67(8.2), 41(10), 39(9.3).
10	123(37), 108(100), 107(6.7), 93(10), 80(10), 67(11), 67(6.1), 41(12.2), 39(11).
11	151(4.5), 150(29.5), 136(11), 135(100), 107(11), 80(10.5), 79(6.5), 68(10), 53(6), 41(8), 39(8.5).

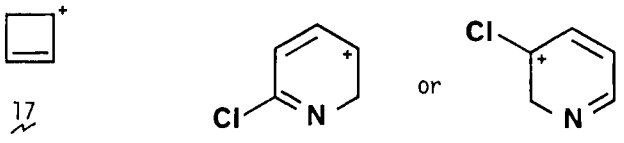
The base peak in the mass spectrum,[5] at 40°, of 2-chloropyrrole (1) is the molecular ion, which shows two major modes of fragmentation. One involves loss of a neutral HCN molecule, to yield an ion radical *m/e* 74, which loses a chlorine radical and cyclizes to afford the cyclopropenyl ion, *m/e* 39 (12). The second mode of fragmentation involves loss of a chlorine radical *before* loss of HCN, to produce *m/e* 66, 13, which further fragments to 12. These processes appear to be approximately equally favorable.

In the mass spectrum of 2-chloro-1-methylpyrrole (2), the molecular ion, *m/e* 115, is the base peak, and the abundance of the azafulvinium species, *m/e* 114, 14 is low. The molecular ion does lose a methyl radical to afford a fragment *m/e* 100. Also important is the loss of chlorine radical and subsequent rearrangement to a pyridinium species of the type 15 or 16 at *m/e* 80.

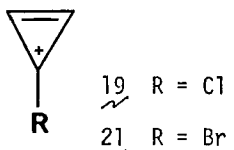


These can fragment by loss of HCN, as observed previously for 1-methylpyrrole[3,4], to produce the species *m/e* 53, 17. The azafulvinium species 14 undergoes loss of HCl to afford an ion *m/e* 78.

This process may occur before or after ring expansion to a pyridinium species 18, but it is of interest that the fragment ion *m/e* 78 is the base peak in the mass spectrum of 2-chloropyridine. Further fragmentation by loss of HCN gives rise to the ion at *m/e* 51, of unknown structure. It is also noteworthy that the chlorocyclopropenyl ion, *m/e* 73, 19 has an abundance of 15%, strong evidence for this ion being the product of a fragmentation of pyrrolic (azafulvinium) rather than a pyridinium species, since it is present as only 2% of the base peak in the mass spectrum of 2-chloropyridine.



17 18



19 R = Cl
21 R = Br

20

As in the mass spectrum of 1-benzylpyrrole 6, the base peak in the mass spectra of 1-benzyl-2-chloro-and 1-benzyl-2-bromopyrrole, 3 and 4, is the tropylium species, *m/e* 91, 20. The molecular ion, in the case of the 2-chloro derivative, is 26%, and in the case of the 2-bromo derivative only 13% of the base peak. The other major fragment is a species, *m/e* 65, (11.5% of the base peak in each case) resulting from loss of both substituents. It is somewhat

surprising that the cyclopropenyl ion 12 has only a low abundance (5%) in the spectrum of each of these compounds.

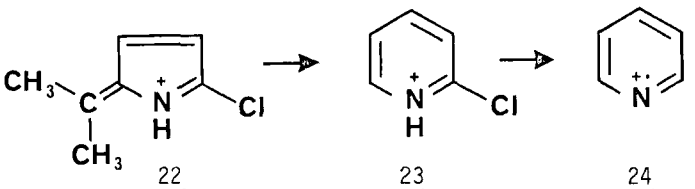
The mass spectrum of 5-chloropyrrole 2-carboxaldehyde (5) has two peaks at M^+ and M^+-1 of almost equal intensity which are the base peaks. Loss of halogen radical from the molecular ion does not occur to any great extent (<2%); rather, loss of carbon monoxide to afford an ion *m/e* 100 is followed by loss of HCN to give the chlorocyclopropenyl ion, *m/e* 73, 19. The fragment ion at *m/e* 66, 13, is also quite abundant and probably arises from *m/e* 101 by loss of halogen radical.

The spectrum of 5-bromopyrrole-2-carboxaldehyde (6) consists of four strong peaks of almost equal intensity due to the two bromine isotopes at *m/e* 173 and 175. Their corresponding M^+-1 species fragment in a similar way to the corresponding chloro compound by loss of carbon monoxide, to give an ion *m/e* 144; the latter loses HCN to afford the bromocyclopropenyl ion, *m/e* 117, 21, along with corresponding fragments containing the ^{81}Br isotope at *m/e* 146 and 119, respectively.

The mass spectrum of 5-chloro-1-methylpyrrole-2-carboxaldehyde (7) exhibits very strong M^+ and M^+-1 peaks, the latter being the base peak, *m/e* 142. This peak gives rise to two abundant fragments at *m/e* 114 (14.5%), by loss of carbon monoxide, and *m/e* 78, (24.2%), by loss of HCl and subsequent ring expansion. The most abundant fragment, is the chlorocyclopropenyl ion (19) (31.5%).

The molecular ion in the mass spectrum of 5-chloro-2-*t*-butylpyrrole (8) at 40°, is less than 20% of the base peak, *m/e*

142, 22. Further loss of one-carbon fragments from this species takes place to successively produce species at *m/e* 126 and *m/e* 114. The latter is the pyridinium species 23, which can either lose a chlorine radical with hydrogen radical rearrangement to afford *m/e* 79, 24, or HCl, as described previously to yield the ion *m/e* 78. Loss of halogen radical from the base peak is also observed, affording a species, *m/e* 107.

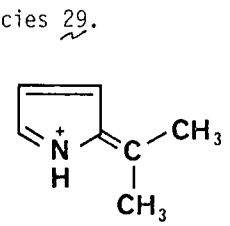


22 23 24

The most abundant fragments, after the base peak, are the ions at *m/e* 41 and 39. Since these fragments occur to the extent of less than 5% in 2-chloropyridine, considerable fragmentation of the pyrrolic species 22 must occur, before it rearranges to the pyridinium species 23.

Of the *t*-butyl compounds whose mass spectra were examined, only 3-*t*-butylpyrrole (9) has a molecular ion which is a fairly large percentage of the base peak. As in the thiophene series[2], the molecular ion is only 35% of the base peak in the mass spectrum of 2-*t*-butylpyrrole (10). The base peaks in the parent compounds are thought to be due to ions of the type 25 and 26. Further loss of one-carbon fragments then takes place to produce species at *m/e* 93 and *m/e* 80, the latter probably being the ring-expanded pyridinum species 27. The secondary mode of fragmenta-

tion of the molecular ion is one involving complete loss of the t-butyl group with concomitant double hydrogen radical migration to the ring[2], to afford a protonated pyrrole species at *m/e* 68, 28. That this ion has approximately the same abundance for both 2- and 3-*t*-butylpyrrole is strong evidence that it is in fact the protonated pyrrole species, rather than the ring fragmented species 29.



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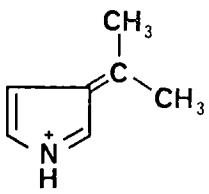

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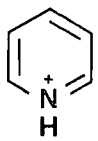

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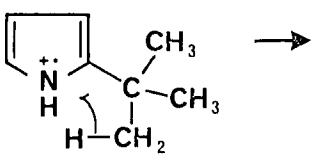

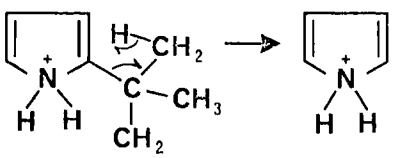

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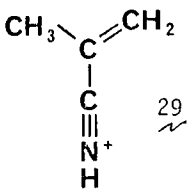

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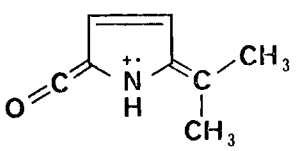

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A molecule containing a *t*-butyl group and a formyl group would be expected to show a comparatively small molecular ion, and indeed in the case of 5-*t*-butylpyrrole-2-carboxaldehyde (11), it is only 4.5% of the base peak. The latter, at M^+-16, (*m/e*

135), arises from rapid loss of the formyl hydrogen and methyl radical, to afford a very stable species 30. Further fragmentations of the base peak are straightforward, by loss of carbon monoxide to *m/e* 107, followed by loss of two one-carbon fragments to the ion, *m/e* 80. It is surprising that the *m/e* 68 species is so abundant (10% of the base peak), since this fragment, thought to be due to a protonated pyrrole species 28, would then arise from *triple* hydrogen radical migration to the ring.

ACKNOWLEDGEMENTS

The author is grateful to Dr. G.F. Smith for his advice and encouragement, and to the Science Research Council for a maintenance grant.

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Received - 9/2/75
Accepted - 9/15/75