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# MASS SPECTRAL FRAGMENTATION OF MONOCYCLIC 2-PYRONES

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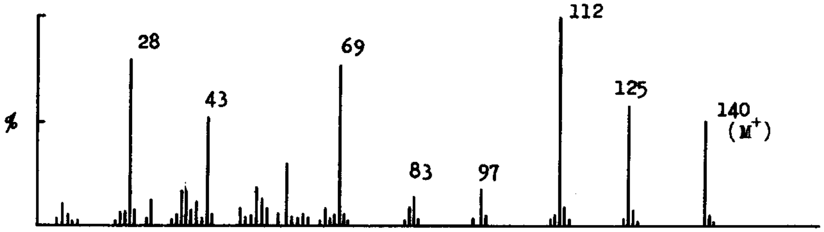
Although the mass spectral fragmentation patterns for a variety of heteroaromatic compounds have been discussed (1,2), little attention was paid to those for monocyclic 2-pyrones. We now wish to report in a preliminary form the behavior of several monocyclic 2-pyrone derivatives upon electron impact.

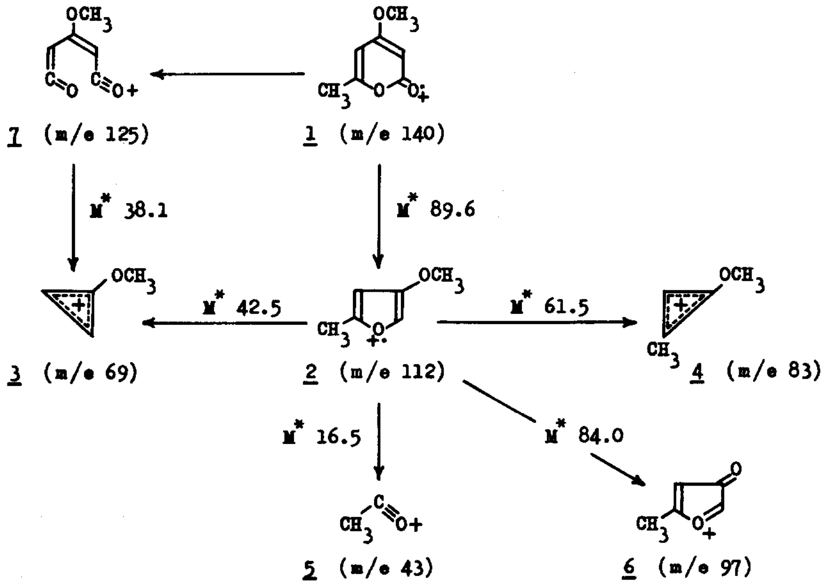
In Scheme 1 is shown the fragmentation pattern of 4-methoxy-6-methyl-2-pyrone as a pertinent example. Most of transformations are confirmed by the existence of appropriate metastable ion peaks, the values of which are indicated in the Scheme.

The primary step of the skeletal change is expulsion of carbon monoxide from the molecular ion 1 (m/e 140) with generation of an electron deficient furan derivative 2 (m/e 112). This important pathway was encountered in all 2-pyrones we have examined. The furan 2 then undergoes rupture between carbon-oxygen bond in two different directions yielding stable cyclopropenyl cations, 3 (m/e 69) and 4 (m/e 83), respectively (3). A similar cleavage would also afford acetyl cation 5 (m/e 43). Other fragmentation of the furan 2 is loss of a methyl radical from a suitably situated methoxyl group to give an ion 6 (m/e 97).

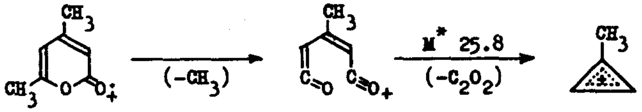
FIG. 1. Mass Spectrum of 4-Methoxy-6-methyl-2-pyrone



SCHEME 1. Fragmentation of 4-Methoxy-6-methyl-2-pyrone

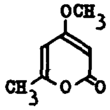
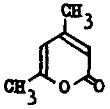
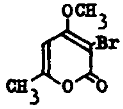
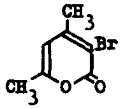
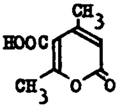
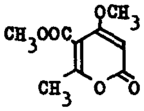
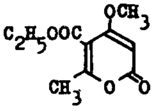
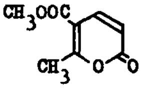
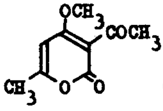
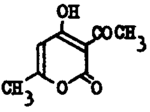
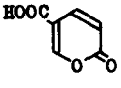
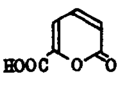
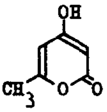
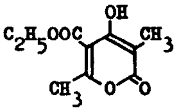
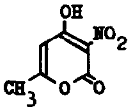


An intense M-15 peak (m/e 125) is attributed to a cation 7. The further loss of 56 mass units ($C_2O_2$) gives rise to an ion of m/e 69, which is assigned as 3. The simultaneous loss of the $C_2O_2$ fragment (probably 2 CO) from 7 is rather unusual but no other combination of peaks accounted for a prominent metastable ion peak at m/e 38.1. One precedent of the similar process has been reported (4). The same type of fragmentation was observed in other 2-pyrones such as 4,6-dimethyl-2-pyrone (9 → 10).



8 (m/e 124) 9 (m/e 109) 10 (m/e 53) ,

We have examined the following 2-pyrones and found that essentially the same fragmentation schemes are applicable. Thus, the characteristic fragmentation pathways of 2-pyrones are the expulsion of carbon monoxide from a given molecular ion affording a furan derivative, followed by the breakdown of this species to a cyclopropenyl cation (or cations). In certain cases, however, some minor modifications and/or some additional fragmentation processes are required in addition to well-defined side-chain fragmentations.

Substitution of bromine at $C_3$ gave a quite revealing result. Because of the natural abundance of bromine isotopes, one can easily identify the fragment ions having bromine atom. This is shown in the spectrum of 3-bromo-4,6-dimethyl-2-pyrone (FIG. 2 and TABLE 1). The fragmentation mode is in accordance with our expectation.

Introduction of a hydroxyl group at $C_4$ does not alter the fragmentation patterns substantially. The only difference is the intervention of successive hydrogen transfer reactions of this hydroxyl hydrogen atom, and these pathways are confirmed by deuterium labeling experiments. Important ions in the spectrum of 4-hydroxy-6-methyl-2-pyrone and its deuteriated isomer are summarized in TABLE 2. For this compound we did not observe any fragment predicted by the retro-Diels-Alder cleavage of the ring. Such a process is pronounced in the fragmentation of hydroxy-coumarin derivatives (5).

FIG. 2. Mass Spectrum of 3-Bromo-4,6-dimethyl-2-pyrone

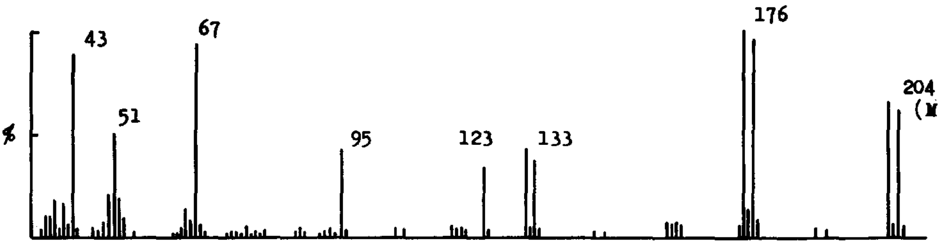
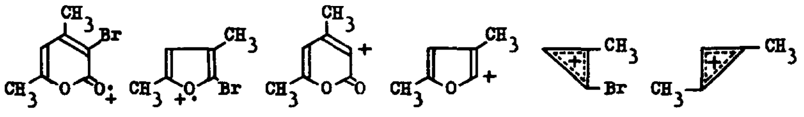
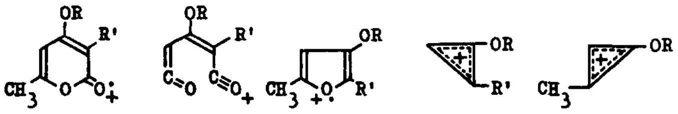


**TABLE 1. Important Fragment Ions of 3-Bromo-4,6-dimethyl-2-pyrone**

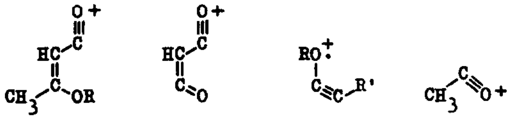


| (m/e) | 204,202 | 176,174 | 123 | 95 | 133,131 | 67 |
|---|---|---|---|---|---|---|

**TABLE 2. Important Fragment Ions of 4-Hydroxy-6-methyl-2-pyrone**

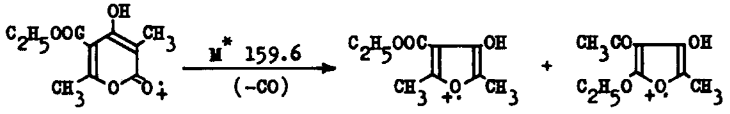


| (m/e) | | | | | | |
|---|---|---|---|---|---|---|
| | R = R'= H | 126 | 111 | 98 | 55 | 69 |
| | R = R'= D | 128 | 113 | 100 | 57 | 70 |



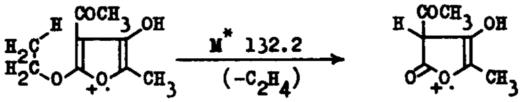
| (m/e) | | | | | |
|---|---|---|---|---|---|
| | R = R'= H | 85 | 69 | 42 | 43 |
| | R = R'= D | 86 | 69 | 44 | 43 |

When a given 2-pyrone has a carbonyl group at $C_5$, this carbonyl group could participate the furan ring formation in an intermediate ion, and the expulsion of carbon monoxide from a molecular ion affords two isomeric furans. An example is shown below.



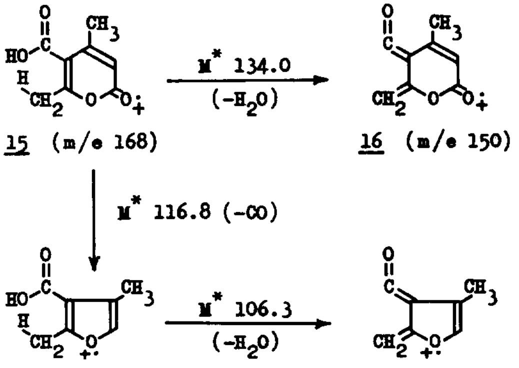
11 (m/e 212) 12 (m/e 184) 13 (m/e 184)

Particularly in this case, subsequent elimination of an ethylene molecule (28 mass units) to give an ion of m/e 156 is explicable only by the isomeric furan 13.



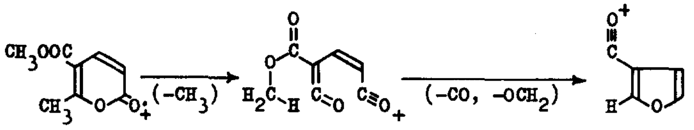
13 (m/e 184) 14 (m/e 156)

In the fragmentation of 2-pyrones having a carboxyl or a carboalkoxyl group at $C_5$ and a methyl group at $C_6$, the following type of fragmentation takes place. This type of cleavage occurs even in the furan stage (17→18).



17 (m/e 140) 18 (m/e 122)

It is of interest to note the behaviour of the M-15 fragment of these 2-pyrones. If the $C_5$-side chain is a carboalkoxyl group, a hydrogen transfer reaction from this ester alkyl group occurs with formal loss of the side chain in this fragment ion (20 → 21).



19 (m/e 168)  20 (m/e 153)  21 (m/e 95)

A more detailed discussion as to the precise mechanisms of each fragmentation reactions will be reported elswhere (6).

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6. The mass spectra of the present work were measured by Hitachi Mass Spectrometer Model RMU-6C, using an all-glass inlet system. The ionizing energy was kept at 80 e.V. and the ionizing current at 80 µA. We gratefully acknowledge the Grant from the Toyo-Rayon Co. Ltd. for purchase of the mass spectrometer.