

## Mass Spectra of some substituted 2-Chloro-pyridones.

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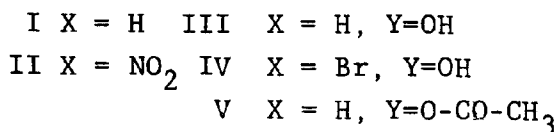
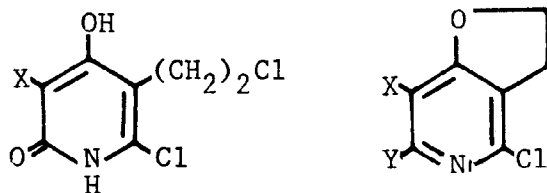
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**Summary:** Mass spectra of 2-chloro-3-(2'-chloroethyl)-4-hydroxy-6-pyridone, 2-chloro-3-(2'-chloroethyl)-5-nitro-4-hydroxy-6-pyridone, 2-chloro-1,6,4',5'-tetrahydro-6-oxo-furano(3',2'-3,4)-pyridine, 2-chloro-1,6,4',5'-tetrahydro-5-bromo-6-oxo-furano(3',2'-3,4) pyridine and 6-acetoxy-2-chloro-4',5'-dihydrofurano(3',2'-3,4) pyridine (I-V) have been studied and their fragmentation patterns have been rationalized. In all these compounds a bicyclic ion has been found to be very stable which loses chlorine (except in compound II) to give a very stable ion of mass 136.

Spiteller and Friedmann<sup>1</sup> have reported that 3-hydroxy and 4-hydroxy pyridines lose CO and HCN but 2-pyridone only loses CO. It has been found<sup>2</sup> that the presence of other groups profoundly modifies the fragmentation of pyridones. Rawi<sup>3</sup> has reported the fragmentation of 4-chloro-2,6-dihydroxy pyridine. Helmut and his coworkers<sup>4</sup> reported that the breakdown of substitution in the pyridine ring is a common feature.

In the present investigation the mass spectra of some 2-chloro pyridones (I to V) have been studied and their fragmentation patterns have been suggested.



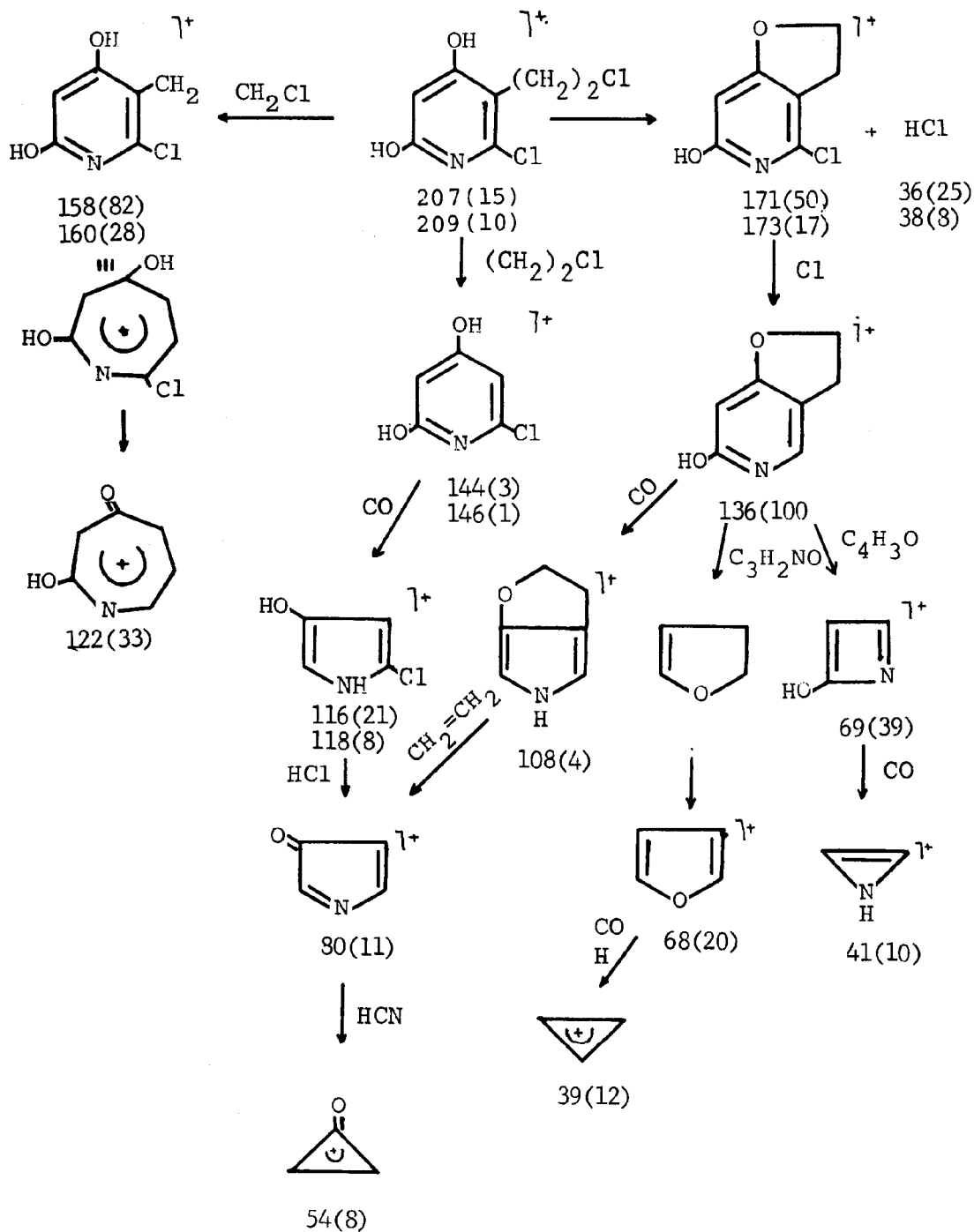
*Mass spectrum of 2-Chloro-3-(2'-chloroethyl)-4-hydroxy-6-pyridone (I)*

The important feature of the fragmentation of this compound is the ready loss of HCl from the molecular ion (207, 15%) to give a strong peak of bicyclic ion (171,50%) and a quite intense peak for HCl (36,25%). This bicyclic ion loses chlorine to give the base peak (136,100%). It is interesting to note that compound (I) even in its chemical reactions has shown a great tendency

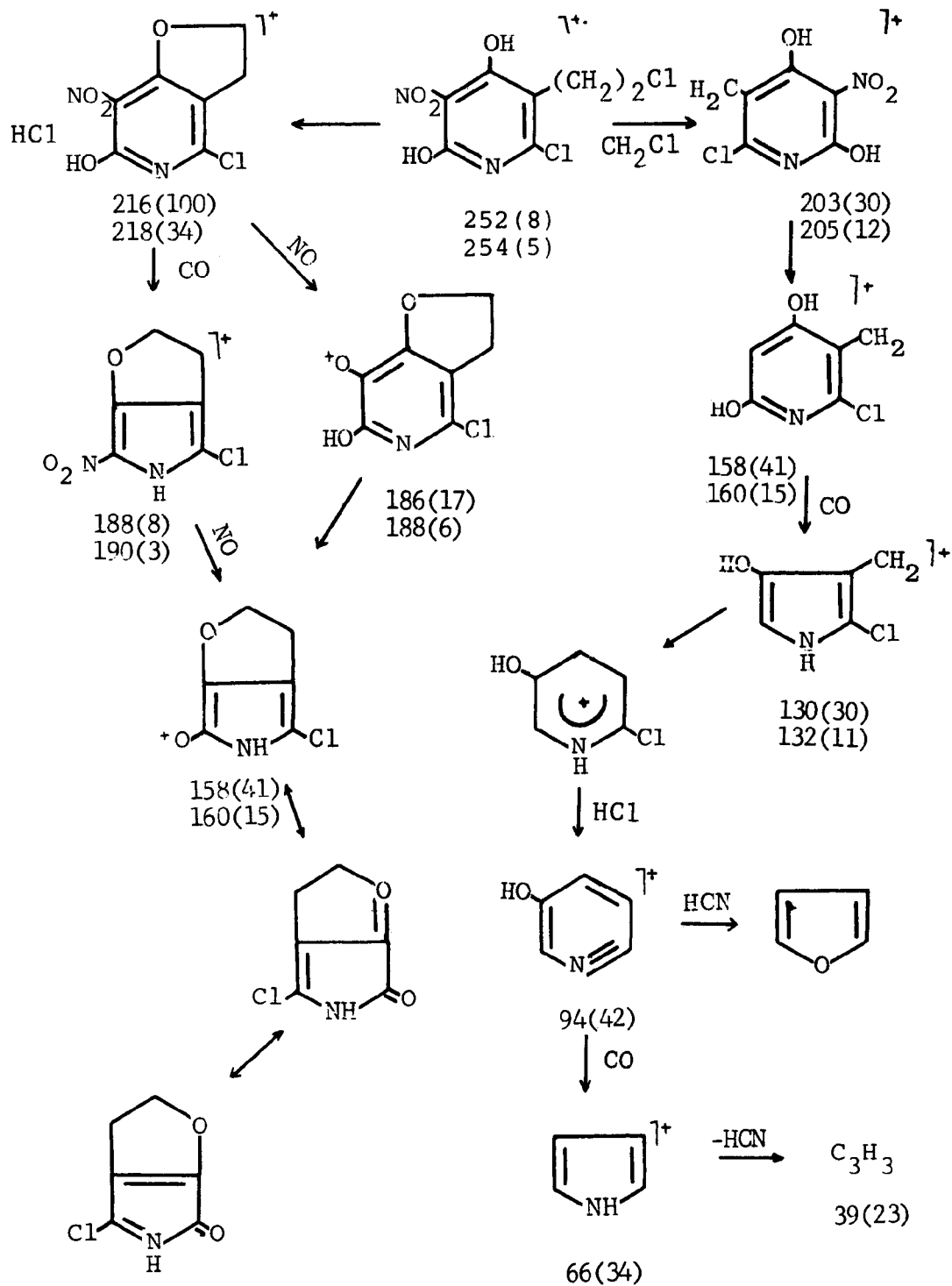
to lose HCl giving bicyclic compound (III<sup>5</sup>). The molecular ion also loses CH<sub>2</sub>Cl to give an intense peak at 158 (82%) leading to azabenzyl ion or azatropylium ion. Thus chlorine attached to alkyl chain is eliminated in the very beginning of fragmentation but aryl chlorine is removed at a later stage. The compound has also been found to lose CO but at quite later stages. Bergman and Dov Diller<sup>6</sup> has also reported that loss of CO in 5-substituted-6-phenyl-2-pyridones did not take place until the substituent at C<sub>5</sub> has been broken off. Loss of HCN has not been noted. The fragmentation pattern of compound I has been rationalized in the scheme No. 1.

*Mass spectrum of 2-chloro-3-(2'-chloroethyl)-5-nitro-4-hydroxy-6-pyridone (II)*

In this molecule also the most characteristic fragmentation involves the loss of HCl from molecular ion (252,8%) producing a bicyclic ion (216,100%) and HCl (36,85%). The other important path of fragmentation involves the loss of CH<sub>2</sub>-Cl due to β cleavage giving an intense peak of azatropylium ion of mass 203 (30%). It looks that this ion at 203 loses nitro group but picks up one hydrogen giving a strong ion of mass 158 (41%). The loss of both NO<sub>2</sub> and NO has been observed. The loss of CO is also an important feature of this spectrum. The remarkable difference between the fragmentation of compound (I) and this compound is that while in the former case both fragments (M-HCl)<sup>+</sup> and (M-CH<sub>2</sub>Cl)<sup>+</sup> lose ring chlorine giving ions free of chlorine but in compound (II) ring chlorine is retained upto the last stages of fragmentation. There is a prominent peak at mass 30 (17%) which is the characteristic peak of the



Scheme I



Scheme II

nitro compounds.

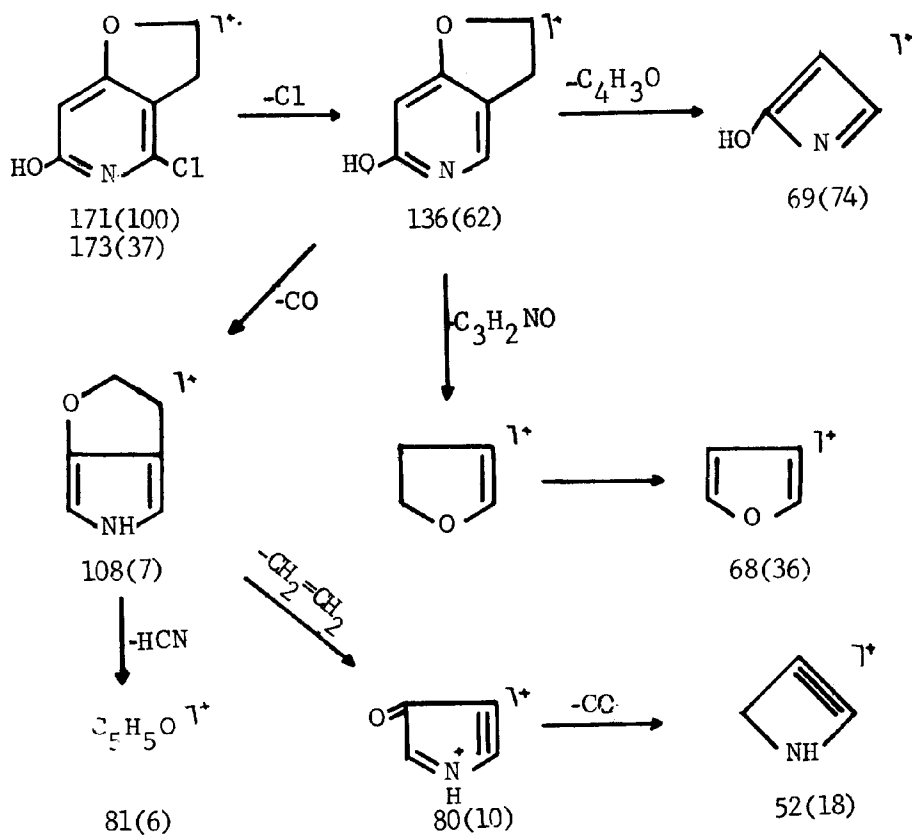
The following scheme (No.2.) is suggested for the important fragmentation of compound (II).

*Mass spectrum of 2-chloro-1,6,4',5'-tetrahydro-6-oxo-furano (3',2'-3,4)-pyridine (III):*

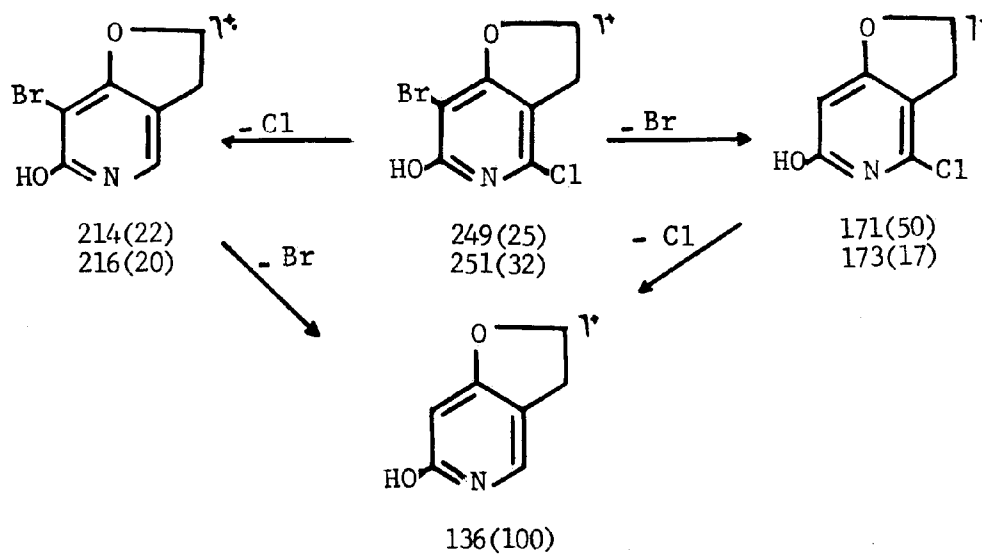
The molecular ion is the base peak (171). It is interesting to note that in the mass spectrum of compound (I) the molecular ion after losing HCl gives this peak (171, 50%) of high intensity. After losing HCl, compound (II) also gives the same type of bicyclic ion representing the base peak. Further breakdown of the molecular ion shows a great resemblance to the breakdown of (M-HCl)<sup>+</sup> ion of compound (I). Fragmentation of compound (III) has been rationalized in scheme No. 3.

*Mass spectrum of 2-chloro-1,6,4',5'-tetrahydro-5-bromo-6-oxo-furano (3',2'-3,4) pyridine (IV):*

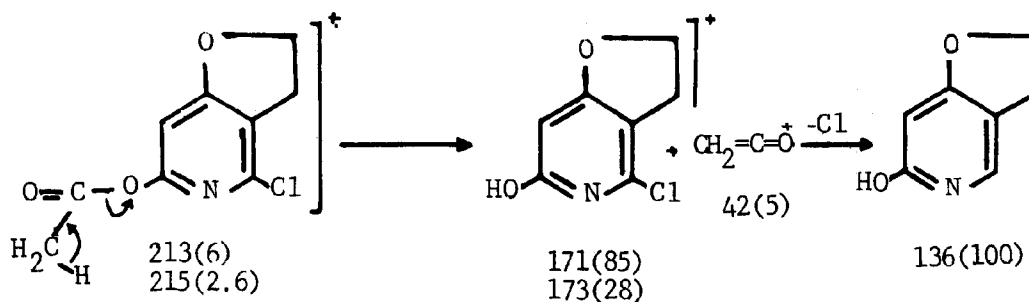
The characteristic fragmentation of the parent ion (249, 25%) is the loss of chlorine leading to an ion of mass 214 (22%), 216 (22%) and then the loss of bromine with picking one hydrogen to give the most intense peak at 136 (100%). The parent ion also loses bromine with picking one hydrogen to give a very intense peak at 171 (50%). This (M-Br)<sup>+</sup> ion can also lose chlorine to give the base peak at 136. The fragmentation pattern of the bicyclic ion of mass 136 is quite similar to the fragmentation pattern of the same ion in the compounds (I) and (III). The important fragmentation features of this compound have been shown in the following scheme No. 4.



Scheme III.



Scheme IV



Scheme V

*Mass spectrum of 6-Acetoxy-2-chloro-4'5'-dihydro furano (3',2'-3,4) pyridine (V)*

The parent peak is very weak (213, 6%). The parent ion loses ketene ( $\text{H}_2\text{C}=\text{C}=\text{O}$ ) through the rearrangement to give very intense peaks at 171 and 173 (85% and 28% respectively). This ion loses chlorine to give the base peak at 136 (100%). The mass spectrum of this compound is relatively simple. There are peaks at 68, 69, 52 like in the mass spectra of compounds, I, III, and IV but relatively of low intensities. There is an intense peak at 43 (38%), most probably, due to acetyl ion ( $\text{H}_3\text{C}-\text{CO}$ )<sup>+</sup>.

In all the compounds studied in this investigation the bicyclic ion has been found to be highly stable. This

stable ion loses chlorine (except in compound II) to give a very stable ion of mass 136 and in most of the cases it is the base peak. Except in compound (II) in the other four compounds the stable ion of mass 136 shows a good resemblance in its further fragmentation.

#### Acknowledgement

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