

Mass Spectra of some Pyrano-1,3-oxazines (Part-I)

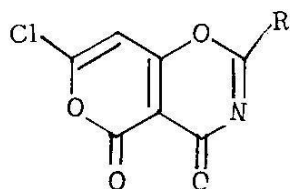
N.A.ZAIDI*, J.M.AL-KATTI AND F.H.SAEED

*Chemistry Department, Faculty of Science,
Post Box 9480, Benghazi, Libya.

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Summary: Under electron impact the fragmentation of 7-chloro-4,5-dioxo-2-cyclohexyl-4H,5H-pyrano[3,4-e] [1,3] oxazine (I), 7-chloro-4,5-dioxo-2-(1'-Phenyl cyclopentyl)-4H,5H-pyrano [3,4-e] [1,3]oxazine (II) and 7-chloro-4,5-dioxo-2-t.butyl-4H, 5H-pyrano[3,4-e] [1,3] oxazine(III) has been studied. The most prominent fission in these three compounds involves the breaking of bond α to the oxazine ring giving abundant ions of substituent at C_2 and a bicyclic pyrano oxazine m/e 198. In compounds II and III the ions from substituent at C_2 make the base peaks of the spectra. The ion of mass 198 loses CO_2 in all these compounds. Fragmentation similar to retro Diels-Alder reaction has also been observed of variable importance in these compounds. The higher mass regions in the spectra of compounds II and III have smaller peaks due to facile fragmentation of side chains. Chlorine is retained till last stages of fragmentation.

Formation of a new bicyclic system of pyrano-1,3-oxazines have been reported from the reactions of malonyl dichloride and some nitriles[1,2,3]. Though mass spectrometry of pyrones and of 1,2-oxazine derivatives have been reported [4] but mass spectrometric studies of these new bicyclic pyrano-1,3-oxazines is not available in the chemical literature. In the present work electron impact induced fragmentation of 7-chloro-4,5-dioxo-2-cyclohexyl-4H, 5H-pyrano [3,4-e] [1,3] oxazine (I), 7-chloro-4,5-dioxo-2-(1'phenyl cyclopentyl)4H,5H-pyrano [3,4-e] [1,3] oxazine (II) and 7-chloro-4,5-dioxo-2-t.butyl-4H, 5H-pyrano[3,4-e] [1,3] oxazine (III) is reported.



Mass spectrum of 7-Chloro-4,5-dioxo-2-cyclohexyl-4H,5H-pyrano [3,4-e] [1,3] oxazine [I].

The spectrum shows relatively a larger number of intense peaks. The molecular ion (281,17%) undergoes fragmentation by different pathways. The most prominent fragmentation of molecular ion involves the breaking of cyclohexyl substituent. The charge may be retained on either fragment giving bicyclic ion (198, 63%) and cyclohexyl ion (83, 40%). The bicycle ion of mass 198 loses CO_2 to give an ion of mass 154 (24%) which subsequently loses Cl and CN to produce an intense peak at m/e 93 (68%). Molecular ion also seems to lose C_5H_8 radical which may be cyclopentene, giving a very stable bicyclic ion of mass 213 (91%). This bicyclic ion may lose CO to give an ion at m/e 185 (15%). Alternatively the bicyclic ion m/e 213 may be rearranged to 2-methyl-pyrano-oxazine which loses $[CH_3CN]$ (41,100%) to produce a ketene of mass 172 (38%). This ketene m/e 172 may also be produced by the fragmentation of molecular ion involving

cleavage similar to retro Diels-Alder reaction yielding ketene and cyclohexyl cyanide ion m/e 109 (27%). This type of cleavage has been shown in 4-pyrones [5] and also in flavones by Barnes and Occolowitz[6]. There is a quite intense peak also at m/e 226 (34%) which may be due to loss of $[C_4H_7]$ from molecular ion. The fragmentation of cyclohexyl ion follows the usual pattern of fragmentation of cycloalkanes. Presence of many intense peaks at lower mass region of the spectrum is due to fragmentation of cyclohexyl ion. Fragmentation of compound (I) is rationalized in scheme No.1

Mass Spectrum of 7-Chloro-4,5-dioxo-2-(1'phenylcyclopentyl)-4H,5H-pyrano [3,4-e][1,3] oxazine (II)

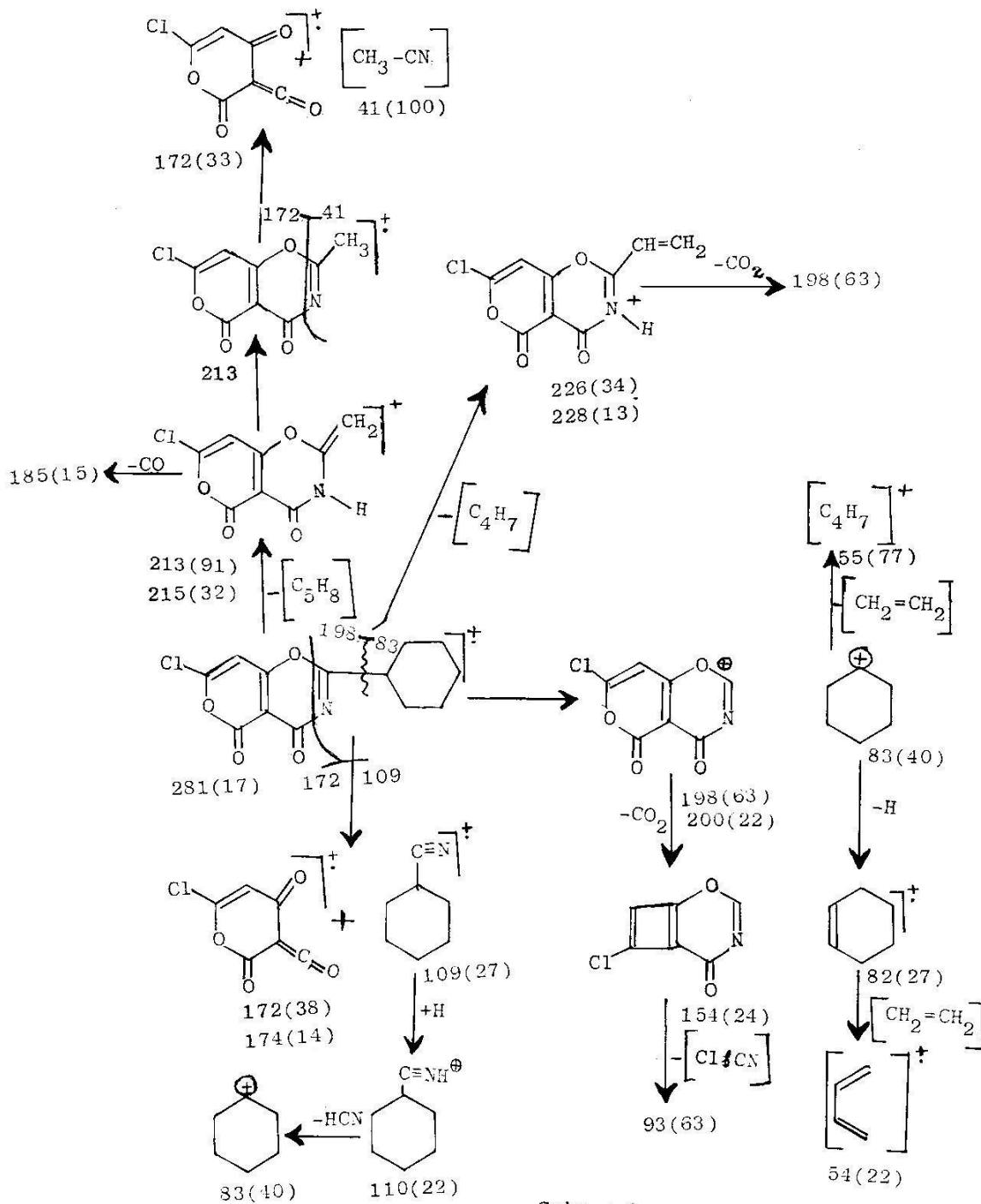
Molecular ion (343,18%) showed two main alternate patterns of fragmentation. The most important fragmentation of molecular ion involves the breaking of substituent at C_2 giving phenyl cyclopentyl ion (145,100%) and a bicyclic pyrano-oxazine ion (198,18%). The other less important fragmentation of molecular ion is similar to retro Diels-Alder reaction yielding 1-cyano-1-phenyl cyclopentane (171,4.6%) and a ketene fragment. The charge seems to be preferentially retained by cyanide fragment. The ion of mass 145 shows the usual fragmentation of an alkyl substituted benzene ion giving quite intense peaks in the mass spectrum. The bicyclic ion at m/e 198 loses CO_2 producing ion of mass (154,5%). The loss of CO_2 from bicyclic ion of mass 198 can occur either from oxazine ring through rearrangement involving migration of oxygen or from pyran ring. Important features of fragmentation of compound II are shown in Scheme 2.

Mass Spectrum of 7-Chloro-4,5-dioxo-2-t.butyl-4H,5H-pyranol[3,4-e][1,3] oxazine (III).

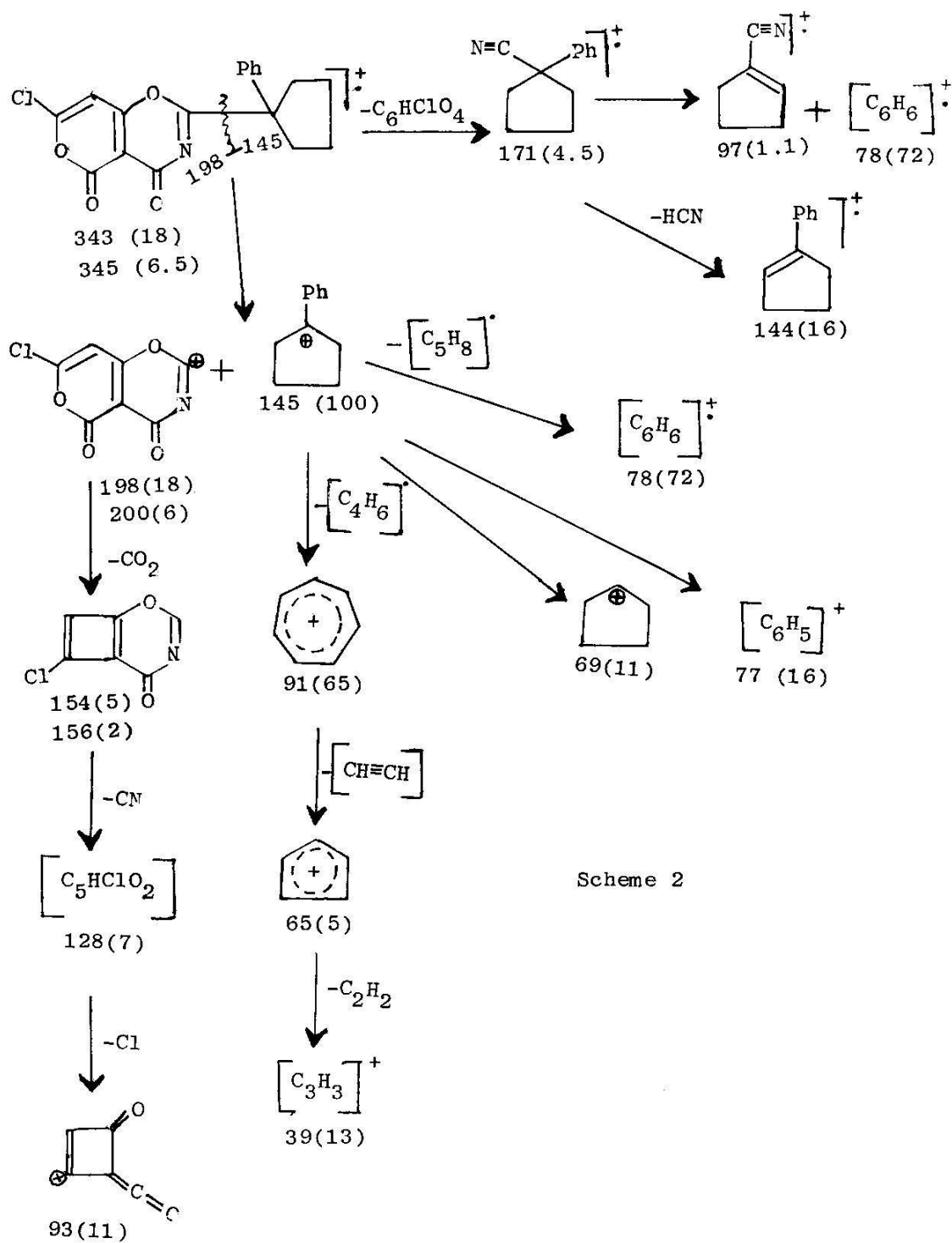
This oxazine gives a very weak

molecular ion (225, 0.8%). The main fragmentation of molecular ion involves the breakage of side chain giving base peak at m/e 57 (100%) and a quite weak ion (198,4.3%). Base peak represents the well known very stable tertiary butyl carbonium ion m/e 57. Fragmentation of side chain is so facile that in the higher mass region only very few and very small peaks occur. In the whole spectrum the fragmentation of tertiary carbonium ion is dominant. The ion m/e 198 loses CO_2 to give an ion m/e 154(3) which subsequently loses CO giving an ion of mass 126 (4.5). There is relatively quite intense peak at m/e 84 which may be due to tertiary butyl cyanide + H because aliphatic nitriles have a substantial tendency to pick up one hydrogen [7]. There is an intense peak at m/e 43 (42%) which is most probably due to $C_3H_7^+$. In branched alkanes there is high probability of such rearrangements[8]. It seems possible that the side chain rearranges and then yields $C_3H_7^+$. Fragmentation pattern of this compound (III) is shown in scheme No.3.

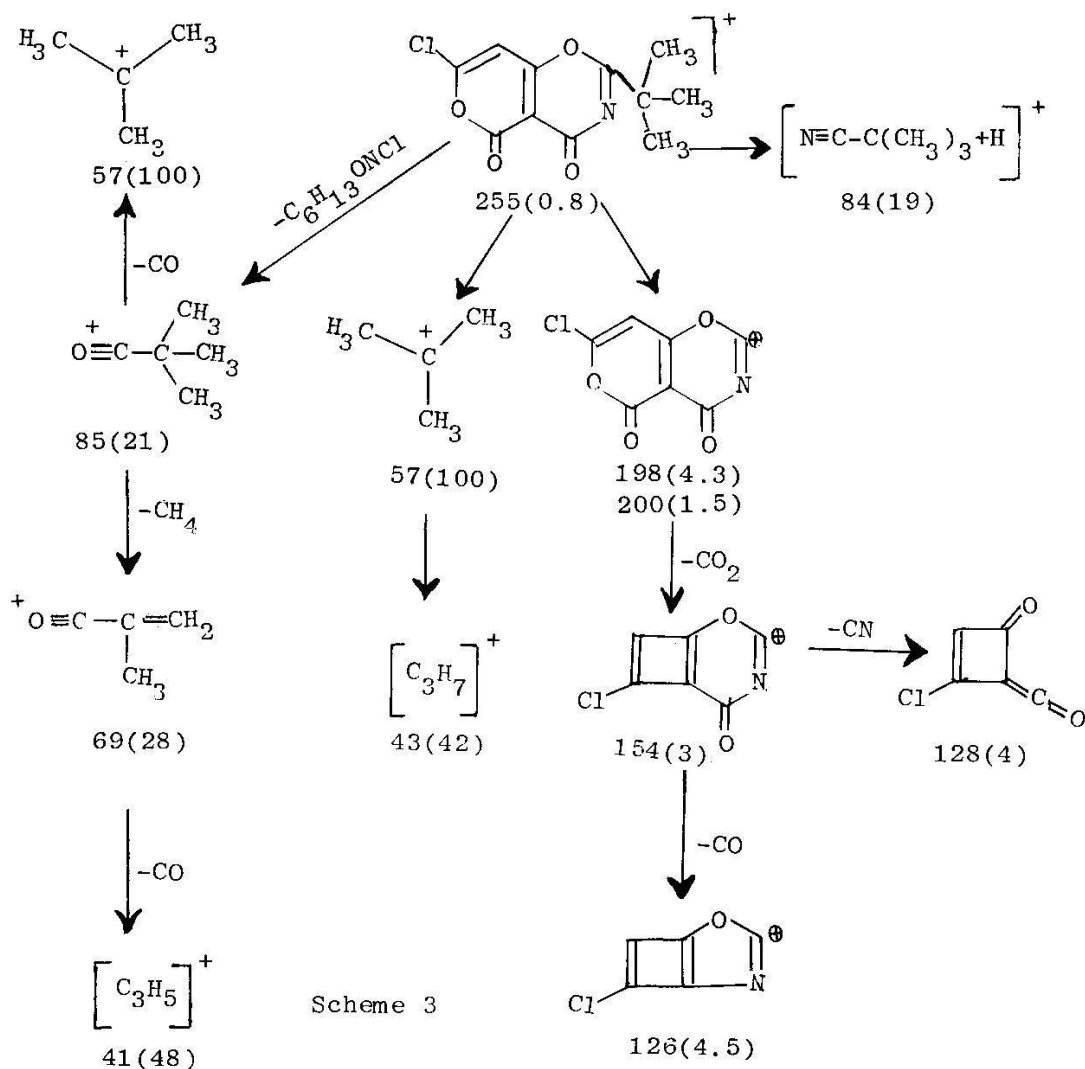
In all the three pyrano-oxazines studied the most important fragmentation involves α -cleavage of substituent at C_2 . The positive charge can be retained by either fragment. The relative intensities of the ions of substituents show the order of their relative stabilities. In compound (I) it is a secondary carbonium ion (63%) while in compound (II) and (III) these are tertiary carbonium ions and make base peaks of the spectra. The loss of CO_2 or CO from molecular ion has not been observed. Loss of chlorine is observed only at late stages. Fragmentation similar to retro Diels-Alder reaction is quite prominent in compound (I) but it is of relatively minor importance in compounds (II) and (III). In compounds (II) and (III) the higher mass regions have smaller peaks and fragmentation of side groups dominates the spectra.



Scheme 1



Scheme 2



Acknowledgement

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