

MASS SPECTROMETRY OF THREE ISOMERIC HYDROXYPHENYLPYRIDINIUM CHLORIDES

Hamdi M.R. El-Mouafi

*Organic Chemistry Department, Faculty of Pharmacy,
Cairo University, Egypt.*

ABSTRACT:

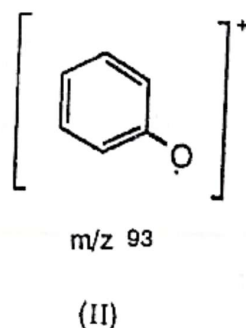
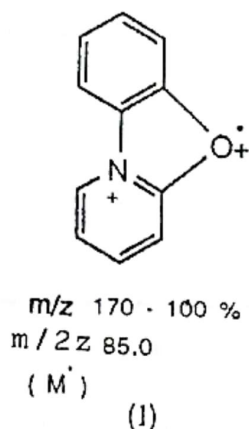
2-,3- and 4-Hydroxyphenylpyridinium chlorides were prepared for comparing their behaviour under electron-impact. No molecular ion peaks were observed in their spectra and all exercised loss of hydrogen chloride at different rates. The peaks at m/z 171 and m/z 172 were highly abundant in the structure of 2- rather than in the 3- and 4-isomers.

INTRODUCTION AND DISCUSSION

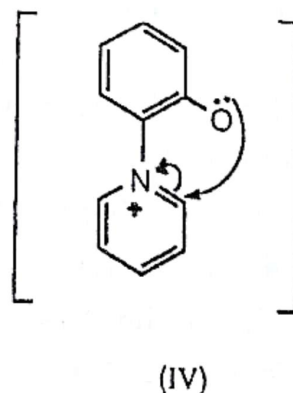
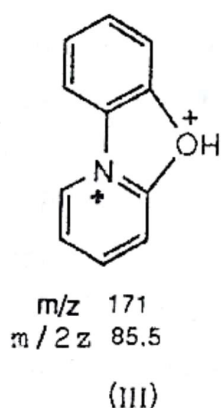
The study of the behaviour of 2-,3- and 4-hydroxyphenylpyridinium chlorides under electron-impact necessitated the preparation of such compounds in fairly pure state. They were prepared by the reaction of 2,4-dinitrophenylpyridinium chloride with 2-,3- and 4-aminophenols, respectively in the presence of pyridine⁽¹⁾.

2,4-Dinitrophenylpyridinium chloride was prepared from pyridine and 2,4-dinitrochlorobenzene⁽²⁾. The structure of the three isomers was confirmed by combustion analysis, N.M.R. and mass spectrometry. The behaviour of the three isomers under electron-impact revealed that they all lost hydrogen chloride at different rates. The ion at m/z 36 represented the base peak of the spectrum of the 3-isomer, 37.4% of the base peak of the 2-isomer, while in the 4-isomer it was only 4.1% of the base peak of the spectrum. No parent ion peaks at m/z 207 were noticed in the three spectra.

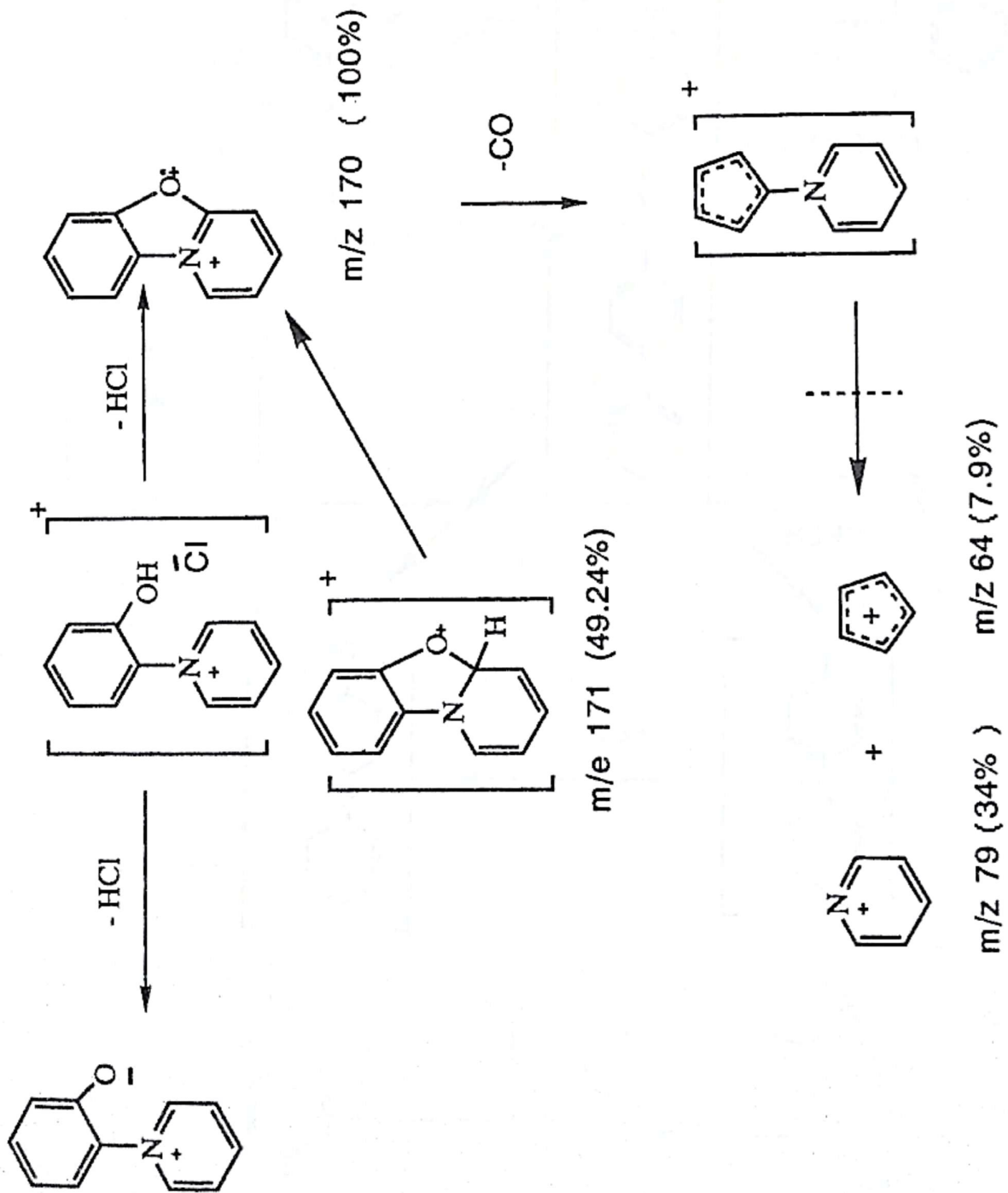
The base peak of the spectrum of the 2-isomer was at m/z 170 (100%). This might be originated by the loss of a hydrogen from the ion at m/z 171 (M-36), forming the stable cyclic ion (I)⁽³⁾. The absence of the peak at m/z 93, present in the other two spectra due to simple fission of the parent molecular ion to give fragment (II), is in favour of our suggestion.



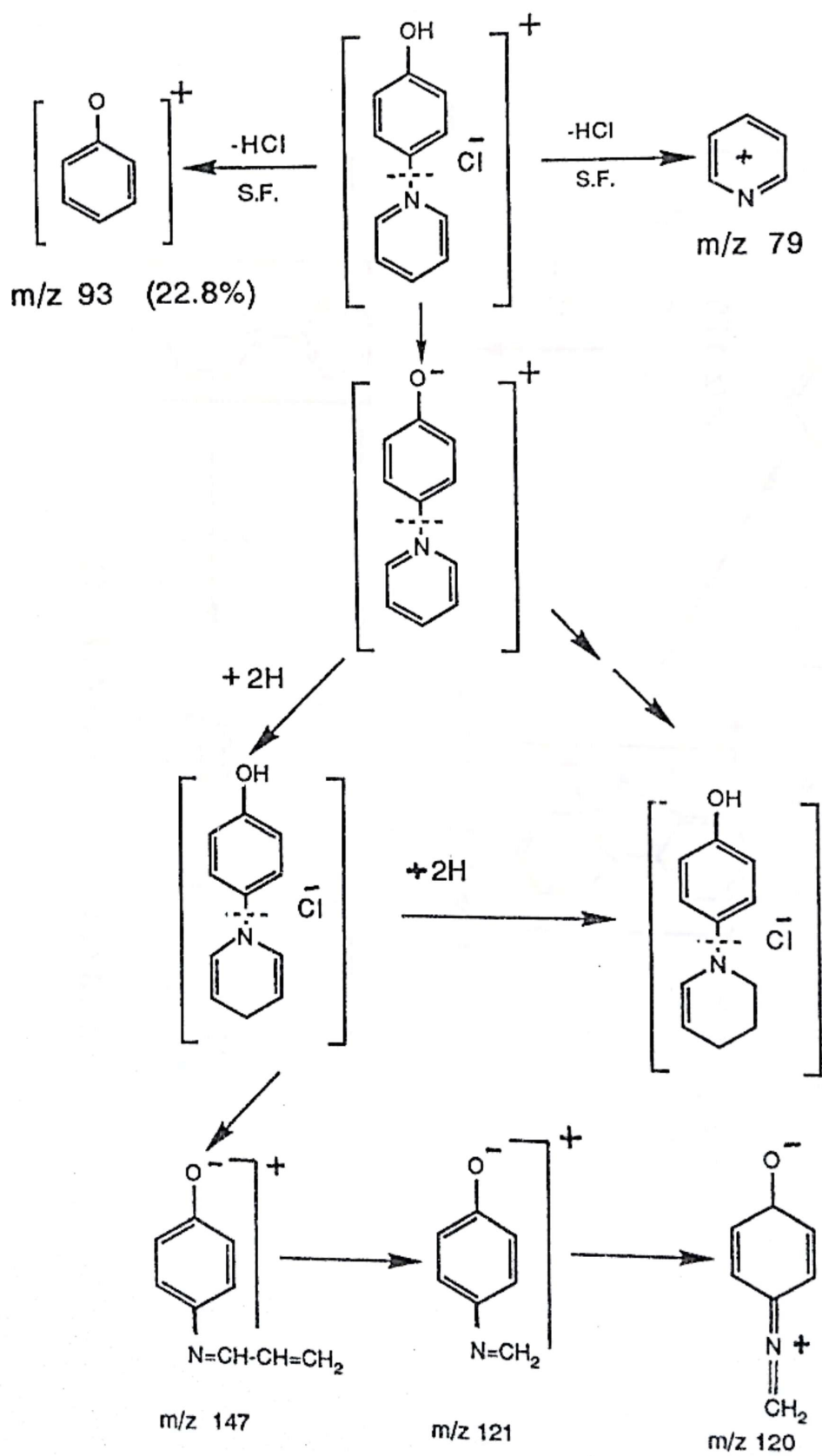
The appearance of ions at $m/2z$ 85.5 and at $m/2z$ 85 confirms our suggestion, as they might be originating from the doubly charged ions (I) and (III). Furthermore, the absence of ions at m/z 145 and m/z 147, which are all reduction products of the corresponding original ions, is another proof of ring formation leading to the stable oxazolo-structure (I). Ring formation is possible due to spatial proximity in addition to the extremely low electron density at position 2- of the pyridinium structure (IV).



The fragmentation of the ion originating from 2-hydroxyphenyl pyridinium chloride is suggested to be shown in scheme (A).

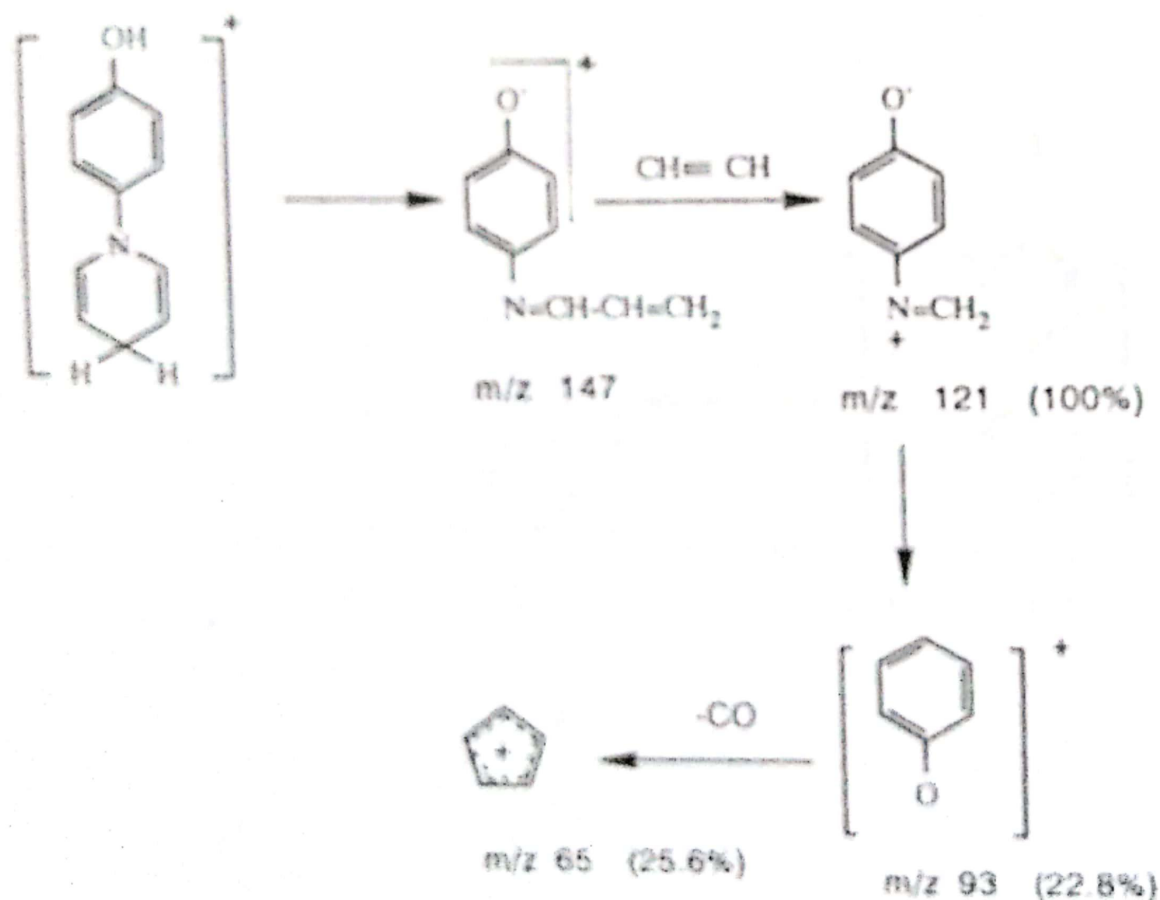


Scheme (A)

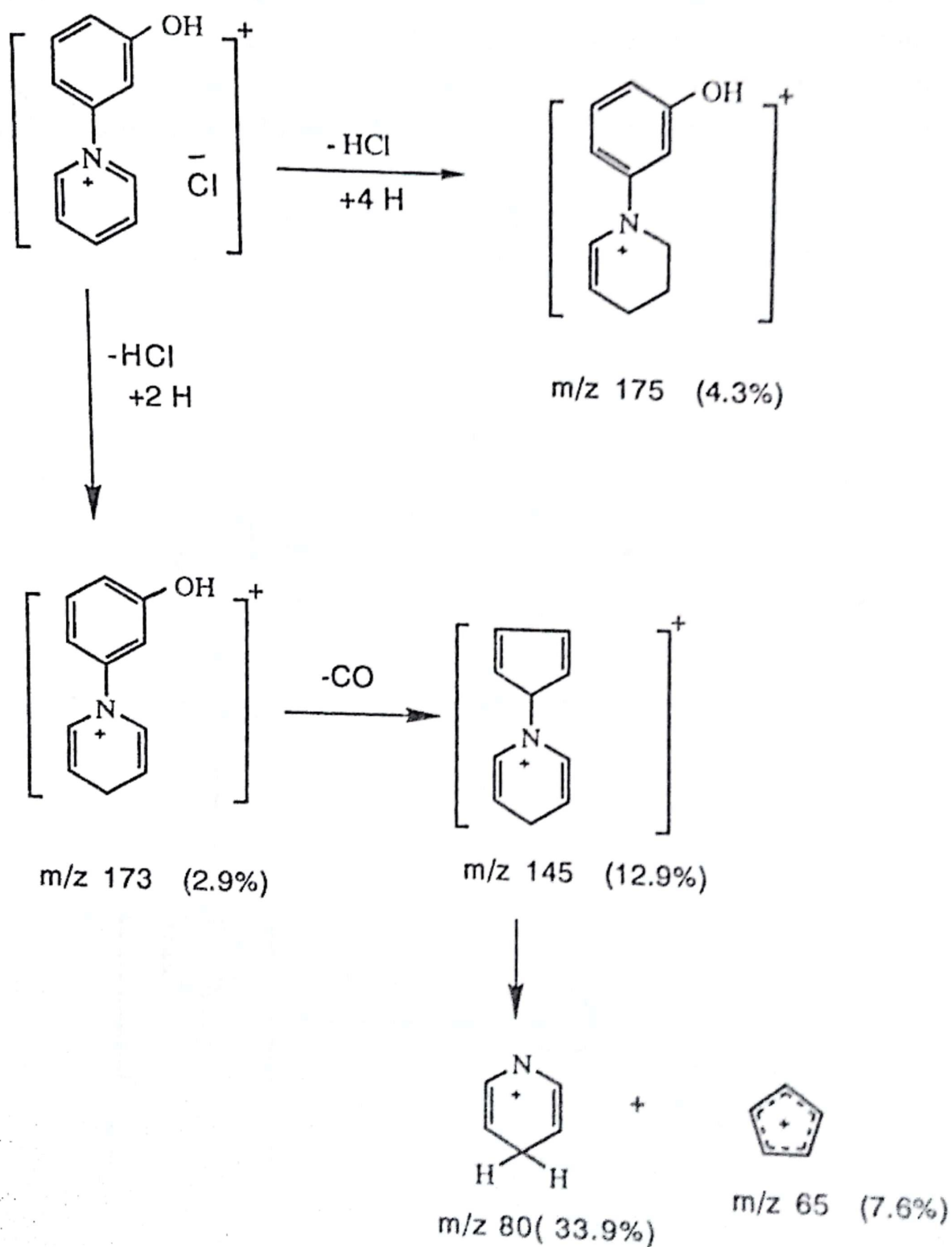


Scheme (B)

The 4-isomer, on the other hand, shows no peak at m/z 171 due to loss of hydrogen chloride elements. Instead an $M + 1$ peak at m/z 172 of low intensity (3.5%) is noticed. Peaks at m/z 173 (1.3%) and m/z 175 (56%) appear in the spectrum, the last one represents the tetrahydro ion produced by hydrogenation of the M-36 peak of our compound. The high abundance observed reflects the stability of the tetra- more than the dihydro-ion. The base peak of the spectrum is at m/z 121, which may be produced by fragmentation of the tetrahydro ion as in scheme (B) or the dihydro-ion as in scheme (C).



Scheme (C)



Scheme (D)

The 3-isomer, shows a very rapid loss of hydrogen chloride element, appears as a base peak of the spectrum at m/z 36. No peak is noticed at m/e 171. That gives an indication of the easy hydrogenation to the di-,tri-, and tetrahydro derivatives, m/z 173 as (2.9%), m/z 174 (33%) and m/z 175 (4.3%) respectively. The dihydro-ion (m/z 173), losses CO to give an ion at m/z 145 (12.9%) of the base peak⁽⁴⁾ (scheme D).

On the contrary in the case of the 4-isomer, the peak at m/z 93 is totally absent, this indicates that simple fission leading to this ion does take place at any rate. Simple fission of the benzene-pyridine bond takes place only after elimination of CO from the ion at m/z 173 to give the ion m/z 80 (33.95%) and m/z 65 (7.6%) of the base peak. Peaks at m/z 81 (1%) and m/z 82 (4.4%), are noticed due to simple fission of reduced products as in scheme D.

Trials to reduce 4-hydroxyphenyl pyridinium chloride in order to investigate the behaviour of the resulting products in a genuine sample were done. Unfortunately, the reduction could not be controlled to the steps of the di- or tetrahydro-derivatives but mixtures of di-,tetra- and hexahydro-derivatives were always obtained. Although sodium borohydride, sodium dithionite and sodium amalgam, were used as reducing agents under different conditions and in different alkaline media, all trials were unsuccessful.

EXPERIMENTAL

Melting points were uncorrected and mass spectra were carried out using an AEL-MS 902 apparatus with an AET data system. Micronalyses were carried out at Alfred Bernhardt Microanalytical Laboratorie, W. Germany.

General Methods of Preparation:

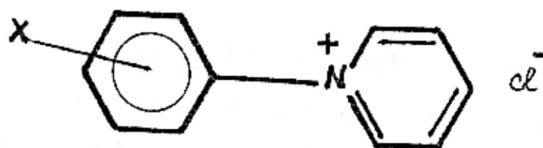
Hydroxyphenyl pyridinium chloride (I):

2,4-Dinitrophenylpyridinium chloride (0.015 mol, 3 g), and 2,3-or-4-aminophenol (0.02 mol, 2.2 g), in dry pyridine (20 ml) were heated for 1-2

hours at 100°C. Acetone was added (in excess) to the reaction mixture after cooling. The formed solid was separated and washed with dry acetone several times, then dried and recrystallized from appropriate solvent after treatment with charcoal (Table 1):

No.	X	M.P.°C.	Solvent	Analysis		
				%C	%H	%N
1-	4-OH	215-216	Methanol	*C 63.76	4.83	6.75
2-	2-OH	212-214	Ethanol			
3-	3-OH	> 300	Ethanol/Benzene	*C 63.76	4.83	6.75
			Ethanol/Pet.ether	*F 63.74	5.15	6.67

*C: Calculated, *F: Found.



4-Hydroxy derivative:

Phenyl protons; at δ 7.81, δ 7.65, δ 7.49 and δ 7.33.

Pyridyl protons; δ 8.85-9.18 (α -pyridyl protons), multiplet centered at 8.5-8.7 (α -pyridyl protons) and doublet at δ 8.53 δ 8.3 (β -pyridyl protons).

Hydroxyl proton; singlet at δ 8.1.

2-Hydroxy derivative:

Phenyl protons; multiplet at δ 7.83-7.17, pyridyl protons; two multiplets at δ 9.12- 8.6 and δ 8.53 - 8.12. Hydroxyl protons; singlet at δ 8.3.

3-Hydroxy derivative:

Phenyl protons; multiplet at δ 7.75 - 7.17.

Phenyl protons; multiplet at δ 9.16 - 8.38.

Hydroxyl proton; singlet at δ 8.1

REFERENCES

- 1- N.E. Grigor'eva and M.D. Yavlinskii (Kharkov-State University) Ukrain khim zuhr, 18, 82-8, (1952); C.A. 48, 11411 a (1954).
- 2- Fischer and Hammer; J. Chem. Soc., 189 (1939).
- 3- M.E. Rose and R.A.W. Johnstone, Mass Spectrometry for Chemists and Biochemists; Cambridge University Press, 1982, 10-7, p. 231.
- 4- M.E. Rose and R.A.W. Johnstone, Ibid; 1982, 10-8, p. 239.

دراسة طيف الكتلة للثلاث نظائر هيدروكسي فنيل بيريدينيوم كلورايد

حمدي المتولي رجب الموافي

قسم الكيمياء العضوية - كلية الصيدلة - جامعة القاهرة

تم تحضير كلوريدات ٢-، ٣-، و ٤- هيدروكسي بيريدينيوم لدراسة خواصها تحت التأثير الالكتروني وذلك عن طريق دراسة طيف الكتلة لهذه المواد . لم يلاحظ وجود الأيون الجزيئي في التحليل الطيفي وقد فقد كلوريد الهيدروجين من هذه المركبات بمعدلات مختلفه . ووجد أن الكتلة عند ١٧١ و ١٧٢ كان مكثف كثافة عاليه في حالة المركب النظير - ٢ على عكس المركبات المتناظرة - ٣ ، ٤ .