COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

TOME : 29 ANNÉE : 1983

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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Mass Spectra Of Mercurated Products Of Mono And Diquinolinyl Phosphates

By

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(Received April 21 1983, and accepted June, 9 1983)

SUMMARY

The behaviour of some mercurated products of mono and diquinolinyl phosphates under electron impact were studied. Fragmentation took place via α and β cleavage. The proposed structures were confirmed. As previously reported all spectra have the oxine ion at m/e 145 instead of oxinate ion m/e 144.

INTRODUCTION

The behaviour of organophosphorus compounds under electron impact has been extensively investigated, this is clearly reflected in the recent review published by Granoth in this field(1). The early study on the fragmentation of dialkylmercurials reported by Dibeler and Mohler(2). Most of the work on organomercury compounds dealt with ionisation potentials and appearence potentials of simple fragments formed by carbon-mercury bond cleavage(3). The mass spectra of some aromatic and aliphatic mercury compounds has been reported(4,5).

The present work was directed to study mass spectra of some mercurated compounds formed by mercuration of mono and diquinolinyl phosphate in order to report the behaviour of these compounds under electron impact.

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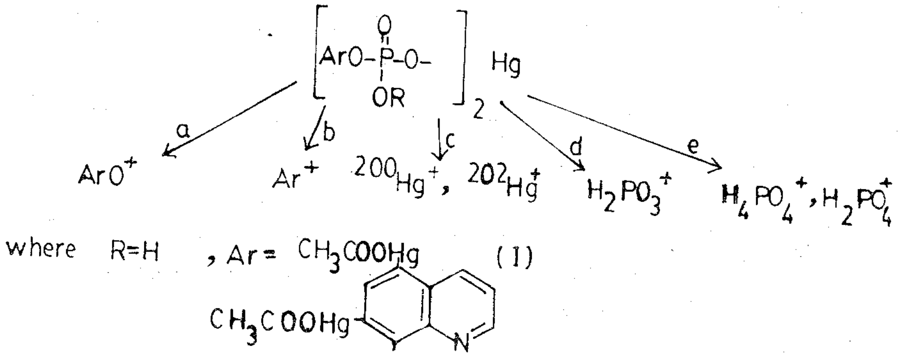
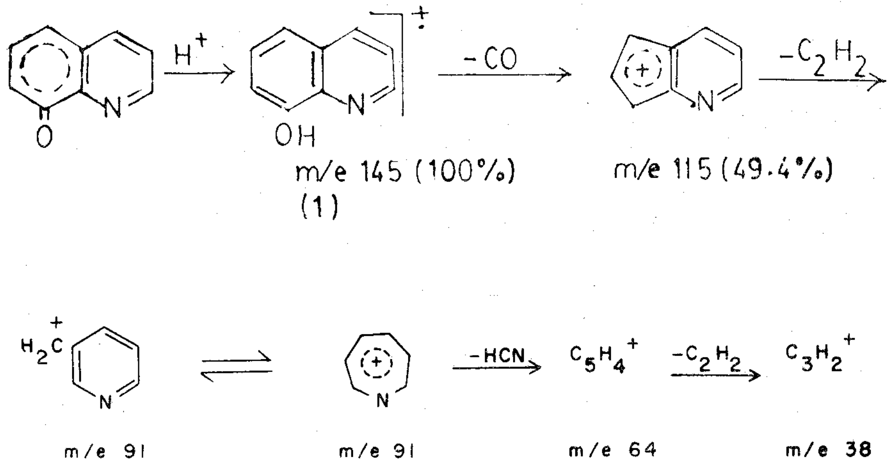
RESULTS AND DISCUSSION

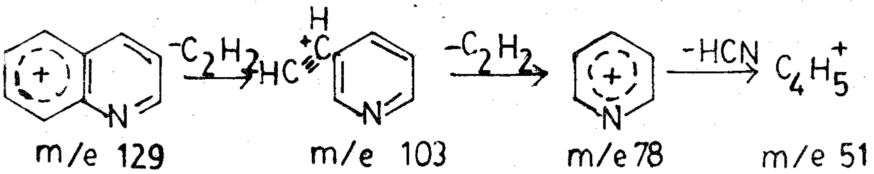
The general fragmentation of the mercuri bis (5,7-acetoxy-mercuri-quinolinyl) phosphate (I) can be described as follows:



The fragmentation according to (a) is due to α- cleavage with respect to $>$P = O and cleavage of C-Hg bonds to give CH_3COOHg^+ m/e 260 (1 %) (The low % may be attributed to further fragmentation) and give (1) by a gain of proton which fragmented as follows:

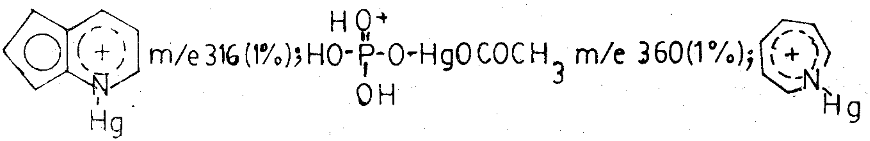


The fragmentation obtained due to β-cleavage is (2) and fragmented as follows:



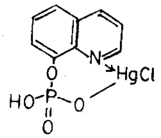
The low intensity can be attributed to further fragmentation. The intense peak at m/e 202 (43.3 %), m/e 200 (31.9 %), m/e 272 (35.05 %) m/e 45 (33 %), m/e 43 (30.9 %), m/e 60 (21.6 %), m/e 64 (16.49 %) and m/e 39 (11.3 %) were attributed to $^{202}Hg^+$, $^{200}Hg^+$, $HC \equiv C - Hg - \overset{HO^{+}}{\overset{\|}{C}} - CH_3$, $CH_3C \equiv O^+ . H_2$, $CH_3C \equiv O^+$, $AcOH^+$, $C_5H_4^+$, HC_2N^+ respectively.

It is clear that $^{200}Hg^+$ and $^{202}Hg^+$ ions enter in the formation of other molecular ions, such as $HC \equiv C - Hg - \overset{O_{+}}{\overset{|||}{C}} - CH_3$ m/e 272 (35.05 %)



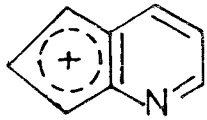
m/e 292 (1 %); $C_4H_3Hg^+$ m/e 251 (1 %); $HO-P-\overset{OH}{\overset{|}{O}}-Hg^+$ m/e 281 (1%). The spectrum shows also small peaks at m/e 81 (1 %) and m/e 99 (8.2 %) derived from fragmentation from the directions d and e due to α-, β- cleavage and β, β-cleavage and gain of protons with the formation of $H_2PO_3^+$ and $H_4PO_4^+$. The small peaks at m/e 41 (1 %) and m/e 40, attributed to CH_3CN^+ and $H_2C_2N^+$.

For compound (II), fragmentation took place via the same



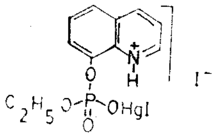
(II)

routes as compound (I). The base peak at m/e 145 (100 %) attributed to oxine ion and not the oxinate ion(6).

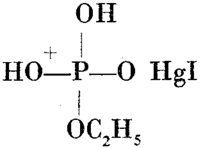
The intense peaks at m/e 177 (60.8 %), m/e 36 (45.3 %), m/e 63 (15.4 %), m/e 91 (19.51 %), 272 (15.4 %) attributed to  H Cl+, $C_5H_3^+$,  and $H.Hg^+Cl_2$.

The small peaks at m/e 235 (1 %), m/e 72 (1 %), m/e 78 (1 %) and m/e 51 (1 %) can be attributed to $HgCl^+$, HCl_2^+,  , $C_4H_3^+$.

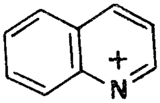
Mass spectrum of compound (III) follows the general fragmentation.



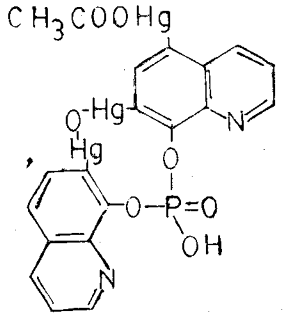
(III)

The small peaks at m/e 200 and m/e 202 attributied to $^{200}Hg^+$, $^{202}Hg^+$ indicate that fragmentation took place with the liberation of mercury as metal and not as ions, also $^{200}Hg^+$ and $^{202}Hg^+$ ions entered in the formation of other molecular ions, e.g. H_2HgI^+ m/e 329, 

$$HO\overset{+}{—}\underset{\substack{|\\OC_2H_5}}{\overset{\substack{OH\\|}}{P}}—O\ HgI$$

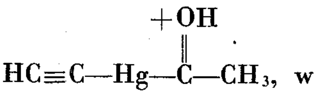
4m/e 54,  m/e 328, and $C_4H_3Hg^+$ m/e 253.

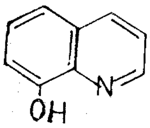
Mass spectrum for compound (IV) shows that the base peak is

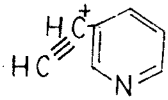


(IV)

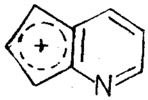
attributed to $^{202}Hg^+$ at m/e 202 (100 %) which appears to be due to cleavage of Hg–C, Hg–O and Hg–$OCOCH_3$ bonds. Fragmentation took place via α and β-cleavage with respect to $>P=O$ to give the different fragments.

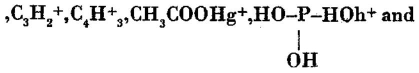
The intense peak at m/e 200 (79.3 %) and m/e 272 (43.3 %) are due to $^{200}Hg^+$ and  $HC\equiv C{-}Hg{-}\overset{+OH}{\overset{\|}{C}}{-}CH_3$, while the small peaks at m/e 145 (3 %), m/e 103 (18.3 %), m/e 60 (8.04 %), m/e 43 (10.3 %), m/e 36 (1 %), m/e 81 (1 %), m/e 91 (1 %), m/e 117 (1 %), m/e 64 (1 %) m/e 38 (1 %), m/e 51 (1 %), m/e 261 (1 %), m/e 281 (1 %) and m/e 266 (1 %) are attributed to

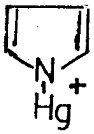




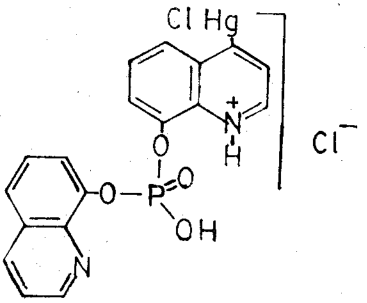
, $CH_3COOH.H, CH_3\equiv O$,C^{-7}, $H_2PO^+_3$.




,$C_3H_2^+$,$C_4H^+_3$,CH_3COOHg^+,$HO{-}\underset{OH}{\underset{|}{P}}{-}HOh^+$ and

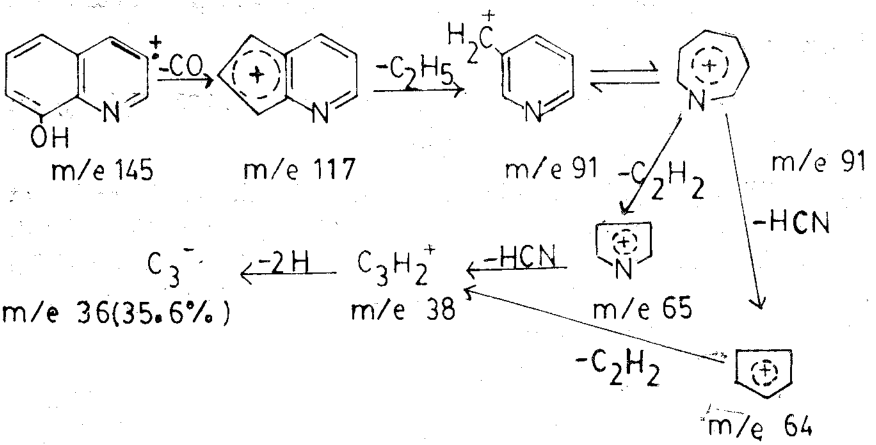


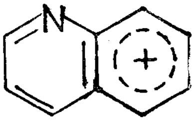
The base peak for compound (V) is the oxine ion m/e 145 (100 %) which attributed to α-cleavage with respect to $>P=O$.

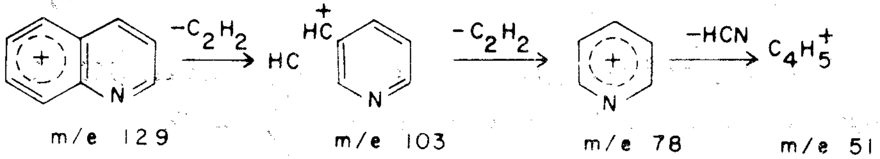


(V)

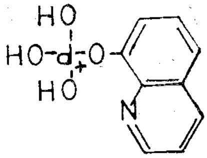
The intense peak at m/e 117 (51 %) is attributed to the fragmentation of the oxine ion as follows:



β-Clavage gave rise to  m/e 129. Its fragmentation is as follows:



The peaks at m/e 202, m/e 200, m/e 99 and m/e 241 are attributed to $^{200}Hg^+$, $^{202}Hg^+$, $H_4PO_4^+$ and



The molecular ion peaks cannot be observed in all spectra and this is attributed to the unstability of these compounds in the mass spectrometer. We notice that instead of oxinate ion m/e 144 the oxine ion m/e 145 appears in all the spectra. This phenomenon has been noticed in the mass spectra for chelated acetylacetone where the peak at m/e 99 disappeared and instead the acetylacetone ion at m/e 100 appears(8). The explanation is that the unstable oxinate ion gain hydrogen atom and change to the oxine ion which arrived to the ion collector in mass spectrometer with the formation of the peak at m/e 145. This was infered also by Kidani et al(6) for chelated 8-hydroxyquinoline where m/e 145 appeared.

EXPERIMENTAL

The mercurated organophosphorus compounds weie previosuly prepared(9).

The mass spectra were determined on a Varian MAT. SM 1B with data system SS 100 mass spectrometer operating at 70 ev, mass resolution approximately 1000 and ion source of 200 C. For all samples the direct inlet system was used. For each sample two mass spectra were carried out, one with correct peak heights ratios and the other was registered with higher sensitivity to show small peaks.

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