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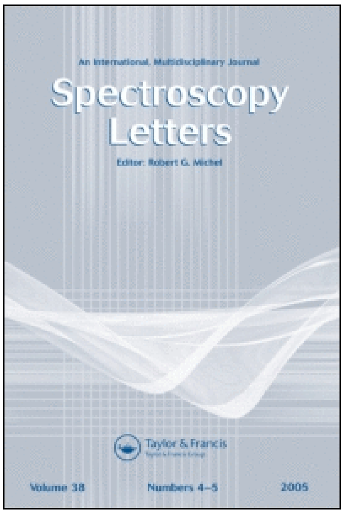

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Isomerism and Beckmann Rearrangement Reactions of α-Benzilmonoxime. A Comparative Kinetic and Stability Study

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Isomerism and Beckmann Rearrangement Reactions of α-Benzilmonoxime. A Comparative Kinetic and Stability Study.

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ABSTRACT

The isomerism of α-benzilmonoxime I is investigated by the measurements of their mass spectra and the integrated ion current curves at temperature 200 °C. Evidences of isomerisation and Beckmann rearrangement reactions of I under electron impact source are given. The high stability of solid I on storage is explained on the basis of hydrogen bonding. A comparative stability constant as measured kinetically in term of half life period between I and benzophenone oxime IV is investigated.

INTRODUCTION

Several methods[1-5] had been applied to identify the syn and anti isomers of oximes, particularly as spectroscopical and physical method. In the former method, a differences in the I.R[1], U.V[2] and N.M.R[3] spectra of the pair isomeric oximes had observed·later, Majer and Azzouz[4] had developed a new method for the assignement of isomeric aldoximes by mass spectrometry .In latter method a differences in dipole moment[5] and recently of rate constant[6] of Beckmann rearrangement of some hetrocyclic aldoxime were observed .

It is well known that oximes can undergo rearrangement to the corresponding anilides in acidic media[7]. The behavior of benzophenone oximes towards electron impact had been investigated by several groups[8-10]. It was claimed that benzophenome oxime undergoes a rearrangement to benzanilide in the mass spectrometer ion source. This rearrangement was suggested to be of the Beckmann type but caused by electron impact and to be a property of molecule ion. However , doubts had been expressed as to whether this rearrangement takes place in the gas phase subsequent to ionization or in solid state prior to evaporation. This led Majer and Azzouz[11] to sure for the latter mechanism .Further mass spectrometric evidence supplemented by I.R studies showed that in solid state at room temperature , benzophenone oxime had a life time of about 600 hours .

An extension of these studies it is decided to study the isomerism and mass spectra of I under electron impact source. Factor governing the stability of I and some related compound, on a storage and at room temperature is considered .

EXPERIMENTAL

Apparatus:

All mass measurements were carried out using A.E.I. MS902 mass spectrometer fitted with a direct insertion probe.Samples admitted to the source in the form of 2% solution in acetone by means of Hamilton micro syringe.

All absorption measurement were made on PYE UNICAM SP 8000 spectrophotometers using a matched 2-cm silica cells.Temperature control during measurement was achieved by connecting a thermostat of the type Julabo Paratherm PT 40 PS to the cell housing of the spectrophotometer .The I.R spectra were recorded on PYE UNICAM SP 1100 spectrophotometer .

Materials:

Benzil was obtained from Fluka and used as supplied without further purification .It was converted to α and β-benzilmonoxime I and II by using a standard method[12].Their mass spectra show a molecular ion peaks at m/z 225 and their precise mass measurement gave an atomic composition of $C_{14}H_{11}NO_2$. Pure I and II have a m.p 139°C and 101°C respectively .

N-Benzoyl benzamide III was prepared[13] by the reaction of benzoyl chloride with benzamide in the presence of pyridine . Product obtained as white needles has a m.p 144°C .It mass spectrum shows a molecular ion peak at m/z 225 and precise mass measurement gave an atomic composition of $C_{14}H_{11}NO_2$.

Kinetic measurement:

A similar procedure was followed to that described elsewere[14] by mixing 1ml of each of perchloric acid(6.324M) and oxime (10^{-3}M) . The mixture was completed to 10ml by distilled water .The decay of benzophenone oxime IV and I were measured at 234 nm and 254 nm respectively .Rate constants at 10°C were evaluated from pseudo first order plot .

RESULTS AND DISCUSSION

The possibility of isomerism in I is performed by measuring the integrated ion current curves[4,11] at m/z 225.5µL of 2% acetone solution of I is admitted to the ion source at a temperature of 200°C, the results are shown in Fig 1.a . It shows three maxima at a time t_m of 17,23 and 28 seconds respectively .These maxima are possibily originated from three different species having the same molecular constitution , but with different heats of sublimation[4].

Early study[11] proves that IV isomerised to benzanilide under electron impact source.This interesting result encourage to prepare a fresh sample of III followed by measuring its molecule ion current curve as above under a similar experimental conditions.It shows a single maximum at a time of 17 seconds .In other words I is isomerised to the corresponding III .Such reaction is formally analogous to the Beckmann rearrangement of oximes to amides which occurs with the ground state molecules in acidic media [7]. However , doubts have been expressed as to whether this isomerisation take place in the gas phase subsequent to ionisation or in solid state prior to evaporation by thermal mechanism.In this it is suggested that the latter mechanism could be the predominant and it agress with similar study[11].

To confirm that the first maximum in Fig.1 is for the rearranged I and to investigate the origin of second and third maxima in Fig.1 , a several mass spectra of I at t_m values indicated above with a mass spectrum of III are recorded .Accordingly 20 μg samples of I and III are admitted separately to the ion source from a direct insertion probe at a temperature 200°C as in Fig.2. A satisfactory molecular ion peak at m/z 225 and a base at m/z 105 are observed as in Fig.2.a. A precise mass measurement of last peak shows the existence of ion $phCO^+$. A comparison of

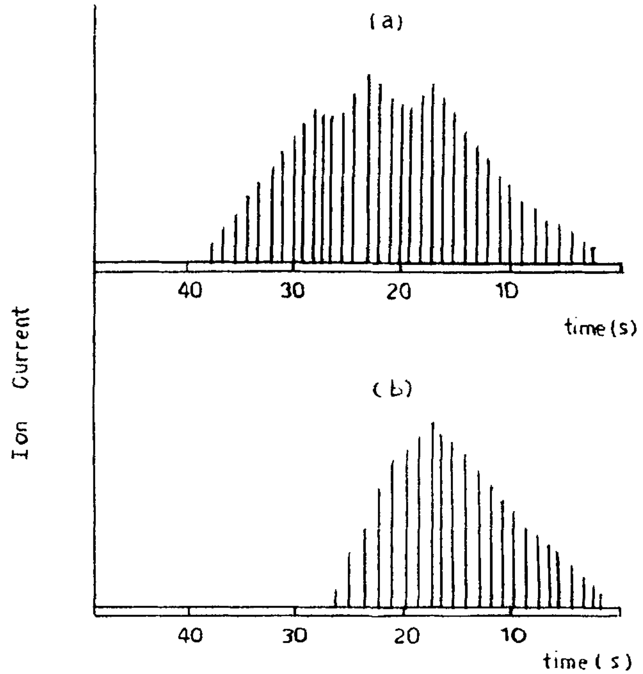

Fig. 1 ION Current Curves at
m /z 225 for :

a – α – Benzilmonoxime

b – N – Benzoyl-benzamide

mass spectra of III with that of I at t_m 17 seconds show they are almost identical , Fig.2 (a and b). This will add an additional evidence of the rearrangement[8-10] of I to III . The mass spectra of I at t_m values of 23 and 28 seconds show a base peak at m/z 103 .This ion after precise mass measurement show the composition of $phCN^+$. A comparison of the mass spectra of I at t_m values 23 and 28

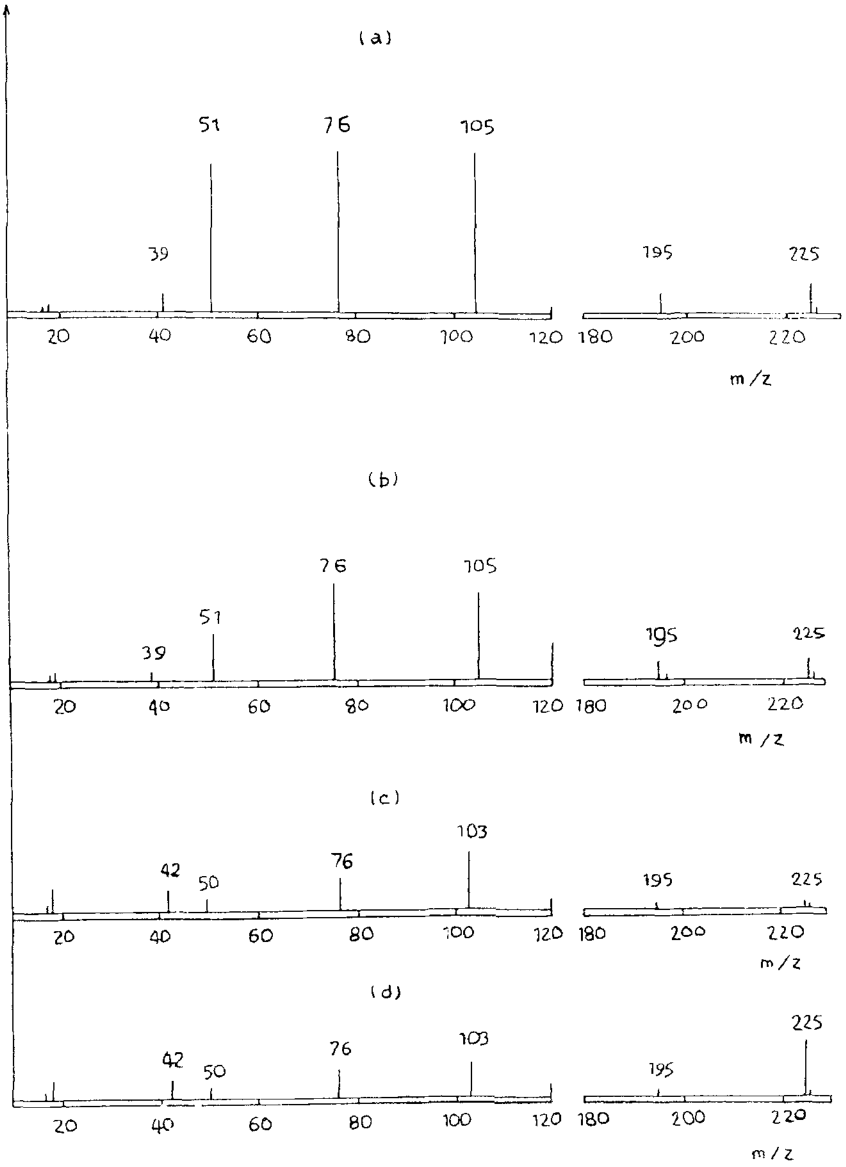

Fig.2 Mass spectra at temperature 200°C of :

a- N-Benzoyl-benzamide

b- α-Benzilmonoxime at t_m 17 sec.

c- = = = 23 =

d- = = = 28 =

seconds show they have similar mass peaks as in Fig.2 (C and d) . However , they have higher , lower or the same peaks intensity . These results realize that possibily I is isomerised in the ion source of the mass spectrometer to the corresponding II by thermal action[15]. Now when a mass spectrum of pure II is recorded at temperature of 200°C , it gives identical spectrum to that obtained for I at t_m value of 28 seconds .This will add a second confirmation of thermal isomerisation of I to the corresponding II.

Finally it can be concluded from the foregoing discussion that when I is admitted to the EI source , it is partially rearranged to the corresponding III , through Beckmann reaction .Other fraction of I is thermally isomerised to II. The remainder fraction of I is remained in its state . The heats of sublimation of III , I and II are significantly different .This permits the isomerism of I to be determined[4,16].

A comparison of stability of solids I and IV on storage seem to be of interest . A sample of solid I was kept in a stoppered flask at room temperature and left for about 10 years. Then after a fresh sample of I is prepared .The I.R of 0.01M solutions of both old and new I in dichloromethane are measured and compared .The results show they completely identical with absorption bands at 1610(m), 1650(s) ,3400(b) and 3180(m)cm^{-1}. These bands can be assigned respectively for azomethine group, a hydrogen bonded carbonyl group[17], a hydroxyl group and the intermolecular hydrogen bonding[17] probably existing between the hydroxyl group and the carbonyl group .

To look for the factor which plays the major role in the high stability of I on storage .This led to measure the I.R spectrum of IV under the same experimental condition as above.

The result proves the disappearance of hydrogen bonding band in IV. In other words I may exist as polymer[4] in solid state by intermolecular hydrogen bonding which inreases its stability .

To confirm the idea of hydrogen bonding in I even in solution , so it is worthy to measure the stability kinetically in terms of half life $t_{0.5}$. Accordingly Beckmann rearrangment reaction is performed to I and IV separately after addition of excess perchloric acid[14]. Evaluated rate constants for pseudo first order rearrangement reaction have a values of $8.5 \times 10^{-6} min^{-1}$. and $0.57 min^{-1}$. respectively .Hence $t_{0.5}$ for I and IV have a values of about 8000 min. and 1 min. respectively .When a similar kinetic study is conducted with II , the experiment proves that no Beckmann rearrangement reaction occurs , hence rate constant and $t_{0.5}$ can not be evaluated .This is an expected result due to fact that compound II is known to exist in an intramolecular hydrogen bonding[1] resulting to an abnormal stability .

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