

Studies on Arylhydrazones. Part XVI: synthesis of Heterocyclic Compound from Diethylmesoxalate-*o*-Carboxyphenylhydrazone.

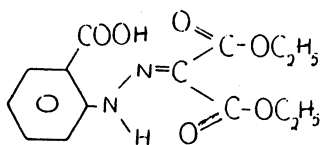
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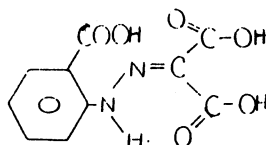
The use of diethylmesoxalate-*o*-carboxyphenyl-hydrazone (I) as a starting material for the synthesis of heterocyclic compound has been studied. Coupling product on fusion with NaOH at 130°C gives fully hydrolysed product. However fusion of compound (I) with NaOH at 220°C gives heterocyclic product. The fused products were characterised on the basis of elemental analysis, IR, ¹H NMR and electron impact studies.

INTRODUCTION

The coupling product obtained by the coupling of aryldiazonium salts with active methylene compounds known as complex arylhydrazones serve as starting materials or intermediates for the synthesis of several important classes of heterocyclic compounds by cyclisation reactions¹⁻³. The use of coupling product have been made by several works in the synthesis of some benzodiazines and related compounds; but survey of literature indicates that no attempt have been made for use of coupling product diethylmesoxalate-*o*-carboxyphenyl-hydrazone (I) obtained by the coupling of diazonium salt of anthranilic acid with diethyl malonate in the synthesis of heterocyclic compound. This prompted us to use coupling product (I) as a starting material for the synthesis of heterocyclic compounds.



(I)



(II)

EXPERIMENTAL

The coupling product (I) was synthesised under the same experimental conditions as adopted by Fernandes *et al.*⁴

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Fusion at 130°C: The paste of recrystallised diethylmesoxalate-*o*-carboxy-phenylhydrazone (I) with aq. NaOH was heated in oil bath at 130°C for 35 minutes with constant stirring. The fused mass was extracted with conc. HCl, filtered and repeatedly washed with water and finally dried in air.

Fusion at 220°C: The paste of recrystallised diethylmesoxalate-*o*-carboxy-phenylhydrazone (I) with aq NaOH was heated in oil bath at 220°C for 30 minutes with constant stirring. The fused mass was extracted with HCl, filtered out and finally washed with water. It was then dried in air.

RESULTS AND DISCUSSION

The fused mass obtained after fusion at 130°C was found to be hydrolysed product (II). The characterisation of hydrolysed product (II) has been done during present course of investigation on the basis of analytical and spectral studies. The analysis of yellow coloured hydrolysed product (II) corresponds to molecular formula $C_{10}N_2O_6H_8$.

The compound (II) exhibits medium to strong intensity bands in the region 3280 cm^{-1} (m), 3140 cm^{-1} (m), 3060 cm^{-1} (m), 1710 cm^{-1} (m), 1675 cm^{-1} (s) and 1595 cm^{-1} (s). The medium band in the region 3060 cm^{-1} may be assigned to H—bonded $\nu(N-H)$ vibration⁵. The bands observed at 3280 cm^{-1} and 3140 cm^{-1} have its origin in the O—H stretching vibration region of two different types of —COOH group (H—bonded and non H—bonded). The $>C=O$ stretching is a characteristic frequency of carboxylic group. The dipole moment derivatives of the COO^- in-plane bending mode and $C=O$ stretching mode are very large splitting with marked frequency differences may be expected for these modes. Further it is known that the out-of-plane $>C=O$ stretching mode should have a higher frequency than that of the in-plane mode⁶. The characteristic bands appearing at 1710 cm^{-1} and 1675 cm^{-1} are assigned to $>C=O$ stretching vibration. O—H in-plane bending and C—O stretching vibration appears at 1440 cm^{-1} and 1300 cm^{-1} respectively. The OCO rocking vibration appear at 770 cm^{-1} and 660 cm^{-1} . The O—H out-of-plane bending vibrations and $>C=O$ out-of-plane bending vibration give rise to bands at 840 cm^{-1} and 700 cm^{-1} respectively. C—OH in-plane bending vibrations and C—OH out-of-plane bending vibrations are assigned⁷ at frequencies 378 cm^{-1} and 222 cm^{-1} respectively. The bands at 1595 cm^{-1} is assigned to $\nu(C=N)$ vibration.

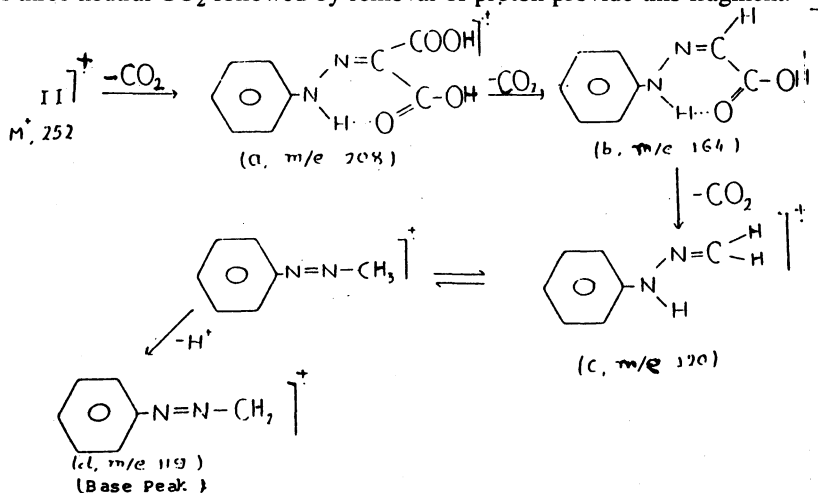
The structure of compound (II) was also corroborated by 1H NMR evidence. It resonance at around $\delta(14.2)$. The phenylamino proton in these types of unchelated compounds resonates between $\delta(5-7)$ (Solvent dependent). However, when intramolecular H—bonding occurs, the N—H proton suffers a characteristic deshielding⁵ and observed at around $\delta 14.2$. The resonance at $\delta 9.2$ is assignable for single carboxylic proton. Resonance in the region $\delta(7-8.5)$ could be assigned to aromatic protons.⁵

In electron impact studies, the M^+ appears at 25 having relative intensity 360.6 which confirms the molecular formula of the compound (II) to be $C_{10}H_8N_2O_6$. This also gave a peak at 253 of $(M + 1)^+$ ion but no peak for $(M + 2)^+$ ion was

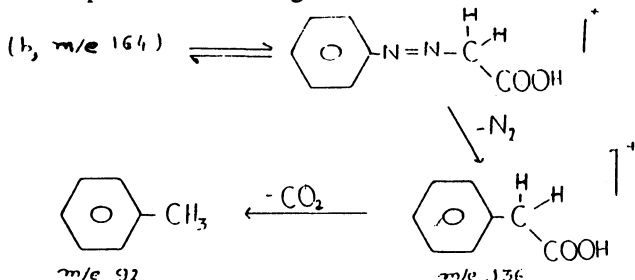
observed in the case indicating the non-resolution of peak due to isotopic abundance of oxygen atoms present in the molecule. The different fragment ions (excluding the peak of low abundances) in case of (II) are as follows:

m/e : 90, 91, 92, 119 (Base Peak), 136, 164, 190, 208 and 234.

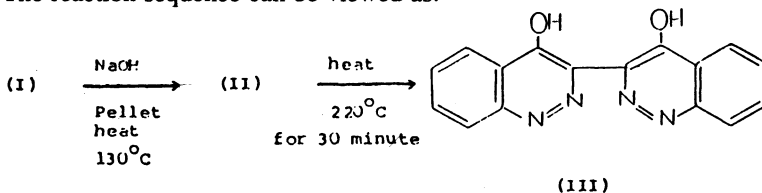
The base peak at m/e 119 could not be obtained directly from M^+ . Migration of three neutral CO_2 followed by removal of proton provide this fragment.



Loss of neutral nitrogen molecule of mass 28 is a common feature of this class of azo compound.⁸ Compound (II) does not show $(M - 28)^+$ peak. From this evidence it may be concluded that the (II) do not exist in azo form. The peak at m/e 136 was found in (II). Which may form by loss of neutral N_2 from fragment (b, m/e 164). Presence of peak at m/e 136 shows that the compound (II) may exist in azo-form. These are however, spectroscopic evidences⁸ to show that hydrazones may undergo thermal isomerisation to azo compounds prior to fragmentation. The fragment obtained at m/e 164 also undergoes similar thermal rearrangement to azo form to some extent and produce another fragment at m/e 136 as shown below:

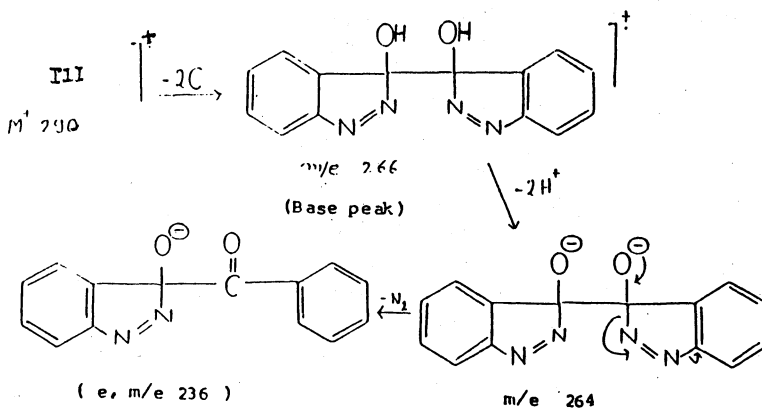


The fused mass obtained after fusion at 220° was to be heterocyclic compound (III). The reaction sequence can be viewed as:

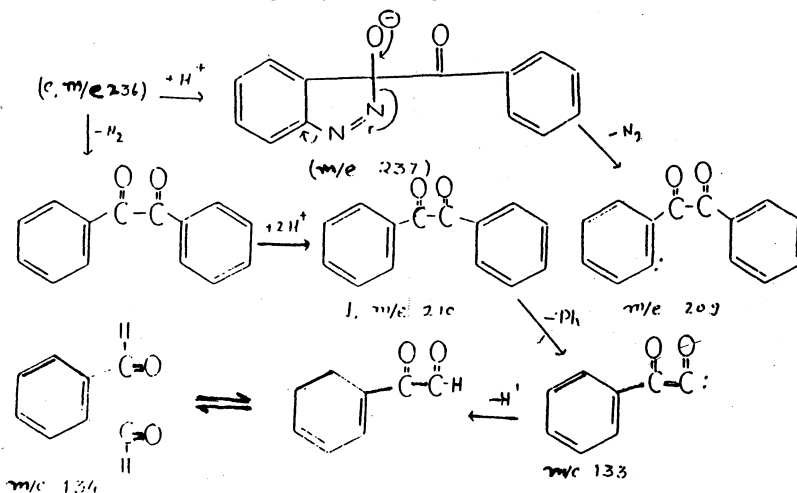


The characterisation of product (III) has been done on the basis of following evidences:

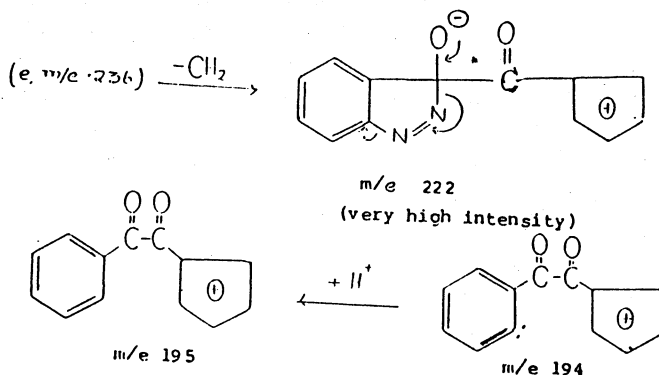
The elemental analysis of product (III) corresponds to molecular formula $C_{16}H_{10}N_4O_2$. On close examination of mass spectrol spectra of (III), it has been found that M^+ appears at 290 which confirms the molecular formula $C_{16}H_{10}N_4O_2$. The base peak is at m/e 266 which can form by elimination of two neutral carbon from two heterocyclic rings resulting in the formation of five membered ring. The ion at m/e 236 which is expected to form by double deprotonation of following by loss of neutral nitrogen from base peak has been observed in very high intensity in the present case.



The peak at m/e 209 and m/e 210 of moderate intensities are due to loss of another neutral nitrogen molecule from second heterocyclic ring according to the scheme shown below. Significant peaks of very high intensity at m/e 133 and 134 are observed due to loss of phenyl ring fragment (f) followed by protonation.



The fragment (e, m/e 236) can undergo a skeletal rearrangement to form ion at m/e 222. The latter ion further undergo fragmentation to give an ion at m/e 194 of moderate intensity by loss of neutral nitrogen.



On comparison of IR spectra of compound (II) and (III) it has been observed that (II) shows two strong bands at 1710 cm^{-1} and 1675 cm^{-1} , which is assigned to $>C=O$ stretching vibration. Disappearance of these two $>C=O$ vibration in the spectra of (III) indicates that at 220°C cyclisation of (II) takes place. In compound (II) $\nu(\text{N—H})$ peak appears at 3060 cm^{-1} . Disappearance of this peak in (III) is an additional supporting evidence for cyclisation of (II) at higher temperature. The band observed at 3370 cm^{-1} and 3160 cm^{-1} as a medium band have its origin in the O—H stretching vibration region of two different O—H groups. O—H in-plane bending and C—O stretching vibration appears at 1409 cm^{-1} and 1250 cm^{-1} as a strong band respectively. The O—H out-of-plane bending vibrations give rise to band at 860 cm^{-1} as a strong band. The broad band at 1325 cm^{-1} shows the interaction of O—H bending and C—O stretching of phenolic group. A broad band around 1550 cm^{-1} corresponds to the overlapping of aromatic $\nu(\text{C}=\text{C})$ and (C—H) bending vibrations. The azo group stretching vibration is assigned at 1610 and 1630 cm^{-1} .

In proton magnetic resonance spectra of compound (II), N—H proton singlet observed at $\delta 14.2$. Absence of N—H proton singlet in ^1H NMR spectra of compound (III), indicates that at higher temperature cyclisation of compound (II) takes place. Compound (III) display a multiplet in the region $\delta 7\text{--}8$ which may be assigned to the aromatic ring proton. A singlet at $\delta 5$ corresponds to the phenolic proton.

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