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Electron Impact Studies on the *N*-formylderivative of Ethyl Cyano-2-*o*-aminophenylhydrazono Acetate

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Mass spectral studies on the *N*-formylderivative of ethyl cyano-2-*o*-aminophenylhydrazono acetate have been carried out and their fragmentation patterns have been rationalised. None of the products shows the ion of highest abundance, *i.e.*, the base peak as the molecular ion. The base peak is at m/e 107.

Key Words: Electron studies, *N*-formylderivative, Ethyl cyano-2-*o*-aminophenylhydrazono acetate.

INTRODUCTION

Complex hydrazones serve as starting materials for the synthesis of several important classes of heterocyclic compound by cyclization reactions[1–3]. In continuation of our investigation, the electron impact studies on the N-formyl derivative of ethyl cyano-2-*o*-aminophenylhydrazono acetate have been carried out and their fragmentation patterns are described in this communication.

Braude *et al.*[4] made the suggestion that catalytic hydrogen transfer to a variety of organic acceptors might be possible under mild conditions. The important reaction variables were determined, the preparation of catalysts systematized and the applications broadened.

Braude *et al.*[5] also reported the striking discovery that ethylenic and acetylenic linkages could be reduced in high yield and purity by refluxing with cyclohexene in tetrahydrofuran at 65°C in the presence of palladium black.

At high temperatures, especially in the presence of catalysts, almost any organic compound can donate hydrogen (catalytic cracking), but this has little potential for controlled synthesis. Similarly, at sufficiently high temperatures (300°C) even benzene can serve as acceptor A and be reduced to cyclohexene. Hence the choice of donor is generally determined by the case of reaction and availability. The chosen compounds tend to be hydroaromatics, unsaturated terpenes and alcohols.

No attempts have been made on the reduction of nitro group attached to the benzene ring of complex arylhydrdzones. Therefore we are describing in this communication interesting findings by catalytic transfer hydrogenation method by using 10% Pd-C as a catalyst, various H donors and solvent.

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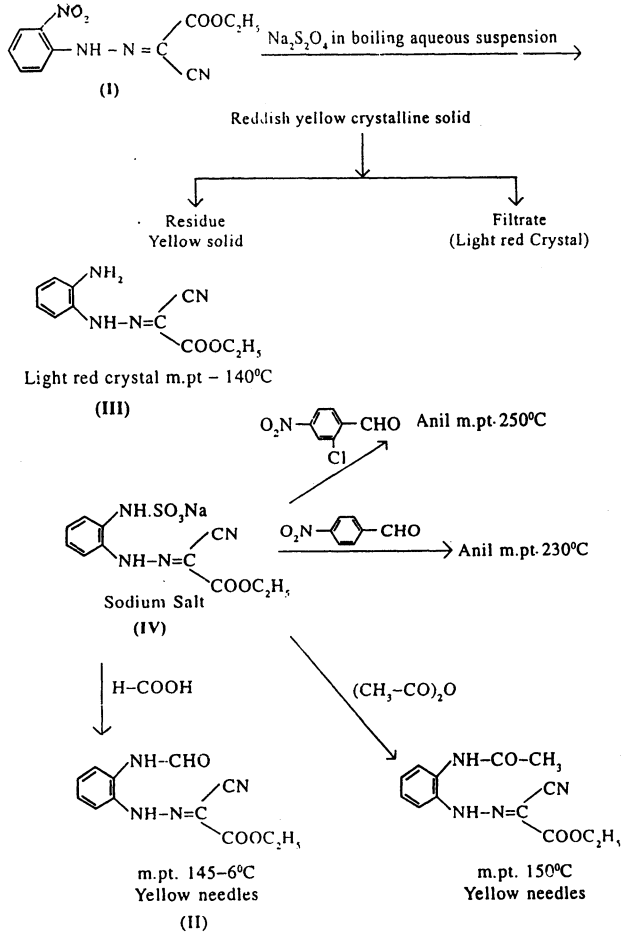
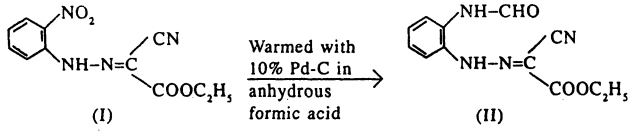


The characterization of the various reduction products obtained in all the above cases has been done during the present course of investigation on the basis of (a) elemental analysis, (b) IR spectral studies, (c) ^{1}H NMR, and (d) mass spectral studies.

Ethyl 2-cyano-2-*o*-nitrophenylhydrazono acetate **(1)** on reduction with 10% Pd-C and anhydrous formic acid gave yellow crystals of N-formyl derivative of the amino compound **(2)** in 50% yield.

The identity of the N-formyl derivative is confirmed by its IR, ^{1}H NMR and also by examining the fragmentation pattern in its mass spectrum.



EXPERIMENTAL

Infrared spectra were recorded on Bruker IFS66v FT-IR spectrometer and Perkin-Elmer No. PE-257 spectrometer using KBr pellets. NMR spectra were

recorded on Jeol AMX-40U model spectrophotometer using TMS as the internal standard. Mass spectra were recorded on MASPEC system (MSW/9629) spectrometer.

Ethyl 2-cyano-2-(*o*-nitrophenylhydrazono) acetate (1)

o-Nitroaniline (13.8 g, 0.1 mol) was dissolved in concentrated hydrochloric acid (25 mL) and diazotized by slow addition of sodium nitrite (7.0 g) in water (7 mL) at 0–5°C. The filtered benzene diazonium salt was run gradually into the cooled solution of ethylcyano acetate (9.3 g, 0.1 mol) in acetone (200 mL) and water (100 mL) containing sodium acetate (18.0 g). The yellow precipitate was collected by filtration after stirring the mixture for further 1 h, in 88% yield, having m.p. 129–130°C. The main product showed two spots on TLC of which the intensity of slower moving component was greater than that of the faster moving one.

Preparation of N-Formyl derivative of ethyl cyano-2-*o*-aminophenylhydrazono acetate (2)

Ethyl 2-cyano-2-*o*-nitrophenylhydrazono acetate **(1)** (250 mg) was dissolved in anhydrous formic acid (15 mL), warmed and then added portionwise 10% Pd-C (100 mg) with occasional stirring. The content was heated for 5 min and filtered hot. On evaporation of the solvent, a yellow crystalline solid was obtained which was recrystallized from aqueous ethanol, m.p. 145°C, yield 50%. The compound gave a single spot on TLC.

RESULT AND DISCUSSION

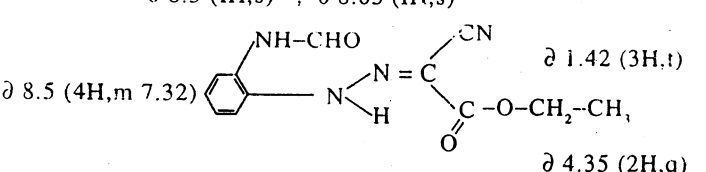
IR spectral studies

The two (NH) stretching frequencies of N-formylderivative were observed in the region 3200 and 2900 cm^{-1} as a medium and broad band respectively. These bands were assigned as NH stretching vibrations of (NHCHO) and (—NH—N=C<) group respectively. The bands at 2250 (s), 1660 (s) and 4590 cm^{-1} (s) can be assigned as ν(C=N), ν(C=O) and ν(C=N) stretching vibrations respectively.

The characteristic IR absorptions are in confirmity of the structure[6, 7]

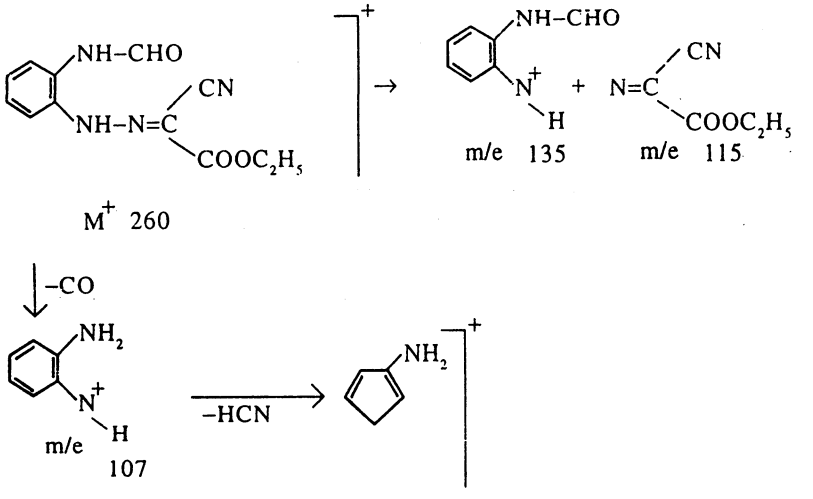
^{1}H NMR spectral studies

^{1}H NMR structure of the N-formylderivative showed resonances at δ 8.5 (s, 1H) as singlet (NH of amino group attached with aldehyde). Four aromatic protons in the form of multiplet showed resonances at δ 7.32. Three ester methyl protons and two ester methylene protons appeared as triplet and quartet respectively at δ 1.42 and δ 4.35. The resonance at 8.05 could be assigned to aldehydic proton.

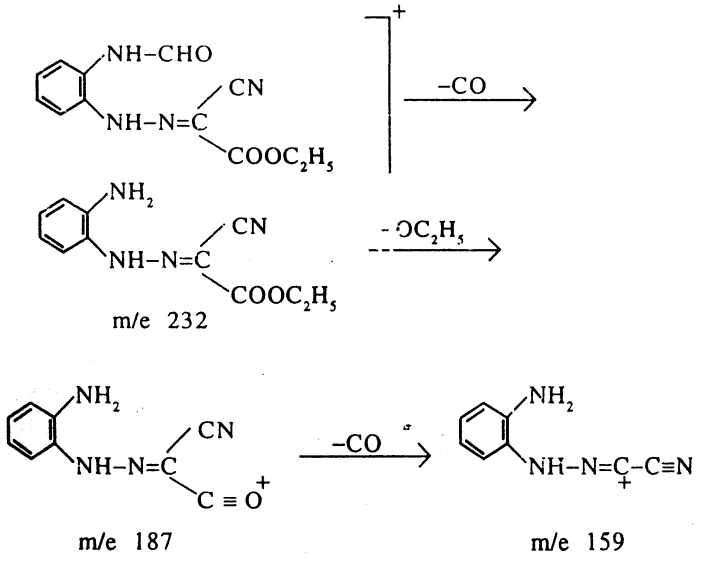


The mass spectrum of the compound **(2)** was examined and showed that the M^+ appears at 260. The observed mass of M^+ was found to be in agreement and confirming the molecular formula $C_{12}H_{12}N_4O_3$.

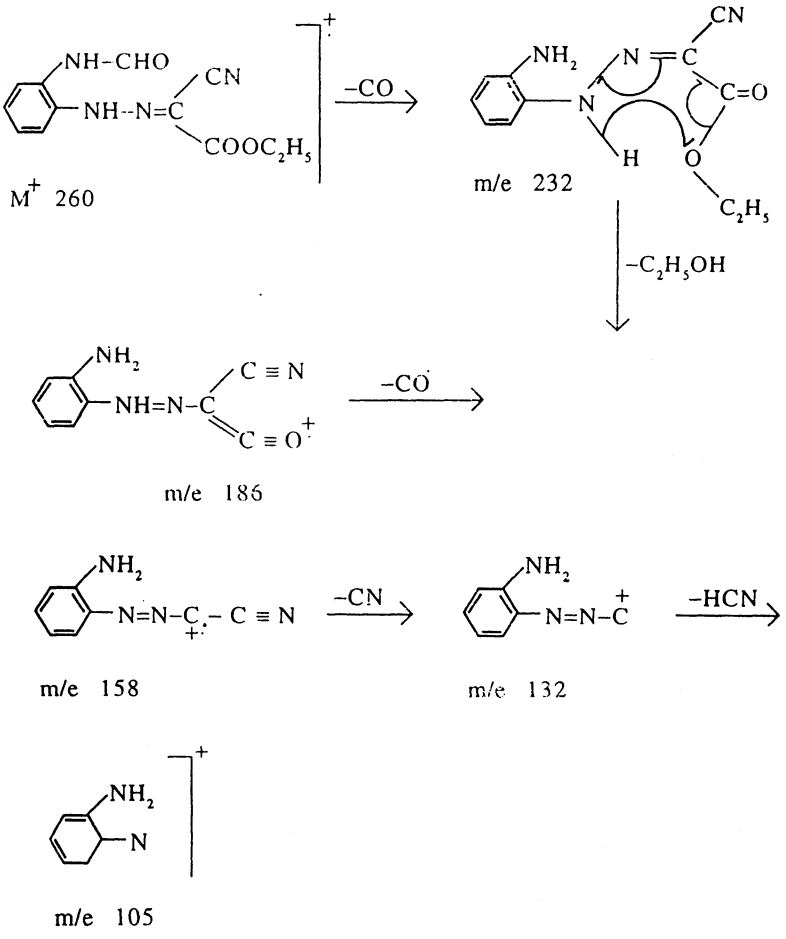
The formation of base peak at M/e 107 is due to cleavage of N-N bond of hydrazo group followed by elimination of CO group.



Fragmentation from the ester group depends upon effective charge localisation as carbonyl oxygen or alkyl oxygen and also to some extent on imino nitrogen (—N=C<).



Loss of mass 74 can be attributed to the elimination of CO group followed by the loss of C_2H_5OH from the ester function after H-transfer and indeed, this mode of fragmentation is also taking place because the ion further produces fragments which are consistent with its structure.



M$^+$ 260

m/e 232

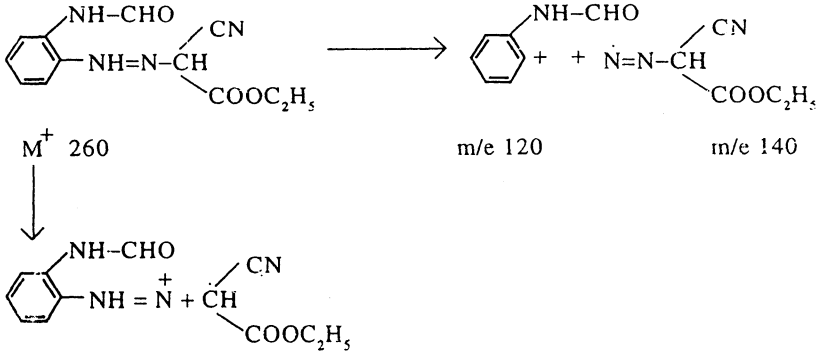
m/e 186

m/e 158

m/e 132

m/e 105

Loss of neutral molecule of mass 28 (m/e 232) was observed which is a common feature of this class of azo compounds[8].



M$^+$ 260

m/e 120

m/e 140

m/e 148

m/e 112

The peaks of m/e 140 and m/e 112 were not observed but peaks at m/e 120 and 148 were present. Although the intensity of these ions is quite low, the fragmentation mode shows that the coupled products may exist in the azo form. However, there are spectroscopic evidences[9, 10] to show that hydrazones may undergo thermal isomerisation to azo compounds prior to fragmentation.

Abundances of ions at m/e 120 and 148 are very low indicating that isomerisation of hydrazo to azo compounds occurs to some extent in the inlet source of mass spectrometer prior to fragmentation under the probe condition.

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