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Studies on Arylhydrazones Part XV: Reduction of Ethyl 2,3-dioxo-2-*o*-nitrophenylhydrazono Butyrate

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Reduction of ethyl 2,3-dioxo-2-*o*-nitrophenylhydrazono butyrate was carried out using various reducing agents such as $FeSO_4/NH_3$, NH_4Cl/Zn dust, Sn/HCl, Zn/CH_3COOH, Zn/HCl, $SnCl_2/HCl$, H_2S/alc. NH_3 and sodium dithionite. In all the above methods of reduction, the reduction with $Na_2S_2O_4$ was proved to be an efficient and excellent method due to easier process, a much better yield of amino compound in spite of the formation of the sodium salt of *o*-sulphamic acid to a greater extent. Reduction product (amino compound) was isolated and characterised by physical and spectral methods. Finally the amino compound was established by forming the N-formyl and N-acetyl derivatives from the sodium salt of *o*-sulphamic acid and the various condensation products (anils) with different aldehydes.

INTRODUCTION

The reduction of nitro group attached to the aromatic nucleus of complex arylhydrazones has attracted the attention of chemists in past.[1-5] In our previous communication[6], reduction of diethyl mesoxalate-*o*-nitrophenylhydrazone has been reported by us. In continuation with our previous work[6], the present paper deals with the characterization of the product obtained by the reduction (using various reducing agents such as $FeSO_4/NH_3$, NH_4Cl/Zn dust, Sn/HCl, $SnCl_2/HCl$, H_2S/alc. NH_3 and $Na_2S_2O_4$) of compound (I). During the course of present investigation in an attempt for reductive cyclisation [to synthesis heterocyclic compounds of various ring sizes specially a seven-membered ring (benzotriazepine)] we have chosen ethyl 2,3-dioxo-2-*o*-nitrophenylhydrazono butyrate but contrary to our expectation the amino compound was isolated in varying yields along with various side-products.

EXPERIMENTAL

The details regarding experimental procedure have been described in our previous communication.[6]

RESULTS AND DISCUSSION

The filtrate obtained after reduction of ethyl 2,3-dioxo-2-*o*-nitrophenylhydrazono butyrate (I) with $FeSO_4/NH_3$, on cooling, gave a red precipitate which

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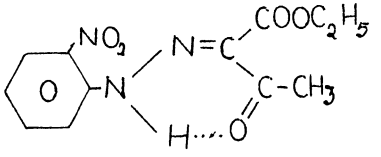
on crystallisation with petroleum ether (60–80°C) furnished orange red crystals in 10% yield. Only traces of orange red crystals were obtained in case of reduction with Zn/CH_3COOH, Zn/HCl, Sn/HCl, $SnCl_3$/HCl. In all the above cases, the main product was found to be a metal complex. Characterization of these complexes are under investigation and will be reported elsewhere.

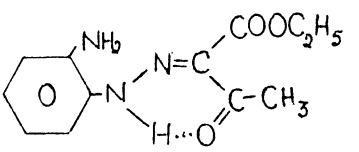
Hydrazone (I) was refluxed with ethanol and liquor ammonia. The contents were filtered hot and the filtrate on cooling gave an unidentified yellow solid (m.p. 159–160°C), which was filtered. The filtrate on extraction with ether gave orange red crystals in 30% yield.

Like in case of diethyl mesoxalate-2-*o*-nitrophenylhydrazone[6], the reduction with sodium dithionite was found to be the most effective method due to easier process, a much better yield of orange-red crystals (50% yield) in spite of the formation of sodium salt of 2-sulphamic acid (III) to a greater extent.

The orange red crystalline compound (mp. 108°C) on the basis of elemental analysis corresponds to molecular formula $C_{12}H_{15}N_3O_3$ which indicates the possibility of the formation of ethyl 2,3-dioxo-2-*o*-aminophenylhydrazono butyrate (II).



(I)



(II)

In order to identify the orange-red crystalline product obtained by reduction, the IR spectra of hydrazone (I) and orange-red product obtained after reduction was compared. IR spectra of (I) shows characteristic absorptions at 3160 cm^{-1} (m), 1690 cm^{-1} (s), 1610 cm^{-1} (s) and 1600 cm^{-1} (s) which may be assigned to νNH (—NH—N=C<), ν (>C=O) (ester). ν (>C=O) (H-bonded) and ν(N=C) respectively.[7-9] These bands (except ν(N—H)) remain almost unaffected in the spectra of the orange red crystalline product ruling out any isomeric change (passing it to azo form) during the course of reduction. The ν(N—H) frequency suffers an appreciable decrease in frequency after reduction and appears at around 3080 cm^{-1}. In addition to these, there are two new medium bands at around 3340 cm^{-1} and 3440 cm^{-1} in the spectra of orange-red crystalline product. These are assigned to asymmetric and symmetric modes of amino group respectively. Appearance of new peak at 1100 cm^{-1} is assignable to deformation mode of NH_2 group[10]. However, due to presence of several peaks in this region δ(N—H) deformation peak is not beyond doubt. Thus on the basis of aforesaid results, it could be inferred that during the course of reduction, nitro group is converted into amino group.

The UV spectrum of (I) and orange red crystalline product shows two strong absorptions in the vicinity of 210 ± 10 nm and 240 ± 5 nm due to the presence of two different types of >C=O group. Again the absorption in the region

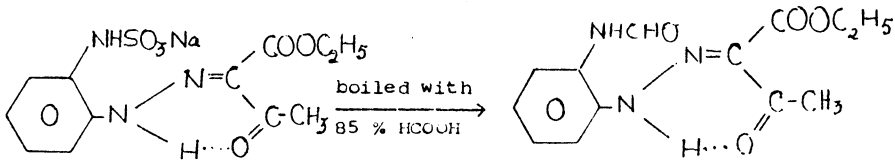
335–360 nm is characteristic of phenylhydrazone (—NH—H=C<) π–π^* transition.[10] In the UV spectra of these compounds the characteristic absorption band of phenyl azo group in the region 270–280 nm is not observed which is sufficient enough to reject any possibility of the azo form of the compound.[10]

^{1}H NMR spectrum of orange-red crystalline product fully supports it to be ethyl 2,3-dioxo-2-*o*-aminophenylhydrazono butyrate(II). It showed resonances at δ5.43 singlet for two amino protons and δ 6.175–7.125 multiples for four protons which could be assigned to four aromatic protons. The resonance at δ 4.12–4.50, δ 2.625 and δ 1.14 could be assignable to ester methylene (2H, q), ketomethyl (3H, s) and ester methyl (3H, t) protons respectively.[11] When intramolecular H-bonding occurs the phenylamino proton suffers a characteristic deshielding[11] and observed at around δ 1.2 and when intramolecular H-bond does not occur it shows resonance at δ 7.0. In the present case, the characteristic N—H signal was not observed because the spectrum was not run up to δ 14.

From the above evidences, it may be concluded that the reduced product (orange-red crystalline product) is ethyl 2,3-dioxo-2-*o*-aminophenylhydrazono butyrate (II).

The structure of amino compound (II) was also confirmed by formation of N-formyl and N-acetyl derivatives and also by the formation of condensation products (anils) with different aldehydes.

The sodium salt of ethyl 2,3-dioxo-2-phenylhydrazono-*o*-sulphamic acid (III) obtained in case of reduction with $Na_2S_2O_4$, on boiling with 85% formic acid, gave yellow needles of N-formyl derivative (IV) (m.p. 145°C) of the amino compound in 70% yield. The characteristic IR absorptions are in conformity with the compound[7–9]. The absorptions due to ν(C=O) (ester), ν(C=O) (keto) and ν(N=C) vibration are obtained at 1700 cm^{-1} (s), 1650 cm^{-1} (s) and 1600 cm^{-1} (s) respectively. In addition it exhibits two bonds in the region 3450 cm^{-1} (b) and 3225 cm^{-1} (m) assigned as two NH stretching vibrations. The shift in one NH can be attributed to intramolecular H-bonding.

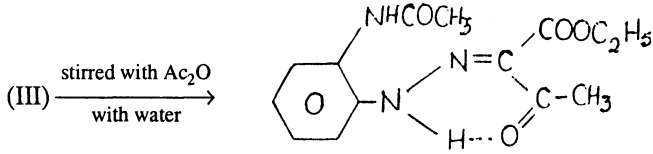


(III) (IV)

On ^{1}H NMR examination, N-formyl derivative (IV) showed resonances at δ 15.215 (s), 9.0 (s), 8.45 (s), 7.2 (m), 4.4 (q), 1.6 (s) and 1.4 (t). The resonance at δ 1.6, 1.4 and 4.4 are assignable for three keto methyl protons, three ester methyl protons and two ester methylene protons respectively. Four aromatic protons showed resonance at δ 7.2. Single resonance at δ 8.45 and δ 9.0 are due to aldehydic proton and NH proton attached with aldehydic group. The phenyl amino proton in this type of unchelated compound resonates between δ 5–7 (solvent dependent)[11]. However, when intramolecular H-bonding occurs, the NH

proton suffers a characteristic deshielding and observed at around δ 13.[11] In the present case the characteristic NH signal was observed at δ 15.2.

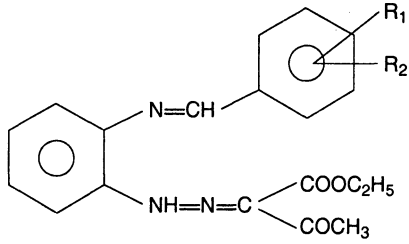
The yellow product (m.p. 168–9°C) from the reaction of sodium salt (III) with acetic anhydrode is the N-acetyl derivative (V) which is confirmed by its IR and ^{1}H NMR examination.



(V)

The characteristic IR absorptions of compound (V) were observed at 3275 cm^{-1} (b), 1705 cm^{-1} (m), 1670 cm^{-1} (s) and 1600 cm^{-1} (w) together with typical absorptions due to the aromatic nucleus. The bond at 3275 cm^{-1} is obviously due to ν(N—H) vibration of —$NHCOCH_3$ and —NH—N=C group and that the three bands at 1705 cm^{-1}, 1670 cm^{-1} and 1600 cm^{-1} are due to three different ν(C=O) groups. The two ν(N—H) vibrations could not be separated probably due to their coupling and yielded a broad band in the region 3275 cm^{-1}.

TABLE-1
PHYSICAL CONSTANTS AND ANALYTICAL DATA OF ANILS



Compound (Colour)	m.p. (°C)	Yield (%)	Molecular formula	% Analysis Found (Calcd.) C	H	N
(a) R_1 = *p*-NO_2, R_2 = H (Orange yellow)	180	70	$C_{19}H_{18}N_4O_5$	59.02 (59.68)	4.12 (4.71)	14.30 (14.65)
(b) R_1 = *p*-Cl, R_2 = H (Yellow)	170	60	$C_{19}H_{18}N_3O_3Cl$	61.01 (61.37)	4.52 (4.84)	11.20 (11.30)
(c) R_1 = 2-Cl, R_2 = 5-NO_2 (Deep yellow)	165	55	$C_{19}H_{17}N_4O_5Cl$	54.61 (54.74)	4.01 (4.08)	13.30 (13.44)
(d) R_1 = *m*-NO_2, R_2 = H (Yellow)	174	50	$C_{19}H_{18}N_4O_5$	59.00 (59.68)	4.30 (4.71)	14.10 (14.65)

^{1}H NMR of yellow compound fully supports it to be N-acetyl derivative (V). Its ^{1}H NMR gave resonances at δ 4.21 (q) for two ester methylene protons and resonances at δ 1.4, 2.75 and 2.81 for protons of ester methyl, keto methyl and acetamido methyl respectively. The resonance at δ 14.6(s) for one proton can be assigned to NH group (H-bonded) and single acetamido NH proton appeared in this case as singlet at δ 9.84. The aromatic proton appears at δ 7.5 (m).

On condensation with different substituted benzaldehyde, the sodium salt (III) gave yellow crystals of different types of anils. The physical constant and analytical data of anils are listed in Table-1.

The characteristic IR absorption is in conformity with the structure. The bond in the vicinity of 3100 ± 100 cm^{-1} is due to NH stretching vibration. In addition it also gave absorptions around 1680 cm^{-1} (s), 1630 cm^{-1} (s) and 1575 cm^{-1} (b) for ν(C=O) (ester), ν(C=O) (chelated) and ν(N=C) respectively[7-9].

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