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Studies on Arylhydrazones, Part-XIV: Reduction of Diethyl Mesoxalate-*o*-Nitrophenylhydrazone

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The present communication deals with the characterisation of the product obtained by the reduction (using various reducing agents such as $FeSO_4/NH_3$, NH_4Cl/Zn dust, Sn/HCl, $SnCl_2/HCl$, $H_2S/$ alcoholic NH_3 and $Na_2S_2O_4$) of diethyl mesoxalate-*o*-nitrophenylhydrazone. Contrary to our expectation the amino compound was isolated in varying yields along with various side products. 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. The characterisation of *o*-aminophenylhydrazones obtained in all the above cases has been done during the present course of investigation on the basis of elemental and spectral studies.. Finally, the amino compound was established by forming the various derivatives from the sodium salt of *o*-sulphamic acid *e.g.* N-formyl, N-acetyl, N-benzoyl, N-phthaloyl and the various condensation procucts with different aldehydes, the intentity of which was confirmed by elemental and spectral analysis.

INTRODUCTION

During the course of the present investigation in an attempt for reductive cyclisation, we have chosen diethyl mesoxalate-*o*-nitrophenylhydrazone for the following reasons:

(a) The reduction compound diethyl mesoxalate-*o*-aminophenylhydrazone was isolated by Trave and Bianchetti[1] as a crystalline solid (m.p. 82°C), but we have isolated it as a red oil. On purification of red oil by column chromatography, we get red crystals (m.p. 55°C). The amino compound was not characterised by Trave and Bianchetti.[1]

(b) To synthesise heterocyclic compounds of various ring sizes specially a seven-membered ring (benzotriazepine).

Thus keeping in mind the above facts we tried to reduce the arylhydrazones by using reducing agents such as $FeSO_4/NH_3$, NH_4Cl/Zn dust, Sn/HCl, $SnCl_2/$

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HCl, H_2S/alc. NH_3 and $Na_2S_2O_4$. But contrary to our expectations the amino compound was isolated in varying yields along with various side products.

EXPERIMENTAL

Melting/decomposition points were determined in sulphuric acid bath in open capillaries and are uncorrected. IR spectra are recorded on Perkin-Elmer 157 or 577 model in Nujol Mull or KBr disc. ^1H nmr measured in $CDCl_3$ solution using TMS as an internal reference on the Varian EM-360 60 MHz and Varian FT 80A instrument. TLC was done routinely to check the purity of the products.

Compound I was prepared by known method.[2, 3]

Reduction with $FeSO_4/NH_3$

A hot saturated solution of $FeSO_4$ (10 mL) was added to a suspension of compound I (0.001 mol) in liquor NH_3 (10 mL). The reaction mixture was heated on water bath and evaporated to dryness to obtain a black residue. The chloroform extract of the black residue gave a trace amount of red oil on evaporation.

Reduction with NH_4Cl/Zn dust

0.008 mol of compound I was dissolved in ethyl acetate and a saturated solution of NH_4Cl (10 mL) was added followed by Zn dust (1 g). The reaction mixture was shaken for 1 h. The contents were filtered and the filtrate, on evaporation of the upper layer of ethyl acetate, gave a trace amount of red oil.

Reduction with Sn/HCl

0.001 mol of compound I was mixed with granulated Sn (1 g) and conc. HCl (10 mL). The reaction mixture was boiled on water bath till the disappearance of starting material, then cooled and filtered. The filtrate was made alkaline with 2N NaOH solution and extracted with chloroform from which reduced product could not be separated out even in trace amount.

Reduction with $SnCl_2$/HCl

0.001 mol of compound I was stirred with a solution of $SnCl_2$ (3 g) in 5 mL of conc. HCl and heated on water bath until no precipitate was formed on addition of water. The contents were diluted with water (50 mL), heated nearly to boiling and a current of H_2S gas was passed until all the tin was precipitated as sulphide. The ppt. was filtered; the filtrate was concentrated and extracted with chloroform. The chloroform extract, on evaporation in open air, produced red oil (10% yield).

Reduction with H_2S/alc. NH_3

0.001 mol of compound I was dissolved in ethanol (10 mL). Liquor ammonia 1 mL was added and H_2S gas was passed for 15 min in warm solution. The test tube was then immersed in boiling water for 5 min and again H_2S was passed. The process was repeated till the starting material vanished in TLC. Approximately 1 h was needed for the complete disappearance of starting material. This was diluted and H_2S gas was passed for further 15 min to the warm solution, cooled and filtered. The filtrate, on evaporation of ethyl alcohol, gave red oil (30% yield).

Reduction with sodium dithionite

0.001 mol of compound I was mixed with a small quantity of water and warmed gently. Sodium dithionite was added to it in very small portions with constant stirring and warming until the completion of reaction.. The completion of reaction was tested by TLC examination. After completion of reaction, the reaction mixture was kept in a desiccator for complete dryness. The dried solid mass was then finally extracted with chloroform which gave red oil (50% yield) on evaporation. The residue left after extraction was found to be the sodium salt of diethyl mesoxalate-2-phenylhydrazono-*o*-sulphamic acid (III).

Preparation of N-formyl derivative (IV)

0.01 mol of sodium salt of *o*-sulphamic acid (III) of the coupling product was boiled with anhydrous formic acid (10 mL) for 5 min and filtered hot. The filtrate was left in open air for 2 days for complete evaporation of formic acid. Evaporated solid on recrystallisation with aq. ethanol gave yellow crystals of N-formyl derivative (IV) (m.p. 120–122°C) in 60% yield.

Preparation of N-acetyl derivative (V)

0.01 mol of compound III was boiled with 5 mL of acetic anhydride for 2 min and filtered hot. The filtrate was left in open air for complete dryness. A yellow solid was obtained in 50% yield which was recrystallised from aq. ethanol (m.p. 130–131°C).

Preparation of N-benzoyl/N-phthaloyl derivative

0.001 mol of compound III was fused with 0.001 mol of benzoic anhydride/phthalic anhydride for 5 min, cooled, diluted with water (20 mL) and filtered. A yellow solid was obtained which was recrystallised from aq. ethanol (yield 50%).

M.p. of N-benzoyl derivative 120°C. M.p. of N-phthaloyl derivative 215°C

Preparation of condensed product (Anils) of compound III with different aldehydes

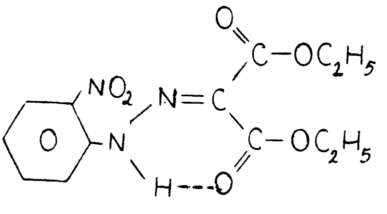
Suspension of 0.002 mol of compound III and 0.002 mol of an aldehyde in glacial acetic acid (30 mL) was refluxed on water bath for 1 h using a crystal of *p*-toluene sulphonic acid as a catalyst. The contents were filtered hot when a yellow solid was precipitated. It was filtered and recrystallised from aq. acetic acid.

RESULTS AND DISCUSSION

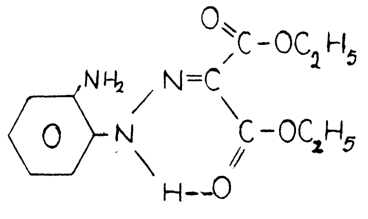
The red oily compound, on purification by column chromatography, gave orange-red crystal (m.p. 55°C) which was found to be diethyl mesoxalate-*o*-aminophenylhydrazone (II). Thus of all the methods of reduction, the reduction with

$Na_2S_2O_4$ proved to be an efficient and excellent method due to easier process, a much better yield of reduction product inspite of the formation of the sodium salt (III) of the reduction product to a greater extent.

The orange red crystalline compound on the basis of elemental analysis corresponds to the molecular formula $C_{13}N_3O_4H_{17}$ which indicates the possibility of the formation of diethyl mesoxalate-*o*-aminophenylhydrazone (II).



(I)



(II)

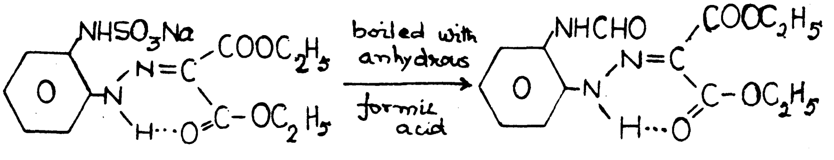
The characteristic IR absorption of compound I was observed at 3080 cm^{-1}, 1710 cm^{-1} and 1660 cm^{-1} together with typical absorptions due to aromatic nucleus. The bands at 1710 cm^{-1} and 1660 cm^{-1} are obviously due to two $>C{=}O$ stretching vibrations and the small band at 3080 cm^{-1} is due to ν(N—H)[2, 4]. In general free ester carbonyl group displays ν(C═O) at around 1770 cm^{-1}. The lowering of two ν(C═O) frequencies in compound I is explained by the presence of α,β-unsaturation in former but α,β-unsaturation and H-bonding in latter.[2, 4] The azomethine band is assigned at 1605 cm^{-1} as a strong band. All the above vibrational frequencies are not shifted appreciably in the case of orange-red crystal. Thus it is inferred that during reduction, isomeric change (passing it to azo form) does not take place. The orange-red crystals display a strong band around 3420 cm^{-1} and 3240 cm^{-1} which is neither present in compound I nor expected for water molecule (water molecule always display broad hump) are assigned to asymmetric and symmetric (N—H) modes of amino group respectively.[2] The appearance of new peak around 100 cm^{-1} is assignable to deformation mode of NH_2 group. Thus it is authentically confirmed that during the course of reduction, nitro group is converted into amino group.

The UV spectra of orange-red crystals show two strong absorption in the vicinity of 210 nm and 240 nm due to presence of two different type of $>C{=}O$ group. Again the absorption in the region 335–260 nm *i.e.* characteristic of phenylhydrazone ($>N{-}N{=}C<$) π-π^* transition.[2, 5, 6] In the UV spectra of the characteristic absorption band of phenylazo group in the region 270–280 nm were not observed which is sufficient enough to rule out any possibility of the azo form of the compound II.[2, 5, 6]

The ^1H nmr spectrum of organge-red crystal showed resonances at δ 12.9, 12.4, 6.7 to 7.7, 4.6, 4.35, 4.1, 1.4 and 1.1. Single resonances at δ 12.9 and 4.6 are due to single chelated N—H proton and protons of the amino group respectively.[7, 8] Four aromatic protons in the form of multiplets showed resonance at δ 6.7 to 7.7. Three ester methyl non-bonded protons appeared as triplet at δ 1.1 and δ 1.4 respectively. Similarly two ester methylene bonded and two ester methylene non-bonded protons appeared as quartet at δ 4.35 and δ 4.1 respectively.[7,8]

On these evidences, the orange-red crystalline product was characterised as diethyl mesoxalate-*o*-aminopheynylhydrazone (II). Finally the structure of amino compound II was established by forming various derivatives from the sodium salt of diethyl mesoxalate-2-phenylhydrazone-*o*-sulphamic acid (III) *e.g.* N-formyl, N-acetyl, N-benzoyl, N-phthaloyl and various condensation products with different aldehhydes, the identities of which were confirmed by elemental and spectral analysis.

The compound III on reaction with anhydrous formic acid gave light yellow needles of N-formyl derivative (IV) of the amino compound.

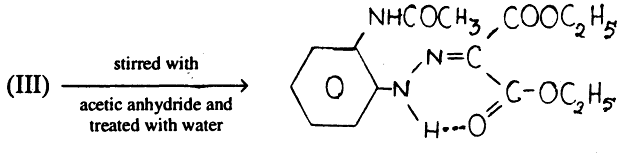


(III) (IV)

The characteristic IR absorption is in confirmity with the structure IV. Bands at 3200 cm^{-1} (m) and 3450 cm^{-1} (b) are due to NH stretching vibrations.[2,4] In addition it also gave absorption at 1720 cm^{-1} (m), 1660 cm^{-1} (s) and 1600 cm^{-1} (s) for >C=O (aldehydic), >C=O (ester) and N=C stretching vibrations.[2,4]

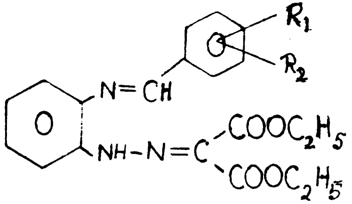
Single resonances at δ 12.67 and δ 10.1 in ^{1}H nmr are due to single NH (chelated) proton and protons of NH group attached to the aldehydic group. Four aromatic protons in the form of multiplets[7,8] showed resonance at δ 7.2; six ester methyl protons and four ester methylene protons appeared as triplet and quartet respectively at δ 1.3 and 4.3 and single aldehydic proton was at δ 8.3 as a singlet.[7,8]

The pale yellow product (V), m.p. 130–131°C (yield 50%) from the reaction of III with acetic anhydride showed IR bands at 3140 cm^{-1} (m) and 3560 cm^{-1} (s) for N—H chelated and free N—H stretching vibrations respectively.[2,4] Three strong bands at 1700 cm^{-1}, 1650 cm^{-1} and 1600 cm^{-1} can be assigned as a ν(C=O) (ester), νC=O (ester, H-bonded) respectively.[2,4]



(V)

TABLE-1
PHYSICAL CONSTANTS AND ANALYTICAL DATA OF ANILS



Compund	Colour	m.p. (°C)	Yield (%)	Molecular formula	Analytical data, found (calcd.) %		
					C	H	N
(a) $R_1 = p$-Cl, $R_2 = H$	deep yellow	210	70	$C_{20}H_{20}N_3O_4Cl$	59.73 (59.77)	4.90 (4.98)	10.02 (10.46)
(b) $R_1 = p$-NO_2, $R_2 = H$	yellow	233	55	$C_{20}H_{20}N_4O_6$	58.20 (58.25)	4.05 (4.85)	13.02 (13.59)
(c) $R_1 = p$-OCH_3, $R_2 = H$	light yellow	253	65	$C_{21}H_{23}N_3O_5$	63.20 (63.47)	5.30 (5.79)	10.40 (10.57)
(d) $R_1 = m$-NO_2, $R_2 = H$	light yellow	243	50	$C_{20}H_{20}N_4O_8$	53.01 (54.50)	4.55 (4.50)	12.10 (12.61)
(e) $R_1 = 2$-Cl, $R_2 = 5$-NO_2	deep yellow	234	60	$C_{20}H_{19}N_4O_6Cl$	53.04 (53.75)	4.21 (4.25)	12.50 (12.54)
(f) $R_1 = p$-N-$(CH_3)_2$, $R_2 = H$	chocolate brown	60	75	$C_{22}H_{26}N_4O_4$	64.05 (64.39)	6.20 (6.34)	13.05 (13.65)
(g) {R_1, $R_2 = m$-, p-O-CH_2-O- (piperonal)	yellow needles	165	50	$C_{21}H_{21}N_3O_6$	60.13 (61.31)	4.85 (5.10)	10.59 (10.21)
(h) $R_1 = m$-OCH_3, $R_2 = p$-OCH_3	yellow	180	50	$C_{21}H_{20}N_3O_6$	61.04 (61.46)	4.80 (4.87)	10.10 (10.24)

^{1}H NMR spectra of compound V revealed resonance at δ 12.2 (characteristic of H-bonded proton) and at δ 9.3 (NH of $NHCOCH_3$) as a singlet.[7, 8] Indistinguishable ester methylene (four) proton and methyl (six) proton signals were obtained at δ 4.09 and 1.26 as quartet and triplet respectively.[7, 8] Four aromatic protons in the form of multiplets showed resonance at δ 6.76. Three methyl protons of acetyl group showed resonance at δ 2.13.[7, 8] On these evidences the product were characterised as N-acetyl derivative (V) of compound III.

The compound III, on reaction with benzoic anhydride in the same manner, affords yellow coloured N-benzoyl derivative (m.p. 120°C, yield 50%) of the compound III. IR absorption at 3250 (b) cm^{-1}, 3460–3400 (b) cm^{-1}, 1720 (s) cm^{-1}, 1665 (m) cm^{-1} and 1605 (m) cm^{-1} evidently due to ν(N—H) (chelated), ν(N—H) (free), ν(C=O) (ester), ν(C=O) and ν(N=C) vibrations.[2, 4]

In the same compound III, on reaction with phthalic anhydride, gave very light yellow needles of phthaloyl derivative of compound III (m.p. 215°C, yield 60%) which showed the usual bands at 3240 cm^{-1} (b) and 3500 cm^{-1} (b) for chelated N—H and free N—H groups. The bands at 1795, 1730, 1685 and 1635 cm^{-1} are assignable to four C=O groups and 1610 cm^{-1} (s) for N=C.[2, 4]

Similar observations were made in the case of condensation products of compound III with different aldehydes. Compound III, when refluxed with an aldehyde (substituted benzaldehyde) in acetic acid/ethanol gave yellow crystals of condensed products, the identities of which were established by IR spectral studies.

The physical constant and elemental analysis of all the above condensed products (anils) are listed in Table-1. In IR spectra, the bands at around 315 ± 50 cm^{-1} is obviously due to ν(N—H) vibration. The two strong bands at around 1680 cm^{-1} and 1620 ± 20 cm^{-1} can be attributed to two different types of >C=O group. The lowering of two >C=O stretching frequencies are due to α,β-unsaturation in the former and α,β-unsaturation and H-bonding in the latter.[2, 4, 9, 10]

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