

Research Paper :

Catalytic transfer hydrogenation studies on Arylhydrazones

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ABSTRACT

The catalytic transfer hydrogenation studies on several arylhydrazones, prepared by coupling aryl diazonium salts with diethylmalonate and acetyl acetone have been carried out. It has been found that even under a variety of reaction conditions the reduction of diethyl mesoxalate-2-o-nitrophenylhydrazone or pentane-2,3,4- trioxo-3-o-nitrophenylhydrazone in anhydrous formic acid as a solvent and as a hydrogen donor with 10 per cent pd-C as a catalyst produces the N-formyl derivative of the free amino compound.

KEY WORDS : Catalytic Transfer hydrogenation studies, N- formyl derivative

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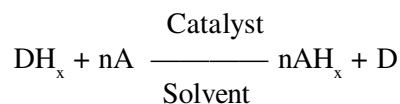
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The synthetically and industrially important reduction of nitro compounds has been effected in many ways¹⁻³ (Entwistley *et al.*, 1977, Coutts and Edwards, 1966 and Rylander, 1970). The reduction of nitro group attached to the aromatic nucleus of complex arylhydrazones (I) has been accomplished by various research groups⁴⁻⁶ (Cadagon *et al.*, 1970, Campbell and Rees, 1969 and Rissi *et al.*, 1968) . During the present course of investigation to design new synthetic strategies to different benzofused heterocyclic compounds⁷ (Selvi and Perumal, 2002), an attempt was made to reduce the hydrazones (I) by catalytic transfer hydrogenation. But contrary to the expectations, the N-formyl derivative of free amino compound⁸ (Prasad and Singh, 2004) was furnished. Its broad scope as well as the easy access to N-formyl

derivatives should make this methodology widely applicable in organic synthesis.

Catalytic transfer reductions are a considerable technical improvement over rather messy traditional reduction with metal and acid and appear to be selective than regular catalytic hydrogenation⁹ (Braude *et al.*, 1954).

It is the reduction of an organic compound by use of a hydrogen donor in the presence of a catalyst. The reaction can be generalised as follows:

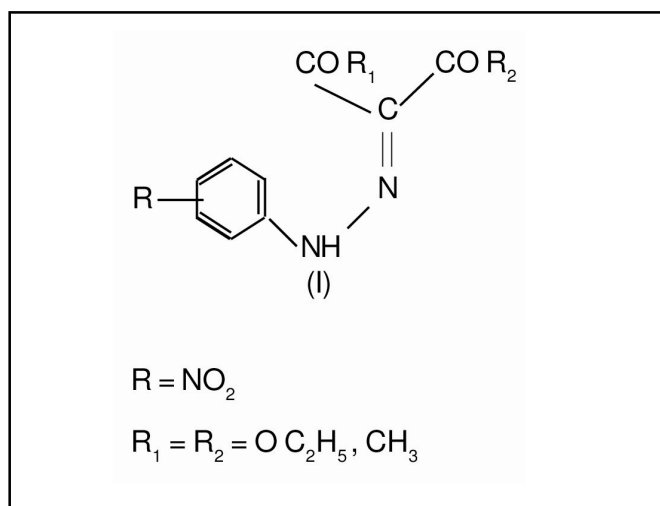


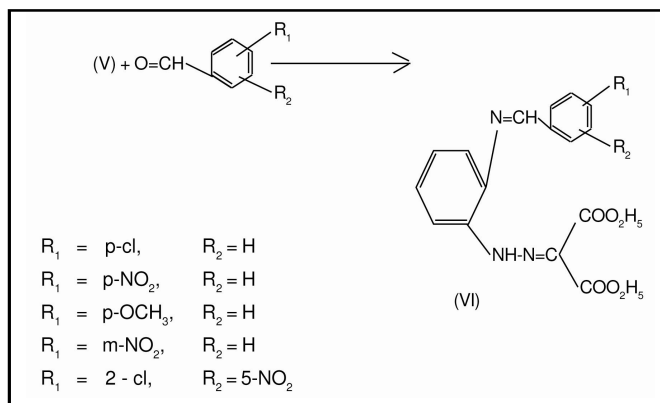
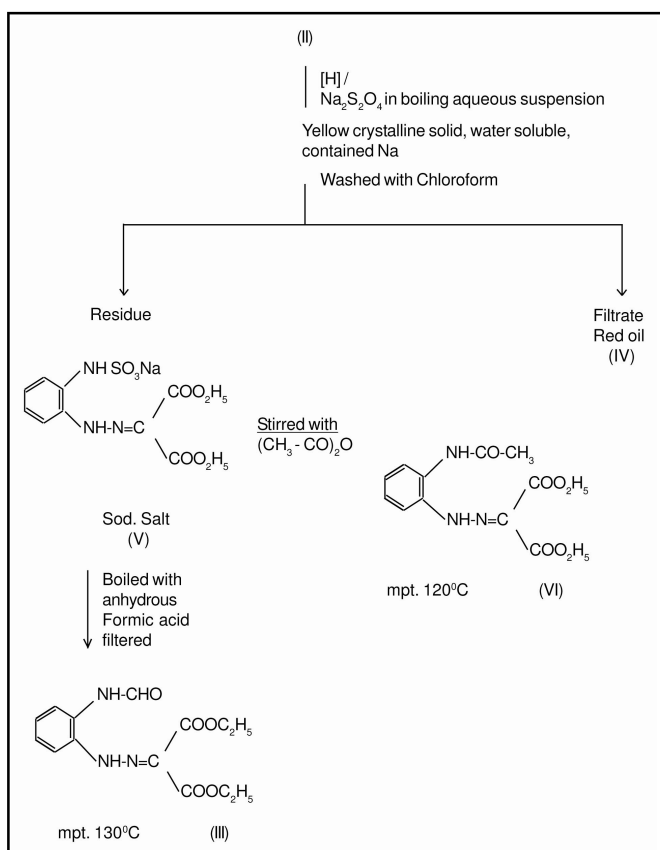
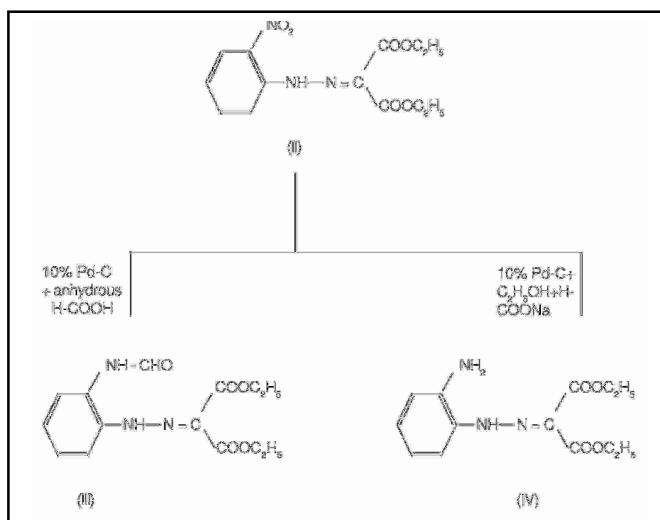
The donor compound DH_x can be any organic compound whose oxidation potential is sufficiently low so that hydrogen transfer can occur under mild conditions.

The early pioneering work by Braude⁹ was largely ingored because of poor yields and long reaction times, but the situation has changed considerably following the appearance of a stimulating review and the introduction of greater catalyst loadings and different hydrogen donors.

The reduction of diethylmesoxalate-2-o-nitrophenylhydrazone (II) in anhydrous formic acid as a solvent and as a hydrogen donor with 10 per cent Pd-C produced the N- formyl derivative of the free amino compound (III). By using ethanol as a solvent and sodium formate as a hydrogen donor, the free amino compound (IV) was obtained as a red oil.

The compounds (III) and (IV) were the same

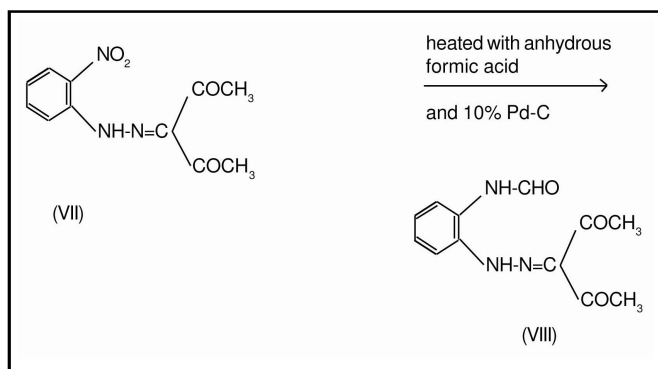




compounds as confirmed by TLC and by reduction of (II) with Na₂S₂O₄ in our laboratory¹⁰ (Prasad, 1995) by the following sequence of reactions.

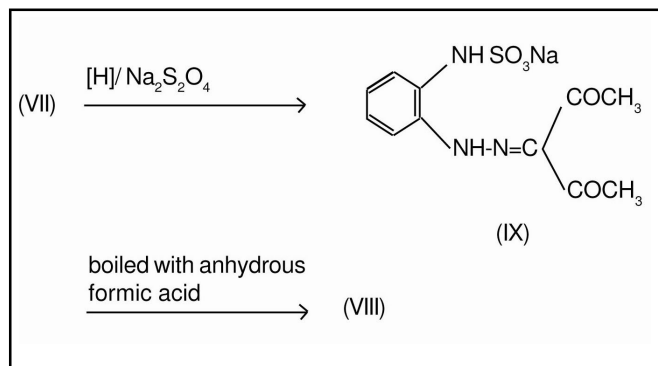
Like wise the CTH was carried out on pentane-2,3,4-trioxo-3-o-nitrophenylhydrazone by using 10 per cent Pd-C as a catalyst, various H-donors and solvents.

The results are summarised below in the present communication.



The compound VII, on reduction with 10 per cent Pd-C by using anhydrous formic acid both as a solvent and as a H donor gave a dark orange semi-solid. This, on crystallisation with aqueous ethanol, gave red crystals of N-formyl derivative (VIII).

The identity of the compound (VIII) was examined on the basis of elemental analysis, IR, mass and ¹H nmr spectral measurements.



Further the identity of the compound was confirmed by comparing an authentic sample of the pure N-formyl derivative formed by the sodium dithionite reduction of the hydrazide (VII) followed by treatment with hot anhydrous formic acid.

EXPERIMENTAL METHODOLOGY

Melting points were measured in open capillaries and are uncorrected. Infrared spectra were recorded on Perkin-Elmer spectrometer using KBr pellets. N.M.R. spectra were recorded on Ft-80A and Bruker WM-400

Table 1 : H. donors and solvent

Sr. No.	Name of solvent	H donor	Name of the product	Colour	% of yield
1.	Anhydrous formic acid	Formic acid	N-formyl derivative m.pt. 200 ^o C	Red	70
2.	Petroleum ether (60 ^o -80 ^o)	Sodium formate	Free amino compound, m.pt 117 ^o C	Red	60
3.	Ethylalcohol and acetic acid	Sodium formate	Free amino compound 117 ^o C	Deep red	50
4.	Ethyl alcohol	Sodium formate	Free amino compound	Light red	50
5.	Isopropyl alcohol (R.T.)	Isopropyl alcohol	Noreaction	-	-
6.	Acetic acid (R.T)	Acetic acid	Noreaction	-	-

model using TMS as the internal standard. Mass spectra were recorded on MASPEC system spectrometer. Analytical thin layer chromatography was performed on precoated sheets of silica GelG of 0.25mm thickness.

The arylhydrazone was prepared by the method available in literature.

– Preparation of N-formyl derivative of diethylmesoxalate-2-o-amino phenylhydrazone (III)- The compound (I) (600mg) dissolved in anhydrous formic acid (20ml) was heated on a water bath for one minute and 10 per cent Pd-C (300mg) was added portion wise with occasional stirring. The contents were heated again for 4 minutes and filtrate hot. The colour of the filtrate was light yellow on evaporation of the solvent, a yellow crystalline solid (400g, 66%) was obtained which was recrystallised from aqueous ethanol. This gave one spot on the TLC m.p.t. 120^oC.

– Preparation of Pentane - 2,3,4-trioxo-3-o nitrophenylhydrazone (VII).

O-Nitroniline (13.8 gm, 0.1 mole) was diazotised and coupled with acetylacetone (10ml, 0.1 mole) by the method indicated above. Pentane-2,3,4-trioxo-3-o-nitrophenylhydrazone was obtained as yellow plates (from acetic acid) in 95 per cent yield, m.pt. 174^oC (Literature 173^oC).

– Preparation of N-formyl derivative of Pentane-2,3,4- trioxo-3-o-amino phenylhydrazone (VIII).

The compound (750 mg) was dissolved in anhydrous formic acid (15ml) and heated in a boiling water bath for 1 minute, added portionwise 10 per cent Pd-C (300mg) with occasional stirring and again heated for about 3 minutes and filtered hot. A dark orange red semi solid was obtained. This, on crystallisation with aqueous ethanol produced a red crystalline solid which gave one single spot at the base on TLC in benzene containing ethanol (3 drops) yield 70 per cent, mpt. 200^oC.

EXPERIMENTAL FINDINGS AND ANALYSIS

Analytical and spectral data of the product obtained after treatment of (I) with anhydrous formic acid, 10 per cent Pd-C are as follows:

Elemental analysis:

Found C = 54.71% N = 13.02% H = 5.51%
 Calculated for C = 54.72% N = 13.06% H = 5.53%
 (C₁₄H₁₇N₃O₅)
 IR spectrum (In Nujol)
 3200 cm⁻¹ (s, NHStr), 2850 Cm⁻¹ (s, C-H Str)
 1750 cm⁻¹ (s, ester) C=O), 1660 Cm⁻¹ (s, C=NStr)
 1450 cm⁻¹ (b, N=C Str.)

¹Hnmr spectral data:

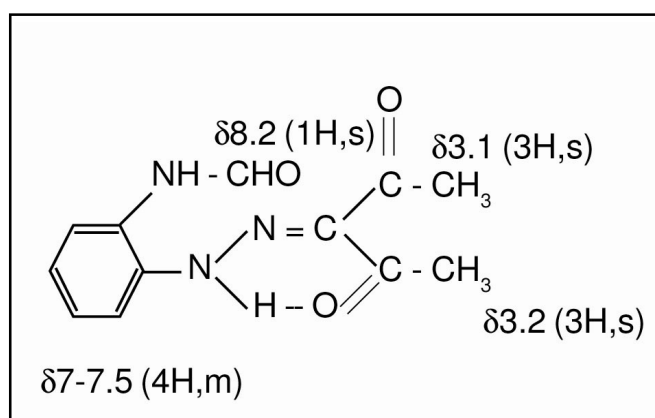
d_{8.5} (S, 1H) NH bonded or (s, 1H) aldehydic proton.
 d_{1.35} (q, 6H) estermethyl, d 4.3 (q, 4H) ester methylene
 d_{7.73} (m, 4H) aromatic protons
 Reduction of VII with anhydrous formic acid and 10% Pd-C.

Elemental analysis:

Found C=58% H=5.1% N=17.05%
 Calculated for C=58.29% H=5.26% N=17.06%
 (C₁₂H₁₃N₃O₃)

IR spectrum:

3300 cm⁻¹ (m, N-H str. of NH-CHO), 2900 cm⁻¹ (sh, NH-N=C unchelated str.), 2600 Cm⁻¹ (w, NH of chelated
 NH-N=C Str), 1600 Cm⁻¹ (s) 1500 cm⁻¹ (s)
 (V_{C=O}, V_{O-H} banded) and 1450 Cm⁻¹ (V_{N=C} str)



¹H NMR Spectrum:

$\delta_{3.01}$ (3H,s), $\delta_{3.2}$ (3H,s) methyl protons,
 $\delta_{7-7.5}$ (4H,m) aromatic protons, $\delta_{8.2}$ (1H,s) aldehydic proton.

The ¹H nmr spectrum showed resonances at $\delta_{3.01}$ and $\delta_{3.2}$ as a singlet which were assigned six methyl protons. Four aromatic protons in the form of multiplets showed resonance at $\delta_{7-7.5}$. The resonance at 8.2 was assigned to the aldehydic proton. The resonance of NH proton of formamido gr. as a singlet was not visible in the spectrum which meant that it was hidden under the peak of the aldehydic proton. Further the resonance of NH proton which is H bonded intramolecularly to Ketomethyl was not observed as the ¹Hnmr spectrum was not run upto δ_{15} .

Mass spectrum:

The mass spectrum of the compound (VIII) was examined and showed that the M⁺ appears at 247. The observed mass of M⁺ was found to be in agreement confirming the molecular formula C₁₂H₁₃N₃O₃.

The formation of the base peak at m/e 43 may be explained by fragmentation from the far end of the molecule containing COCH₃ functional group. The assignment is further substantiated by the formation of fragments at m/e 204, m/e 134 and m/e 106.

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