

An Efficient Reduction of Quinones by Formate-Palladium/Carbon System¶

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Ammonium formate in presence of palladium-carbon is an efficient system for catalytic transfer hydrogenation of several functional groups under mild conditions. However, this system was not found effective for reduction of quinones to hydroquinones, although reduction could be effected with phosphinic acid, phosphinates or cyclohexene as donors. A reexamination of this reaction suggested that formates were good hydrogen donors in this reduction but the reaction was inhibited due to quinhydrone formation. A simple expedient of maintaining low concentration of quinone during catalytic transfer hydrogenation reduction gave excellent yields of the hydroquinone. Compared to formates, formic acid was found to be a poor hydrogen donor.

Key Words: Catalytic transfer hydrogenation, Reduction, Ammonium formate, Reduction of quinones.

INTRODUCTION

Reduction of quinones to hydroquinones is extensively used in industry and in research. A variety of methods, electrolytic, dissolving metals, reducing reagents and catalytic hydrogenation besides other methods achieve this reduction¹. Catalytic hydrogenation is the most cost effective and "clean" method for quinone reduction in industrial scale. In the laboratory use of highly inflammable hydrogen gas is less preferred. Catalytic transfer hydrogenation (CTH) reductions are increasingly becoming popular as safe hydrogenation/reduction methods operable under mild conditions. Catalytic transfer hydrogenation reductions can be done under heterogeneous as well as homogeneous conditions. High degree of enantio-selectivity has also been achieved in the reduction of pro-chiral substrates. The methods have been reviewed²⁻⁴. In heterogeneous CTH, Pd-carbon catalyst is the most popular catalyst.

The hydrogen donors include cyclo-olefins, hydroaromatics, hydride donors, phosphinic acid, phosphinates, formic acid and formate salts besides several others. Formates are becoming increasingly popular due to low cost, easy accessibility, and good donor efficiency for a wide variety of functional group reductions. The subject has been reviewed⁵. Catalytic transfer hydrogenation reduction of quinones

¶Dedicated to the memory of Late Dr. G.C. Joshi.

has been reported⁶ in presence of Pd-carbon catalyst in benzene, ethanol or tetrahydrofuran solvent. Phosphinic acid, sodium phosphinate or cyclohexene were found as good hydrogen donors. However formic acid and its salts were found to be ineffective⁶. In view of the efficient reduction of a wide variety of substrates with ammonium formate donor under CTH conditions it was desirable to re-examine its efficiency in the reduction of quinones.

EXPERIMENTAL

All chemicals and solvents were A.R. or C.P. grade. Quinones used as substrates in catalytic transfer hydrogenation (CTH) reduction study were synthesized from precursor hydroquinones or phenols. Quinone and their reduction products were characterized by their physical properties, IR and NMR.

IR were run in Perkin-Elmer FTIR 1760X instrument. ¹H NMR spectra were run in JEOL JNM FX-100 instrument in CDCl₃ solution with TMS as internal standard. Thin layer chromatography was done on silica gel plates and spots were developed by iodine vapours. Hydroquinone in the reduction product of 1,4-benzoquinone was estimated by bromometric titration of aqueous extract.

General procedure: Catalytic transfer hydrogenation reduction of quinones with ammonium formate donor.

Method A: Two examples of this method are described below:

Reduction of 1,4-benzoquinone: In a two neck round bottom flask fitted with a condenser, a nitrogen purge tube and a magnetic bar were taken 10 mL of methanol benzene mixture (70:30) and 0.93 g ammonium formate dissolved in 1 mL water. Pd-carbon (10 %) 100 mg was added after stirring for 15 min under nitrogen followed by 1.08 g (10 mmol) *p*-benzoquinone (after 30 s). The mixture was stirred for 4 h at room temperature. The catalyst was removed by filtration through a sintered disk under suction and the filtrate evaporated under reduced pressure to give 1.15 g crude solid product. The residue was extracted with water and the extract (pink solution) taken in a standard volumetric flask. An aliquot of this solution was titrated against standard bromide-bromate solution using ASTM bromometric estimation procedure⁷ of modified hydroquinone estimation method⁸. Amount of bromine consumed is directly proportional to hydroquinone present which was found to be 43 % by weight of *p*-benzoquinone taken.

Reduction of 2,5-di-*t*-butyl-1,4-benzoquinone: In the reaction assembly described earlier were taken 300 mg (4.5 mmol) of ammonium formate and 15 mL methanol. 50 mg of Pd-C catalyst was added while stirring under nitrogen followed by 660 mg (3 mmol) of 2,5-di-*t*-butyl-1,4-benzoquinone. Stirring under nitrogen was done for 0.5 h at room temperature and the reaction mixture was filtered to remove the catalyst. The filtrate was concentrated by evaporating the solvent and residue triturated with water (3 mL) and extracted with ether (3 × 10 mL). The combined ether extracts were washed with saturated brine, dried over Na₂SO₄, filtered and solvent evaporated to give 500 mg (76 %) of crude product. Recrystallization

from benzene-hexane gave 458 mg (69 %) of white crystalline solid, m.p. 216-217 °C (Lit.⁹ 217-219 °C). Characterized by FTIR and ¹H NMR.

Method B: The experimental set up was similar as for direct addition method described earlier except that the quinone was added slowly as a solution in the reaction solvent to the stirred mixture of the hydrogen donor and catalyst in the same solvent. The reduction of 1,4-benzoquinone is described as an example.

Methanol (20 mL) was taken in the reaction flask along with 950 mg (15 mmol) of ammonium formate under nitrogen. 10 % Pd-C catalyst (100 mg) was added and a solution of 1.08 g (10 mmol) of 1,4-benzoquinone in 20 mL benzene was added after 30 s dropwise with stirring under nitrogen at room temperature in 10 min. After another 10 min of stirring the reaction mixture was filtered and worked up as in method A. Bromometric analysis gave 92.0 % hydroquinone.

Method C: The reduction of trimethyl-1,4-benzoquinone is described as an example.

A solution of 750 mg (5 mmol) trimethyl benzoquinone in 15 mL methanol was added dropwise to a refluxing mixture of 475 mg (7.5 mmol) ammonium formate and 100 mg 10 % Pd-C in 15 mL methanol under nitrogen (30 s after addition of catalyst). Total addition time 5 min. The reaction was cooled after 5 min and filtered to remove the catalyst.

Work up of the filtrate as for 2,5-di-*t*-butyl-1,4-benzoquinone gave 706 mg (93 %) of the recrystallized product, m.p. 166-167 °C (Lit.¹⁰ 168-170 °C), identical with authentic sample of trimethyl-1,4-hydroquinone (TLC).

RESULTS AND DISCUSSION

Catalytic hydrogen transfer using formic acid or formate salts using Pd-carbon catalyst is believed to follow the following mechanism:



Hydrogen may be either adsorbed on palladium metal or present as palladium hydride (Pd-H) species.

It has been found by several workers that formates are better donors than formic acid itself. A definite study¹¹ offers explanation for this observation. The observation by Entwistle *et al.*⁶ that ammonium formate Pd-C system does not reduce quinones to hydroquinones was rather in contrast to other related reductions in which ammonium formate has been shown to be efficient donor⁶. We examined the reduction of 1,4-benzoquinone and 4 other alkyl substituted 1,4-quinones with ammonium formate as donor and Pd-carbon catalyst in methanol at room temperature. Benzoquinone itself gave low yields of 1,4-hydroquinone. However yields were fair to good with

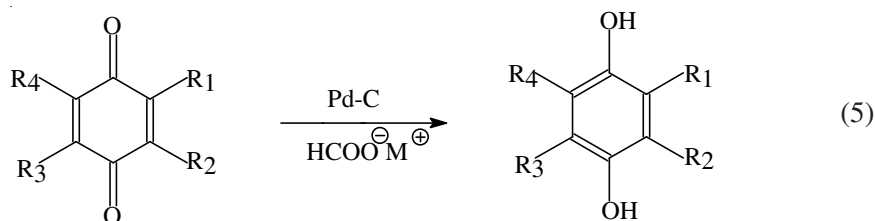
alkyl substituted benzoquinones and diphenoquinone. Reduction was studied under different conditions using ammonium formate as donor and also with two other formates and formic acid as donor. Results are given in Table-1.

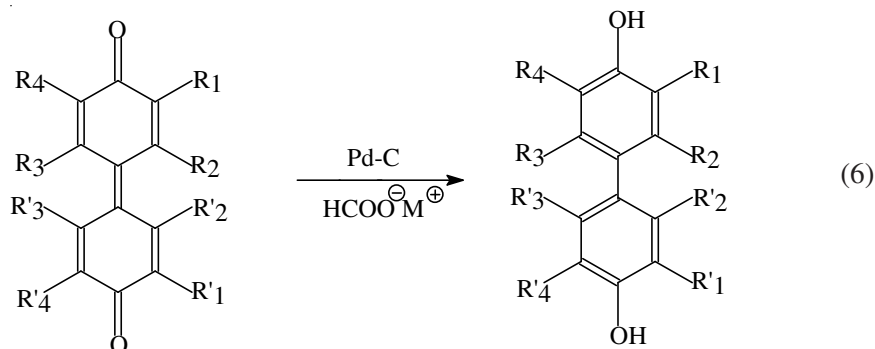
TABLE-1
CATALYTIC TRANSFER HYDROGENATION REDUCTION OF QUINONES

Quinone	Donor	Solvent [#] (temp.)	Method*	Hydroquinone yield (wt %)	m.p. °C (Lit. ^{ref} m.p. °C)
a	Ammonium formate	MeOH-benz. (70:30), RT	A	43 (Titration)	Not isolated
a	-do	-do- (1:1), RT	B	92 (-do-)	-do-
a	-do-	-do- (1:1), Reflux	C	98.5 (-do-)	-do-
a	Potassium formate	-do-	B	98.2 (-do-) (2-3 min)	-do-
a	Triethylammonium formate	-do-	B	99.5 (-do-)	-do-
a	Formic acid	-do-	B	42.3 (-do-)	-do-
b	Ammonium formate	MeOH (RT)	A	22 (Isolated cryst.)	125-126 Lit. ¹² 126-127
b	-do-	-do-(RT)	B	54.8 (-do-)	125-126 Lit. ¹² 126-127
b	-do-	-do-(reflux)	C	81.0 (-do-)	125-126 Lit. ¹² 126-127
c	-do-	THF (RT)	A	67.8 (-do-)	167-168 Lit. ¹⁰ 168-170
c	-do-	MeOH (reflux)	C	93 (-do-)	167-168 Lit. ¹⁰ 68-170
d	-do-	MeOH (RT)	A	76 (-do-)	95-96 L ¹³ 94-96
e	-do-	MeOH (RT)	A	76 (-do-)	216-217 Lit. ⁹ 217-219
f	-do-	THF	A	95 (Isolated crude)	184-185 Lit. ¹⁴ 185

a: 1,4-Benzoquinone; b: Methyl-1,4-benzoquinone; c: Trimethyl-1,4-benzoquinone; d: 2,6-Di-*t*-butyl-1,4-benzoquinone; e: 2,5-Di-*t*-butyl-1,4-benzoquinone; f: 3,3',5,5'-tetra-*t*-butyl-diphenoquinone; *See experimental section for details; #MeOH= Methyl alcohol, RT = Room temp. *ca.* 25 °C, THF = Tetrahydrofuran.

Reduction of 1,4-benzoquinone would then be straight forward 1,4-addition:





Conclusion

Ammonium formate is an efficient hydrogen donor in CTH reduction of 1,4-quinones to corresponding hydroquinones using Pd-C catalyst. Good to very good yields of hydroquinones are obtained by a simple procedure that ensures low concentration of quinone during the reaction. Further increase in yield can be obtained with much shorter reaction times at reflux temperatures of methanol. Very good yields were obtained in the reduction of highly hindered quinones and diphenoquinone. As expected the formates are superior donors in this reduction compared to formic acid.

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