N-Hydroxyphthalimide as an Effective Mediator for the Oxidation of Alcohols by Electrolysis

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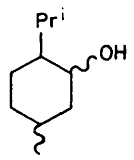
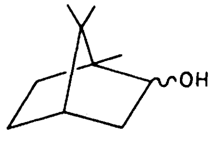
N-Hydroxyphthalimide is shown to be an effective electron carrier in the electrochemical oxidation of alcohols to the corresponding carbonyl compounds.

Electrochemical oxidation of alcohols to the corresponding carbonyl compounds has been successfully achieved by making use of electron carriers (mediators), such as halogen ions,[1] and organic compounds with[2] or without[3] photoexcitation. In our study on the anodic oxidation of hydroxamic acids, we found that the oxidation of *N*-hydroxyphthalimide (NHPI) was not a two-electron oxidation unlike those observed for other hydroxamic acids,[4] and most of the starting NHPI was recovered from the solution after the passage of two Faradays (F) of electricity per mole of compound. During the electro-



(1)



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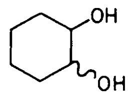

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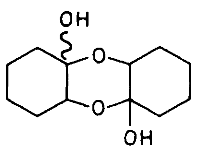

(4)

Table 1. Yield of ketones from secondary alcohols.

Alcohol	Yield (%) of ketone	NHPI recovered (%)
Ph_2CHOH	96	90
PhCH(Me)OH	87	74
Cyclohexanol	94	60
(1)	58	25
(2)	91	66
MeCH(OH)Et	88	84
MeCH(OH)-CH(OH)Me	59[a] (diketone) 9[a] (hydroxyketone)	11
(3)	30[b] [of (4)]	12

[a] 3.9 F/mol based on the alcohol. [b] 1.7 F/mol based on the alcohol.

lysis the solution became yellow, but the colour disappeared on addition of an alcohol. The results suggest that the oxidation intermediate of NHPI will work as an electron carrier to oxidize alcohols. Further investigation showed NHPI to be an effective organic electron carrier in the electrochemical oxidation of alcohols; *i.e.*, NHPI has a low oxidation potential in the presence of added base and a high number of turnovers and a high current efficiency without the assistance of photo-excitation.[2] NHPI has an oxidation peak at 1.44 V *vs.* S.C.E. (saturated calomel electrode) at a glassy-carbon electrode in acetonitrile containing 0.1 M $NaClO_4$, and in the presence of pyridine an extra peak[4,5] develops at 0.85 V.

The oxidation of the secondary alcohols was performed as follows: 5 mM of NHPI, 20 mM of alcohol, and 5 mM of pyridine were dissolved in 40 ml of acetonitrile containing 0.1 M $NaClO_4$ in an undivided cell. The electrodes used were a glassy-carbon plate anode (50 × 15 × 2 mm), a glassy-carbon cylinder cathode (45 × 3 mm ϕ), and an S.C.E. reference electrode. 2 F of electricity per mole of alcohol were passed at an anode potential of 0.85 V. The products were confirmed as carbonyl compounds by forming their 2,4-dinitrophenylhydrazone derivatives and their quantities estimated by g.c. of the solution after electrolysis. (Table 1).

In the case of the oxidation of benzhydrol even 0.05 mol. equiv. of NHPI relative to the alcohol gave an almost quantitative yield of benzophenone, and a water content up to 30% v/v did not affect the yield of the ketone.

Table 2. Yields of aldehydes from primary alcohols.

Alcohol	Solvent	$E_{app.}$[a]	Yield[b] of aldehyde	NHPI recovered (%)
$PhCH_2OH$	MeCN	0.85	49	43
EtOH	EtOH	1.00	93	46
Pr^nOH	Pr^nOH[c]	1.40	17	13
Bu^nOH	Bu^nOH[c]	1.40	9	14

[a] Applied potential, V *vs.* S.C.E. [b] Current yield, 16 F/mol based on NHPI (5 mM). [c] Lutidinium perchlorate was used as a supporting electrolyte.

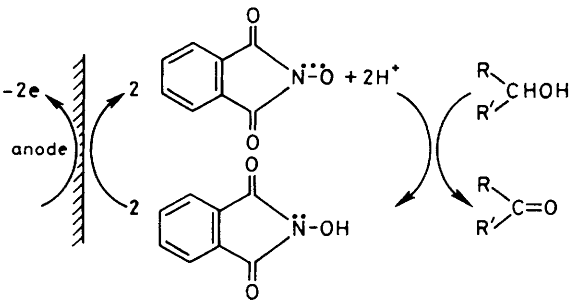

Figure 1

In the oxidation of primary alcohols, the yields of the products were rather poor except for ethanol (Table 2) even when the electrolysis was performed in the alcohol as a solvent.

The esters reported as the main product from the oxidation by other similar methods[1a] were also obtained in the present method, but only in low or negligible yields.

These results show that NHPI is a good mediator with high current efficiency and turnover number for the oxidation of alcohols (except for n-propanol and n-butanol) to the corresponding carbonyl compounds.

The oxidation process can be depicted as in Figure 1. The phthalimide N-oxyl is efficient for oxidation of secondary alcohols and at room temperature the reaction goes to completion in reasonable time. The analogous hydroxyimide, *N*-hydroxysuccinimide, is much less efficient for the oxidation of these alcohols.

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