Communications to the Editor

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ANODIC OXIDATION OF COMPOUNDS HAVING BENZYLIC OR ALLYLIC CARBON AND α-CARBON TO HETERO ATOM USING N-HYDROXYPHTHALIMIDE AS A MEDIATOR

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Benzylic, allylic carbons and the carbon α to hetero atoms are electrochemically oxidized to the corresponding carbonyl group in the presence of N-hydroxyphthalimide under mild conditions.

KEYWORDS——anodic oxidation; mediator; N-hydroxyphthalimide; benzylic carbon; allylic carbon; ether; sulfide; amide

N-Hydroxyphthalimide (NHPI) is known to be an effective electron carrier for the electrochemical oxidation of alcohols to the corresponding carbonyl compounds under mild condition.[1) Under an assumed mechanism of the reaction, NHPI was thought to be a versatile catalyst for the oxidation of various organic compounds by electrolysis.

The present communication shows by new examples tested to date that the method is promising in the field of organic reactions. Procedures used are essentially the same as described before.[1) Equimolar amounts of pyridine against NHPI, and about twice molar amounts of pyridine against substrate are used in the electrolysis in an undivided cell and in a divided cell, respectively. Initially the current for the electrolysis in the divided cell was much higher than that in an undivided cell because of the larger amount of pyridine, and the time required for the electrolysis in the divided cell was considerably shorter than that in the undivided cell. The yields of oxidation products in the two methods, however, were not significantly different. Identification of most of the products and the NHPI recovered were performed by the use of GLC or HPLC. Comparisons were made with authentic samples. **2**, **6**, and **7** isolated from the solution after electrolysis showed spectroscopic (IR and ^{1}H NMR) properties in agreement with the assigned structures and correct elemental analysis.

Oxidation of benzyl alkyl ethers gave the corresponding esters in which the benzyl carbon was oxidized. p-MeO-benzyl-n-octyl ether oxidized in a nitrogen atmosphere gave p-MeO-bezaldehyde and n-octyl alcohol as the main products as described for the debenzylation from the protected alcohols.2) The dependence of the yields of benzoates on the amount of electricity consumed and the effect of atmosphere suggest that the esters are produced via participation of molecular oxygen in the reaction of the carbon radical at the benzyl position. Since esters are easily hydrolysed to give alcohols, the present method also provides a mild debenzylation reaction for the protected alcohols.

α-Carbon to the oxygen in cyclic ether was similarly oxidized to give lactone. Cyclic sulfide was also oxidized to give thiolactone and a lesser amount of sulfoxide. The benzylic and allylic positions were attacked to give carbonyl compounds. Many oxidations in the present study are similar to those observed for autoxidation,3) but the present method does not require special conditions other than NHPI, photo excitation; high pressure and elevated temperature, and the conditions are mild.

Table. Products from Electrolysis a)

Compds.	F/mol b)	Products	Yield(%) c)	NHPI recovered(%)
$PhCH_2OMe$	1.8 d)	$PhCO_2Me$	84	50
$PhCH_2O\text{-}Amyl^i$	2.0 d)	$PhCO_2\text{-}Amyl^i$	65	65
		PhCHO	11	
$p\text{-}MeO\text{-}PhCH_2O\text{-}Octyl^n$	2.0 d)	$p\text{-}MeO\text{-}PhCO_2\text{-}Octyl^n$	84	47
	2.0 d,e)	$p\text{-}MeO\text{-}PhCO_2\text{-}Octyl^n$	9	69
		p-MeO-PhCHO	65	
		$Octyl^n\text{-}OH$	72	
(1) f)	2.0 g)	**(2)** f)	77	88
	2.5 g)	**(2)** f)	83	80
$PhCH_2Me$	2.0 g)	PhCOMe	80	39
$Ph(CH_2)_2Me$	1.7 g,h)	$PhCOCH_2Me$	64	14
Cyclohexene	1.5 g)	2-Cyclohexene-1-one	44	50
Tetraline	2.0 g)	α-Tetralone	68	36
Fluorene	0.7 g,h)	Fluorenone	17	trace
(3) i)	2.0 g)	**(4)** i)	72	33
(5) j)	2.0 d,k)	**(6)** j)	26	1)
		(7) j)	15	
(8) m)	1.7 g,h)	**(9)** m)	30	20
		(10) m)	20	
Tetrahydrofurane	0.67 g,n)	γ-Lactone	11	38

a) 5 mM of NHPI and 20 mM of compounds were used unless otherwise stated.

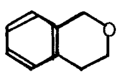
b) Electricity passed per mole of compounds.

c) See text. Based on compounds.

d) Electrolyzed in an undivided cell.

e) Electrolyzed in an atmosphere of nitrogen.

f) (1):



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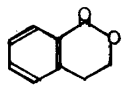
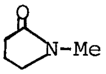


g) Electrolyzed in a divided cell.

h) Electrolysis did not proceed further.

i)

(3):



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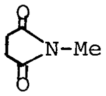
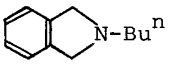


j) 10 mM of NHPI and 20 mM of 5 were used.

(5):



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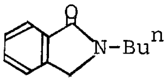

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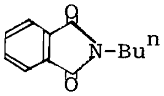
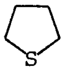


k) $Et(Bu^n)_3NBF_4$ was used as a supporting electrolyte.

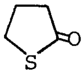
l) Not determined.

m)

(8):



(9):



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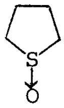

n) 5 mM of NHPI and 60 mM of tetrahydrofurane were used. Electrolysis was interrupted when the electricity consumption reached the value described.

REFERENCES AND NOTES

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