Tetrahedron Letters No. 2, pp 165 - 168.
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0040-4039/79/0108-0165$02.00/0

ELECTROCHEMICAL OXIDATION OF ALCOHOLS USING IODONIUM ION AS AN ELECTRON CARRIER[1]

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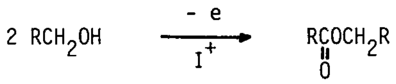
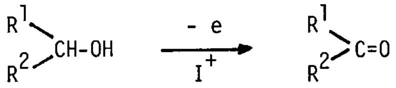
The electrochemical oxidation of alcohols has not satisfactorily been accomplished[2] because of their relatively high oxidation potentials.[3] We wish to report herein a simple and efficient electrochemical process for the oxidation of primary and secondary alcohols to the corresponding esters (eq. 1) and ketones (eq. 2), respectively, where an iodonium ion behaves as a catalytic electron carrier as shown in Figure 1.

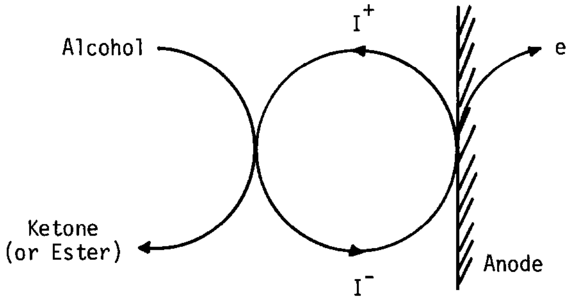


$$2\ RCH_2OH \xrightarrow[I^+]{-\ e} R\underset{O}{\underset{\|}{C}}OCH_2R$$ ··················(1)



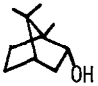
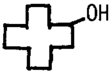
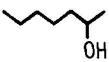
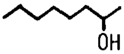
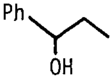
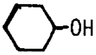
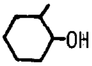
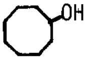
$$R^1R^2CH\text{-}OH \xrightarrow[I^+]{-\ e} R^1R^2C{=}O$$ ··················(2)

Figure 1



A general procedure is as follows. Into a cell equipped with platinum or carbon electrodes were put an aqueous solution of 2.49 g (0.015 mole) of potassium iodide in 15 ml of water and 0.06 mole of an alcohol.[4] When the alcohol is hardly soluble in water or is solid at room temperature, *t*-butanol and/or hexane are necessary as co-solvents. The cell was cooled with a water jacket and a constant current was passed through the two phase solution with vigorous stirring. After 4-15 *F*/mole of electricity was passed,[5] the organic layer was separated and the aqueous layer was extracted with three portions of ether. The combined organic and ethereal layers were washed with aqueous sodium thiosulfate. The products were isolated by distillation and identified by comparison with authentic samples. The results are listed in Table 1.

Table 1. Electrochemical Oxidation of Alcohols Using Iodonium Ion

Run	Alcohol	Alcohol/KI	Co-Solvents	Passed Electricity (*F*/mole)	Yield[a,b] of Ketone or Ester (%)
1.		4.0	*t*-BuOH/*n*-hexane	14	84 (93)[c]
2.		4.0	*t*-BuOH/*n*-hexane	15	83 (91)[c]
3.		4.0	*t*-BuOH	13	75 (89)[c]
4.		4.0	*t*-BuOH	10	84 (99)[c]
5.		10.0	*t*-BuOH	5.7	76 (92)[c]
6.		4.0	*t*-BuOH/*n*-hexane	12	79 (~100)[c]
7.		4.0	*t*-BuOH	8	60 (74)[c]
8.		4.0	*t*-BuOH/*n*-hexane	21	52 (57)[c]
9.		4.0	*t*-BuOH/*n*-hexane	12	59 (69)[c]
10.		4.0	none	11	72 (80)[d]
11.		10.0	none	4.7	83 (83)[d]
12.		4.0	*t*-BuOH	9	79 (83)[d]
13.		4.0	*t*-BuOH/*n*-hexane	7	84 (84)[d]

(a) Based on alcohol.

(b) Yields in parentheses are based on the consumed alcohol.

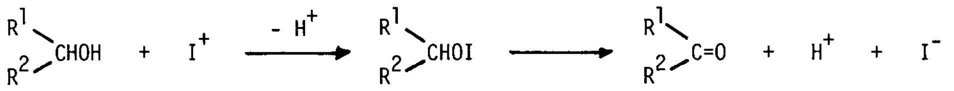
(c) Ketone.

(d) Ester.

One of the important characteristics of this new oxidation is that the reaction proceeds with a small equivalent of potassium iodide as shown in Table 1, and especially runs 5 and 11 clearly exemplify that the oxidation of alcohols can be achieved by only one-tenth equivalent of potassium iodide.

Although the detailed mechanism of the oxidation is not necessarily clear, iodonium ion generated by the electrooxidation of iodide ion seems to behave as the oxidizing agent[6] as shown in eq. 3 and eq. 4, since the anode potential (0.6-0.8 V *vs.* SCE) is sufficient for the oxidation of iodide ion.[7]

$$I^- \xrightarrow{-2e} I^+ \quad \cdots\cdots\cdots\cdots (3)$$

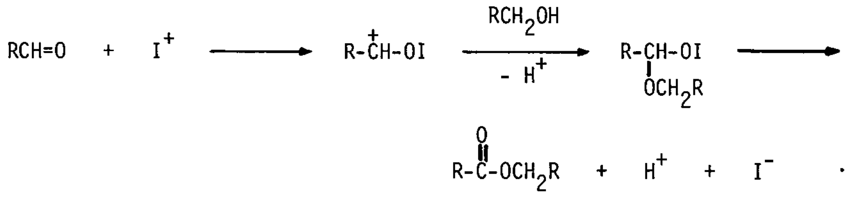


$$R^1R^2CHOH + I^+ \xrightarrow{-H^+} R^1R^2CHOI \longrightarrow R^1R^2C{=}O + H^+ + I^- \quad \cdots\cdots\cdots\cdots (4)$$

The iodide ion formed from the iodonium ion (eq. 4) is again oxidized at an anode to the iodonium ion, so that the function of the iodonium ion is some kind of catalytic oxidizing agent and, at the same time, an electron carrier.

Another remarkable characteristic of this anodic oxidation is that primary alcohols can be converted directly to esters (eqs. 5 and 6). The intermediary aldehydes were hardly isolated.

$$R\text{-}CH_2OH + I^+ \xrightarrow{-H^+} R\text{-}CH_2OI \longrightarrow R\text{-}CH{=}O + H^+ + I^- \quad \cdots\cdots\cdots\cdots (5)$$



$$RCH{=}O + I^+ \longrightarrow R\text{-}\overset{+}{C}H\text{-}OI \xrightarrow[-H^+]{RCH_2OH} R\text{-}\underset{OCH_2R}{\underset{|}{C}}H\text{-}OI \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2R + H^+ + I^- \quad \cdots\cdots\cdots\cdots (6)$$

This electrochemical method using iodonium ion as an electron carrier may possess high potentiality in organic synthesis, since it requires only a small equivalent of potassium iodide, whereas most of the hitherto known oxidations usually require more than one equivalent of oxidizing agents, which often give troublesome problems at the stage of working up.

Studies on the mechanism and the extention to the oxidation of other functional groups are in progress.

References and Notes

1. Electroorganic Chemistry. 37.
2. N. L. Weinberg, "Technique of Electroorganic Synthesis" Part I, p. 435, John Wiley & Sons, New York, 1974.
3. P. C. Scholl, *Tetrahedron*, **32**, 303 (1976).
4. Alcohols used in the present study are not miscible with water. Oxidation of alcohols miscible with water will be reported elsewhere.
5. Yields at the stage where 2 *F*/mole of electricity was passed were some 60 %, and the excess of electricity was consumed to increase the yields.
6. The chemical oxidation of alcohols using iodonium ion has been reported in
   (a) U. E. Diner, *J. Chem. Soc. (C)*, **1970**, 676 and
   (b) J. B. Chattopodhyaya and A. V. R. Rao, *Tetrahedron Lett.*, **1973**, 3735.
7. G. Dryhurst and P. J. Elving, *Anal. Chem.*, **39**, 606 (1967).

(Received in Japan 19 October 1978)