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Electroorganic Chemistry. XXVI.[1] Electrooxidation of Enamines, Haloolefins, and Enol Ethers

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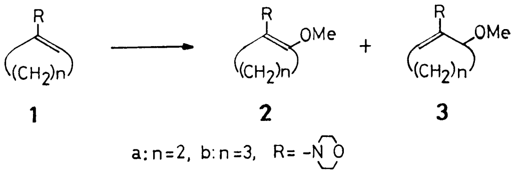
Synopsis. Electrooxidation of enamines in methanol afforded two types of methoxylated enamines. Similar treatment of enol ethers gave trimethoxylated compounds. The products formed by the electrolysis of haloolefins in acetic acid were α-acetoxy haloolefins and α-acetoxy ketones.

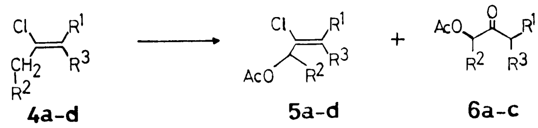
Because of mild reaction conditions and non-polluting nature, anodic oxidation is a highly promising method for the oxidation of organic compounds. The electrooxidation of some alkenes[2] or enol esters[3] has been studied from both synthetic and mechanistic points of view. The utility of electrooxidation in organic synthesis prompted us to extend it to the oxidation of such olefinic systems as enamines, haloolefins, and enol ethers.

Anodic Oxidation of Enamines. As shown in Scheme 1 the anodic oxidation of enamines **1a** and **1b** gave two types of enamine, namely, the methoxylated compounds at the vinylic **2** and allylic **3** positions of the starting enamine, though the two compounds were hardly separated from each other by distillation or gas chromatography. A mixture of the products **2b**+**3b** was identified by comparison of its NMR and IR spectra with those of the mixture of enamines **2b**+**3b** prepared independently from 2-methoxy-1-cyclohexanone[4] by the standard method.[5] Furthermore, the hydrolysis[5] of the mixture of products gave 2-methoxy-1-cyclohexanone in 80% yield. The elemental analysis of the product mixture **2a**+**3a** or **2b**+**3b** gave a satisfactory result.



Scheme 1.

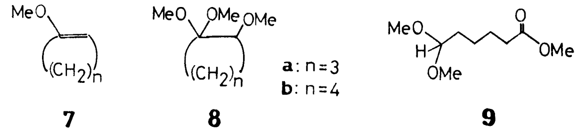
Anodic Oxidation of Haloolefins. Haloolefins **4a**—**d** were anodically oxidized to afford haloolefins **5** acetoxylated at the allylic position and the α-acetoxyketones **6** as shown in Scheme 2.



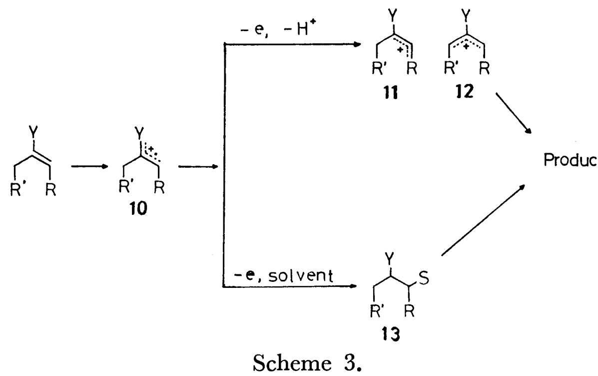
a: R^1=H, R^2, R^3=-$(CH_2)_2$-,
b: R^1=H, R^2, R^3=-$(CH_2)_3$-,
c: R^1=H, R^2=n-C_5H_{11}, R^3=H,
d: R^1=Cl, R^2, R^3=-$(CH_2)_3$-

Scheme 2.

Anodic Oxidation of Enol Ethers. Enol ethers **7a** and **7b** were electrooxidized to give the trimethoxylated compounds **8**. Upon hydrolysis with aqueous hydrochloric acid, compound **8b** gave 2-methoxy-1-cyclohexanone[4] in 73% yield. Furthermore, **8b** could be anodically oxidized easily to the acetal ester **9**, which can hardly be obtained by the conventional chemical methods.



Reaction Pathway. The reaction pathways might be as shown in Scheme 3 in which the initiation step is the electron-transfer to the anode from the conjugating olefinic system involving a hetero atom and a double bond. Further reactions of the first intermediate **10** can be controlled by several factors such as the nature of substituent Y and solvents, and reaction conditions. The products determining intermediates, however, would be allylic cations **11** and **12**, and a cation **13**. No product was formed from the allylic cation **11** formation, of which has been observed in the anodic oxidation of alkenes.[2] This method of oxidation of such olefinic compounds is promising for the synthesis of ketone derivatives hardly obtainable by other methods.



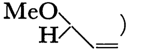
Scheme 3.

Experimental

Materials. Enamines, haloolefins and enol ethers were prepared from the corresponding ketones by reported methods.[5-7] The spectroscopic data of NMR and IR and the result of elemental analysis of the compounds (**2**, **3**, **5**, **6**, **8**, and **9**) are summarized in Table 1.

Electrooxidation of Enamines. Anodic oxidation of an enamine (50 mmol) in methanol (50 ml) containing sodium

Table 1. Spectroscopic data of NMR and IR, and the results of elemental analysis of compounds (**2**, **3**, **5**, **6**, **8**, **9**)

Product	IR cm^{-1}	NMR (CCl_4) δ	Calcd for:	Calcd (Found) (%)		
				C	H	N
2a+**3a**	1645, 1120	1.65—2.50 (m), 2.94 (m, -NCH_2-), 3.28 (s, -OCH_3), 3.49 (t, -OCH_3), 3.72 (t, -OCH_2), 4.44 (m,  MeO H)	$C_{10}H_{17}NO_2$	65.54, (65.44,	9.35, 9.45,	7.63 7.70)
2b+**3b**	1650, 1111	1.75—2.10 (m), 2.80 (m, -NCH_2-), 3.33 (s, -OCH_3), 3.57 (s, -OCH_3), 3.72 (t, -OCH_2-), 4.56 (m), 4.65 (t)	$C_{11}H_{19}NO_2$	66.97, (66.77,	9.71, 9.95,	7.10 7.13
Product	IR	NMR		C	H	Cl
5a	1730, 1620, 1240	2.10 (s, 3H, acetyl), 1.7—2.9 (m, 8H), 5.30 (t, 1H, H+OAc), 5.93 (b.s, 1H, olefinic)	$C_7H_9O_2Cl$	52.35, (52.37,	5.65, 5.78,	22.08 22.30)
6a	1740, 1715, 1240	2.20 (s, 3H, acetyl), 1.57—2.63 (m, 6H), 5.00 (t, 1H, H+OAc)	$C_7H_{10}O_3$	59.99, (59.98,	5.75 6.01)	
5b	1740, 1650, 1240	2.0 (s, 3H, acetyl), 1.4—2.4 (m, 6H), 5.2 (t, 1H, H+OAc), 6.0 (t, 1H, olefinic)	$C_8H_{12}O_2Cl$	55.04, (55.14,	6.35, 6.45,	20.31 20.19)
6b	1730, 1715, 1240	2.05 (s, 3H, acetyl), 1.5—2.6 (m, 8H), 5.0 (t, 1H, H+OAc)	$C_8H_{12}O_3$	61.52, (61.32,	8.63 8.55)	
5c	1740, 1640, 1240	0.80—1.50 (m, 9H), 2.00 (s, 3H, acetyl), 5.35 (b.s, 1H, H+OAc), 5.30 (m, 2H, olefinic)	$C_9H_{15}O_2Cl$	56.69, (56.58,	7.93, 8.01,	18.59 18.63)
6c	1730, 1720, 1240	0.70—1.50 (m, 9H), 2.00 (s, 3H, acetyl), 2.10 (s, 3H, acety), 4.80 (t, 1H)	$C_9H_{10}O_3$	62.76, (62.86,	9.36 9.50)	
5d	1740, 1640, 1240	1.70—2.00 (m, 9H), 2.05 (s, 3H, acetyl), 2.30—2.70 (m, 2H, allylic), 4.6 (t, 1H)	$C_8H_{10}O_2Cl_2$	49.96, (50.02,	4.82, 4.70,	33.92 33.92)
Materials	IR	NMR		C	H	
8a	2840, 1280, 1100	1.23—2.50 (m, 6H), 3.13 (s, 6H, methoxy), 3.33 (s, 3H, methoxy), 3.20—3.35 (m, 1H, H+OAc)	$C_8H_{16}O_3$	59.98, (60.05,	10.07 9.97)	
8b	2840, 1250, 1100	1.20—2.00 (m, 8H), 3.16 (s, 6H, methoxy), 3.30 (s, 3H, methoxy), 3.20—3.30 (m, 1H, H+OAc)	$C_9H_{18}O_3$	62.04, (62.14,	10.41 10.29)	
9	2840, 1730, 1170, 1130	1.20—2.25 (m, 8H), 3.33 (s, 6H, methoxy), 3.70 (s, 3H, methoxy), 4.30 (t, 1H, H-C(CH_3)$_2$)	$C_9H_{18}O_4$	56.82, (56.77,	9.54 9.39)	

methoxide (50 mmol) as a supporting electrolyte was carried out with carbon rod electrodes at room temperature. After 3 *F*/mol of electricity had been passed, methanol was removed by evaporation, and the residue was washed with three portions of ether. The combined ethereal solution was filtrated and distilled.

Electrolysis of ***1a*** (7.65 g, 50 mmol) at the anode potential of 1.65—1.75 V *vs.* SCE gave a mixture of **2a** and **3a** (6.95 g); bp 101—104 °C/mmHg.

*Enamine (**1b**) (8.35 g, 50 mmol) was electrooxidized* at the anode potential of 1.90—2.20 V *vs.* SCE to give a mixture of **2b** and **3b** (7.29 g); bp 121—124 °C/mmHg.

Electrolysis of Haloolefins. Electrolysis of a haloolefin (50 mmol) in acetic acid containing potassium acetate was carried out according to the reported method.[8] The amount of electricity passed through the cell was 5.5 *F*/mol. The product was analyzed after it had been separated by gas chromatography.

Anodic Oxidation of ***4a*** (5.125 g, 50 mmol) gave **5a** (2.81 g) and **6a** (0.945 g). **5a** and **6a**: Bp 100—120 °C/20 mmHg.

Electrolysis of Enol Ethers. A solution of an enol ether (50 mmol) in methanol (50 ml) containing sodium methoxide (50 mmol) as a supporting electrolyte was electrooxidized with carbon rod electrodes at room temperature until 3.5 *F*/mol of electricity was passed. After the usual work-up, the product was obtained by distillation.

Anodic oxidation of **7a** yielded **8a** (3.60 g). **8a**: Bp 71—73 °C/11 mmHg.

Electrolysis of ***7b*** gave **8b**: Bp 83—85 °C/13 mmHg.

1,1,2-Trimethoxycyclohexane (**8b**) (1.74 g, 10 mmol) was anodically oxidized according to the reported method[9] to give **9**, yield being 75%. **9**: Bp 121—123 °C/18 mmHg.

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