REDUCTIVE CONVERSION OF NITRO ALKENES TO KETONES AND/OR OXIMES IN AN AQUEOUS HClo₄-CH₂Cl₂-DIOXANE-(Pb) SYSTEM

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Electrochemical and chemical reduction of nitro alkenes in an aqueous $\text{HClO}_4-\text{CH}_2\text{Cl}_2$ -dioxane-(Pb) system afforded ketones and oximes in good yields, each of which can be obtained selectively by treating with either aqueous formaldehyde or hydroxylamine as a proper workup process, respectively.

Nitro alkenes <u>1</u>, readily prepared by the condensation of aldehydes with nitro alkanes,¹⁾ are synthetically equivalent to the corresponding ketones <u>2</u> and oximes <u>3</u>. Namely, nitro alkenes <u>1</u> can be converted to <u>2</u> and/or <u>3</u> by the reduction with Fe-dilute HCl,^{2a)} Zn-AcOH,^{2b)} TiCl₃-NH₄OAc-aqueous methanol,^{2c)} and others.³⁾ Electrolytic reduction of <u>1</u> to <u>2</u> and/or <u>3</u> has been also investigated by several groups.⁴⁾ However, the product selectivity and the yield for the desired products <u>2</u> and <u>3</u> are not satisfactory in a practical sense.⁵⁾ In this communication, we describe some of potential procedures for the reductive conversion of <u>1</u> to <u>2</u> or <u>3</u> assisted with lead in an aqueous HClO₄-CH₂Cl₂-dioxane system, which involve electrochemical and chemical methods followed by a proper workup process.



The electrochemical reduction was carried out in an undivided cell fitted with two lead electrodes $(1.5 \times 2 \text{ cm}^2)$. A typical electrolysis procedure is as follows: To a solution of nitro alkene <u>la</u> ($\mathbb{R}^1 = \mathbb{p}$ -chlorophenyl; $\mathbb{R}^2 = CH_3$, 0.53 mmol) in dichloromethane (2 ml) and dioxane (0.5 ml) was added aqueous 20% perchloric acid (10 ml) and the two-phase solution was electrolyzed under vigorous stirring at 10 mA/cm², changing the current direction every 30 s by a commutator, at room temperature. After passage of 3 F/mol of electricity, aqueous 37% formaldehyde (1 ml) was added and the stirring was continued for additional 20 min without passing current. The usual workup of the organic phase afforded the ketone <u>2a</u> ($\mathbb{R}^1 = \mathbb{p}$ -chlorophenyl; $\mathbb{R}^2 = CH_3$) in 93% yield (Procedure **A**: entry 1 in the Table).

On the other hand, after the electrolysis (3.5 F/mol of electricity passed), the organic phase was separated from the aqueous phase and treated with $NH_2OH \cdot HCl$ (300 mg) and sodium acetate (370 mg) at room temperature for 2 h, affording the corresponding oxime <u>3a</u> ($R^1 = p$ -chlorophenyl; $R^2 = CH_3$) in 90% yield (Procedure B: entry 2 in the Table). Apparently, the initial product of the reduction was a mixture of <u>2</u> and <u>3</u> and the suitable workup of the products allowed to isolate either <u>2</u> or <u>3</u> respectively.⁶

Actually, the transformation of 1 into 2 or 3, which is a four-electron reduction process, 7) consumed 2-3.5 F/mol of electricity and after the electrolysis (ently 1 in the Table) lead(II) salts were obtained from the aqueous layer.⁸⁾ This suggests that the reduction of 1 to 2 or 3 (Procedure A and B) involves both electrochemical reduction and chemical reduction with electrochemically activated lead(0). In fact, the reduction of 1 with lead in the same media occurred smoothly without passing current.⁹⁾ Thus, prior to the reduction the current (10 mA/cm^2) was passed between two lead electrodes in aqueous 20% perchloric acid for 10 min in order to activate the metal surface. To this solution a dichloromethane solution of la was added and the mixture was stirred for 30 min at room temperature. Workup in accordance with that of Procedure A afforded 2a in 90% yield (Procedure C: entry 3 in the Table). The treatment of la in the same media with lead¹⁰⁾ without activating its surface resulted in the recovery of most of la along with a small amount of 2a (\sim 10%) after stirring for 1 h.

Electrochemical reduction of $\underline{1}$ proceeded mainly when the electrolysis was

entry	nitro al R ^l	lkene R ²		procedure ^{a)}	electricity F/mol	product, ketone <u>2</u>	yeild % ^{b)} oxime <u>3</u>
							<u>.</u>
1	cı-	сн ₃ -	<u>la</u>	А	3	93	
2			<u>la</u>	В	3.5		91
3			<u>la</u>	с		91	
4			<u>la</u>	D	4.3	83	
5	$\langle \rangle$	сн ₃ -	<u>1b</u>	А	3	80	
6			<u>1b</u>	В	3		75
7			<u>1b</u>	с		76	
8			<u>lb</u>	D	4	73	
9	сн₃о-√_>-	сн ₃ -	lc	Α	3	87	
10			lc	В	3		88
11			lc	С		80	
12			lc	D	4.4	74	
13	СН=СН-	сн ₃ -	<u>ld</u>	A	2	70	
14			<u>ld</u>	В	3		55
15			<u>1d</u>	С		71	
16			<u>1d</u>	D	4.1	63	
17	с _{6^н13} -	сн ₃ -	le	A	2.7	81	
18			le	В	3		67
19			<u>le</u>	С		88	
20			le	D	4	80	
21	с ₆ н ₁₃ - сн ₃ со (^{(CH} 2)2 ⁻	<u>lf</u>	A	3	95	
22			<u>lf</u>	D	4	75	

Table Reduction of Nitro Alkenes in an Aqueous HClO₄-CH₂Cl₂-dioxane-(Pb) System

a) Procedure A: worked up with aqueous 37% formaldehyde; B: worked up with NH₂OH.HCl-NaOAc; C: reduction with lead activated by electrolysis prior to use;
 D: using lead cathode and platinum anode.

b) Isolated yields after column chlomatography on SiO₂ (hexane-AcOEt: $10/1 \sim 5/1$).

carried out by using lead cathode and platinum anode without changing the current direction (Procedure D in the Table). In this case, 4-4.5 F/mol of electricity was required to complete the reduction and no detectable amount of lead(II) salts were recovered from the aqueous layer.

The results of the reduction of nitro alkenes $\underline{1}$ in Procedure A-D are summarized in the Table. The combination of aqueous perchloric acid and lead cathode is essential to each procedure, since the use of other materials as electrodes (cathode-anode: Pt-Pt, Cu-Pt, Cu-Cu, C-C, and stainless (SUS 27)stainless) brought about no appreciable amount of reduction products $\underline{2}$ and $\underline{3}$ and the use of aqueous 10% sulfuric acid or aqueous 10% chloric acid resulted in the complete recovery of the starting materials.

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- 3) Ordinary, metal-acids reduction of $\underline{1}$ has been carried out at high temperature (\sim 100 °C) and the yields of 2 and/or 3 are insufficient (50-70% yields).
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- 5) The reported electrolytic reduction of nitro alkenes has been carried out in a divided cell under a strict control of the electrode potential and/or pH of the electrolysis medium.
- 6) Usual workup of the electrolyte afforded a mixture of <u>2a</u> and <u>3a</u> (59/33) in 92% yield.
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- Lead(II) salts disolved in the aqueous layer was recovered as precipitates of lead(II) sulfate (226 mg).
- 9) Reduction of nitro alkenes with lead has not yet been reported.
- 10) Purchased from Kishida Chemical Co. Ltd., Osaka.

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