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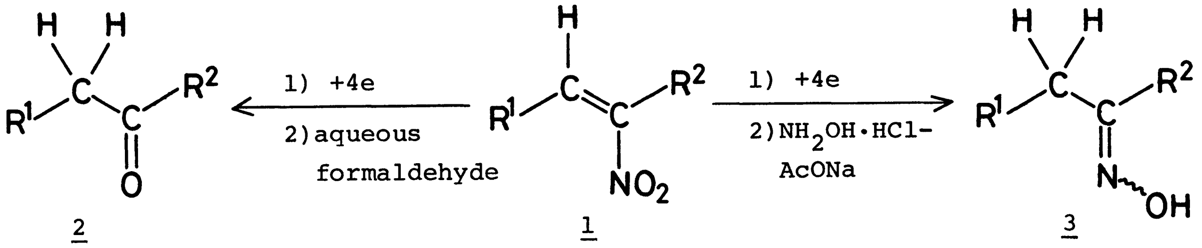
REDUCTIVE CONVERSION OF NITRO ALKENES TO KETONES AND/OR OXIMES IN AN AQUEOUS $HClO_4$-CH_2Cl_2-DIOXANE-(Pb) SYSTEM

Sigeru TORII,* Hideo TANAKA, and Tetsuo KATOH
Department of Industrial Chemistry, School of Engineering,
Okayama University, Tsushima, Okayama 700

Electrochemical and chemical reduction of nitro alkenes in an aqueous $HClO_4$-CH_2Cl_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 1, readily prepared by the condensation of aldehydes with nitro alkanes,[1)] are synthetically equivalent to the corresponding ketones 2 and oximes 3. Namely, nitro alkenes 1 can be converted to 2 and/or 3 by the reduction with Fe-dilute HCl,[2a)] Zn-AcOH,[2b)] $TiCl_3$-NH_4OAc-aqueous methanol,[2c)] and others.[3)] Electrolytic reduction of 1 to 2 and/or 3 has been also investigated by several groups.[4)] However, the product selectivity and the yield for the desired products 2 and 3 are not satisfactory in a practical sense.[5)] In this communication, we describe some of potential procedures for the reductive conversion of 1 to 2 or 3 assisted with lead in an aqueous $HClO_4$-CH_2Cl_2-dioxane system, which involve electrochemical and chemical methods followed by a proper workup process.



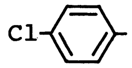
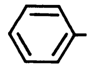
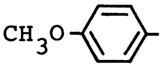
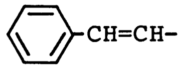
The electrochemical reduction was carried out in an undivided cell fitted with two lead electrodes (1.5 × 2 cm^2). A typical electrolysis procedure is as follows: To a solution of nitro alkene 1a (R^1 = p-chlorophenyl; R^2 = CH_3, 0.53 mmol) in dichloromethane (2 ml) and dioxane (0.5 ml) was added aqueous 20% perchloric acid (10 ml) and the two-phase solution was electrolyzed under vigorous stirring at 10 mA/cm^2, 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 2a (R^1 = p-chlorophenyl; 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 3a (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 2 and 3 and the suitable workup of the products allowed to isolate either 2 or 3 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 1a 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 1a in the same media with lead$^{10)}$ without activating its surface resulted in the recovery of most of 1a along with a small amount of 2a (~10%) after stirring for 1 h.

Electrochemical reduction of 1 proceeded mainly when the electrolysis was

Table Reduction of Nitro Alkenes in an Aqueous $HClO_4$-CH_2Cl_2-dioxane-(Pb) System

entry	nitro alkene			procedure[a)]	electricity	product, yeild %[b)]	
	R^1	R^2			F/mol	ketone 2	oxime 3
1		CH_3-	1a	A	3	93	--
2			1a	B	3.5	--	91
3			1a	C	--	91	--
4			1a	D	4.3	83	--
5		CH_3-	1b	A	3	80	--
6			1b	B	3	--	75
7			1b	C	--	76	--
8			1b	D	4	73	--
9		CH_3-	1c	A	3	87	--
10			1c	B	3	--	88
11			1c	C	--	80	--
12			1c	D	4.4	74	--
13		CH_3-	1d	A	2	70	--
14			1d	B	3	--	55
15			1d	C	--	71	--
16			1d	D	4.1	63	--
17	C_6H_{13}-	CH_3-	1e	A	2.7	81	--
18			1e	B	3	--	67
19			1e	C	--	88	--
20			1e	D	4	80	--
21	C_6H_{13}-	$CH_3CO(CH_2)_2$-	1f	A	3	95	--
22			1f	D	4	75	--

a) Procedure **A**: worked up with aqueous 37% formaldehyde; **B**: worked up with $NH_2OH\cdot HCl$-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 SiO_2 (hexane-AcOEt: 10/1~5/1).

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 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 2 and 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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2) a) H. B. Hass, A. G. Susie, and R. L. Heider, J. Org. Chem., 15, 8 (1950);
b) D. Nightingale and J. R. James, J. Am. Chem. Soc., 66, 325 (1944);
c) J. E. McMurry and J. Melton, J. Org. Chem., 38, 4367 (1973), and references cited therein.
3) Ordinary, metal-acids reduction of 1 has been carried out at high temperature (~100 °C) and the yields of 2 and/or 3 are insufficient (50-70% yields).
4) a) J. Armand and O. Convert, C. R. Hedb. Seances Acad. Sci., Ser. C, 286, 842 (1969); b) C. Bellec, R. Colan, S. Deswarte, J. Dore, and C. Viel, ibid., 281, 885 (1975); c) I. A. Avnitskaya, K. K. Babievskii, V. M. Belikov, E. V. Zaporozhets, V. T. Novikov, M. Foishin, and M. Ya, Electrokhimiya, 11, 661 (1975); d) T. Shono, H. Hamaguchi, H. Mikami, and H. Nogusa, 45th National Meeting of the Chemical Society of Japan, Tokyo, April 4, 1982, Abstr. Vol. 2, p. 1038.
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 2a and 3a (59/33) in 92% yield.
7) J. Wiemann and O. Convert, C. R. Hebd. Seances Acd. Sci., Ser. C, 258, 4285 (1964).
8) 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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