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One-Step Deoxygenation of Alcohols into Alkanes by a 'Double Electrolysis' in the Presence of a Phosphine†

Hatsuo Maeda, Toshihide Maki, Kaoru Eguchi, Takashi Koide and Hidenobu Ohmori*

Faculty of Pharmaceutical Sciences, Osaka University
1-6 Yamadaoka, Suita, Osaka 565, Japan.

Abstract: Deoxygenation of primary and secondary alcohols was effectively achieved in one-step by constant current electrolysis of a mixture of a phosphine, an alcohol, and Et_4NBr in CH_3CN with one compartment cell at room temperature under N_2 atmosphere.

Recently, we have found that a carboxylic acid can be partially reduced into the corresponding aldehyde without over-reduction by 'Double electrolysis'[1] in the presence of Ph_3P.[2] According to the proposed mechanism,[2b] electrochemical reduction of a hardly reducible compound can be easily achieved by the 'Double electrolysis,' that is, such a compound will be activated by converting it to the corresponding phosphonium ion through anodic oxidation of a phosphine (R'_3P) and the latter ion will be cathodically reduced *in situ* to afford the desired product as in the case of a carboxylic acid. Thus, we have examined the possibility of the electrochemical preparation of an alkane (**2**) from an alcohol (**1**) through the 'Double electrolysis' effected by anodic oxidation of R'_3P. It has been shown that an alcohol is not susceptible to a direct cathodic reduction unless a strong electron-withdrawing group is present on the carbon adjacent to the hydroxy group.[3] The investigation is intriguing by the following reasons: a) the conversion of **1** into **2** generally requires two-step reactions, which compromise a tedious derivatization of **1** using rather expensive reagents followed by the reductive C-O bond cleavage although the process is important for the synthesis of biologically active deoxygenated compounds[4] and is still one of the objects for recent synthetic researches;[5] b) although 'Double electrolysis' has drawing great attention owing to the inability of common organic reactions to realize a process consisted simultaneously of oxidation and reduction, that is, the electrolysis takes full advantage of the privilege conferred on electrochemistry, only few examples have been reported;[6] and hence it should be important to develop 'Double electrolyses' applicable to a variety of synthetic

$$\underset{\mathbf{1}}{\mathrm{ROH}} \xrightarrow[\mathrm{R'_3P,\ Et_4NX\ in\ CH_3CN}]{\text{Constant current electrolysis in one compartment cell}} \underset{\mathbf{2}}{\mathrm{RH}}$$

$$\left(\mathrm{R'_3P} + \mathbf{1} \xrightarrow[\text{at anode}]{-2e,\ -H^+} \mathrm{R'_3\overset{+}{P}{-}O{-}R} \xrightarrow[\text{at cathode}]{+2e,\ +H^+} \mathrm{R'_3PO} + \mathbf{2} \right)$$

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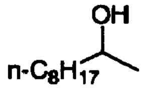
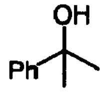
† This paper is dedicated to Professor Yasumitsu Tamura on the occasion of his 70th birthday.

reactions. In this paper, we describe that the 'Double electrolysis' in the presence of R'$_3$P can be utilized as a versatile synthetic tool to transform 'free' alcohols into the corresponding alkanes in one-step.

The effects of electrolysis conditions on the deoxygenation of primary, secondary, and tertiary alcohols were explored first, utilizing 1-decanol, 2-decanol, and 2-phenyl-2-propanol as model compounds, and the results are summarized in Table 1. The electrolysis was carried out as follows. A mixture of a phosphine (R'$_3$P) (6 mmol), an alcohol (3 mmol), and Et$_4$NX (3 mmol) in CH$_3$CN (30 ml) was subjected to constant current electrolysis (CCE) in one compartment cell equipped with two graphite plates as an anode and a cathode (12.5 cm^2 each) under N$_2$ atmosphere at room temperature. As a solvent CH$_3$CN was found to be superior to CH$_2$Cl$_2$ which was often employed in the electrolysis of phosphines to give favorable results.[2,7] After the electricity of 4 or 5 F / mol had been passed, the electrolyte was analyzed by GLC.

Table 1. Effects of the electrolysis conditions upon the deoxygenation of 1-decanol, 2-decanol, and 2-methyl-2-propanol by CCE

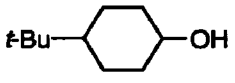
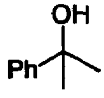
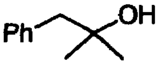
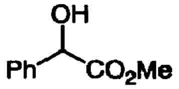
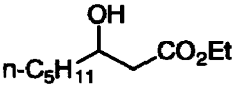
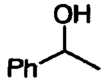
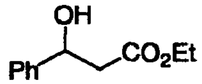
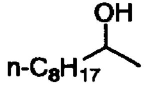
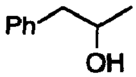
Run	1	R' in R'$_3$P	X in Et$_4$NX	Current (mA)	Electricity (F / mol)[a]	Yield of 2 (%)[b]
1	CH$_3$(CH$_2$)$_9$OH	Ph	ClO$_4^-$	25	5	trace
2	″	″	BF$_4^-$	″	″	trace
3	″	″	Cl$^-$	″	″	66
4	″	″	Br$^-$	″	″	94
5	″	″	I$^-$	″	″	74
6	″	″	Tos$^-$	″	″	7
7	″	″	Br$^-$	″	4	70
8	″	Bu	″	″	5	68
9	″	PhO	″	″	″	80
10	″	—	″	″	″	0
11		Ph	Br$^-$	25	5	51 (7)[c,d]
12	″	Bu	″	″	″	93
13	″	PhO	″	″	″	61 (11)[c,d]
14		Ph	Br$^-$	25	5	22 (48)[e]
15	″	Bu	″	″	″	0 (0)[e]
16	″	PhO	″	″	″	28 (57)[e]
17	″	Ph	″	50	″	60 (27)[e]
18	″	PhO	″	″	″	79 (trace)[e]
19	″	″	″	100	″	72 (11)[e]

a) Against the amount of 1. b) Determined by GLC. c) The number in the parenthesis shows the yield of 1-decene. d) The formation of 2-decene was also recognized in a small amount. e) The number in the parenthesis shows the yield of α-methyl stylene.

Among the readily available tetraethyl ammonium salts examined as the supporting electrolyte in the formation of n-decane (runs 1~6), those with halide ions as the counter anion gave satisfactory results and above all Et_4NBr induced the most successful transformation.[8] The results in runs 4 and 7 suggest that the electricity of 5 F/mol of the alcohol is enough to obtain the products in an excellent yield. With respect to the identity of a phoshpine, Ph_3P turned out to be the choice in this case (runs 4, 8, and 9). A control experiment without a phosphine did not afford n-decane at all (run 10), indicating that an anodic process including a phosphine is indispensable for the present reaction. In the deoxygenation of 2-decanol, an effective formation of n-decane from the secondary alcohol without giving the elimination products, 1- or 2-decene, was induced not by Ph_3P or $(PhO)_3P$ but by Bu_3P (runs 11~13). On the other hand, the deoxygenation of a tertiary alcohol, dimethylphenyl carbinol, was realized only in the presence of Ph_3P or $(PhO)_3P$; and yet it was spoiled by the formation of a large amount of an elimination product, α-methyl stylene (runs 14~16). Fortunately, CCE using those phosphines at a higher electrolysis current was found to achieve the formation of cumene in a fair yield (runs 17~19) and $(PhO)_3P$ was the choice between the two, taking the formation of less amount of the by-product into consideration (runs 17 and 18).

Based on the results obtained so far, the present electrolysis was applied to the transformation of various alcohols into alkanes. The results are summarized in Table 2. Various benzyl alcohols were deoxygenated in good yields regardless of the situation of branching at benzylic carbons (runs 2, 6, and 10) and esters as well as a cathodically reducible aromatic bromide were tolerated under the conditions (runs 3,

Table 2. Electrochemical One-Step Deoxygenation of Alcohols (**1**) into the Corresponding Alkanes (**2**) Effected by the Presence of R_3P

Run		1	Method[a)]	Yield of 2 (%)[b)]	Run		1	Method[a)]	Yield of 2 (%)[b)]
1	**a**	$CH_3(CH_2)_9OH$	A	94	9	**i**		B	48
2	**b**	$p\text{-}CH_3O\text{-}PhCH_2OH$	A[c)]	96	10	**j**		C	79
3	**c**	$p\text{-}Br\text{-}PhCH_2OH$	A[c)]	89	11	**k**		C'	19 (59)[d,e)]
4	**d**	$PhCH_2CH_2OH$	A	83	12	**l**		A[c)]	85
5	**e**	$CH_2{=}CH(CH_2)_8OH$	A	70	13	**m**		C	59
6	**f**		A[c)]	86	14	**n**		C	60
7	**g**		B	93					
8	**h**		B	86					

a) CCE by method A, B, C and C' was carried out under the conditions shown in run 4, 12, 18, and 19 in Table 1, respectively. b) Determined by GLC. c) The electricity of 4 F / mol was passed. d) The number in the parenthesis shows the yield of 2-methyl-1-phenyl-1-propene determined by GLC. e) The formation of 2-methyl-1-phenyl-2-propene was also recognized although its yield was not determined.

12, and 14). In the case of primary and secondary aliphatic alcohols, the alkanes were obtained in fair to moderate yields and functional groups such as olefin and ester caused no problem in the transformation. The electrochemical reaction of an aliphatic tertiary alcohol **1k** gave the corresponding alkane in a low yield with a dehydrated compound as a major product (run 11).

In summary, the present method has been shown to transform various alcohols into alkanes except for an aliphatic tertiary one without any tedious derivatization, just by making proper use of the electrolysis conditions. Thus, a 'Double electrolysis' in the presence of phosphines has proved to be quite general as a useful tool to form C-H from C-OH not only in carboxylic acids but also in simple alcohols. Further work is under way in order to examine the possibility of the present electrolysis as a preparation method of biologically interesting deoxy-derivatives from more complicated alcohols and to shed light on the mechanism of the transformation.

Acknowledgement. This work was supported in part by a Grant-in-Aid for Scientific Research (05235228) on Priority Areas (No. 236) from the Ministry of Education, Science, and Culture, Japan.

References and Notes

1. Although our electrolysis will be classified as one of the electrochemical reactions called 'Paired electrolysis,' it is considered reasonable to name it 'Double electrolysis' alternatively. cf. Baizer, M. M. *Organic Electrochemistry*, 3rd ed., Baizer, M. M.; Lund, H., Marcel Dekker, Inc., New York, 1991, p.1421.
2. a) Maeda, H.; Maki, T.; Ohmori, H. *Tetrahedron Lett.*, **1992**, *33*, 1347-1250. b) Maeda, H.; Maki, T.; Ohmori, H. *Chem. Pharm. Bull.*, in the press.
3. For example, Lund, H. *Acta Chem. Scand.*, **1960**, *14*, 1927-1938.
4. Hartwig, W. *Tetrahedron*, **1983**, *39*, 2609-2645.
5. For example, a) Barton, D. H. R.; Parekh, S. I.; Tse, C.-L. *Tetrahedron Lett.*, **1993**, *34*, 2733-2726. b) Nishiyama, K.; Oba, M. *Tetrahedron Lett.*, **1993**, *34*, 3745-3748.
6. a) Wille, H. J.; Knittel, D.; Kastening, B.; Mergel, J. *J. Appl. Electrochem.*, **1980**, *10*, 489-494. b) Iwasaki, T.; Nishitani, T.; Horikawa, H.; Inoue, I. *J. Org. Chem.*, **1982**, *47*, 3799-3802. c) Baizer, M. M.; Nonaka, T.; Park, K.; Saito, Y.; Nobe, K. *J. Appl. Electrochem.*, **1984**, *14*, 197-208.
7. a) Ohmori, H.; Maeda, H.; Kikuoka, M.; Maki, T.; Masui, M. *Tetrahedron*, **1991**, *47*, 767-776. b) Maeda, H.; Kawaguchi, T.; Masui, M.; Ohmori, H. *Chem. Pharm. Bull.*, **1990**, *38*, 1389-1391.
8. As to the cations of supporting electrolyte, the solubilities of most metal and tetramethylammonium halides are poor in CH_3CN. Though Bu_4NBr gave similar results as Et_4NBr, the former salt is more expensive.

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