Tetrahedron Letters No. 23, pp 2157 - 2160. 0040-4039/79/0601-2157$02.00/0

SELECTIVE TRANSFORMATION OF ALIPHATIC ALCOHOLS TO ALKANES BY ELECTROREDUCTIVE METHOD[1]

Tatsuya Shono,* Yoshihiro Matsumura, Kenji Tsubata, and Yoshihiro Sugihara
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Sakyo, Kyoto 606, Japan

A new highly selective transformation of ROH to RH was accomplished by electrochemical reduction of methanesulfonates of ROH. Other functional groups such as ester, olefin, nitrile, epoxide, and aromatic nucleus were inert in this electrochemical reduction.

Reduction of aliphatic alcohols to the corresponding alkanes is one of the most important transformations in organic synthesis.[2] The methods hitherto known generally involve conversion of the hydroxyl group to better leaving groups followed by reductive elimination of the leaving groups. However, typical methods exemplified by LAH reduction of tosylates,[3] hydrogenolysis of isoureas[4] or reduction of phosphates with alkali metals in liquid ammonia[5] are not necessarily operative in reduction of alcohols containing other reducible functional groups such as ester, nitrile, epoxide, olefin, and/or aromatic nucleus.

In this paper, we wish to report a new selective transformation of ROH to RH by means of electrochemical reduction of methanesulfonates of ROH[6] in which the functional groups reducible under vigorous conditions exist in the group R.

$$\underset{\mathbf{1}}{\mathrm{R{-}OH}} \longrightarrow \underset{\mathbf{2}}{\mathrm{ROMs}} \xrightarrow{+\,e} \underset{\mathbf{3}}{\mathrm{RH}}$$

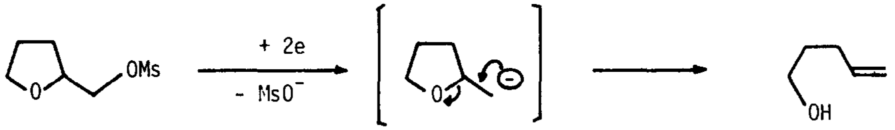
Starting methanesulfonates (**2**) were prepared from alcohols (**1**) according to the conventional method.[8,9] Into a divided cell equipped with a lead cathode and a platinum anode was added a solution of 50 ml of dry DMF containing tetraethylammonium *p*-toluenesulfonate (1.7 mmol) as a supporting electrolyte, and the solution was kept at 5° to 10° by cooling with ice-water bath. In order to avoid hydrolysis of methanesulfonates prior to the electroreduction,[10] they were slowly added into the electrolysis system. Thus, a solution of **2** (5 mmol) in dry DMF (5 ml) was added dropwise into the cathodic solution over a period of 2 hr.

When the addition was completed, 3 *F*/mol of electricity had been passed.[11] After additional 1 *F*/mol of electricity was passed, the corresponding alkanes (**3**) were obtained in the yields shown in Table I. All products gave satisfactory physical and spectroscopic data for assigned structures.

The reduction mechanism may be explained in terms of electron transfer to the mesylate group at the initiation step followed by elimination of the methanesulfonate anion and further reduction of the resulted alkyl radical (R·) to the carbanion (R^-) as proposed in the reduction with arene anion radicals,[12] although no reduction wave of **2** is observed in the potential range more anodic than -2.50 V *vs.* SCE.[13]

$$\underset{\mathbf{2}}{R\text{—}OMs} \xrightarrow{+\,e} R\cdot \; + \; MsO^- \xrightarrow{+\,e} R^- \longrightarrow RH$$

Although the formation of a radical as the first intermediate is not conclusive, the formation o a carbanion is likely, since the formation of coupling product (R—R) was not observed, whereas the electroreduction of **4** gave the ring opened product (**6**) which is supposed to be resulted from the concerted ring opening of the carbanion (**5**).

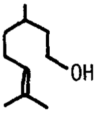
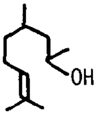
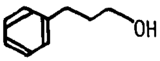
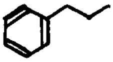
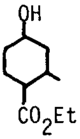
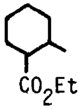
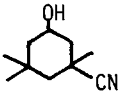
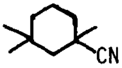
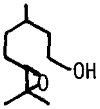
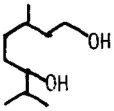
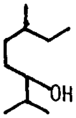


4 **5** **6**

64 % yield

The selectivity and yield of this electrochemical transformation of ROH to RH are remarkable in organic synthesis, and further mechanistic investigation is in progress.

Table I. Transformation of Alcohols to Alkanes

Alcohols (**1**)	*F*/mol	Alkanes (**3**)	Yield[a] (%)
$CH_3(CH_2)_{10}CH_2OH$	4	$CH_3(CH_2)_{10}CH_3$	81[b]
	4		85[b]
	4		63[b]
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$	4	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3$	70[c]
	4		83[b]
	4		57[c]
	4		71[c]
	4		87[b]
	4.8		72[c]

a. Overall yield from alcohol. b. Determined by glc. c. Isolated yield.

References and Notes

1. Electroorganic Chemistry. 38.
2. I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley-Interscience, New York, 1971; D. H. R. Barton and S. W. McCombie, *J. Chem. Soc.*, **1975**, 1574; T. Tsuchiya, I. Watanabe, M. Yoshida, F. Nakamura, T. Usui, M. Kitamura, and S. Umezawa, *Tetrahedron Lett.*, **1978**, 3365.
3. For example, K. B. Wiberg and J. G. Pfeiffer, *J. Am. Chem. Soc.*, **92**, 553 (1970).
4. E. Vowinkel and I. Büthe, *Chem. Ber.*, **107**, 1353 (1974).
5. R. E. Ireland, D. C. Muchmore, and U. Hengartner, *J. Am. Chem. Soc.*, **94**, 5098 (1972).
6. The electrochemical reduction of toluenesulfonates of alcohols is known to yield not the corresponding alkanes but toluenesulfinic acid and starting alcohols.[7]
7. L. Horner and H. Neumann, *Chem. Ber.*, **98**, 3462 (1965); P. Yousefzadeh and C. K. Mann, *J. Org. Chem.*, **33**, 2716 (1968).
8. R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).
9. Tlc showed only one spot and spectra (ir and nmr) characteristic to the sulfonate group were obtained.
10. The cathodic solution was basic when the electrolysis was completed.
11. The cathode potential was -2.5—-2.7 V *vs.* SCE.
12. J. R. Garnson, S. Schulenberg, and W. D. Closson, *Tetrahedron Lett.*, **1970**, 4397.
13. The measurement of the reduction potential of methanesulfonates was carried out under the following conditions; Substrate, 0.1 M; Solvent, DMF; Supporting Electrolyte, 0.05 M Et_4NCl; Dropping mercury electrode.

(Received in Japan 28 February 1979)