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A FACILE TRANSFORMATION OF ESTER GROUPS TO VINYL GROUPS BY THE ELECTROREDUCTIVE METHOD[1)]

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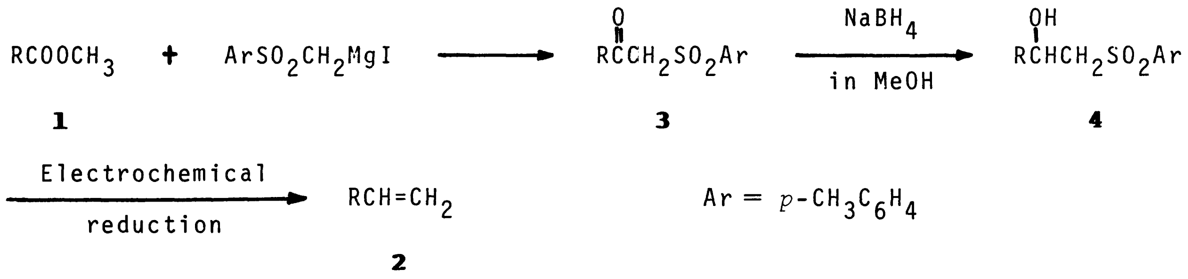
A facile method of the transformation of esters to vinyl compounds was developed by using the electroreductive 1,2-elimination as a key step. β-Hydroxysulfones were electrochemically reduced to vinyl compounds in good yields. Hydroxyolefins could be also prepared from the corresponding lactones.

A simple transformation of an ester group of esters (**1**) to a vinyl group without any modification of the substrate R is quite desirable in organic syntheses.[2)] We wish to report herein a facile transformation of **1** to olefins (**2**) by using the electroreductive 1,2-elimination[3,4)] as a key step (Scheme I).

Scheme I

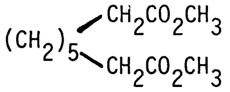
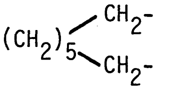
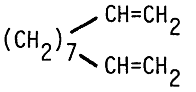
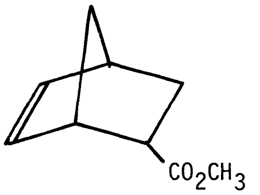
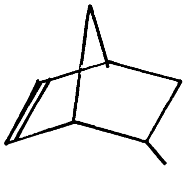
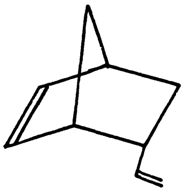
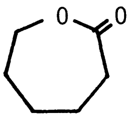
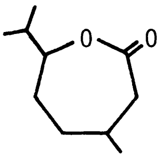
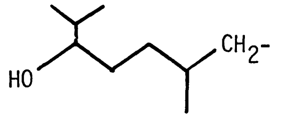
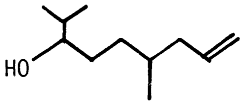
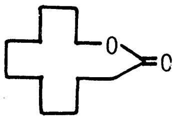
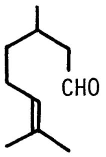
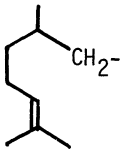
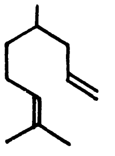


$$\underset{\mathbf{1}}{RCOOCH_3} + ArSO_2CH_2MgI \longrightarrow \underset{\mathbf{3}}{R\overset{O}{\overset{\|}{C}}CH_2SO_2Ar} \xrightarrow[\text{in MeOH}]{NaBH_4} \underset{\mathbf{4}}{R\overset{OH}{\overset{|}{C}}HCH_2SO_2Ar}$$

$$\xrightarrow[\text{reduction}]{\text{Electrochemical}} \underset{\mathbf{2}}{RCH{=}CH_2} \qquad Ar = p\text{-}CH_3C_6H_4$$

β-Ketosulfones (**3**), synthesized by the reaction of starting esters (**1**) with *p*-tolylsulfonylmethylmagnesium iodide,[6)] were easily reduced with methanolic $NaBH_4$ to β-hydroxysulfones (**4**) in quantitative yields. In a divided cell equipped with a lead cathode and a platinum anode, the electroreductive 1,2-elimination of **4** to **2** was accomplished by passing 4 *F*/mol of electricity through a solution of **4**

Table I. Electroreductive Synthesis of Olefins from Esters, Lactones, and Aldehydes

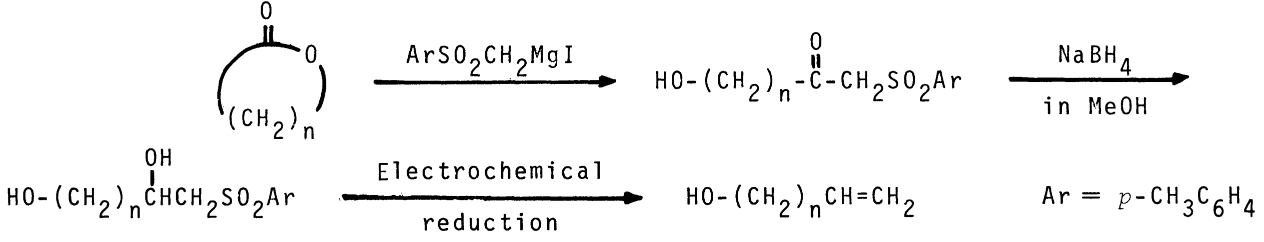
Entry	Starting Compound	$\mathrm{R\underset{OH}{C}HCH_2SO_2\text{-}(\mathit{p})\text{-}CH_3C_6H_4}$ R (Yield,[a] %)	Product (Yield,[b] %)
1	$\mathrm{CH_3(CH_2)_{16}CO_2CH_3}$	$\mathrm{CH_3(CH_2)_{16}\text{-}}$ (73)	$\mathrm{CH_3(CH_2)_{16}CH{=}CH_2}$ (82)
2	$\mathrm{\phi CH_2CH_2CO_2CH_3}$	$\mathrm{\phi CH_2CH_2\text{-}}$ (93)	$\mathrm{\phi CH_2CH_2CH{=}CH_2}$ (74)
3	 $\mathrm{(CH_2)_5}<\begin{matrix}\mathrm{CH_2CO_2CH_3}\\\mathrm{CH_2CO_2CH_3}\end{matrix}$	 $\mathrm{(CH_2)_5}<\begin{matrix}\mathrm{CH_2\text{-}}\\\mathrm{CH_2\text{-}}\end{matrix}$ (74)	 $\mathrm{(CH_2)_7}<\begin{matrix}\mathrm{CH{=}CH_2}\\\mathrm{CH{=}CH_2}\end{matrix}$ (87)[c]
4	$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3}$	$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_6CH_2\text{-}}$ (85)	$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH{=}CH_2}$ (74)
5		 (83)	 (76)
6		$\mathrm{HO(CH_2)_4CH_2\text{-}}$ (71)	$\mathrm{HO(CH_2)_5CH{=}CH_2}$ (73)
7		 (73)	 (73)[d]
8		$\mathrm{HO(CH_2)_{10}CH_2\text{-}}$ (80)	$\mathrm{HO(CH_2)_{11}CH{=}CH_2}$ (80)
9	$\mathrm{CH_3(CH_2)_8CHO}$	$\mathrm{CH_3(CH_2)_7CH_2\text{-}}$ (75)	$\mathrm{CH_3(CH_2)_8CH{=}CH_2}$ (70)
10		 (68)	 (71)[e]
11	$\mathrm{\phi CH_2CH_2CHO}$	$\mathrm{\phi CH_2CH_2\text{-}}$ (78)	$\mathrm{\phi CH_2CH_2CH{=}CH_2}$ (74)

[a] Isolated yields from **1**. [b] Isolated yields of the elimination. [c] The amount of electricity passed was 8 *F*/mol. [d] Bp 120 - 125 °C/20 - 22 mm. [e] Bp 77 - 80 °C/20 - 22 mm.

(5 mmol) in DMF (40 ml) containing tetraethylammonium *p*-toluenesulfonate (1.2 mmol) as a supporting electrolyte. The cathode potential was -2.4 ~ -2.6 V vs. SCE. Usual work-up gave vinyl compounds (**2**) in satisfactory yields. The results are shown in Table I.

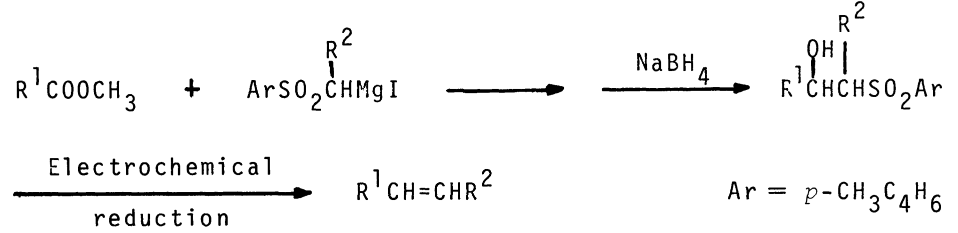
A divinyl compound (entry 3) and vinyl olefins (entries 4 and 5) as well as simple vinyl compounds (entries 1 and 2) could be prepared from the corresponding starting esters. Furthermore, the versatility of this method was shown by the formation of hydroxyolefins, of which syntheses from reasonable starting compounds might be troublesome by other methods. Thus, according to the Scheme II, lactones gave hydroxyolefins in satisfactory yields (entries 6,7, and 8).

Scheme II



This electroreductive method is obviously applicable to the conversion of an aldehyde group to a vinyl groups, since hydroxysulfones can be obtained directly by the reaction of aldehydes with *p*-tolylsulfonylmethylmagnesium iodide[8)] (entries 9,10 and 11). All the products were identified by the spectroscopic and elemental analyses.

Inner olefins could also be prepared by this method.



$$R^1COOCH_3 + ArSO_2CH(R^2)MgI \longrightarrow \xrightarrow{NaBH_4} R^1CH(OH)CH(R^2)SO_2Ar \xrightarrow[\text{reduction}]{\text{Electrochemical}} R^1CH=CHR^2 \qquad Ar = p\text{-}CH_3C_4H_6$$

$R^1 = C_9H_{18}$, $R^2 = CH_3$, overall yield 50 %
(*cis* 25 %, *trans* 75 %)

$R^1 = C_6H_5CH_2CH_2$, $R^2 = CH_3$, overall yield 52 %
(*cis* 31 %, *trans* 69 %)

Because of the simplicity and the generality, the novel method described herein would be remarkably promising in organic syntheses.

References and Notes

1) Electroorganic Chemistry 32.
2) A possible transformation of **1** to **2** may be the reduction of **1** to aldehydes followed by the Wittig reaction.
3) a) P. Martigny, M. A. Michel, and J. Simonet, *J. Electroanal. Chem.*, 73, 373 (1976).
   b) Electroreductive 1,2-elimination has mainly been known for *vic*-dihalides. For reviews, see "Organic Electrochemistry" edited by M. M. Baizer, Marcel Dekker, Inc., New York, 1973.
4) The 1,2-elimination of hydroxysulfones has been known to be feasible for some simple compounds by the reduction with Na-Hg.5)
5) a) M. Julia and J. M. Paris, *Tetrahedron Lett.*, 1973, 4833.
   b) B. M. Trost and Y. Matsumura, *J. Org. Chem.*, 42, 2036 (1977).
6) β-Ketosulfones (**3**) were prepared by the method of L. Field.7)
7) L. Field, J. E. Lawson, and J. W. McFarland, *J. Am. Chem. Soc.*, 78, 4389 (1956).
8) L. Field, *J. Am. Chem. Soc.*, 74, 3919 (1952).

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