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ELONGATION OF CARBONYL COMPOUNDS BY UTILIZING ELECTROREDUCTION AS A KEY STEP[1)]

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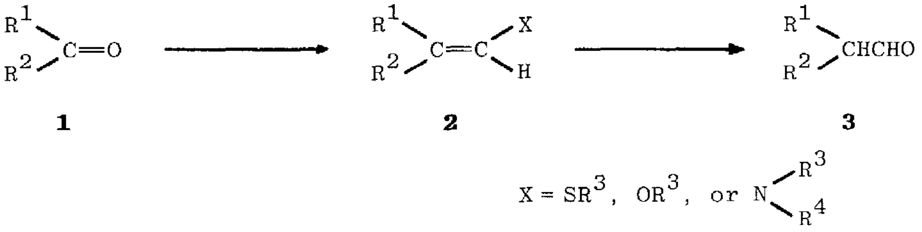
The transformation of aldehydes, ketones and esters to the next higher homologous aldehydes was accomplished by utilizing electroreductive 1,2-elimination as a key step.

The conversion of carbonyl compounds (**1**) into unsaturated compounds like compounds (**2**) has been known to be one of the key steps[2)] for aldehyde elongation (**1→3**), which is often required in organic synthesis.

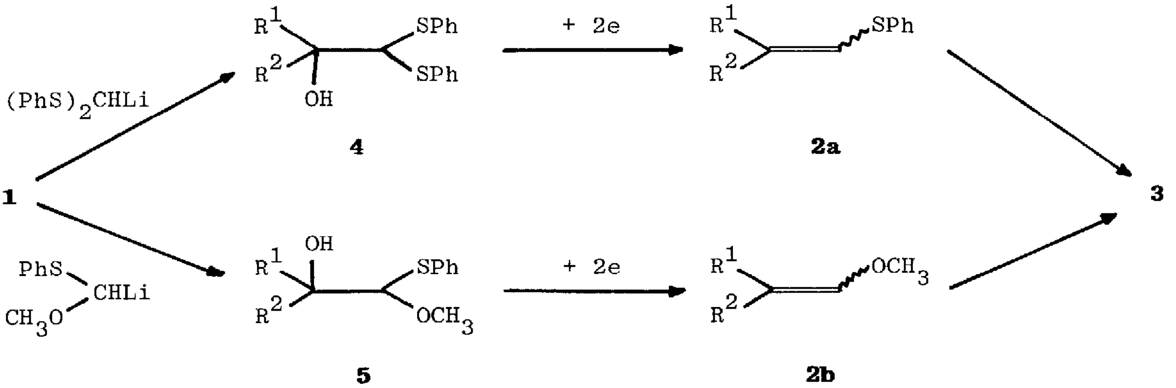

······(1)

1 **2** **3**

We report herein a new facile synthetic method of **2** ($X = OCH_3$ and SPh) in which the key step is the formation of **2** from hydroxysulfides like **4** or **5** through the electroreductive 1,2-elimination of phenylthio and hydroxyl groups, which we have found in the previous study.[3)]

This method leads to the elongation of aldehydes, ketones and esters to the next higher homologous aldehydes. Scheme 1 illustrates the sequence of the synthesis of vinyl sulfides (**2a**), and vinyl ethers (**2b**) from aldehydes or ketones.

Scheme 1



R^1 and R^2=alkyl or hydrogen

β-Hydroxysulfides (**4** or **5**) can be synthesized by the reaction of **1** with bisphenylthiomethyllithium$^{4)}$ or methoxyphenylthiomethyllithium$^{5)}$ according to known procedures.$^{6)}$ The electroreductive transformation of **4** or **5** to **2** was accomplished as follows.

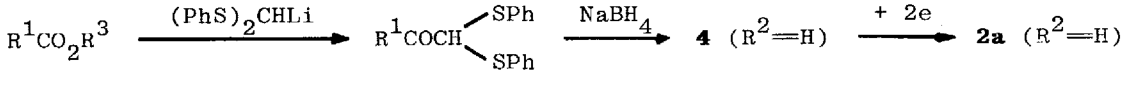
A solution of **4** or **5** (10 mmol) dissolved in dry DMF (40 ml) containing tetraethylammonium *p*-toluenesulfonate was placed into a divided cell equipped with a platinum anode and a lead cathode.

After 4 *F*/mol of electricity$^{7)}$ was passed, the reaction mixture was worked up to give **2a** or **2b** in moderate or high yields, which are shown in the Table 1 along with yields of **4** and **5**.

The fact that the yields of **2a** are generally lower than **2b** may be explained by the difference of stability of **2a** and **2b** under the reduction conditions.$^{8)}$

Furthermore, the versatility of this method is exemplified by the transformation of esters (**6**) to vinylsulfides (**2a**) as shown in Scheme 2.

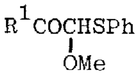
Scheme 2



R^3=CH_3 or CH_2CH_3

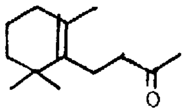
Esters **6** were easily transformed to **4** (R^2 = H) through the reaction with bisphenylthiomethyllithium$^{4)}$ followed by reduction with methanolic $NaBH_4$.

The reaction of methoxyphenylthiomethyllithium with **6**, however, gave the desired compound **8** in a poor yield. Yields of **2a** ($R^2 = H$) from **6** are summerized in Table 2.



$R^1COCH(OMe)SPh$ **8**

Table 1. Yields[a,b] of β-Hydroxysulfides and Unsaturated Compounds.

Carbonyl Compounds (**1**)	**4**	**2a**	**5**	**2b**
$PhCH_2CH_2CHO$	87	61	93	96
$n\text{-}C_9H_{19}CHO$	92	68	96	98
$n\text{-}C_6H_{13}CHO$	88	60	97	90
citronellal	87	63	88	98
cyclohexanone	77	61	99	92
$CH_3COCH_2CH(CH_3)_2$	—	—	94	91
	—	—	99	92

a) Isolated yields (%). b) All products gave satisfactory spectroscopic data and elemental analysis for assigned structures.

Table 2. Synthesis of Unsaturated Sulfides from Esters.[a,b]

Esters (**6**)	**7**	**4** ($R^2 = H$)	**2a** ($R^2 = H$)
$PhCH_2CH_2CO_2CH_3$	87	99	61
$n\text{-}C_7H_{15}CO_2CH_2CH_3$	95	98	77
$CH_3O_2C(CH_2)CO_2CH_3$	81	98	69[c]

a) Isolated yields(%).
b) All products gave satisfactory spectroscopic data and elemental analysis for assigned structures.
c) The isolated yields were caluculated at the stage when 6 *F*/mol of electricity was passed.

Because of the simplicity of the manipulation and good yields, this method is promising in the synthesis of homologous aldehydes from ketones, aldehydes or esters.

References and Notes

1) Electroorganic Chemistry. 43.

2) The elongation of carbonyl compounds has been accomplished by several methods: (a) The conversion of glycidic ester, M. S. Newman and B. J. Magerlain, *Org. Reactions*, **5**, 413 (1949). (b) The ring opening of epoxides, E. J. Corey and M. Chavkovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962). (c) The Wittig Reaction, S. G. Levine, *J. Am. Chem. Soc.*, **80**, 6150 (1958), A. Maercker, *Org. Reactions*, **14**, 270 (1965); A. F. Kluge, *Tetrahedron Lett.*, **1978**, 3629, and references cited therein. The methods (a) and (b) are, however, not necessarily satisfactory in yields, and furthermore, all the methods cited above are not applicable to the transformation of esters to their next higher homologues aldehydes.

3) T. Shono, Y. Matsumura, S. Kashimura, and H. Kyutoku, *Tetrahedron Lett.*, **1978**, 2807.

4) E. J. Corey and D. Seebath, *J. Org. Chem.*, **31**, 4097 (1966).

5) B. M. Trost and C. H. Miller, *J. Am. Chem. Soc.*, **97**, 7182 (1975).

6) The reaction of **1** with bisphenylthiomethyllithium or methoxyphenylthiomethyllithium was carried out in a similar way to the Corey's method.$^{4)}$

7) Cathode potential was - 2.5 V *vs.* SCE.

8) Unsaturated sulfides were consumed to some extent under the reduction conditions, whereas unsaturated ethers were stable.

9) The reaction of **6** with bisphenylthiomethyllithium was carried out according to the reported procedure.$^{5)}$

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