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ELECTROREDUCTIVE SYNTHESIS OF OLEFINS FROM β-HYDROXYSULFIDES[1]

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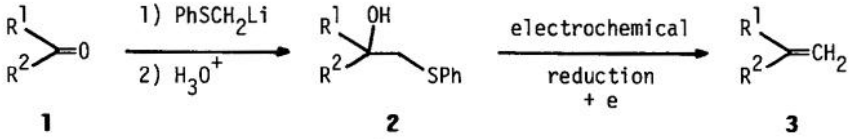
Reductive elimination of groups including sulfur from organosulfur compounds has been extensively studied[2] from the viewpoint of organic synthesis. The elimination of hydroxyl and phenylthio groups from β-hydroxysulfides (**2**) leads to the convenient route to the synthesis of olefins, and several reducing agents[3] have been recently exploited for this transformation.

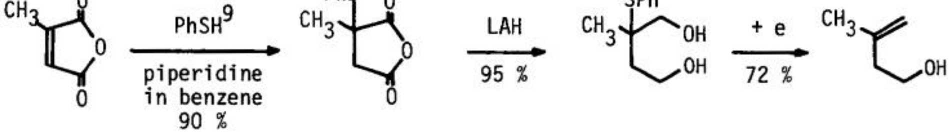
We wish to report herein a new 1,2-elimination[4] of β-hydroxysulfides (**2**) to the corresponding olefins (**3**) by electroreductive method in which electron itself behaves as a reducing agent.



$\cdots\cdots\cdots(1)$

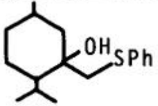
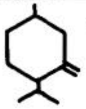
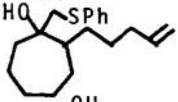
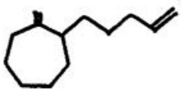
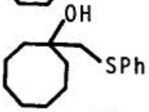
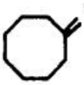
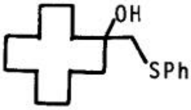
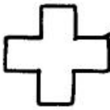
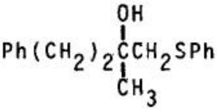
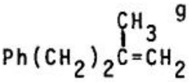
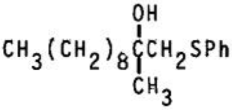
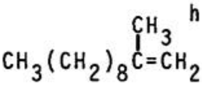
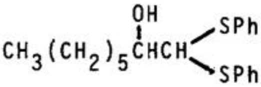
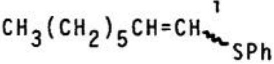
A typical procedure for the electroreductive transformation of **2** to **3** is as follows. β-Hydroxysulfide (10 mmol) dissolved in dry dimethylformamide (40 ml) containing tetraethylammonium *p*-toluenesulfonate (4.0 g) as a supporting electrolyte was reduced in a divided cell equipped with a platinum anode and a lead cathode. The cathode potential was -1.8—-2.2 V *vs.* SCE. After 4 *F*/mol of electricity was passed, the reaction mixture was worked up to give the corresponding olefin in good yield. Results are summarized in Table 1. All products gave satisfactory results in elemental and spectroscopic analyses.[7]

Furthermore, this method is applicable to the following skeletal conversion.[8]



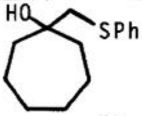
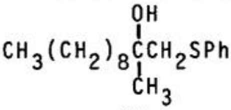
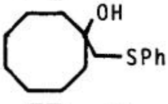
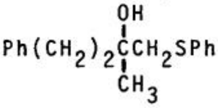
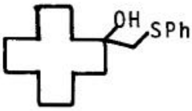
$\cdots\cdots\cdots(2)$

Table 1. Electroreductive Synthesis of Olefins

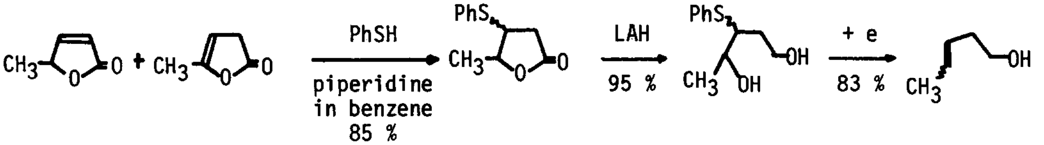
β-Hydroxysulfides[a]	Yields (%)[b]	Olefins	Yields (%)[b]
	51	 c	80
	72	 d	92
	54	 e	68
	60	 f	70
 $Ph(CH_2)_2C(OH)(CH_3)CH_2SPh$	53	 $Ph(CH_2)_2C(CH_3)=CH_2$ g	90
 $CH_3(CH_2)_8C(OH)(CH_3)CH_2SPh$	74	 $CH_3(CH_2)_8C(CH_3)=CH_2$ h	96
 $CH_3(CH_2)_5CH(OH)CH(SPh)_2$	88	 $CH_3(CH_2)_5CH=CH\sim SPh$ i	60

a. ref. 5; b. Isolated yields; c. ref. 7a; d. ref. 7b; e. ref. 7c; f. ref. 7d; g. ref. 7e; h. ref. 7f; i. ref. 7g.

Table 2. Reduction Peak Potentials[a] of Some β-Hydroxysulfides

β-Hydroxysulfides	Ep (V *vs.* SCE.)	β-Hydroxysulfides	Ep (V *vs.* SCE.)
	-2.15	 $CH_3(CH_2)_8C(OH)(CH_3)CH_2SPh$	-1.80
	-1.87	 $Ph(CH_2)_2C(OH)(CH_3)CH_2SPh$	-1.80
	-1.75		

a. Conditions of the measurement are as follows. Solvent, DMF; supporting electrolyte, 0.05 M Et_4NCl; substrate, 0.05 M; scanning rate, 100 mV/sec; anode and cathode, Pt.



····(3)

In order to clarify the mechanism of this 1,2-elimination, the reduction peak potentials of some β-hydroxysulfides were measured (Table 2).

The fact that the reduction peak potentials of β-hydroxysulfides were observed in the range of -1.75—-2.15 V *vs.* SCE., while those of alkyl phenyl sulfides bearing no β-hydroxy group showed far negative values[10] suggests that the initiation step involves the electron transfer to β-hydroxysulfides followed by the concerted elimination of both hydroxyl and phenylthio groups. Further mechanistic study based on the relationship between reduction potential and structure is in progress.

Because of its generality and simplicity, the present method may possess high potentiality in the synthesis of olefins.

References and Notes

1. Electroorganic Chemistry 33.
2. For example, (a) A. W. Burgstahler and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **85**, 173 (1963); (b) J. Wolinsky, R. L. Marhenke, and E. J. Eustace, *J. Org. Chem.*, **38**, 1428 (1973); (c) M. Brink, *Synthesis*, **1975**, 807; (d) T. Shono, Y. Matsumura, S. Kashimura, and H. Kyutoku, *Tetrahedron Lett.*, **1978**, 1205.
3. (a) I. Kuwajima and M. Uchida, *Tetrahedron Lett.*, **1972**, 649; (b) I. Kuwajima, S. Sato, and Y. Kurata, *ibid.*, **1972**, 737; (c) R. C. Sowerby and R. M. Coates, *J. Am. Chem. Soc.*, **94**, 4758 (1972); (d) Y. Watanabe, M. Shiono, and T. Mukaiyama, *Chem. Lett.*, **1975**, 871; (e) B. Lythgoe and I. Waterhouse, *Tetrahedron Lett.*, **1977**, 4223; (f) T. Mukaiyama and M. Imaoka, *Chem. Lett.*, **1978**, 413.
4. T. Shono, Y. Matsumura, S. Kashimura, and H. Kyutoku, Abstracts of the 6th Symposium on Organosulfur and Phosphorus Chemistry, Japan, 1978, p.17.
5. β-Hydroxysulfides were prepared according to the known method,[6] and their spectral data were reasonable for the assigned structures.

6. E. J. Corey and D. Seebach, *J. Org. Chem.,* **31**, 4097 (1966).

7. (a) bp 102-106 °C/90 Torr: IR (neat); 3070, 1640, and 895 cm^{-1}: NMR (CCl_4), δ 4.7-4.3 (2H, broad d., $>\!\!=CH_2$), 2.5-0.7 (18H, m., $-CH_2-C=C-$, $-CH_2-$, and $-CH_3$): MS, m/e 152 (M^+); (b) bp 110-115 °C/15 Torr: IR (neat), 3060, 1635, 910, and 810 cm^{-1}: NMR (CCl_4), δ 6.0-4.5 (5H, m., $>\!\!=CH_2$ and $-CH=CH_2$), 2.6-0.7 (17H, m., $-CH_2-$): MS, m/e 178 (M^+); (c) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *J. Am. Chem. Soc.,* **84**, 3164 (1962). IR (neat); 3080, 1630, and 890 cm^{-1}: NMR (CCl_4), δ 4.7-4.5 (2H, broad s., $>\!\!=CH_2$), 2.4-1.9 (4H, m., $-CH_2-C=C-$), 1.8-1.3 (10H, m., $-CH_2-$): MS, m/e 124 (M^+); (d) B. Waegell and J. Casanova, *Bull. Chim. Soc. Fr.,* **1971**, 1295. IR (neat), 3070, 1635, and 890 cm^{-1}: NMR (CCl_4), δ 4.8 (2H, broad s., $>\!\!=CH_2$), 2.2-1.8 (4H, t., $-CH_2-C=C-$), 1.7-1.0 (18H, broad s., $-CH_2-$): MS, m/e 180 (M^+); (e) P. Warric, Jr. and W. H. Saunder, Jr., *J. Am. Chem. Soc.,* **84**, 4095 (1962). IR (neat), 3070, 3020, 1640, 1595, and 885 cm^{-1}: NMR (CCl_4), δ 7.4-6.8 (5H, broad s., $-C_6H_5$), 4.8-4.6 (2H, broad s., $>\!\!=CH_2$), 2.9-2.2 (4H, m., $-CH_2-$), 1.9-1.8 (3H, s., $=\!\!<_{CH_3}$): MS, m/e 146 (M^+); (f) F. Mitarb, *J. Polymer. Sci.,* **3**, 45 (1948). IR (neat), 3060, 1640, and 880 cm^{-1}: NMR (CCl_4), δ 4.7-4.5 (2H, broad s., $=CH_2$), 2.3-1.8 (2H, m., $=C-CH_2-$), 1.7-1.6 (3H, s., $=\!\!<_{CH_3}$), 1.6-0.7 (17H, m., $-CH_2-$ and $-CH_3$): MS, m/e 168 (M^+); (g) This product was isolated by column chromatography. IR (neat), 3060, 3010, 1580, 740, and 690 cm^{-1}: NMR (CCl_4), δ 7.3-7.0 (5H, m., C_6H_5-), 6.1-5.3 (2H, m., $-CH=CH-SPh$), 2.4-1.8 (2H, m., $-C=C-CH_2-$), 1.7-0.6 (11H, m., $-CH_2-$ and $-CH_3$).

8. All intermediates and products described in equations 2 and 3 gave satisfactory spectroscopic data for assigned structures.

9. The substitution of phenylthio group preferentially took place on the more substituted carbon.

10. M. M. Baizer, Ed., "Organic Electrochemistry", Marcel Dekker, New York, N. Y., 1970, p. 750.