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NEW SYNTHETIC REACTION BY ELECTROLYSIS. III.1)
α-ACETOXYLATION OF SULFIDE

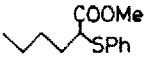
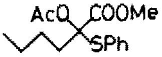
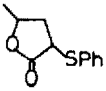
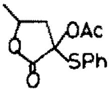
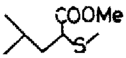
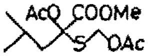
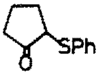
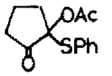
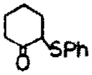
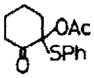
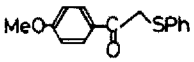
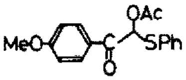
Junzo Nokami, Muyu Hatate, Shoji Wakabayashi, and Rokuro Okawara
Okayama University of Science, Ridai, Okayama, 700 Japan

Summary: Sulfides are directly converted effectively to the corresponding α-acetoxy sulfides by electrolysis in acetic acid.

α-Acetoxy sulfides have been employed as ketone (or aldehyde) synthon in organic synthesis. They are usually derived by Pummerer rearrengement2) of sulfoxides which were prepared from corresponding sulfides by the oxidation using various peroxides. The α-acetoxylation of ß-keto sulfide by lead tetraacetate has been reported resently.3) In this communication, we describe one step conversion of a sulfide to the α-acetoxy sulfide by electrolysis in acetic acid with sodium acetate.4) By the present finding, almost all the typical oxidation reactions of sulfur compounds (at sulfur5) or α-carbon6)) can be replaced by electrolytic procedures.

A typical reaction carried out was as follows. Octyl phenyl sulfide (5 g, 17 mmol) was dissolved in acetic acid (5 ml) with

Table 1 Acetoxylation of Sulfide

Sulfide	AcONa (mol equiv)	Electricity^a) (F/mol)	Product	Yield (%)
	1/3	2.5		71
	1/2	2.2		24
				40
	1/3	2.5		78
	1/3	2.0		78
	1/3	2.5		49
				9
	1/4	2.3		50
	1/5	3.0		62
	1	2.5		55

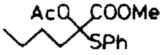
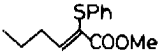
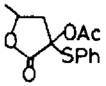
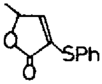
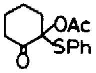
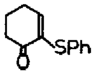
a) Current density; 0.05 A/cm^2

sodium acetate (0.05 g, 6 mmol), and electrolyzed without cooling by using platinum electrodes (3 cm^2) with stirring. After appropriate amount of electricity was passed (see Table 1), acetic acid was removed under reduced pressure. The residue was washed with aqueous sodium carbonate and extracted with ether. The pure α-acetoxy sulfide (71%) was obtained by column chromatography (SiO_2, ether-hexane (1/4)). Typical results are listed in Table 1.

Pyrolysis (Table 2) of the α-acetoxy sulfide (neat) at 80-145°C for 1.5-2 hr gave the αß-unsaturated sulfide in good yield.

These reactions are employed effectively for synthesis[7] of Pellitorine, Prostaglandin intermediate, and Pyrenophorin.

Table 2 Pyrolysis of α-Acetoxy Sulfide

Acetoxy Sulfide	Product	Yield(%)
		97
		94
		82
		82
		66[a]

a) Overall yield from methyl α-(phenylthio)decanoate without isolation of α-acetoxy sulfide. bp 163-6°C/0.45 Torr.

References and Notes

1) Part I. J. Nokami, M. Kawada, R. Okawara, S. Torii, and H. Tanaka, Tetrahedron Lett., 1045(1979); Part II. J. Nokami, T. Yamamoto, M. Kawada, M. Izumi, N. Ochi, and R. Okawara, ibid., 1047(1979).

2) K. Iwai, M. Kawai, H. Kosugi, and H. Uda, Chem. Lett., 385(1974); T. Numata, J. Syn. Org. Chem. Jpn., 36, 845(1978); and references cited therein.

3) B. M. Trost and G. S. Massiot, J. Am. Chem. Soc., 99, 4405(1977).

4) Sodium acetate seems to be the best supporting electrolyte for our purpose.

5) For instances, we could list up the following reports. F. Magno et al., J. Electroanal. Chem., 30, 375(1971); S. Torii et al., Tetrahedron Lett., 4513(1972); J. Nokami et al., ibid., 3659(1979); S. Torii et al., J. Org. Chem., 44, 2938(1979).

6) Oxidation at α-carbon with C-C bond cleavage; S. Torii et al., J. Org. Chem., 43, 5020(1978); J. Nokami et al., Chem. Lett., 1283(1978), Tetrahedron Lett., 1045(1979).
Oxidation at α-carbon without C-C and C-S bond cleavage; This report.

7) J. Nokami et al., to be published.

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