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PYROLYSIS OF β-HYDROXY SULFOXIDES TO KETONES

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In recent years, the pyrolysis of α-sulfinyl compounds to the corresponding α,β-unsaturated compounds has gained interest because of its availability in organic syntheses.1) We recently deviced a facile reaction of a new type Grignard reagent(1), derived from ethyl α-phenylsulfinylacetate and alkylmagnesium halides, with aldehydes to give the corresponding α-ethoxycarbonyl-β-hydroxy sulfoxides(2).2) During the course of our experiments concerned with the desulfurization of 2, we have now found a novel elimination accomplishing the conversion of 2 to β-keto esters(3) (Scheme 1). Namely, when 2 was heated under reflux in benzene for 2-4 hr, 3 was obtained in satisfactory yields together with a small amount of its tautomer. The typical results are compiled in Table 1. Incidentally, in the case, phenyl benzenethiolsulfonate and diphenyl disulfide were also obtained. The formation of these compounds may be due to the disproportionation of benzenesulfenic acid initially formed.3)

Scheme 1

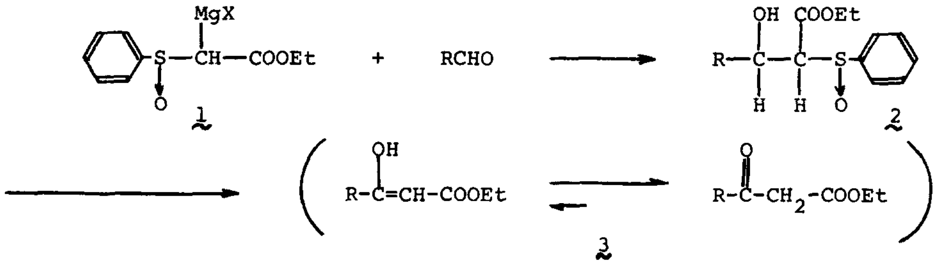
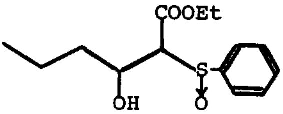
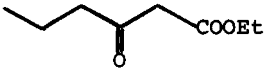
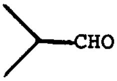
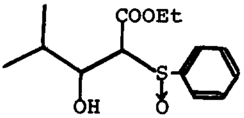
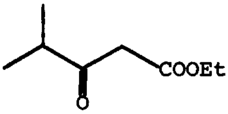
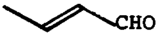
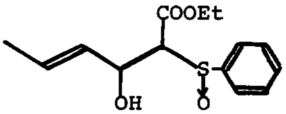
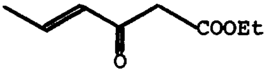
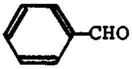
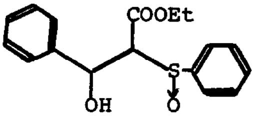
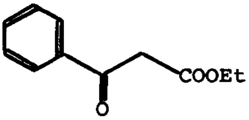


Table 1 Syntheses of β-Keto Esters

Aldehydes	β-Hydroxy sulfoxides(yield %)[a]		β-Keto esters(yield %)[a]	
		(95)		(75)
		(97)		(83)
		(90)		(90)
		(84)		(95)

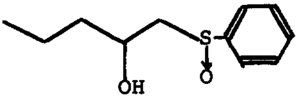
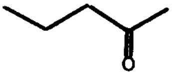
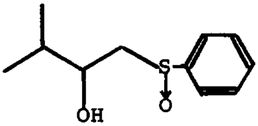
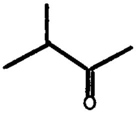
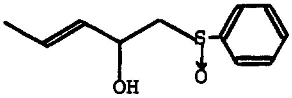
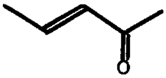
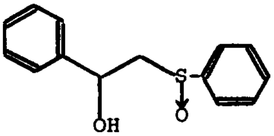
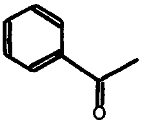
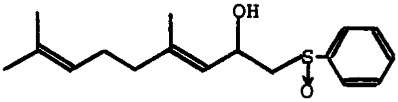
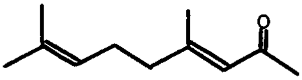
a) Satisfactory nmr, ir, and elemental analyses were obtained for all products.

Moreover, we have found that the common β-hydroxy sulfoxides such as 4 also display the feature of the same type of elimination affording methyl ketones(5) in good yields when heated at much higher temperatures(150-160°C) without solvent. The pyrolysis was carried out in a distillation tube and the product was distilled continuously(Scheme 2). The results are summarized in Table 2.

Scheme 2

4 5

Table 2 Syntheses of Methyl Ketones (**4**~**5**)

β-Hydroxy sulfoxides a) (yield b) %)		Methyl ketones (yield b) %)	
	(95)		(80)
	(95)		(88)
	(93)		(82)
	(95)		(95)
	(84)		(74)

a) The β-hyroxy sulfoxides (**4**) were prepared by the reaction of α-sulfinyl-carbanion with aldehydes according to the method reported by Tsuchihashi et al.4)

b) Satisfactory nmr, ir, and elemental analyses were obtained for all compounds.

Inspection of these results reveals that the pyrolysis proceeds obviously through the initial formation of enol compound. In the case of **2**, we think, the ease of the elimination may be due to the fact that the enol form of β-keto esters is more stable than that of single carbonyl compounds.

Further study on the application for organic syntheses of this finding is in progress.

References and Notes

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4) G.Tsuchihashi, S.Iriuchijima, and M.Ishibashi, Tetrahedron Lett.,4605(1972); Since it is known that β-hydroxy sulfoxides are obtained from the cooxidation of α-olefins and thiols with oxygen,5) this pyrolysis is of great advantage to convert α-olefins to methyl ketones.

5) S.Iriuchijima, K.Maniwa, T.Sakakibara, and G.Tsuchihashi, J.Org.Chem.,39, 1170(1974).