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PYROLYSIS OF ß-HYDROXY SULFOXIDES. II.
SYNTHESIS OF ALLYLIC ALCOHOLS

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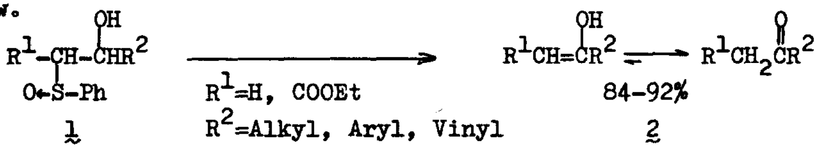
It has been reported[1] briefly that the pyrolysis under a mild condition of ß-hydroxy methylsulfoxides gives ketones smoothly. This sort of intramolecular reaction which may proceed through the elimination of the sulfenic acid has recently been noticed. We have described[2] the formation of a ketone with accompanying tautomer by the pyrolysis (R^1=H: distillation at 150-160°C under reduced pressure. R^1=COOEt: reflux in benzene) of ß-hydroxy phenylsulfoxides as shown below.



$$R^1\text{-}\underset{O\leftarrow S\text{-}Ph}{\underset{|}{CH}}\text{-}\overset{OH}{\overset{|}{C}}HR^2 \xrightarrow[R^2=\text{Alkyl, Aryl, Vinyl}]{} R^1CH{=}\overset{OH}{\overset{|}{C}}R^2 \rightleftharpoons R^1CH_2\overset{O}{\overset{\|}{C}}R^2$$

1 R^1=H, COOEt; R^2=Alkyl, Aryl, Vinyl; 84-92% 2

Recently, similar results of pyrolysis with α-chloro-ß-hydroxy phenylsulfoxides have also been reported.[3]

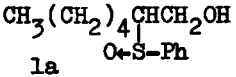
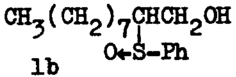
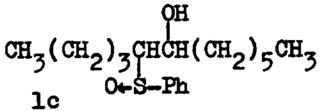
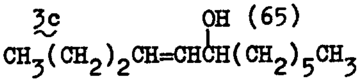
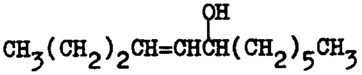
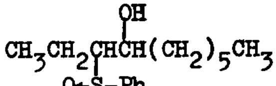
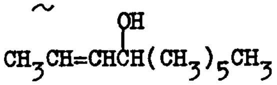
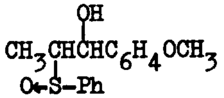
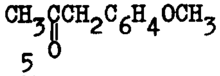
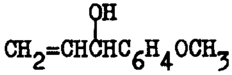
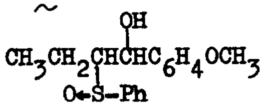
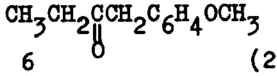
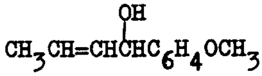
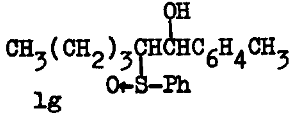
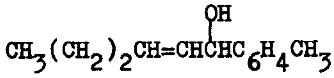
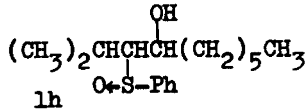
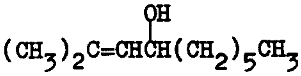
Now, we have found further that the product of this type of reaction with α-alkyl sulfoxides (R^1=alkyl in 1)[4] is not limited to the ketone but the allylic alcohol (see 3a or 3c in Table 1) is formed. As shown in Table 1, the satisfactory yield of allylic alcohols has been obtained by the pyrolysis condition in refluxing xylene with suspended sodium carbonate. Even such compounds 1e-f which give 5 and 6 by mere thermal decomposition can be converted with good yield to allylic alcohols 3e-f.

A typical procedure is as follows. The sulfoxide (1 mmol) in xylene (1 ml) with suspended sodium carbonate (excess, finely powdered) was refluxed with stirring for 1 hour. The mixture was filtered through an active alumina (300 mesh, 2 g) column, and washed with dichloromethane (5 ml). Removal of the solvent from the methanol filtrate (ca. 10-15 ml) under reduced pressure gave only an allylic alcohol, which was found to be geometrically pure (E).

References and Notes

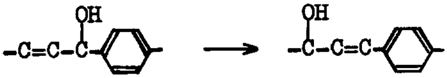
1) G. A. Russell, E. Sabourin, and G. J. Mikol, J. Org. Chem., 31, 2854(1966).
2) J. Nokami, N. Kunieda, and M. Kinoshita, Tetrahedron Lett., 2841(1975).
3) V. Reutrakul and W. Kanghae, Tetrahedron Lett., 1225(1977).
4) α-Alkyl-ß-hydroxy phenylsulfoxides were prepared by a convenient method from substituted α-phenylsulfenylacetyl chlorides; J. Nokami, Y. Takagi, and R. Okawara, to be published.

Table 1

Sulfoxides	Pyrolysis Products (Yield %) At 130-180°C under reduced pressure	In refluxing xylene with suspended Na_2CO_3
 $CH_3(CH_2)_4\underset{O\leftarrow S-Ph}{CH}CH_2OH$ 1a	$CH_3(CH_2)_3CH{=}CHCH_2OH$ 3a (70)	
 $CH_3(CH_2)_7\underset{O\leftarrow S-Ph}{CH}CH_2OH$ 1b		$CH_3(CH_2)_6CH{=}CHCH_2OH$ 3b (94)
 $CH_3(CH_2)_3\underset{O\leftarrow S-Ph}{CH}\overset{OH}{CH}(CH_2)_5CH_3$ 1c	3c (65)  $CH_3(CH_2)_2CH{=}CH\overset{OH}{CH}(CH_2)_5CH_3$ $CH_3(CH_2)_2(CH{=}CH)_2(CH_2)_4CH_3$ 4 (10)	 $CH_3(CH_2)_2CH{=}CH\overset{OH}{CH}(CH_2)_5CH_3$ 3c (88)
 $CH_3CH_2\underset{O\leftarrow S-Ph}{CH}\overset{OH}{CH}(CH_2)_5CH_3$ 1d		 $CH_3CH{=}CH\overset{OH}{CH}(CH_3)_5CH_3$ 3d (82)
 $CH_3\underset{O\leftarrow S-Ph}{CH}\overset{OH}{CH}C_6H_4OCH_3$ 1e	 $CH_3\underset{O}{\overset{\Vert}{C}}CH_2C_6H_4OCH_3$ 5 (trace)	 $CH_2{=}CH\overset{OH}{CH}C_6H_4OCH_3$ 3e (79)
 $CH_3CH_2\underset{O\leftarrow S-Ph}{CH}\overset{OH}{CH}C_6H_4OCH_3$ 1f	 $CH_3CH_2\underset{O}{\overset{\Vert}{C}}CH_2C_6H_4OCH_3$ 6 (21)	 $CH_3CH{=}CH\overset{OH}{CH}C_6H_4OCH_3$ 3f (72)
 $CH_3(CH_2)_3\underset{O\leftarrow S-Ph}{CH}\overset{OH}{CH}C_6H_4CH_3$ 1g		 $CH_3(CH_2)_2CH{=}CH\overset{OH}{CH}C_6H_4CH_3$ 3g (75)
 $(CH_3)_2CH\underset{O\leftarrow S-Ph}{CH}\overset{OH}{CH}(CH_2)_5CH_3$ 1h		 $(CH_3)_2C{=}CH\overset{OH}{CH}(CH_2)_5CH_3$ 3h (70)

5, 6, The formation of these oxygen migrated products appears to be a result from preferential dehydration of the benzylic alcohols(1e-f).

3e, 3f, 3g These alcohols are unstable, the skeletal structure changes clearly in a few weeks as indicated below.



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