

## Reactions of Sulphoxides with Sulphonyl Halides

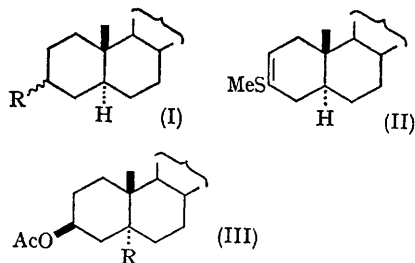
By D. NEVILLE JONES,\* M. J. GREEN, and M. A. SAEED

(Department of Chemistry, The University, Sheffield, 10)

THE conversion of sulphoxides into  $\alpha$ -chloro-sulphides by acyl halides and thionyl chloride,<sup>1</sup> and into  $\alpha$ -acetoxy-sulphides by acetic anhydride<sup>2</sup> constitutes a class of reactions related to the Pummerer rearrangement.<sup>3</sup> Further examples of this type of reaction are provided by recent reports of the conversion of dimethyl sulphoxide into chloromethyl methyl sulphide by arylsulphonyl chlorides.<sup>4</sup> We now report that sulphoxides undergo two reactions with sulphonyl chlorides which are not analogous to the Pummerer rearrangement. One involves deoxygenation without  $\alpha$ -chlorination, and the other results in the elimination of an alkylsulphinyl group to give olefins.

$3\alpha$ -Phenylsulphinyl- $5\alpha$ -cholestane (I; R =  $3\alpha$ -SOPh) was deoxygenated to  $3\alpha$ -phenylthio- $5\alpha$ -cholestane (I; R =  $3\alpha$ -SPh) in methanesulphonyl chloride solution.  $3\beta$ -Phenylsulphinyl- $5\alpha$ -cholestane, and  $3\alpha$ - and  $3\beta$ -methylsulphinyl- $5\alpha$ -cholestane were likewise deoxygenated to the corresponding sulphides. The reaction was complete after 18 hr. at room temperature for the phenyl

sulphoxides, and after 40 hr. for the methyl sulphoxides. In pyridine solution, with a tenfold molar excess of methanesulphonyl chloride, the reactions were complete in 15 min., but the product compositions were altered; deoxygenation of the phenyl sulphoxides was accompanied by some



inversion at C-3, whilst the methyl sulphoxides reacted to give 3-methylthio- $5\alpha$ -cholest-2-ene (II) as well as the products of deoxygenation. Some sulphide of inverted configuration was also formed from the  $3\alpha$ -(methyl sulphoxide). The structure

TABLE  
*Reaction of steroidal sulphoxides with methanesulphonyl chloride*

Sulphoxide	Solvent	Products <sup>a</sup>		
		(I; R = 3 $\alpha$ -SPh)	(I; R = 3 $\beta$ -SPh)	(II)
(I; R = 3 $\alpha$ -SOPh)	.. .. . none	62	0	0
(I; R = 3 $\beta$ -SOPh)	.. .. . none	0	60	0
(I; R = 3 $\alpha$ -SOPh)	.. .. . pyridine	56	8	0
(I; R = 3 $\beta$ -SOPh)	.. .. . pyridine	2	65	0
		(I; R = 3 $\alpha$ -SMe)	(I; R = 3 $\beta$ -SMe)	(II)
(I; R = 3 $\alpha$ -SOMe)	.. .. . none	58	0	0
(I; R = 3 $\beta$ -SOMe)	.. .. . none	0	60	0
(I; R = 3 $\alpha$ -SOMe)	.. .. . pyridine	7	3	50
(I; R = 3 $\beta$ -SOMe)	.. .. . pyridine	0	33	35
		(III; R = SMe)	3 $\beta$ -Acetoxy-5 $\alpha$ -cholest-4- and -5-ene.	
(III; R = SOMe)	.. .. . pyridine	37	41	

<sup>a</sup> Percentage yields in columns.

of the vinyl sulphide (II) was established by Raney nickel desulphurization to 5 $\alpha$ -cholest-2-ene, and by hydrolysis to 5 $\alpha$ -cholestan-3-one. 3 $\beta$ -Acetoxy-5 $\alpha$ -methylsulphinylcholestan (III; R = SOMe) with methanesulphonyl chloride in pyridine gave the sulphide (III; R = SMe) and a mixture of 3 $\beta$ -acetoxycholest-4- and -5-ene. The results are collected in the Table.

For the reactions in pyridine solution very similar results were obtained when toluene-*p*-sulphonyl chloride was used instead of methanesulphonyl chloride. The reactions were performed

with the *R*- and *S*-diastereomeric sulphoxides, and the identity of the results for each pair of diastereoisomers indicated that the reactions were independent of the stereochemistry at sulphur.

We believe that sulphonium ions such as (I; R = +SMe-OSO<sub>2</sub>Me) are involved as intermediates in these reactions, and their varying modes of decomposition will be discussed in a future publication.

(Received, May 19th, 1967; Com. 492.)

<sup>1</sup> F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, 1955, **77**, 572.

<sup>2</sup> W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, 1963, **28**, 2686.

<sup>3</sup> R. Pummerer, *Ber.*, 1910, **43**, 1401.

<sup>4</sup> E. H. Amonoo-Neizer, S. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 6250; R. E. Boyle, *J. Org. Chem.* 1966, **31**, 3880.