

STEREOSELECTIVE PUMMERER REACTION OF 4-p-CHLOROPHENYLTHIANE S-OXIDE
 WITH ACETIC ANHYDRIDE

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Among many examples of the Pummerer reaction of S-oxides of sulfur-heterocycles with acetic anhydride, stereoselective (or stereospecific) Pummerer reactions were reported only in the following two cases of five-membered sulfur-heterocycles, i.e., S-oxides of thiosugar derivatives,¹⁾ and S-oxides of 1,3-oxathiolane derivatives.²⁾ Now we wish to report a first example of stereoselective Pummerer reaction of the S-oxides of a simple six-membered sulfur-heterocycle.

When conformationally fixed 4-p-chlorophenylthiane S-oxide (1) was heated with a large excess of acetic anhydride at 100°C, the corresponding oily axial α -acetoxy sulfide (2a) was found to be formed stereoselectively from both the trans sulfoxide (1t) and the cis sulfoxide (1c). (runs 3 and 4 in Table) Meanwhile, the stereoselectivity of the reaction was found to be changed dramatically by addition of dicyclohexylcarbodiimide (DCC) or 2,6-lutidine into the media. (runs 5-11) For example, the treatment of the sulfoxide with acetic anhydride in the presence of a five molar amount of DCC gave the corresponding crystalline equatorial α -acetoxy sulfide (2e) stereoselectively. (runs 8 and 9)

These interesting findings on the stereoselectivity in the Pummerer reaction suggest that the equatorial α -acetoxy sulfide (2e) is a kinetically controlled product and an acid-catalyzed isomerization of the equatorial α -acetoxy sulfide (2e) to the thermodynamically stable α -acetoxy sulfide (2a) is involved during the reaction if in the absence of DCC or 2,6-lutidine (runs 1-4), which may act as a scavenger of acetic acid formed along the reaction.³⁾

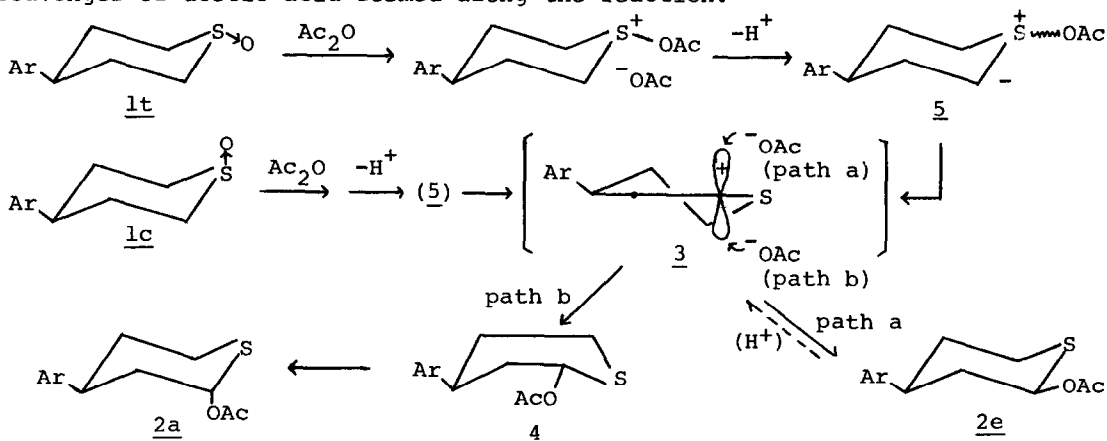


Table The Pummerer reaction of the thiane S-oxide (1) with Ac₂O at 100°C

Run	Sulfoxide	Acid-scavenger (ratio) ^a	Reaction time (hr)	Products(%)	
				<u>2</u> (<u>2e</u> : <u>2a</u>) ^b	vinyl sulfide ^c
1	<u>1t</u>	-	0.75 ^d	40 (1 : 1)	
2	<u>1c</u>	-	0.75 ^d	40 (1 : 1)	
3	<u>1t</u>	-	3	70 (1 : 15)	23
4	<u>1c</u>	-	3	71 (1 : 15)	21
5	<u>1t</u>	DCC (1)	4	78 (2 : 1)	20
6	<u>1c</u>	DCC (1)	4	77 (2 : 1)	20
7	<u>1t</u>	DCC (3)	4	85 (9 : 1)	11
8	<u>1t</u>	DCC (5)	4	83 (13 : 1)	9
9	<u>1c</u>	DCC (5)	6	83 (14 : 1)	12
10	<u>1c</u>	2,6-lutidine (5)	4.5	81 (5 : 2)	15
11	<u>1c</u>	2,6-lutidine (10)	4.5	86 (5 : 1)	12

a: ratio = acid scavenger/sulfoxide (1) b: the ratio(2e : 2a) was determined by NMR measurement c: α , β -unsaturated 4-p-chlorophenylthiane d: the starting sulfoxide (1) was recovered in ca. 50% yield

The stereoselective reaction would proceed through the formation of the sulfur-stabilized carbonium ion intermediate (3), which is then attacked by external acetoxy group preferentially from the upper direction (path a) to give the equatorial α -acetoxy sulfide (2e), while the attack from the bottom side (path b) to give the boat-formed α -acetoxy sulfide (4) is less favorable kinetically and eventually undergoes conformation change to give the axial isomer (2a). The acid-catalyzed isomerization of (2e) to (2a) is considered to proceed via the carbonium ion intermediate (3).

The reaction was also found to proceed via an intermolecular acetoxy migration in view of the following ¹⁸O tracer experiments. Namely, when the ¹⁸O-labeled trans sulfoxide (1t) (1.09 ex.atom%) was heated with a large excess of acetic anhydride alone at 100°C for 45 min (about half completion), the recovered sulfoxide, contaminated with no cis sulfoxide, was found to have retained completely the original ¹⁸O-content (1.09 ex.atom%), while the Pummerer product (2) (mixture of 2e and 2a ; 2e/2a = 1) was found to retain only 1.2% of ¹⁸O (0.01 ex.atom%) of the original sulfoxide. Similarly the cis sulfoxide (1c) (0.50 ex. atom%) gave the product (2) which is incorporated with only 0.02 ex.atom% of ¹⁸O.

References and Note

1. J.E. McCormick and R.S. McElhinney, J. Chem. Soc., Perkin I, 2533 (1976).
2. S. Glue, I.T. Kay and M.R. Kipps, J. Chem. Soc., Chem. Commun., 1158 (1970).
3. DCC is considered to have acted only as an effective acid scavenger like 2,6-lutidine, since when (+) N,N-dimethyl-p-tolylsulfanyl-acetamide was heated with acetic anhydride either in absence or in presence of DCC, the corresponding (-) α -acetoxy sulfide was found to be formed.⁴⁾
4. T. Numata, O. Itoh and S. Oae, Annual Meeting of Japan Chem. Soc., 2I 29 (1978), Nagoya.

(Received in Japan 17 October 1978)