

FACILE PUMMERER REARRANGEMENT OF SULFOXIDE  
IN AN ACETIC ANHYDRIDE-TRIFLUOROACETIC ANHYDRIDE MIXTURE

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The Pummerer rearrangement of sulfoxide under the influence of an acidic catalyst gives an  $\alpha$ -substituted sulfide.<sup>1)</sup> Recently, the rearrangement with hot acetic anhydride was applied to the conversion of an  $\alpha$ -sulfinylmethylene carbon to an aldehyde group.<sup>2)</sup> This method, however, cannot be applied to the sulfoxide with an active hydrogen atom at a  $\beta$ -position, because it undergoes the elimination reaction to an olefin at high temperature.<sup>3)</sup>

We have found that, when the rearrangement is carried out in acetic anhydride containing trifluoroacetic anhydride (TFAA),  $\alpha$ -acetoxysulfide can readily be obtained at lower temperature.

General Procedure: TFAA (15 mmol) was dissolved in acetic anhydride (10 ml) and kept standing for 5 hours at room temperature. Sulfoxide I (10 mmol), and, a few minutes later, 2,6-lutidine (20 mmol) were added to the mixture, and then, were kept being stirred for 0.5-3 hours at room temperature. After removal of acetic anhydride under reduced pressure, the solution was extracted with benzene, and washed with dil. hydrochloric acid, a  $\text{NaHCO}_3$  solution and water. After removal of benzene,  $\alpha$ -acetoxysulfide II was obtained by preparative layer chromatography (silica gel). Some experimental data obtained (Method A) are shown in Table.

Table. Rearrangement of I,  $\text{R-CH}_2\text{CH}_2\text{-S-C}_6\text{H}_4\text{-X-p}$  to II,  $\text{R-CH}_2\text{CH-S-C}_6\text{H}_4\text{-X-p}$   
 $\text{O}$   $\text{O-COCH}_3$

R	X	Method A		Method B*	
		Yield(%)	Reaction Time(hr)	Yield(%)	Reaction Time(hr)
$\text{C}_6\text{H}_5\text{O-}$	H	76	0.5	77	7
$\text{C}_2\text{H}_5\text{O-}$	H	87	0.5	81	7
$\text{CH}_3(\text{CH}_2)_3\text{-}$	H	84	0.5	62	7
$\text{C}_6\text{H}_5\text{S-}$	H	56	0.5	45	7
$(\text{C}_2\text{H}_5\text{OCO})_2(\text{C}_2\text{H}_5)\text{C-}$	H	60	3	40	7
$(\text{CH}_3)_2(\text{NO}_2)\text{C-}$	H	64	3	38	11
$\text{C}_6\text{H}_5\text{O-}$	Cl	63	0.5	60	9

\* I(10 mmol) and  $\text{NaOCOCH}_3$  (30 mmol) in acetic anhydride (30 ml) were refluxed.<sup>2)</sup>

