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 α -substituted sulfide.¹⁾ Recently, the rearrangement with hot acetic anhydride was applied to the conversion of an α -sulfinylmethylene carbon to an aldehyde group.²⁾ This method, however, cannot be applied to the sulfoxide with an active hydrogen atom at a β -position, because it undergoes the elimination reaction to an olefin at high temperature.³⁾

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

<u>General Procedure</u>: 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 NaHCO₃ solution and water. After removal of benzene, α -acetoxysulfide II was obtained by preparative layer Chromatography (silica gel). Some experimental data obtained (Method A) are shown in Table.

		Method A		Method B*	
R	x	Yield(%)	Reaction Time(hr)	Yield(%)	Reaction Time(hr)
C _c H _c O-	Н	76	0.5	77	7
с ₆ н ₅ 0- с ₂ н ₅ 0-	Н	87	0.5	81	7
сн ₃ (Сн ₂) ₃ -	н	84	0.5	62	7
C ₆ H ₅ S-	н	56	0.5	45	7
(C ₂ H ₅ OCO) ₂ (C ₂ H ₅)C-	н	60	3	40	7
(CH ₃) ₂ (NO ₂)C-	н	64	3	38	11
C ₆ H ₅ O-	Cl	63	0.5	60	9

Table. Rearrangement of I, $R-CH_2CH_2-S-C_6H_4-X-p$ to II, $R-CH_2CH-S-C_6H_4-X-p$

* I(10 mmol) and NaOCOCH₃ (30 mmol) in acetic anhydride (30 ml) were refluxed²⁾

The Pummerer rearrangement in an acetic anhydride-TFAA mixture more quickly gave II in higher yield than that without TFAA. Futhermore, it gave neither olefin nor disulfide resulting from the thermal elimination reaction. Interest-ingly, any α -trifluoroacetoxysulfide was not detected. A plausible reaction mechanism seems to be as follows;

$$(CH_{3}CO)_{2}O + (CF_{3}CO)_{2}O \longrightarrow 2 CH_{3}COOCOCF_{3}$$

$$(1)^{4}$$

$$R-CH_{2}CH_{2}-S-R' + CH_{3}COOCOCF_{3} \longrightarrow R-CH_{2}CH_{2}-\frac{1}{5}-R', OCOCF_{3} \longrightarrow R-CH_{2}CH_{2}-\frac{1}{5}-R', OCOCF_{3} \longrightarrow R-CH_{2}CH_{2}-\frac{1}{5}-R', OCOCF_{3} \longrightarrow R-CH_{2}CH_{2}-\frac{1}{5}-R', CH_{2}CH_{2}-\frac{1}{5}-R', CH_{2}-\frac{1}{5}-R', CH_{2$$

The following factors seem to play an important role in this smooth reaction, that is, a trifluoroacetate anion CF_3COO^- is an excellent leaving group, and an acetate anion CH_3COO^- is a stronger nucleophile than CF_3COO^- .

The following results are consistent with the above-mentioned mechanism; (i) I and acetyltrifluoroacetate in acetonitrile gave II at room temperature in reasonable yield.

(ii) I in TFAA did not give α -trifluoroacetoxysulfide in good yield because of the weak nucleophilicity of a trifluoroacetate anion.

(iii) When I and TFAA were added to acetic anhydride, and kept standing at room temperature, II was obtained in good yield, but it took several hours probably because the equilibrium (1) is not promptly reached.

All sulfoxides shown were easily prepared by Michael addition to vinyl aryl sulfoxide. This means that the following aldehyde synthesis using vinyl aryl sulfoxide is possible;

References

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