Pergamon

Tetrahedron Letters, Vol. 35, No. 21, pp. 3575-3576, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)E0591-K

A NOVEL ASYMMETRIC PUMMERER REACTION INDUCED BY ETHOXY VINYL ESTER

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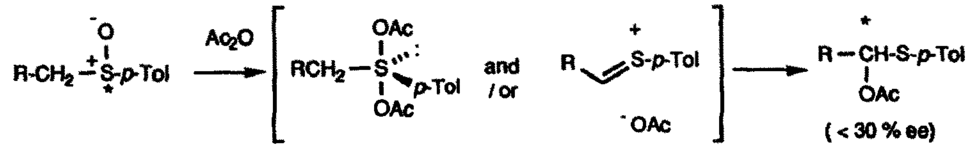
Abstract: Ethoxy vinyl ester is a novel efficient reagent for the asymmetric Pummerer reaction having high enantioselectivity and high yield.

The Pummerer rearrangement is widely used for the preparation of α-acyloxysulfides from sulfoxides by treatment of acid anhydrides, acids, or acid halides.[1] Although the asymmetric Pummerer rearrangement is of significant importance due to the chiral transfer from optically active sulfoxides to the α-carbon of the sulfur, the extent of asymmetric induction never exceeded 30 % e.e. This is probably due to the formation of a sulfurane intermediate and the dissociation of the intimate ion pair by reaction with the generated acetate anion (eq. 1).[2] Although the addition of 1,3-dicyclohexylcarbodiimide (DCC) as an effective scavenger of acetic acid increased enantioselectivity, the chemical yield significantly decreased[3] and the Pummerer reaction of chiral benzyl tolylsulfoxide in the presence of DCC gave only the racemic adduct.[4] Recently, we reported the first highly asymmetric silicon-induced Pummerer-type reaction of chiral sulfoxides using *O*-methyl-*O*-*tert*-butyldimethylsilyl ketene acetal (**1**), which gave chiral α-siloxysulfides under mild conditions in high yield (eq. 2).[5] The main reason for this high asymmetric induction seems to be the absence of sulfurane formation. Therefore, we now examined a novel asymmetric Pummerer reaction using a similar type of acyl-induced reagent, ethoxy vinyl ester (**2**), which is known as a powerful acylating reagent[6] for active hydrogen compounds such as alcohols, amines, and carboxylic acids and found **2** caused the highly asymmetric Pummerer rearrangent of chiral sulfoxides (**3**) leading to α-acetoxysulfides (**4**).



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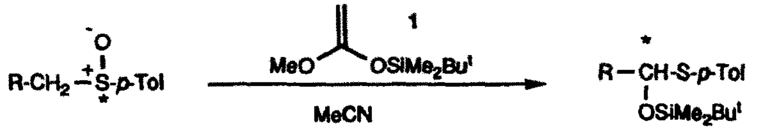
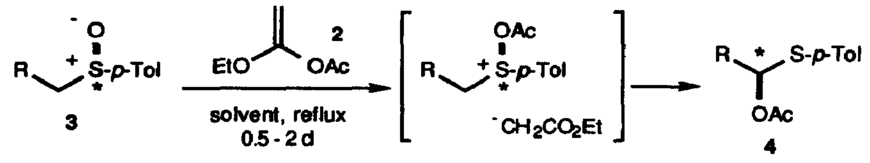


—(2)

Treatment of *R*-**3a** with **2** in refluxing $(CH_2Cl)_2$, benzene or toluene gave chiral *R*-α-acetoxysulfide (*R*-**4a**) in considerably high e.e. (Table 1). Observed e.e.'s and yields were higher than those of the reported asymmetric Pummerer rearrangement using acid anhydrides in all cases. Although the asymmetric induction of the present asymmetric Pummerer reaction is slightly lower than the silicon-induced Pummerer reaction, it is quite interesting to increase the asymmetric induction by preventing the formation of the sulfurane intermediate. The difference in e.e. of both reactions may come from the releasing character of the O-Si and O-acyl groups or the intimate ion character of the O-Si and O-acyl anion pairs.[5b)]

Table 1. Pummerer Reaction of Chiral Sulfoxides (3) with Ethoxy Vinyl Ester (2).



3	R	Solvent	4	Product % Ee (% Yield)	 $[\alpha]_D$ (*c*, acetone)	Reported Method % Ee (% Yield)
R-**3a**	$CONMe_2$	$(CH_2Cl)_2$	*R*-**4a**	68 [a] (72)	-35.4 (0.51)	65(35)
		benzene		72 [a] (52)	-38.2 (0.82)	
		toluene		84 [a] (34)	-46.5 (0.50)	
R-**3b**	CO_2Et	$(CH_2Cl)_2$	*R*-**4b**	77 [b] (58)	-57.6 (0.91)	70 (10)
		benzene		76 [b] (43)	-57.0 (1.0)	
		toluene		71 [b] (42)	-53.4 (1.5)	
S-**3c**	$P(O)(OMe)_2$	$(CH_2Cl)_2$	*S*-**4c**	75 [b] (44)	-12.5 (1.5)	24 (73)
		toluene		69 [b] (38)	-11.5 (1.5)	
R-**3d**	Ph	toluene	*R*-**4d**	20 [a] (64)	-5.29 (1.6)	0 (10)

[a] E.e. value was determined from ^1H-NMR ($CDCl_3$) with $Eu(hfc)_3$.
[b] E.e. value was calculated from the reported $[\alpha]_D$ value. See Ref. 2-4.

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(*Received in Japan* 29 *January* 1994)