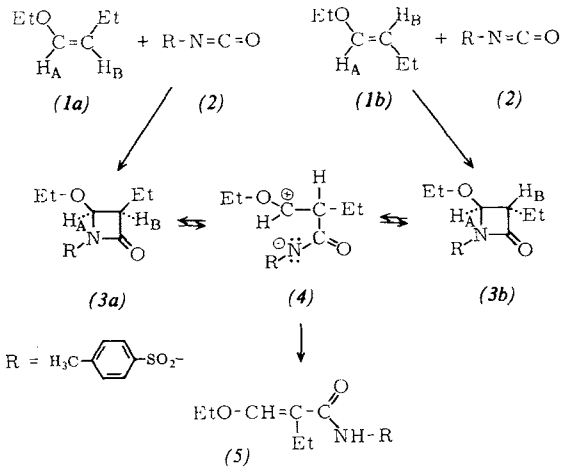


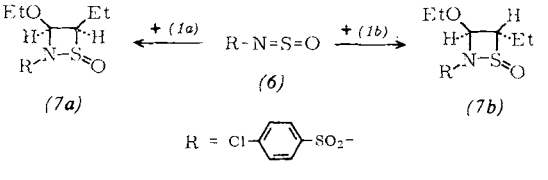
Reaction of (2) with (1a)			Reaction of (2) with (1b)		
Reaction time (min)	(3a) (%)	(3b) (%)	Reaction time (min)	(3a) (%)	(3b) (%)
1	95	—	1	10	90
3	90	10			
7	80	20	5	15	85
10.5	75	25			
18	65	36			
23	54	46	24	20	80
62	30	70	63	23	77
1440	27	73	1440	27	73

The proportions of the β-lactams *(3a)* and *(3b)* formed (see table) can be obtained from the newly appearing resonance signals of the proton H_A in *(3a)* or *(3b)* with an accuracy of about ± 4 %. *(3a)*: H_A gives a doublet at $\tau = 4.5$, J_{AB} 5.3 Hz; *(3b)*: H_A gives a doublet at $\tau = 4.81$, $J_{AB} = 2$ Hz. The structures *(3a)* and *(3b)* are assigned on the basis of the coupling constants J_{AB} [4].

From the table it can be seen that *(1a)* reacts stereospecifically with *(2)* and that *(1b)* reacts stereoselectively, but that after somewhat more than an hour an equilibrium mixture containing 27 % of *(3a)* and 73 % of *(3b)* is formed from either pure *(1a)* or pure *(1b)*. The isomerization *(3a)* $\rightleftarrows$ *(3b)* is formulated as occurring by way of a resonance-stabilized polar intermediate *(4)*.

When kept for several days in $DCCl_3$ the equilibrium mixture of *(3a)* and *(3b)* rearranges to the thermodynamically more stable compound *(5)*, the compound *(4)* being again assumed as intermediate.

Enol ethers combine with *N*-sulfinylsulfonamides to give 1,2-thiazetidine 1-oxides *(7)* [5]. NMR spectroscopic studies conducted during this cycloaddition in $DCCl_3$ show a stereospecific reaction of both *(1a)* and *(1b)*. The products *(7a)* and *(7b)* do not isomerize and do not rearrange on long storage in $DCCl_3$.



The results show that in the reaction of enol ethers with polar reagents the kinetically controlled cycloaddition occurs largely synchronously. Quite possibly, different bond lengths are to be considered for the transition state [6]. Depending on the ring strain, isomerization and removal of a proton occur,

Stereochemistry of the Cycloaddition of Sulfonyl Isocyanates and *N*-Sulfinylsulfonamides to Enol Ethers [1]

By *F. Effenberger* and *G. Kiefer* [*]

4-Alkoxyazetidin-2-ones *(3)* are formed on cycloaddition of sulfonyl isocyanates to enol ethers under mild conditions [2]. We have now studied the stereochemistry of this reaction in order to decide between a synchronous mechanism, as proposed by *Huisgen et al.* [3] for the cycloaddition of ketenes to enol ethers, and a two-stage reaction involving an intermediate compound of type *(4)*.

The *cis*- and *trans*-1-butenyl ethyl ethers *(1a)* and *(1b)*, which are separable by preparative gas chromatography, were treated separately in $DCCl_3$ with *p*-tosyl isocyanate *(2)* in the molar proportions 1:1, and the progress of the reaction was followed by NMR spectroscopy (Table).

One minute after the reactants had been mixed the signals of *(1a)* (H_A = doublet at $\tau = 4.18$, H_B = quadruplet at $\tau = 5.74$; $J_{AB} = 6.3$ Hz) and *(1b)* (H_A = doublet at $\tau = 3.82$, H_B = 2 triplets at $\tau = 5.32$; $J_{AB} = 12.6$ Hz) had disappeared, whence it is concluded that there is very rapid reaction with *(2)*.

both under thermodynamical control, to give a stable substitution product.

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