

EPOXIDATION OF *cis/trans*-ENOL ESTERS BY DIMETHYLDIOXIRANE: KINETICS

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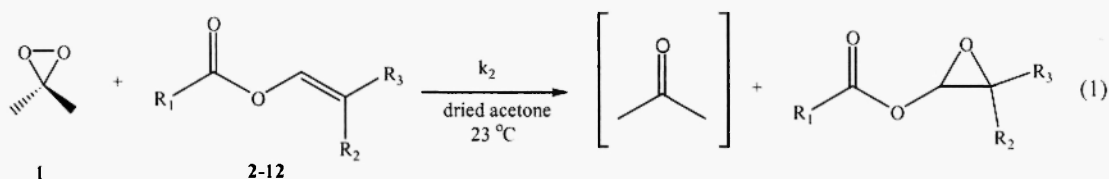
Abstract. The epoxidation of a series of *cis/trans*-enol esters with R groups of varying steric bulk by dimethyldioxirane in dried acetone at 23 °C produced the corresponding *cis/trans*-epoxides as the sole observable products. The kinetics study showed k_{cis} / k_{trans} ratios of 1.6 to 2.5. The k_2 values for the *cis*-compounds were essentially identical while those for the *trans*-compounds showed a consistent decrease with increasing steric bulk.

Introduction

Dimethyldioxirane, either *in situ*¹ or in an isolated solution,² has been shown to be a versatile and useful oxidation reagent for a broad scope of synthetic applications.³ Epoxidation is one of the most investigated reactions of dimethyldioxirane. Epoxidation by dimethyldioxirane, **1**, has been shown to be stereospecific and postulated to occur via a concerted electrophilic process with a "spiro" transition state.⁴ The epoxidation of simple alkenes and α,β -unsaturated carbonyl compounds by **1** has been extensively investigated.³ Previous studies have shown this electrophilic process to be affected by steric effects within a series and by electronic effects between series.⁵ However, the epoxidation of enol esters by **1** has not been extensively investigated other than that for isolated reports.⁶ We report here the results of a kinetics study of the epoxidation of a series of *cis/trans*-enol esters with substituents of varying steric bulk by dimethyldioxirane in dried acetone.

Results and Discussion

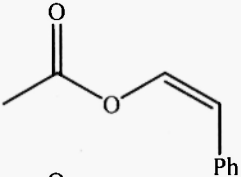
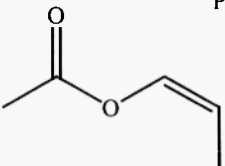
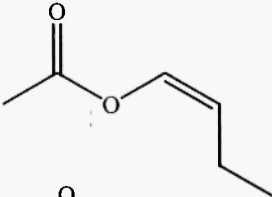
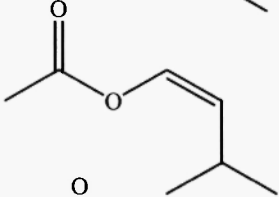
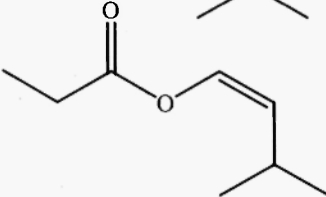
The epoxidation of a series of *cis* (**2-6**) and *trans* (**7-12**) substituted enol esters at 23 °C by dimethyldioxirane (**1**) produced the corresponding epoxides as the sole products in all cases (reaction 1).



cis ($R_3 = H$) R_1, R_2 : (2) Me, Ph; (3) Me, Me; (4) Me, Et; (5) Me, *i*Pr; (6) Et, *i*Pr
trans ($R_2 = H$) R_1, R_3 : (7) Me, Ph; (8) Me, Me; (9) Me, Et; (10) Me, *i*Pr; (11) Et, *i*Pr; (12) Me, *t*Bu

The epoxides were identified and characterized by comparison of the spectral data with literature values.⁷ Kinetic studies were carried out at 23 °C in dried acetone using UV techniques. The k_2 values for **2**, **7**, and **12** were determined from the pure starting material. The k_2 values for **3-6**, **8-11** were determined from pure *cis/trans* mixtures.⁸ In selected cases, k_2 values were checked under pseudo first order conditions with 1:10 and 10:1 ratios of dioxirane to enol ester and were found to be identical (within experimental error $\pm 5\%$). The kinetic results for the *cis* and *trans* series enol esters are listed in Tables 1 and 2.

Table 1. Second order rate constants for the epoxidation of *cis* enol esters (**2-6**) by dimethyldioxirane in dried acetone at 23 °C.

Entry	Compound	k_2 (M ⁻¹ s ⁻¹)	k_2 (rel) ^a
2		$1.9 \pm 0.2 \times 10^{-2}$	0.24
3		$3.0 \pm 0.1 \times 10^{-2}$	$\equiv 1.0$
4		$8.1 \pm 0.3 \times 10^{-2}$	1.0
5		$7.9 \pm 0.2 \times 10^{-2}$	0.99
6		$7.1 \pm 0.2 \times 10^{-2}$	0.89

^a normalized for the series;

The *cis*-phenyl substituted enol ester, **2**, is considerably less reactive than the *cis*-alkyl substituted enol esters. A similar trend is observed⁵ with the *cis*-phenyl substituted alkenes and *cis*-alkyl substituted alkenes. The k_2 values (R=alkyl) for *cis*-enol esters **3-6** are essentially identical. These kinetic results are consistent with those found for the *cis*-alkenes.^{5b} Overall, the k_2 values for *cis*-enol esters were found to be

less than those of corresponding *cis*-alkenes⁴ and considerably greater than those of α,β -unsaturated carbonyl compounds.⁵

Table 2. Second order rate constants for the epoxidation of *trans* enol esters (7-12) by dimethyldioxirane in dried acetone at 23 °C.

Entry	Compound	k_2 (M ⁻¹ s ⁻¹)	k (rel) ^a	k_{cis}/k_{trans}
7		$1.2 \pm 0.2 \times 10^{-2}$	0.24	1.6
8		$5.0 \pm 0.1 \times 10^{-2}$	$\equiv 1.0$	1.6
9		$4.7 \pm 0.3 \times 10^{-2}$	0.94	1.7
10		$3.6 \pm 0.2 \times 10^{-2}$	0.74	2.2
11		$2.8 \pm 0.2 \times 10^{-2}$	0.58	2.5
12		$6.7 \pm 0.2 \times 10^{-3}$	0.13	N/A

^a normalized for the series

The *trans*-phenyl substituted enol ester, 7, is considerably less reactive than the *trans*-methyl substituted enol ester but more reactive than 12. For the *trans* series (7-12), a consistent decrease in k_2 is observed with increasing steric bulk of the R groups. In the enol ester series, the *trans*-enol esters are found to be slightly less reactive than the corresponding *cis*-enol esters. However, as steric bulk increased in the series, the *cis/trans* ratio increased, e.g. for enol esters 3/8, the *cis/trans* ratio was 1.6 while that for 6/11 was 2.5. In contrast, for simple alkenes, k_{cis}/k_{trans} ratios for the epoxidation by 1 of 7-22 have been found.⁴ A plot of k_{rel} *trans*-enol esters vs. k_{rel} *trans*-alkenes, showed the k_2 results for the *trans*-enol esters to be ~70% less sensitive to steric effects than the corresponding *trans*-alkenes.^{5b} Thus, the lower k_{cis}/k_{trans}

ratios in the present study are partially due to a decrease in sensitivity to steric effects in the enol ester series and the increased reactivity of the *trans* compounds.

In summary, the *cis*- and *trans*- enol esters (**2-12**) are slightly less reactive than the corresponding alkenes⁵ and considerably more reactive than the corresponding α,β -unsaturated carbonyl compounds.^{5b} The *trans*-enol esters are more reactive and less sensitive to steric influences than the corresponding *trans*-alkenes. Two factors that influence the *cis/trans*-enol ester ratio are: 1) the steric effects of the OAc group on the *trans*-enol ester and 2) the increased reactivity of the *trans*-enol ester.

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8. The six alkyl *cis/trans* compounds are reported⁷ as mixtures in the literature. The *cis/trans* ratios obtained: (3/8) 46:54; (4/7) 39:61; (5/8) 37:63; (6/9) 35:65 were in good agreement with the published results. Rate constants were determined from partial oxidations, product and kinetic studies and calculated employing the product and starting material *cis/trans* ratios.

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