KINETICS OF EPOXIDATION OF α,β-UNSATURATED CARBONYL COMPOUNDS AND ENOL ESTERS BY DIMETHYLDIOXIRANE

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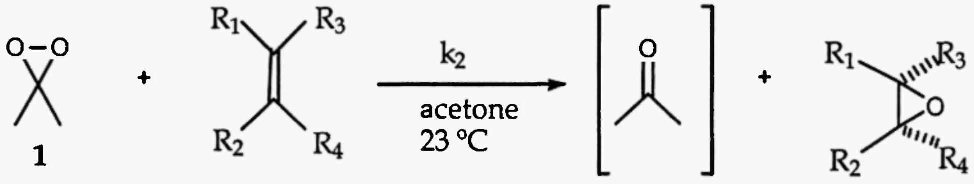
Abstract. Kinetic data for epoxidation of several series of α,β-unsaturated carbonyl compounds and enol esters by dimethyldioxirane in dried acetone are reported.

Introduction

Dioxiranes are efficient oxygen-atom transfer reagents for a wide variety of organic substrates.[1] Numerous synthetic transformations have been performed either in situ[2] or in isolated[3] solution with these powerful oxidants. In particular, dimethyldioxirane has been found to be a versatile epoxidizing agent.[1] The reaction of dimethyldioxirane with a wide variety of alkenes including α,β-unsaturated compounds has been shown to be electrophilic and stereospecific.[1] For simple epoxidation, a concerted "spiro" transition state process[4] has been generally accepted. Structural influences on alkene epoxidation have been extensively investigated.[5] Limited kinetic data on epoxidation of α,β-unsaturated compounds with dimethyldioxirane are available.[6] We report here the results of a kinetics study of the epoxidation of several series of α,β-unsaturated carbonyl compounds and enol esters by dimethyldioxirane in dried acetone.

Results and Discussion

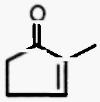
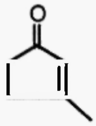
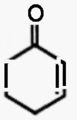
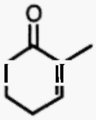
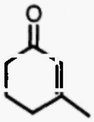
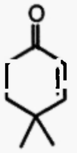
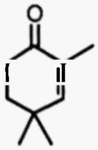
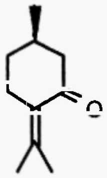
The reaction of dimethyldioxirane (**1**) with a series of α,β-unsaturated ketones **2-14**, α,β-unsaturated esters **15-20** and enol esters **21-25** produced the corresponding epoxides in essentially quantitative yields (reaction 1). The epoxides were isolated and characterized by comparison of spectral data with

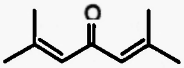
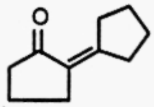
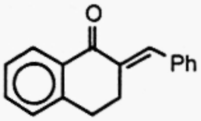
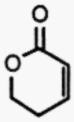
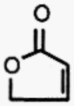
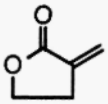
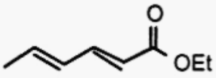
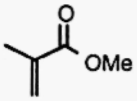
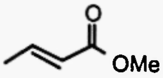
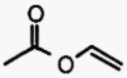
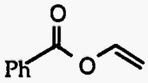
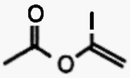
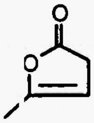
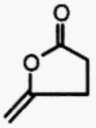


(1)

R_1 = R-(O)C **2-14**, R_1 = R-O-(O)C **15-20**, R_1 = R-(O)C-O **21-25** literature values. Kinetics studies were carried out in dried acetone at 23 °C employing UV techniques. The reactions were found to be of the first order with respect to both 1 and the substrates. The k_2 values determined under pseudo first order conditions with 10:1 or 1:10 ratios of dioxirane to substrate were identical. The kinetics results are listed in Table 1.

Table 1. Second Order Rate Constants for Epoxidation of α,β -Unsaturated Carbonyl Compounds **2-20** and Enol Esters **21-25** by Dimethyldioxirane **1** in Dried Acetone at 23°C.

Entry	α,β-Unsaturated Ketone	Structure	k_2 $M^{-1}s^{-1}$
2	2-cyclopentenone		$2.1 \pm 0.1 \times 10^{-4}$
3	2-methyl-2-cyclopenten-1-one		$9.3 \pm 0.2 \times 10^{-4}$
4	3-methyl-2-cyclopenten-1-one		$3.0 \pm 0.1 \times 10^{-4}$
5	2-n-pentyl-2-cyclopenten-1-one		$7.2 \pm 0.1 \times 10^{-4}$
6	2-cyclohexen-1-one		$8.7 \pm 0.2 \times 10^{-4}$
7	2-methyl-2-cyclohexen-1-one		$2.4 \pm 0.4 \times 10^{-3}$
8	3-methyl-2-cyclohexen-1-one		$2.0 \pm 0.3 \times 10^{-3}$
9	4,4-dimethyl-2-cyclohexen-1-one		$8.9 \pm 0.3 \times 10^{-4}$
10	2,4,4-trimethyl-2-cyclohexen-1-one		$1.8 \pm 0.1 \times 10^{-3}$
11	(R)-(+)-pulegone		$1.2 \pm 0.1 \times 10^{-2}$ [a]

12	phorone		$1.6 \pm 0.1 \times 10^{-2}$ [b]
13	2-cyclopentylidene-cyclopentanone		$3.9 \pm 0.4 \times 10^{-2}$
14	2-benzylidene-1-tetralone		$7.3 \pm 0.1 \times 10^{-3}$
15	5,6-dihydro-2H-pyran-2-one		$1.8 \pm 0.1 \times 10^{-4}$
16	2(5H)-furanone		$2.3 \pm 0.2 \times 10^{-3}$
17	α-methylene-γ-butyrolactone		$1.9 \pm 0.1 \times 10^{-3}$
18	ethyl sorbate		$2.4 \pm 0.1 \times 10^{-2}$ [b,c]
19	methyl methacrylate		$3.9 \pm 0.3 \times 10^{-4}$
20	methyl crotonate		$2.3 \pm 0.2 \times 10^{-3}$
21	vinyl acetate		$8.6 \pm 0.1 \times 10^{-3}$
22	vinyl benzoate		$1.1 \pm 0.1 \times 10^{-2}$
23	isopropenyl acetate		$1.7 \pm 0.1 \times 10^{-2}$
24	α-angelicalactone		$4.1 \pm 0.2 \times 10^{-1}$
25	γ-methylene-γ-butyrolactone		$3.7 \pm 0.2 \times 10^{-1}$

a) 2:1 Ratio of disasteriomeric epoxides. b) k_2 value for monoepoxidation. c) γ,δ-double bond epoxidation

For the α,β-unsaturated ketone series, **2-14**, the 5-ring compounds have lower k_2 values than the structurally analogous 6-ring compounds. For cyclic α,β-unsaturated compounds, formal increased methyl substitution has a slightly greater effect at the α-position than that at β. However, the magnitude of the increase in k_2's is generally smaller than that observed for simple alkenes.[5] Entries **11-13** are the most reactive compounds in the α,β-unsaturated ketone series. As expected, α,β-unsaturated esters[7] **15-20** are less reactive than the corresponding ketones while the enol esters are more reactive.

Our kinetic study of the epoxidation of chalcones by 1 indicated[6] that the reaction proceeded via an electrophiiic process. The observed sensitivity to structural variation for the present series of α,β-unsaturated compounds and enol esters is consistent with the electrophiiic mechanism. As noted for alkenes, the process is sensitive to steric influences.

In conclusion, the k_2 values for epoxidation of α,β-unsaturated compounds and enol esters by dimethyldioxirane show considerable variation with structure. The relative reactivity of the substrates is high enough to be of synthetic utility.

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References and Notes

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(7) Diethyl fumarate and maleate were found to be unreactive under the conditions employed in this study.

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