

## EPOXIDATION OF CHALCONES WITH *t*-BUTYL HYDROPEROXIDE IN PRESENCE OF AN IRON(III) SCHIFF BASE COMPLEX

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### ABSTRACT

Epoxidation of chalcone, 4-methoxy-, 4'-chloro-, 4'-bromo-, 3'-nitro-, 4'-methyl-3-nitro-, and 3'-nitro-3-nitrochalcones has been carried out with *t*-butyl hydroperoxide using *N, N'*-ethylenebis(salicylideneiminato)iron(III)- $\mu$ -oxo-*N, N'*-ethylenebis(salicylideneiminato)iron(III) complex as a catalyst. The effects of solvents, temperature, quantity of catalyst and different substituents on the yield of epoxides have also been studied. A probable free radical mechanism has been proposed.

### INTRODUCTION

SIGNIFICANT amount of work has been done on the preparation, characterization and industrial applications of epoxides<sup>1-4</sup>. Information concerning the role of metal complexes in oxidation has been gained from studies of their reactions with alkyl hydroperoxides under nonautoxidizing conditions<sup>5-7</sup>. *t*-Butyl hydroperoxide (TBHP) is thermally more stable and is less sensitive to contamination by metals than either organic peracids or hydrogen peroxide and is, therefore, safer to handle<sup>8,9</sup>. The present communication deals with the epoxidation reaction of chalcones with TBHP in presence of (Fe salen)<sub>2</sub>O complex as a catalyst.

### EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 399 IR spectrometer and UV-visible spectra on a Beckman Du-6, UV/vis spectrophotometer. <sup>1</sup>H NMR and mass spectra were recorded on a Varian 80-FT and spectra were obtained from a Jeal JMS-D mass spectrometer. Homogeneity and purity of the products were checked by TLC.

All reagents used were of analytical grade. Solvents were distilled and dried before use. Melting points are uncorrected. The *N, N'*-ethylenebis(salicylideneiminato)iron(III)- $\mu$ -oxo-*N, N'*-ethylenebis(salicylideneiminato)iron(III) complex was synthesized by reported methods<sup>10</sup>.

#### Synthesis of substrates

Various substrates (1a-1g) were synthesized following reported methods<sup>11</sup>. Chalcone (1a), 4-methoxychalcone (1b), 4'-chlorochalcone (1c), 4'-bromochal-

cone (1d), 3'-nitrochalcone (1e), 4'-methyl-3-nitrochalcone (1f) and 3'-nitro-3-nitrochalcone (1g) had melting points 56, 61, 138, 119, 145, 230 and 158° respectively.  $\mu$ (KBr) 1645-1695 (-C=O), 1610-1630 (-C=C-) and 965-985 cm<sup>-1</sup> (-C-H-);  $\lambda_{\max}$ (EtOH) 251-309 nm.

#### Epoxidation of substrates (1a-1g)

Chalcone (2.4 mmol), benzene (50 ml), catalyst (0.5 mmol), 10% aqueous NaOH (5 ml) and 80% TBHP (5 ml) were stirred at room temperature for 24-50 h. The TBHP and aqueous NaOH were added after 26 and 40 h. The reaction was monitored by TLC. The catalyst was filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated off, washed with H<sub>2</sub>O, 10% Na<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>O, and then dried. After evaporation of the solvent, the crude product was eluted on a silica gel column using CH<sub>2</sub>Cl<sub>2</sub> as eluant. The product thus obtained was crystallized from methanol.

### RESULTS AND DISCUSSION

The rate of epoxidation of substrates (1a-1g) is enhanced by electron donating groups as they elevate the energy of the  $\pi$  bond (HOMO), whereas electron withdrawing groups decrease the same and retard the rate of epoxidation (table 1). Most of the substrates under study have an electron withdrawing group and so the olefinic bond has lower electron density than in the unsubstituted chalcone. These substrates particularly do not undergo epoxidation in the absence of the catalyst. Thus (Fe salen)<sub>2</sub>O tends to improve the yield of the epoxides of electron-poor olefins. In the epoxidation process, pH also plays an important role. For example, 4-

**Table 1** Epoxidation of chalcones with TBHP and  $(Fe\ salen)_2O$  carried out at room temperature in benzene

	Substrate	Time (h)	Yield (%)
1a	Chalcone	30	79
1b	4-Methoxychalcone	24	82
1c	4'-Chlorochalcone	40	42
1d	4'-Bromochalcone	36	51
1e	3'-Nitrochalcone	35	60
1f	4'-Methyl-3-nitrochalcone	40	70
1g	3'-Nitro-3-nitrochalcone	38	35

methoxychalcone on epoxidation afforded the epoxide in 82% yield when the pH of the reactants was maintained between 7 and 8 (table 2).

The solvent also affects the yield of the epoxides. From table 3, it is evident that the rate decreases with decrease in the dielectric constant of the solvent.

The low yield of the epoxides at high temperatures is probably due to the decomposition of the

oxidizing agent. The most suitable temperature for the reaction was found to be  $\sim 22^\circ C$  (table 4).

In the absence of the catalyst, epoxides were obtained in negligible amounts. The optimum substrate : catalyst ratio has been found to be  $2.4 \times 10^{-3} : 0.5 \times 10^{-3}$ . As the amount of catalyst is decreased, the rate of epoxidation also decreases (table 5).

The epoxidation of chalcones using TBHP, diethyl tartrate and iron(III) schiff base complex was carried out following Sharpless oxidation method<sup>12</sup>. However, no asymmetric induction was observed in these cases.

The IR spectra of the epoxides show the characteristic bands of the oxirane ring in the range  $1220-1255\text{ cm}^{-1}$  and those of the carbonyl group at  $1650-1690\text{ cm}^{-1}$ . The  $^1H$  NMR spectra in  $CDCl_3$  show characteristic doublets at  $\delta$  4.40-4.67 and 4.03-4.36 ppm for three-membered ring protons.

In order to finally ascertain whether free radicals

**Table 2** pH Dependence of the epoxidation of chalcones at room temperature

Chalcone	4-Methoxy-chalcone		4'-Chloro-chalcone		4'-Bromo-chalcone		3'-Nitro-chalcone		4'-Methyl-3-nitrochalcone		3'-Nitro-3-nitrochalcone	
	pH	Time (h)	Yield (%)	pH	Time (h)	Yield (%)	pH	Time (h)	Yield (%)	pH	Time (h)	Yield (%)
	5.0	40	0	5.0	40	0	5.0	50	0	5.0	45	0
	6.0	38	25	6.0	38	35	6.2	45	10	6.1	45	18
	7.5	30	79	7.8	24	82	7.6	40	42	7.9	36	51
	9.3	30	0	9.3	30	0	9.0	40	0	9.1	35	0
	5.0	30	0	5.0	30	0	5.0	40	0	5.0	30	0
	6.0	35	22	6.0	35	22	6.0	45	0	6.0	35	22
	7.5	40	70	7.5	40	70	7.5	38	35	7.5	38	35
	9.0	50	0	9.0	50	0	9.0	50	0	9.0	50	0

**Table 3** Solvent effect on the epoxidation of chalcones at room temperature

Solvent	Dielectric constant	Chalcone		4-Methoxy-chalcone		4'-Chloro-chalcone		4'-Bromo-chalcone		3'-Nitro-chalcone		4'-Methyl-3-nitrochalcone		3'-Nitro-3-nitrochalcone	
		Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
Dichloromethane	9.08	30	83	20	88	35	55	38	58	36	65	35	76	40	42
Benzene	2.284	30	79	24	82	40	42	36	51	35	60	40	70	38	35
Carbon tetrachloride	2.238	35	75	35	80	35	39	35	42	38	52	45	65	35	80
Cyclohexene	2.220	38	67	40	70	35	32	40	38	38	45	40	51	40	25

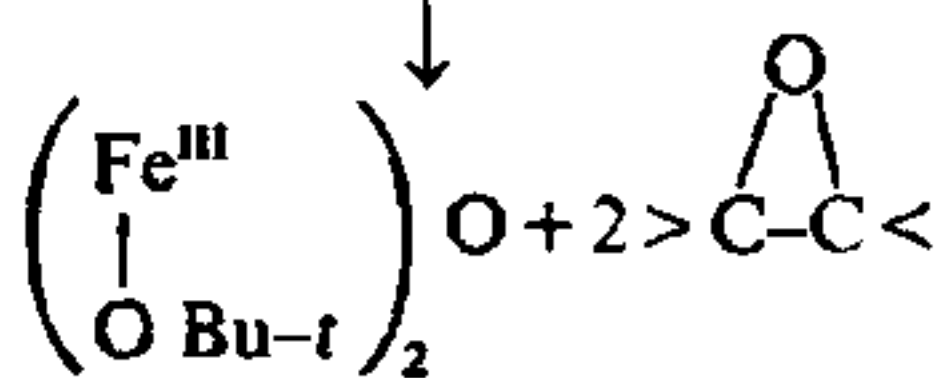
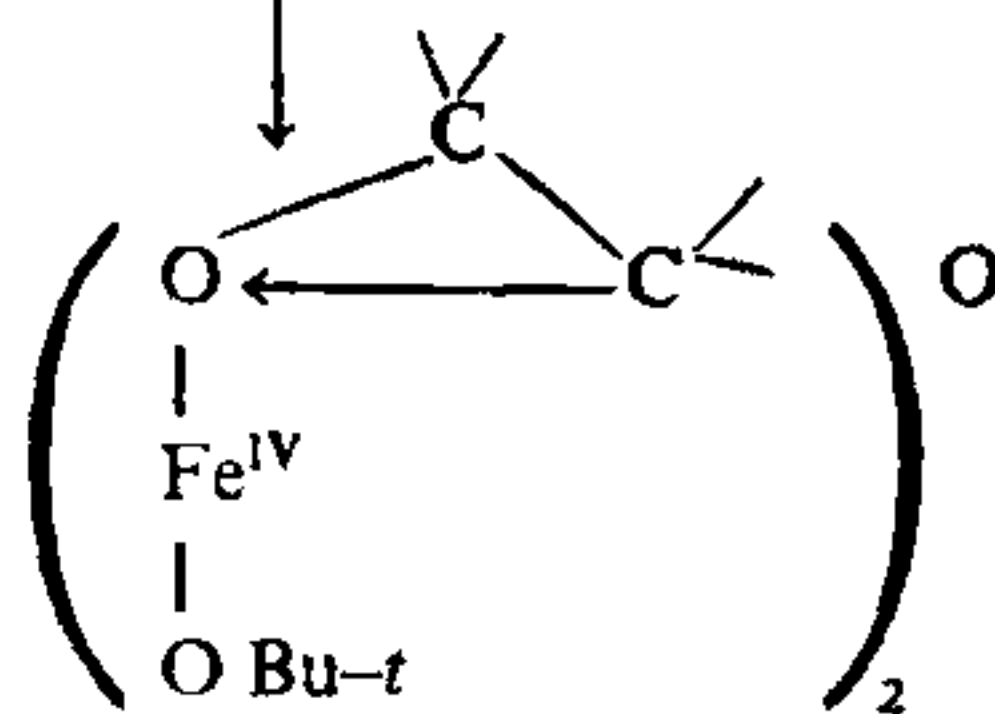
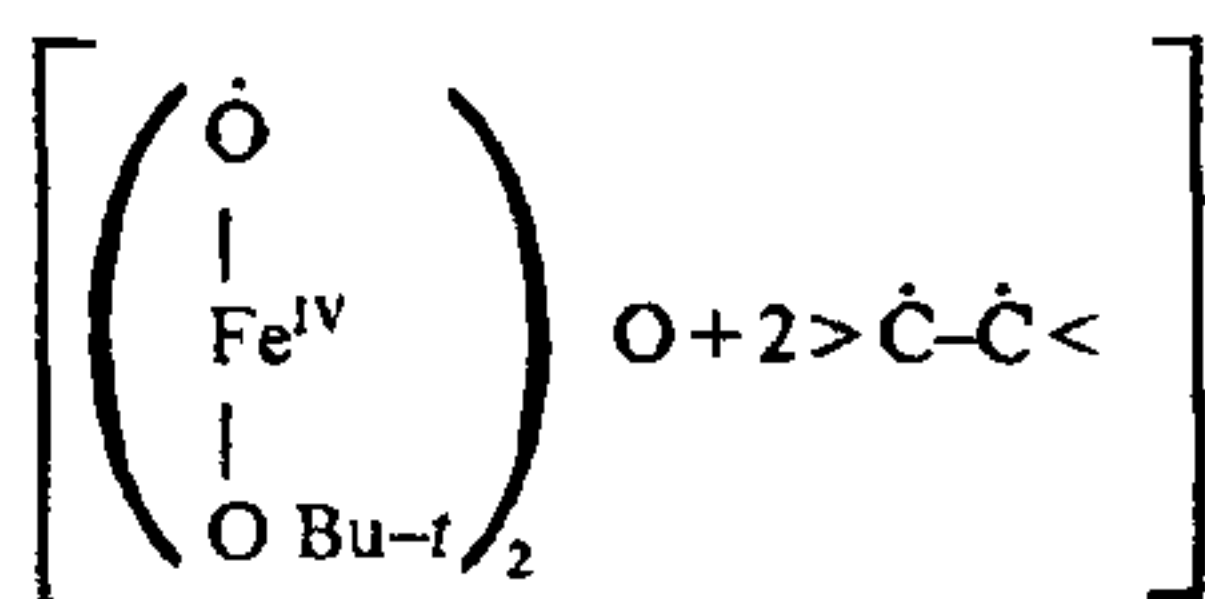
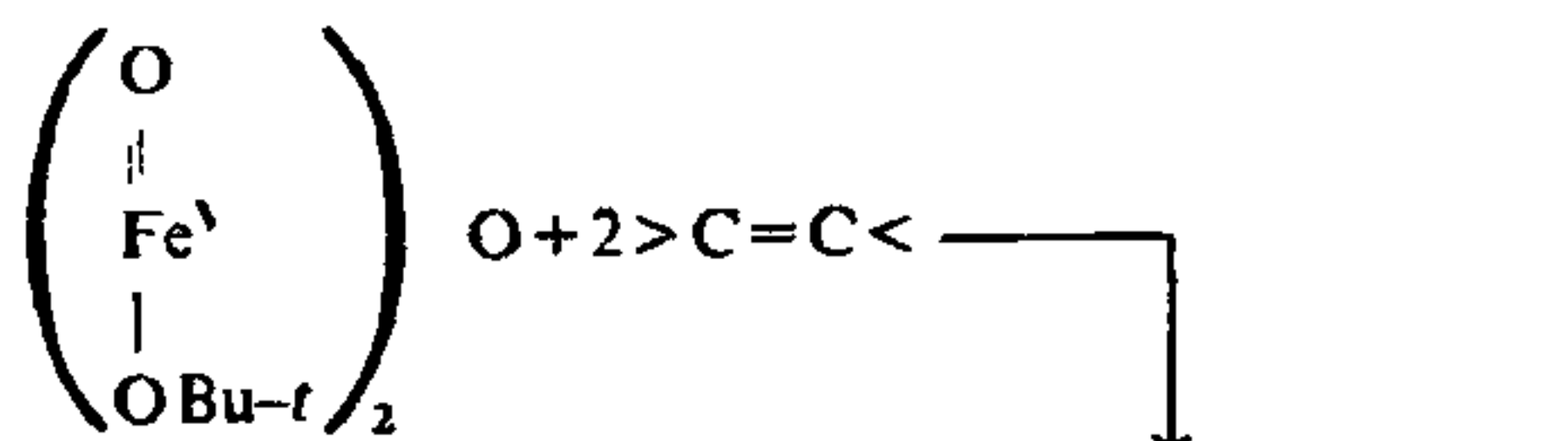
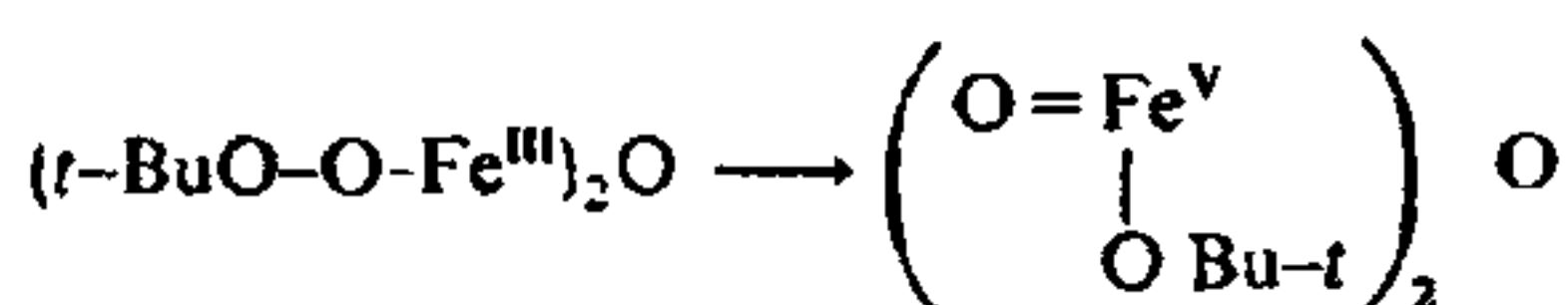
**Table 4** Temperature effects on the epoxidation of chalcones

Temperature ( $^\circ C$ )	Chalcone		4-Methoxy-chalcone		4'-Chloro-chalcone		4'-Bromo-chalcone		3'-Nitro-chalcone		4'-Methyl-3-nitrochalcone		3'-Nitro-3-nitrochalcone	
	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
0	85	46	80	52	80	30	90	35	80	38	82	40	80	15
25	30	79	24	82	40	42	36	51	35	60	40	70	38	35
40	55	20	50	33	50	8	50	15	50	18	50	19	50	5
60	64	15	55	20	60	5	60	10	62	12	60	14	60	0

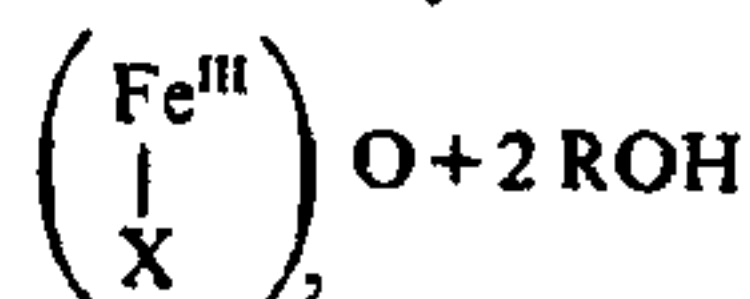
**Table 5** Effect of substrate catalyst ratio on the rate of epoxidation of chalcones at room temperature

Substrate (mmol)	Catalyst (mmol)	Chalcone		4-Methoxy-chalcone		4'-Chloro-chalcone		4'-Bromo-chalcone		3'-Nitro-chalcone		4'-Methyl-3-nitrochalcone		3'-Nitro-3-nitrochalcone	
		Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
48	0.5	35	75	28	78	42	40	40	45	35	50	35	62	40	25
24	0.5	30	79	24	82	40	42	36	51	35	60	40	70	38	35
24	0.2	35	32	35	40	40	18	42	20	40	25	40	28	45	10
24	0.4	32	45	30	55	38	20	40	24	40	30	35	33	40	12

play any role in these reactions. The effect of radical traps was studied on adding diphenylpicrylhydrazyl,



HX

**Scheme 1**

a well-known radical scavenger, to the reacting system. The rate of the reaction was observed to decrease. This amply proves that these reactions involve a radical mechanism.

Thus homolytic catalysis occurring in these reactions involves a one-electron process, in which free radicals are intermediates. Rapid decomposition of TBHP occurs in presence of trace amounts of the iron catalyst. A mechanism for this process of epoxidation can be proposed (scheme 1), involving the formation of an oxorion(V) species, which is an active oxidant. This participates in a 1,2-addition to the olefinic double bond.

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