

Epoxidation of Chalcones with *t*-Butylhydroperoxide in Presence of a Cobalt(II) Schiff Base Complex

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The epoxidation of some chalcones, i.e. 3-nitrochalcone, 4'-methoxy-3-nitrochalcone, 4'-hydroxy-4-methoxychalcone, 3'-aminochalcone, 3'-amino-3-nitrochalcone, 2-methoxychalcone and 2-hydroxy-chalcone has been carried out with *t*-butylhydroperoxide using cobalt(II) Schiff base complex as a catalyst. The effects of solvent, temperature, different substituents and quantity of catalyst on the yield of the epoxides have also been studied. A probable free radical mechanism has been proposed.

In recent years, epoxides have evinced much interest in view of their varied usefulness as reagents, intermediates and end-products. The epoxidation of alkenes and related compounds with organic per-acids and hydrogen peroxide catalysed by transition metal complexes of Mo, W, V, Ti, Ni etc. has been extensively studied by several workers¹⁻³. The metal-catalysed homolytic decomposition of alkyl hydroperoxidic intermediates is the most common pathway for the catalysis of liquid-phase autoxidation. Information concerning the role of metal complexes in oxidation has been gained from the separate studies of their interactions with alkyl hydroperoxides under nonautoxidising conditions⁴. Cobalt complexes are effective catalysts and have attracted attention in various oxidation processes⁵. The reversible complexation of molecular oxygen by aminocobalt(II) salts has been known since long⁶ and these complexes behave as reversible oxygen carriers⁷. No work however, seems to have been done on the epoxidation of chalcones employing a cobalt(II) Schiff base complex as a catalyst. The present communication concerns with the epoxidation of chalcones with *t*-butylhydroperoxide using *N,N'*-ethylenebis(salicylaldimine-5-sulphonato)cobalt(II) complex as a catalyst.

Experimental

Infrared spectra were recorded on a Perkin Elmer 399 spectrophotometer, electronic spectra on a Beckman DU-6 spectrophotometer and mass spectra on a Jeal JMS-D spectrometer. pH was recorded on a control dynamics APX 175 E/c-pH meter. 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. *N,N'*-Ethylenebis(salicylaldimine-5-sulphonato)cobalt(II) complex was prepared by the reported method⁸.

Synthesis of substrate : Chalcone (**1a** ; m.p. 56°), 3-nitrochalcone (**1b** ; 149°), 4'-methoxy-3-nitrochalcone (**1c** ; 147°), 4'-hydroxy-4-methoxychalcone (**1d** ; 200°), 3'-aminochalcone (**1e** ; 185°), 3'-amino-3-nitrochalcone (**1f** ; 148°), 2-methoxychalcone (**1g** ; 90°) and 2-hydroxychalcone (**1h** ; 141°) were synthesised following the reported methods⁹ ; ν_{\max} (KBr) 1 645–1 695 (C=O), 1 610–1 630 (C=C) and 965–985 cm^{-1} (CH) ; λ_{\max} (EtOH) 251–309 nm.

Epoxidation of 1a–h : A mixture of chalcone (2.4 mmol), benzene (50 ml), catalyst (0.5 mmol), 10% aqueous NaOH (5 ml) and 80% *t*-butyl hydroperoxide (5 ml) was stirred at room temperature for 24–58 h. Requisite amounts of triethanolamine were added to maintain the pH at 8–9. A 80% *t*-butyl hydroperoxide (5 ml) and a 10% aqueous NaOH (5 ml) were further added after 26 and 50 h. The reaction was monitored by tlc. The catalyst was filtered and washed with dichloromethane. The organic layer was separated and subsequently washed with water, 10% Na_2SO_3 and H_2O and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the crude product was eluted on a silica gel column using dichloromethane as eluant. It was crystallised from methanol.

Chalcone epoxide (2a) : m.p. 88° ; ν_{\max} (KBr) 1 685 (C=O), 1 235 (oxirane ring), 895 (C–O), 760 and 690 cm^{-1} ; δ (CDCl_3) 4.30 (1H, d, *J* 2 Hz), 4.05 (1H, d, *J* 2 Hz) and 7.35–8.15 (10H, m, ArH) ; λ_{\max} (EtOH) 250 nm ; *m/e* 224 (M^+). **3-Nitrochalcone epoxide (2b) :** m.p. 126° ; ν_{\max} (KBr) 1 690 (C=O), 1 510 (NO_2), 1 340 (NO_2), 890 (C–O) and 1 226 cm^{-1} (oxirane ring) ; δ (CDCl_3) 4.35 (1H, d, *J* 2 Hz), 4.10 (1H, d, *J* 2 Hz) and 7.30–8.30 (9H, m, ArH) ; λ_{\max} (EtOH) 255 nm ; *m/e* 269 (M^+). **3'-Nitro-4-methoxychalcone epoxide (2c) :** m.p. 138° ; ν_{\max} (KBr) 1 685 (C=O), 1 230 (oxirane ring), 889 (C–O), 2 820 (OMe) and 1 345 cm^{-1} (NO_2) ; δ (CDCl_3) 4.40 (1H, d, *J* 2 Hz), 4.0 (1H, d, *J* 2 Hz), 3.93 (3H, s, OMe) and 7.3–8.0 (8H, m,

ArH); λ_{\max} (EtOH) 252 nm; m/e 299 (M^+).
 4'-Hydroxy-4-methoxychalcone epoxide (2d): m.p. 140°; ν_{\max} (KBr), 1 665 (C=O), 1 265 (oxirane ring), 893 (C-O), 2 950 (OMe), 3 420 (OH), 745 and 690 cm^{-1} ; δ (CDCl_3) 3.85 (1H, d, J 2 Hz), 3.70 (1H, d, J 2 Hz), 3.90 (OMe) and 7.70–6.65 (8H, m, ArH); λ_{\max} (EtOH) 265 nm; m/e 270 (M^+).
 3'-Aminochalcone epoxide (2e): m.p. 201°; ν_{\max} (KBr) 1 680 (C=O), 1 255 (oxirane ring), 3 500 (NH_2) and 890 cm^{-1} (C-O); δ (CDCl_3) 4.05 (1H, d, J 2 Hz), 3.80 (1H, d, J 2 Hz) and 7.90–6.70 (9H, m, ArH); λ_{\max} (EtOH) 254 nm; m/e 239 (M^+).
 3'-Amino-3-nitrochalcone epoxide (2f): m.p. 250°; ν_{\max} (KBr) 1 690 (C=O), 1 225 (oxirane ring), 3 450 (NH_2), 1 505 (NO_2), 1 345 (NO_2), 880 (C-O), 750 and 695 cm^{-1} ; δ (CDCl_3) 4.2 (1H, d, J 2 Hz), 4.0 (1H, d, J 2 Hz) and 7.6–6.9 (9H, m, ArH); λ_{\max} (EtOH) 265 nm; m/e 284 (M^+).
 2-Methoxychalcone epoxide (2g): m.p. 165°; ν_{\max} (KBr) 1 675 (C=O), 1 260 (oxirane ring), 2 850 (OMe), 895 (C-O), 765 and 695 cm^{-1} ; δ (CDCl_3) 4.0 (1H, d, J 2 Hz), 3.9 (1H, d, J 2 Hz) and 7.80–6.85 (9H, m, ArH); λ_{\max} (EtOH) 258 nm; m/e 254 (M^+).
 2-Hydroxychalcone epoxide (2h): m.p. 125°; ν_{\max} (KBr) 1 690 (C=O), 1 250 (oxirane ring), 3 425 (OH), 780 and 690 cm^{-1} ; δ (CDCl_3) 4.1 (1H, d, J 2 Hz), 3.90 (1H, d, J 2 Hz) and 7.95–6.90 (9H, m, ArH); λ_{\max} 260 nm; m/e 240 (M^+).

Results and Discussion

The epoxidation of 1a–h in presence of N,N' -ethylenebis(salicylaldimine-5-sulphonato)cobalt(II) complex in general affords better yields. However, the rate of epoxidation is enhanced by electron-donating groups, as they elevate the energy of the π -bond (HOMO) whereas electron-withdrawing groups decrease the energy of the π -bond and retard the rate of epoxidation (Table 1). Cobalt(II) Schiff base acts as catalyst in enhancing the rate and yield of epoxidation in electron-poor olefins.

TABLE 1—EPOXIDATION AT ROOM TEMPERATURE IN BENZENE

pH=8–9			
Compd. no.	Substrate	Time h	Yield %
1a	Chalcone	35	82
1b	3-Nitrochalcone	56	58
1c	4'-Methoxy-3-nitrochalcone	45	70
1d	4'-Hydroxy-4-methoxychalcone	24	98
1e	3'-Aminochalcone	30	86
1f	3'-Amino-3-nitrochalcone	50	65
1g	2-Methoxychalcone	28	89
1h	2-Hydroxychalcone	30	84

The concentration of the base is found to affect the yield of epoxides. For example, 4'-hydroxy-4-methoxychalcone on epoxidation afforded the epoxides in 98% yield when pH of the reactants was maintained at 8–9 (Table 2). The solvent also affects the yield of the epoxides. From Table 3, it is evident that the rate of epoxidation decreases with

TABLE 2—pH-DEPENDENCE OF EPOXIDATION OF CHALCONES AT ROOM TEMPERATURE

Substrate	pH	Time h	Yield %
Chalcone	6.0	40	0
	7.2	38	41
	8.5	35	82
	10.0	45	0
3-Nitrochalcone	6.0	64	0
	7.0	59	29
	8.8	56	58
	10.2	60	0
4'-Methoxy-3-nitrochalcone	6.0	50	0
	7.0	46	36
	8.7	45	70
	10.0	55	0
4'-Hydroxy-4-methoxychalcone	6.0	48	0
	7.0	30	45
	8.8	24	98
	10.2	25	0
3'-Aminochalcone	6.1	40	0
	7.3	35	48
	8.9	30	86
	10.2	42	0
3'-Amino-3-nitrochalcone	6.0	40	0
	7.0	50	35
	8.8	50	65
	10.2	45	0
2-Methoxychalcone	6.0	48	0
	7.0	28	44
	8.7	28	89
	10.0	30	0
2-Hydroxychalcone	6.0	45	0
	7.0	38	43
	8.6	30	84
	10.0	40	0

the decrease in dielectric constant of the medium. The low yield of the epoxides at high temperatures is probably due to the decomposition of the oxidising agent. The most suitable temperature for the reaction was, however, found as $\sim 22^\circ$ (Table 4). In absence of the catalyst, poor yields of the epoxides were obtained. The optimum substrate–catalyst ratio has been found to be $2.4 \times 10^{-2} : 0.5 \times 10^{-2}$. As the amount of catalyst is decreased, the rate of epoxidation also decreases (Table 5).

The ir spectra of the epoxides show the characteristic bands of oxirane ring at 1 220–1 265 cm^{-1} and those of the carbonyl group at 1 650–1 690 cm^{-1} . The ^1H nmr spectra (CDCl_3) reveal characteristic doublets at δ 3.85–4.67 and 3.70–4.36 for three-membered ring protons.

In order to find out if free radicals play any role in these reactions, the effect of radical traps was studied. When diphenylpicrylhydrazyl (a well-known radical scavenger) was added to the reacting system, the rate of reaction was observed to be very low and yield of the epoxide was found to be negligible. This may be due to decrease in the number of radicals, which form complexes with the radical scavenger. Thus it may be suggested that these reactions involve a radical mechanism.

Cobalt compounds have two oxidation states of comparable stability and are able to include efficient

TABLE 3—SOLVENT EFFECT ON EPOXIDATION OF CHALCONES AT ROOM TEMPERATURE

Solvent	Dielectric constant	Chalcone		3-Nitro-chalcone		4'-Methoxy-3-nitrochalcone		4'-Hydroxy-4-methoxychalcone	
		Time h	Yield %	Time h	Yield %	Time h	Yield %	Time h	Yield %
Dichloromethane	9.080	30	86	54	60	40	75	20	100
Benzene	2.284	35	82	56	58	45	70	24	98
Carbon tetrachloride	2.238	35	72	58	52	50	68	35	80
Cyclohexane	2.220	40	66	58	50	52	64	40	78
		3'-Amino-chalcone		3'-Amino-3-nitrochalcone		2-Methoxy-chalcone		2-Hydroxy-chalcone	
Dichloromethane	9.080	25	90	40	70	25	92	30	88
Benzene	2.284	30	86	50	65	28	89	30	84
Carbon tetrachloride	2.238	35	75	55	58	30	78	35	73
Cyclohexane	2.220	40	70	55	55	35	72	40	69

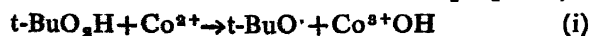
TABLE 4—TEMPERATURE EFFECT ON EPOXIDATION OF CHALCONES

Temp. °C	Chalcone		3-Nitro-chalcone		4'-Methoxy-3-nitrochalcone		4'-Hydroxy-4-methoxychalcone	
	Time h	Yield %	Time h	Yield %	Time h	Yield %	Time h	Yield %
0	88	42	95	25	90	40	70	55
25	35	82	56	58	45	70	24	98
45	60	20	60	8	60	18	50	30
65	60	10	65	2	65	8	50	22
	3'-Amino-chalcone		3'-Amino-3-nitrochalcone		2-Methoxy-chalcone		2-Hydroxy-chalcone	
0	80	50	95	30	76	52	82	48
25	30	86	50	65	28	89	30	84
45	55	25	60	12	52	27	58	22
65	50	18	65	5	51	20	55	15

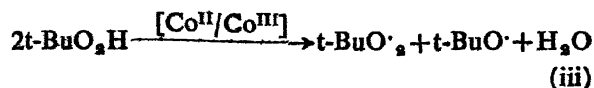
TABLE 5—EFFECT OF SUBSTRATE : CATALYST RATIO ON THE RATE OF EPOXIDATION OF CHALCONES AT ROOM TEMPERATURE

Substrate mmol	Catalyst mmol	Chalcone		3-Nitro-chalcone		4'-Methoxy-3-nitrochalcone		4'-Hydroxy-4-methoxychalcone	
		Time h	Yield %	Time h	Yield %	Time h	Yield %	Time h	Yield %
4.8	0.5	35	75	56	50	45	65	24	96
2.4	0.5	35	82	56	58	45	70	24	98
4.8	0.2	50	35	60	20	50	30	50	45
4.8	0.4	85	45	90	30	90	41	85	60
		3'-Amino-chalcone		3'-Amino-3-nitrochalcone		2-Methoxy-chalcone		2-Hydroxy-chalcone	
4.8	0.5	35	84	50	58	28	86	35	78
2.4	0.5	30	86	50	65	28	89	30	84
4.8	0.2	50	40	60	25	50	42	50	37
4.8	0.4	90	52	90	35	85	55	90	49

catalytic decomposition of alkylhydroperoxides^a. A probable free radical mechanism can be proposed,



The net transformation constitutes a catalytic-decomposition of t-butylhydroperoxide into alkoxy and alkylperoxy radicals, i.e.



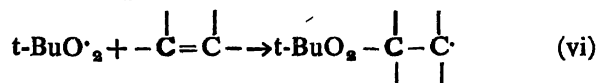
The radical chain decomposition of t-butylhydroperoxide can be shown as



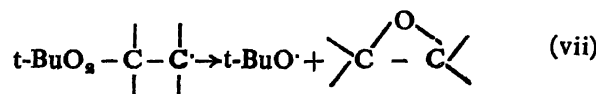
Under these circumstances, the metal ion acts as an initiator rather than as a catalyst. In general, metal complexes catalyse oxidation by generating chain-initiating radicals via reaction (i) or (ii). In nonpolar solvents, reaction (ii) constitutes the slower, rate-determining step, and the cobalt catalyst is present mainly in the trivalent oxidation state.

The commencement of the cobalt-catalysed autoxidation is accompanied by the oxidation of Co^{II} to Co^{III} as the transformation can be easily observed by the change in colour from pale-violet or pink of Co^{II} species to the dark-green of Co^{III} .

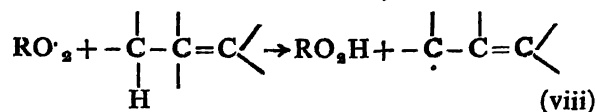
The epoxidation process may occur by the following steps,



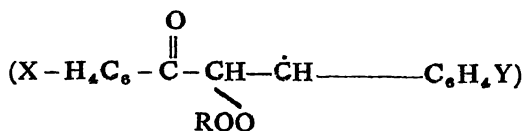
Addition of the alkylperoxy radical to the double bond of the chalcones can be followed by the unimolecular decomposition of the β -alkylperoxyalkyl radical, affording epoxide and an alkoxy radical,



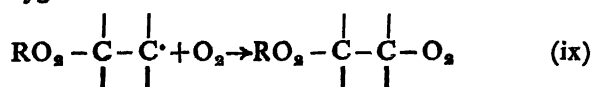
The absence of the labile C-H bonds in chalcones under study renders the radical chain propagation step (viii) via hydrogen abstraction extremely unfavourable,



The low stability of the intermediate adduct formed by addition of the alkylperoxy radical to the double bond, i.e.



makes unimolecular cleavage to epoxide more favourable than via the bimolecular reaction with dioxygen as



Thus, the epoxidation process occurs via steps (i), (ii), (iii), (iv), (v), (vi) and (vii) and the epoxides are obtained in good yield.

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