Oxidation of Alkenes and Sulphides with a Series of Hydroperoxides having Electron-withdrawing Substituents at the α-Position

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The oxidations of alkenes and sulphides with a series of hydroperoxides, α-hydroperoxy-α-methoxyacetophenone (**1**), α-hydroperoxy-α,α-diphenylacetophenone (**2**), methyl α-hydroperoxy-α,α-diphenylacetate (**3**), and α-hydroperoxy-α,α-diphenylacetonitrile (**4**), were undertaken in a systematic fashion. The data revealed the following. (a) The reactions of electron-rich alkenes (**11a** and **b**) with hydroperoxides (**1**)—(**4**) are most likely to proceed by a mechanism similar to that with peracids, as do the oxidations of sulphides (**5a**—**e**). (b) For the reaction of less reactive alkenes (**11f**—**k**) with hydroperoxide (**1**) in the presence of oxygen, epoxidation by benzoylperoxyl radical contributes to a significant extent. The reaction with hydroperoxide (**2**) at 60 °C also seems to proceed by a mechanism involving benzoylperoxyl radical, whereas a molecular epoxidation mechanism is important for the reaction at 30 °C. Perhaps in accord with this, the reaction of 1,1-disubstituted ethylenes (**11c**—**e**) with hydroperoxides (**1**) and (**2**) results in the formation of considerable amounts of benzoylated products (**13**) and (**14**). (c) For the epoxidation with hydroperoxides (**3**) and (**4**), however, a molecular epoxidation process seems to predominate. The exception is the reaction of hydroperoxide (**3**) with (*Z*)-2-phenylbut-2-ene and (*Z*)-stilbene, having very poor reactivity, in which a peroxyl radical, produced by hydrogen abstraction from the hydroperoxide (**3**), plays an important role in the epoxidation.

Since hydroperoxides are of relevance to the chemistry of 4a-hydroperoxyflavins, and because they are also important intermediates in oxygen activation in Nature,[1] the behaviour of such compounds having electron-withdrawing substituents at the α-position, *e.g.*, methyl α,α-diphenyl-α-hydroperoxyacetate,[2a,b] α-hydroperoxy-α,α-diphenylacetonitrile,[2a,b] α-alkoxy hydroperoxides,[2c] hexafluoro-2-hydroperoxypropan-2-ol,[2d] and benzylazobenzene α-hydroperoxide[2e] has attracted much attention.[2f] These hydroperoxides can effectively epoxidize alkenes. On the basis of kinetic studies and product distributions for 2,3-dimethylbut-2-ene oxidation,[2a,b,e] these reactions are considered to proceed by a mechanism similar to that of peracid epoxidation (a molecular epoxidation mechanism).[3]

We report herein that in the case of α-hydroperoxy-α-methoxyacetophenone (**1**) and α-hydroperoxy-α,α-diphenylacetophenone (**2**), however, epoxidation with peroxyl radicals competes with a molecular epoxidation process, the extent of each process being a marked function of the nature of the alkenes. Even in the epoxidation of some di- and tri-substituted ethylenes by methyl α-hydroperoxy-α,α-diphenylacetate (**3**), a mechanism involving peroxyl radicals is still important. The epoxidation with α-hydroperoxy-α,α-diphenylacetonitrile (**4**), however, seems to proceed by a molecular epoxidation mechanism.[2b]

Results and Discussion

Oxidation of Sulphides.—The oxidation of sulphides to sulphoxides is well known to be readily accomplished with peracids, hydrogen peroxide, and organic hydroperoxides.[4] We therefore investigated first the reactions of sulphides with hydroperoxides (**1**)—(**4**) [equation (1) and Table 1]. The reactions of hydroperoxide (**1**) with sulphides (**5a**—**e**) in methylene dichloride at 25 °C proceeded smoothly to give the corresponding sulphoxides (**6a**—**e**) almost quantitatively. The by-product was phenylglyoxal (**7**). The reactions of *p*-substituted phenyl methyl sulphides (**5b**—**d**) also followed pseudo-first-order kinetics. The rate increased as the substituent became increasingly electron-donating. This trend was exactly the same as that observed for the reactions with *m*-chloroperbenzoic acid MCPBA (Table 2). The reaction of diphenyl sulphide (**5e**) with hydroperoxide (**1**) was first-order with respect to both the sulphide and the hydroperoxide (Figure 1).

Treatment of sulphides (**5a** and **c**) with hydroperoxides (**2**) or (**3**) led to quantitative formation of the corresponding sulphoxides (**6a** and **c**) together with α-hydroxy-α,α-diphenylacetophenone (**8**) and methyl α-hydroxy-α,α-diphenylacetate (**9**), respectively. From the reaction of sulphide (**5c**) with hydroperoxide (**4**), sulphoxide (**6c**) was obtained quantitatively, along with α-hydroxy-α,α-diphenylacetonitrile [(**10**); isolated as

$$R^1SR^2 \xrightarrow{(1)-(4)} R^1S(O)R^2 \qquad (1)$$

(**5**) **a**; $R^1 = R^2 = CH_2Ph$; **b**; $R^1 = 4\text{-}MeC_6H_4$, $R^2 = Me$; **c**; $R^1 = Ph$, $R^2 = Me$; **d**; $R^1 = 4\text{-}ClC_6H_4$, $R^2 = Me$; **e**; $R^1 = R^2 = Ph$

(**6**) **a**; $R^1 = R^2 = CH_2Ph$; **b**; $R^1 = 4\text{-}MeC_6H_4$, $R^2 = Me$; **c**; $R^1 = Ph$, $R^2 = Me$; **d**; $R^1 = 4\text{-}ClC_6H_4$, $R^2 = Me$; **e**; $R^1 = R^2 = Ph$

PhCOCH(OMe)OOH (**1**) | $Ph_2C(OOH)COPh$ (**2**) | $Ph_2C(OOH)CO_2Me$ (**3**) | $Ph_2C(OOH)CN$ (**4**)

PhCOCHO (**7**) | $Ph_2C(OH)COPh$ (**8**) | $Ph_2C(OH)CO_2Me$ (**9**) | $Ph_2C(OH)CN$ (**10**)

Table 1. Oxidation of sulphides[a]

Sulphide	Oxidant	Sulphoxide (% yield)	By-products (% yield)	Recovered sulphide (%)
(5a)	(1)	(6a) (87)	(7) (78)	12
(5b)	(1)	(6b) (~100)	c	
(5c)	(1)	(6c) (~100)	(7) (89)	
(5d)	(1)	(6d) (~100)	c	
(5e)	(1)	(6e) (93)	c	
(5a)	(2)	(7a) (91)	(8) (75)	5
(5c)	(2)	(6c) (89)	(8) (90)	11
(5a)	(3)	(6a) (~100)	(9) (93)	
(5c)	(3)	(6c) (95)	(9) (93)	
(5c)	(4)	(6c) (86)	(17a) (88)	13
(5a)	$PhCOCl-KO_2$[b]	(6a) (68)	(17f) (40)	23
(5a)	$PhCOCl-KO_2$[b,d]	(6a) (30)	(17f) (15), (18) (43)	46
(5b)	$PhCOCl-KO_2$[b]	(6b) (36)	c	26
(5c)	$PhCOCl-KO_2$[b]	(6c) (18)	c	21
(5d)	$PhCOCl-KO_2$[b]	(6d) (23)	c	45
(5e)	$PhCOCl-KO_2$[b]	(6e) (32)	c	66

[a] Reaction with an equimolar amount of a hydroperoxide in CH_2Cl_2 or $CDCl_3$ at 25 °C for 24 h, unless otherwise noted. [b] Reaction of sulphide with a mixture of PhCOCl (2 mol equiv.) and KO_2 (5 mol equiv.) in the presence of 18-crown-6 (0.4 mol equiv.) in CH_2Cl_2 at 15 °C for 1 h. [c] The by-products were not determined. [d] Reaction with a mixture of PhCOCl (1 mol equiv.) and KO_2 (3 mol. equiv.) in the presence of 18-crown-6 (0.4 mol equiv.) in CH_2Cl_2.

Table 2. Relative reactivities of sulphides

Oxidant	4-MeC_6H_4SMe	C_6H_5SMe	4-ClC_6H_4SMe
(1)[b]	1.9	1	0.5
(2)[b]	1.4	1	0.6
(3)[b]	1.4	1	0.6
(4)[b]	1.5	1	0.7
(5)[b]	1.3	1	0.8

[a] Relative rates under conditions of pseudo-first-order kinetics. [b] Determined by competitive reactions between two sulphides.

Table 3. Oxidation of tetra-alkyl-substituted ethylenes[a]

Alkene	Oxidant	Reaction time (h)	Epoxide (% yield)	By-product (% yield)
(11a)	(1)	6	(12a) (95)	(7) (90)
(11a)	(2)	24	(12a) (80)	(8) (72)
(11a)	(3)	24	(12a) (92)	(9) (88)
(11a)	(4)	7	(12a) (95)	(17a) (93)
(11b)	(1)	6	(12b) (90)	(7) (90)
(11b)	(2)	24	(12b) (85)	(8) (83)
(11b)	(3)	36	(12b) (80)	(9) (75)
(11b)	$PhCOCl-KO_2$[b]	1	(12b) (47)	c

[a,b,c] See the footnotes in Table 1.

benzophenone] (Table 1). For a series of *p*-substituted phenyl methyl sulphides (**5b**—**d**), the reactivity of the sulphides increased with increasing electron-donating ability of the substituents (Table 2). The reactions of methyl phenyl sulphide (**5c**) with hydroperoxides (**2**)—(**4**) followed pseudo-first-order kinetics, as did the reaction with hydroperoxide (**1**). The order of reactivity of hydroperoxides (**1**)—(**4**) followed the sequence (**4**) [25] > (**1**)[9] > (**2**) [2.6] > (**3**) [1] (Figure 2).

All these data are in accord with the oxidation of sulphides with hydroperoxides (**1**)—(**4**) proceeding by a mechanism similar to that of oxidation with peracids, *i.e.*, oxygen transfer *via* electrophilic attack of hydroperoxide on sulphide.[2a]

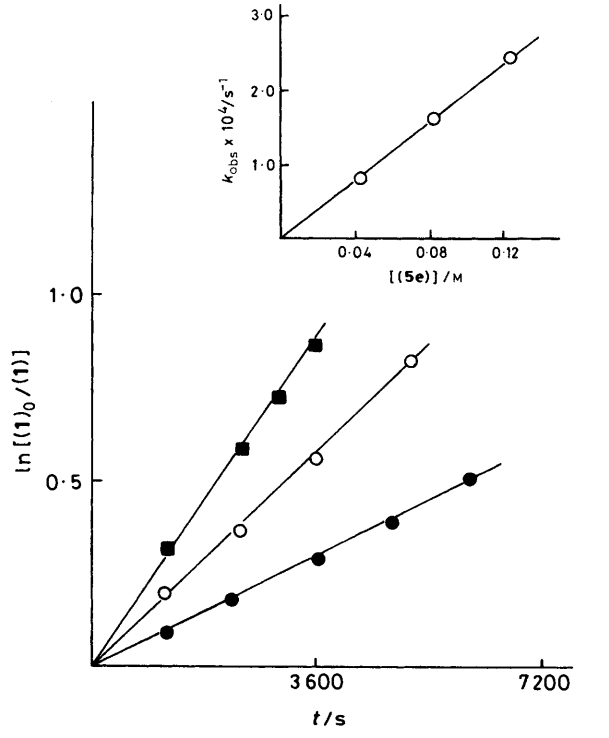


Figure 1. Plots of K_{obs} for the reaction of diphenyl sulphide (**5e**) with hydroperoxide (**1**). The initial concentrations of hydroperoxide (**1**) was 0.02M. Initial concentrations of sulphide (**5e**) were 0.24M (■), 0.16M (○), and 0.08M (●)

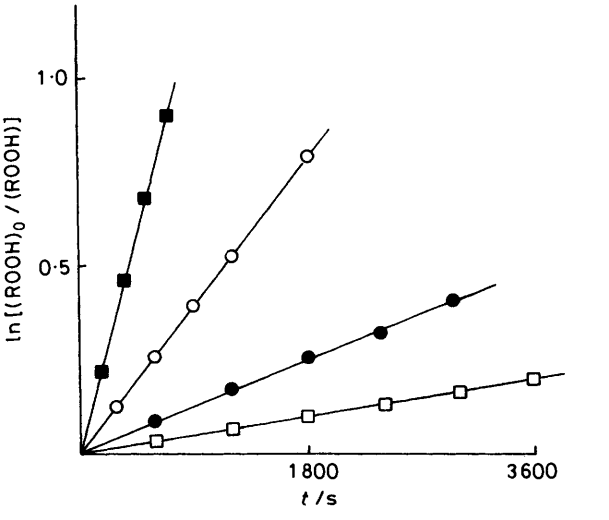


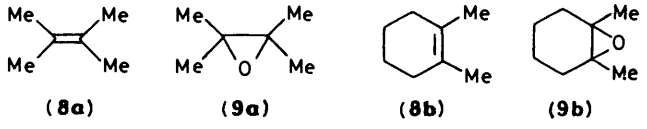
Figure 2. The kinetics for the reaction of methyl phenyl sulphide (**5c**) with hydroperoxides (**1**)—(**4**). The initial concentrations of hydroperoxide and sulphide were 0.02M and 0.08M, respectively: (1) (○), (2) (●), (3) (□), (4) (■)

Reaction of Tetra-alkyl-substituted Ethylenes.—Treatment of 2,3-dimethylbut-2-ene (**11a**) with hydroperoxides (**1**)—(**4**) in $CDCl_3$ at 25 °C afforded the corresponding epoxide (**12a**) almost quantitatively. The by-products were phenylglyoxal (**7**), α-hydroxy-α,α-diphenylacetophenone (**8**), methyl α-hydroxy-α,α-diphenylacetate (**9**), and α-hydroxy-α,α-diphenylacetonitrile (**10**), respectively (Table 3). The reaction followed pseudo-first-

Table 4. Oxidation of 1,1-disubstituted ethylenes[a]

Alkene	Oxidant	Reaction conditions	Products (% yield)	Recovered alkene (%)
(11c)	(1)	O_2, 25 °C, 24 h	(13a) (24), (15) (4), (16) (1), (17a) (17), (18) (36), (19) (80)	36
(11c)	(1)	Ar/25 °C, 24 h	(13a) (22), (17a) (15), (18) (38), (19) (80)	34
(11c)	(2)	O_2, 25 °C, 24 h	(13a) (15), (17a) (76), (8) (27), (18) (9)	45
(11c)	(2)	Ar, 25 °C, 24 h	(13a) (15), (17a) (81), (18) (21), (18) (12)	43
(11c)	(3)	O_2, 60 °C, 7 h[d]	(12c) (90), (9) (85)	
(11c)	(4)	O_2, 30 °C, 6 h	(12c) (40), (17a), (41)[e]	58
(11c)	PhCOCl–KO_2[b]	O_2, 10 °C, 1 h	(12c) (42)[c]	
(11d)	(1)	O_2, 25 °C, 24 h	(14) (15), (17b) (28), (18) (38), (19) (70)	28
(11d)	(1)	Ar, 25 °C, 24 h	(14) (10), (17b) (41), (18) (21), (19) (70)	36
(11d)	(2)	O_2, 25 °C, 24 h	(13b) (8), (14) (12), (17a) (33), (17b) (37), (8) (42), (19) (13)	19
(11d)	(2)	Ar, 25 °C, 24 h	(13b) (6), (14) (16), (17a) (47), (17b) (25), (18) (21), (18) (11)	39
(11e)	(1)	O_2, 25 °C, 20 h	(12e) (4), (13c) (12), (17c) (7), (19) (49), (19) (65)	54
(11e)	(3)	O_2, 60 °C, 12 h[d]	(12e) (20), (9) (19)[f]	75

[a,b,c] See the footnotes in Table 1. [d] Reaction in CCl_4. [e] Hydroperoxide (4) was recovered (55%). [f] Hydroperoxide (3) was recovered (72%).



order kinetics (Figure 3). The order of reactivity followed the sequence (1) [69] > (4) [59] > (2) [1.7] > (3) [1].[2a] From 1,2-dimethylcyclohexene (**11b**), epoxide (**12b**) was obtained in good yield (Table 3). These results can be rationalised in terms of electrophilic oxygen-atom transfer from hydroperoxides (**1**)—(**4**) to electron-rich alkenes (**11a** and **b**).*

Reaction of 1,1-*Disubstituted Ethylenes.*—In sharp contrast to the reaction of alkenes (**11a** and **b**), the reaction of 1,1-diphenylethylene (**11c**) with hydroperoxide (**1**) did not give the corresponding epoxide (**12c**). Instead, 3-hydroxy-3,3-diphenylpropiophenone (**13a**) was obtained in 24% yield, together with 4-benzoyl-1,1,3,3-tetraphenylbut-1-ene (**15**) (4%), benzil (**16**) (1%), benzophenone (**17a**) (17%), benzoic acid (**18**) (36%), and methyl formate (**19**), (80%). A considerable amount of the starting alkene (**11c**) was also recovered (36%) [equation (2) and Table 4]. The reaction was first-order with respect to both the alkene (**11c**) and the hydroperoxide (**1**) (Figure 4). The product composition observed in the reaction under anaerobic conditions was much the same as that observed in the reaction under aerobic conditions. As will be seen later, for the reaction

* Radical-initiated autoxidation of 2,3-dimethylbut-2-ene by O_2 is known to yield the allyl hydroperoxides and the corresponding allylic alcohols as well as the epoxide (D. E. Van Sickel, F. R. Mayo, R. M. Arluck, and M. G. Syz, *J. Am. Chem. Soc.*, 1967, **89**, 967).

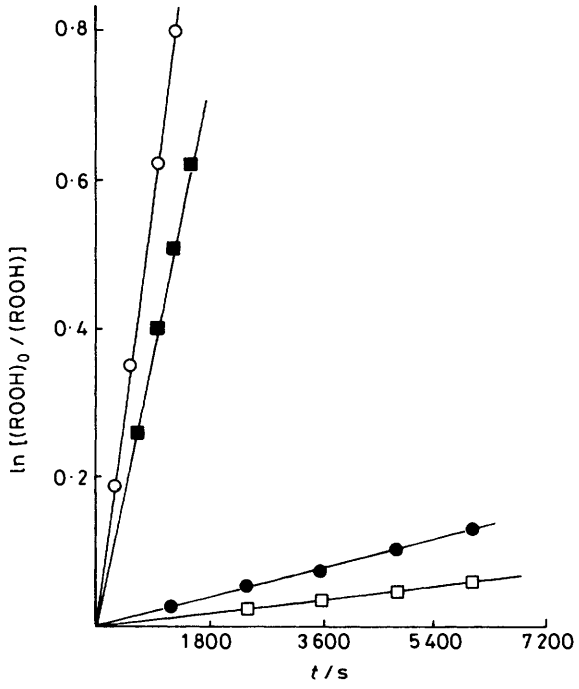


Figure 3. The kinetics for the reaction of 2,3-dimethylbut-2-ene (**11a**) with hydroperoxides (**1**)—(**4**). The initial concentrations of (**11a**) and hydroperoxide (were 0.04M and 0.25M, respectively: (**1**) (○), (**2**) (●), (**3**) (□), (**4**) (■)

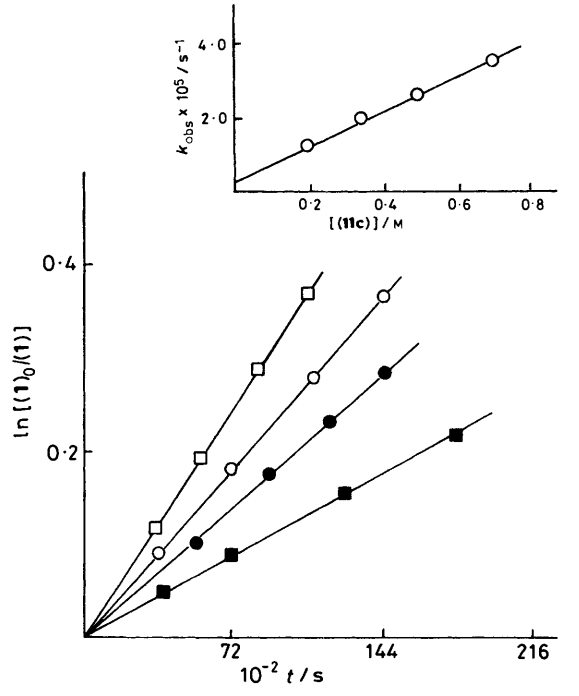


Figure 4. Plots of k_{obs} for the reaction of 1,1-diphenylethylene (**11c**) with hydroperoxide (**1**). Initial concentration of hydroperoxide (**1**) was 0.1M. Initial concentration of alkene (**11c**) was 0.7M (□), 0.5M (○), 0.35M, (●), and 0.2M (■)

of 2-methyl-3-phenylbut-2-ene (**11f**), however, the presence or absence of oxygen molecules exerted a remarkable influence on the course of the reaction. Alkenes (**11d** and **e**) also yielded the corresponding benzoylated products (**14**) or (**13b** and **c**) (Table

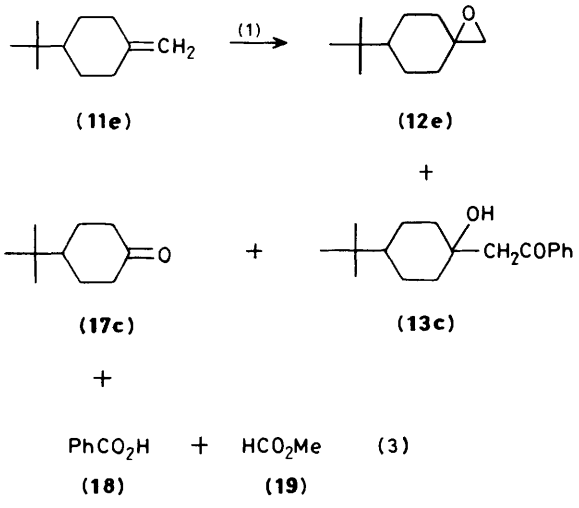
$$(4\text{-}RC_6H_4)_2C{=}CH_2 \xrightarrow{(1)} (4\text{-}RC_6H_4)_2C(OH)CH_2COPh +$$
(11) c; R = H (13) a; R = H
d; R = OMe b; R = OMe

$$(4\text{-}MeOC_6H_4)_2C{=}CHCOPh + PhCOCH_2C(Ph)_2CH{=}CPh_2 +$$
(14) (15)

$$PhCOCOPh + (4\text{-}RC_6H_4)_2C{=}O + PhCO_2H + HCO_2Me$$
(16) (17) a; R = H (18) (19)
b; R = OMe

(2)

4). From alkene (**11e**) the corresponding epoxide (**12e**) was also isolated but in only 4% yield [equation (3)].



(11e) (12e)

+

(17c) + (13c)

+

$$PhCO_2H + HCO_2Me \quad (3)$$
(18) (19)

A mechanism illustrated in Scheme 1 would rationalise the formation of two benzoylated products (**13**) and (**14**). 1,1-Diarylethylenes would induce decomposition of hydroperoxide (**1**) to afford a mixture of benzoyl radical (**20**) and hydroxyl radical along with methyl formate (**19**).* Attack of benzoyl radical on an alkene (**11**), followed by coupling with hydroxyl radical, would yield a ketone (**13**). Dehydration of this product (**13**) would result in the formation of the α,β-unsaturated ketone (**14**). A brief comment is made here concerning the formation of the C–C-cleavage product, benzophenone (**17a**), from 1,1-diphenylethylene. Since compound (**17a**) is produced in the absence of oxygen, it is clear that this product (**17a**) is not the result of autoxidation of 1,1-diphenylethylene. A possible precursor of benzophenone (**17a**) would be 1,2-diphenylethylene oxide (**12c**); treatment of epoxide (**12c**) with hydroperoxide (**1**) provides an 80% yield of benzophenone (**17a**). The mechanistic detail for this transformation is, however, obscure. The reaction of epoxide (**12c**) with hydroperoxide (**2**) also yields benzophenone (**17a**) in good yield.

The reaction of 1,1-disubstituted ethylenes (**11c** and **d**) with hydroperoxide (**2**) also resulted in the formation of considerable amounts of benzoylated products (**13**) and (**14**) (Table 4), suggesting that these reactions also proceed by a mechanism

$$PhCOCH(OMe)OOH \longrightarrow Ph\dot{C}(O) + HCO_2Me + {}^{\cdot}OH$$
(1) (20) (19)

$$(20) + CH{=}CAr_2 \longrightarrow PhCOCH_2\dot{C}AR_2$$
(11) c; Ar = Ph
d; Ar = 4-MeOC6H4

$$PhCOCH_1\dot{C}Ar_2 + {}^{\cdot}OH \longrightarrow PhCOCH_2C(OH)Ar_2$$
(13) a; Ar = Ph
b; Ar = 4-MeOC6H4

$$(13b) \xrightarrow{H_2O} (4\text{-}MeOC_6H_4)_2C{=}CHCOPh$$
(14)

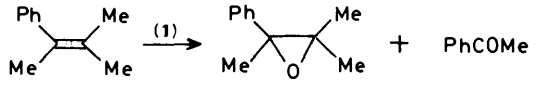
$$Ar_2C{=}CH_2 \xrightarrow{(1)} Ar_2C\text{—}CH_2$$
(12) c; Ar = Ph
d; Ar = 4-MeOC6H4

$$(12c \text{ and } d) \xrightarrow{(1)} Ar_2C{=}O$$
(17) a, Ar = Ph
b; Ar = 4-MeOC6H4

Scheme 1.

involving benzoyl radical. From the reactions of alkenes (**11c**) and (**11e**) with hydroperoxide (**3**), however, the corresponding epoxides (**12c**) and (**12e**) were obtained, together with methyl α-hydroxy-α,α-diphenylacetate (**9**). Hydroperoxide (**4**) can also epoxidize 1,1-diphenylethylene (Table 4).

Reaction of 1,2-*Disubstituted*, 1,1,2-*Trisubstituted, and* 1,1,2,2-*Tetrasubstituted Ethylenes* (**11f**—**k**).—The reaction of 2-methyl-3-phenylbut-2-ene (**11f**) with hydroperoxide (**1**) under aerobic conditions afforded epoxide (**12f**) in 31% yield, together with C–C-cleavage products, acetophenone (**17d**) (12%) and acetone (**17e**) (11%), benzoic acid (**18**) (55%), methyl formate (**19**) (60%), and phenylglyoxal (**7**) (11%). Alkene (**11f**) and hydroperoxide (**1**) were recovered in 34 and 20%, respectively [equation (4) and



(11f) (12f) (17d)

+

$$HCO_2Me + PhCO_2H + Me_2C{=}O$$
(19) (18) (17e)

+

PhCOCHO (4)
(7)

Table 5]. This is in marked contrast to the results of the reaction of 2,3-dimethylbut-2-ene (**11a**) which led to the exclusive formation of epoxide (**12a**) together with phenylglyoxal (**7**), and the reaction of 1,1-diphenylethylene (**11c**) which resulted in the formation of considerable amounts of benzoylated product (**13a**). When the reaction of alkene (**11f**) was undertaken in the absence of oxygen, however, small amounts of epoxide (**12f**) (10%) and phenylglyoxal (**7**) (10%) were obtained together with benzoic acid (**18**) (65%), methyl formate (**19**) (70%), and alkene

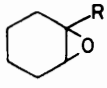
* The rate of decomposition of t-butyl hydroperoxide is well known to be significantly accelerated in the presence of alkenes (C. Walling and L. Heaton, *J. Am. Chem. Soc.*, 1965, **87**, 38). In connection with this, Schuster has revealed that electron-rich compounds, *e.g.*, diphenylanthracene, induce the decomposition of some cyclic peroxides by electron-transfer (G. B. Schuster, *Acc. Chem. Res.*, 1979, **12**, 366). A similar mechanism would operate for the alkene-induced decomposition of hydroperoxide (**1**). As will be seen later, in the absence of alkene the rate of decomposition of (**1**) is very slow.

Table 5. Oxidation of alkenes (**11f—i**)[a]

Alkene	Oxidant	Reaction conditions	Products (% yield)	Recovered hydroperoxide (%)	Recovered alkene (%)
(**11f**)	(**1**)	O_2, 25 °C, 6 h	(**12f**) (31), (**17d**) (12), (**17e**) (11), (**7**) (11), (**18**) (55), (**19**) 60)	20	34
(**11f**)	(**1**)	Ar, 25 °C, 6 h	(**12f**) (10), (**7**) (10), (**18**) (65), (**19**) (70)	10	64
(**11g**)	(**1**)	O_2, 25 °C, 6 h	(**12g**) (17), (**18f**) (3), (**7**) (4), (**19**) (70), (**19**) (75)	7	61
(**11h**)	(**1**)	O_2, 25 °C, 6 h	(**12h**) (30), (**7**) (8), (**18**) (58), (**19**) (70)		17
(**11h**)	(**1**)	Ar, 25 °C, 6 h	(**12h**) (8), (**7**) (8), (**18**) (66), (**19**) (65)		63
(**11i**)	(**1**)	O_2, 25 °C, 6 h	(**12i**) (38), (**7**) (8), (**18**) (60), (**19**) (65)		20
(**11f**)	(**2**)	O_2, 30 °C, 15 h	(**12f**) (27), (**8**) (25)	65	57
(**11f**)	(**2**)	Ar, 30 °C, 15 h	(**12f**) (30), (**8**) (28)	66	68
(**11f**)	(**2**)	O_2, 60 °C, 15 h[c]	(**12f**) (52), (**8**) (18), (**17a**) (50), (**18**) (48), (**17d**) (11)	18	16
(**11f**)	(**2**)	Ar, 60 °C, 15 h[c]	(**12f**) (36), (**8**) (37), (**17a**) (42), (**18**) (48)	10	45
(**11g**)	(**2**)	O_2, 30 °C, 15 h	(**12g**) (30), (**8**) (32)	65	62
(**11h**)	(**2**)	O_2, 30 °C, 30 h	(**12h**) (46), (**8**) (46), (**17a**) (6), (**18**) (4)	50	50
(**11h**)	(**2**)	O_2, 60 °C, 15 h[c]	(**12h**) (35), (**8**) (18), (**17a**) (75), (**18**) (70)		33
(**11i**)	(**2**)	O_2, 30 °C, 30 h	(**12i**) (26), (**8**) (24), (**17a**) (5), (**18**) (5)	52	41
(**11f**)	(**3**)	O_2, 60 °C, 16 h[c]	(**12f**) (60), (**9**) (58)	40	35
(**11g**)	(**3**)	O_2, 60 °C, 16 h[c]	(**12g**) (52), (**9**) (50)	46	40
(**11h**)	(**3**)	O_2, 60 °C, 16 h[c]	(**12h**) (53), (**9**) (48)	32	38
(**11h**)	(**3**)	Ar, 60 °C, 16 h	(**9h**) (48), (**9**) (48)	40	45
(**11i**)	(**3**)	O_2, 60 °C, 16 h[c]	(**12i**) (50), (**9**) (50)	32	46
(**11h**)	(**4**)	O_2, 30 °C, 8 h	(**12h**) (77), (**17a**) (80)	10	20
(**11f**)	PhCOCl–KO_2[b]	O_2, 15 °C, 1 h	(**12f**) (34), (**17d**) (16), (**18**) (10)		9
(**11g**)	PhCOCl–KO_2[b]	O_2, 15 °C, 1 h	(**12g**) (29), (**17f**) (1), (**18**) (18)		17
(**11h**)	PhCOCl–KO_2[b]	O_2, 15 °C, 1 h	(**12h**) (59), (**18**) (11)		
(**11i**)	PhCOCl–KO_2[b]	O_2, 15 °C, 1 h	(**12i**) (13), (**18**) (17)		

[a,b] See the footnotes in Table 1. [c] Reaction in CCl_4.

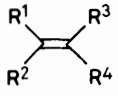
(**11h**); R = Ph
i; R = Me



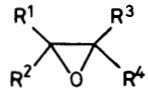
(**12h**); R = Ph
i; R = Me

PhCHO

(**17f**)



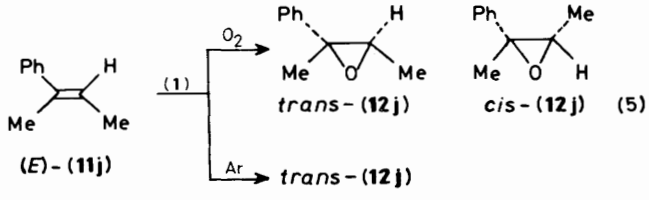
(**11f**); R^1 = Ph, R^2 = R^3 = R^4 = Me
g; R^1 = Ph, R^2 = H, R^3 = R^4 = Me
(*E*)-(**11j**); R^1 = Ph, R^2 = R^4 = Me, R^3 = H
(*Z*)-(**11j**); R^1 = Ph, R^2 = R^3 = Me, R^4 = H
(*Z*)-(**11k**); R^1 = R^3 = Ph, R^2 = R^4 = H



(**12f**); R^1 = Ph, R^2 = R^3 = R^4 = Me
g; R^1 = Ph, R^2 = H, R^3 = R^4 = Me
trans-(**12j**); R^1 = Ph, R^2 = R^4 = Me, R^3 = H
cis-(**12j**); R^1 = Ph, R^2 = R^3 = Me, R^4 = H
trans-(**12k**); R^1 = R^4 = Ph, R^2 = R^3 = H

(**11f**) (64% recovery). The lack of C–C-cleavage products, (**17d**) and (**17e**), was also noteworthy. Exactly the same trends were observed for the reaction of 1-phenylcyclohexene (**11h**). Judging from the amounts of recovered hydroperoxide (**1**), the rate of decomposition of compound (**1**) under aerobic conditions is much the same as that under anaerobic conditions. In the absence of alkene, however, the decomposition of hydroperoxide (**1**) at 30 °C was very slow: after 24 h, around 5% of the hydroperoxide (**1**) had decomposed into benzoic acid and methyl formate. These results would imply that an alkene induces decomposition of hydroperoxide (**1**) probably *via* O–O bond fission and, moreover, oxygen molecules do not exert a significant influence on the rate of the decomposition.

To elucidate the stereochemistry of the epoxidation, the reactions of (*E*)- and (*Z*)-2-phenylbut-2-ene (**11j**) and (*Z*)-stilbene (*Z*)-(**11k**) were performed (Table 6). Treatment of (*E*)- or (*Z*)-(**11j**) with hydroperoxide (**1**) under aerobic conditions led to the formation of an *E*—*Z* mixture of 2-phenylbut-2-ene oxide (**12j**). From (*Z*)-stilbene, *trans*-(**12b**) was obtained exclusively. The reaction of (*E*)-(**11j**) under anaerobic conditions, however, gave exclusively *trans*-(**12j**) but in only small amounts [equation 5)]. In connection with this, it is noted that the benzoylperoxyl



(5)

radical, generated *in situ* from a mixture of benzoyl chloride and potassium superoxide in the presence of 18-crown-6,[5]

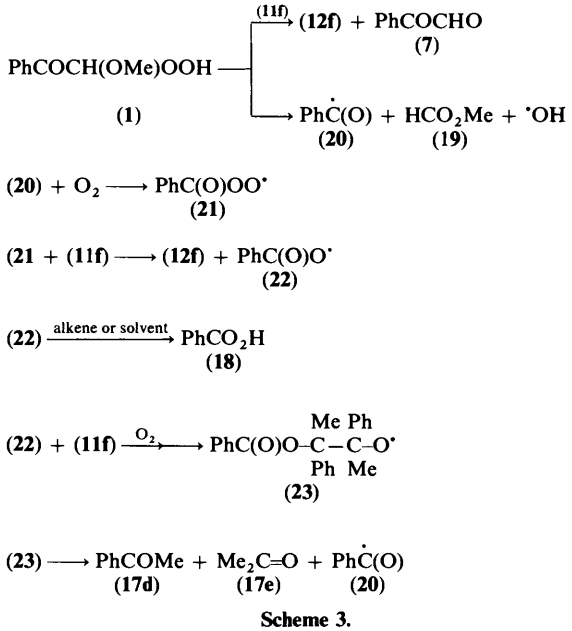
Table 6. Stereochemistry of oxidation of (*E*/*Z*)-2-phenylbut-2-ene (**11j**) and (*Z*)-stilbene (**11k**)[a]

Alkene	Oxidant	Reaction conditions	Epoxide yield (%)	Epoxide *trans*:*cis* ratio	By-products (% yield)	Recovered alkene (%)	Recovered hydroperoxide (%)
(*E*)-(**11j**)	(**1**)	O_2, 30 °C, 6 h	37	3:1	(**7**) (5), (**17d**), (30), (**18**) (37), (**19**) (72)	8	
(*E*)-(**11j**)	(**1**)	Ar, 30 °C, 6 h	12	1:0	(**7**) (10), (**18**) (74), (**19**) (77)	71	
(*E*)-(**11j**)	(**2**)	O_2, 60 °C, 6 h[c]	50	2:1	(**8**) (18), (**17a**) (33), (**17d**) (16), (**18**) (13)	16	24
(*E*)-(**11j**)	(**2**)	O_2, 30 °C, 15 h	36	1:0	(**8**) (38), (**17a**) (10), (**17d**) (10), (**18**) (7)	16	49
(*E*)-(**11j**)	(**2**)	Ar, 60 °C, 6 h[c]	37	1:0	(**8**) (38), (**17a**) (35), (**18**) (35)	30	12
(*E*)-(**11j**)	(**3**)	O_2, 60 °C, 20 h[c]	51	1:0	(**9**) (50), (**17d**) (13)	13	19
(*E*)-(**11j**)	(**3**)	Ar, 60 °C, 20 h[c]	38	1:0	(**9**) (35)	33	35
(*E*)-(**11j**)	(**4**)	O_2, 30 °C, 7 h	78	1:0	(**17a**) (80)	10	8
(*E*)-(**11j**)	PhCOCl–KO_2[b]	O_2, 10 °C, 1 h	48	2:1	(**17d**) (13), (**18**) (30)		
(*Z*)-(**11j**)	(**1**)	O_2, 30 °C, 6 h	32	1:1	(**7**) (5), (**17d**) (18), (**18**) (32), (**19**) (69)	23	
(*Z*)-(**11j**)	(**2**)	O_2, 60 °C, 6 h[c]	25	2:5	(**8**) (32), (**17a**) (30), (**17d**) (8), (**18**) (18)	42	22
(*Z*)-(**11j**)	(**3**)	O_2, 60 °C, 20 h[c]	37	1:1	(**9**) (38), (**17d**) (5)	43	40
(*Z*)-(**11j**)	(**3**)	Ar, 60 °C, 20 h[c]	35	1:1	(**9**) (36)	45	46
(*Z*)-(**11j**)	(**4**)	O_2, 30 °C, 7 h	45	0:1	(**17a**) (48)	40	38
(*Z*)-(**11j**)	PhCOCl–KO_2[b]	O_2, 10 °C, 1 h	46	3:2	(**17d**) (13), (**18**) (20)		
(*Z*)-(**11k**)	(**1**)	O_2, 40 °C, 10 h	20	1:0	(**17f**) (5)	47	
(*Z*)-(**11k**)	(**2**)	O_2, 60 °C, 14 h[c]	10	1:0	(**17f**) (5)	66	40
(*Z*)-(**11k**)	(**3**)	O_2, 60 °C, 20 h[c]	10	1:0		80	64
(*Z*)-(**11k**)	(**4**)	O_2, 60 °C, 18 h[c]	30	0:1	(**17a**) (30)	68	60
(*Z*)-(**11k**)	PhCOCl–KO_2[b]	O_2, 10 °C, 1 h	14	1:0	(**17f**) (6), (**18**) (16)	58	

[a,b] See the footnotes in Table 1. [c] Reaction in CCl_4.

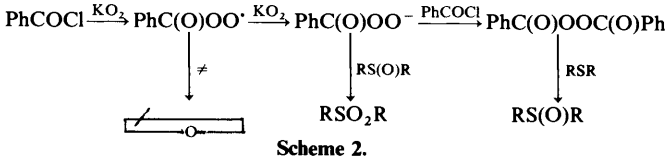
epoxidizes alkenes, the reaction being non-stereospecific (Tables 5 and 6).*

Since it is well known that epoxidation by peracids proceeds stereospecifically[3] and, in direct contrast, epoxidation by peroxyl radicals is non-stereospecific,[6] the oxidation by hydroperoxide (**1**) could be interpreted as the participation of two alternative epoxidation processes, *i.e.*, molecular epoxidation and epoxidation by peroxyl radicals, the extent of each process being a marked function of reaction conditions (Scheme 3).



Scheme 3.

* On the basis of the following results, the oxidation by a mixture of benzoyl chloride and potassium superoxide in the presence of 18-crown-6 can be rationalized by a mechanism illustrated in Scheme 2. (a) The possible oxidants in this system would be benzoylperoxyl radical, benzoylperoxy anion, and benzoyl peroxide (D. T. Sawyer and J. S. Valentein, *Acc. Chem. Res.*, 1981, **14**, 393). The competitive reaction between 2-methyl-3-phenylbut-2-ene (**11f**) and methyl phenyl sulphoxide (**6c**) indicates that the rate of disappearance of alkene (**11f**) is much faster than that of sulphoxide (**6c**), suggesting that benzoylperoxyl radical rather than benzoylperoxy anion is the major oxidant in this system. (b) The competitive reaction between alkene (**11f**) and methyl phenyl sulphide (**5c**) reveals that alkene (**11f**) is around three times more reactive than sulphide (**5c**). Since it is known that benzoylperoxyl radical is ineffective in sulphide oxidation, ref. 6, the active species oxidizing sulphide in this system would be benzoyl peroxide (Table 1). In accord with this, treatment of sulphide (**5c**) with an equimolar amount of benzoyl peroxide leads to the formation of the corresponding sulphoxide (**6c**) in *ca.* 70% yield.



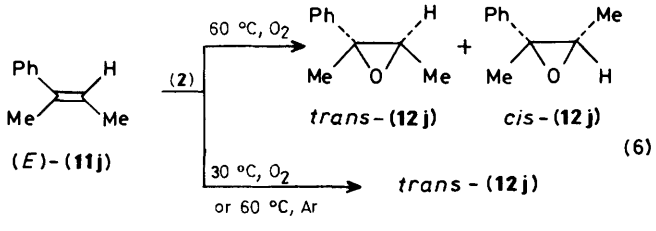
Scheme 2.

In the reaction in the absence of oxygen, a molecular epoxidation process is considered to be important, since the epoxidation is stereospecific and moreover, the epoxide yield is in good agreement with that of phenylglyoxal (**7**).

The non-stereospecificity in epoxidation under aerobic con-

ditions implies that a mechanism involving peroxyl radicals is important in the presence of oxygen molecules. Since alkene-induced decomposition of hydroperoxide (**1**) would result in the formation of benzoyl radical (as exemplified by the reaction of 1,1-diphenylethylene) and, moreover, since benzoylperoxyl radical, produced from benzoyl radical and oxygen molecule, is an extremely effective epoxidizing agent,[6] we deduced that benzoylperoxyl radical (**21**) is responsible for the non-stereospecific epoxidation.* Oxygen-atom transfer from the peroxyl radical (**21**) to alkene leads to the formation of epoxide and benzoyloxyl radical (**22**). Benzoyloxyl radical, thus formed, would abstract hydrogen atom from alkene or solvent to yield benzoic acid (**18**). Although the details are obscure, an alternative reaction involving benzoyloxyl radical (**22**) could be the production of C–C-cleavage products (**17**) by β-fission of the intermediary β-benzoyloxyalkoxyl radical (**23**) (Scheme 3).[6,7] The formation of small amounts of phenylglyoxal (**7**), however, would imply that even under aerobic conditions a molecular epoxidation process contributes to the reaction mechanism, but to a small extent. The remarkable difference in the product compositions between 1,1-disubstituted ethylenes (**11c—e**) and alkenes (**11f—k**) leads us to deduce that, for steric reasons, addition of benzoyl radical to alkenes (**11f—k**) is retarded and, consequently, the radical is forced to couple with an oxygen molecule to provide benzoylperoxyl radical, which in turn epoxidizes alkenes (**11f—k**).

The reaction of alkenes (**11f—i**) with hydroperoxide (**2**) at 30 °C under aerobic conditions was very slow. The products were a mixture of only the corresponding epoxide and α-hydroxy-α,α-diphenylacetophenone (**8**) (Table 5), suggesting that the epoxidation proceeds by a mechanism similar to that with peracids. In accord with this, treatment of (*E*)-2-phenylbut-2-ene (*E*)-(**11j**) with hydroperoxide (**2**) under the same conditions resulted in exclusive formation of epoxide (**12f**) with a *trans*-configuration. When the reaction of (*E*)- or (*Z*)-(**11j**) was performed at 60 °C, however, a cis–*trans* mixture of epoxide (**12j**) was obtained [equation (6) and Table 6]. From (*Z*)-stilbene (*Z*)-(**11k**), *trans*-(**12k**) was obtained exclusively.



(6)

These results led us to deduce that in the presence of oxygen the reaction of alkenes with hydroperoxide (**2**) at 60 °C proceeds by a mechanism involving peroxyl radicals. If consideration is given to the fact that benzoyl radical is likely to be produced from hydroperoxide (**2**) under these conditions,[8] it would be reasonable to suspect that, in the reaction with hydroperoxide (**2**) also, benzoylperoxyl radical would play an important role in the epoxidation. It is worth noting that the yield of α-hydroxy-α,α-diphenylacetophenone (**8**), a reasonable by-product formed from hydroperoxide (**2**) by molecular epoxidation, is significantly lower than that of the epoxide major product. As might be expected, only *trans*-(**12j**) was obtained when the reaction of (*E*)-(**11j**) with hydroperoxide (**2**) was performed at 60 °C in the absence of oxygen, a reaction in which benzoylperoxyl radical cannot be produced (Table 6).

The reactions of alkenes (**11f—i**) with hydroperoxide (**3**) were very slow. The epoxidation at 60 °C gave, however, the corresponding epoxides (**12f—i**) in good yield, together with methyl α-hydroxy-α,α-diphenylacetate (**9**) (Table 5). Treatment of (*E*)-2-phenylbut-2-ene (*E*)-(**11j**) with hydroperoxide (**3**) gave exclusively *trans*-(**12j**). The presence or absence of oxygen did not affect the product composition. In contrast, a *cis–trans* mixture of epoxide (**12j**) was obtained from the less reactive alkene (*Z*)-(**11j**) (Table 6).† (*Z*)-Stilbene, having the least reactivity, yielded only *trans*-(**12k**). These results would imply that the epoxidation of reactive alkenes (**11f—i**) and (*E*)-(**11j**) is most likely to proceed by a molecular epoxidation mechanism, whilst a process involving peroxyl radicals would be important for the epoxidation of (*Z*)-(**11j**) and (*Z*)-(**11k**).

Since methyl α,α-diphenyl-α-hydroxyacetate (**12**) is the major by-product from the reaction of (*Z*)-(**8j**) or *cis*-(**8k**) (the yield is in good agreement with that of the epoxide) and the epoxidation does not require the presence of oxygen molecules, the most likely epoxidizing agent in this reaction would be peroxyl radical (**25**) (Scheme 4). Alkoxyl radical (**24**), first formed by

$$\underset{(3)}{Ph_2C(OOH)CO_2Me} \longrightarrow \underset{(24)}{Ph_2C(CO_2Me)O^{\bullet}} + {}^{\bullet}OH$$

$$(24) + (3) \longrightarrow \underset{(9)}{Ph_2C(OH)CO_2Me} + \underset{(25)}{Ph_2(CO_2Me)OO^{\bullet}}$$

$$(25) + (Z)\text{-}(11j) \longrightarrow \textit{trans}\text{-}(12j) + \textit{cis}\text{-}(12j) + (24)$$

Scheme 4.

decomposition of hydroperoxide (**3**), would abstract hydrogen from hydroperoxide (**3**) to provide the alcohol (**19**) and peroxyl radical (**25**). The peroxyl radical (**25**) would then react with alkene to provide epoxide and regenerate alkoxyl radical (**24**).

The reactions of (*E–Z*)-(**11j**) and (*Z*)-(**11k**) with α-hydroperoxy-α,α-diphenylacetonitrile (**4**) were stereospecific,[2b] suggesting that epoxidation with hydroperoxide (**4**) is most likely to proceed by a mechanism similar to that with peracids (Table 6).

Thus, our study of a series of hydroperoxides (**1**)—(**4**) has revealed that the reaction of alkenes with these hydroperoxides having electron-withdrawing substituents at the α-position is much more complex than had previously been considered.[2] Two alternative mechanisms, *i.e.*, molecular epoxidation and the one involving peroxyl radicals, are possible depending on the structures of the hydroperoxides and alkenes. The remarkable difference in behaviour between hydroperoxides (**1**) and (**2**) and hydroperoxides (**3**) and (**4**) can be rationalized in terms of the relative stabilities of the possible radical intermediates produced from the reaction of alkenes with these hydroperoxides (**1**)—(**4**). The relative stabilities of free radicals X$^{\bullet}$, judged from the dissociation energies of X–H bonds, increase in the order $^{\bullet}CN$ (129) < $RO^{\bullet}$ (104) < $^{\bullet}CO_2Me$ (95) < $ROO^{\bullet}$ (90) < PhC(O) (87) (units in kcal mol^{-1}).[7] Since the benzoyl radical is much more stable than an alkoxyl radical, alkene-induced O–O-bond fission of hydroperoxides (**1**) and (**2**) is most likely to be accompanied by spontaneous ejection of a carbonyl moiety [methyl formate from (**1**) and benzophenone from (**2**)] to yield benzoyl radical, followed by rapid reaction with an oxygen molecule to provide benzoylperoxyl radical, which in turn epoxidizes the alkene. Judging from the reactivity of hydroperoxides (**1**)—(**4**) toward 2,3-dimethylbut-2-ene (**11a**), hydroperoxide (**1**) seems to have a high ability to epoxidize alkenes by a molecular epoxidation mechanism, but nevertheless it favours a process involving benzoylperoxyl radical. Probably

* In addition to epoxidation with benzoylperoxyl radical, an autoxidation process would contribute in part to formation of the epoxide (F. R. Mayo, *Acc. Chem. Res.*, 1968, **1**, 193).

† The order of reactivity of alkenes, judged qualitatively from the amounts of unchanged hydroperoxide (**3**), followed the sequence (**11h**) > (**11i**) > (*E*)-(**11j**) ≃ (**11f**) ≃ (**11g**) > (*Z*)-(**11j**) > (*Z*)-(**11k**).

the anomalously easy O–O-bond fission of hydroperoxide (**1**) is the reason.* In the case of $Ph_2C(CO_2Me)O^{\bullet}$ (**24**), however, hydrogen abstraction from hydroperoxide (**3**) to yield $Ph_2C(CO_2Me)OO^{\bullet}$ (**25**) and alcohol (**9**) is more favourable than ejection of benzophenone to produce the less stable $^{\bullet}CO_2Me$. Consequently, in the epoxidation of the very unreactive alkenes (*Z*)-(**11j**) and (*Z*)-(**11k**) by a poor epoxidizing agent (**3**), in which a molecular epoxidation process is expected to be very slow, epoxidation by the peroxyl radical (**25**) would play an important role. Hydroperoxide (**4**), having a much higher epoxidizing ability, however, epoxidizes even these alkenes, (*Z*)-(**11j**) and (*Z*)-(**11k**), by a mechanism similar to that with peracids.

Experimental

^{1}H N.m.r. spectra were obtained with a JNM-PS-100 spectrometer for $CDCl_3$ solutions. Mass spectra were obtained with a Hitachi RMU-6H spectrometer and i.r. spectra with a Hitachi 215 spectrophotometer. G.l.c. analysis was carried out on a Hitachi 164 gas chromatograph.

Materials.—α-Hydroperoxy-α-methoxyacetophenone (**1**),[9a] α-hydroperoxy-α,α-diphenylacetophenone (**2**),[10] methyl α-hydroperoxy-α,α-diphenylacetate (**3**),[10] and α-hydroperoxy-α,α-diphenylacetonitrile (**4**),[11] were prepared by the reported methods. Compound (**1**) had m.p. 68—69 °C (decomp.) (from ethyl acetate–hexane), δ_H 3.63 (3 H, s), 5.60 (1 H, s), 7.13—8.00 (5 H, m), and 9.00 (1 H, s). Compound (**2**) had m.p. 116—117 °C (from benzene–hexane), δ_H 7.18—8.08 (15 H, m) and 8.96 (1 H, s); $\nu_{max.}$ 3 370 and 1 680 cm^{-1}. Compound (**3**) had m.p. 73—74 °C (from benzene–hexane), δ_H 3.83 (3 H, s), 7.33 (10 H, m), and 9.70 (1 H, s); $\nu_{max.}$ 3 450 and 1 720 cm^{-1}. Compound (**4**) had m.p. 84—86 °C (lit.,[2a] 87—88 °C) (from benzene–hexane), δ_H 7.40 (10 H, m) and 9.00 (1 H, s); $\nu_{max.}$ 3 300 cm^{-1}.

Methyl *p*-tolyl sulphide (**5b**) and *p*-chlorophenyl methyl sulphide (**5d**) were prepared by the methods of Balfe *et al.*[12] Compound (**5b**) had b.p. 90 °C (30 mmHg), δ_H 2.20 (3 H, s), 2.32 (3 H, s), and 6.98—7.23 (4 H, m).[13] Compound (**5d**) had b.p. 119 °C (0.3 mmHg), δ_H 2.37 (3 H, s) and 6.97—7.23 (4 H, m).[15] Alkenes (**11b**), (**11d—i**), (*E*)-(**11j**) were prepared by the reported methods.[15—21] Compound (**11b**) had b.p. 136 °C (lit.,[15] 135.9—136.5 °C), δ_H 1.58 (6 H, s) and 1.91 (8 H, m). Compound (**11d**) had m.p. 143—145 °C (lit.,[16] 140—141.5 °C) (from ethanol), δ_H 3.77 (6 H, s), 5.23 (2 H, s), and 6.66—7.33 (8 H, m). Compound (**11e**) had b.p. 70 °C (10 mmHg), δ_H 0.83—2.51 (18 H, m) and 4.48 (2 H, s).[17] Compound (**11f**) had b.p. 89 °C (30 mmHg) [lit.,[18] 91—92 °C (25 mmHg)], δ_H 1.57 (3 H, s), 1.77 (3 H, s), 1.90 (3 H, s), and 7.10 (5 H, m). Compound (**11g**) had b.p. 106 °C (50 mmHg) [lit.,[19] 103 °C (25 mmHg)], δ_H 1.83 (3 H, s), 1.87 (3 H, s), 6.20 (1 H, s), and 7.11 (5 H, m). Compound (**11h**) had b.p. 96 °C (4 mmHg) [lit.,[20] 124—125 °C (10 mmHg)], δ_H 1.47—2.53 (8 H, m), 6.00 (1 H, s), and 7.00—7.50 (5 H, m). Compound (**11i**) had b.p. 110—111 °C, δ_H 1.33—2.20 (11 H, m) and 5.27 (1 H, s). Compound (*E*)-(**11j**) had b.p. 90 °C (25 mmHg) [lit.,[21] 94 °C (29.5 mmHg)], δ_H 1.77 (3 H, d, *J* 6.8 Hz), 1.98 (3 H, s), 5.73 (1 H, q, *J* 6.8 Hz), and 7.13 (5 H, m). Compound (*Z*)-(**11j**); had b.p. 86 °C (25 mmHg) [lit.,[21] 77 °C (29.5 mmHg)], δ_H 1.56 (3 H, d, *J* 7.0 Hz), 1.97 (3 H, s), 5.45 (3 H, q, *J* 7.0 Hz), and 6.83—7.40 (5 H, m).

Oxidation of Sulphides with Hydroperoxides (**1**)—(**3**).—A mixture of a sulphide (0.5 mmol) and a hydroperoxide (0.5 mmol) in $CDCl_3$ (1 ml) was stirred at 25 °C for 24 h. Then an appropriate amount of diphenylmethane [δ_H 2.47 (2 H, s)] or acetophenone [δ_H 3.90 (3 H, s)] was added as an internal standard. By ^{1}H n.m.r. spectroscopy, the amounts of sulphoxide, recovered sulphide, phenylglyoxal [(**7**), with methanol co-ordination], α-hydroxy-α,α-diphenylacetophenone (**8**), and methyl α-hydroxy-α,α-diphenylacetate (methyl benzilate) (**9**) were determined. The glyoxal (**7**) had δ_H 3.52 (3 H, s). The benzoin (**8**) had m.p. 84—86 °C (lit.,[22] 87—88 °C), δ_H 4.90 (1 H, s) and 7.00—7.90 (15 H, m); $\nu_{min.}$ 3 500 and 1 670 cm^{-1}. Methyl benzilate (**9**) had m.p. 70—71 °C (from benzene–hexane), *m/z* 242 (M^+); δ_H 3.64 (3 H, s), 4.25 (1 H, s), and 7.00—7.65 (10 H, m); $\nu_{max.}$ 3 500 and 1 730 cm^{-1}.

Reaction of Sulphide with Hydroperoxide (**4**).—A mixture of a sulphide and hydroperoxide (**4**) in $CDCl_3$ was stirred at 25 °C for 24 h. The amounts of sulphoxide and recovered sulphide were determined by ^{1}H n.m.r. spectroscopy. The yield of benzophenone (**17a**) was determined by g.l.c.

Reaction of 1,1-*Diphenylethylene* (**11c**) *with Hydroperoxide* (**1**).—A mixture of alkene (**11c**) (5 mmol) and hydroperoxide (**1**) (5 mmol in CH_2Cl_2) (6 ml) was stirred at 25 °C for 24 h. The yield of methyl formate [(**19**); δ_H 3.72 (3 H, s)] was determined by ^{1}H n.m.r. spectroscopy. The amounts of recovered alkene, benzophenone (**17a**), and benzil (**16**) were determined by g.l.c. Then the neutral products were chromatographed on a column of silica gel. The first fraction contained recovered alkene (**11c**). From the second fraction was obtained 4-*benzoyl*-1,1,3,3-*tetraphenylbut*-1-*ene* (**15**), m.p. 172 °C (from benzene–hexane) (Found: C, 90.4; H, 6.1. $C_{35}H_{28}O$ requires C, 90.48; H, 6.07%); *m/z* 464 (M^+); δ_H 4.54 (2 H, s), 6.02 (1 H, s), and 7.23 (25 H, m). The third fraction contained benzophenone (**17a**) and benzil (**16**). From the fourth fraction was obtained 3-*hydroxy*-3,3-*diphenylpropiophenone* (**13a**), m.p. 117—119 °C (from benzene–hexane) (Found: C, 82.9; H, 6.1. $C_{21}H_{18}O_2$ requires C, 83.42; H, 6.00%); *m/z* 302 (M^+); δ_H 3.67 (2 H, s), 5.16 (1 H, s), and 6.84—8.08 (15 H, m); $\nu_{max.}$ 3 475 and 1 670 cm^{-1}. Benzoic acid was isolated from the acid layer.

Reaction of Alkene (**11d**) *with Hydroperoxide* (**2**).—The reaction of alkene (**11d**) with hydroperoxide (**2**) was undertaken at 25 °C for 24 h. The neutral products were chromatographed on a column of silica gel. The first fraction contained recovered alkene (**11d**). From the second fraction was obtained 4,4′-dimethoxybenzophenone (**17b**), m.p. 141—143 °C (from benzene–hexane) (lit.,[23] 143 °C); *m/z* 242 (M^+); δ_H 3.87 (6 H, s) and 6.83—7.80 (8 H, m). The third fraction contained 2-*benzoyl*-1,1-*bis*-(4-*methoxyphenyl*)*ethylene* (**14**), m.p. 95—97 °C (from benzene–hexane) (Found: C, 80.2; H, 5.9. $C_{23}H_{20}O_3$ requires C, 80.21; H, 6.03%); *m/z* 344 (M^+); δ_H 3.77 (3 H, s), 3.84 (3 H, s), and 6.68—8.00 (14 H, m); $\nu_{max.}$ 1 655 cm^{-1}. From the fourth fraction was obtained 3-hydroxy-3,3-bis-(4-methoxyphenyl)-propiophenone (**13b**), m.p. 137—140 °C (from benzene–hexane); *m/z* 362 (M^+); δ_H 3.70—3.88 (8 H, m), 4.08 (1 H, s), and 6.73—7.87 (13 H, m); $\nu_{max.}$ 3 450 and 1 720 cm^{-1}. The fifth fraction contained the alcohol (**8**).

Reaction of 4-*Methylene*-1-*t*-*butylcyclohexane* (**11e**) *with Hydroperoxide* (**1**).—A mixture of alkene (**11e**) and hydroperoxide (**1**) in CH_2Cl_2 was stirred at 25 °C for 24 h. The amounts of recovered alkene, epoxide (**12e**), and 4-t-butylcyclohexanone (**17c**), were determined by g.l.c. Column chromatography of the neutral products on silica gel afforded the alcohol (**13c**), m.p. 125—127 °C (from benzene–hexane); *m/z*

* Hydroperoxide (**1**) decomposes at around 70 °C, providing mainly a mixture of benzoic acid and methyl formate.[9a] The relevant α-hydroperoxy-α-methoxyacetone is not stable even at room temperature. CIDNP studies reveal the generation of acetyl radical.[9b] In marked contrast, hydroperoxide (**2**) is very stable (m.p. 115—116 °C) and its thermal decomposition could only be attained at temperatures above 240 °C.[8]

274 (M^+); δ_H 0.77—2.60 (18 H, m), 3.03 (2 H, s), 3.67 (1 H, s), and 7.10—8.13 (5 H, m); $\nu_{max.}$ 3 500 and 1 670 cm^{-1}.

Reaction of (E)-2-*Phenylbut*-2-*ene* (E)-(**11j**) *with Hydroperoxide* (**1**) *under Aerobic Conditions.*—The reaction of alkene (*E*)-(**11j**) (0.5 mmol) with hydroperoxide (**1**) (0.5 mmol) in $CDCl_3$ (1 ml) was undertaken in a 20 ml round-bottomed flask equipped with a reflux condenser and magnetic stirring bar. After the reaction was complete (6 h) the amounts of recovered alkene (*E*)-(**11j**) [δ_H 1.77 (3 H, s)], acetophenone (**17d**) [δ_H 2.47 (3 H, s)] epoxides, *trans*-(**12j**) [δ_H 1.37 (3 H, d)] and *cis*-(**12j**) [d_H 0.90 (3 H, d)], phenylglyoxal (**7**) [δ_H 3.52 (3 H, s)], and methyl formate (**19**) [δ_H 3.72 (3 H, s)] were determined by comparison of the characteristic signals in the ^1H n.m.r. spectra (internal standard: diphenylmethane).

Reaction of (E)-2-*Phenylbut*-2-ene (E)-(**11j**) *with Hydroperoxide* (**2**) *under Aerobic Conditions.*—The reaction of (*E*)-(**11j**) with hydroperoxide (**2**) was undertaken at 60 °C for 6 h. The amounts of recovered alkene (*E*)-(**11j**), epoxides *trans*-(**12j**) and *cis*-(**12j**), acetophenone (**17d**), and α-hydroxy-α,α-diphenylacetophenone (**8**) were determined by ^1H n.m.r. spectroscopy. The amount of recovered hydroperoxide (**2**) was determined by an iodometric titration of part of the crude products. The remainder was treated with Me_2S to convert hydroperoxide (**2**) into the alcohol (**8**), and then the yield of benzophenone (**17a**) was determined by g.l.c. [otherwise, a part of the recovered hydroperoxide (**2**) decomposed into benzophenone (**17a**) during g.l.c. analysis or column chromatography and consequently the correct value of the yield of benzophenone could not be obtained].

Reaction of Alkene (*E*)-(**11j**) *with Hydroperoxide* (**3**) *under Anaerobic Conditions.*—A CCl_4 (2 ml) solution of alkene (*E*)-(**11j**) (0.5 mmol) and hydroperoxide (**3**) (0.5 mmol) in a high-pressure glass vessel was frozen (liquid nitrogen) and evacuated three times at 10^{-5} mmHg, and the vessel was then warmed to 60 °C. After 20 h, the amounts of epoxide *trans*-(**12j**), alcohol (**9**), and recovered alkene (*E*)-(**11j**) were determined by ^1H n.m.r. spectroscopy.

Oxidation of Alkenes with a Mixture of Benzoyl Chloride and Potassium Superoxide.—Into a 50 ml flask containing an alkene (1 mmol), benzoyl chloride (2 mmol), 18-crown-6 (0.4 mmol), and CH_2Cl_2 (20 ml) was added KO_2 (5 mmol) during 5 min. After 1 h, ether was added and the mixture was poured onto ice-cold aqueous potassium hydroxide, and extracted with three portions of ether. Work-up of the extracts gave products which were separated by column chromatography and analysed by ^1H n.m.r. spectroscopy or g.l.c.

Kinetics.—Reactions of hydroperoxides (**1**)—(**4**) with sulphides (**5b**—**e**), 2,3-dimethylbut-2-ene (**11a**), and 1,1-diphenylethylene (**11c**) were followed by determination of the decrease in hydroperoxide with time *via* an iodometric assay.

Physical Properties of Products.—The products were characterized by comparison of their physical properties with those of authentic samples prepared by the reported methods. Compound (**6a**) had m.p. 133—134 °C (from benzene–hexane), δ_H 3.83 (4 H, s) and 7.33 (10 H, m).[24] Compound (**6b**) had b.p. 120 °C (5 mmHg), δ_H 2.27 (3 H, s), 2.40 (3 H, s), and 7.03—7.93 (4 H, m).[25] Compound (**6c**) had b.p. 95 °C (5 mmHg) [lit.,[25] 78—79 °C (0.1 mmHg)], δ_H 2.67 (3 H, s) and 7.00—7.90 (5 H, m). Compound (**6d**) had b.p. 135 °C (5 mmHg), δ_H 2.70 (3 H, s) and 7.30—7.73 (4 H, m).[25] Compound (**6e**) had m.p. 69—71 °C (from benzene–hexane) (lit.,[26] 70—71 °C).

Epoxide (**12b**) had b.p. 150—151 °C, δ_H 1.23 (6 H, s) and 1.30—2.00 (8 H, m).[27] Epoxide (**12c**) had m.p. 53—55 °C (from ethanol) (lit.,[28] 52—54 °C), δ_H 3.25 (2 H, s) and 7.30 (10 H, m). Epoxide (**12e**) had b.p. 95—98 °C (10 mmHg), δ_H 0.90 (9 H, s), 1.00—2.10 (9 H, m), and 2.45 (2 H, s).[29] Epoxide (**12f**) had b.p. 128 °C (20 mmHg), δ_H 0.95 (3 H, s), 1.43 (3 H, s), 1.62 (3 H, s), and 7.07—7.50 (5 H, m). Epoxide (**12g**) had b.p. 120—122 °C (20 mm Hg), δ_H 1.05 (3 H, s), 1.45 (3 H, s), 3.82 (1 H, s), and 7.17—7.43 (5 H, m). Epoxide (**12h**) had b.p. 118 °C (0.5 mmHg), δ_H 1.10—2.33 (8 H, m), 2.87 (1 H, s), and 7.00—7.50 (5 H, m).[30] Epoxide (**12j**) had b.p. 138—142 °C (lit.,[27] 137—138 °C), δ_H 1.07—2.00 (11 H, m) and 2.73 (1 H, s). Epoxide *trans*-(**12j**) had b.p. 72 °C (1 mmHg), δ_H 1.37 (3 H, d, *J* 5.6 Hz), 1.60 (3 H, s), 2.90 (1 H, q, *J* 5.6 Hz), and 7.00—7.50 (5 H, m).[31] Epoxide *cis*-(**12j**) had b.p. 77—80 °C (2 mmHg), δ_H 0.90 (3 H, d, *J* 5.2 Hz), 1.90 (3 H, s), 2.97 (1 H, q, *J* 5.2 Hz), and 7.07—7.43 (5 H, m).[32] Epoxide *trans*-(**12k**) had m.p. 68—69 °C (from ethanol) (lit.,[33] 69—69.5 °C), δ_H 3.63 (2 H, s) and 7.00—7.34 (10 H, m). Epoxide *cis*-(**12k**) had m.p. 36—37 °C (from ethanol) (lit.,[33] 37—37.5 °C), δ_H 4.13 (2 H, s) and 6.93—7.13 (10 H, m).

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Received 24*th June* 1985; *Paper* 5/1059