

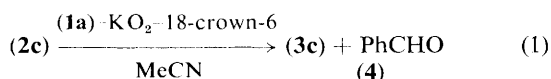
Oxidation of Alkenes and Sulphoxides with a Mixture of Potassium Superoxide and Diethyl Chlorophosphate

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The reaction of potassium superoxide with diethyl chlorophosphate in the presence of 18-crown-6 ether gave at least two oxidizing agents, one of which was electrophilic and used in the oxidation of alkenes, whilst the other, nucleophilic in type, was important in the oxidation of sulphoxides.

Superoxide ion acts as a nucleophile in the displacement reactions of acyl derivatives and sulphonyl chlorides to give the corresponding peroxy radicals $RC(=O)OO\cdot$ and $RSO_2OO\cdot$. These species, in the presence of excess of superoxide ion, are transformed into the peroxy anions $RC(=O)OO^-$ and RSO_2OO^- ,¹⁻⁴ that oxidise organic substrates by routes accordant with their nature.^{4,5} We therefore thought it would be interesting to study the oxidation mode with the relevant biologically important phosphorus peroxidic species.⁶ The desired species were generated *in situ* by mixing potassium superoxide with diethyl chlorophosphate (**1a**) in the presence of 18-crown-6 ether in acetonitrile, and then adding the alkenes or sulphoxides [reaction (1)]. The data in Table 1 indicate



that the oxidation proceeded smoothly to give the expected epoxides (**3**) or sulphones (**6**).[†] Diethyl pyrophosphate (**1b**) also could be used successfully in place of (**1a**).

Competitive experiments (Table 2) provided information which suggested that the system contained at least two oxidizing agents, one a radical (electrophilic nature) and the other nucleophilic. The results may be summarised as follows. (a) The reactivity of the series of 4,4'-disubstituted stilbenes (**2a—d**) decreases in the order (**2a**) ($R = \text{OMe}$) > (**2b**) ($R = \text{Me}$) > (**2c**) ($R = \text{H}$) > (**2d**) ($R = \text{Cl}$).[‡] (b) Both *trans*-(**2c**) and *cis*-stilbene (**2e**) gave only the *trans*-epoxide (**3c**).[§]

[†] In the absence of (**1a**), oxidation of (**2c**) and (**5c**) did not proceed.

[‡] This trend is the same as that found in the photo-induced hydroxylation of substituted benzenes by triethyl phosphite and molecular oxygen, in which the intermediate $(RO)_4POO\cdot$ has been postulated.⁷

[§] The same results have been obtained in reactions with the benzoylperoxy radical.⁸

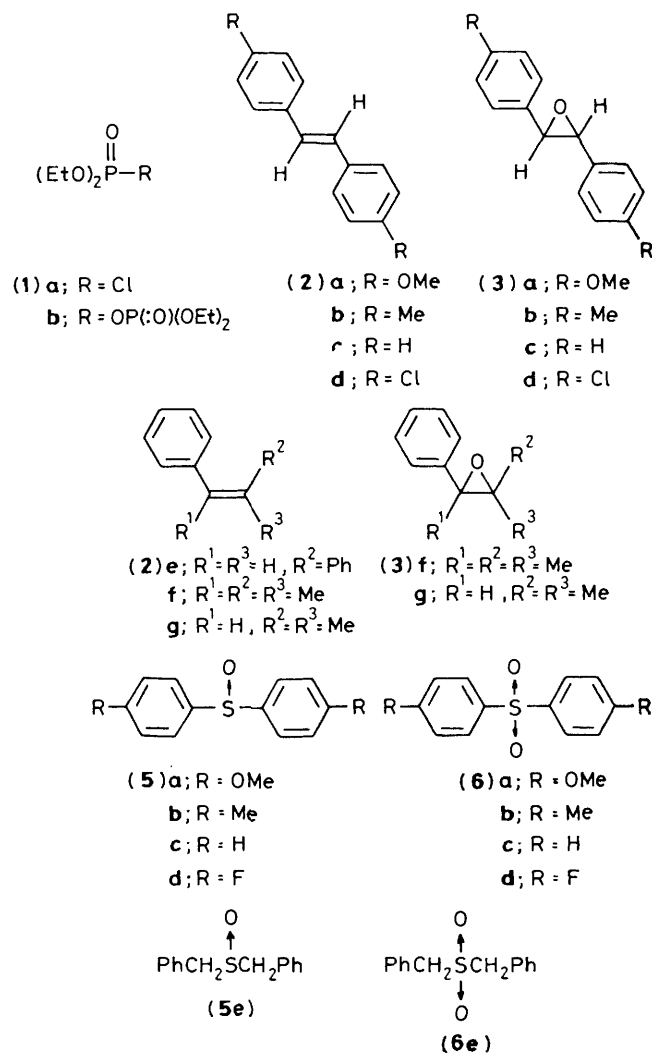


Table 1. Oxidation of alkenes and sulphoxides.^a

Substrate	Phosphate (1)	Temp./°C	Time/h	Yield [%] ^b	
				Epoxide or Sulphone	Recovery
(2c)	a	0	5	(3c) [45(41) ^d]	(2c) [10(7) ^d] ^e
(2c)	b	0	5	(3c) [17]	(2c) [43]
(2e) ^c	a	0	3	(3c) [20]	(2e) [65]
(2f) ^c	a	0	5	(3f) [25]	(2f) [25]
(2f) ^c	b	0	5	(3f) [17]	(2f) [43]
(2g)	a	0	5	(3g) [24]	(2g) [28]
(5c)	a	20	4	(6c) [73]	(5c) [22]
(5e)	a	20	5	(6e) [23]	(5e) [68]

^a Potassium superoxide (5 mmol) was added to a solution of the phosphate (2 mmol), the substrate (1 mmol), and 18-crown-6 ether (0.4 mmol) in acetonitrile (20 ml), and the mixture was stirred for an appropriate time under argon. ^b Determined by n.m.r. spectroscopy. ^c Benzene was used as the co-solvent (1:1 v/v). ^d Isolated yield. ^e Benzaldehyde (4) was isolated in 5% yield.

Table 2. Competitive reactions.^a

Substrates	Time/h	Yield [%] ^b	
		Epoxides or sulphones	Recoveries
(2a) + (2b) ^c	1	(3a) [30], (3b) [13]	(2a) [32], (2b) [64]
(2b) + (2c) ^c	2	(3b) [45], (3c) [28]	(2b) [17], (2c) [48]
(2c) + (2d) ^c	2	(3c) [32], (3d) [18]	(2c) [49], (2d) [63]
(5a) + (5b)	4	(6a) [52], (6b) [55]	(5a) [37], (5b) [37]
(5b) + (5c)	4	(6b) [30], (6c) [41]	(5b) [68], (5c) [57]
(5c) + (5d)	1.5	(6c) [24], (6d) [51]	(5c) [66], (5d) [46]
(2c) + (5c) ^c	2.5	(3c) [42], (6c) [41]	(2c) [36], (5c) [53]

^a A mixture of potassium superoxide (5 mmol), (1a) (2 mmol), the substrates (0.5 mmol of each), and 18-crown-6 ether (0.4 mmol) in acetonitrile was stirred at 20 °C for an appropriate time. ^b Determined by g.l.c. analysis. ^c Benzene was used as the co-solvent (1:1, v/v).

(c) The reactivity order of a series of 4,4'-disubstituted diphenyl sulphoxides, however, follows the sequence (5d) (R = F) > (5c) (R = H) > (5b) (R = Me) > (5a) (R = OMe),[¶] these substituent effects on the rates being the reverse of those observed in the oxidation of the stilbenes (2a–d). These results can be best rationalized in terms of the participation of both the radical (EtO)₂P(=O)OO• (in the oxidation of alkenes) and the anion (EtO)₂P(=O)OO⁻ (important in sulphoxide oxidation). Judging from the yield of the epoxide (3c) and that of the sulphone (6c) in the competitive experiment between (2c) and (5c), these two intermediates exist in comparable amounts in the system.

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[¶] This trend is the same as that observed in the oxidation of diaryl sulphoxides by potassium t-butyl peroxide.⁹