Photo-sensitized Oxidation of Sulphur and Pyridinium Ylides. Oxygen Atom Transfer to Divalent Sulphur[1]

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Summary Methylene Blue sensitized photo-oxidation of dimethyl oxosulphonium and pyridinium bis(methoxycarbonyl)methylides in chloroform gave dimethyl sulphoxide and pyridine as the main products respectively, together with dimethyl mesoxalate; the photo-oxidation of diphenyl sulphide afforded diphenyl sulphoxide, and the results indicate that an oxygen atom is transferred to diphenyl sulphide from oxenoid rather than from 1,2-dioxetan intermediates.

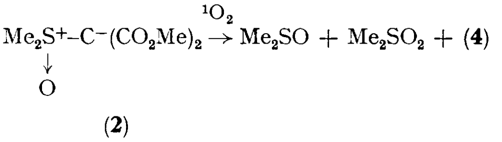
SINCE Hamilton[2] proposed that an oxenoid was the oxidizing agent in mixed function mono-oxidase systems, simple oxenoid model systems have been developed. One of the most studied of the oxenoid reagents is the carbonyl oxide system which is a key intermediate in oxygen transfer reactions. Carbonyl oxides, produced in the photo-oxidation of diazo compounds, transfer an oxygen atom to saturated hydrocarbons[3] and naphthalene.[4] Similar oxygen atom transfer reactions were observed in the studies of α-carbonyl carbonyl oxides produced in the ozonization of alkynes.[5] However, up to date, only these simple models of oxenoid systems have been studied.

Here we report oxygen atom transfer from oxenoid intermediates to diphenyl sulphide in the reaction of singlet oxygen with the ylides (**1**)–(**3**).

Methylene Blue sensitized photo-oxidation of (**3**) (*ca.* 0·5 mmol in 30 ml of CHCl$_3$) was carried out in a water-cooled Pyrex tube by external irradiation with a 300 W halogen lamp. After irradiation for 2 h, two products, pyridine (82%) and dimethyl mesoxalate (**4**) (81%) were obtained by g.l.c. Pyridine is known to be eliminated in the photo-oxidation of some pyridinium salts,[6] and a similar type of amine elimination has been reported in the autoxidation of phenacyl ammonium ylides.[7] Similarly, the photo-sensitized oxidation of (**2**) gives dimethyl sulphoxide (66%), dimethyl sulphone (16%), and (**4**) (58%). The low yields of dimethyl sulphone from the photo-oxidation of (**2**) suggest that the reaction does not involve predominantly a 1,2-dioxetan intermediate, as recent studies on the oxidation of phosphonium ylides by singlet oxygen[8,9] have shown that the resultant 1,2-dioxetan disproportionates to give the phosphine oxide. By analogy, the 1,2-dioxetan formed from (**2**) should afford mainly dimethyl sulphone. In these ylides, oxidative cleavage of the C–N and C–S bonds is the main reaction pathway, which affords oxenoid intermediates. Photo-sensitized oxidation of (**1**) gave dimethyl sulphoxide (60%), dimethyl sulphone (38%), and (**4**) (82%). Probably dimethyl sulphoxide and dimethyl sulphone arose from the oxidation of the resulting dimethyl sulphide. Photo-oxidation of (**1**)–(**3**) without any sensitizer did not occur under the same reaction conditions. Addition of DABCO (1,4-diazabicyclo[2.2.2]octane) (singlet oxygen quencher) to the ylides (4 : 1) completely inhibited the photo-sensitized oxidation of (**1**) and (**2**), and slightly inhibited that of (**3**) [no product was found for (**1**) and (**2**), and 48% of pyridine was detected for (**3**)]. Singlet oxygen must be the reaction intermediate in these reactions.†

$$\mathrm{Me_2S^+{-}C^-(CO_2Me)_2 \xrightarrow{^1O_2} Me_2SO + Me_2SO_2 + O{=}C(CO_2Me)_2}$$

(**1**) (**4**)



$$\mathrm{\underset{\substack{\downarrow\\ O}}{Me_2S^+}{-}C^-(CO_2Me)_2 \xrightarrow{^1O_2} Me_2SO + Me_2SO_2 + (\mathbf{4})}$$

(**2**)

$$\mathrm{C_5H_5N^+{-}C^-(CO_2Me)_2 \xrightarrow{^1O_2} C_5H_5N + (\mathbf{4})}$$

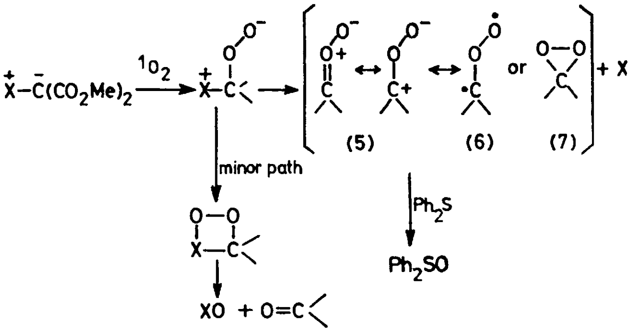
(**3**)

To elucidate the nature of the oxenoid intermediates, intermolecular oxygen atom transfer reactions were carried out by adding various olefins, aromatic hydrocarbons, and sulphides. Among them, diphenyl sulphide was found to be one of the best oxygen atom acceptors; it is known to be a good trapping agent for 1,2-dioxetan intermediates.[10] The ylides (**1**)–(**3**) with diphenyl sulphide (ratio 1 : 4) were photo-oxidized with Methylene Blue in chloroform and gave diphenyl sulphoxide as the oxygen atom transfer product. Diphenyl sulphide is unreactive towards singlet oxygen,[11] and control experiments showed that no diphenyl sulphoxide was formed in the absence of ylide under the reaction conditions. Moreover, oxygen atom transfer from the products, dimethyl sulphoxide or dimethyl sulphone, was excluded. One mechanism for the oxidation of diphenyl sulphide involves the intermediacy of an oxenoid, which might be the zwitterion (**5**), the diradical (**6**), or possibly the cyclic peroxide (**7**) (Scheme).[12]

TABLE. Photo-sensitized oxidation of the ylides (**1**)–(**3**) with $\mathrm{Ph_2S}$ (irradiation time; 2 h)[a]

Ylide	$\mathrm{Ph_2SO}$/%	$\mathrm{Me_2SO}$/%	$\mathrm{Me_2SO_2}$/%	(**4**)/%	$\mathrm{C_5H_5N}$/%
(**1**)	53	67	18	63	—
(**2**)	39	78	10	33	—
(**3**)	45	—	—	34	72

[a] Yields were based on ylides and determined by g.l.c. analyses. Solvent; $\mathrm{CHCl_3}$



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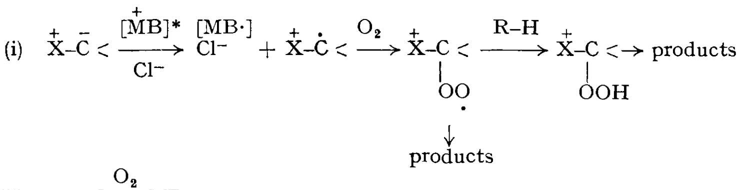
† A referee suggested an alternative reaction mechanism which would involve electron abstraction from the ylide by photo-excited Methylene Blue, followed by reaction of the ylide radical with triplet oxygen to give a peroxide radical.



$$\text{(i)}\quad \mathrm{\overset{+}{X}{-}\overset{-}{C}< \xrightarrow[Cl^-]{[\overset{+}{MB}]^*} \underset{Cl^-}{[MB\cdot]} + \overset{+}{X}{-}\overset{\cdot}{C}< \xrightarrow{O_2} \overset{+}{X}{-}\underset{\substack{|\\ OO\cdot\\ \downarrow\\ products}}{C}< \xrightarrow{R{-}H} \overset{+}{X}{-}\underset{\substack{|\\ OOH}}{C}< \rightarrow products}$$

$$\text{(ii)}\quad \mathrm{\underset{Cl^-}{[MB\cdot]} \xrightarrow{O_2} \underset{Cl^-}{[MB^+]}}$$

However, the photo-sensitized oxidation of the ylides was not affected by addition of 2,6-di-t-butyl-*p*-cresol (radical scavenger: ylide 2 : 1). Such a radical mechanism can be neglected, and moreover, addition of DABCO inhibited the reaction. These results indicate that singlet oxygen must be the reactive intermediate.

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