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A Novel Base-catalysed Oxidation of Sulphides with an α-Azohydroperoxide

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The α-azohydroperoxide (**1**) in the presence of pyridine oxidises aryl sulphides cleanly to sulphoxides; the dioxirane (**2**) is proposed as the intermediate.

Hydroperoxides are known to oxidise sulphides to sulphoxides in neutral and acidic media.[1–3] We report a new type of sulphoxidation with α-azohydroperoxide (**1**) in basic media.

When a benzene solution of (**1**) (10^{-2} M) and thioanisole (10^{-1} M) was stirred in the presence or absence of pyridine (10^{-2} M) at room temperature for 12 h, methyl phenyl sulphoxide was formed together with benzaldehyde, benzoic acid, *N*-(4-bromophenyl)benzohydrazide (**3**), and 4-bromobiphenyl. The yields (excluding 4-bromobiphenyl) are given in Table 1. By a similar reaction, diphenyl sulphide gave diphenyl sulphoxide together with several other products (Table 1). Sulphones were not formed in these reactions. It is important to note that the product distribution in the presence and absence of pyridine differs substantially. Diphenyl sulphoxide and methyl phenyl sulphoxide were formed together with a considerable amount of benzaldehyde in the presence of pyridine, while the benzohydrazide (**3**) was produced with the sulphoxides in the absence of pyridine (Table 1). In the former case the amounts of sulphoxide and benzaldehyde were approximately equal as were the amounts of sulphoxide and the hydrazide (**3**) in the latter reaction. In addition, in the reaction of thioanisole, 4-bromobiphenyl was formed in 20% yield (isolated yield) in the presence of pyridine, while, in the absence of pyridine, 4-bromobiphenyl could not be detected in the reaction mixture. In contrast, di-n-butyl sulphide behaves differently. The sulphoxide was formed together with a considerable amount of (**3**) both in basic and neutral media.

These differences can be explained if there are two different modes of reaction; one is direct oxygen transfer from (**1**),[1–3] and the other is oxygen transfer from the dioxirane intermediate (**2**) [or the carbonyl oxide (**4**)] which is generated from (**1**) by the action of a base (Scheme 1).[4] The former mechanism gives an equal amount of sulphoxide and (**3**) *via* (**5**),[4,5] while the latter gives sulphoxide and benzaldehyde. All these reactions occur competitively depending on the rates of the reactions k_1—k_4 (Scheme 1).

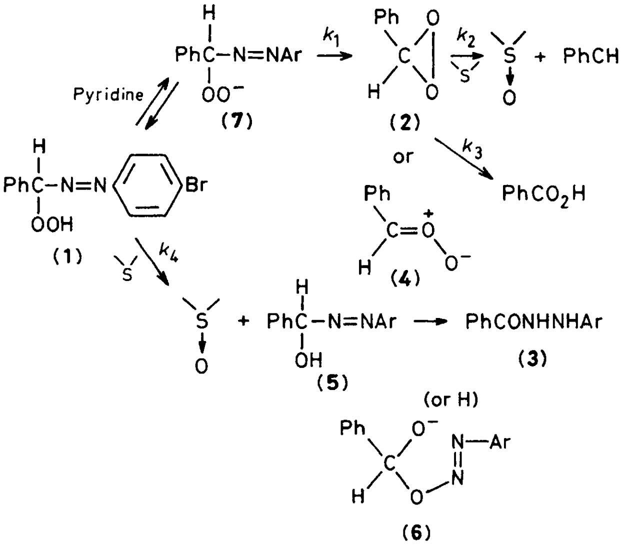
Table 1. Oxidation of sulphides with α-azohydroperoxide (**1**).

Sulphide	Pyridine	Sulphoxide (%)[a]	PhCHO (%)[a]	$PhCO_2H$ (%)[a]	PhCONHNHAr (**3**) (%)[a]
Ph_2S	+[b]	67	52	31	5
	+[c]	74	8	3	61
PhSMe	+	54	40	39	10
	–	73	8	0	66
$Bu^n{}_2S$	+	89	5	13	58
	–	80	4	0	74

[a] Yield is based on (**1**) and measured by h.p.l.c. [b] In the presence of pyridine. [c] In the absence of pyridine.

A time-dependent study of diphenyl sulphide indicated that the rate of sulphoxide formation in neutral solution was initially (up to 6 h) slow and then fast, while the sulphoxide formation in basic solution occurred rapidly from the beginning of the reaction at 26 °C (Figure 1). After 10 h, however, the yields in both neutral and basic media were comparable. The apparent rate of sulphoxidation at the initial stage of the reaction is much faster in basic than neutral media at 26 °C (Figure 1). The slow sulphoxidation of diphenyl sulphide by hydroperoxides in neutral media has been reported.[3]

It is interesting, however, that in spite of this ready reaction of diphenyl sulphide in basic media, the yield of sulphoxide at the end of the reaction is lower in basic media than in neutral



Scheme 1

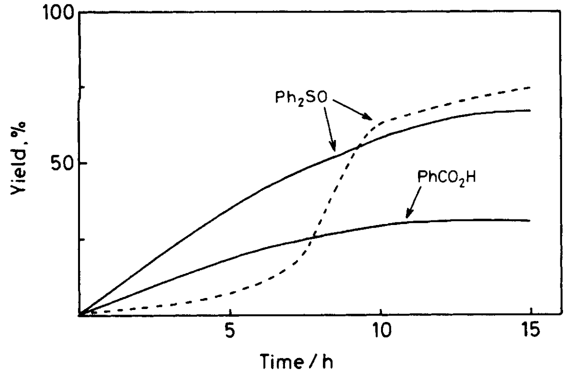


Figure 1. Time-dependent study of the oxidation of diphenyl sulphide with (**1**) in the presence (——) and the absence (– – –) of pyridine.

media (Figure 1 and Table 1). This is because sulphoxidation occurs *via* the dioxirane intermediate (**2**) in basic media, and the oxygen transfer from (**2**) to sulphide competes with the intramolecular rearrangement to benzoic acid.[4] In fact, the ratio of the sulphoxide and benzoic acid was 2:1 throughout the reaction (Figure 1). In contrast, there is no such competing reaction in neutral media, and hence the final yield of sulphoxide was higher. A similar result was observed for thioanisole.

On the other hand, a reactive sulphide such as di-n-butyl sulphide which has high electron density on the sulphur atom and is reactive toward electrophiles, behaves differently. A comparison of the yields in Table 1 indicates that direct oxygen transfer from (**1**) to di-n-butyl sulphide is dominant even in basic media, giving rise to di-n-butyl sulphoxide together with a considerable amount of (**3**) (Table 1).

We have previously reported that in the pyridine-catalysed reaction of the α-azohydroperoxide (**1**) a new oxidant is generated, assigned as the dioxirane (**2**) or the carbonyl oxide (**4**) which epoxidizes olefins or isomerizes to benzoic acid.[4] All our present observations agree with this; the sulphoxidations of diphenyl sulphide and thioanisole in basic solution are accounted for by the mechanism involving (**2**) or (**4**) as a reactive oxenoid in Scheme 1. However, the possibility of alternative oxenoids such as (**6**) can not be ruled out completely at the moment. The oxenoid (**6**) is derived from the peroxy anion (**7**) by a Criegee-type rearrangement[6,7] of the azo group to the α-oxygen atom with a simultaneous attack of the β-oxygen atom on the methine carbon atom. The dioxirane (**2**) could then be derived from (**6**) by elimination of the azo group.

Recently, sulphoxidation by reactive oxenoids such as carbonyl oxides generated from diazo compounds with singlet oxygen[8] and from other sources[9] has been reported. Our present observations are of interest in this respect.

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