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A FACILE PREPARATION OF SULPHOXIDES BY THE BENTONITE-ASSISTED OXIDATION OF SULPHIDES WITH MAGNESIUM MONOPEROXYPHTHALATE IN AN APROTIC SOLVENT

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ABSTRACT: The title oxidation has been investigated in acetonitrile. The substrates examined include alkyl aryl, diaryl, dialkyl, and cyclic sulphides, which afforded the corresponding sulphoxides in good to excellent yields under neutral and mild conditions.

A newly developed peroxy acid derivative, magnesium monoperoxyphthalate (for short *MMPP*), was originally manufuctured as a bleaching agent in a detergent because of mild oxidative property.1) The commercial chemical, available as the hexahydrate,2) is a free-flowing white

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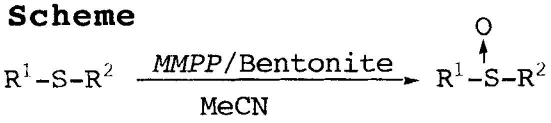
powder, and its physicochemical profile has been illustrated recently.(3,4) Since the pioneering work of Heaney's group,(5) considerable attention has been devoted to *MMPP* as a substitute of *mCPBA*, and many interesting facets of *MMPP* chemistry have been disclosed.(6,7) A variety of approaches were elaborated to effect the reactions, however, these processes were performed in an aqueous alcoholic medium or under phase-transfer conditions. No evaluation of synthetic potential of *MMPP* in aprotic solvents thus has been made to date owing to its negligible solubility. Consequently, *MMPP* chemistry in a water-free medium still remains unexplored.

During our continuous work concerning peroxy acid oxidations,(8,9) we have become aware of a considerable promotive function of an inorganic support material upon the reaction with an oxidant insoluble in organic solvents,(9) which is expected to accommodate the solubility problem associated with *MMPP*. It is worth noting at this point that the oxidising miliues of the foregoing reactions(9) are reminiscent of those of supported reagent systems, and therefore the product isolation is very facile. By introducing this novel and experimentally simple procedure, we now report that *MMPP* become efficient oxidant in an aprotic solvent with the aid of a bentonite, and that such reagent system is convenient to use and capable of performing a clean sulphide oxidation, and results in a selective formation of the corresponding sulphoxides in good to excellent yields (**Scheme** and Table).

Scheme



$$R^1\text{-S-}R^2 \xrightarrow[\text{MeCN}]{\textit{MMPP}/\text{Bentonite}} R^1\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}R^2$$

The present oxidation can be readily carried out only by mixing *MMPP*, a solvent, and a bentonite with a sulphide. Preliminary experiments have been made to establish the optimal conditions for the selective formation of a sulphoxide in high yield. The satisfactory results were attained by conducting the reaction in acetonitrile at modest temperature (ambient to 303K) by using a slight excess of *MMPP* in the presence of the moist bentonite (detailed in **Experimental Section**). Under such conditions, methyl phenyl sulphide, for an instance, underwent smooth oxidation whereupon, after a single chromatographic isolation, pure methyl phenyl sulphoxide was obtained in 90% yield with no apparent formation of methyl phenyl sulphone (Entry 1). Thus work-up as well as isolation of a sulphoxide did not present any problem. Once again, control experiment showed that the absence of the bentonite causes a rather sluggish reaction and an inferior yield of a sulphoxide and, more seriously, makes efficient isolation of sulphoxides considerably difficult in some cases by contamination of the product mixtures with the oxidant residue. These suggest that the bentonite serves not only as a highly reactive site for *MMPP* facilitating the reaction, but as a trap of the oxidant residue, preventing its diffusion into the solvent during reaction and/or work-up.

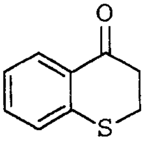
Usefulness of the present procedure for a variety of sulphides is summarised in the Table. The apparent reactivity order of the substituted methyl phenyl sulphides is well consistent with the trend observed in ordinary peroxy acid oxidations (Entries 1-5). But interestingly the electronic property of the *para*-substituents hardly influenced the selectivities and yields of the sulphoxides. It is of special note that, in contrast to previous observations that an olefinic double bond is highly susceptible to epoxidation,[5,6] the present procedure is not deleterious to vinyl (Entry 9) and allyl (Entry 10) functionalities, giving the sulphoxides in good to essentially quantitative yields. The oxidation of typical dialkyl sulphides are also performed (Entries 11-14) wherein they afforded the corresponding sulphoxides in excellent yields, irrespective of a steric bulk or a carbon-chain length of an alkyl group. Benzyl alcohol (Entry 6) or

Table. Oxidation of Sulphides with *MMPP* in Acetonitrile[a)]

Entry No.	Sulphides R^1	R^2	*MMPP* [mmol]	Time [min.]	Sulphoxides [%][b)]
1	Ph	Me	1.04	60	90
2	*p*-$MeOC_6H_4$	Me	1.04	45	87
3	*p*-MeC_6H_4	Me	1.04	60	93
4	*p*-BrC_6H_4	Me	1.04	60	93
5[c)]	*p*-$NO_2C_6H_4$	Me	1.04	15(h)	85
6	*p*-$HOCH_2C_6H_4$	Me	1.04	120	68
7	Ph	Ph	1.12	60	84
8	$PhCH_2$	$PhCH_2$	1.16	60	71[d)]
9	Ph	Vinyl	1.04	90	75
10	Allyl	Allyl	1.04	60	96[e)]
11	*n*-Bu	*n*-Bu	1.04	60	95[e)]
12	*i*-Bu	*i*-Bu	1.04	60	92
13	*s*-Bu	*s*-Bu	1.04	60	87
14	*n*-Octyl	Me	1.04	90	96[e)]
15	Tetrahydrothiophene		1.04	90	67[e)]

a) Under argon and at 303K; 2 mmol of a sulphide, 2 g of the moist bentonite, and 10 mL of acetonitrile were used in every run. b) Isolated yields. c) At ambient temperature (*ca.* 293-294K) for 15 hours. d) Isolated by recrystallization from ethanol/hexane. e) GC yields.

heterocyclic ring (Entry 15) are found intact under the reaction conditions.



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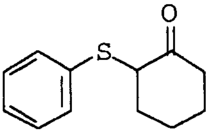

2

Somewhat surprisingly, oxidation of a sulphide with an oxo-functionality such as thiochroman-4-one (**1**) and 2-(phenylthio)-cyclohexanone (**2**) resulted only in the formation of a complex mixture of products, despite that the latter sulphide is convertible to the sulphoxide in fair good yield upon the reaction in aqueous ethanol.10) This failure is assumed to at least in part be responsible for the susceptibility of the carbonyl moiety to Baeyer-Villiger oxidation.5) In this unexpected regard, further work is now in progress to reveal the behaviour of ketonic compounds under the oxidative conditions.

EXPERIMENTAL SECTION

Generals: ^{1}H NMR spectra were measured with a JEOL PMX-60 spectrometer for solutions in carbon tetrachloride or deuteriochloroform. IR spectra were recorded for thin films (neat) or KBr disks on JASCO A-

100 spectrophotometer. GC was carried out on a Shimadzu GC-4CM instrument with a 2 m glass column packed with 3% Silicone OV-17 on Chromosorb GAW-DMCS, with temperature programming.

Starting Materials: *MMPP* was purchased from *Tokyo Chemical Industry Co., Ltd.* [*JAPAN*],$^{2)}$ of which purity was determined by iodometry (*ca.* 86%). The bentonite (*Kukita Yakuhin Kogyo Co., Ltd.* [*JAPAN*]) was carcined at *ca.* 620K for several hours. The moist bentonite was prepared by adding distilled water (2.7 g) to the bentonite (18 g) in portions followed by vigorous shaking of the mixture on every addition for a few minutes untill a free-flowing powder was obtained. All the sulphides, but 2-(phenylthio)-cyclohexanone, were commercial chemicals and were used without purification; their purities were checked by GC analyses prior to use. 2-(Phenylthio)-cyclohexanone was synthesized according to the literature.$^{11)}$

Oxidation Procedure: The following one for methyl phenyl sulphide is representative. In a 30 ml, round-bottom flask were placed the moist bentonite (2.0 g), acetonitrile (6 mL) and *MMPP* (0.52 mmol), and the resultant heterogeneous mixture was magnetically stirred for several minutes. Methyl phenyl sulphide (2 mmol) in acetonitrile (4 mL) was added in a portion and was then the flask deaerated by flushing dry argon. The reaction was initiated by vigorous stirring; *NB*, efficient stirring is indispensable for attaining a superior performance of the reaction. After allowing the reaction at 303K for two hours, the whole mixture was transferred onto a sintered glass funnel, and the insolubles were thoroughly washed with dichloromethane (required *ca.* 100 mL). The combined solvent was rotary-evaporated *in vacuo*, leaving methyl phenyl sulphoxide accompanied with a faint trace of methyl phenyl sulphone. Immediate column chromatography on silica gel (Merk 60) eluting with a combination of hexane and ethyl acetate (2:1 by volume) afforded satisfactorily pure (100% by GC analysis) methyl phenyl sulphoxide in 90% isolated yield.

The other tabulated sulphoxides, except for dibenzyl sulphoxide, were synthesized as described above. Dibenzyl sulphoxide was given by recrystallisation of a crude material from a combined solvent of ethanol and hexane; *m.p.* 408K (uncorrected); *Lit.*,12) 407-408K.

Incidentally, independent reaction employing methyl phenyl sulphide as substrate revealed that use of a quite common bentonite clay, K10 Montmorillonite13) (available from *Aldrich*), in place of the present one leads to almost the same selectivity and yield of the sulfoxide.

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