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EFFICIENT OXIDATION OF SULFIDES TO THE SULFOXIDES USING A NEW SULFINYLPEROXY INTERMEDIATE GENERATED FROM 2-NITROBENZENESULFINYL CHLORIDE AND SUPEROXIDE

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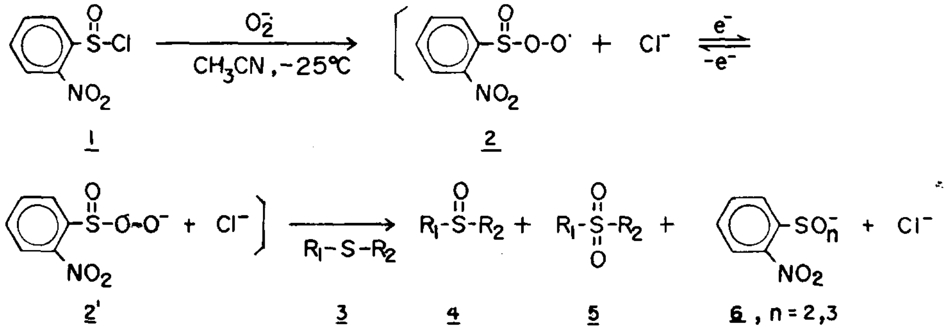
Summary: Various sulfides were found to react with a sulfinylperoxy intermediate generated in situ by the treatment of 2-nitrobenzenesulfinyl chloride with superoxide at -25 °C in acetonitrile to afford the corresponding sulfoxides selectively in excellent yields together with traceable amount of the sulfones under mild conditions.

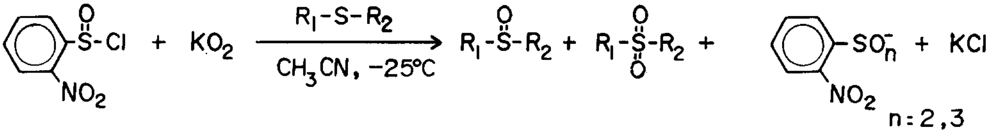
Considerable interest has recently been focused on the use of superoxide ($O_2^{-\cdot}$) for organic synthesis.[1] The physical properties of nucleophilicity, basicity, and radical character of $O_2^{-\cdot}$ appear to have an important role depending on the substrates.[1c] Berger's suggestion[2] that formation of peroxysulfinate was involved as a key intermediate in the strong alkaline auto-oxidation of thiols or disulfides to the sulfinates and sulfonates has been neither isolated nor confirmed.

During a study on activating superoxide,[3] we have now found that various sulfides are readily oxidized to the corresponding sulfoxides in excellent yields under mild conditions by 2-nitrobenzenesulfinylperoxy intermediate 2 which is generated in situ by the treatment of 2-nitrobenzenesulfinyl chloride[4] and potassium superoxide at -25 °C in acetonitrile. Only traceable amount of the sulfones were obtained or observed by ^1H NMR spectrocopy.



It is important and valuable to control the oxidation to the sulfoxides without undergoing further oxidation to the sulfones. The results obtained are summarized in Table I.

Table I. Oxidations of Sulfides to the Sulfoxides[a]



Run	R_1	R_2	Reactn. Time (h)	Yield(%)[b] -SO-	-SO_2-	-S-
1	4-CH_3-C_6H_4	CH_3	5	97	trace	
2	4-CH_3-C_6H_4	CH_2Ph	4	95	"	
3	4-CH_3-C_6H_4	CH_2CH_3	4	96	"	
4	Ph	CH_3	4	92	"	
5	4-Br-C_6H_4	CH_3	5	95	"	
6	4-Cl-C_6H_4	CH_3	5	91	"	
7	4-Cl-C_6H_4	CH_2CH_3	4	94	"	
8	4-Cl-C_6H_4	CH_2Ph	7	94	"	
9	$PhCH_2$	CH_2Ph	5	97	3[c]	
10	α-Naphthyl	CH_3	7	98	2[c]	
11	4-NO_2-C_6H_4	CH_3	8	62	12	24[c]

a. Molar ratio = KO_2:1:3 = 3:1:0.5

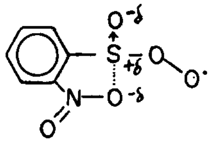
b. Isolated yields

c. Determined by ^1H NMR spectrum

In a general procedure (Run 5), a solution of 2-nitrobenzenesulfinyl chloride (205 mg, 1 mmol) and 4-bromophenyl methyl sulfide (102 mg, 0.5 mmol) in dry acetonitrile (3 ml) was added to a heterogeneous solution of potassium superoxide (216 mg, 3 mmol) in dry acetonitrile (3 ml) at -25 °C with continuous vigorous stirring. After being stirred for 4h at

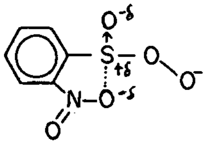
$-25\ ^{o}C$, the reaction mixture was filtered and the solid collected was washed with acetonitrile (10 ml) and then chloroform (10 ml). Concentration of solvent and then the ratio of sulfoxide and sulfone was compared by ^{1}H NMR. Purification by preparative TLC (Merck, silicagel 60 F_{254}, 1mm x 20cm x 20cm, Et_2O:n-hexane = 2:1) gave 4-bromophenyl methyl sulfoxide (105 mg, 95%) and a traceable amount of 4-bromophenyl methyl sulfone. Some other sulfoxides were purified by recrystallization or column chromatography (silica gel, Merck, Kiesel gel 60, 70-230 mesh, CH_2Cl_2:MeOH = 10:1).

The workup is simple and easy: after monitoring the complete reaction by TLC on silica gel, filtration to remove insoluble potassium chloride and 6 and then concentration give a highly pure product. When less than two equivalent amount of 2-nitrobenzenesulfinyl chloride (1) for the sulfide was used, smooth oxidation of sulfides to the sulfoxides occurred almost without further oxidation to the sulfones, except the oxidation of methyl 4-nitrophenyl sulfide (Run 11). Oxidation of sulfides to the sulfoxides in well known to be electrophilic in contrast to the nucleophilic oxidation of sulfoxides to the sulfones.[5] The sulfur atom of methyl 4-nitrophenyl sulfide which contains a strong electron withdrawing group of NO_2 appears to be a weaker electrophile than the other sulfides. The sulfinylperoxy intermediate (2) seems to be stabilized by a neighboring group effect of the nitro group as shown below as in the case of methyl 2-nitrophenyl sulfenate,[6] 2-nitrobenzene selenic anhydride,[7] or 2-nitrobenzeneperoxyseleninic acid.[8]



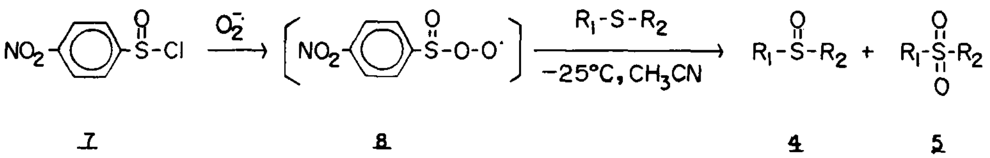
2

OR



2'

Oxidation using 4-nitrobenzenesulfinylperoxy intermediate (8) which is generated from 4-nitrobenzenesulfinyl chloride and superoxide under the same reaction conditions yielded poorer yields than those obtained using 2 as shown below. This may be explained by the lower stability of 8 due to the lack of a neighboring group effect of the nitro group in comparison with that from 2.



R_1	R_2	7 : $O_2^{-\cdot}$: 3	Reactn. Time (h)	Yields -SO-	Yields $-SO_2-$
$4-Me-C_6H_4$	Et	1 : 3 : 0.5	4	41	2
Ph	Me	1 : 3 : 0.5	4.5	40	trace
$4-Cl-C_6H_4$	Me	1 : 3 : 0.5	5	50	2

4-Tolylsulfinylperoxy intermediate generated from 4-tolylsulfinyl chloride and $O_2^{-\cdot}$ meanwhile gave much poorer yields[9] of the sulfoxides than those obtained using 2 or 8. Thus, the nitro group in 2-position of 2 appears to play an important role in accelerating the substitution of chlorine with superoxide anion and also in stabilizing the intermediate, 2 by a neighboring group effect. It is noteworthy that the 2-nitrobenzenesulfinylperoxy intermediate (2 or 2') shows a strong electrophilic character under the basic condition and, moreover that in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) which is known to be a radical capture reagent,[10,11] the oxidation of methyl phenyl sulfide to the sulfoxide was inhibited.[12] The peroxy intermediate is likely to be of a radical character (2) as in the case of 2-nitrobenzenesulfonylperoxy intermediate,[13] acyl peroxy radical,[14] and phenyl nitroso oxide radical (PhNOO·).[15] However, an alternative mechanism involving anion character (2') in the basic condition cannot be ruled out.

Though 2 has not yet been confirmed, it has strong electrophilic oxidizing ability and is stable enough to be widely used for the efficient oxidation of sulfides to the sulfoxides under mild conditions.

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