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Direct Oxidation of Arenes to Arene Oxides by 2-Nitrobenzene Peroxysulfur Intermediate Generated from 2-Nitrobenzenesulfonyl Chloride and Superoxide

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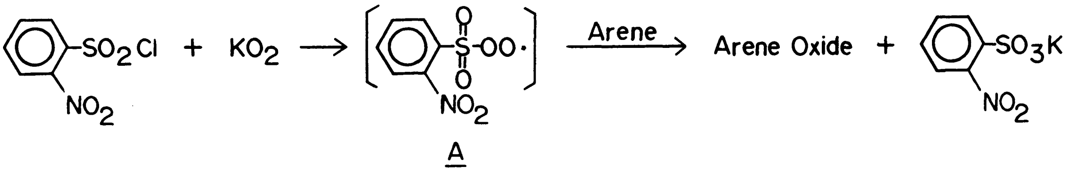
Acenaphthylene, phenanthrene, and pyrene, which are inert with superoxide itself, were readily oxidized to the corresponding arene oxides by a 2-nitrobenzene sulfonylperoxyl radical intermediate (A) generated from 2-nitrobenzenesulfonyl chloride and potassium superoxide in polar aprotic solvents such as acetonitrile, nitromethane, and dimethylformamide under mild conditions.

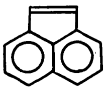
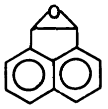
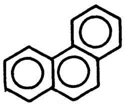
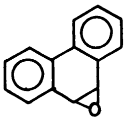
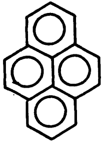
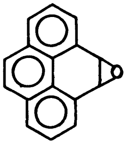
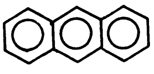
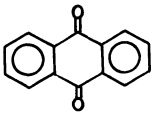
Since arene oxides and their subsequent metabolites have been implicated as the intermediates which are responsible for the carcinogenicity and mutagenicity of polyaromatic hydrocarbons, there have been considerable interests both in the related chemical reactions and in understanding how they are formed physiologically.[1)] In many attempts to synthesize arene oxides by direct oxidation, few of successful works have been reported.[1)] The discovery of superoxide dismutase which may protect the living cells against the toxic effects of superoxide and the possibility that superoxide might be an important intermediate in aerobic life provided a new impetus for studies on the superoxide reactivities.[2,3)]

Recently it was reported that 2-nitrobenzene peroxysulfur intermediate, generated *in situ* by the treatment of 2-nitrobenzenesulfonyl chloride with superoxide, could be an oxidizing agent for the epoxidation of olefins[4)] and for the desulfurization of thiocarbonyl compounds to carbonyl compounds[5)] which are important *in vivo* metabolic processes catalyzed by monooxygenases.[6)]

In this communication, we report that various arenes reacted with 2-nitrobenzene peroxysulfur intermediate (A) under mild conditions to give the corresponding arene oxides. Polyaromatic compounds such as acenaphthylene (1), phenanthrene (2), and pyrene (3), which are inert to superoxide itself, were readily oxidized to the corresponding arene oxides by A as shown in Table 1.

Table 1. Oxidation of Arenes with 2-Nitrobenzene Peroxysulfur Intermediate in Acetonitrile at -30 °C[a)]



Run	Arene	Solvent	Temp/°C	Time/h	Product	Yield/%[b)]
1	 1	CH_3CN	-30	12	 1'	95
2	 2	CH_3CN	-30	10	 2'	50[c)]
3	 3	CH_3CN	-30	10	 3'	15[c)]
4	3	DMF	-30	22	3'	10[c)]
5	 4	CH_3CN	0-r.t.	20	 4'	70[d)]
6	4	DMF	-30	8	4'	70

a) Molar ratio (Arene : $ArSO_2Cl$: KO_2 = 1:2:8). b) Isolated yields. c) Yields were determined by ^1H-NMR. d) The starting material (4) is not very soluble at -30 °C in acetonitrile. Thus the reaction was carried out at 0-25 °C.

In a general procedure (run 1), a solution of 2-nitrobenzenesulfonyl chloride (222 mg, 1 mmol, CH_3CN; 3 ml) was added to a suspension of superoxide (290 mg, 4 mmol) in dry acetonitrile(3 ml) and then acenaphthylene solution (76 mg, 0.5 mmol, CH_3CN; 2 ml) was added. The reaction mixture was stirred at -30 °C with good stirring. After being stirred for 10 h at -30 °C, the reaction mixture was poured into cold 10% aqueous sodium chloride solution. The mixture was extracted with methylene chloride(10 ml x 3), dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure to give acenaphthylene oxide (1') (79 mg, 95%).[9)] Anthracene was oxidized to anthraquinone under the same conditions except using dry dimethyl formamide because of its poor solubility at -30 °C in acetonitrile. Previously, a few syntheses of arene oxides from arenes by the direct oxidation with aqueous sodium hypochlorite,7) m-CPBA in buffered solution,8) or dimethyldioxirane9) were reported. These syntheses of arene oxides by direct oxidation were carried out using phase transfer catalysts in two layer system of organic solvent and water under slightly basic buffered solution because the highly strained arene oxides are unstable under acidic conditions.

However, our oxidation system can be conducted in aprotic organic solvents under mild (-30 $^{\circ}C$) and basic conditions, where superoxide is well known to be a quite strong base.3a) Acenaphthylene oxide which is unstable under acidic conditions is known to be more stable under basic conditions.8) Thus we could isolate acenaphthylene oxide in higher yields than those of the reported methods7,10) perhaps due to the stability of the product under basic conditions.

It is noteworthy that there are contrasted solvent effects among acetonitrile, nitromethane, dimethyl formamide, pyridine, and tetrahydrofuran as shown in Table 2.

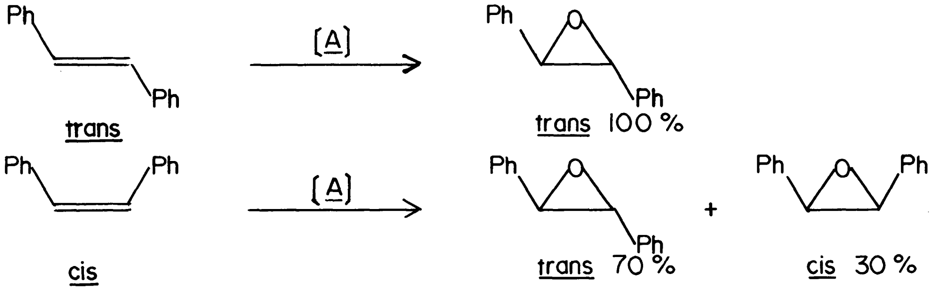
Table 2. Oxidation of Acenaphthylene with 2-Nitrobenzene Peroxysulfur Intermediate in Various Solvents at -30 $^{\circ}C$ for 10 h[a)]

$$\text{Acenaphthylene}(\underline{1}) \xrightarrow[-30^{\circ}\text{C}/10\ \text{h}]{[\underline{\text{A}}]} \text{Acenaphthylene Oxide}(\underline{1}')$$

Solvent	Yield/%[b)]
CH_3CN	> 95
CH_3NO_2[c)]	> 95
DMF	100[d)]
Pyridine	Small amount[e)]
THF[f)]	0

a) Molar ratio (Acenaphthylene : $ArSO_2Cl$: KO_2 = 1:2:8). b) Isolated yields. c) Nitromethane reacted violently with superoxide at 25 $^{\circ}C$ to give unidentified product, but inert to superoxide at -30 $^{\circ}C$. d) Determined by ^1H-NMR. e) Pyridine is also polar aprotic solvent and may be good solvent for KO_2. But pyridine itself was found to be oxidized to the corresponding N-oxide in more than 50% yield. f) No reaction occurred probably due to the poor solubility of KO_2 in THF: starting material was recovered quantitatively.

Metal peroxides have been considered to be little dissolved in organic solvents and usually used in the presence of crown ethers to increase the solubility of metal superoxide. Potassium superoxide is now turned out to be soluble enough in aprotic solvents such as CH_3CN, CH_3NO_2, and DMF without using crown ether catalysts. The peroxysulfur intermediate is likely to be of a radical character (A), rather than anion, like the case of acylperoxy radical ($ArC(O)OO\cdot$)[12] and phenyl nitroso oxide radical ($PhNOO\cdot$)[13] from the fact that oxidation of cis-stilbene by A gave both trans- (70%) and cis-oxides (30%) under the same conditions.[11]



The scope and mechanism of the oxidation are under investigation. This work was supported by a generous grant from the KOSEF and partially KAIST.

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