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Communications to the Editor

stituted cation (ion 9) with that of the substituted cations, it also indicates that the substituents in fused benzene ring exerted a considerable influence on the charge delocalization.

The difference of a chemical shift of the ortho protons in ion (1) which containes one methoxy groups at C-5 give a slightly large $\Delta\delta H_o$ value (1.44 ppm) relative to that of ion (2) (1.37 ppm) which contains also one methoxy group at C-6. This result reveals large charge delocalization into *p*-fluorophenyl ring in case of ion (1). In other word, the 6 substituent is much more effective to charge decloaization through homobenzylic participation.

Surprisingly, the $\Delta\delta H_o$ value for the ion (3) shows exceptionnally high compared to that of the ion (4), even though these cations have two methoxy groups in fused benzene ring. In series of methyl substituted cations, their nature in cationic intermediates is a very similar to that of methoxy substituted cations.

From the result of ^1H nmr studies, we confirm that the position of substituent in fused benzene ring is a very impor-

tant factor to the charge delocalization in substituted benzonorbonenyl cations. Unfortunately, the ^1H nmr data does not appear to provide the precise structure of cationic intermediate. To help resolve this problem, the ^{13}C nmr studies on these cations are currently under investigation.

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Chemoselective Oxidation of Sulfides to Sulfones with Selenium Dioxide–Hydrogen Peroxide

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Chemoselective conversion of sulfides to sulfones would provide synthetic chemists with a useful tool since organosulfur compounds are widely used in organic synthesis. Most commonly used oxidizing agents for sulfides to sulfones such as H_2O_2, MCPBA, and $KMnO_4$ have limitations: incomplete conversion to sulfoxides or oxidation of other functional groups.

We have found that SeO_2-H_2O_2 system is a chemoselective oxidizing agent for conversion of sulfides to sulfones. Neither this system nor its application to oxidation of organic compounds is new.[1,2] In fact, SeO_2-H_2O_2 system has been used for selective oxidation of sulfides to sulfoxides by Mikolajczyk[3] and for oxidation of secondary amines to nitrones by Murahashi.[4] However, in contrast with Mikolajczyk's report, SeO_2-H_2O_2 system in the present work efficiently oxidized sulfides to sulfones but did not affect other functional groups such as double bonds and hydroxy groups. A representative example is the oxidation of crotyl phenyl sulfide. To a mixture of crotyl phenyl sulfide (0.164g, 1.00 mmol) and selenium dioxide (0.222g, 2.00 mmol) in methanol (2 ml) was added dropwise an aqueous 30% hydrogen peroxide solution (0.227g, 2.00 mmol) at room temperature. Tlc of the reaction mixture indicated that the starting material disappeared quickly and the product was the mixture of the sulfoxide and the sulfone in almost 1:1 ratio. The sulfoxide was converted into the sulfone in 1 hr. The reaction mixture was partitioned between methylene chloride and water layers. Glc analysis of the organic layer indicated the yield of sulfone

Table 1. Oxidation of Sulfides to Sulfones with SeO_2-H_2O_2[a]

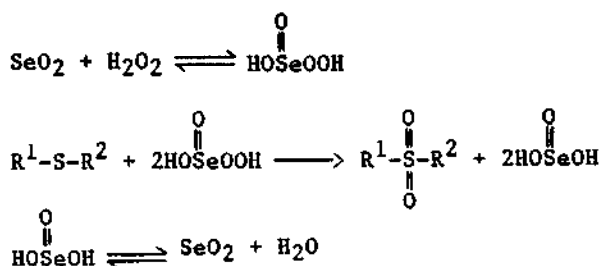| Entry	Sulfide	Product	Yield, %[b,c]
1			70(75)
2			73(76)
3			72(78)
4			80(82)
5			85(88)
6			72

[a]Oxidation completed within 1 hr at room temperature. [b]Isolated yields. [c]Yields in parentheses are isolated ones.

was 75%. The product in organic layer was purified on a silica gel column to afford pure crotyl phenyl sulfone (0.137g,

70%).

Results of the oxidation are summarized in Table 1 and these examples illustrate the chemoselectivity of SeO_2-H_2O_2 system. Entries 1 and 2 illustrate that double bonds are unaffected by this reagent system. No evidence of epoxidation was observed. Superiority of this system is well demonstrated in the oxidation of a hydroxy sulfide (entry 6). Oxidation of the hydroxy sulfide with MCPBA, H_2O_2 and H_2O_2-protic acid or Lewis acid afforded only sulfoxides or decomposition products. $KMnO_4$ and RuO_4 oxidized not only the sulfide group but also the hydroxy group to give a mixture of products.

Trude oxidizing species in SeO_2-H_2O_2 system used in the present work must be peroxyselenous acid (H_2SeO_4) which would be reduced back to H_2SeO_3 and quickly regenerated by H_2O_2 during reaction and thus, a catalytic amount of SeO_2 should be enough for the completion of the reaction. In fact, a catalytic amount of SeO_2 completely oxidized sulfides to sulfones although a little longer reaction time was required. The reason for the discrepancy between the present and Mikolajczyk's results is not clear but the present results clearly indicate that SeO_2-H_2O_2 system is the stronger oxidizing agent than H_2O_2 and a lot more chemoselective than $KMnO_4$ or RuO_4.

$$SeO_2 + H_2O_2 \rightleftharpoons HO\overset{\overset{O}{\|}}{Se}OOH$$

$$R^1-S-R^2 + 2HO\overset{\overset{O}{\|}}{Se}OOH \longrightarrow R^1-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-R^2 + 2HO\overset{\overset{O}{\|}}{Se}OH$$

$$HO\overset{\overset{O}{\|}}{Se}OH \rightleftharpoons SeO_2 + H_2O$$

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