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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### STUDY OF THE MECHANISM FOR THE REARRANGEMENT OF THIOLSULFINATE WITH ACETIC ANHYDRIDE BY $^{13}\text{C}$ AND $^{18}\text{O}$ -TRACER EXPERIMENTS

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$$\begin{array}{c}
 \text{PhCH}_2\underset{\downarrow \text{O}}{\text{SS}}\text{CH}_2\text{Ph} + \text{Ac}_2\text{O} \xrightleftharpoons[60^\circ\text{C}]{\text{AcOH}} [\text{PhCH}_2\overset{\text{OAc}}{\underset{|}{\text{S}}} - \text{S} - \underset{\text{H}}{\underset{|}{\text{CH}}}\text{Ph}] \longrightarrow \text{PhCH}_2\overset{\text{+}}{\underset{\text{OAc}}{\underset{|}{\text{S}}}} - \text{S} - \underset{\ominus}{\text{CH}}\text{Ph} \\
 (\text{I}) \\
 \longrightarrow \text{PhCH}_2\overset{\text{O}}{\underset{\downarrow}{\text{S}}} - \underset{\text{SAc}}{\underset{|}{\text{CH}}}\text{Ph} + \text{Recovered-(1)} \qquad \qquad \qquad (1) \\
 (\text{II})
 \end{array}$$

In order to shed further light in understanding the mechanism of this reaction, we have carried out a  $^{13}\text{C}$  tracer experiment using  $^{13}\text{C}$ -labeled compound(I). The results revealed that the amount of  $^{13}\text{C}$  in both the sulfoxide and the recovered thiolsulfinate(I) decreased down to 76% and 62% respectively at 60% conversion of the reaction. Furthermore, when the reaction was carried out in the presence of 10 molar excess of methyl acrylate, the product obtained was methyl-3-(1-phenylmethanesulfinyl)propionate in 83% yield. Thus, these results suggest strongly that the initial formation of the sulfenyl acid via the pyrolytic decomposition of the thiolsulfinate.