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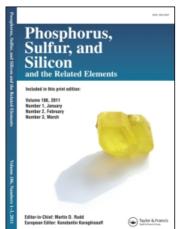
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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Furukawa, Naomichi , Morishita, Tsuyoshi , Akasaka, Takeshi and Oae, Shigeru(1979) 'STUDY OF THE MECHANISM FOR THE REARRANGEMENT OF THIOLSULFINATE WITH ACETIC ANHYDRIDE BY ¹³C AND ¹⁸O-TRACER EXPERIMENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 99

To link to this Article: DOI: 10.1080/03086647908080323 URL: http://dx.doi.org/10.1080/03086647908080323

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

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Recently, we found that benzyl phenylmethanethiolsulfinate(I) reacts with acetic anhydride at 60°C to afford the rearranged sulfoxide, i.e., an almost 1:1 mixture of both erythro and threo-1-(acetoxylthio)benzyl benzyl sulfoxides(II) in a substantial yield.

PhCH₂SSCH₂Ph + Ac₂O
$$\stackrel{60 \text{°C}}{\longrightarrow}$$
 [PhCH₂S-S-CHPh $\stackrel{+}{\longrightarrow}$ PhCH₂S-S-CHPh $\stackrel{-}{\longrightarrow}$ OAc

(I)

PhCH₂S-CHPh + Recovered-(1)

O SAc

(II)

Based on the deuterium tracer experiment, the mechanism of this rearrangement was proposed to proceed via the initial equilibrium formation of the intermediate(A) or (B) by acetylation of (I) with acetic anhydride, followed by the subsequent proton-removal from the sulfenyl carbon by acetate, like in the Pummerer or the Wittig rearrangement, eventually affording (II) as shown in eq-(1). In order to shed further light in understanding the mechanism of this reaction, we have carried out a ¹³C tracer experiment using 13 C-labeled compound(I). The results revealed that the amount of ¹³C in both the sulfoxide and the recovered thiolsulfinate(I) decreased down to 76% and 62% respectively at 60% conversion of Furthermore, when the reaction was carried out in the presence of 10 molar excess of methyl acrylate, the product obtained was methy1-3-(1-phenylmethanesulfiny1)propionate in 83% Thus, these results suggest strongly that the initial formation of the sulfenyl acid via the pyrolytic decomposition of the thiolsulfinate.