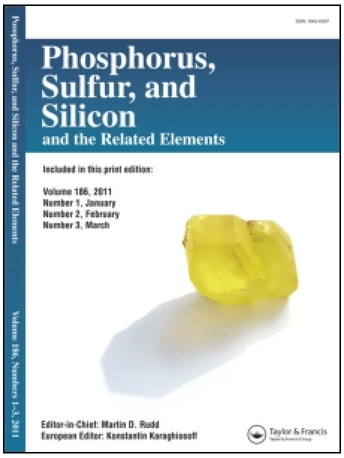

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STUDY OF THE MECHANISM FOR THE REARRANGEMENT OF THIOLSULFINATE WITH ACETIC ANHYDRIDE BY ^{13}C AND ^{18}O-TRACER EXPERIMENTS

Naomichi Furukawa[a]; Tsuyoshi Morishita[a]; Takeshi Akasaka[a]; Shigeru Oae[a]
[a] Department of Chemistry, Tsukuba University, Ibaraki, Japan

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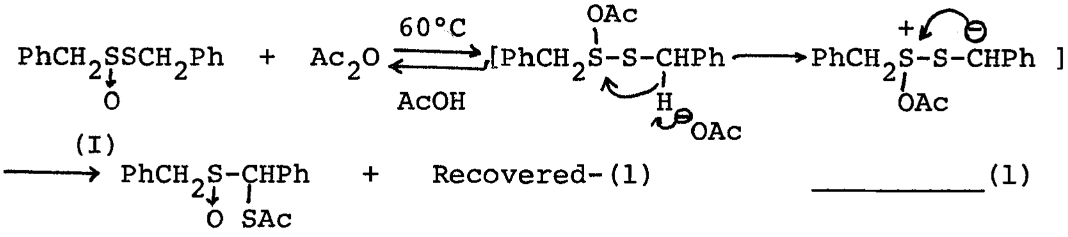
STUDY OF THE MECHANISM FOR THE REARRANGEMENT OF THIOLSULFINATE WITH ACETIC ANHYDRIDE BY ^{13}C and ^{18}O-TRACER EXPERIMENTS

Naomichi Furukawa, Tsuyoshi Morishita, Takeshi Akasaka and Shigeru Oae
Department of Chemistry, Tsukuba University, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan

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.



(I)

(II)

(1)

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 ^{13}C tracer experiment using ^{13}C-labeled compound(I). The results revealed that the amount of ^{13}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.