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Study of the Mechanism for the Rearrangement of Thiolsulfinate with Acetic Anhydride by ^{13}C- and ^{18}O-Tracer Experiments

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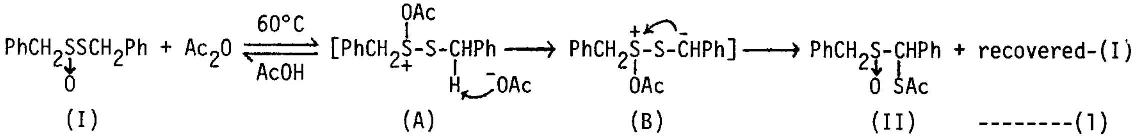
Recently, we found that benzyl phenylmethanethiolsulfinate (I) reacts with acetic anhydride at 60°C to afford the rearranged sulfoxide, i.e., an almost 1:1 mixture of both erythro and threo 1-(thioacetoxy)benzyl benzyl sulfoxides (II) in a substantial yield.[1)]



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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).

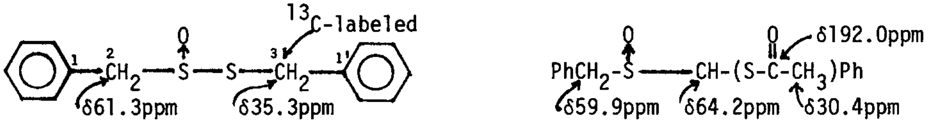
In this paper we wish to report the refined, somewhat revised mechanism for this rearrangement, based on our additional ^{13}C- and ^{18}O-tracer experiments and detailed product analyses.

Recently, Block and his coworkers proposed an interesting mechanism of the pyrolysis of some alkyl thiolsulfinate, which involves the initial formation of the sulfenic acid and thioaldehyde.[2)] Our reaction appears to be quite similar to that of Block's Ei reaction though the products are quite different from those of the Block's. A big question is whether the reaction proceeds via an intramolecular process like Eq-(1) or through some other intermolecular process involving carbon-skeletal migration as suggested by Block.

In order to shed further light in understanding the mechanism of this reaction,[3)] we have carried out a ^{13}C tracer experiment using ^{13}C-labeled compound (I) which was prepared starting from $Ba^{13}CO_3$ enriched with 90% ^{13}C.

Before starting the reaction, the ^{13}C-labeled-(I) was diluted with non-labeled-(I) down to around 30-50% ^{13}C enrichment and this diluted compound was treated with Ac_2O-AcOH for 1-2 h. After the reaction, the rearranged sulfoxide (II)$^{4)}$ and the recovered-(I) were separated by column chromatography and the position and the content of ^{13}C of the starting-(I), the recovered-(I) and II were determined by ^{13}C-nmr or ^{1}H-nmr due to ^{13}C satelite method.$^{5)}$ Major chemical shifts of the ^{13}C in both I and II are summarized in Scheme I.

Scheme I. (Chemical shifts were measured in $CDCl_3$ using TMS as an internal standard).



(C-1 or C-1'; δ136.1ppm) (I) (II)

The contents of ^{13}C were determined by comparing their relative intensities (peak hights or areas) of the respective carbon atoms in both compounds having natural abundance with those of the ^{13}C enriched compounds$^{6)}$: for example in the case of I, the peak at δ136.1ppm (C-1 or C-1') was taken as the standard and its peak hight was compared with that of C-2 (δ61.3ppm) and C-3 (δ35.3ppm). The results obtained are summarized in the Table.

Table. The Contents of ^{13}C of the Thiolsulfinate (I) and Sulfoxide (II).$^{a)}$

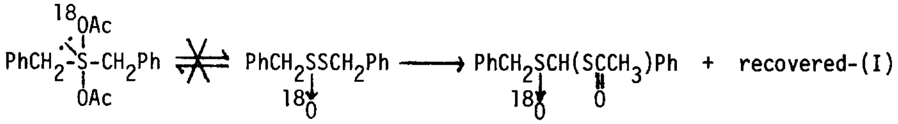
React.time	Starting (I)		Product (II)		Recovered (I)	
(h)	Sulfenyl	Sulfinyl	Methine	Methylene	Sulfenyl	Sulfinyl
2	32.0(100)	-0.04	24.5(76)	-0.24	19.8(62)	0.33
$2^{b)}$	55.0(100)	-	43.0(78)	-	27.0(50)	-
$1^{b)}$	55.0(100)	-	53.0(96)	-	45.0(82)	-
$2^{c)}$	85.0(100)	-	64.0(75)	-	75.0(88)	-

a) The error should be less than ± 5%. b) ^{1}H-nmr method. c) D-experiment.

These results revealed that the amount of ^{13}C in both the sulfoxide (II) and the recovered-(I) decreased down to 76% and 62% respectively at 60% conversion of the reaction. However, when the reaction was stopped after 1 h which corresponds to 40% conversion, the amounts of ^{13}C found in the sulfoxide (II) was 96% while that of the recovered-(I) was 82%. These observations indicate clearly that there is a definite carbon scrambling during the reaction and the reaction cannot be explained by the simple H-D exchange as suggested in Eq-(1). Furthermore, ^{13}C was found solely in the sulfenyl side or the methine position of the sulfoxide (II) and the recovered-(I) respectively but not in the sulfinyl side within experimental error, thus, indicating explicitly that the oxygen migration from sulfinyl sulfur to sulfenyl sulfur does not take place during the reaction. Meanwhile, the contents of D of both the compound (I) and (II) were found to have decreased as the decrease of the ^{13}C, however, the trend of the decrease is different from that of ^{13}C. Apparently, there is a large kinetic isotope effect at the initial H-abstraction which kept D-atoms preferentially in the compound (I).

In order to understand the mechanism further, we have carried out the following reaction. When the reaction was carried out at the normal condition (Ac_2O-AcOH at 60°C) in the presence of 10 molar excess of methyl acrylate, the product obtained was methyl-3-(1-phenylmethanesulfinyl)-propionate in 83% yield. This indicates clearly the incipient formation of the sulfenic acid which is trapped by the electrophilic olefin to afford the addition compound as in the pyrolysis of the sulfoxide$^{7)}$ or the thiolsulfinate.$^{8)}$

Furthermore, in order to see the fate of sulfinyl oxygen, ^{18}O-labeled-(I) was prepared and treated under the similar reaction condition as described above. The results obtained are shown below. According to the results, the contents of ^{18}O of both the sulfoxide (II) and the recovered-(I) did not change within experimental error, thus, indicating clearly that ^{18}O exchange involving the initial O-acylation followed by the sulfurane-like intermediate (C) did not take place during the reaction unlike the Pummerer reaction of sulfoxide$^{9)}$ or the ^{18}O exchange of sulfinate with trichloroacetic anhydride.$^{10)}$



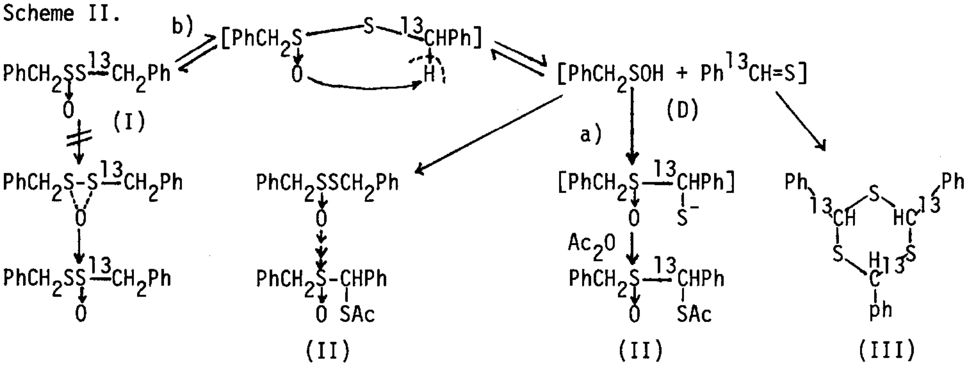
$$PhCH_2\overset{^{18}OAc}{\underset{OAc}{S}}{-}CH_2Ph \not\rightleftharpoons PhCH_2\underset{^{18}O}{S}SCH_2Ph \longrightarrow PhCH_2\underset{^{18}O}{S}CH(S\underset{O}{C}CH_3)Ph + \text{recovered-(I)}$$

(C) (I) 0.833 atom%(100%) (II) 0.856(102.8) 0.855(102.6)

Thus, both the tracer experiments and the product analysis suggest strongly the initial formation of the sulfenic acid as an unstable intermediate which reacts further with another sulfenic acid molecule to result in the decrease of the ^{13}C in the recovered-(I) as suggested by others.$^{11)}$ Therefore, the ^{13}C enriched thiolsulfinate would be diluted continuously during the reaction and hence the content of ^{13}C of the sulfoxide (II) decreases gradually during the prolonged reaction time.

Thereofore, the most likely mechanism for this rearrangement is shown in the following Scheme II: namely, the initial step is the Ei process just like the simple pyrolysis of I, affording α-toluenesulfenic acid and thiobenzaldehyde, probably in the cage of acetic anhydride. The sulfenic acid and thiobenzaldehyde once formed then react mainly to afford the rearranged sulfoxide (II) (process-a) or to return to the original thiolsulfinate (process-b). Meanwhile, some of the sulfenic acid and thiobenzaldehyde may escape from the cage and disproportionate or trimerize to the starting compound (I) or the trithiane (III). The initial step is undoubtedly an equilibrium between I and the intermediate (D) in view of the fact that when the reaction was carried out in the presence of D_2O, the recovered-(I) was found to have taken up 20% D in its sulfenyl side at 26% conversion of the reaction. Consequently the mechanism of the whole process may be illustrated by Scheme II.

Scheme II.



References and Footnotes

1) N.Furukawa, T.Morishita, T.Akasaka, and S.Oae, Tetrahedron Lett., 1977, 1653.
Similar p-tolylmethyl p-tolylmethanethiolsulfinate, p-tolylmethyl phenylmethanethiolsulfinate afforded the rearranged sulfoxides with Ac_2O. However, it was very hard to separate the isomers.

2) E.Block and J.O'Connor, J.Am.Chem.Soc., 96, 3929 (1974).

3) In order to clarify this point, one of the best way is the cross-over experiment. We tried the reaction by using 1:1 mixture of benzyl phenylmethanethiolsulfinate and p-methyl substituted thiolsulfinate. After the reaction, however, it was hard to separate the mixed isomers by preparative thin layer or high speed liquid chromatography.

4) Both erythro and threo isomers were obtained. For ^{13}C-measurement one isomer having m.p. 85.0-86.0°C was separated and subjected to the analysis.

5) The coupling constants of ^{13}C-^{1}H is large and therefore it is possible to measure the content of ^{13}C by ^{1}H-nmr.

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8) E.Block, J.Am.Chem.Soc., 94, 642 (1972).

9) S.Oae and M.Kise, Tetrahedron Lett., 1967, 1409.

10) J.Drabowicz and S.Oae, Tetrahedron, 34, 63 (1978).

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