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STEREOSELECTIVE PUMMERER REARRANGEMENT OF PHENYLSULFINYLCYCLOPROPANES WITH ACETIC ANHYDRIDE(1)

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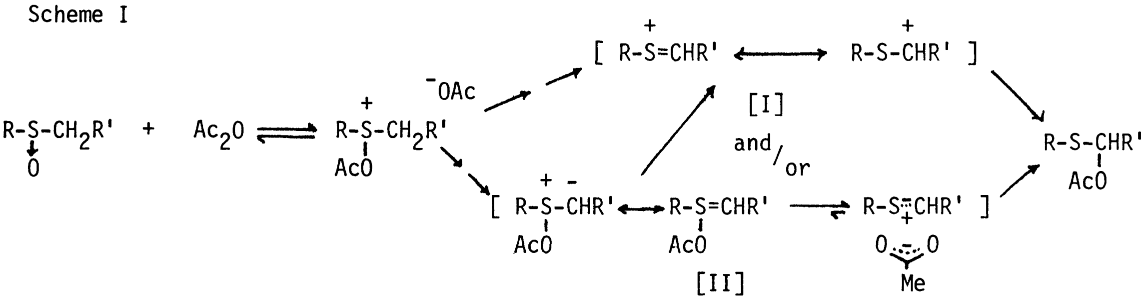
The Pummerer reaction of cis- and trans-2-phenyl-1-(phenylsulfinyl)cyclopropanes and cis, syn- and cis, anti-2,3-dimethyl-1-(phenylsulfinyl)cyclopropanes afforded the stereoselective products.

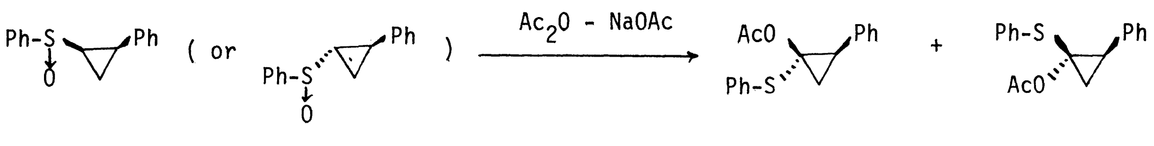
Numerous works concerning the Pummerer rearrangement have been reported(2) and the mechanism for the rearrangement is considered to proceed via either a carbonium ion [I] or an ylide - ylene [II] after the α-proton removal as shown below (Scheme I).

Scheme I

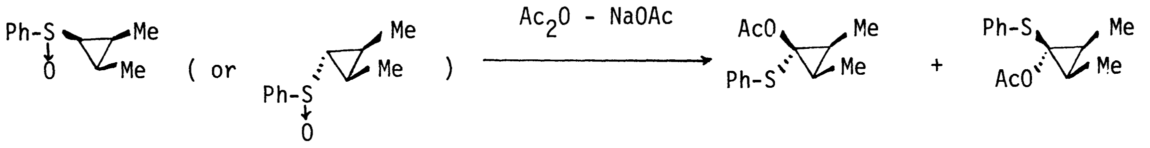


Earlier it was suggested that the rearrangement involves a carbonium ion [I]. Recently however, we found that the Pummerer reaction of phenylsulfinylcyclopropanes or (phenylsulfinylmethyl)-cyclopropane with acetic anhydride afforded 1-acetoxy-1-(phenylthio)cyclopropanes or (α-acetoxyphenylthiomethyl)cyclopropane in high yields but no ring opening product, which is expected to be formed, if the reaction would involve a carbonium ion.(1) Meanwhile the methanolyses(3) and acetolyses of 1-chloro-1-phenylthiocyclopropanes afforded both the corresponding acetoxy-cyclopropanes and ring opening allylic products.(1) In view of the difference in product distribution between the solvolyses and the Pummerer reaction of cyclopropyl compounds, we suggested that the Pummerer rearrangement does not proceed via a carbonium ion [I] but via an ylide - ylene - ion pair [II]. Recent work of Kay et al. on the Pummerer reaction of 1,3-oxathiolan-5-one S-oxides,(4) that of optically active o-benzylsulfinylbenzoic acid by Allenmark et al.(5) and our work of optically active 4-(cyanomethylsulfinyl)toluene with acetic anhydride to give partially optically active α-acetoxysulfide on α-carbon atom(6) also seem to suggest the ylide - ion pair process and clearly rule out the carbonium ion process. In order to seek further evidence to support the ylide - ylene - ion pair mechanism, we prepared cis- and trans-2-phenyl-1-(phenylsulfinyl)cyclopropanes,(**1a**) and (**1b**), and cis, syn- and cis, anti-2,3-dimethyl-1-(phenylsulfinyl)cyclopropanes,(**1c**) and (**1d**), and sujected them to the Pummerer reactions with acetic anhydride containing anhydrous sodium acetate. We found that the Pummerer

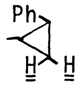
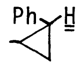
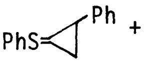
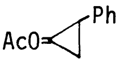
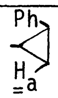
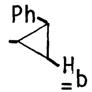
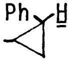
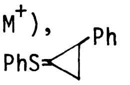
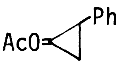
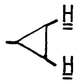
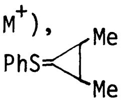
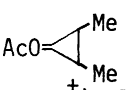
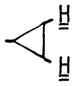
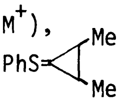
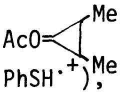
Table I. Reaction of Phenylsulfinylcyclopropanes, (**1a-d**), with Acetic Anhydride containing Anhydrous Sodium Acetate at 170°C for 3 h



(**1a**) (**1b**) (**2a**) (**2b**)



(**1c**) (**1d**) (**2c**) (**2d**)

Sulfoxides	Products and Yields(%), (ratio)	IR Spectra (cm^{-1})	100 MHz NMR Spectra($CDCl_3$) (δ-ppm), (J cps)	MASS Spectra($^m/_e$),
(**1a**)	(**2a**) + (**2b**), 84 (69 : 31)	1760 1230 1140	1.50-1.88(m)() and 1.78(s) and 2.05(s)(CH_3CO_2-) 5H, 2.64-2.88(q)1H(), 6.96-7.50(m)10H(Ph-, PhS-)	284(M$^+$), 225(PhS$^+$), 175(AcO$^+$), 110(PhSH$^{\cdot +}$), 109 (PhS$^+$), 43(Ac$^+$)
(**1b**)	(**2b**) only, 88	1760 1230 1140	1.59(q)1H(), J_{ax} = 8.86 J_{bx} = 9.93 1.89(q)1H(),J_{ab} = 7.18 2.05(s)3H(CH_3CO_2-), 2.75(q)1H(), 6.92-7.60(m)10H(Ph-, PhS-)	284(M$^+$), 225(PhS$^+$), 175(AcO$^+$), 110(PhSH$^{\cdot +}$), 109(PhS$^+$), 43(Ac$^+$)
(**1c**)	(**2c**) + (**2d**), 92 (76 : 24)	1750 1220 1150	0.80-1.12(m)6H(), 1.36-1.60 (m)2H(), 2.00(s) and 2.08(s) 3H(CH_3CO_2-), 7.0-7.6(m)5H(PhS-)	236(M$^+$), 177(PhS$^+$), 127(AcO$^+$), 110(PhSH$^{\cdot +}$), 109 (PhS$^+$), 43(Ac$^+$)
(**1d**)	(**2d**) only, 93	1750 1220 1150	0.96-1.10(m)6H(), 1.40-1.66 (m)2H(), 2.00(s)3H(CH_3CO_2-) 7.0-7.5(m)5H(PhS-)	236(M$^+$), 177(PhS$^+$), 127(AcO$^+$), 110(PhSH$^{\cdot +}$), 109(PhS$^+$), 43(Ac$^+$)

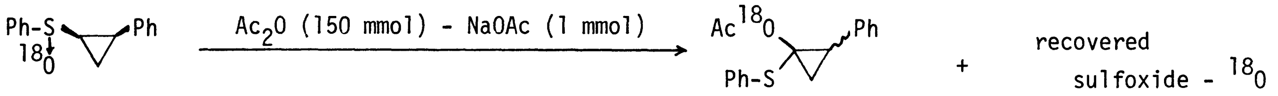
reactions of these compounds proceeded stereoselectively affording the rearranged products, (2a-d), in high yields, and hence we wish to describe these stereochemical results of the Pummerer reaction of (1a-d),together with some ^{18}O tracer experiments and discuss briefly the reaction mechanism involving an ylide - ylene - ion pair.

The Pummerer reactions of (1a-d)$^{7)}$ were carried out at 170 °C for 3 h. The products, their yields thus obtained, their IR, NMR, and MASS spectra are shown in Table I.

The remarkable feature of the reaction is that the Pummerer rearrangement of the trans- or cis, anti-cyclopropyl sulfoxide ((1b) or (1d)) afforded (2b) or (2d) as the sole product. The structure of (2b) or (2d) was confirmed by its IR, NMR, and MASS spectra(see Table I). Meanwhile, from the reaction of sterically crowded cis- or cis, syn-cyclopropyl sulfoxide ((1a) or (1c)), a mixture of two stereoisomers ((2a) and (2b) or (2c) and (2d)) was obtained with ratio of 69 : 31 or 76 : 24, respectively. These products were not isomerized at the reaction conditions employed. These observations indicate that the acetate anions attack predominantly the α-carbon from the back side of the proton removed. The compound (1a) or (1c) is thermodynamically much less stable than the corresponding trans- or cis, anti-counter part (1b) or (1d) due to the steric repulsion of the substituents.$^{7-c,d)}$ Therefore, in the case of (1a) or (1c), after the initial proton removal partial isomerization of the resulting carbanion to (1b) or (1d) would take place besides the Pummerer reaction to give stereoselective products.

In order to examine whether the rearrangement is either intra- or intermolecular, cis-2-phenyl-1-(phenylsulfinyl)cyclopropane labeled with ^{18}O was prepared$^{8)}$ and subjected to the reaction. The reaction was stopped at 40 % conversion of the sulfoxide and then ^{18}O analyses of both the product and the recovered sulfoxide were carried out as usual. The results of ^{18}O analyses are shown below(Scheme II).

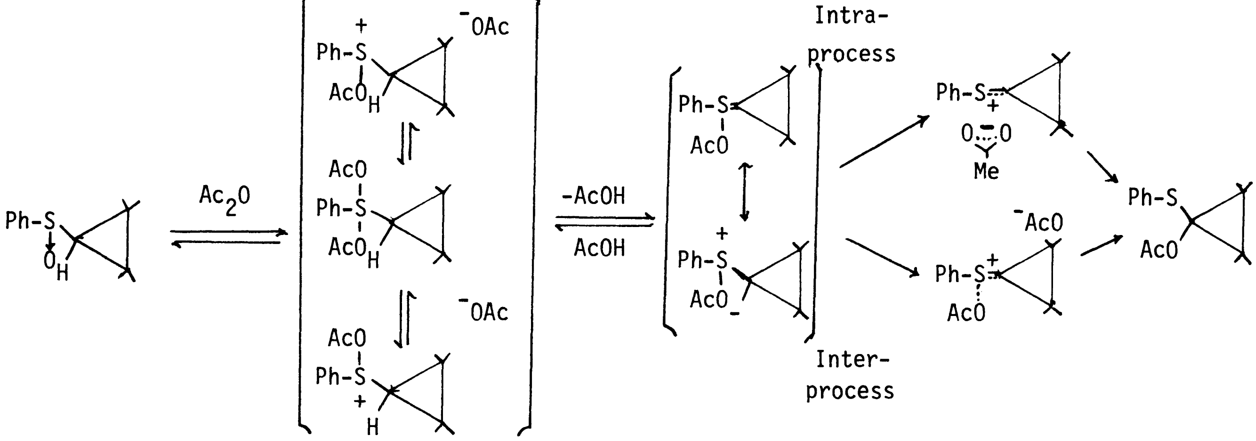
Scheme II



(4 mmol)		
Excess atom	Excess atom	Excess atom
1.04	0.05 (9.6 %)	0.21 (20.2 %)

The large loss of ^{18}O in the recovered sulfoxide revealed that the S_N2 type ^{18}O-exchanged reaction on sulfur atom$^{9)}$ occurs faster than the Pummerer reaction and obscured the detailed nature of the rearrangement. Yet the acetate retained a significant amount(nearly 10 % out of 20 % ^{18}O of the recovered sulfoxide) of ^{18}O from the sulfoxide. Thus both stereochemical and ^{18}O experiments suggest clearly that the Pummerer reaction of phenylsulfinylcyclopropanes with acetic anhydride proceeds via an ylide - ylene - ion pair [II] but not via a free carbonium ion [I] as shown below(Scheme III).

Scheme III



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REFERENCES AND NOTES

1) Part II : preceding paper T. Masuda, T. Numata, N. Furukawa, and S. Oae, Chem. Lett., 1977, in press.

2) a) C. R. Johnson and W. G. Phillips, J. Am. Chem. Soc., 91, 682 (1970).
   b) T. Durst, Adv. Org. Chem., 6, 285 (1969), and references cited therein.

3) U. Schöllkopf, E. Ruban, P. Tonne, and K. Riedel, Tetrahedron Lett., 5077 (1970).

4) S. Glue, I. T. Kay, and M. R. Kipps, J. Chem. Soc., Chem. Commun., 1158 (1970).

5) B. Stridsberg and S. Allenmark, Acta Chem. Scand., B 28, 591 (1974), ibid., B 30, 219 (1976).

6) T. Numata and S. Oae, Tetrahedron Lett., 1337 (1977).

7) a) cis- and trans-2-Phenyl-1-(phenylthio)cyclopropanes$^{7-b)}$ or cis, syn- and cis, anti-2,3-dimethyl-1-(phenylthio)cyclopropanes$^{10)}$ were separated by column packed with silica-gel and then phenylsulfinylcyclopropanes,(1a-d), were obtained by usual oxidation (H_2O_2 - AcOH) of the corresponding sulfides.
   b) cis-2-Phenyl-1-(phenylthio)cyclopropane synthesized according to the method of Truce et al.$^{11)}$ was also contained about 2 -3 % of trans-isomer(from GLC (chemi-column OV-101, 20 m)).
   c) trans- or cis, anti-Sulfoxides, (1b) or (1d), was also prepared by isomerization of cis- or cis, syn-sulfoxide, (1a) or (1c), with potassium t-butoxide in t-butanol under reflux for 12 h.
   d) Schöllkopf et al.$^{3)}$ reported that in the methanolyses of cis,syn- and cis, anti-1-chloro-2,3-dimethyl-1-(phenylthio)cyclopropanes the cyclopropyl product was only cis, anti-2,3-dimethyl-1-methoxy-1-(phenylthio)cyclopropane.

8) a) S. Oae and S. Kawamura, Bull. Chem. Soc. Jpn., 36, 164 (1963).
   b) R. J. Gritter and D. J. Carey, J. Org. Chem., 29, 1160 (1964).

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

10) U. Schöllkopf, G. J. Lehmann, J. Paust, and H. D. Härtl, Chem. Ber., 97, 1527 (1964).

11) W. E. Truce and V. V. Badiger, J. Org. Chem., 29, 3277 (1964).

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