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NON-CARBONIUM ION CHARACTER OF THE INTERMEDIATE IN THE PUMMERER REACTION OF PHENYLSULFINYLCYCLOPROPANES AND (PHENYLSULFINYLMETHYL)CYCLOPROPANE WITH ACETIC ANHYDRIDE

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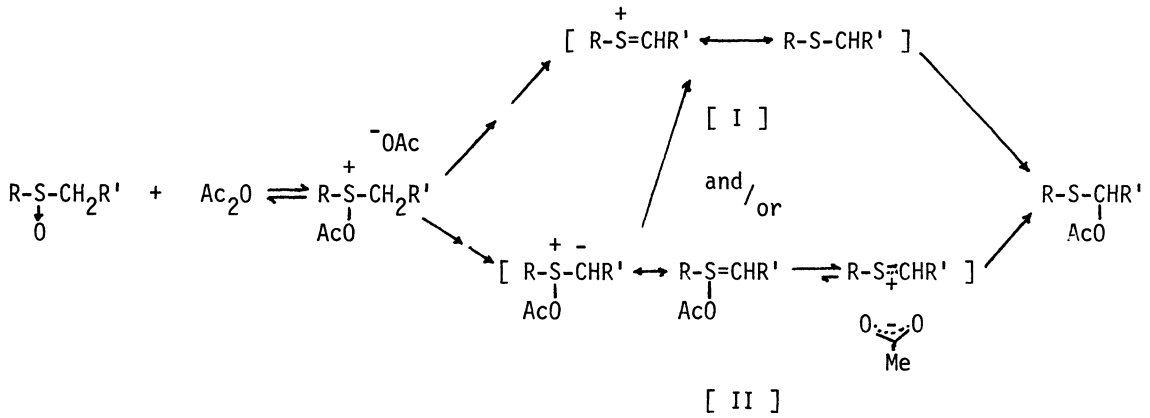
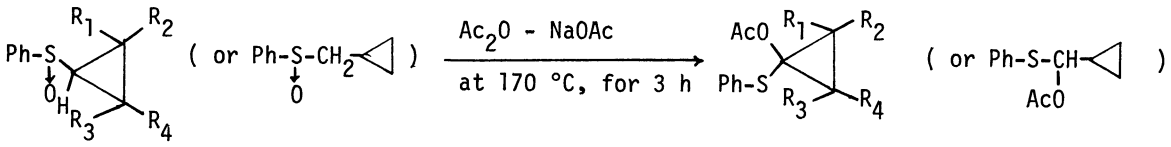
The Pummerer reaction of phenylsulfinylcyclopropanes and (phenylsulfinylmethyl)-cyclopropane with acetic anhydride afforded 1-acetoxy-1-(phenylmercapto)-cyclopropanes and (α-acetoxyphenylmercaptomethyl)cyclopropane in high yields unlike in the acetolysis of 1-chloro-1-(phenylmercapto)cyclopropanes. Thus, the Pummerer reaction is considered to proceed via an ylide - ylene - ion pair.

Numerous investigations on the Pummerer rearrangements of sulfoxides with acid anhydride have been carried out and the general scheme of the rearrangements seems to involve the initial formation of acetoxy sulfonium ion as illustrated below.[1)]



One of the remaining questions is whether the actual intermediate after the proton - removal is a carbonium ion stabilized by the sulfur's lone pair electron [I] or an intermediate having an ylide - ylene like structure [II]. If the reaction would proceed via [I], which involves the carbonium ion that would be obtained by the solvolysis of α-halosulfides, the resulting products should be non-stereoselective.[2)] Recently, Kay et al.[3)] and Allenmark et al.[4)] investigated the stereochemistry of the Pummerer reactions and found that the Pummerer rearrangement of 1,3-oxathiolan-5-one S-oxides or optically active o-benzylsulfinylbenzoic acid gives the product, in which stereoselectivity is observed around α-carbon attached to the sulfur atom. Based on these observations, they proposed that the reactions proceed via the ylide - ion pair intermediate [II] but not the free carbonium ion [I]. Our recent work on the Pummerer reaction of optically

Table I. Reactions of Phenylsulfinylcyclopropanes, (1)a-d, and (Phenylsulfinylmethyl)cyclopropane, (3), with Acetic Anhydride containing Sodium Acetate at 170 °C for 3 h



(1)a-d (3) (2)a-d (4)

Starting Sulfoxides (1)a-d and (3) R_1 R_2 R_3 R_4	Products, (2)a-d and (4) Yields(%)	IR Spectra (cm^{-1})	NMR Spectra ($CDCl_3$) (δ-ppm)	MASS Spectra ($^m/_e$)
(1)a H H H H	(2)a 95	1770 1240 1160	1.38(m)4H( ) 2.10(s)3H(CH_3CO_2-) 7.3-7.7(m)5H(Ph-S-)	208(M^+), 149(PhS- $^+$), 110($PhSH^{\cdot+}$), 109(PhS^+), 99(AcO- $^+$), 43(Ac^+)
(1)b Me H H Me	(2)b 90	1760 1220 1150	0.9-1.5(m)8H( ) 1.91(s)3H(CH_3CO_2-) 7.0-7.5(m)5H(Ph-S-)	236(M^+), 127(AcO- $^+$), 110($PhSH^{\cdot+}$), 109(PhS^+), 43(Ac^+)
(1)c Me Me H H	(2)c 92	1750 1230 1110	1.05(d)2H( ) 1.21(s)3H and 1.31(s)3H (and) 2.05(s)3H(CH_3CO_2-) 7.1-7.5(m)5H(Ph-S-)	236(M^+), 127(AcO- $^+$), 110($PhSH^{\cdot+}$), 109(PhS^+), 43(Ac^+)
(1)d H Me H Me	(2)d 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(Ph-S-)	236(M^+), 127(AcO- $^+$), 110($PhSH^{\cdot+}$), 109(PhS^+), 43(Ac^+)
(3)	(4) 96	1750 1230	0.45-0.75(m)4H( ) 1.20-1.45(m)1H( ) 1.95(s)3H(CH_3CO_2-) 5.55(d)1H(PhS-CH(OAc)-) 7.0-7.5(m)5H(Ph-S-)	222(M^+), 162(Ph-S-CH- $^{\cdot+}$), 85($^+$), 43(Ac^+)

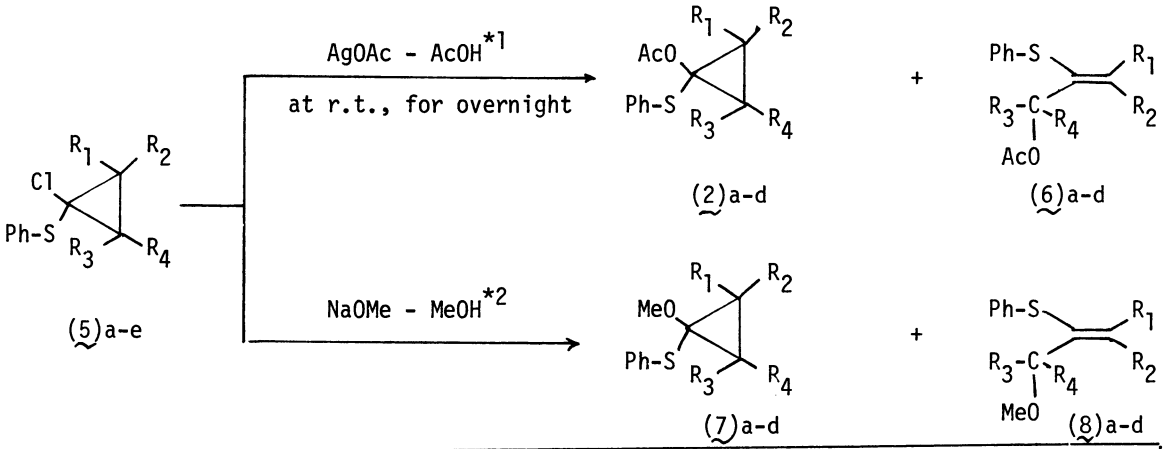
active 4-(cyanomethylsulfinyl)toluene to afford asymmetrically induced α-cyano-p-tolylmercaptomethyl acetate also suggests that the reaction does not proceed via the free carbonium ion [I].[5)]

In order to shed further light on the mechanism of this reaction, we prepared phenylsulfinylcyclopropanes and (phenylsulfunylmethyl)cyclopropane[6)] and subjected them to the Pummerer reaction with acetic anhydride, since both cyclopropyl and cyclopropylmethyl cations are known to lead mainly to ring opening. We found, however, that the Pummerer reactions of these sulfoxides afford non-ring opening products in high yields. This communication describes the results of these experiments and a brief discussion on the intermediate in the reaction.

Generally the reaction was carried out as follow. Phenylsulfinylcyclopropane, (1)a, (5 mmole) was heated with 20 ml of acetic anhydride containing anhydrous sodium acetate (500 mg) at 170 °C for 24 h. The usual workup afforded the product which was purified further by preparative thin layer chromatography. The only product obtained in 95 % yield was 1-acetoxy-1-(phenylmercapto)-cyclopropane (bath temp. 100 °C/ 4×10^{-2} mmHg, by bulb to bulb distillation). The structure of the product was determined by IR, NMR, and MASS spectra. The Pummerer rearrangements of the other sulfoxides, (1)b-d and (3), were carried out at 170 °C for 3 h similarly. The products thus obtained and their spectrum data are shown in Table I.

One of the remarkable features of the reactions is that the reaction gave the non-ring opening products in high yields but no noticeable amount of ring opening products. If the

Table II. Solvolyses of 1-Chloro-1-(phenylmercapto)cyclopropanes, (5)a-e



	R_1	R_2	R_3	R_4	Yields (%) (2)a-d*1		(7)a-d*2		(6)a-d*1		(8)a-d*2	
(5)a	H	H	H	H	(2)a	93			(6)a	-		
(5)b	Me	H	H	Me	(2)b	21	(7)a	72	(6)b	73	(8)a	27
(5)c	Me	Me	H	H	(2)c	trace	(7)b	95	(6)c	89*3	(8)b	5*4
(5)d	H	Me	H	Me	(2)d	trace	(7)c	10	(6)d	93	(8)c	90
(5)e	Me	H	Me	H			(7)d	25			(8)d	70

*1 By us

*2 By Schöllkopf et al.[2)]

*3 A mixture of R_1=Me, R_2=Me, R_3=H, R_4=H and R_1=H, R_2=H, R_3=Me, R_4=Me was obtained with ratio of 35 : 65 from NMR spectra.

*4 A mixture of R_1=Me, R_2=Me, R_3=H, R_4=H and R_1=H, R_2=H, R_3=Me, R_4=Me

rearrangements would proceed via a free carbonium ion like [I], cyclopropane ring should open up at least partially to afford the allylic compounds. Actually when 1-chloro-1-(phenylmercapto)-cyclopropanes, (5)a-d, were subjected to acetolyses with silver acetate in acetic acid, main products obtained were the allylic compounds, (6)b-d, besides cyclopropyl compounds, (2)b-d, except in the case of (5)a. For example, 1-chloro-1-(phenylmercapto)-2,3-trans-dimethyl-cyclopropane, (5)b (2 mmole),was reacted with 2 mole excess of silver acetate at r.t. for overnight in 10 ml of acetic acid. The usual workup afforded the products which were purified further by preparative thin layer chromatography. The acetolyses of the other 1-chloro-1-(phenylmercapto)cyclopropanes, (5)a, c and d, were also carried out similarly. The yields and the structures of the products were determined by GLC, IR, NMR, and MASS spectra. The results on the acetolyses are listed in Table II. Schöllkopf et al.[2] also reported similar results in methanolyses of 1-chloro-1-(phenylmercapto)cyclopropanes, (5)b-e (see Table II).

The cyclopropyl carbonium ions formed by the solvolyses, though substantially stabilized by the adjacent sulfur atom, would be highly strained and hence would give the ring opening products such as (8)c and (8)d. If the Pummerer rearrangement would proceed via the carbonium ion [I] like in the solvolyses, the products should be a composite of both allylic and cyclopropyl compounds. However, this was not the case, and thus, the mechanism of the Pummerer rearrangement of this system is quite different from that of the similar solvolyses. We believe that the Pummerer rearrangement proceeds not via the free carbonium ion such as [I] but via the ylide - ylene - ion pair [II].

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