Stereochemical and Kinetic Studies on the Pummerer Reaction of Arylsulphinylcyclopropanes and Phenylsulphinylmethylcycloalkanes with Acetic Anhydride [1]

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The Pummerer reactions of arylsulphinylcyclopropanes and phenylsulphinylmethylcycloalkanes with acetic anhydride containing anhydrous sodium acetate afforded 1-phenylthio-1-acetoxycyclopropanes and [acetoxy(phenylthio)methyl]cycloalkanes, respectively, in high yields but no ring opening products. The Pummerer reactions of *trans*- and *cis*-1-phenyl-2-phenylsulphinylcyclopropanes and *cis,anti*- and *cis,syn*-1,2-dimethyl-3-(phenylsulphinyl)cyclopropanes gave the corresponding stereoselective products. The pseudo-first-order rate constants for the Pummerer reaction were determined using a large excess of acetic anhydride. A Hammett correlation of the rates with σ values gives a **U** shape curve, whereas the enthalpy and the entropy of activation for the reaction of phenylsulphinylcyclopropane are $\Delta H^{\ddagger}$ 41.3 kcal mol^{-1} and $\Delta S^{\ddagger}$ +10.4 cal mol^{-1} K^{-1}, respectively. Hydrogen–deuterium kinetic isotope effects were found to be rather small (k_H/k_D 1.13, 1.24, and 1.49 for *p*-MeO-H-, and *m*-CF_3-phenylsulphinyl[1-^{2}H]cyclopropanes, respectively). An ^{18}O tracer study indicated that there was marked oxygen exchange during the reaction but the products were found to retain a substantial proportion of the ^{18}O of the original sulphoxides. These observations suggest that the reaction proceeds *via* an ylide–ion pair intermediate, after initial formation of acetoxysulphonium salts.

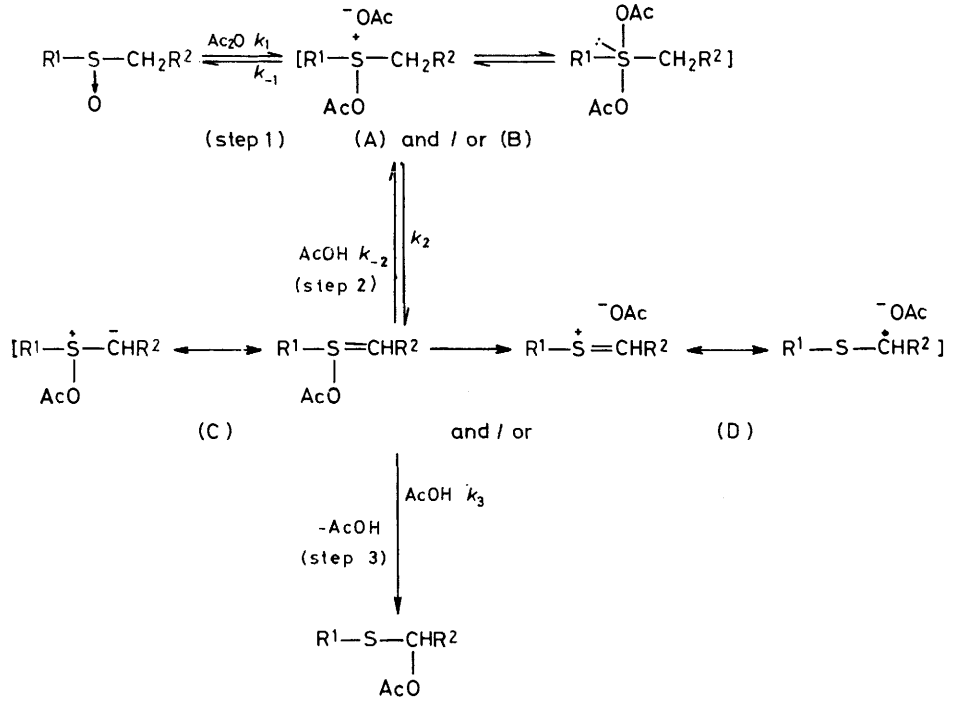
GENERALLY, the Pummerer reaction [2] has been considered to proceed *via* initial formation of a sulphonium salt (A) by acetylation of the sulphinyl oxygen with acetic anhydride (step 1), followed by subsequent proton removal by acetate anion from (A) (step 2), either simultaneous or stepwise cleavage of the S–O bond, and the final recombination of the reaction intermediate (C or D) with acetate anion (step 3) (Scheme 1).

Meanwhile, one important question which remains to be solved is whether the intermediate after proton removal is a carbonium ion stabilized by the sulphur lone

[1] Preliminary reports, T. Masuda, T. Numata, N. Furukawa, and S. Oae, *Chem. Letters*, 1977, 745, 903.

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

pair electrons (D) or an intermediate having an ylide–ion pair like structure (C). Recently, Pummerer reactions leading to stereoselective products [3,4] and involving



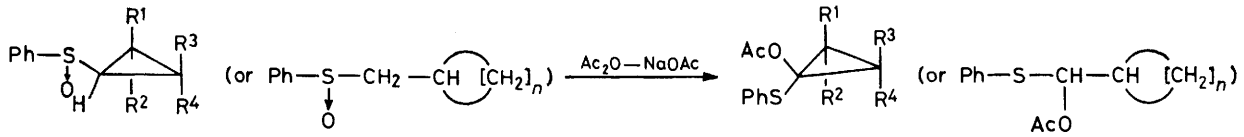
SCHEME 1

asymmetric induction [5] have been reported, suggesting that a carbonium ion like (D) is not involved in the reactions.

In order to elucidate further the mechanism and the stereochemical course of the Pummerer reaction, a number of arylsulphinylcyclopropanes and phenylsulphinylmethylcycloalkanes were prepared and subjected to reaction with acetic anhydride containing anhydrous sodium acetate. This paper presents detailed accounts of the product analyses, results of kinetic and ^{2}H and ^{18}O tracer experiments of the reaction of arylsulphinylcyclopropanes with acetic anhydride, and also their implications in understanding the mechanism of the Pummerer reaction.

TABLE 1

Reaction of phenylsulphinylcyclopropanes (1a—g) and phenylsulphinylmethyl)cycloalkanes (3a and b) with acetic anhydride containing anhydrous sodium acetate at 170 °C for 3 h



	Sulphoxide					Product (%) (ratio)	
	R^1	R^2	R^3	R^4	n		
(1a) *	H	H	H	H		(2a)	95
(1b)	Me	H	H	Me		(2b)	90
(1c)	Me	Me	H	H		(2c)	92
(1d)	H	Ph	H	H		(2d)	88
(1e)	Ph	H	H	H		(2d + e)	84 (31 : 69)
(1f)	H	Me	H	Me		(2f)	93
(1g)	Me	H	Me	H		(2f + g)	92 (24 : 76)
(3a)					2	(4a)	96
(3b)					3	(4b)	84

* This reaction was carried out at 170 °C for 24 h.

RESULTS

The Pummerer reactions of phenylsulphinylcyclopropanes (1) with acetic anhydride containing anhydrous

[3] S. Glue, I. T. Kay, and M. R. Kipps, *Chem. Comm.*, 1970, 1158.

[4] B. Stridsberg and S. Allenmark, *Acta Chem. Scand.* (*a*) 1974, **B28**, 591; (*b*) 1976, **B30**, 219.

[5] T. Numata and S. Oae, *Tetrahedron Letters*, 1977, 1337.

sodium acetate were carried out at 170 °C for 3 h and the products thus obtained are summarized in Table 1.

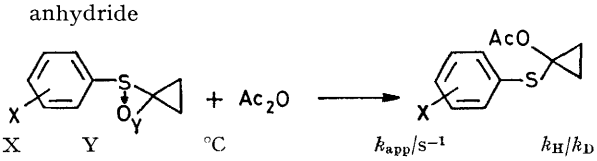
Kinetics and Hammett Correlation.—The rate of the Pummerer reaction of arylsulphinylcyclopropanes with acetic anhydride was followed spectrophotometrically,[6] by measuring the u.v. spectrum of the starting sulphoxide and that of the final compound, *i.e.*, thiophenolate obtained by quenching the reaction mixture with aqueous KOH solution.* The rates were found to be well correlated by the pseudo-first-order kinetic equation (ii) † when a large excess of acetic anhydride was used. The rate constants for the reaction thus obtained are summarized in Table 2. The activation parameters calculated for the reaction of phenylsulphinylcyclopropane with acetic anhydride were $\Delta H^{\ddagger}$ 41.3 kcal mol^{-1} and $\Delta S^{\ddagger}$ +10.4 cal mol^{-1} K^{-1}.

The effects of substituents on the reaction rate were examined for several *para*- and *meta*-substituted arylsulphinylcyclopropanes under similar reaction conditions and the results are also shown in Table 2. The Hammett plot using σ values did not give a straight line but instead a U shaped curve.

Hydrogen–Deuterium Kinetic Isotope Effects.—In order to examine the possibility of proton removal as the rate-determining step, kinetic isotope effects were measured using 1-deuteriated *para*- and *meta*-substituted arylsulphinylcyclopropanes and values of k_H/k_D of 1.13, 1.24, and 1.49 for the *p*-MeO, H, and *m*-CF_3 compounds, respectively, were obtained (see Table 2).

TABLE 2

Rate constants for the reaction of *para*- or *meta*-substituted arylsulphinylcyclopropanes (4 mmol) with acetic anhydride



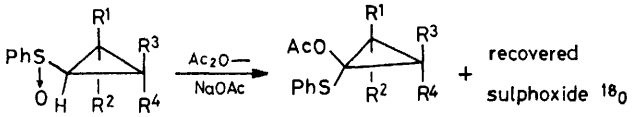
X	Y	°C	k_{app}/s^{-1}	k_H/k_D
H	H	160.00 ± 0.05	2.43 ± 0.10 × 10^{-6}	
H	H	170.00 ± 0.05	6.70 ± 0.22 × 10^{-6}	1.24
H	D	170.00 ± 0.05	5.39 ± 0.08 × 10^{-6}	
H	H	180.00 ± 0.05	2.12 ± 0.17 × 10^{-5}	
p-MeO	H	170.00 ± 0.05	1.06 ± 0.12 × 10^{-3}	1.13
p-MeO	D	170.00 ± 0.05	9.35 ± 0.16 × 10^{-6}	
p-Me	H	170.00 ± 0.05	9.47 ± 0.32 × 10^{-5}	
p-Cl	H	170.00 ± 0.05	8.43 ± 0.55 × 10^{-6}	
m-CF_3	H	170.00 ± 0.05	1.21 ± 0.05 × 10^{-5}	
m-CF_3	D	170.00 ± 0.05	8.13 ± 0.27 × 10^{-6}	1.49

$\Delta H^{\ddagger}$ 41.3 kcal mol^{-1}; $\Delta S^{\ddagger}$ +10.4 cal mol^{-1} K^{-1}; γ 0.999 (at 170 °C)

^{18}O *Tracer Experiments.*—In order to see whether or not acetoxy migration proceeds *via* an intra- or an intermolecular path, ^{18}O tracer experiments on the reactions of ^{18}O-labelled phenylsulphinylcyclopropane and ^{18}O-labelled *cis*-1-phenyl-2-phenylsulphinylcyclopropane with acetic anhydride containing anhydrous sodium acetate were carried out at 170 °C; the reactions were stopped at *ca.* 70 and 40% completion, respectively. In the reaction of ^{18}O-labelled phenylsulphinylcyclopropane, the recovered sulphoxide was found to have lost *ca.* 95% ^{18}O. In the reaction of ^{18}O-labelled *cis*-1-phenyl-2-phenylsulphinylcyclopropane, the recovered sulphoxide was found to have retained *ca.* 20% of ^{18}O while the rearranged 1-acetoxycyclopropyl product thus obtained was found to have retained *ca.* 10% ^{18}O (see Table 3).

TABLE 3

^{18}O tracer experiments for the reaction of ^{18}O-labelled phenylsulphinylcyclopropane and *cis*-1-phenyl-2-phenylsulphinylcyclopropane (4 mmol) with acetic anhydride (150 mmol) containing anhydrous sodium acetate (1 mmol)



Starting sulphoxide							
R^1	R^2	R^3	R^4	^{18}O Excess atom %	Reaction conditions	^{18}O Excess atom % of 1-acetoxy-cyclo-propane	^{18}O Excess atom % of recovered sulphoxide
H	H	H	H	1.21	170 °C; 10 h (*ca.* 70% completion)	0.03 (5.0%)	0.05 (4.1%)
Ph	H	H	H	1.04	170 °C; 1 h (*ca.* 40% completion)	0.05 (9.6%)	0.21 (20.2%)

DISCUSSION

One of the characteristic features of the reaction is that the cyclopropyl derivatives (2) were formed in high yields but no noticeable amount of any ring opening product. This means that a free carbonium ion such as (D) is not formed in the Pummerer reaction, since (D) once formed should open up at least partially affording some ring opening products. Both we [1] and Schöllkopf *et al.*[8] found that the products obtained were the corresponding allylic and cyclopropyl compounds for both acetolysis and methanolysis of 1-chloro-1-phenylthiocyclopropane which gives initially the free carbonium ion, substantially stabilized by the adjacent sulphur atom but highly strained. Thus, the intermediate in the Pummerer reaction should be quite different from that in the solvolyses. The Pummerer reactions of other phenylsulphinylmethylcycloalkanes (3) also afforded the corresponding [acetoxy(phenylthio)methyl]cycloalkanes (4) in high yields (Table 1) but no ring opening product. Here again the reaction does not appear to proceed *via* the free carbonium ion, *i.e.*, cyclopropyl- or cyclobutylmethyl cation,[9] since these cations once formed should open up at least partially to afford ring enlargement or fission products.

* Alkaline hydrolysis of 1-acetoxy-1-phenylthiocyclopropane afforded thiophenolate since the alkaline hydrolysis of 1-chloro-1-phenylthiocyclopropane gave thiophenol and carboxylic acid.[7]

† According to the proposed mechanism shown in Scheme 1, the kinetic equations (i) and (ii) can be derived by the steady-state method. If step 3 is the rate-determining step equation (i) applies and this reduces to (ii) for [Sulphoxide] ≪ [Ac_2O].

$$\text{Rate} = \frac{k_1k_2k_3}{k_1k_{-2} + k_{-1}k_3 + k_2k_3}\,[\text{Sulphoxide}]\,[Ac_2O] \quad \text{(i)}$$

$$\text{Rate} = k_{app}\,[\text{Sulphoxide}] \quad \text{(ii)}$$

[6] S. Oae and M. Kise, *Tetrahedron Letters*, 1968, 2261; *Bull. Chem. Soc. Japan*, 1970, **43**, 1426.

[7] U. Schöllkopf, F. P. Woener, and E. Wiskott, *Chem. Ber.*, 1966, **99**, 806.

[8] U. Schöllkopf, E. Ruban, P. Tonne, and K. Riedel, *Chem. Ber.*, 1970, 5077.

[9] (*a*) J. D. Roberts and V. C. Chembers, *J. Amer. Chem. Soc.*, 1951, **73**, 5034; (*b*) A. Streitwieser, jun., *Chem. Rev.*, 1956, **56**, 571.

Another marked feature of the reaction was that the Pummerer reaction of (1d or f) afforded only (2d or f) quantitatively.* The product, (2d)† or (2f), shows one singlet for the $MeCO_2$ group at δ 2.05 or 2.00 in the n.m.r. spectra. On the other hand, the reaction of sterically crowded (1e or g) gave a mixture of two stereoisomers (2d and e) or (2f and g). The product mixture, (2d and e) or (2f and g), shows two distinguishable singlets for the $MeCO_2$ group at δ 2.05 and 1.78 ‡ or 2.00 and 2.08 in the n.m.r. spectra. The ratio (2d) : (2e) or (2f) : (2g), calculated from the ratio of the peak areas of the $MeCO_2$ signals, was 31 : 69 or 24 : 76. Thus, in the reactions of (1e and g), (2e and g) were the preferred products over (2d and f). These results reveal clearly that acetate anion attacks the α-carbon predominantly from the back side of the proton removed. The derivative (1e or g) is thermodynamically much less stable than the corresponding (1d or f) due to steric repulsion of the substituents.§ Therefore, in the case of (1e or g), after the initial proton removal, partial isomerization of the resulting carbanion to (1d or f) takes place besides the normal Pummerer reaction which should afford stereoselective products. Thus, although the stereoselectivity is not 100% in each case, the reaction may be described as proceeding *via* a stereoselective route.

Kinetic measurements were carried out and the results obtained with various substituted cyclopropyl derivatives under various conditions are compared with those of previous studies.[14] The results are summarized in Table 4.

TABLE 4

Kinetic data for Pummerer reactions

Reaction	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal mol^{-1} K^{-1}	k_H/k_D	ρ Value	k (at 120 °C) (k_{rel})
p-$CH_3C_6H_4S(O)CH_3$ + Ac_2O[6]	21.2	−20.7	2.9	−1.60	1.77×10^{-4} (1)
o-HO_2C–$C_6H_4S(O)CH_3$ + Ac_2O[14a]	21.6	−11.3	1.07		2.45×10^{-2} (138)
$C_6H_5\overset{+}{S}\overset{-}{C}(CO_2CH_3)_2CH_3$ + Ac_2O[14b]	21.3	−22.2	1.57	−0.76	8.35×10^{-5} (0.47)
$CH_3S(O)CH_3$ + $(C_6H_5CO)_2O$[14c]	14.2	−10.2	1.21	+1.40	6.88×10^{2} (3.89×10^{6})
$C_6H_5\overset{+}{S}\overset{-}{C}(CO_2CH_3)_2CH_3$ + $(C_6H_5CO_2)_2$[14b]	17.3	−18.7	1.35	−0.98	1.63×10^{-1} (9.21×10^{2})
1(a—g) + Ac_2O	41.3	+10.4	1.24	U shaped	1.70×10^{-8} (9.60×10^{-5})

The rate of the reaction of the cyclopropyl phenyl system is *ca.* 10^4 times smaller than that of methyl *p*-tolyl sulphoxide. This large rate deceleration reflects on both the activation enthalpy and entropy. The $\Delta H^{\ddagger}$ value for the present reaction is *ca.* 20 kcal mol^{-1} larger than that obtained for the reaction of methyl *p*-tolyl sulphoxide with acetic anhydride (21.2 kcal mol^{-1}); furthermore, the $\Delta S^{\ddagger}$ value for the reaction is positive. The unusual values of the activation parameters seem to suggest that the mechanism for the cyclopropyl system is somewhat different from that of, *e.g.*, the methyl *p*-tolyl system.

The small kinetic isotope effect indicates that proton removal is not the rate-determining step of the reaction. This may mean that there is a possibility of ready proton exchange between the sulphoxide and the medium. Indeed, the results of quenching of the reaction of phenylsulphinyl[1-^{2}H]cyclopropane with acetic anhydride in the presence of acetic acid indicate clearly that hydrogen–deuterium exchange actually takes place during the reaction though to a small extent. Therefore, proton abstraction is not the rate-determining step in this reaction. However, the mode of this reaction is somewhat different from that of the Pummerer-type reaction of methylphenylsulphonium methylide with acetic anhydride. In the reaction of the ylide $C_6H_5\overset{+}{S}\overset{-}{C}(CO_2Me)_2CD_3$ with acetic anhydride in the presence of acetic acid, the ylide recovered was found to have lost *ca.* 80% of its deuterium content after 20% completion of the reaction; the Pummerer reaction of methylphenylsulphonium methylide proceeds *via* an *E*1cB path.[14b]

The Hammett plot using σ values shows a U shaped curve. This reveals that the rate-determining step of the reaction varies upon changing the substituent. It appears that proton abstraction by acetate is just as important as S–O bond cleavage in the energy profile of the reaction.

In order to examine whether the reaction proceeds *via* an intra- or an inter-molecular path, ^{18}O tracer experiments were carried out. A large loss of ^{18}O in the recovered sulphoxide reveals that S_N2-type ^{18}O exchange on the sulphur atom [6,15] takes place faster than the Pummerer reaction perhaps due to the relatively high temperature. However, in the case of ^{18}O-labelled *cis*-1-phenyl-2-phenylsulphinylcyclopropane, the product acetate still retained a significant amount (nearly 10% out of 20% ^{18}O in the recovered sulphoxide) of the ^{18}O label in the starting sulphoxide. The result reveals that a substantial portion of the acetoxy migration proceeds *via* both intra- and inter-molecular paths.

* Conclusive evidence for the presence of a cyclopropyl ring is provided by the high field chemical shifts of the cyclopropyl ring protons [10] and the magnitudes of the geminal and vicinal coupling constants.[11]

† The n.m.r. spectrum of (2d) is of the readily analysable abx type [12] with J_{ax} 8.86, J_{bx} 9.93, and J_{ab} 7.18 Hz and δ_a 1.59, δ_b 1.89, and δ_x 2.75.

‡ The $MeCO_2$ signal at δ 2.05 can be assigned to the shift for (2d) and the peak at δ 1.78 to that of (2e) since the $MeCO_2$ group of (2e) is in the anisotropic region of the 1-phenyl group and hence would shift upfield.[13]

§ *trans- or cis,anti*-sulphoxide (1d or f) was also prepared by isomerization of *cis*- or *cis,syn*-sulphoxide (1e or g) with potassium t-butoxide in butanol under reflux for 12 h.

[10] (*a*) D. J. Patel, M. E. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1963, **85**, 3218; (*b*) K. B. Wiberg and B. J. Nist, *ibid.*, 1961, **83**, 1226.

[11] K. B. Wiberg, D. E. Barth, and P. H. Schertler, *J. Org. Chem.*, 1973, **38**, 378, and references cited therein.

[12] J. A. Pole, W. G. Scheider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' McGraw-Hill, New York, 1959, p. 98.

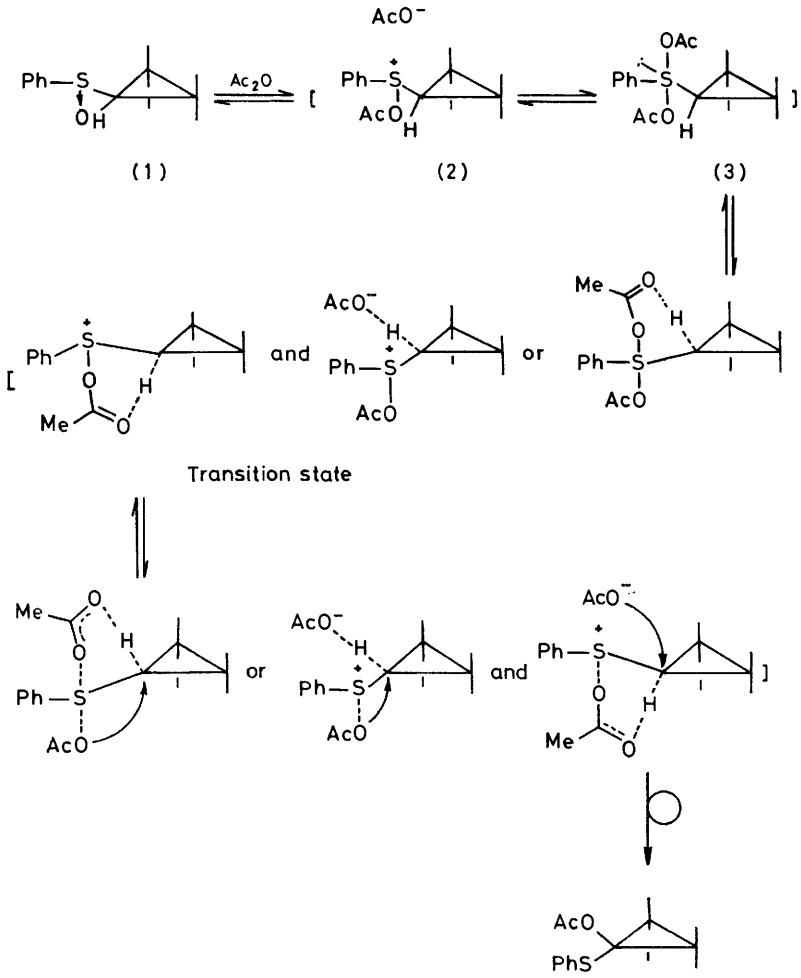
[13] D. T. Longone and A. H. Miller, *Chem. Comm.*, 1967, 447.

[14] (*a*) T. Numata and S. Oae, *Tetrahedron*, 1976, **32**, 2699; (*b*) T. Yagihara and S. Oae, *ibid.*, 1972, **28**, 2765; *Internat. J. Sulfur Chem.*, 1971, **1**, 159; (*c*) S. Iwanami, S. Arita, and K. Takeshita, *J. Synth. Org. Chem. Japan*, 1968, **26**, 375.

[15] M. Kise and S. Oae, *Bull. Chem. Soc. Japan*, 1970, **43**, 1421, 1804.

These kinetic and tracer investigations together with the stereochemistry reveal that the Pummerer reaction of arylsulphinylcyclopropanes with acetic anhydride involves initial formation of the acetoxysulphonium salt (2) or some sulphurane-like intermediate (3), which upon either intra- or inter-molecular proton removal or both, affords an ylide–ion pair. In view of the stereochemical results, the subsequent acetoxy migration is considered to take place intramolecularly from the back side of the proton removal. The rate-determining step or the driving force of this reaction is heterolytic S–O bond fission accompanied by the incipient formation of a S=C double bond between the sulphinyl sulphur and the cyclopropyl ring carbon. This step in the reaction of the cyclopropyl system may require more energy than that of, *e.g.*, the methyl *p*-tolyl system, since double bond formation between sulphur and carbon should result in enormous strain; hence the enthalpy would be exceptionally large for the cyclopropyl system. The oxygen scrambling and the unique stereoselectivity suggest that the formation of sulphonium salt or sulphurane as intermediate is quite facile and the rearrangement seems to start from the sulphonium salt or sulphurane intermediate. Therefore, at the transition state, steric rigidity due to the crowded structure of the reacting intermediate should decrease and this would be reflected in the positive value of the activation entropy.

Thus, the mechanism of this Pummerer reaction is illustrated in Scheme 2.



SCHEME 2

EXPERIMENTAL

Material.—Acetic anhydride and anhydrous sodium acetate were purified by the usual procedures.

para- or meta-Substituted Arylsulphinylcyclopropanes.—Substituted arylsulphinylcyclopropanes were prepared by oxidation with H_2O_2–AcOH of the corresponding sulphides formed by the reaction of *para-* or *meta*-substituted aryl 3-chloropropyl sulphides with sodium amide in liquid ammonia,[16] except for *p*-chlorophenylsulphinylcyclopropane prepared by the reaction of ethyl *p*-chlorobenzenesulphinate with cyclopropylmagnesium bromide in ether. All the substituted phenylsulphinylcyclopropanes thus obtained were purified by g.l.c. (5% silicone OV-17; 1 m; 6 mm i.d.; stainless steel tube; temperature 120—150 °C; H_2 flow 40 ml min^{-1}): *phenylsulphinylcyclopropane* (1a);

[16] W. E. Truce, K. R. Hollister, L. B. Lindy, and J. E. Parr, *J. Org. Chem.*, 1968, **33**, 43.

$\nu_{max.}$ 1 050 cm^{-1} (S=O); δ($CDCl_3$) 0.5—1.4 (4 H, m, cyclopropyl), 1.9—2.4 (1 H, m, CH), and 7.3—7.8 (5 H, m, Ph) (Found: C, 64.8; H, 6.0. $C_9H_{10}OS$ requires C, 65.0; H, 6.1%); p-*tolylsulphinylcyclopropane*; $\nu_{max.}$ 1 050 cm^{-1} (S=O); δ($CDCl_3$) 0.8—1.5 (4 H, m, cyclopropyl), 2.0—2.5 (1 H, m, CH), 2.40 (3 H, s, CH_3), and 7.2—7.7 (4 H, q, aromatic) (Found: C, 66.6; H, 6.7. $C_{10}H_{12}OS$ requires C, 66.6; H, 6.7%); p-*chlorophenylsulphinylcyclopropane*; $\nu_{max.}$ 1 050 cm^{-1} (S=O); δ($CDCl_3$) 0.9—1.6 (4 H, m, cyclopropyl), 2.0—2.4 (1 H, m, CH), and 7.4—8.0 (4 H, q, aromatic); p-*methoxyphenylsulphinylcyclopropane*; $\nu_{max.}$ 1 040 cm^{-1} (S=O); δ($CDCl_3$) 0.6—2.2 (4 H, m, cyclopropyl), 1.9—2.5 (1 H, m, CH), 3.80 (3 H, s, MeO), and 6.7—7.4 (4 H, q, aromatic); and m-*trifluoromethylphenylsulphinylcyclopropane*; $\nu_{max.}$ 1 060 cm^{-1} (S=O); δ($CDCl_3$) 0.9—2.4 (4 H, m, cyclopropyl), 2.0—2.5 (1 H, m, CH), and 7.7—8.0 (4 H, m, aromatic) (Found: C, 51.5; H, 3.8. $C_{10}H_9F_3OS$ requires C, 51.3; H, 3.9%).

Phenylsulphinylcyclopropanes (1b *and* c).—Other phenylsulphinylcyclopropanes can be readily prepared by the reaction of chloromethyl phenyl sulphide and potassium t-butoxide in various olefins.[17] Phenylsulphinylcyclopropanes (1b and c) [18] were obtained by oxidation (H_2O_2–AcOH) of the corresponding sulphides, purified by bulb-to-bulb distillation and then by g.l.c. (5% silicone OV-17; 6 mm i.d.; stainless steel tube; temperature 180 °C; H_2 flow 40 ml min^{-1}) or recrystallization from ether–hexane: trans-1,2-*dimethyl*-3-*phenylsulphinylcyclopropane* (1b), b.p. 150 °C at 3 × 10^{-2} mmHg (bath temp.); $\nu_{max.}$ 1 040 cm^{-1} (S=O); δ($CDCl_3$) 0.9—1.7 (8 H, m, 2MeCH), 1.7—2.2 (1 H, m, CH), and 7.3—7.9 [5 H, m, PhS(O)] (Found: C, 67.5; H, 7.2. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.3%); 1,1-*dimethyl*-2-*phenylsulphinylcyclopropane* (1c), b.p. 150 °C at 3 × 10^{-2} mmHg (bath temp.); $\nu_{max.}$ 1 040 cm^{-1} (S=O); δ($CDCl_3$) 0.9—1.4 (m), 1.07 (s), and 1.39 (s) (8 H, Me_2CCH_2), 1.8—2.4 (1 H, m, CH), and 7.3—7.9 [5 H, m, PhS(O)].

trans- *and* cis-1-*Phenyl*-2-*phenylsulphinylcyclopropanes* (1d *and* e) *and* cis,anti- *and* cis,syn-1,2-*Dimethyl*-3-*phenylsulphinylcyclopropane* (1f *and* g).—A mixture of *trans*- and *cis*-1-phenyl-2-phenylthiocyclopropane * or *cis,anti*- and *cis,syn*-1,2-dimethyl-3-phenylthiocyclopropane was synthesized according to the method of Truce *et al.*[19] or Schöllkopf *et al.*,[16] respectively, and were separated through a column packed with silica gel. The sulphides were then oxidized to the corresponding phenylsulphinylcyclopropanes (1d—g) with H_2O_2–AcOH and purified by recrystallization from ether–hexane or by g.l.c. (5% silicone OV-17; 1 m; 6 mm i.d.; stainless steel tube; temperature 180 °C; H_2 flow 40 ml min^{-1}): trans-1-*phenyl*-2-*phenylsulphinylcyclopropane* (1d), purified by g.l.c.; $\nu_{max.}$ 1 040 cm^{-1} (S=O); δ($CDCl_3$) 1.0—1.9 (2 H, m, CH_2), 2.1—2.8 (2 H, m, 2CH), 6.7—7.4 (5 H, m, Ph), and 7.4—7.9 [5 H, m, PhS(O)]; cis-1-*phenyl*-2-*phenylsulphinylcyclopropane* (1e), m.p. 97—98 °C; $\nu_{max.}$ 1 040 cm^{-1} (S=O); δ($CDCl_3$) 1.5—2.3 (2 H, m, CH_2), 2.4—2.7 (2 H, m, 2CH), and 7.2—7.6 [10 H, m, Ph and PhS(O)] (Found: C, 73.6; H, 5.7. $C_{15}H_{14}OS$ requires C, 74.3; H, 5.8%); cis,anti-1,2-*dimethyl*-3-*phenylsulphinylcyclopropane* (1f), purified by g.l.c.; $\nu_{max.}$ 1 040 cm^{-1} (S=O); δ($CDCl_3$) 0.9—1.3 (6 H, d, 2Me), 1.4—2.2 (3 H, m, 3CH), and 7.4—7.8 [5 H, m, PhS(O)] (Found: C, 68.4; H, 7.2. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.3%); and cis,syn-1,2-*dimethyl*-3-*phenylsulphinylcyclopropane* (1g), m.p. 75—76 °C; $\nu_{max.}$ 1 040 cm^{-1} (S=O); δ($CDCl_3$) 0.9—1.7 (8 H, m, 2MeCH), 1.9—2.4 (1 H, m, CH), and 7.3—7.9 [5 H, m, PhS(O)] (Found: C, 67.8; H, 7.2%).

Phenylsulphinylmethyl-cyclopropane (3a) *and -cyclobutane* (3b).—Phenylthiomethyl-cyclopropane and -cyclobutane were prepared by treating cyclopropylmethyl and cyclobutylmethyl benzenesulphonates with sodium thiophenolate in alcohol. A typical run is as follows. A CH_2Cl_2 solution (50 ml) of benzenesulphonyl chloride (12 g, 68 mmol) was added dropwise to a CH_2Cl_2 solution (100 ml) of cyclopropylmethyl alcohol (5 g) containing pyridine (5.5 g, 70 mmol) at −20 °C and then allowed to react for 4 h. After the CH_2Cl_2 solution was left at room temperature for 2 h, the solution was poured into ice–water and washed with 5% aqueous Na_2CO_3 solution, water, 5% aqueous hydrochloric acid, and water and dried ($MgSO_4$). CH_2Cl_2 was evaporated and the crude cyclopropylmethyl benzenesulphonate was obtained. An alcohol solution (50 ml) containing this product without further purification was added dropwise to an alcohol solution (50 ml) of sodium thiophenolate (0.1 mol) at −5 to 0 °C. The alcohol solution was left at room temperature overnight, the solution was poured into 5% aqueous sodium hydroxide solution, and the product was extracted with hexane. After the solvent was evaporated, phenylthiomethylcyclopropane was obtained. Yields of phenylthiomethylcyclopropane, b.p. 80—82 °C at 5—6 mmHg, and phenylthiomethylcyclobutane, b.p. 96—98 °C at 5 mmHg, were 61 and 68%, respectively. Phenylsulphinylmethyl-cyclopropane (3a) and -cyclobutane (3b) were obtained in 82 and 88% yield, respectively, by oxidation (H_2O_2–AcOH) of the corresponding sulphides: *phenylsulphinylmethylcyclopropane* (3a), m.p. 32—33 °C; $\nu_{max.}$ 1 040 cm^{-1} (S=O); δ($CDCl_3$) 0.1—1.2 (5 H, m, cyclopropyl), 2.71 [2 H, dq, *J* 6, 7, and 12 Hz, S(O)CH_2], and 7.35—7.70 [5 H, m, PhS(O)] (Found: C, 66.7; H, 6.7; S, 17.6. $C_{10}H_{12}OS$ requires C, 66.6; H, 6.7; S, 17.8%); *phenylsulphinylmethylcyclobutane* (3b), m.p. 61—62 °C; $\nu_{max.}$ 1 040 cm^{-1} (S=O); δ($CDCl_3$) 1.5—2.4 (6 H, m, $3CH_2$), 2.4—2.8 [3 H, m, S(O)CH_2CH], and 7.3—7.8 [5 H, m, PhS(O)] (Found: C, 67.8; H, 7.2; S, 16.3. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.3; S, 16.5%).

Reaction of Phenylsulphinylcyclopropanes (1a—g) *and Phenylsulphinylmethylcycloalkanes* (3a *and* b) *with Acetic Anhydride containing Anhydrous Sodium Acetate.*—A typical run is as follows. Phenylsulphinylcyclopropane (1a) (5 mmol) and anhydrous sodium acetate (500 mg) was dissolved in acetic anhydride (20 ml) in a sealed tube. The tube was heated in an oil-bath at 170 °C for 24 h. After the reaction, the tube was broken and acetic anhydride was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (50 ml) and the solution was neutralized with 5% aqueous Na_2CO_3 solution, washed with water, and dried ($MgSO_4$). CH_2Cl_2 was evaporated and the residue was subjected to preparative t.l.c. on silica gel using benzene as eluant. The product was 1-acetoxy-1-phenylthiocyclopropane (2a), purified by g.l.c. (5% silicone OV-17; 1 m; 6 mm i.d.; stainless steel tube; temperature 150 °C; H_2 flow 40 ml min^{-1}) and identified by i.r., n.m.r., and mass spectrometry.

The reactions of other phenylsulphinylcyclopropanes (1b—g) and phenylsulphinylmethylcycloalkanes (3a and b)

* *cis*-1-Phenyl-2-phenylthiocyclopropane synthesized by the method of Truce *et al.*[19] was found to contain *ca.* 2—3% of *trans*-isomer by g.l.c. (OV-101; 20 m).

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were carried out at 170 °C for 3 h, similarly. Products, purified by g.l.c., were identified by i.r., n.m.r., and mass spectrometry: 1-acetoxy-1-phenylthiocyclopropane (2a) $\nu_{max.}$ 1 770 1 240 and 1 160 cm^{-1}; $\delta(CDCl_3)$ 1.38 (4 H, m, cyclopropyl), 2.10 (3 H, s, $MeCO_2$), and 7.3—7.7 (5 H, m, PhS); *m/e* 208 (M^+), 149 [$(M - MeCO_2)^+$], 110 ($PhSH^{\cdot+}$), 109 (PhS^+), 99 [$(M - PhS)^+$], and 43 ($MeCO^+$) (Found: C, 63.7; H, 5.8. $C_{11}H_{12}O_2S$ requires C, 63.4; H, 5.8%); trans-1-*acetoxy*-2,3-*dimethyl*-1-*phenylthiocyclopropane* (2b), $\nu_{max.}$ 1 760, 1 220, and 1 150 cm^{-1}; $\delta(CDCl_3)$ 0.9—1.5 (8 H, m, 2MeCH), 1.91 (3 H, s, $MeCO_2$), and 7.0—7.5 (5 H, m, PhS); *m/e* 236 (M^+), 127 [$(M - PhS)^+$], 110 ($PhSH^{\cdot+}$), 109 (PhS^+), and 43 ($MeCO^+$) (Found: C, 65.8; H, 6.6. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.8%); 1-*acetoxy*-2,2-*dimethyl*-1-*phenylthiocyclopropane* (2c), $\nu_{max.}$ 1 750, 1 230, and 1 110 cm^{-1}; $\delta(CDCl_3)$ 1.05 (2 H, d, CH_2), 1.21 (3 H, s), and 1.31 (3 H, s) (2Me), 2.05 (3 H, s, $MeCO_2$), and 7.1—7.5 (5 H, m, PhS); *m/e* 236 (M^+), 127 [$(M - PhS)^+$], 110 ($PhSH^{\cdot+}$), 109 (PhS^+), and 43 ($MeCO^+$) (Found: C, 65.9; H, 6.7. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.8%); 1-*acetoxy*-2-*phenyl*-1-*phenylthiocyclopropane* (2d), $\nu_{max.}$ 1 760, 1 230, and 1 140 cm^{-1}; $\delta(CDCl_3)$ 1.59 (1 H, q, CH_a), 1.89 (1 H, q, CH_b), 2.05 (3 H, s, $MeCO_2$), 2.75 (1 H, q, CH_x), and 6.92—7.60 (10 H, m, Ph and PhS), J_{ax} 8.86, J_{bx} 9.93, and J_{ab} 7.18 Hz; *m/e* 284 (M^+), 225 [$(M - MeCO_2)^+$], 175 [$(M - PhS)^+$], 110 ($PhSH^{\cdot+}$), 109 (PhS^+), and 43 ($MeCO^+$); (1e) ⟶ (2d + 3), $\nu_{max.}$ 1 760, 1 230, and 1 140 cm^{-1}; $\delta(CDCl_3)$ 1.50—1.88, 1.78, and 2.05 (5 H, m, s, and s, CH_2 and $MeCO_2$), 2.64—2.88 (1 H, q, CH), and 6.96—7.50 (10 H, m, Ph and PhS); *m/e* 284 (M^+), 225 [$(M - MeCO_2)^+$], 175 [$(M - PhS)^+$], 110 ($PhSH^{\cdot+}$), 109 (PhS^+), and 43 ($MeCO^+$) (Found: C, 72.35; H, 5.5. Calc. for $C_{17}H_{16}O_2S$: C, 71.35; H, 6.0%); 1-*acetoxy*-2,3-*dimethyl*-1-*phenylthiocyclopropane* (2f), $\nu_{max.}$ 1 750, 1 220, and 1 150 cm^{-1}; $\delta(CDCl_3)$ 0.96—1.10 (6 H, m, 2Me), 1.40—1.66 (2 H, m, 2CH), 2.00 (3 H, s, $MeCO_2$), and 7.0—7.5 (5 H, m, PhS); *m/e* 236 (M^+), 177 [$(M - MeCO_2)^+$], 127 [$(M - PhS)^+$], 110 ($PhSH^{\cdot+}$), 109 (PhS^+), and 43 ($MeCO^+$); (1g)→(2f + g), $\nu_{max.}$ 1 750, 1 220, and 1 150 cm^{-1}; $\delta(CDCl_3)$ 0.80—1.12 (6 H, m, 2Me), 1.36—1.60 (2 H, m, 2CH), 2.00 (s) and 2.08 (s) (3 H, $MeCO_2$), and 7.0—7.6 (5 H, m, PhS); *m/e* 236 (M^+), 177 [$(M - MeCO_2)^+$], 127 [$(M - PhS)^+$], 110 ($PhSH^{\cdot+}$), 109 (PhS^+), and 43 ($MeCO^+$) (Found: C, 65.8; H, 6.7. Calc. for $C_{13}H_{16}O_2S$: C, 66.1; H, 6.8%); [*acetoxy*(*phenylthio*)*methyl*]*cyclopropane* (4a), $\nu_{max.}$ 1 750 and 1 230 cm^{-1}; $\delta(CDCl_3)$ 0.45—0.75 (4 H, m, cyclopropyl), 1.20—1.45 (1 H, m, CH), 1.95 (3 H, s, $MeCO_2$), 5.55 (1 H, d, SCH), and 7.0—7.5 (5 H, m, PhS); *m/e* 222 (M^+), 162 [$(M - MeCO_2H)^{\cdot+}$], 85 ($C_4H_5S^+$), and 43 ($MeCO^+$) (Found: C, 64.4; H, 6.2. $C_{12}H_{14}O_2S$ requires C, 64.8; H, 6.35%); and [*acetoxy*(*phenylthio*)*methyl*]*cyclobutane* (4b), $\nu_{max.}$ 1 740 and 1 220 cm^{-1}; $\delta(CDCl_3)$ 1.7—2.1 (6 H, m, $3CH_2$), 1.95 (3 H, s, $MeCO_2$), 2.5—2.9 (1 H, m, CH), 6.20 (1 H, d, SCH), and 7.0—7.5 (5 H, m, PhS); *m/e* 236 (M^+), 176 [$(M - MeCO_2H)^{\cdot+}$], 152 [$PhSC(O)Me^{\cdot+}$], 110 ($PhSH^{\cdot+}$), and 43 ($MeCO^+$) (Found: C, 66.4; H, 6.8. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.8%).

1-*Deuteriated* para- *or* meta-*Substituted Arylsulphinylcyclopropanes*.—1-Deuteriated arylsulphinylcyclopropanes were prepared by treating the corresponding sulphoxide in NaOD–D_2O–MeOD at reflux for 12 h. The n.m.r. spectra indicated no appreciable signal for the α-proton at *ca.* δ 1.9—2.4.

^{18}O-*Labelled Phenylsulphinylcyclopropane and* cis-1-*Phenyl*-2-*phenylsulphinylcyclopropane*.— ^{18}O-Labelled phenylsulphinylcyclopropane and *cis*-1-phenyl-2-phenylsulphinylcyclopropane were prepared by the reaction of the corresponding sulphides with bromine in $H_2{}^{18}O$–pyridine–acetic acid solution.[20] The amounts of excess ^{18}O in ^{18}O-labelled phenylsulphinylcyclopropane and in *cis*-1-phenyl-2-phenylsulphinylcyclopropane were determined by the usual ^{18}O analytical method (see Table 3).

Hydrogen–Deuterium Exchange Reaction.—An acetic anhydride solution of 1-deuteriated phenylsulphinylcyclopropane was heated at 170 °C with a 10 molar excess of acetic acid and the reaction was stopped at *ca.* 42 and 68% completion. The n.m.r. spectra of the recovered sulphoxides, separated by column chromatography (silica gel; 300 mesh; chloroform), indicated *ca.* 3 and 11% loss of deuterium from the original sulphoxide.

^{18}O *Tracer Experiments*.—^{18}O-Labelled phenylsulphinylcyclopropane (excess ^{18}O atom % 1.21; 4 mmol) or ^{18}O-labelled *cis*-1-phenyl-2-phenylsulphinylcyclopropane (excess ^{18}O atom % 1.04; 4 mmol) was dissolved into acetic anhydride (150 mmol) containing anhydrous sodium acetate (1 mmol). The solution was heated at 170 °C for 10 h for ^{18}O-labelled phenylsulphinylcyclopropane or 1 h for *cis*-1-phenyl-2-phenylsulphinylcyclopropane (*ca.* 70 or 40% completion, respectively). The results are shown in Table 3.

Kinetic Measurements.—A typical kinetic procedure was as follows. Phenylsulphinylcyclopropane (0.03 mmol) was dissolved in acetic anhydride (15 ml). The solution was divided into 10 portions each of which was sealed in an ampoule. The ampoules were heated in a constant temperature bath (170.00 ± 0.05 °C), taken out at intervals, and cooled in an ice-bath in order to stop the reaction. From each ampoule an aliquot portion (0.1 ml) was pipetted out and hydrolysed with 1N-KOH solution (25 ml). The rates of the reaction were followed spectrometrically, taking advantage of the difference in the u.v. spectra of the starting sulphoxide and the final hydrolysed compounds (*para*- or *meta*-substituted thiophenolates).[6]

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