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THE UNIVERSITY OF ALBERTA

OXYGEN-18 SCRAMBLING IN THE REARRANGEMENT
OF ALLYLIC ARENESULFINATES

by



MARGARET-ANN ARMOUR

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Oxygen-18 Scrambling in the Rearrangement of Allylic Arenesulfinates" submitted by Margaret-Ann Armour, B.Sc., M.Sc., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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.....

To my Mother

ABSTRACT

The rearrangement of allylic arenesulfinates to sulfones has been proposed to occur through a cyclic intramolecular transition state to which there is a contribution from a polar resonance structure. The importance of this resonance structure can be gauged by measuring the degree of oxygen equilibration in the substrate during the rearrangement.

A variety of allylic arenesulfinates has been synthesized having an oxygen-18 label in the sulfinyl-oxygen position. The esters which were recovered after partial reaction in ethanol, 60% ethanol or acetic acid were hydrolyzed and the excess oxygen-18 in the resulting alcohol was determined from the mass spectrum of the alcohol. Excess oxygen-18 was not detected in the alcohols from the allyl, crotyl or α -methylallyl esters during reaction in any of the solvents examined, or in the alcohol from the α,γ -dimethylallyl ester during reaction in ethanol or 60% ethanol.

It is suggested that the rearrangement of these esters proceeds via a cyclic 5-membered transition state in which bond-breaking and bond-making are sufficiently concerted that a discrete ionic intermediate is not involved. The presence of an ion-pair intermediate in the rearrangement of the cinnamyl ester would allow recombination of the α -carbon with either of the oxygens of the sulfinate anion. Such recombination of the ion-pairs formed from the α,γ -dimethylallyl ester and the α -phenylallyl ester would lead to the formation of the diastereoisomer different from the starting ester. The experimental

results from the rearrangement and scrambling of the α -phenylallyl ester are consistent with those calculated using a scheme allowing diastereoisomer interconversion. The incorporation of oxygen-18 into the ether-oxygen position during the rearrangement of the α,γ -dimethylallyl ester in acetic acid may arise by carbon-oxygen bond fission to yield an ion-pair followed by bond formation between the γ -carbon and sulfinyl-oxygen of the starting ester. This process is formally similar to rearrangement via a 6-membered transition state and would lead to the formation of ester which was the same diastereoisomer as the starting material.

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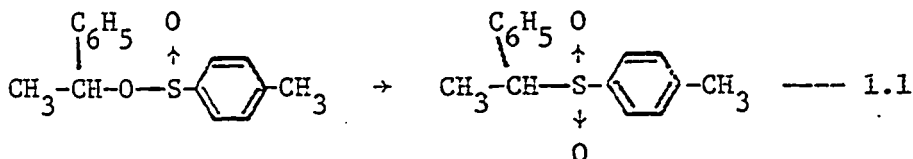
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INTRODUCTION

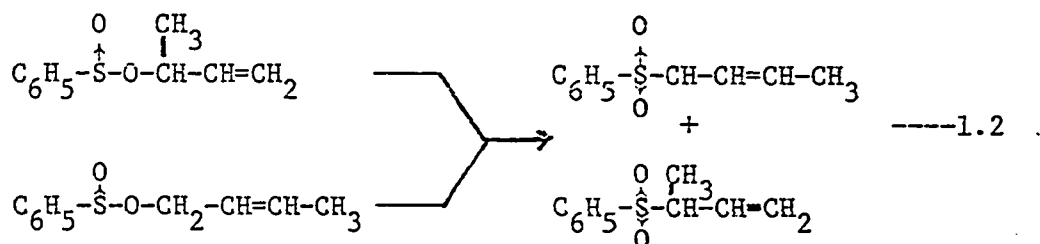
Esters of sulfinic acids have been the subject of investigation by chemists for many years. They were first prepared in 1885 by Otto and Rossing (1) and in 1893 the same workers heated ethyl benzenesulfinate in sealed tubes at 120° to 150° and observed that only decomposition occurred (2). Similarly, in 1925, heating of *l*-2-octyl *p*-toluene-sulfinate was reported (3) to result in partial recovery of the starting material together with decomposition products. However, in 1917, Hinsberg (4) had prepared sulfones by heating the related sulfinic acid and alcohol in acetic acid - hydrochloric acid mixtures, and in 1930, Kenyon and Phillips (5) showed that α -phenylethyl *p*-toluenesulfinate rearranged on standing to α -phenylethyl *p*-tolyl sulfone, (equation 1.1). Kenyon et. al. subsequently investigated the pathway of this rearrangement (6).



When the starting material was optically active ester, the recovered sulfone was completely racemic; the rearrangement was facilitated by increasing the polarity of the solvent, 72% sulfone being recovered from reaction in formic acid, 30% from reaction in nitrobenzene and 9% from reaction in benzene, all at room temperature, and the intermediate could be trapped by added anions. From these observations, which are criteria for the formation of a carbonium ion, it was suggested that ionization of the ester occurred during the reaction. When the rearrangement was allowed to proceed in formic acid with added sodium formate, 10% of the sulfone which was formed was optically active

and had the same configuration as the starting ester. It was proposed that this sulfone was formed by an intramolecular rearrangement.

An intramolecular cyclic route was also one of the possible mechanisms mentioned by Cope, Morrison and Field (7) for the sulfinate to sulfone rearrangement when they obtained low yields of sulfones by heating allyl benzenesulfinate without solvent at 100° for 29 hours, α -methylallyl benzenesulfinate in toluene at 80° for 6½ hours, and crotyl benzenesulfinate in toluene at 100° for 6½ hours. Such an intramolecular rearrangement would have been analogous to the Cope reaction of allylic amine oxides (8,9) and should have given rise to isomerization of the allylic group in addition to rearrangement of the functional group. Since α -methylallyl benzenesulfinate and crotyl benzenesulfinate yielded the same mixture of sulfones which was identified as containing at least 90% crotyl phenyl sulfone and the remainder α -methylallyl phenyl sulfone (equation 1.2), the authors



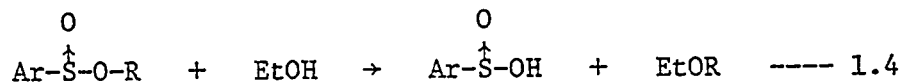
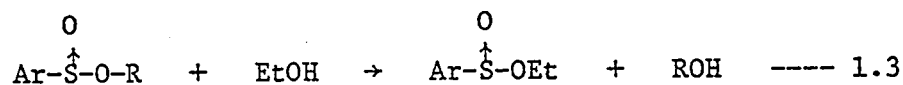
suggested that following their formation, the product sulfones rearranged to the same equilibrium mixture containing predominantly crotyl phenyl sulfone. However, they pointed out that their data did not allow them to rule out either a prior equilibrium of the starting esters followed by rearrangement to sulfones or the formation of a sulfinate anion and resonance stabilized allylic cation which could recombine and would yield the same mixture of products since the same cation would be formed from each ester.

Another mechanistic study of the rearrangement of sulfinic esters was carried out by Wragg, McFadyen and Stevens (10). Using a variety of dimethylphenyl, methylphenyl and phenyl esters, these workers found that rearrangement occurs in acetic acid and nitromethane and in acetonitrile, benzene or toluene only if a little *p*-toluenesulfinic acid is added. Like Kenyon (6), they concluded that the reaction was favoured by ionizing solvents and that substituent effects also suggested an ionic intermediate. They further proposed that the rearrangement was intermolecular since when they heated diphenylmethyl *p*-toluenesulfinate in acetic acid containing *p*-chlorobenzenesulfinic acid, they obtained *p*-chlorophenyl diphenylmethyl sulfone. Hence exchange of anions must have occurred during the reaction. Their observations were consistent with a rate-determining ionization.

Subsequent work in these laboratories on the isomerization and solvolysis of arenesulfinate esters has further elucidated the mechanism of the sulfinate to sulfone rearrangement.

The solvolysis of arenesulfates may occur by either sulfur-oxygen or by carbon-oxygen bond fission. Since, as has been described, sulfones can be obtained, carbon-oxygen bond fission must occur under certain conditions. However, in a study of the solvolyses in ethanol of a series of *p*-methoxyneophyl arenesulfates (11) sulfur-oxygen bond fission was shown to be important when a base such as potassium acetate or sodium ethoxide was present in the reaction mixture. This reaction was very much slower when a weak base such as pyridine or 2,6-lutidine was used. Since sulfur-oxygen bond fission in anhydrous ethanol of the 2,6-dimethylbenzenesulfinate esters would lead to the formation of ethyl 2,6-dimethylbenzenesulfinate, (equation 1.3), while carbon-oxygen bond

fission would not (equation 1.4), the effect of the added base on the



position of bond fission could be judged by following the appearance of the ethyl ester. It was found that the rate of formation of ethyl 2,6-dimethylbenzenesulfinate during the ethanolysis of *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate was reduced one thousand fold when the solution contained 2,6-lutidine in place of potassium acetate. It has also been shown that in systems where carbon-oxygen bond fission will lead to stable products, the type of bond cleavage can be controlled by choosing the appropriate base. For example (12) when allyl 2,6-dimethylbenzenesulfinate was solvolyzed in ethanol in the presence of sodium acetate, the main product was ethyl 2,6-dimethylbenzenesulfinate along with a trace of allyl 2,6-dimethylphenyl sulfone. When the base was changed to 2,6-lutidine, the only detectable product was the sulfone.

The products from the solvolysis of a variety of arenesulfinate esters have been investigated together with the effects on the rates of formation of sulfone and solvolysis products of changes in solvent polarity and the introduction of substituents.

Both sulfone and solvolysis products were obtained from reaction in a variety of solvents of the 2,6-dimethylbenzenesulfinate esters of *t*-butyl (13), α -phenylethyl (13, 14), α -(*p*-methoxyphenyl)-ethyl (13, 14), benzhydryl (13, 15), and 2-aryl 2-propyl (16) alcohols. It was found that the rate of sulfone formation showed a sensitivity

to the ionizing power of the solvent which was similar to that shown by the rate of solvolysis, the slopes of the lines obtained by plotting the logarithm of the rate constant for the solvolysis and rearrangement of benzhydryl 2,6-dimethylbenzenesulfinate against the logarithm of the rate constant for the solvolysis of benzhydryl chloride at 25° being 0.87 and 0.73 respectively. Since the solvolysis of benzhydryl chloride must involve an ionic intermediate (17) the straight line graphs obtained suggest that the reactions of the arenesulfonates also proceed via ionic intermediates.

A further indication of the presence of such intermediates in the rearrangement was given by the fact that introduction of a methoxy group into the aromatic ring of the α -phenylethyl ester increased the rate of both the rearrangement and the solvolysis by four powers of ten. This rate enhancement could be accounted for by increased resonance stabilization of the intermediate carbonium ion by electron release from the p-methoxy group.

Several pieces of evidence indicate that the sulfone is not formed by the recombination of dissociated ions. For example, when the reactant was optically active, diastereomerically pure α -phenylethyl 2,6-dimethylbenzenesulfinate, the sulfone which was produced was also optically active and of over 95% retained configuration, but the ester recovered after partial reaction was a mixture of diastereoisomers. Had dissociated ions been involved in the rearrangement to sulfone the latter would have been expected to have lost most or all of the optical activity associated with the starting material.

Further, the addition of 2,6-dimethylbenzenesulfinate anion to any of the systems did not increase the fraction of sulfone formed as

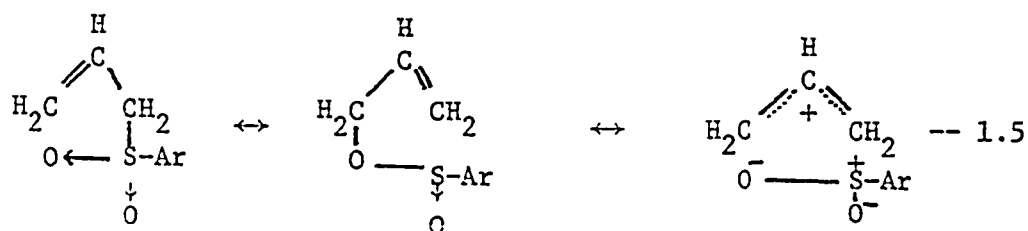
would have been expected if this ion were competing with solvent for the cation.

Only the corresponding sulfone was obtained when trityl 2-methylbenzenesulfinate was allowed to react in carbon tetrachloride, chloroform, nitrobenzene, acetonitrile and dimethylsulfoxide at room temperature (18). The change in rate on changing the solvent suggested that the sulfone was being formed in an ionic reaction. However, in acetonitrile only 45% at most of the intermediates could be diverted to form trityl azide by the addition of tetrabutylammonium azide. Hence most of the sulfone appeared to be being produced from a species which was not readily trappable by azide ion. Trityl 2,6-dimethylbenzenesulfinate on the other hand, yielded only decomposition products, no sulfone being detectable (19). This lack of rearrangement was rationalized on steric grounds. It was further shown that addition of 2,6-dimethylbenzenesulfinate anion in acetonitrile, in the presence of azide ion resulted in a depression of the rate of solvolysis and hence dissociated ions may be present as intermediates in this reaction. However, they were not regarded as the exclusive capturable intermediate.

The rearrangement of allylic arenesulfonates to sulfones was studied by Braverman (12), who showed that allylic rearrangement concomitant with functional group rearrangement occurred to give greater than 72% isolated yields of one sulfone rather than a mixture of isomeric sulfones. The relative rates of reaction of the esters studied was shown to be allyl < crotyl < α -methylallyl = cinnamyl < α,γ -dimethylallyl < α -phenylallyl. This order of reactivity is consistent with a polar transition state. However, the magnitude of the effects of the introduction of the methyl

and phenyl groups was found to be smaller than that observed in the solvolysis of allylic chlorides, reactions which proceed via ionic intermediates (20). For example, α -phenylallyl chloride solvolyzes in 99.5% formic acid at 44.6° about 2×10^9 times faster than allyl chloride (21), while the rearrangement of α -phenylallyl 2,6-dimethylbenzenesulfinate in 60% ethanol at 90° is only about four powers of ten faster than the rearrangement of the allyl ester. Although the rate of rearrangement of the allylic esters was found to be solvent sensitive, the sensitivity was very much less than that observed in the solvolysis of *p*-methoxyneophyl *p*-toluenesulfonate (22) whose rate of solvolysis is the same as its rate of ionization. This, therefore allows a measure of the sensitivity of the reaction to change in solvent which would be expected if ionization were involved.

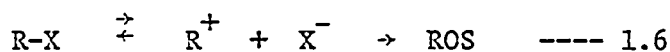
The solvolysis of benzyl 2,6-dimethylbenzenesulfinate can be used as a model for the rearrangement of the allyl ester, since the former formally contains an allyl group. However, the benzyl ester cannot react via a 5-membered cyclic transition state since this would lead to loss of resonance stabilization associated with the aromatic ring. The rate of rearrangement of the allyl ester was found to be faster by about three powers of ten than would have been expected from extrapolation of the data from the benzyl ester. This rate enhancement was explained as due to an intramolecular cyclic rearrangement whose transition state could be written as in equation 1.5.



It was suggested that in the case of allyl 2,6-dimethylbenzenesulfinate, the contribution from the ionic resonance structure might be of little significance, but that its importance would increase with increasing methyl or phenyl substitution of the allylic system.

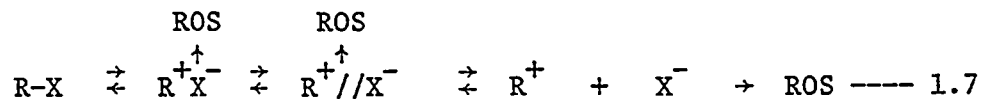
Except in the case of the allyl arenesulfonates, it can be seen from the brief summary of the data amassed on the rearrangement of arenesulfonates to sulfones, that the results are best interpreted in terms of the intermediacy of an ionic species. In the majority of cases, this species does not appear to be dissociated ions, but rather to be ion-pairs.

The presence of such ion-pair species was first considered by Hammett (23) but it remained for Winstein to systematize the idea in a series of papers beginning in 1950. At that time, data on solvolysis reactions had become available which could not be explained using the simple ionization mechanism of Hughes, Ingold and their school (24), (equation 1.6).



where R-X is covalent starting material, and R^+ and X^- represent dissociated ions. Winstein found (25) that, during the acetolysis of optically active norbornyl *p*-bromobenzenesulfonate, the acetate which was formed was completely the *exo* isomer and completely racemic, and the rate of loss of optical activity was several times larger than the rate of formation of *p*-bromobenzenesulfonic acid. This difference in rates could be explained by postulating the presence of ionized but undissociated ion-pairs which would recombine to form racemic starting material, in addition to ionizing further to yield solvolysis products.

In certain systems, it was found possible to distinguish two types of ion-pairs and the scheme of equation 1.7 was proposed (26, 27, 28).



where R-X is covalent starting material, R^+X^- is an intimate ion-pair formed by breaking the R-X bond but without the ions having moved away from one another, $R^+//X^-$ is a solvent separated ion-pair in which one, or a small number of solvent molecules are present between the ions which are still behaving as one kinetic entity, and $R^+ + X^-$ represents the final ionic intermediate which is in the form of dissociated ions.

The presence of two ion-pairs was required to account for the effect on the rate constants in certain systems of added non-common ion salts. For example, in the acetolysis of threo-3-p-anisyl-2-butyl bromobenzenesulfonate (26) the polarimetric rate constant was found to be 4.07 times greater than the titrimetric rate constant, indicating that return to covalent starting material from an ion-pair species was occurring in this system. The rate of loss of optical activity can be equated with the rate of ionization since the ionic intermediates are symmetrical. The addition of 0.02 molar lithium perchlorate to the system resulted in a two and a half fold increase in the titrimetric rate constant, while continued addition of the salt caused a more gradual increase, consistent with a normal salt effect. The latter effect only, was observed on the polarimetric rate constant. The initial "special salt effect" on the titrimetric rate constant has been equated with the partial or complete suppression of ion-pair return

to substrate. Extrapolation to zero of the linear portion of the curve which showed a gradual upslope due to the normal salt effect gave an intercept k_{ext}° which was the value of the titrimetric rate constant with the special salt effect included, but excluding the normal salt effect. If the lithium perchlorate were completely trapping the ion-pair species and preventing their return, this value of the titrimetric rate constant should be the same as the polarimetric rate constant in the absence of added salt. Since the polarimetric rate constant is still larger than the titrimetric rate constant, it was proposed that the added salt traps the solvent separated ion-pair preventing its return, while still permitting return from the intimate ion-pair.

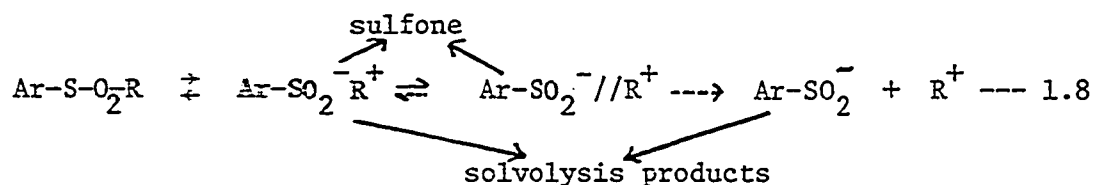
The scheme of equation 1.7 allows such phenomena as anion exchange and common-ion rate depression to be explained and the presence of effects such as these allows conclusions to be drawn about the nature of ionic intermediate present in a given reaction.

Return from dissociated ions to covalent starting material is occurring if common-ion rate depression is observed. If such rate depression is not observed, either dissociated ions are not formed or else they do not return to starting material. The presence of ion-exchange does not lead to a definite conclusion since it can occur with both ion-pairs and dissociated ions. However, the absence of exchange precludes the formation of dissociated ions which return to starting material.

When t-butyl chloride, α -phenylethyl bromide or benzhydryl chloride were solvolyzed in the presence of lutidinium 2,6-dimethylbenzenesulfinate, no sulfone was formed (13) and no mixed products

were obtained when benzhydryl 2,6-dimethylbenzenesulfinate was solvolyzed in the presence of the 4-methylbenzenesulfinate anion (15), thus no exchange of ions occurred during these reactions.

Since neither exchange nor common-ion rate depression were detected in the solvolysis of benzhydryl 2,6-dimethylbenzenesulfinate the mechanism which was proposed for this reaction in ethanol and 80% ethanol included the intermediacy of ion-pairs (equation 1.8).



where $\text{Ar-SO}_2\text{R}^{\ominus}\text{R}^{\oplus}$ is a non-capturable ion-pair, $\text{Ar-SO}_2\text{R}^{\ominus}\text{R}^{\oplus}$ is a capturable ion-pair, and $\text{Ar-SO}_2\text{R}^{\ominus} + \text{R}^{\oplus}$ are dissociated ions, which if formed were shown to react to form solvolysis products only. Thus ion-pair intermediates are important in the solvolysis and rearrangement of several arenesulfonates.

The work to be described herein centres on the investigation of the presence of such intermediates during the rearrangement of allylic arenesulfonates to sulfones. The anion formed by carbon-oxygen bond fission of arenesulfonate esters is polydentate, recombination to form covalent material being possible by the formation of a bond between carbon and either of the two oxygen atoms or the sulfur atom. If an ion-pair species is formed then equilibration of the oxygen is possible and two tools can be used to detect this equilibration. Starting with optically active ester, return by recombination of the carbon with what was originally the sulfinyl-oxygen would result in inversion of the asymmetric centre which is the sulfur atom, and should lead to racemization of the starting ester. Fava (29) has reported that during

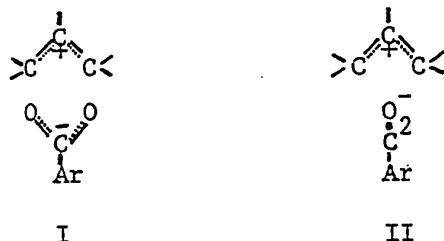
isomerization in acetic acid, optically active sulfinate esters lost optical activity at a rate which was about two and a half times as fast as the rate of formation of sulfone, thus indicating that return from an ionic species was occurring.

Equilibration of the oxygens in the anion and internal return can also be detected by specifically labelling one of the oxygen atoms in the starting ester with oxygen-18 and examining the ester after partial reaction to determine whether scrambling of the label has occurred.

Goering and his co-workers have shown that in non-rearranging systems such as benzhydryl (30), substituted benzhydryl (31,32), α -anisylethyl (61), 2-phenyl-2-butyl (33) and cyclopropylmethyl-carbonyl (34) *p*-nitrobenzoates, ion-pair return associated with solvolysis in aqueous acetone results in equilibration of the carboxyl oxygen atoms and in only partial racemization of optically active substrates. Hence in these systems, the sum of the rate of oxygen equilibration and the rate of formation of solvolysis products is a better measure of the rate of ionization than is the polarimetric rate.

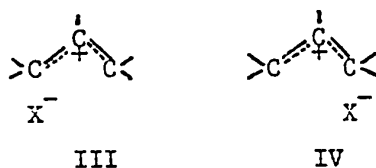
To determine whether or not complete equilibration of the oxygen atoms occurs during ionization, Goering and his co-workers have examined the rate of scrambling of an oxygen-18 label between the oxygen atoms in symmetrical allylic *p*-nitrobenzoates, where the rate of racemization provides an independent measure of the rate of ionization, since in these cases the cation is symmetrical. They found the rates of equilibration and racemization to be equal for trans- α,γ -dimethylallyl (35, 36) and for cis-5-methyl-2-cyclohexenyl (37)

p-nitrobenzoate and therefore suggested that these two rates represented independent measures of the rate of ionization. However, this does not distinguish between the two possible ion-pairs I and II.



In the arrangement I, equilibration of the oxygen atoms either will not occur, or at least will be incomplete for return to the original carbon, whereas in the arrangement II, equilibration will be complete in both isomers. By isolating the ester remaining after partial solvolysis and separating it into its enantiomers, Goering was able to show that in the *cis*-5-methyl-2-cyclohexenyl system, equilibration was complete in both isomers, while in the *trans* - α, γ -dimethylallyl system, return to the original enantiomer resulted in incomplete equilibration. The reason for this difference in behaviour of the two systems is not clear.

In two other allylic systems, the rate of oxygen equilibration has been compared with the rate of racemization. For both *trans*-5-methyl-2-cyclohexenyl (38) and *exo*-bicyclo (3.2.1.)oct-3-en-2-yl (39) *p*-nitrobenzoates, it was found that the rate constant for equilibration was greater than the rate constant for racemization. This result was rationalized by assuming that the intermediate could be represented as a mixture of III and IV.



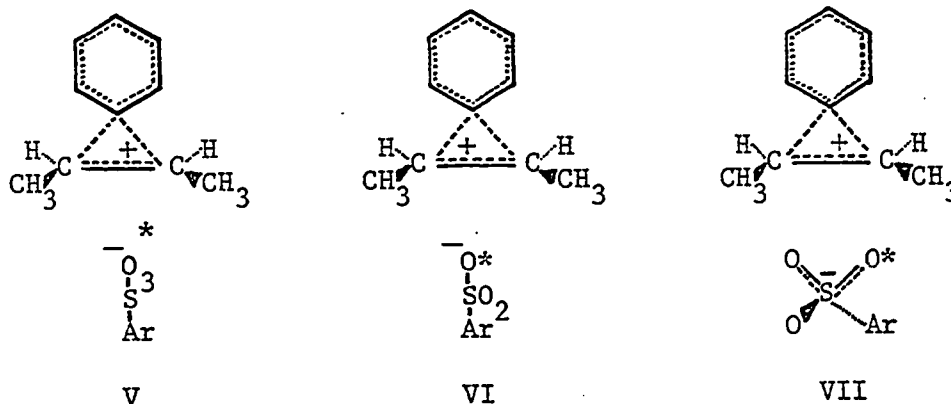
Since the anion is not in the plane of the cation, the two ion-pairs III and IV are enantiomeric and so their return will not result in complete racemization of the starting material.

A comparison of the rate of rearrangement of trans- α -phenyl- γ -methylallyl p-nitrobenzoate to the more stable trans- α -methyl- γ -phenylallyl p-nitrobenzoate with the rates of solvolysis of these two isomers (40) led to the conclusion that ion-pair return associated with the solvolysis of the former ester results in almost complete oxygen equilibration and, further, that the same amount of scrambling occurs when the intermediate ion-pair is formed from either allylic isomer. It would be expected that the more stable, and hence the longer lived the ion-pair intermediate, the more complete would be the oxygen equilibration. This has been shown to be the case for replacement of a methyl by a phenyl group in the allyl cation. Return to the original carbon atom in trans- α,γ -dimethylallyl p-nitrobenzoate results in about 35% equilibration of the oxygen atoms, while for trans- α -phenyl- γ -methyl p-nitrobenzoate, the equilibration is increased to about 85%.

In studying the acetolysis and rearrangement of 2-phenyl-1-propyl p-bromobenzenesulfonate, Winstein (41) did not detect any common-ion rate depression and suggested that the intermediate could be represented as an intimate ion-pair. Denney and Goldstein (42) found that the recovered sulfonate after partial rearrangement of ether-oxygen labelled ester had the same oxygen-18 content as the original ester and hence there is no equilibrating return from an ion-pair back to starting ester. Substitution of a p-methoxy group in the aryl substituent still did not result in common-ion rate depression being observed during the

acetolysis (43) but in this system, a special salt effect was detected and it was proposed that the rearrangement proceeded via a solvent separated ion-pair. Denney and Goldstein (42) suggested that in the acetolysis of ether-oxygen labelled 2-p-methoxy-1-propyl p-toluene-sulfonate complete equilibration of the oxygen-18 label occurred, but in these studies the equilibration was not correlated with an independent measure of ion-pair return.

Goering has studied the acetolysis of two sulfonate esters in which the rate of racemization represents an independent measure of ion-pair return, these being threo-3-phenyl-2-butyl p-toluenesulfonate (44, 45) and endo-bicyclo(3.2.1)-octan-2-yl p-toluenesulfonate (44). In the former case, a symmetric carbonium ion is formed (83) by participation of the phenyl group. No special salt effect was observed on addition of lithium perchlorate and so an intimate ion-pair was proposed as the intermediate. The rate constant for racemization was found to be twice the rate constant for equilibration so that some ion-pair return was occurring without equilibration. Using (+)-threo-3-phenyl-2-butyl p-toluenesulfonate (45) it was shown that internal return in which a p-toluenesulfonate ion rebonds to the original carbon atom is accompanied by about 50% randomization of the sulfonate oxygen atoms. Similar results were obtained when the starting ester was labelled with oxygen-18 in either the sulfonyl or the ether-oxygen positions. Three possible ionic intermediates were considered, V, VI and VII.



In each case, the oxygen which was originally in the ether position is marked with an asterisk.

In intermediate V, complete equilibration of the three oxygen atoms would occur so that the rate constant for equilibration would be the same as the rate constant for racemization; in VI, racemization occurs without equilibration, while in VII, one-quarter of the oxygen-18 label will end up in the ether-oxygen position. For complete scrambling one-third of the label should be on each oxygen, so that if this is the intermediate involved, the rate of equilibration would be three-quarters of the rate of scrambling. Using (+)-threo-3-phenyl-2-butyl p-toluenesulfonate, and examining the distribution of the label in each enantiomer of the racemic ester resulting from ion-pair return, Goering and his co-workers were able to show that the results were consistent with return from a 1:1 ratio of V and VI.

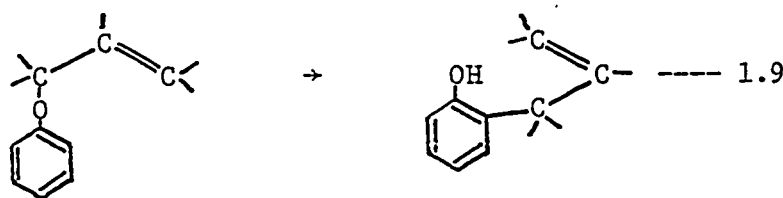
Endo-bicyclo(3.2.1)-octan-2-yl p-toluenesulfonate also forms a symmetric ion-pair (46) and since no special salt effect was observed on acetolysis in the presence of lithium perchlorate intimate ion-pairs were assumed to be involved in the solvolysis. Since the rate constant for equilibration was found to be about one-half of the value of the rate constant for racemization (44), in this system also, some

ion-pair return occurs without oxygen scrambling. In the acetolysis of this substrate, the presence of lithium perchlorate reduced the ratio of the rate constant for equilibration to the rate constant for racemization from 0.47 to 0.39 and the authors suggest that this is due to the presence of more than one ion-pair species which return with different amounts of oxygen equilibration, the intermediate which returns with the most equilibration being diverted by lithium perchlorate.

It has been mentioned that as a result of his studies on the rearrangement of allylic arenesulfinates to sulfones, Braverman (12) proposed that the reaction proceeded via an intramolecular cyclic mechanism, the transition state of which would become increasingly polar with the introduction of groups which would tend to stabilize the incipient carbonium ion.

Similar mechanisms have been proposed for the reactions of several other types of allylic compounds in which rearrangement of the functional group is accompanied by isomerization of the allylic system.

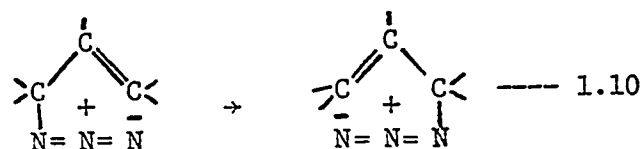
The classic example of a reaction of this general class is the Claisen rearrangement of allyl aryl ethers to allyl phenols (47), (equation 1.9).



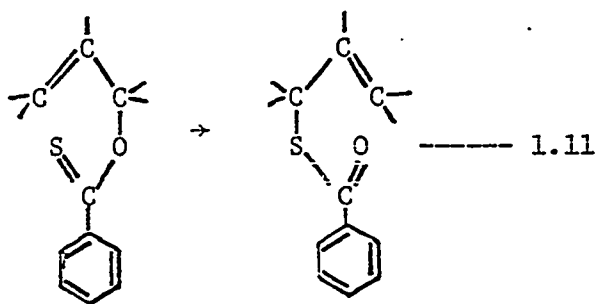
This rearrangement has been shown to proceed via an intramolecular cyclic mechanism, but the reactivity was found to be increased by the presence of electron donating groups on both the allyl group and the aromatic ring (48) and to be slightly enhanced by increased

ionizing power of the solvent (49). Hence, this rearrangement must have a certain, albeit small, amount of polar character.

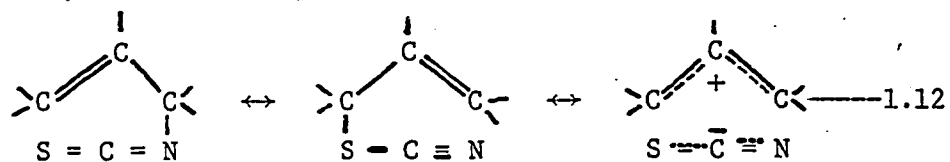
Also displaying a marked insensitivity to solvent and substituent effects are the rearrangement of allylic azides (equation 1.10),



studied by Winstein, (50), the conversion of allylic thionbenzoates to thiolbenzoates (51) (equation 1.11) and the conversion of allylic

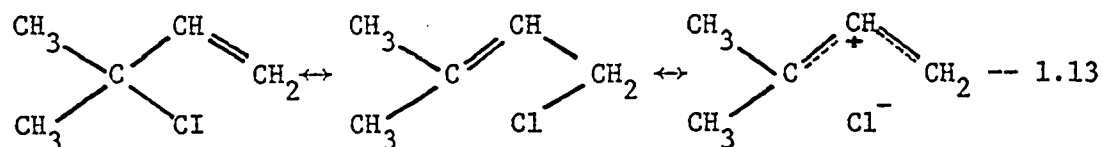


thiocyanates to isothiocyanates (52). The latter rearrangement has been proposed (53) to have a transition state which closely resembles that drawn by Braverman (equation 1.12) except that in this case, a



6-membered cyclic intermediate is involved.

This description of the transition state is very similar to that proposed by Young, Winstein and Goering (20) in the rearrangement of α,γ -dimethylallyl chloride (equation 1.13), the main difference being



the fact that, as indicated by the high sensitivity of the chloride reaction to solvent and structure effects, the ionic contributors to the resonance hybrid are more important in the solvolysis of the chloride than in the rearrangement of the thiocyanate.

The fact, already mentioned, that Goering and his co-workers have been able to detect equilibration of the oxygens during the rearrangement of allylic p-nitrobenzoates, indicates the predominantly ionic character of this transition state.

Hence, as has been pointed out by Winstein (50) there exists a spectrum of merging ion-pair and non-ionic cyclic mechanisms of allylic rearrangements, the non-ionic end of which is very nearly represented by the azide and thiocyanate rearrangements, while the chloride rearrangements are considerably closer to the ionic end.

Braverman's studies (12) have indicated that the rearrangement of allylic arenesulfinates to sulfones has a greater ionic character than that of the azide and thiocyanate rearrangements. It seemed possible that with the introduction of electron releasing groups which would stabilize the allylic carbonium ion, a discrete ion-pair intermediate might be formed, which, by analogy with the work of Goering, should lead to at least partial equilibration of the oxygen atoms of the sulfinate anion.

The work to be reported describes the use of the technique of specific labelling of one of the oxygen atoms of the starting ester with oxygen-18 in order to detect any oxygen equilibration occurring during the rearrangement of a variety of allylic arenesulfinates to sulfones.

CHAPTER I : THE PRODUCTS OF THE THERMAL REACTION OF SOME ALLYLIC
ARENESULFINATES

INTRODUCTION

In their investigation of the thermal stabilities of allyl benzenesulfinate, crotyl benzenesulfinate and α -methylallyl benzenesulfinate, Cope, Morrison and Field (7) isolated low yields of sulfone as one of the products of the reaction. However, the sulfone which was recovered after heating an approximately 1.5 molar solution of crotyl benzenesulfinate in toluene at 100° for $6\frac{1}{2}$ hours was found to be a mixture consisting of approximately 90% of crotyl phenyl sulfone and 10% of α -methylallyl phenyl sulfone. A similar mixture of sulfones was obtained when a 1.5 molar solution of α -methylallyl benzenesulfinate in toluene was heated at 80° for the same length of time.

Cope and his co-workers identified the mixture produced by comparing its physical properties with those of the products of oxidation of crotyl phenyl sulfide and α -methylallyl phenyl sulfide. They found that this oxidation, rather than producing crotyl phenyl sulfone and α -methylallyl phenyl sulfone respectively, gave the same mixture of sulfones from both of the sulfides as judged from the similarity of the infrared spectra. Catalytic hydrogenation of the oxidation product yielded mainly n-butyl phenyl sulfone, but comparison of the infrared spectrum of the hydrogenated material with the infrared spectra of authentic samples of n-butyl phenyl sulfone and 2-butyl phenyl sulfone indicated the presence of about

10% of 2-butyl phenyl sulfone. It was from this analysis that it was concluded that the mixture of unsaturated sulfones contained 10% of α -methylallyl phenyl sulfone.

Since Braverman found (12) that rearrangement of crotyl 2,6-dimethylbenzenesulfinate in 60% ethanol with added 2,6-lutidine resulted in the formation of pure α -methylallyl 2,6-dimethylphenyl sulfone, and that rearrangement under similar conditions of α -methylallyl 2,6-dimethylbenzenesulfinate yielded pure crotyl 2,6-dimethylphenyl sulfone, it was of interest to examine the products of rearrangement of the benzenesulfinate esters under conditions similar to those used by Braverman for the 2,6-dimethylbenzenesulfinate esters.

The advent of nuclear magnetic resonance spectroscopy has greatly facilitated the assignment of structures to products of reactions such as these, which yield mixtures of two or three closely related materials. In the work to be described, this technique has been used to identify the products of rearrangement of the esters under several solvolytic conditions.

RESULTS

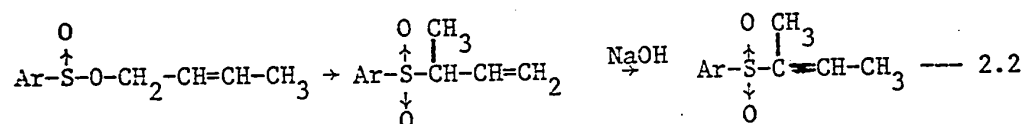
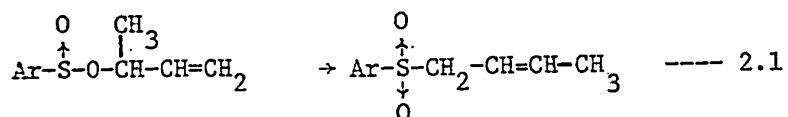
Benzenesulfinic acid was obtained by reduction of benzenesulfonyl chloride using sodium sulfite (54). Reduction of crotonaldehyde with lithium aluminium hydride yielded crotyl alcohol which was assigned a trans configuration on the basis of a very strong band in the infrared spectrum at 962 cm^{-1} (57) and the fact that the refractive index of the liquid was, within the experimental error in agreement with the reported value for trans crotyl alcohol. α -Methylallyl alcohol was prepared by the addition of acrolein to methyl Grignard reagent. Addition of the appropriate alcohol to benzenesulfinyl chloride in pyridine solution resulted in the formation of the benzenesulfinate esters. Owing to its thermal instability the α -methylallyl ester was purified by alumina chromatography, while it was found possible to purify the crotyl ester by distillation in small quantity at low pressure.

A solution of α -methylallyl benzenesulfinate (0.1 M) in 60% ethanol with 2,6-lutidine added was heated at 80° for $6\frac{1}{2}$ hours. The small quantity of unrearranged α -methylallyl ester was decomposed by base-catalyzed hydrolysis and the resulting alcohol was removed under reduced pressure. The nmr spectrum of the product was consistent with its being a pure sample of crotyl phenyl sulfone and a 75% isolated yield of this material was obtained.

A solution of crotyl benzenesulfinate (0.1 M) in 60% ethanol with 2,6-lutidine added was heated at 100° for $6\frac{1}{2}$ hours. Base-

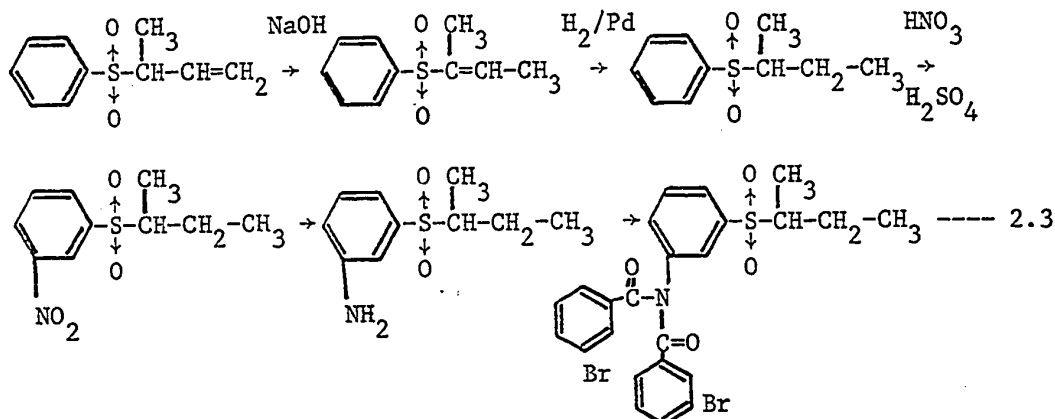
catalyzed hydrolysis of the residual ester was found to isomerize the α -methylallyl phenyl sulfone to the more stable α -methylpropenyl phenyl sulfone and so this residue was chromatographed on alumina. A second chromatography completed removal of the ester. The nmr spectrum of the product indicated that it was a mixture of α -methylallyl phenyl sulfone and a small quantity of α -methylpropenyl phenyl sulfone. The isolated yield of the mixture was 62%.

These results are summarized in equations 2.1 and 2.2.



Since an almost quantitative yield of α -methylallyl phenyl sulfone could be obtained from crotyl benzenesulfinate by heating the ester in 60% ethanol for 24 hours, a sample of the sulfone was obtained in this way. It gave a satisfactory microanalysis and its ir and nmr spectra were consistent with the proposed structure.

When crystalline α -methylallyl phenyl sulfone was stirred with 0.1 molar aqueous sodium hydroxide solution, either for 24 hours at room temperature or for 2 hours on the steambath, a solid resulted which was identified as α -methylpropenyl phenyl sulfone by catalytic hydrogenation (55) to its saturated analogue, 2-butyl phenyl sulfone and conversion of this sulfone to 2-butyl m- (di-3-bromobenzoylamino)- phenyl sulfone, a known derivative, (56) (equation 2.3).



Further confirmation of the identity of the saturated sulfone was obtained when its nmr spectrum was shown to be identical with that of the sulfone prepared by oxidation of 2-butyl phenyl sulfide with hydrogen peroxide.

The nmr spectra of the starting esters and their rearrangement products are detailed in Table I. From an examination of these spectra it seemed possible that mixtures of α -methylallyl phenyl sulfone and crotyl phenyl sulfone could be identified and this possibility was confirmed when synthetic mixtures of the sulfones were prepared and their nmr spectra measured. It was found that 5% of the one sulfone in the presence of 95% of the other could be detected readily, while the detection of 1% of one in the presence of 99% of the other was possible but more doubtful.

In the light of these findings, crotyl benzenesulfinate and α -methylallyl benzenesulfinate were allowed to rearrange under conditions approximating those used by Cope and the products examined.

Solutions in toluene which were approximately 1.5 molar in ester were heated for 6½ hours, the α -methylallyl ester at 80° and the crotyl ester at 100°. After removal of the toluene under reduced pressure, the ir and nmr spectra of the residues were measured.

TABLE I

A Summary of the NMR Spectra of α -Methylallyl, α -Methylpropenyl and Crotyl Arenesulfonates and Sulfones

	=CH-	=CH ₂	-CH-	α -CH	γ -CH ₃
α -methylallyl benzenesulfinate	3.80-4.50 (m)	4.52-5.09 (m)	5.09-5.45 (m)	8.69 (t)	
α -methylallyl phenyl sulfone	3.85-4.50 (m)	4.68-5.21 (m)	6.40 (s)	8.62 (d)	γ -CH ₃ 8.19 (d of d)
α -methylpropenyl phenyl sulfone	2.82-3.33 (m)			8.22 (s)	
crotyl benzenesulfinate	-CH=CH- 4.32-4.65 (m)	-CH ₂ - 5.45-6.30 (m)	γ -CH ₃ 8.35 (d of d)		
crotyl phenyl sulfone	4.41-4.72 (m)	6.25-6.46 (m)	8.38 (d of d)		
α -methylallyl 2,6-dimethyl- benzenesulfinate	=CH- 4.00-4.42 (m)	=CH ₂ 4.55-5.07 (m)	-CH- 5.08-5.37 (m)	ArCH ₃ 7.41 (s)	α -CH ₃ 8.61 (d of d)
α -methylallyl phenyl sulfone	4.02-4.52 (m)	4.73-5.26 (m)	6.36 (q)	7.36 (s)	8.58 (d)
α -methylpropenyl 2,6-dimethyl- phenyl sulfone	3.20-3.42 (m)		α -CH ₃ 8.26 (s)	7.42 (s)	γ -CH ₃ 8.22 (d of d)
crotyl 2,6-dimethylbenzenesulfinate	-CH=CH- 4.15-4.44 (m)	-CH ₂ - 5.50-5.68 (m)	ArCH ₃ 7.43 (s)	γ -CH ₃ 8.29 (d of d)	
crotyl 2,6-dimethylphenyl sulfone	4.45-4.68 (m)	6.26-6.46 (m)	7.38 (s)	8.35 (d of d)	

The signals due to the aromatic protons have been omitted

From the spectra, it was estimated that the residues consisted of about 80% unrearranged ester. After basic hydrolysis of the ester and removal of the acid and alcohol formed, the nmr spectrum of the product from the rearrangement of α -methylallyl benzenesulfinate showed signals due to crotyl phenyl sulfone only, there being no evidence of signals due to α -methylpropenyl phenyl sulfone. On the other hand the nmr spectrum of the product from crotyl benzenesulfinate could be rationalized as due to a mixture of crotyl phenyl sulfone, α -methylallyl phenyl sulfone and α -methylpropenyl phenyl sulfone. The integration of the signals indicated that about 35% of the product was crotyl phenyl sulfone.

The detection of α -methylpropenyl phenyl sulfone in the presence of crotyl phenyl sulfone or α -methylallyl phenyl sulfone from the ir spectrum of a mixture was found to be unsatisfactory. The frequency of the absorption bands due to C-H out-of-plane bending of olefins in the region $800 - 1000 \text{ cm}^{-1}$ is characteristic of the substitution pattern of the olefins. α -Methylallyl and crotyl phenyl sulfone give rise to strong absorptions in this region at 930 cm^{-1} and 968 cm^{-1} respectively, with much less intense absorptions present at 850 cm^{-1} and 990 cm^{-1} for the α -methylallyl phenyl sulfone and 865 cm^{-1} and 930 cm^{-1} for the crotyl phenyl sulfone. α -Methylpropenyl phenyl sulfone shows weak bands only at 835 cm^{-1} and 895 cm^{-1} which makes detection of this sulfone uncertain in the presence of either of the other two.

When 2,6-lutidine was added to neutralize any acid formed by decomposition of the ester, crotyl phenyl sulfone was once again the only product which could be detected after saponification of

the residue from the rearrangement of α -methylallyl benzenesulfinate. However, when crotyl benzenesulfinate was heated in this solution containing base, the nmr spectrum of the product after removal of unrearranged ester was consistent with a mixture of α -methylallyl phenyl sulfone and α -methylpropenyl phenyl sulfone. There was no evidence of the presence of crotyl phenyl sulfone.

Reduction of the concentration of the esters to 0.1 molar in toluene, again with 2,6-lutidine added, resulted in a considerable reduction in the rate of their rearrangement and the time of heating was increased to 42 hours. Saponification of the residues by stirring with 0.1 molar sodium hydroxide at room temperature for 12 hours and removal of the alcohols yielded only one product from each ester; crotyl phenyl sulfone from α -methylallyl benzenesulfinate and α -methylpropenyl phenyl sulfone from crotyl benzenesulfinate.

The products of the thermal rearrangement of 0.1 molar solutions of α -methylallyl 2,6-dimethylbenzenesulfinate and crotyl 2,6-dimethylbenzenesulfinate in toluene and 60% ethanol with 2,6-lutidine added were also analyzed by nmr spectroscopy. The nmr spectra of the starting materials and products are detailed in Table I. The results were similar to those described using the benzenesulfinate esters. Crotyl 2,6-dimethylphenyl sulfone was produced when a solution of α -methylallyl 2,6-dimethylbenzenesulfinate in toluene was heated at 80° for 63 hours, while crystalline α -methylallyl 2,6-dimethylphenylsulfone was obtained by heating a toluene solution of the crotyl ester at 100° for 63 hours. The same products were formed when the solvent was 60% ethanol and the heating period was reduced to 17 hours.

When α -methylallyl 2,6-dimethylphenyl sulfone was stirred with 0.1 molar sodium hydroxide at room temperature for 16 hours, or on the steambath for one hour, α -methylpropenyl 2,6-dimethylphenyl sulfone was formed, and was identified by comparison of its ir and nmr spectra with those of α -methylpropenyl phenyl sulfone.

DISCUSSION

Identification of the products of rearrangement of the α -methylallyl and crotyl esters of benzenesulfinic acid and 2,6-dimethylbenzenesulfinic acid has been made largely on the basis of their nmr spectra and a brief discussion follows of some of the aspects of these spectra.

The nmr signal assigned to the methyl group in α -methylallyl benzenesulfinate is described in Table I as a triplet at τ 8.69. This signal was rationalized as consisting of a pair of doublets having $J=7$ Hertz, two of the signals of which were coincident with each other. Since there are two asymmetric centres present in this ester, the sulfur and the carbon atom, the material prepared was a mixture of diastereoisomers. One of the doublets could then be due to the methyl group of one of the diastereoisomers, the chemical shift difference between the signals being 7 Hertz. Two pieces of evidence support this explanation. The nmr signal due to the α -methyl group of the α -methylallyl 2,6-dimethylbenzenesulfinate was obviously a doublet of doublets, the coupling constant of each pair being 6.5 Hertz, while the chemical shift difference was 8 Hertz. This signal can therefore be explained similarly. If the presence of the pair of doublets is due to a diastereoisomeric mixture, then the signal due to the methyl group of either α -methylallyl phenyl sulfone or α -methylallyl 2,6-dimethylphenyl sulfone in which one of the asymmetric centres, that at the sulfur, has been destroyed, should have collapsed to a doublet. This was found to be the case.

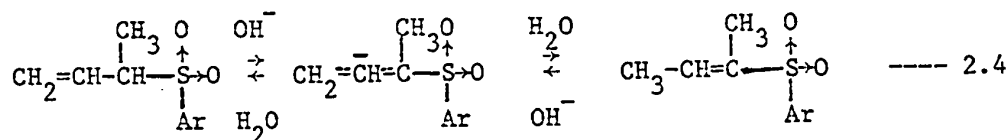
The doublet of doublets observed for the methyl group of crotyl alcohol, the crotyl esters and the crotyl sulfones was not due to a mixture of cis and trans isomers since it has been noted that only the trans alcohol could be detected in the reduction product and approximately equal amounts of the two isomers would have been required to be present to account for the nmr signals. The multiplicity of the signal may be explained by invoking splitting of the expected doublet by coupling of the hydrogens of the methyl group with the cis proton and this is consistent with the very small coupling constant observed ($J = 0.5$ Hertz).

Only under the conditions used by Cope (7) where the rearrangement was allowed to proceed in unbuffered and concentrated toluene solution could the formation of a mixture of sulfones be detected. Under these conditions the product after saponification of the crotyl benzenesulfinate was identified as a mixture containing approximately 35% of crotyl phenyl sulfone, the remainder being α -methylallyl phenyl sulfone and α -methylpropenyl phenyl sulfone. There is considerably less crotyl phenyl sulfone than had been estimated by Cope but before attempting to identify the products, Cope also saponified the unrearranged ester with base and, as will be discussed below, this would lead to isomerization of most or all of the α -methylallyl phenyl sulfone to α -methylpropenyl phenyl sulfone which would be considerably more difficult to detect in the infrared spectrum than α -methylallyl phenyl sulfone itself. Under similar solvent and concentration conditions, α -methylallyl benzenesulfinate rearranged to yield crotyl phenyl sulfone only, a result very similar to that reported by Cope, except that he suggested that this product might contain up to 10% of α -methylallyl phenyl sulfone.

Whenever the reaction mixture contained 2,6-lutidine, the only sulfone produced was that formed by allylic rearrangement in addition to functional group rearrangement. These results agree with those obtained by Braverman (12) and it seems probable that in these cases, the mechanism of the reaction is the same as that outlined by him, namely, a cyclic intramolecular rearrangement with an ionic resonance structure contributing to the transition state.

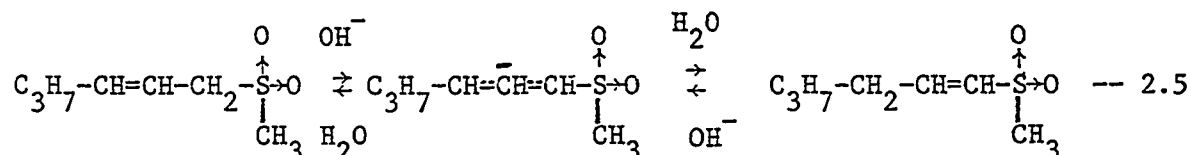
The conditions used by Cope can lead to a more complicated reaction which could include acid catalyzed rearrangement of the ester and acid catalyzed exchange.

The base catalyzed rearrangement of the α -methylallyl phenyl and 2,6-dimethylphenyl sulfones is of some interest. The nmr spectra of the products, α -methylpropenyl phenyl and 2,6-dimethylphenyl sulfones showed a complicated multiplet due to one proton at very low field, (τ 2.83-3.33). Broaddus (58) has measured the nmr spectra of cis and trans 2-hexenyl sulfones and has reported that the signal for the β proton of the trans isomer is at τ 2.9-3.2 while that of both the α and β protons of the cis isomer is at τ 3.6-3.8. The downfield shift of the former signal is attributed to deshielding of the proton by the cis sulfone group. Hence the products of the base-catalyzed rearrangement of the α -methylallyl sulfones were assigned a trans configuration. Their formation in basic solution can be postulated as occurring via an anionic intermediate, (equation 2.4).

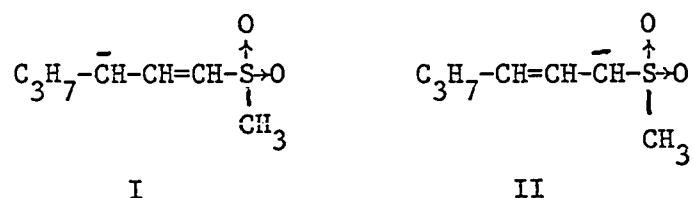


Much effort has been expended in an effort to explain the mode of protonation of allylic anions (59).

Closely related to this system are the 1- and 2-hexenyl methyl sulfones studied by Broaddus (58). The equilibrium between these two sulfones in base is indicated in equation 2.5.

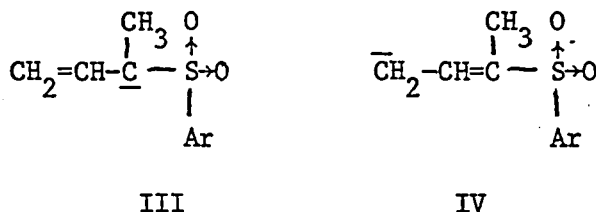


The two major contributors to the resonance stabilized intermediate in this system are I and II. The fact that protonation of II occurs



almost specifically was rationalized on two grounds. Firstly, the contribution of II to the resonance hybrid would be expected to be greater than that of I since the former is destabilized by the presence of an alkyl substituent on the carbon carrying the negative charge. From molecular orbital calculations any participation by d orbitals of the sulfone group has been suggested to affect both allylic positions equally (60), but the inductive effect of this electronegative group will stabilize structure II. Secondly the product of protonation of II, 2-hexenyl methyl sulfone, will be more stable than its double bond isomer 1-hexenyl methyl sulfone, the product of protonation of I. The former has been shown to constitute greater than 99% of an equilibrium mixture (62).

Similar arguments can be used to account for the formation of the α -methylpropenyl phenyl and 2,6-dimethylphenyl sulfones. The main contributing resonance structures to the allylic anion would be III and IV. IV is a primary carbanion, while III will be destabilised by the inductive effect of the methyl group on the



negatively charged carbon and stabilized by the same effect of the sulfone group. Therefore in this case it is somewhat more difficult to deduce the relative distribution of the electron density. However, the product formed by protonation of IV will be thermodynamically more stable than the one formed from III, the double bond being more highly substituted in the former. It is not surprising therefore, that at equilibrium only α -methylpropenyl phenyl sulfone could be detected.

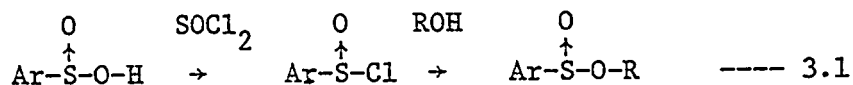
CHAPTER II : THE INVESTIGATION OF OXYGEN-18 SCRAMBLING DURING THE
REARRANGEMENT OF SPECIFICALLY LABELLED ALLYL, CROTYL
AND α -METHYLALLYL 2,6-DIMETHYLBENZENESULFINATES

INTRODUCTION

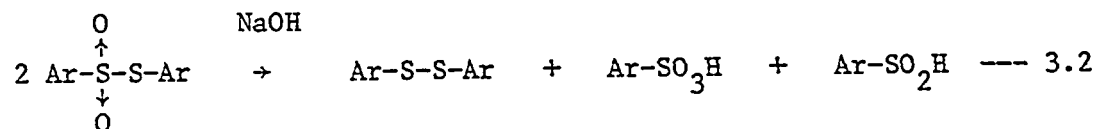
The results obtained by Braverman (12) from his study of the rates and products of rearrangement of a variety of allylic 2,6-dimethylbenzenesulfinates have been used as a basis for the oxygen-18 labelling work to be described in this chapter and in Chapter III. In this chapter, the possibility of the presence of an ion-pair intermediate during the rearrangement of allyl, crotyl and α -methylallyl 2,6-dimethylbenzenesulfinates to sulfones has been investigated. The esters have been prepared having an oxygen-18 label in the sulfinyl-oxygen position and their rates of rearrangement have been measured. The ester remaining after partial rearrangement has been recovered and examined for the presence of an oxygen-18 label in the ether-oxygen position. The results are discussed in the context of the mechanism of the rearrangement.

RESULTS

Allyl, crotyl and α -methylallyl 2,6-dimethylbenzenesulfonates have been synthesized by allowing the corresponding alcohol to react with 2,6-dimethylbenzenesulfinyl chloride in pyridine solution at about -30° in accord with equation 3.1.



If the solution was allowed to become warm during the addition, 2,6-dimethylphenyl 2,6-dimethylbenzenethiosulfonate was formed as an impurity, and could be detected from the ir spectrum since it gave rise to a strong peak at 1335 cm^{-1} . Further, when the allyl ester containing the thiosulfonate impurity was hydrolyzed in 0.1 molar aqueous sodium hydroxide, a very small quantity of a colourless solid precipitated and was identified from its nmr spectrum as 2,6-dimethylphenyl disulfide whose formation can be rationalized as in equation 3.2 (63).



The allyl and α -methylallyl esters were liquids, which, due to their thermal instability, were purified by chromatography on alumina at room temperature. The crotyl ester was a liquid at room temperature but could be crystallized on standing in the refrigerator and was found to have a melting point of about 15° . It too, was purified by chromatography on alumina.

Braverman (12) has shown that when these esters are allowed to react

in ethanol or 60% ethanol with added, 2,6-lutidine, or in acetic acid with added sodium acetate, a greater than 72% yield of the sulfone resulting from allylic isomerization can be isolated. In certain cases he also detected low yields of solvolysis products. His results are collected in Table II.

TABLE II

Yields of Sulfone and Acid Produced During the Reaction of Allyl, Crotyl and α -Methylallyl 2,6-Dimethylbenzenesulfonates.

2,6-Dimethylbenzenesulfonate	Solvent	Base	Temperature	Yield of sulfone	Acid produced
allyl	60% EtOH	2,6-lutidine	90.0°	78.2%	6%
crotyl	60% EtOH	2,6-lutidine	90.0°	85.0%	3.5% ^a
	HOAc	sodium acetate	80.0°	91.5%	
α -methylallyl	60% EtOH	2,6-lutidine	90.0°	72.7%	1%
	HOAc	sodium acetate	80.0°	86.2%	

a - acid produced when sodium acetate used as base.

The rates of disappearance of the esters in ethanol, 60% ethanol and acetic acid were measured by infrared spectroscopy. The chosen wavelength of absorption for each ester is detailed in Table III. In order to determine whether the absorbance obeyed the Lambert Beer Law over the concentration range in which measurements would be made, a standard solution of each ester in ethanol was prepared and aliquots of these solutions were diluted with varying volumes of ethanol to give further solutions of known concentration. Aliquots of each

TABLE III

Absorption Bands of Allyl, Crotyl and α -Methylallyl 2,6-Dimethylbenzenesulfonates Used to Measure the Rate of Disappearance of the Ester.

2,6-Dimethylbenzenesulfonate	ir region scanned microns	ir absorption measured, microns
allyl	9.9-11.5	10.34
crotyl	10.0-11.9	11.15
α -methylallyl	11.5-12.6	12.05

solution were subjected to an extraction procedure. The resulting esters were dissolved in bromoform and the absorption at the appropriate wavelength measured. The results are in Tables IV to VI, and the graphs of absorbance against concentration are shown in Figures 1 to 3. The plots show good linearity and so in addition to verifying the applicability of the Lambert Beer Law under these conditions, they also serve as controls of the extraction procedure.

The results used to calculate the rates of disappearance of the esters in the solvents mentioned are detailed in Tables VII to XIII. 2,6-Lutidine was added to the solutions of the esters in ethanol or 60% ethanol and sodium acetate to the solutions of the esters in acetic acid to prevent catalysis of the reaction by 2,6-dimethylbenzenesulfonic acid, a possible minor product. Graphs of the logarithm of the absorbance against time are shown in Figures 4 to 10. These plots are linear in accord with simple first order kinetics for allyl and crotyl 2,6-dimethylbenzenesulfonates.

TABLE IV

Lambert Beer Law and Extraction Procedure Control for Allyl
2,6-Dimethylbenzenesulfinate. Relationship between Optical
Density and Concentration in Bromoform at 10.34 μ .

(Ester) M	I_0/I	$\log I_0/I$
0.0243	7.368	0.869
0.0202	5.280	0.723
0.0162	3.874	0.589
0.0101	2.787	0.445
0.0061	1.603	0.205

TABLE V

Lambert Beer Law and Extraction Procedure Control for Crotyl
2,6-Dimethylbenzenesulfinate. Relationship Between Optical
Density and Concentration in Bromoform at 11.15 μ .

(Ester) M	I_0/I	$\log I_0/I$
0.02822	5.508	0.741
0.02553	4.477	0.651
0.02058	3.469	0.539
0.01801	2.754	0.440
0.01441	2.388	0.378
0.01205	1.991	0.299
0.00960	1.742	0.241

TABLE VI

Lambert Beer Law and Extraction Procedure Control for α -Methylallyl
2,6-Dimethylbenzenesulfinate. Relationship Between Optical Density
and Concentration in Bromoform at 12.05 μ .

(Ester) M	I_0/I	$\log I_0/I$
0.02798	4.188	0.622
0.02479	3.508	0.545
0.01998	2.825	0.451
0.01749	2.344	0.370
0.01399	2.113	0.325
0.01170	1.849	0.267
0.00932	1.603	0.205

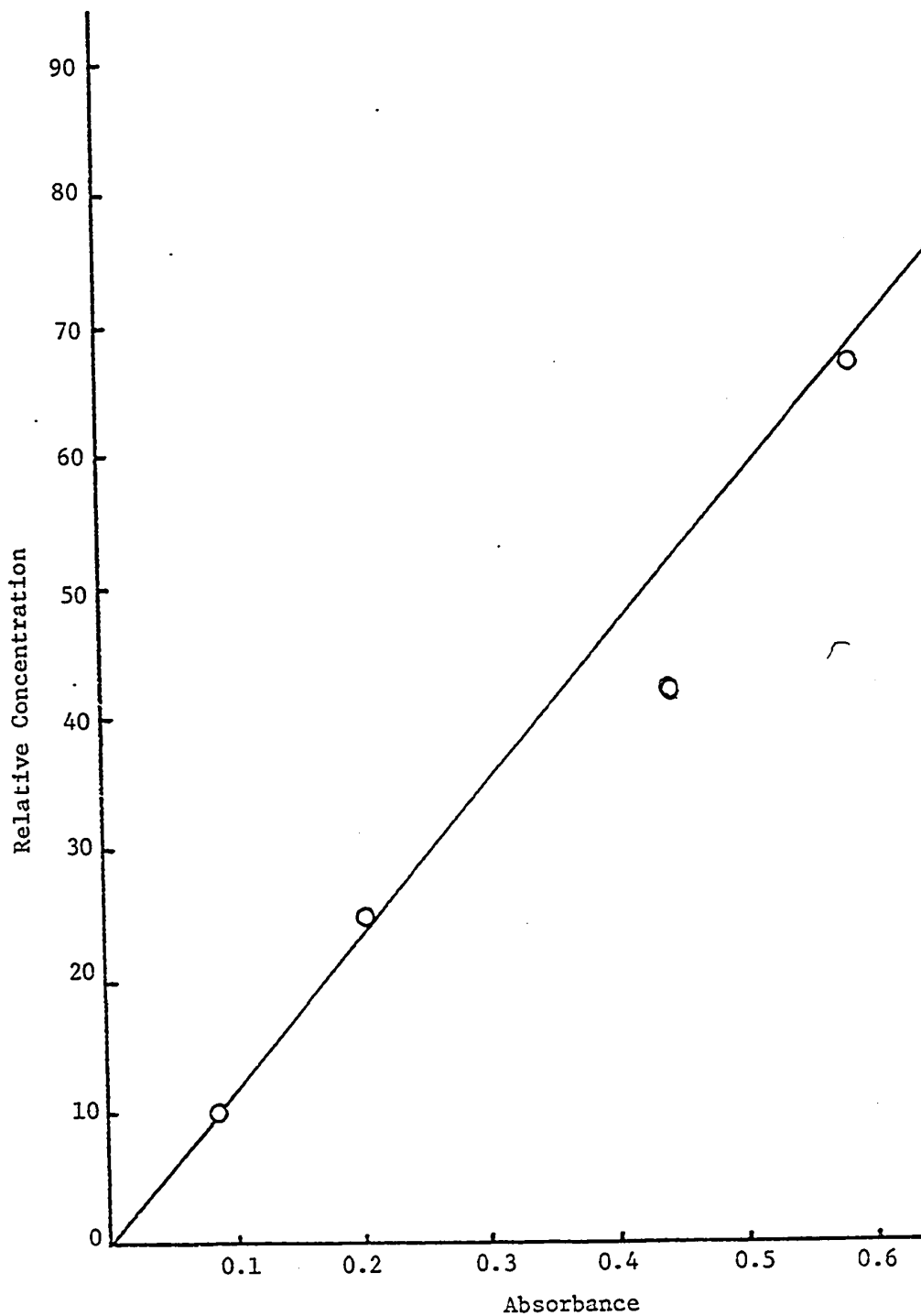


Fig.1 - Lambert Beer Law and Extraction Procedure Control for Allyl 2,6-Dimethylbenzenesulfinate (100 = 0.0243 M)

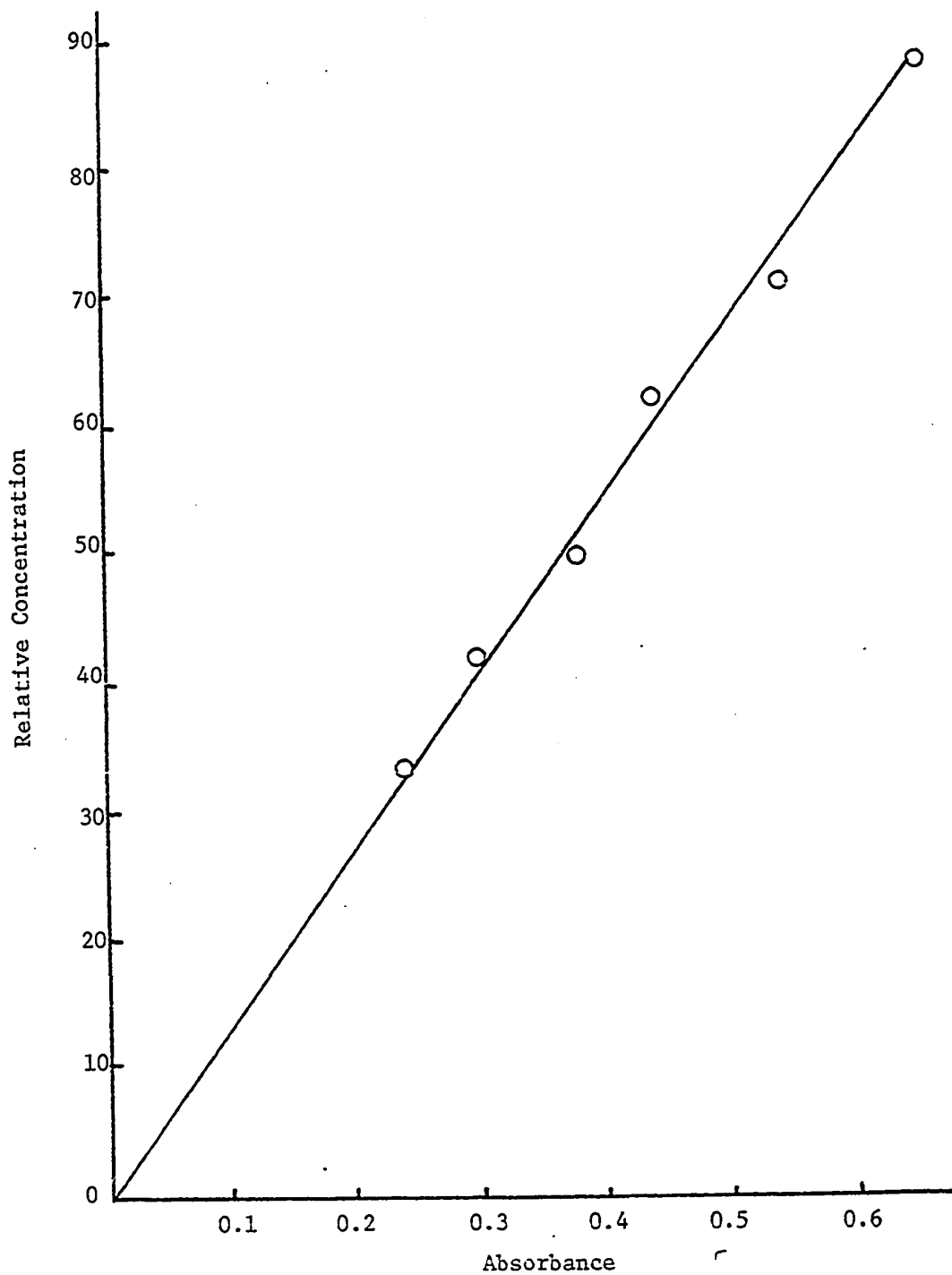


Fig. 2 - Lambert Beer Law and Extraction Procedure Control for Crotyl 2,6-Dimethylbenzenesulfinate (100 = 0.02822 M)

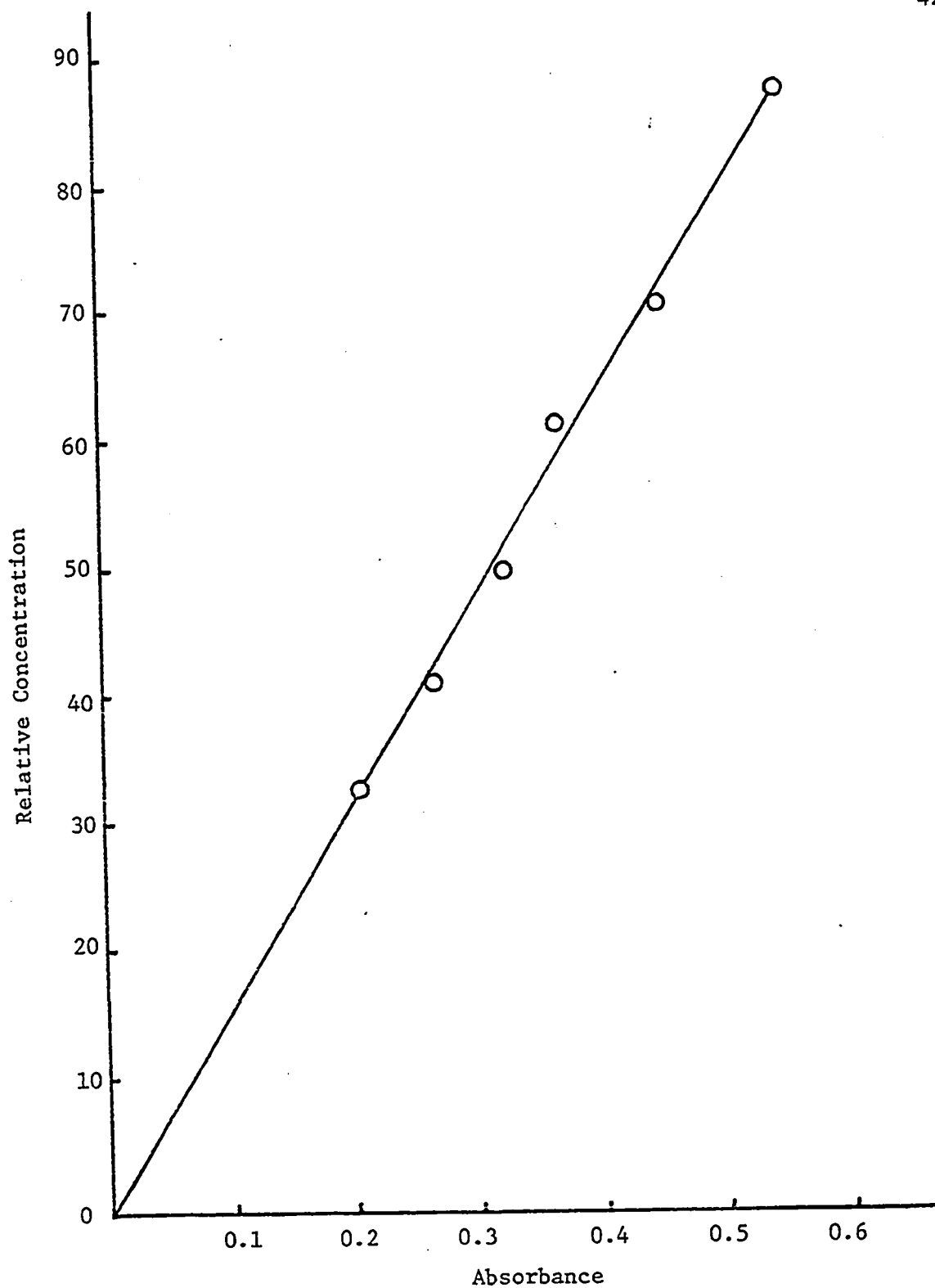


Fig. 3 - Lambert Beer Law and Extraction Procedure Control for α -Methylallyl 2,6-Dimethylbenzenesulfinate (100 = 0.02798 M)

TABLE VII

Rate of Disappearance of Allyl 2,6-Dimethylbenzenesulfinate (0.0219 M)
in 60% Ethanol with Added 2,6-Lutidine (0.0209 M) at 90.0° by
Infrared Spectroscopy.

Time (hour)	I_o/I	$\log \frac{I_o/I}{A_{obs}}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^6$ sec^{-1}	% reaction
0	6.082	0.7840	$\bar{1}.8943$	-	-	-
24	3.564	0.5519	$\bar{1}.7419$	0.1524	4.06	30
48	2.415	0.3829	$\bar{1}.5831$	0.3112	4.15	53
64	2.052	0.3121	$\bar{1}.4943$	0.4000	4.00	60
88	1.573	0.1966	$\bar{1}.2936$	0.6007	4.36	75
112	1.365	0.1351	$\bar{1}.1306$	0.7637	4.34	83

Average value of $k = (4.18 \pm 0.15) \times 10^{-6} \text{ sec}^{-1}$.

TABLE VIII

Rate of Disappearance of Allyl 2,6-Dimethylbenzenesulfinate (0.02385 M)
in Acetic Acid with Added Sodium Acetate (0.02970 M) at 90.0° by
Infrared Spectroscopy.

Time (min.)	I_o/I	$\log I_o/I$ = A_{obs}	$\log A_{obs}$	$\log A_o/A$	$k \times 10^6$ sec^{-1}	% reaction
0	7.133	0.8533	$\bar{1}.9311$	-	-	-
130	6.578	0.8181	$\bar{1}.9129$	0.0182	5.34	4
1048	4.139	0.6169	$\bar{1}.7902$	0.1408	5.15	28
2290	2.448	0.3888	$\bar{1}.5897$	0.3414	5.72	54
3460	1.854	0.2681	$\bar{1}.4283$	0.5028	5.58	68
4220	1.705	0.2316	$\bar{1}.3647$	0.5674	5.16	73
Average value of $k = (5.39 \pm 0.21) \times 10^{-6} \text{ sec}^{-1}$.						

TABLE IX

Rate of Disappearance of Crotyl 2,6-Dimethylbenzenesulfinate (0.02336 M)
in Ethanol with Added 2,6-Lutidine (0.03048 M) at 90.0° by Infrared
Spectroscopy.

Time (sec.)	I_0/I	$\log \frac{I_0}{I}$ $=A_{\text{obs}}$	$\log A_{\text{obs}}$	$\log A_0/A$	$k \times 10^5$ sec^{-1}	% reaction
0	4.767	0.7278	$\bar{1}.8620$	-	-	-
2580	4.135	0.6165	$\bar{1}.7900$	0.072	6.43*	9
5700	3.891	0.5900	$\bar{1}.7709$	0.091	3.68	13
9060	3.192	0.5041	$\bar{1}.7025$	0.159	4.04	26
12600	2.855	0.4556	$\bar{1}.6586$	0.203	4.71	33
17100	2.324	0.3662	$\bar{1}.5637$	0.298	4.01	46
23700	1.891	0.2767	$\bar{1}.4420$	0.420	4.08	59
48000	1.267	0.1028	$\bar{1}.0120$	0.850	4.08	85
Average value of $k = (3.93 \pm 0.16) \times 10^{-5} \text{ sec}^{-1}$.						

* Value not included in average.

TABLE X

Rate of Disappearance of Crotyl 2,6-Dimethylbenzenesulfinate (0.02685 M) in 60% Ethanol with Added 2,6-Lutidine (0.02835 M) at 70.0° by Infrared Spectroscopy.

Time (sec.)	I_o/I	$\log \frac{I_o}{I} = A_{obs}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^5 \text{ sec}^{-1}$	% reaction
0	4.659	0.6683	$\bar{1}.8250$	-	-	-
5040	3.459	0.5389	$\bar{1}.7315$	0.0935	4.27	19
8400	3.195	0.5045	$\bar{1}.7028$	0.1222	3.35	25
13200	2.613	0.4150	$\bar{1}.6180$	0.2070	3.61	38
17280	2.275	0.3570	$\bar{1}.5527$	0.2623	3.50	47
27120	1.776	0.2495	$\bar{1}.3971$	0.4279	3.63	63
40680	1.380	0.1399	$\bar{1}.1459$	0.6791	3.85	79
71160	1.114	0.0467	$\bar{2}.6690$	1.1560	3.74	93

Average value of $k = (3.61 \pm 0.12) \times 10^{-5} \text{ sec}^{-1}$.

TABLE XI

Rate of Disappearance of Crotyl 2,6-Dimethylbenzenesulfinate (0.02686 M)
in Acetic Acid with Added Sodium Acetate (0.03665 M) at 90.0° by
Infrared Spectroscopy.

Time (sec.)	I_o/I	$\log I_o/I$ $=A_{obs}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^5$ sec^{-1}	% reaction
0	7.489	0.8744	$\bar{1}.9417$	-	-	-
2400	4.908	0.6909	$\bar{1}.8394$	0.1023	9.82	21
4200	3.936	0.5951	$\bar{1}.7746$	0.1671	9.49	32
5100	3.641	0.5612	$\bar{1}.7492$	0.1925	8.69	36
6240	3.158	0.4994	$\bar{1}.6985$	0.2432	8.98	43
12600	2.017	0.3047	$\bar{1}.4839$	0.4578	8.37	65
17460	1.604	0.2130	$\bar{1}.3120$	0.6297	8.31	76
23940	1.297	0.1271	$\bar{1}.0531$	0.8376	8.55	87

Average value of $k = (8.89 \pm 0.46) \times 10^{-5} \text{ sec}^{-1}$.

TABLE XII

Rate of Disappearance of α -Methylallyl 2,6-Dimethylbenzenesulfinate
(0.02278 M) in 60% Ethanol with Added 2,6-Lutidine (0.02790 M) at
70.0^o by Infrared Spectroscopy.

Time (sec.)	$\log \frac{I_o}{I}$ = A_{obs}	A_{ext}	A_{calc}	$\log A_{calc}$	$\log A_o/A_{calc}$	$k \times 10^6$ sec^{-1}	% reaction
0	0.5414	0.3758	0.1656	$\bar{1}.2191$	-	-	-
300	0.4938	0.3483	0.1455	$\bar{1}.1629$	0.0562	4.31	12
600	0.4585	0.3304	0.1281	$\bar{1}.1075$	0.1116	4.28	23
1200	0.3863	0.2911	0.0952	$\bar{2}.9786$	0.2405	4.62	44
1800	0.3414	0.2564	0.0750	$\bar{2}.8751$	0.3440	4.40	55
2400	0.2896	0.2254	0.0592	$\bar{2}.7723$	0.4468	4.29	64
3600	0.2104	0.1758	0.0346	$\bar{2}.5391$	0.6800	4.35	79

Average value of $k = (4.38 \pm 0.09) \times 10^{-4} \text{ sec}^{-1}$.

Calculation of rate of disappearance of slow reacting diastereoisomer
overleaf.

TABLE XII (Contd.)

Slow reacting diastereoisomer

Time (sec.)	I_o/I	$\log I_o/I$ $=A_{obs}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^4$ sec^{-1}	% reaction
0	3.479	0.5414	$\bar{1}.575$	-	-	-
1200	2.434	0.3863	$\bar{1}.464$	0.111	2.13	23
2400	1.926	0.2846	$\bar{1}.353$	0.222	2.13	40
5040	1.371	0.1320	$\bar{1}.1362$	0.438	2.00	64
5400	1.335	0.1255	$\bar{1}.0988$	0.476	2.03	68
7200	1.246	0.0938	$\bar{2}.9722$	0.603	1.93	75
10200	1.106	0.0437	$\bar{2}.6405$	0.934	2.11	88
12600	1.054	0.0229	$\bar{2}.3598$	1.215	2.12	93
17280	1.023	0.0099	$\bar{2}.9956$	1.579	2.13	97

Average value of $k = (2.09 \pm 0.07) \times 10^{-4} \text{ sec}^{-1}$.

Ratio of fast to slow reacting diastereoisomer in starting ester = 0.44

TABLE XIII

Rate of Disappearance of α -Methylallyl 2,6-Dimethylbenzenesulfinate
(0.02713 M) with Added Sodium Acetate (0.04470 M) in Acetic Acid at
70.0° by Infrared Spectroscopy.

fast reacting diastereoisomer

Time (sec.)	$\log \frac{I_o}{I}$ = A_{obs}	A_{ext}	A_{calc}	$\log A_{calc}$	$\log A_o/A_{calc}$	$k \times 10^4$ sec^{-1}	% reaction
0	0.6549	0.5117	0.1432	$\bar{1}.156$	-	-	-
300	0.6021	0.4775	0.1247	$\bar{1}.0960$	0.060	4.61*	7
630	0.5651	0.4581	0.1070	$\bar{1}.0294$	0.1266	4.63*	10
900	0.5513	0.4406	0.1107	$\bar{1}.0441$	0.1119	2.86	23
1200	0.5177	0.4246	0.0931	$\bar{2}.9689$	0.1861	3.57	35
2100	0.4631	0.3793	0.0838	$\bar{2}.9230$	0.2330	2.56	42
3600	0.3713	0.3133	0.0580	$\bar{2}.7634$	0.3926	2.51	60
4800	0.3040	0.2685	0.0355	$\bar{2}.5502$	0.6058	2.91	75
6900	0.2248	0.2016	0.0202	$\bar{2}.3054$	0.8506	2.84	86
Average value of $k = (2.89 \pm 0.25) \times 10^{-4} sec^{-1}$							

* Value not included in average.

Calculation of rate of disappearance of slow reacting diastereoisomer
overleaf.

TABLE XIII (Contd.)

slow reacting diastereoisomer

Time (sec.)	I_o/I	$\log I_o/I$ $=A_{obs}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^4$ sec^{-1}	% reaction
0	4.517	0.5117	$\bar{1}.709$	-	-	-
9600	1.4005	0.1464	$\bar{1}.1656$	0.5434	1.30	71
13500	1.2343	0.0913	$\bar{2}.9605$	0.7485	1.28	82
16260	1.1548	0.0626	$\bar{2}.7966$	0.9024	1.28	88
21600	1.0741	0.0315	$\bar{2}.4983$	1.2107	1.29	94
Average value of $k = (1.29 \pm 0.01) \times 10^{-4} \text{ sec}^{-1}$.						

Ratio of fast to slow reacting diastereoisomer in starting ester, 0.28

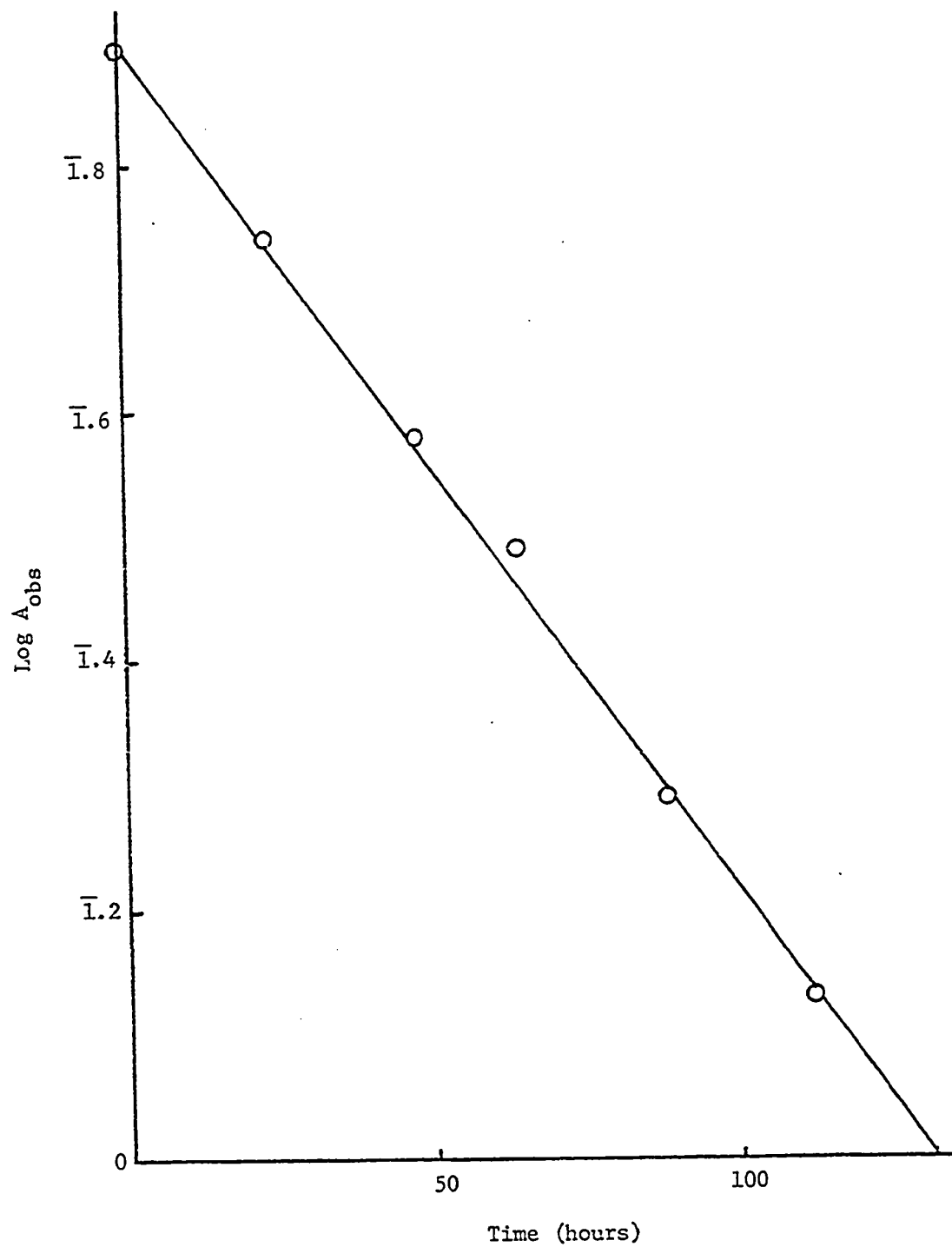


Fig. 4 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of Allyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol at 90.0° (Table VII).

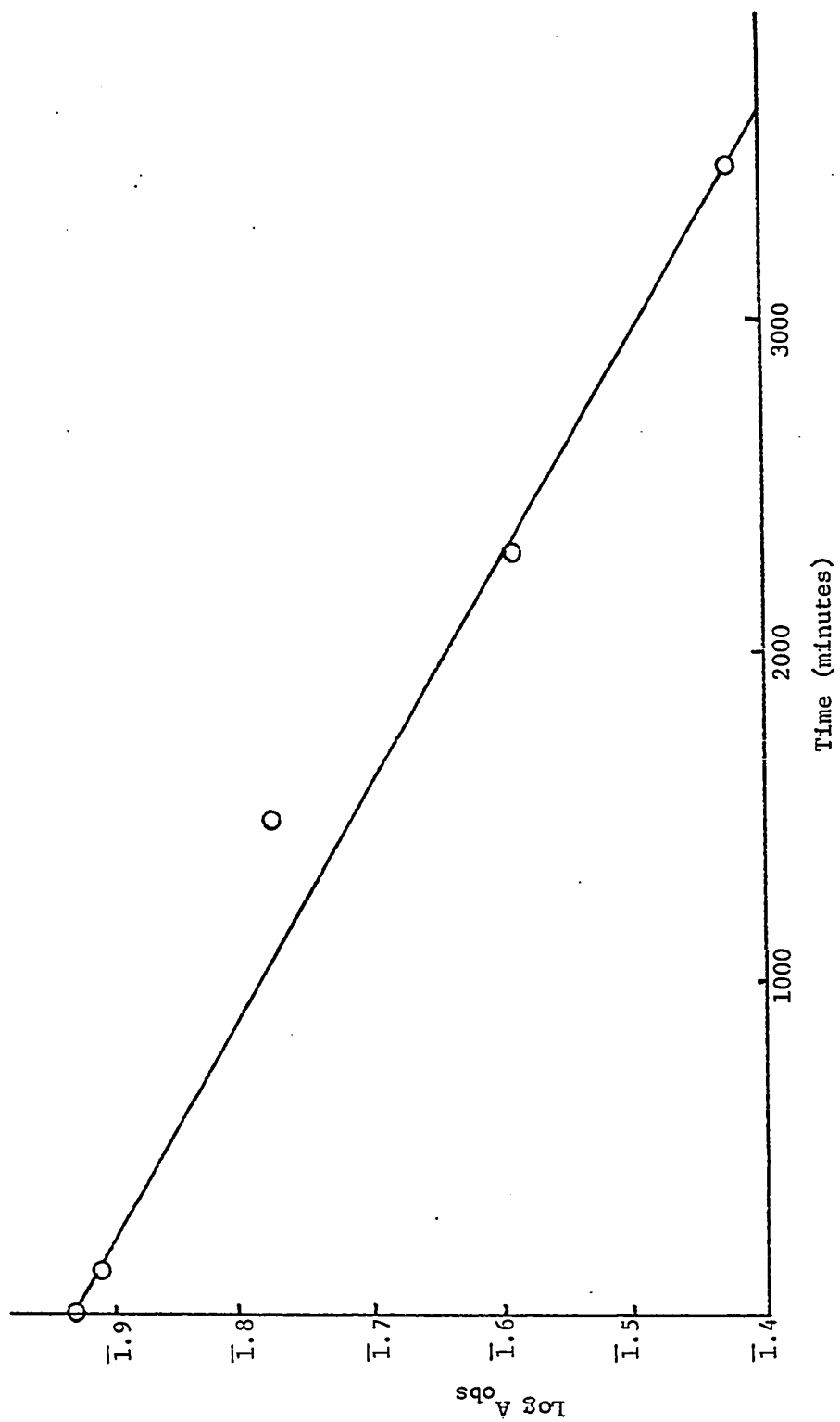


Fig. 5 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of Allyl 2,6-Dimethylbenzenesulfinate in Acetic Acid at 90.0° (Table VIII).

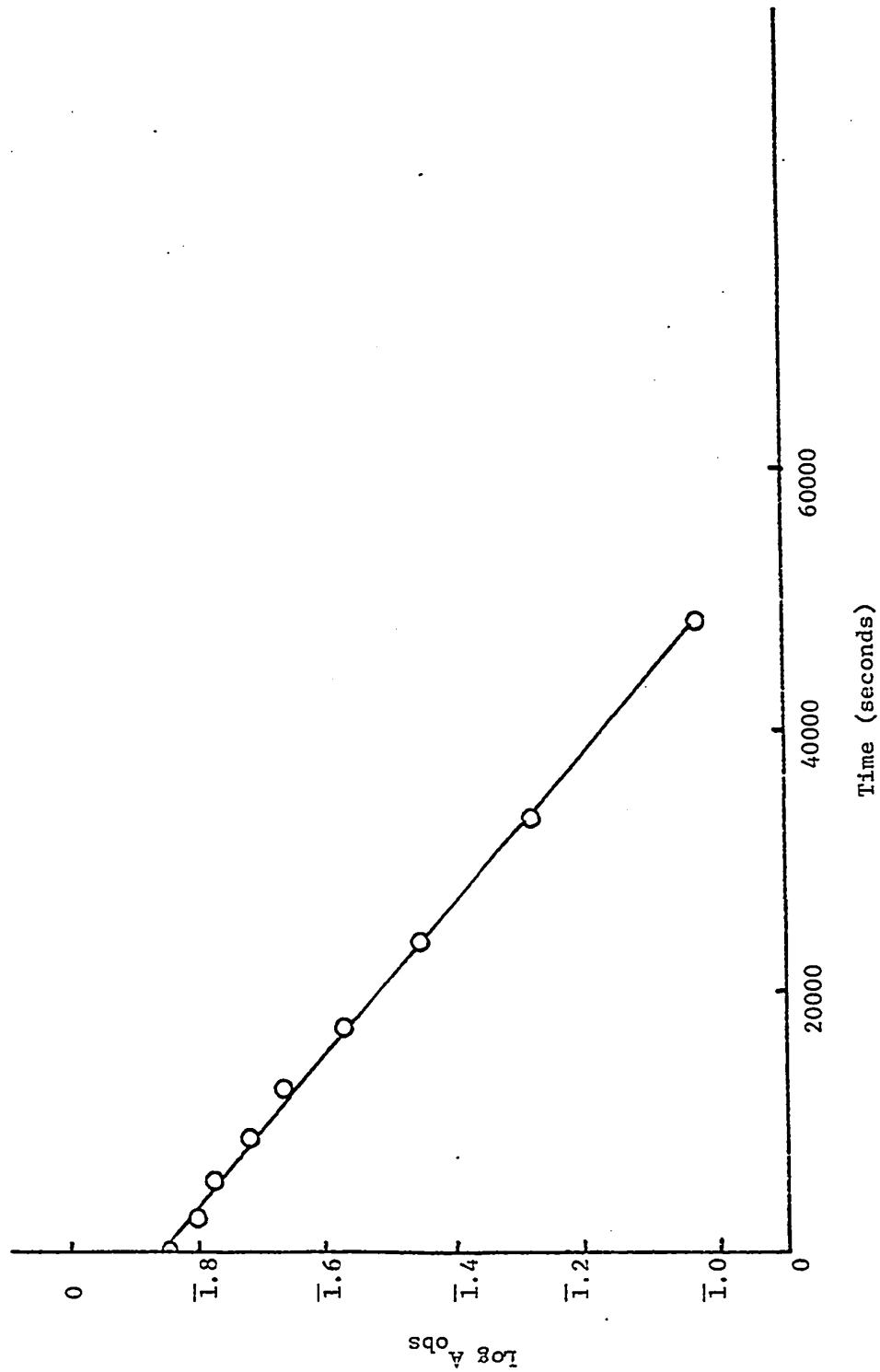


Fig. 6 - Plot of Log A_{obs} Against Time for the Rearrangement of Crotyl 2,6-Dimethylbenzenesulfinate in Ethanol at 90.0° (Table IX).

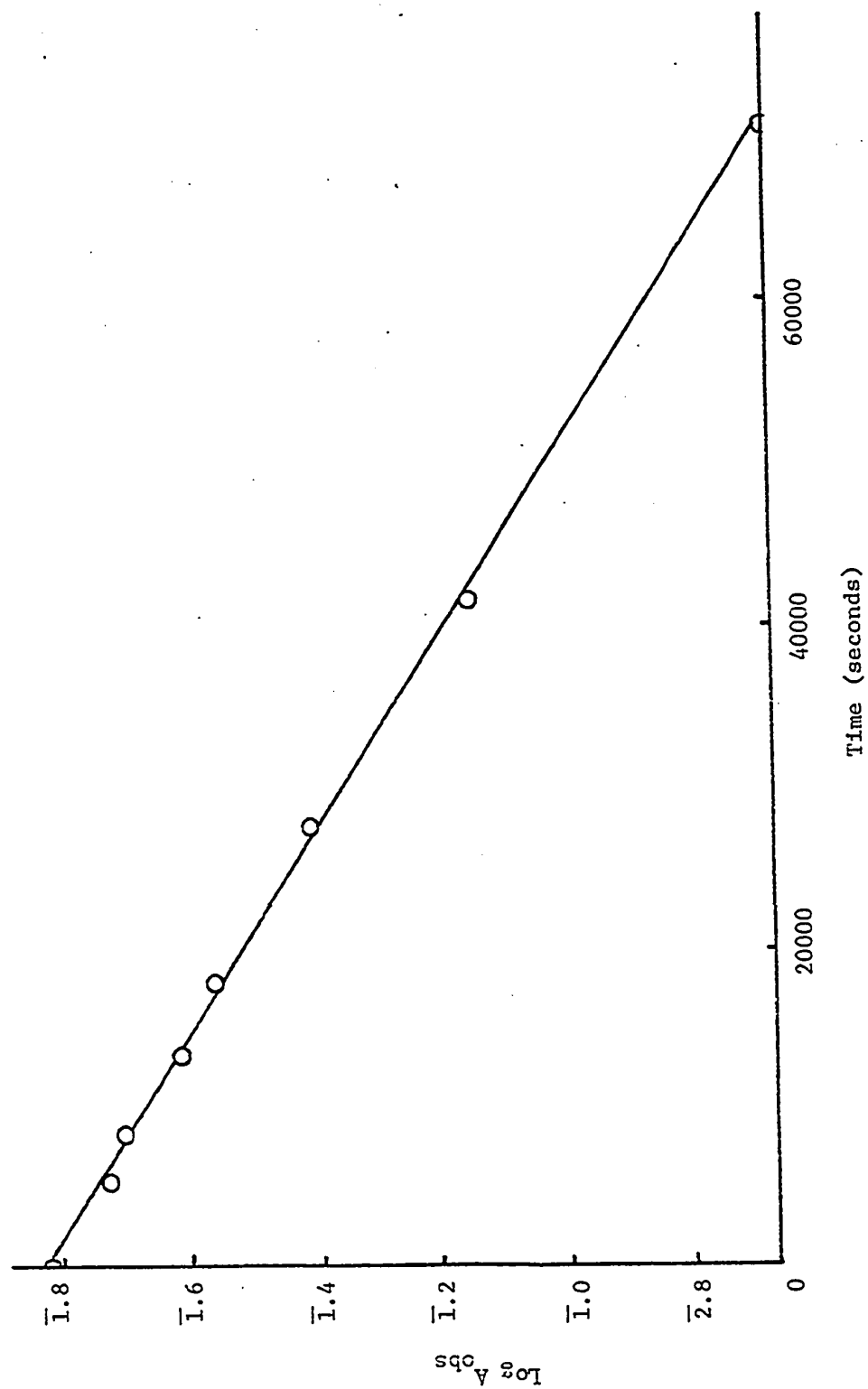


Fig. 7 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of Crotyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol at 70.0° (Table X)

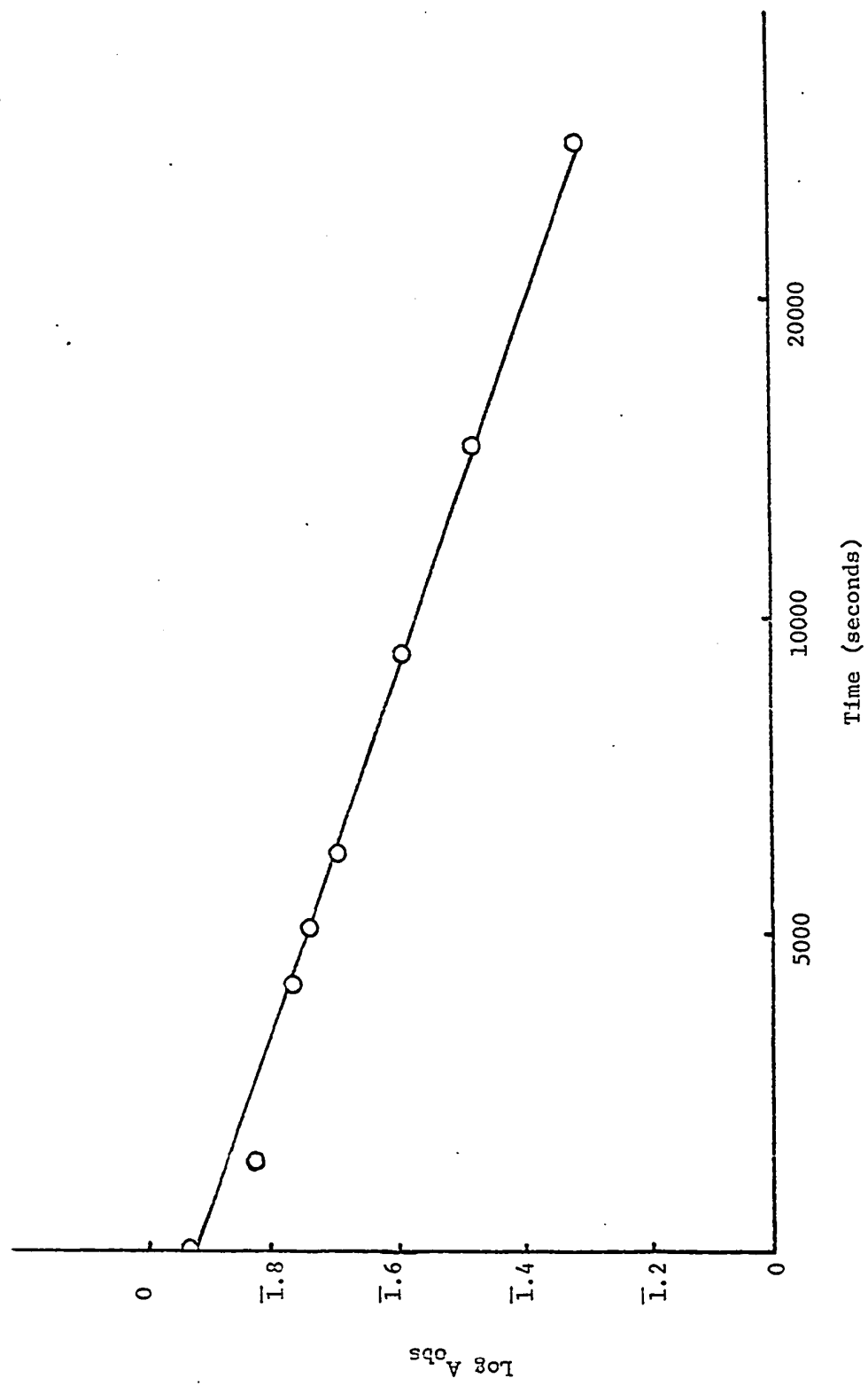


Fig. 8 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of Crotyl 2,6-Dimethylbenzenesulfinate in Acetic Acid at 90.0° (Table XI).

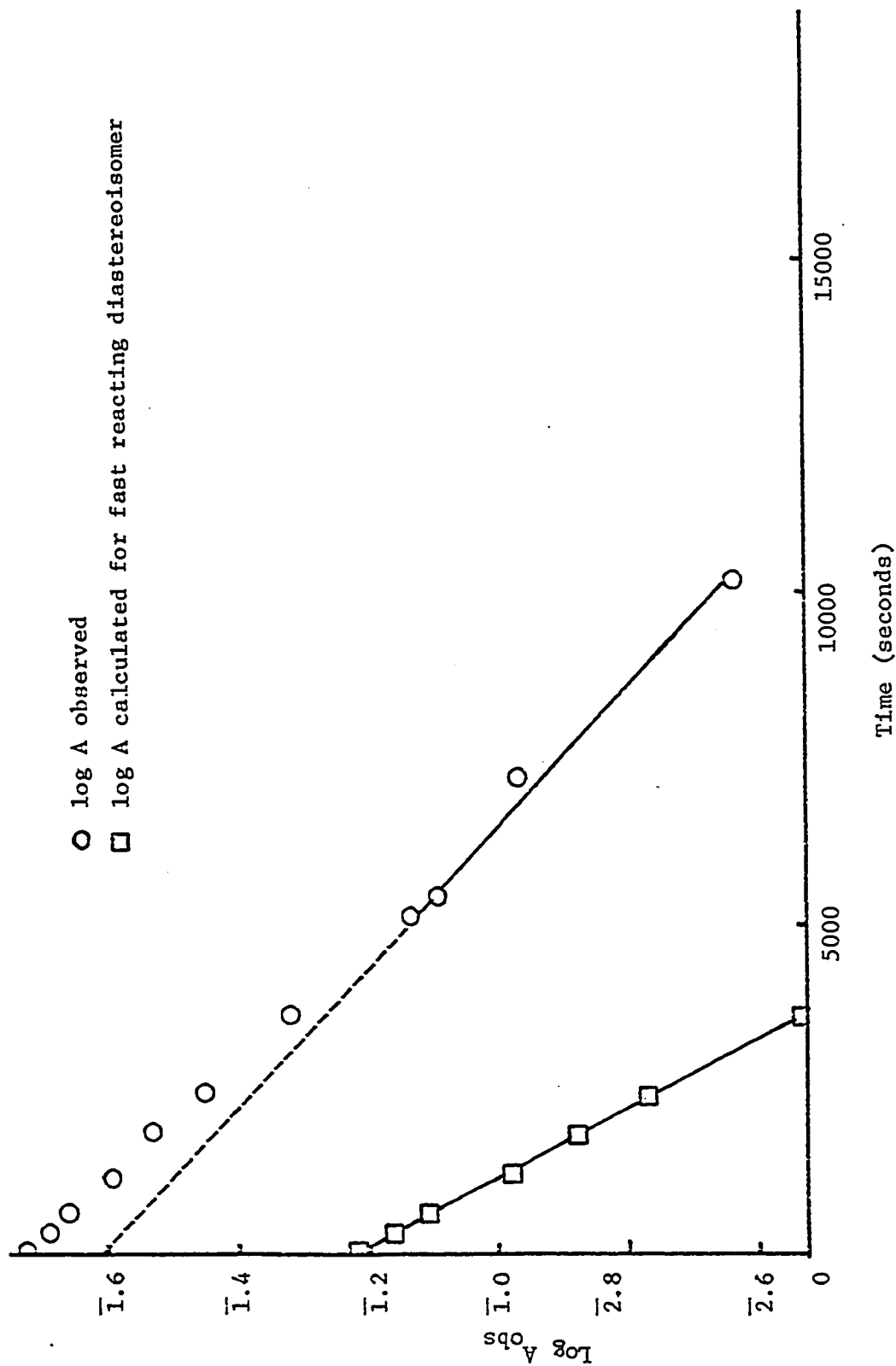


Fig. 9 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of α -Methylallyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol at 70.0° (Table XII).

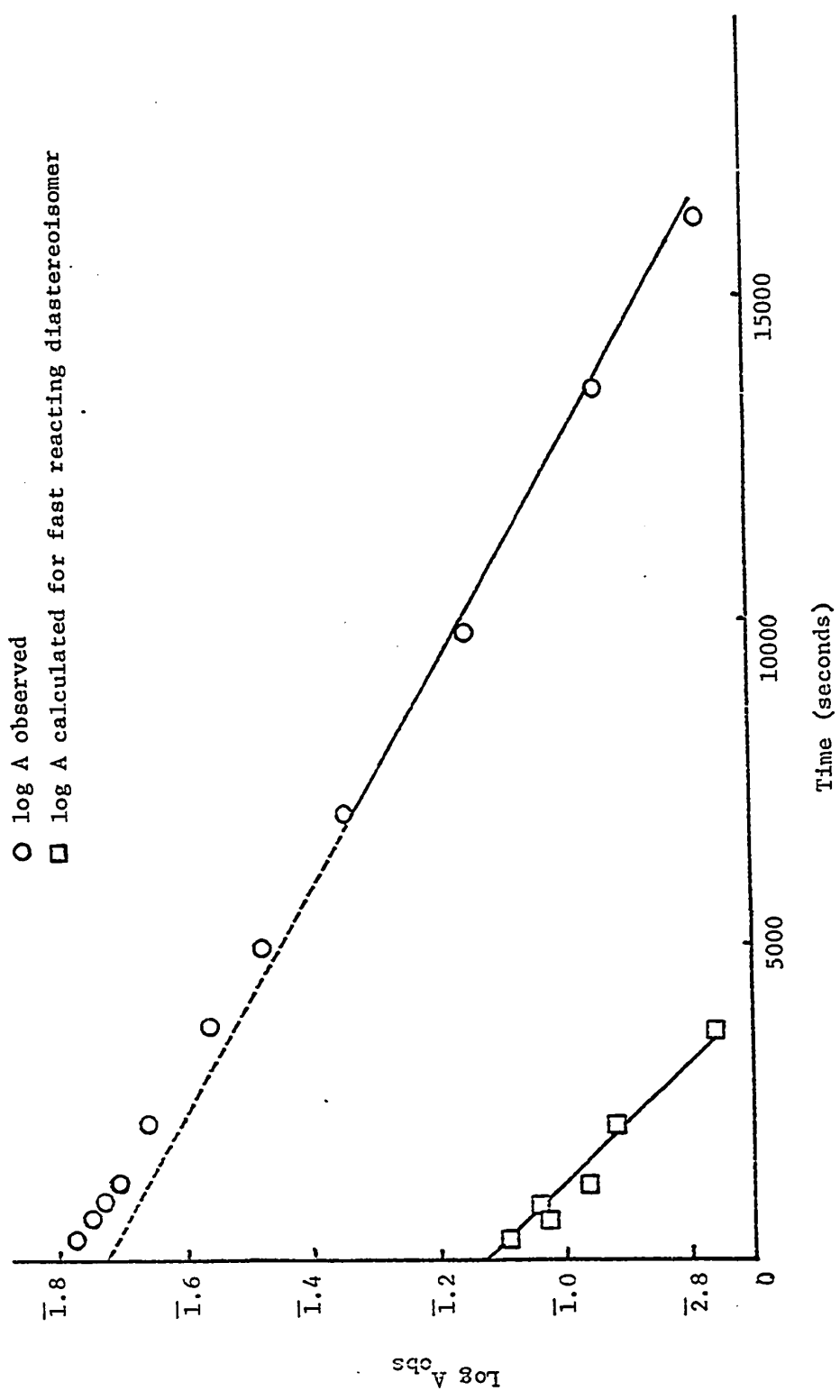


Fig. 10 - Plot of Log A_{obs} Against Time for the Rearrangement of α -Methylallyl 2,6-Dimethylbenzenesulfinate in Acetic Acid at 70.0° (Table XIII).

Accordingly, the rate constants for disappearance of these esters were calculated using equation 3.3.

$$k = \frac{2.303}{t} \log \frac{A_0}{A} \quad \text{--- 3.3}$$

where A_0 is the absorbance of the ester at time zero and A is the absorbance of the ester at time t . The values obtained are included in Tables VII to XIII.

As has been mentioned in Chapter I, α -methylallyl 2,6-dimethylbenzenesulfinate contains two asymmetric centres, the carbon atom of the allyl moiety and the sulfur atom. Hence, this ester exists in four optically active forms or two pairs of diastereoisomers. The two members of each pair will react at precisely the same rate. However, the diastereoisomers will react at different rates. It is to be expected then, that the graphs of the logarithm of the absorbance against time for this ester will no longer be straight lines. As can be seen from Figures 9 and 10, they are initially curved, becoming linear as time increases. The absorbance of this ester includes contributions from both pairs of diastereoisomers, one of which will be called the fast reacting diastereoisomer and the other the slow reacting diastereoisomer. If the assumption is made that there is no interconversion between the diastereoisomers, then after a certain length of time, all of the fast reacting diastereoisomer will have disappeared, and the absorbance should be due to the slow reacting diastereoisomer only. If the rates of disappearance of the diastereoisomers differ by a factor of 2 or more, then it is possible in practice to obtain separate rates of rearrangement for the fast and slow reacting diastereoisomers. After all of the fast reacting diastereoisomer has rearranged, the graph of the logarithm of the

absorbance against time should be a straight line whose slope will be the rate constant for disappearance of the slow reacting diastereoisomer. By extrapolating this straight line portion of the graph to zero time and assuming that the extinction coefficients of the diastereoisomers are the same, the logarithm of the absorbance due to the slow reacting diastereoisomer at any time can be read from the graph. The contributions of the slow reacting diastereoisomer to the absorbance at time t , given as A_{ext} values in Tables XII and XIII were subtracted from the observed absorbance (A_{obs}), also at time t , and the absorbance due to the fast reacting diastereoisomer (A_{calc}) was obtained. When the logarithm of this calculated absorbance was plotted against time, a straight line graph resulted whose slope was the rate constant for rearrangement of the fast reacting diastereoisomer.

A summary of the rate constants obtained is presented in Table XIV. The order of reactivity, and in general, the absolute values of the rate constants are in agreement with those found by Braverman (12).

Oxygen-18 Labelling

The esters were also synthesized having the sulfinyl oxygen labelled with oxygen-18. The isotope was introduced by hydrolyzing the acid chloride in the presence of oxygen-18 labelled water and using this labelled acid to prepare the ester. In this manner, the label was introduced specifically in the sulfinyl-oxygen position. The method is illustrated in equation 3.4.

TABLE XIV

Summary of Rate Constants for Rearrangement of Allyl, Crotyl and α -Methylallyl 2,6-Dimethylbenzenesulfonates.

Ester	Solvent	Base	Temp, °C,	$k \times 10^5$ (sec ⁻¹)	
allyl	60% EtOH	a	90.0°	0.42 ± 0.02	0.46 ± 0.02 ^e
allyl	HOAc	b	90.0°	0.54 ± 0.02	0.65 ± 0.03 ^e
crotyl	EtOH	a	90.0°	3.93 ± 0.16	
crotyl	60% EtOH	a	70.0°	3.61 ± 0.12	16.6 ± 0.7 ^f
crotyl	HOAc	b	90.0°	8.89 ± 0.46	9.37 ± 0.42 ^e
α -methylallyl	60% EtOH	a	70.0°	43.8 ± 0.9 ^c	20.9 ± 0.7 ^d
α -methylallyl	60% EtOH	a	90.0°	235 ± 7 ^{c,e}	64.5 ± 1.5 ^{d,e}
α -methylallyl	HOAc	b	70.0°	28.9 ± 2.5 ^c	12.9 ± 0.1 ^d
α -methylallyl	HOAc	a	90.0°	-	39.4 ± 1.3 ^{d,e}

a - 2,6-lutidine

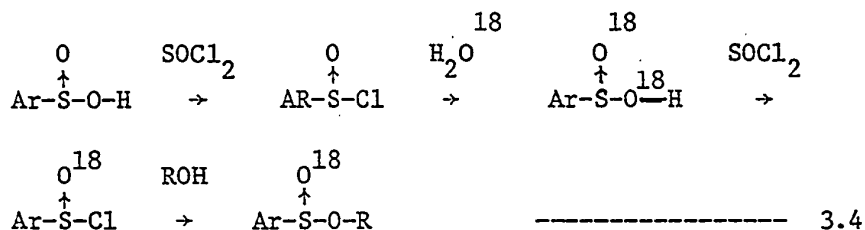
b - sodium acetate

c - fast reacting diastereoisomer

d - slow reacting diastereoisomer

e - values taken from ref. 12

f - run at 90.0°, value taken from ref. 12



The ir and nmr spectra of the labelled esters were superimposable on those of their unlabelled counterparts, and the refractive indices were the same within the experimental error.

The atom excess oxygen-18 in the sulfinyl-oxygen position of the esters was determined using an Unterzaucher apparatus, modified as suggested by Oita and Conway (64) and by Denney and Greenbaum (65). In this process, approximately 15 mg of each ester was pyrolyzed to carbon monoxide which was oxidized by iodine pentoxide to carbon dioxide. The latter was collected in a modified break seal which was suitable for attachment to the mass spectrometer. From the ratio of the peaks at mass 44 and 46 in the mass spectrum of the carbon dioxide, the percent excess oxygen-18 present in the samples could be calculated using the formulae of Goering (36) as detailed below. Each run was made in triplicate and as a control, the mass spectrum of a sample of natural carbon dioxide was measured along with each batch of samples containing oxygen-18.

$$\text{Atom percent excess oxygen-18 in sample} = 100(X - 0.00204)$$

$$\text{where } X = \frac{R'}{1 + R'}$$

$$R' = \frac{R_s}{R_t} \times 0.00409 - 0.00204$$

R_s = 46/44 peak ratio in mass spectrum of sample,

R_t = 46/44 peak ratio in mass spectrum of natural
carbon dioxide.

A sample calculation of the atom excess oxygen-18 in crotyl
2,6-dimethylbenzenesulfinate labelled with oxygen-18 in the
sulfinyl-oxygen position (notebook ref. III-66) is presented.

In CO_2 from ester,

$$\frac{\text{Peak at mass 46}}{\text{Peak at mass 44}} = 0.01396$$

In natural CO_2 ,

$$\frac{\text{Peak at mass 46}}{\text{Peak at mass 44}} = 0.00392$$

$$R' = \frac{0.01396 \times 0.00409}{0.00392} - 0.00204$$

$$= 0.01253$$

$$\text{Atom fraction oxygen-18} = \frac{0.01253}{1.01253}$$

$$= 0.01237$$

$$\text{Atom excess oxygen-18} = 100(0.01237 - 0.00204)$$

$$= 1.033\%$$

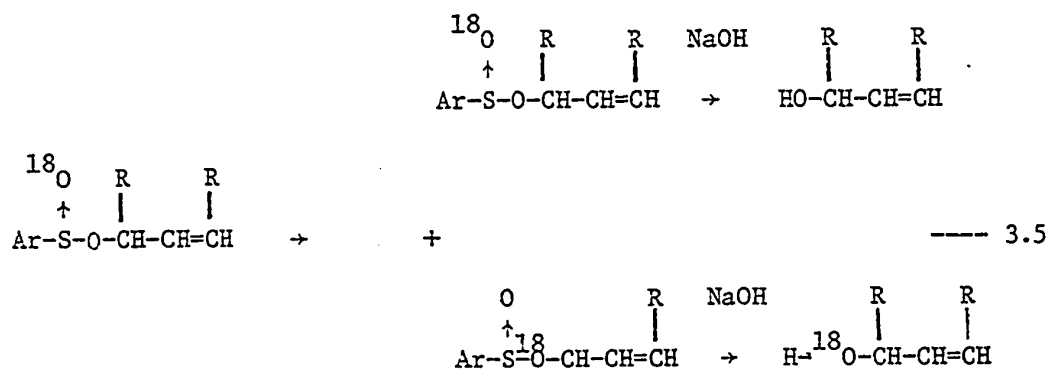
Atom excess oxygen-18 in sulfinyl oxygen position

$$= 2.066\%$$

The percent atom excess oxygen-18 in the sulfinyl-oxygen position
of the esters, synthesized by the method described above using water which

contained 5% water labelled with oxygen-18, varied between 1.98 and 2.50.

Since the presence of oxygen-18 in the ether position of unrearranged ester recovered after partial reaction would give information on the ionization of the system, it was required to measure the rate of appearance of the label in this position. The general method used to accomplish this was to allow partial formation of sulfone to occur, to recover the remaining ester, hydrolyze it by sulfur-oxygen bond fission to a mixture of acid and alcohol and to extract and purify the alcohol. The presence of excess oxygen-18 in the alcohol was detected from the mass spectrum of the carbon dioxide samples formed from the alcohol on pyrolysis, as was described for the determination of excess oxygen-18 in the esters. The oxygen in the alcohol was the ether-oxygen of the ester (67) so that any excess oxygen-18 in the alcohol reflects the presence of oxygen-18 in the ether position of the ester (equation 3.5).



The rates of scrambling of oxygen-18 were measured during rearrangement of the esters in 60% ethanol, acetic acid and, in the case of the crotyl ester, also in anhydrous ethanol. For the

determination of each point in the run, a solution containing approximately one gram of ester in about 150 ml of solvent was required. This solution was sealed in a pressure bottle and suspended in a constant temperature bath at the appropriate temperature. After the required time the solution was worked up as described in the experimental section.

Any allyl alcohol, α -methylallyl alcohol or crotyl alcohol which had been produced by solvolysis during the rearrangement was removed during the work-up procedure by warming the residue under low pressure. In acetic acid, Braverman (12) detected traces of acetates in the sulfones formed by rearrangement of the esters. In the method used for the detection of oxygen-18 scrambling, the acetates would be hydrolyzed by the base along with the unrearranged ester and hence the corresponding alcohol would be produced from both sources. However, the acetates were sufficiently volatile that they could be removed by distillation under reduced pressure prior to hydrolysis.

The 2,6-dimethylbenzenesulfinate esters resulting from the work-up were hydrolyzed under a variety of conditions. It has been shown that using sodium ethoxide as the basic catalyst for the hydrolysis may result in oxygen-18 scrambling during the hydrolysis, (15). As a result the catalyst used in these experiments was sodium hydroxide. Conditions of solvent, temperature and the strength of the base were sought such that complete hydrolysis of the ester would occur in a given time; the combinations of these variables used for each ester are listed in Table XV. When labelled ester which had been dissolved in one of the solvents and immediately worked up was hydrolyzed under the specified conditions, the resulting alcohol contained no excess oxygen-18, and

so no scrambling of the label was occurring during either the work-up or the hydrolysis.

TABLE XV

Conditions for Hydrolysis of Allyl, Crotyl and α -Methylallyl 2,6-Dimethylbenzenesulfinates.

Ester	Solvent	Base Conc.	Temp.	Time
allyl	water	0.2 M	100°	1 hour
crotyl	water	0.2 M	25°	12 hours
α -methylallyl	water	0.2 M	25°	12 hours

The alcohols produced by the hydrolysis were isolated by ether extraction of the basic solution followed by preparative gas chromatography. Details of the column temperature and packing for each case are in Table XVI.

TABLE XVI

Conditions for Preparative Gas Chromatography of Allyl, Crotyl and α -Methylallyl 2,6-Dimethylbenzenesulfinates.

Ester	Column Packing	Temp.	Helium Flow, (cc/min)
allyl ^a	Ucon Oil	100°	25
crotyl ^b	Ucon Oil	119°	100
α -methylallyl ^b	Ucon Oil	111°	120

a- Varian Aerograph A 90P-3 Gas Chromatograph

b- Perkin Elmer Vapor Refractometer Model 154

The recovered alcohols were shown by their ir and nmr spectra, gc retention times and refractive indices to be identical with authentic samples. No impurities could be detected.

Approximately 10 mg samples of each alcohol were converted to carbon dioxide using the modified Unterzaucher method, and the excess oxygen-18 in the carbon dioxide and hence in the alcohol, was calculated in the same manner as that described for the calculation of the excess oxygen-18 in the esters. From these values, again run in triplicate for each sample of alcohol, and from the amount of labelling in the starting esters, the fraction of ester containing oxygen-18 in the ether oxygen position (F_{scr}) could be obtained; equation 3.6.

$$F_{scr} = \frac{2 \times \text{atom percent oxygen-18 in alcohol}}{\text{atom percent excess oxygen-18 in sulfinyl oxygen position of starting ester.}} \quad \text{--- 3.6}$$

The results of the scrambling experiments are in Tables XVII to XXIII. No scrambling of the label was detected during the rearrangement of these esters and so only the values of the ratio of the peaks at mass 46 to the peaks at mass 44 for the alcohol are given along with the value of the ratio for natural carbon dioxide.

There are two possible reasons for the absence of excess oxygen-18 in the alcohols from hydrolysis of the esters recovered after partial rearrangement. Firstly, there may have been no scrambling of the label during the rearrangement, or secondly, carbon-oxygen bond fission may have occurred during the hydrolysis. A direct method of testing for such bond fission would be to label the ether oxygen

TABLE XVII

Results from Scrambling of Oxygen-18 in Allyl 2,6-Dimethylbenzene-sulfinate - sulfinyl-¹⁸O (0.02830 M) in 60% Ethanol with Added 2,6-Lutidine (0.02878 M) at 90.0°.

Run no	Time (hour)	% atom excess oxygen-18 in alcohol	% reaction
I-58-A	0	0.00408	-
I-67-A	17	0.00407	22
I-67-B	24	0.00408	30
I-68-A	48	0.00407	53
I-68-B	73	0.00413	68
I 69-A	98	0.00408	86
I-69-B	112	0.00408	93

% Atom excess oxygen-18 in starting ester = 1.978

Measured % atom excess oxygen-18 in natural carbon dioxide = 0.00408

TABLE XVIII

Results from Scrambling of Oxygen-18 in Allyl 2,6-Dimethylbenzene-sulfinate - sulfinyl-¹⁸O (0.02385 M) in Acetic Acid with Added Sodium Acetate (0.02970 M) at 90.0°.

Run No.	Time (min.)	% atom excess oxygen-18 in alcohol	% reaction
I-230-A	130	0.00400	4
I-230-B	1048	0.00391	28
I-230-C	2290	0.00394	54
I-230-D	3460	0.00385	69
I-230-E	4220	0.00384	73

% Atom excess oxygen-18 in starting ester = 2.702

Measured % atom excess oxygen-18 in natural carbon dioxide = 0.00400

TABLE XIX

Results from Scrambling of Oxygen-18 in Crotyl 2,6-Dimethylbenzene-sulfinate - sulfinyl-¹⁸O (0.03035 M) in Ethanol with Added 2,6-Lutidine (0.02860 M) at 90.0°.

Run No.	Time (sec.)	% atom excess oxygen-18 in alcohol	% reaction
III-138-A	2520	0.00397	9
III-138-B	8400	0.00394	29
III-138-C	18900	0.00392	54
III-138-D	28200	0.00393	67

% Atom excess oxygen-18 in starting ester - 2.066

Measured % atom excess oxygen-18 in natural carbon dioxide = 0.00392

TABLE XX

Results from Scrambling of Oxygen-18 in Crotyl 2,6-Dimethylbenzene-sulfinate - sulfinyl-¹⁸O (0.02685 M) in 60% Ethanol with Added 2,6-Lutidine (0.02835 M) at 70.0°.

Run no.	Time (min.)	% atom excess oxygen-18 in alcohol	% reaction
II-226-A	140	0.00411	25
II-226-B	452	0.00403	63
II-226-C	678	0.00402	79

% Atom excess oxygen-18 in starting ester = 4.056

Measured % atom excess oxygen-18 in natural carbon dioxide = 0.00395

TABLE XXI

Results from Scrambling of Oxygen-18 in Crotyl 2,6-Dimethylbenzene-sulfinate - sulfinyl-¹⁸O (0.02945 M) in Acetic Acid with Added Sodium Acetate (0.03294 M) at 90.0°.

Run no.	Time (sec.)	% atom excess oxygen-18 in alcohol	% reaction
II-250-A	2400	0.00401	41
II-250-B	5100	0.00415	36
II-250-C	8100	0.00400	50
II-250-D	12600	0.00398	65
II-250-E	17700	0.00405	76

% Atom excess oxygen-18 in starting ester = 4.056

Measured % atom excess oxygen-18 in natural carbon dioxide = 0.00394

TABLE XXII

Results from Scrambling of Oxygen-18 in α -Methylallyl 2,6-Dimethylbenzenesulfinate - sulfinyl- ^{18}O (0.02278 M) in 60% Ethanol with Added 2,6-Lutidine (0.02790 M) at 90.0°.

Run no.	Time (Min.)	% atom excess oxygen-18 in alcohol	% reaction
II-225-A	20	0.00401	20
II-225-B	40	0.00398	40
II-225-C	120	0.00404	75

% atom excess oxygen-18 in starting ester = 4.224

Measured % atom excess oxygen-18 in natural carbon dioxide = 0.00395.

TABLE XXIII

Results from Scrambling of Oxygen-18 in α -Methylallyl, 2,6-Dimethylbenzenesulfinate - sulfinyl- ^{18}O (0.02693 M) in Acetic Acid with Added Sodium Acetate (0.03079 M) at 70.0°.

Run no.	Time (sec.)	% atom excess oxygen-18 in alcohol	% reaction	
			FRD	SRD
II-262-A	900	0.00392	22	
II-262-B	2100	0.00392	40	
II-262-C	3600	0.00395	60	
II-262-D	5400	0.00400	80	
II-262-E	8100	0.00409		60

% Atom excess oxygen-18 in starting ester - 4.224

Measured % atom excess oxygen-18 in natural carbon dioxide = 0.00392

of the starting ester with oxygen-18 and to determine whether the alcohol produced on hydrolysis contained a comparable degree of labelling. If carbon-oxygen bond fission were occurring to any extent, then part or all of the label would be lost.

Oxygen-18 labelled allyl alcohol was prepared by solvolyzing allyl bromide in sodium hydroxide solution labelled with oxygen-18. The percent oxygen-18 in the alcohol was not measured. Addition of the labelled alcohol to a pyridine solution of unlabelled 2,6-dimethylbenzenesulfinyl chloride yielded, after work-up allyl 2,6-dimethylbenzenesulfinate which was labelled in the ether-oxygen position with 1.108 atom percent excess oxygen-18. After hydrolysis the alcohol contained 1.052 atom percent excess oxygen-18. Hence insignificant loss of the label from the ether-oxygen position is occurring and the hydrolysis is via sulfur-oxygen rather than carbon-oxygen bond cleavage.

DISCUSSION

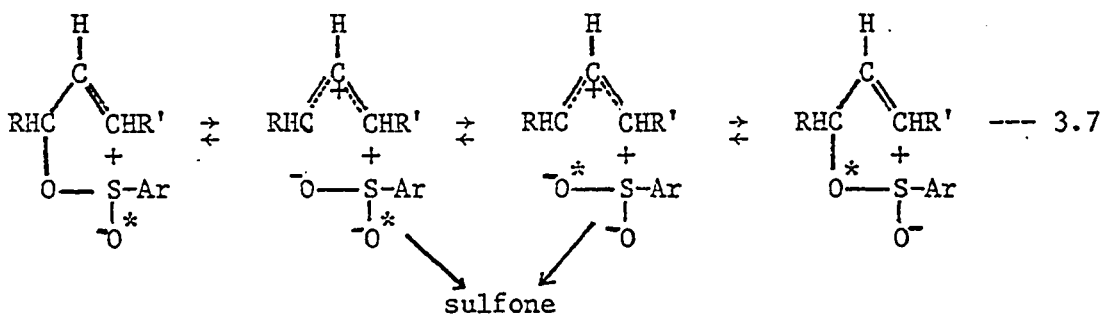
The major products of rearrangement of allyl, crotyl, and α -methylallyl 2,6-dimethylbenzenesulfonates under the reaction conditions are allyl, α -methylallyl and crotyl 2,6-dimethylphenyl sulfones respectively, thus a large fraction of the reaction is occurring via fission of the carbon-oxygen bond and subsequent formation of a carbon-sulfur bond. However, as has been summarized in Table II, minor amounts of solvolysis products have been detected in addition to the sulfone, and their possible mode of formation will be discussed briefly.

The acid produced during the rearrangement of the esters in 60% ethanol could have arisen from either carbon-oxygen or sulfur-oxygen bond fission. It has been shown (69) that in the solvolysis of *p*-methoxyneophyl 2,6-dimethylbenzenesulfonate in 60% ethanol at 90.0° acetate ion is 6.5 times more efficient than 2,6-lutidine in effecting sulfur-oxygen bond fission. Braverman (12) found that, in the rearrangement of allyl 2,6-dimethylbenzenesulfonate, also in 60% ethanol at 90.0°, 4 times more acid was produced in the presence of acetate ion than in the presence of 2,6-lutidine. He therefore concluded that the acid produced during this rearrangement arose from sulfur-oxygen rather than carbon-oxygen bond fission. Similar results were obtained in the rearrangement of the crotyl and α -methylallyl esters and hence similar conclusions were reached concerning the mode of formation of the acid.

Since the reaction of interest in this work, the rearrangement of the sulfonate esters to sulfones, occurs via carbon-oxygen bond

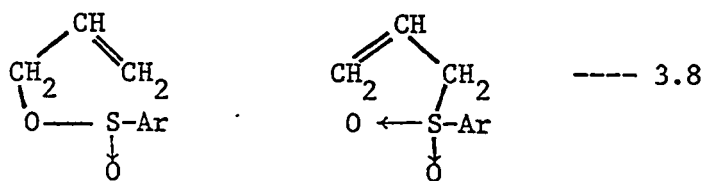
fission, the occurrence of sulfur-oxygen bond fission was depressed by the use of 2,6-lutidine as added base in the solvent systems ethanol and 60% ethanol, while since in acetic acid, the addition of 2,6-lutidine would give rise to acetate ion, sodium acetate itself was added.

It has been described in the introduction how an oxygen-18 labelling technique can be used to detect the presence in a reaction of ionic intermediates which return to covalent starting material. This technique can be employed in systems such as these arenesulfinate esters which give rise to a polydentate anion. A general scheme for rearrangement of the arenesulfinate esters to sulfones involving an ionic intermediate which would result in scrambling of the oxygen-18 label in the ester is illustrated in equation 3.7.

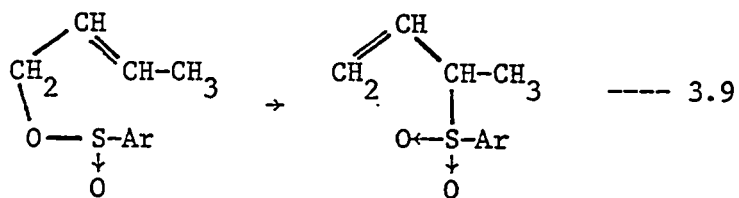


The asterisk denotes an oxygen-18 label.

Allyl 2,6-dimethylbenzenesulfinate rearranges to allyl, 2,6-dimethylphenyl sulfone in 60% ethanol and in acetic acid (equation 3.8).

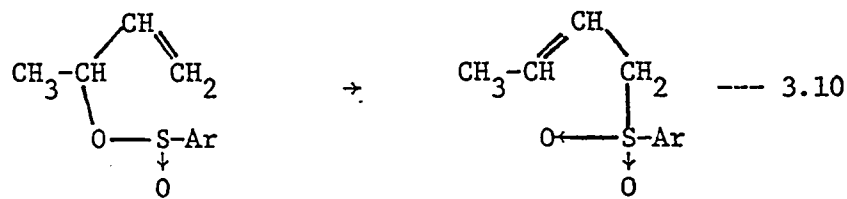


The rate of rearrangement of the crotyl ester to α -methylallyl 2,6-dimethylphenyl sulfone (equation 3.9) is approximately 15 times faster than the rate of rearrangement of the allyl ester.



This rate enhancement is attributed to the presence of the γ -methyl group on the allyl moiety, but, as was mentioned in the introduction, comparison of this rate increase with that caused by the introduction of a methyl group in allylic reactions which involve ionic intermediates shows that it is considerably less than would be expected if the rearrangement proceeded via an ionic intermediate.

Two asymmetric centres are present in α -methylallyl 2,6-dimethylbenzenesulfinate, and hence it was obtained as a mixture of diastereoisomers. The separate rates of rearrangement of the diastereoisomers to crotyl 2,6-dimethylphenyl sulfone (equation 3.10) were deduced from the infrared data and were found to differ by a factor of about 2 in both 60% ethanol and in acetic acid, the only solvents in which the ester was studied. It can be seen from Figures 9 and 10 that a reasonable separation of the rates appeared to have been achieved, straight lines



being obtained when the logarithm of the absorbance of the fast reacting diastereoisomer was plotted against time. It might be noted that the constitution of the starting ester deduced from the absorptions due to the fast and slow reacting diastereoisomers at zero time was quite similar in both runs, although separate preparations were used for each run. The figures suggested the presence of over 70% of the slow reacting diastereoisomer. The rate of rearrangement of the slow reacting diastereoisomer is approximately 5 times greater than the rate of rearrangement of the crotyl ester.

No scrambling of the oxygen-18 label was detected during the rearrangement of the allyl, crotyl or α -methylallyl esters in any of the solvent systems employed. The allyl ester was synthesized with an oxygen-18 label in the ether-oxygen position and it was shown that there was no loss of the label during work-up or ester hydrolysis. Therefore, hydrolysis of the ester must have occurred via sulfur-oxygen bond fission. The conditions used for the hydrolysis of the crotyl and α -methylallyl esters were similar to the conditions used to hydrolyze the allyl ester and hence sulfur-oxygen bond fission should also occur during the hydrolysis of these esters. Since excess oxygen-18 was detected in the alcohols produced by hydrolysis of the α,γ -dimethylallyl, cinnamyl and α -phenylallyl esters recovered after partial rearrangement, sulfur-oxygen bond fission must have occurred during their hydrolysis.

These esters would be more subject to carbon-oxygen bond fission than the crotyl or α -methylallyl esters and so the hydrolysis of the latter esters should occur via sulfur-oxygen bond fission.

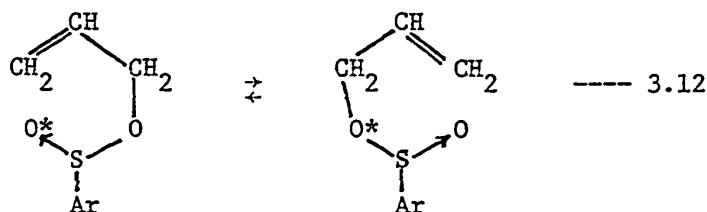
There are two possible explanations for the absence of oxygen-18 scrambling. Firstly, an ion-pair intermediate could be formed which does not return to covalent starting material, or secondly, the rearrangement could proceed via a 5-membered cyclic transition state without the intermediacy of an ionic species. Several considerations allow a choice to be made between these possibilities. The rates of rearrangement of all three esters to the corresponding sulfone have been shown to be faster than would be expected from a purely ionic mechanism, (12). For example, the enhancement in the rate of rearrangement of the allyl ester is ca three powers of ten over an ionic reaction. This rate acceleration was attributed to an extra driving force during the rearrangement which was suggested to be the partial formation of the carbon-sulfur bond in the transition state. Some measure of the degree of charge separation in the transition state can be gained from the sensitivity of the rearrangement to the ionizing power of the solvent. Using the equation suggested by Smith, Fainberg and Winstein (equation 3.11) (22), the sensitivity of the rearrangement can be correlated with that of the rate of ionization of p-methoxyneophyl p-toluenesulfonate.

$$\log k_{\text{rearr}} = a \log k_1 + b \quad \text{---- 3.11}$$

where k_{rearr} is the rate constant for rearrangement of the sulfinate ester, and k_1 is the rate constant for ionization of p-methoxyneophyl

p-toluenesulfonate. The ρ value was suggested to be a measure of the relative sensitivity of a reaction to the ionizing power of the solvent, and was found to be 0.38 for the allyl ester. This value can be compared to a value of 0.94 for *cis*-5-methyl-2-cyclohexenyl acid phthalate which has been interpreted to react by an ion-pair mechanism, (70). The lack of oxygen-18 scrambling during the rearrangement of the allyl, crotyl and α -methylallyl 2,6-dimethylbenzenesulfinates is therefore attributed to the fact that the making and breaking of bonds in the transition state is sufficiently concerted that a discrete ion-pair intermediate is not formed.

The absence of oxygen-18 incorporation into the ether position of the esters precludes rearrangement via a 6-membered transition state to yield the starting ester having the oxygen-18 label in the ether-oxygen position, as illustrated for the allyl ester in equation 3.12.



The asterisk denotes an oxygen-18 label. This type of rearrangement has been observed by Goering in his study of allylic *p*-nitrobenzoates (35, 37, 38, 39). In the sulfinate systems, a 5-membered cyclic transition state will lead to the formation of a stable sulfone, while in the nitrobenzoate systems, there is no driving force for such functional group rearrangement. This 6-membered rearrangement can also be ruled out for the crotyl and α -methylallyl esters which have

asymmetric allylic groups, from the fact that only one sulfone is produced rather than the mixture of two allylic isomers which would be expected if prior isomerization of the starting material were possible. The assumption of no interconversion between the diastereoisomers of the α -methylallyl ester, made in the determination of their rates of rearrangement from the ir spectral data, must be correct since such interconversion would lead to scrambling of the label. This point will be discussed further in Chapter III with reference to the two other esters which exist in diastereoisomeric form α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate and α -phenylallyl 2,6-dimethylbenzenesulfinate.

CHAPTER III : THE DETERMINATION OF OXYGEN-18 SCRAMBLING DURING THE
REARRANGEMENT OF SPECIFICALLY LABELLED CINNAMYL,
 α,γ -DIMETHYLALLYL AND α -PHENYLALLYL 2,6-DIMETHYLBENZENE-
SULFINATES.

INTRODUCTION

Evidence indicating the absence of oxygen equilibration during the rearrangement of allyl, crotyl and α -methylallyl 2,6-dimethylbenzenesulfinates has been presented and discussed in Chapter II. This chapter presents a continuation of studies of oxygen equilibration during the rearrangement of allylic arenesulfinates . Cinnamyl, α,γ -dimethylallyl and α -phenylallyl 2,6-dimethylbenzenesulfinates have been synthesized having an oxygen-18 label in the sulfinyl-oxygen position. The rates of rearrangement of the allylic esters and the rates of incorporation of the oxygen-18 label into the ether-oxygen position of the esters during the rearrangement in ethanol, 60% ethanol and acetic acid have been measured. The presence of oxygen equilibration during the reaction of the esters in several of the solvents has been detected and will be discussed in the context of the mechanism of the reactions.

RESULTS

Cinnamyl alcohol was commercially available. α,γ -Dimethylallyl alcohol was obtained by reaction of crotonaldehyde with methyl Grignard reagent. α -Phenylallyl alcohol was also prepared by a Grignard reaction between phenyl magnesium bromide and acrolein. The 2,6-dimethylbenzenesulfinate esters were prepared by allowing the appropriate alcohol to react with 2,6-dimethylbenzenesulfinyl chloride in pyridine at about -30° .

The α,γ -dimethylallyl ester was a liquid and was purified by chromatography on alumina at room temperature. The α -phenylallyl ester, also a liquid, could be purified on alumina at -70° , but since, even under these conditions, considerable loss of material by rearrangement resulted, it was normally used without purification. This ester could not be obtained free of a small amount (indicated by the nmr spectrum to be less than 2%), of cinnamyl 2,6-dimethylphenyl sulfone. The cinnamyl ester was a low-melting solid which was readily crystallizable from pentane-ether.

The products of the reactions of these esters in 60% ethanol, ethanol and acetic acid have been examined by Braverman (12). His results are collected in Table XXIV. As in the reactions of allyl, crotyl and α -methylallyl 2,6-dimethylbenzenesulfates, reported in Chapter II, the major products of the reactions of these esters are sulfones in which the allylic group has isomerized. Low yields of solvolysis products were also detected.

Some additional results have now been collected on the formation of solvolysis products during the reaction of α -phenylallyl 2,6-

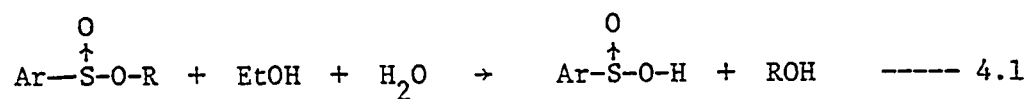
TABLE XXIV

Yields of Sulfone and Acid Produced During the Reaction of Cinnamyl, α,γ -Dimethylallyl and α -Phenylallyl 2,6-Dimethylbenzenesulfonates.

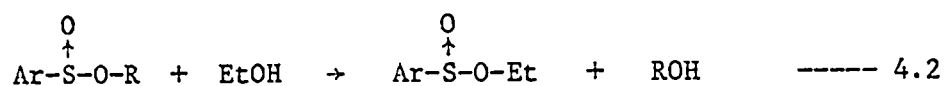
2,6-Dimethyl- benzenesulfonate	Solvent	Base	Temp. °C	Yield of Sulfone	Acid Produced
cinnamyl	60% EtOH	2,6-lutidine	90.0	89%	5.8% (6.4%) ^a
	HOAc	sodium acetate	90.0	86.2%	
α,γ -dimethylallyl	60% EtOH	2,6-lutidine	70.0		1.3%
	HOAc	sodium acetate	80.0	70.2%	7.2%
	EtOH	2,6-lutidine	70.0	82.5%	0%
α -phenylallyl	60% EtOH	2,6-lutidine	25.0	87%	9.8%

a - result from present work

dimethylbenzenesulfonate in 60% ethanol and in anhydrous ethanol, and the reaction of α,γ -dimethylallyl 2,6-dimethylbenzenesulfonate in acetic acid. In 60% ethanol, carbon-oxygen bond fission will give rise to the corresponding alcohol and 2,6-dimethylbenzenesulfonic acid, (equation 4.1) while sulfur-oxygen bond fission may result

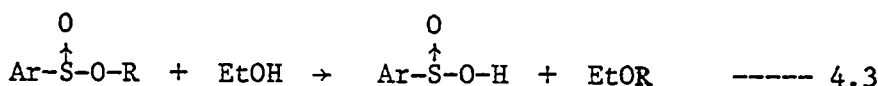


either in the formation of the same products or in ester interchange, (equation 4.2). Therefore the amount of acid produced as determined



by titration with base, represents an upper limit to the degree of carbon-oxygen bond fission which occurred. When α -phenylallyl 2,6-dimethylbenzenesulfinate (0.02538 M) was allowed to react in 60% ethanol with 2,6-lutidine added, for 10 half lives, 9.8% acid was produced. Using sodium acetate as the added base in place of 2,6-lutidine, the yield of acid was 10.4%.

In anhydrous ethanol, sulfur-oxygen bond fission will give rise to ethyl 2,6-dimethylbenzenesulfinate and alcohol (equation 4.2) while carbon-oxygen bond fission will give rise to the free acid and an ether (equation 4.3).



A sample of the ethyl ester was prepared by the addition of ethanol to a cold solution of 2,6-dimethylbenzenesulfinyl chloride in pyridine. Its ir and nmr spectra were measured and compared with those of the residue from the reaction of α -phenylallyl 2,6-dimethylbenzenesulfinate (0.02683 M) in ethanol with added 2,6-lutidine. No signals due to the ethyl ester could be detected and so the residue contained less than 2% of this ester. The residue from the reaction of the α -phenylallyl ester (0.02568 M) in ethanol with added sodium acetate was estimated to contain approximately 5% of the ethyl ester. Titration with base revealed that no 2,6-dimethylbenzenesulfinic acid had been produced in either of these reactions.

The formation of α,γ -dimethylallyl acetate during the rearrangement of the α,γ -dimethylallyl ester in acetic acid has been measured. α,γ -Dimethylallyl acetate was prepared by the reaction of α,γ -dimethylallyl

alcohol with acetic anhydride in pyridine. The ester was found to be stable to gas chromatography on a column packed with Ucon oil, LB-550-X, at 134° and with helium at a pressure of 15 lbs/sq.in. as the carrier gas. Using cyclohexane as an internal standard, a calibration graph was prepared. The residue from the rearrangement of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate was analyzed by gas chromatography under the same conditions, again with cyclohexane added. It was estimated that, after 10 half lives for the rearrangement, 9% of the products were α,γ -dimethylallyl acetate.

The rates of rearrangement of the cinnamyl and α,γ -dimethylallyl esters in ethanol, 60% ethanol and acetic acid were measured by infrared spectroscopy. The rates of rearrangement of the α -phenylallyl ester in the same three solvents were measured by both ir and nmr spectroscopy. The chosen wavelength of absorption in the infrared for each ester is in Table XXV.

TABLE XXV

Absorption Bands of Cinnamyl, α,γ - Dimethylallyl and α -Phenylallyl 2,6-Dimethylbenzenesulfates Used to Measure the Rate of Disappearance of the Ester.

2,6-Dimethyl- benzenesulfinate	ir region scanned microns	ir absorption measured, microns
cinnamyl	11.5-12.4	12.03
α,γ -dimethylallyl	11.4-12.4	11.85
α -phenylallyl	10.5-11.6	10.80

The applicability of the Lambert Beer Law to these absorptions was tested as described in Chapter II. The results are in Tables XXVI to XXVIII, and the absorbance is plotted against concentration in Figures 11 to 13. It can be seen from these figures that straight lines were obtained.

The rates of rearrangement of the esters using infrared spectroscopy were calculated from the results in Tables XXIX to XXXVII. Graphs of the logarithm of the absorbance against time are shown in Figures 14 to 22. Linear plots were obtained for cinnamyl 2,6-dimethylbenzenesulfinate (Figures 14 to 16) and so the rate constants could be obtained using simple first-order kinetics for the allyl and crotyl esters. The values of the rate constants are included in Tables XXIX to XXXI.

α,γ -Dimethylallyl 2,6-dimethylbenzenesulfinate and α -phenylallyl 2,6-dimethylbenzenesulfinate, like the α -methylallyl ester discussed in Chapter II, contain two asymmetric centres and were obtained as mixtures of diastereoisomers. The rates of rearrangement of the fast and slow reacting diastereoisomers were calculated using the method described for the α -methylallyl ester. The calculations are illustrated in Tables XXXII to XXXVII and the results are presented graphically in Figures 17 to 22.

For the α,γ -dimethylallyl ester in acetic acid, and the α -phenylallyl ester in all three solvents, the rates of rearrangement are sufficiently fast that the results, especially for the fast reacting diastereoisomer are subject to somewhat larger errors than those associated with the rate constants for rearrangement of the other esters. A summary of the rate constants obtained together with values obtained

TABLE XXVI

Lambert Beer Law and Extraction Procedure Control for Cinnamyl
2,6-Dimethylbenzenesulfinate. Relationship Between Optical
Density and Concentration in Bromoform at 12.03 μ .

(Ester) M	I_o/I	$\log I_o/I$
0.02931	3.119	0.494
0.02597	2.851	0.455
0.02093	2.249	0.352
0.01832	2.028	0.307
0.01466	1.824	0.261
0.01225	0.652	0.218
0.00976	0.462	0.165

TABLE XXVII

Lambert Beer Law and Extraction Procedure Control for α,γ -Dimethyl-
allyl 2,6-Dimethylbenzenesulfinate. Relationship Between Optical
Density and Concentration in Bromoform at 11.85 μ .

(Ester) M	I_o/I	$\log I_o/I$
0.0299	4.468	0.650
0.02649	3.354	0.575
0.02135	2.919	0.465
0.01869	2.384	0.372
0.01495	2.131	0.328
0.01250	2.003	0.301
0.00996	1.634	0.213

TABLE XXVIII

Lambert Beer Law and Extraction Procedure Control for α -Phenylallyl-2,6-Dimethylbenzenesulfinate. Relationship Between Optical Density and Concentration in Bromoform at 10.80 μ .

(Ester) M	I_0/I	$\log I_0/I$
0.0295	2.322	0.368
0.02614	2.110	0.324
0.02106	1.863	0.270
0.01844	1.821	0.260
0.01475	1.549	0.190
0.01233	1.515	0.180
0.00982	1.374	0.138

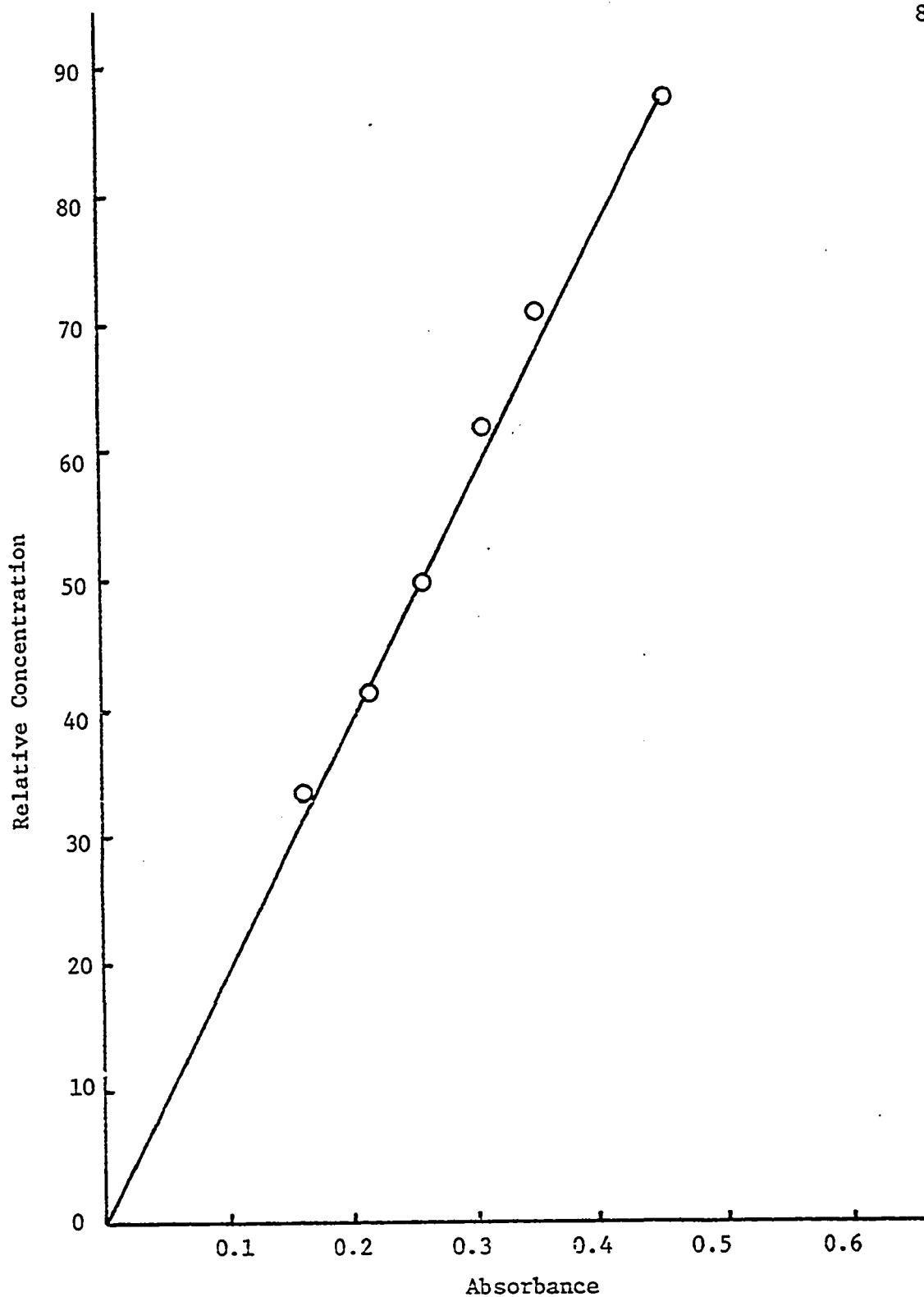


Fig. 11 - Lambert Beer Law and Extraction Procedure Control for
Cinnamyl 2,6-Dimethylbenzenesulfinate (100 = 0.02931 M).

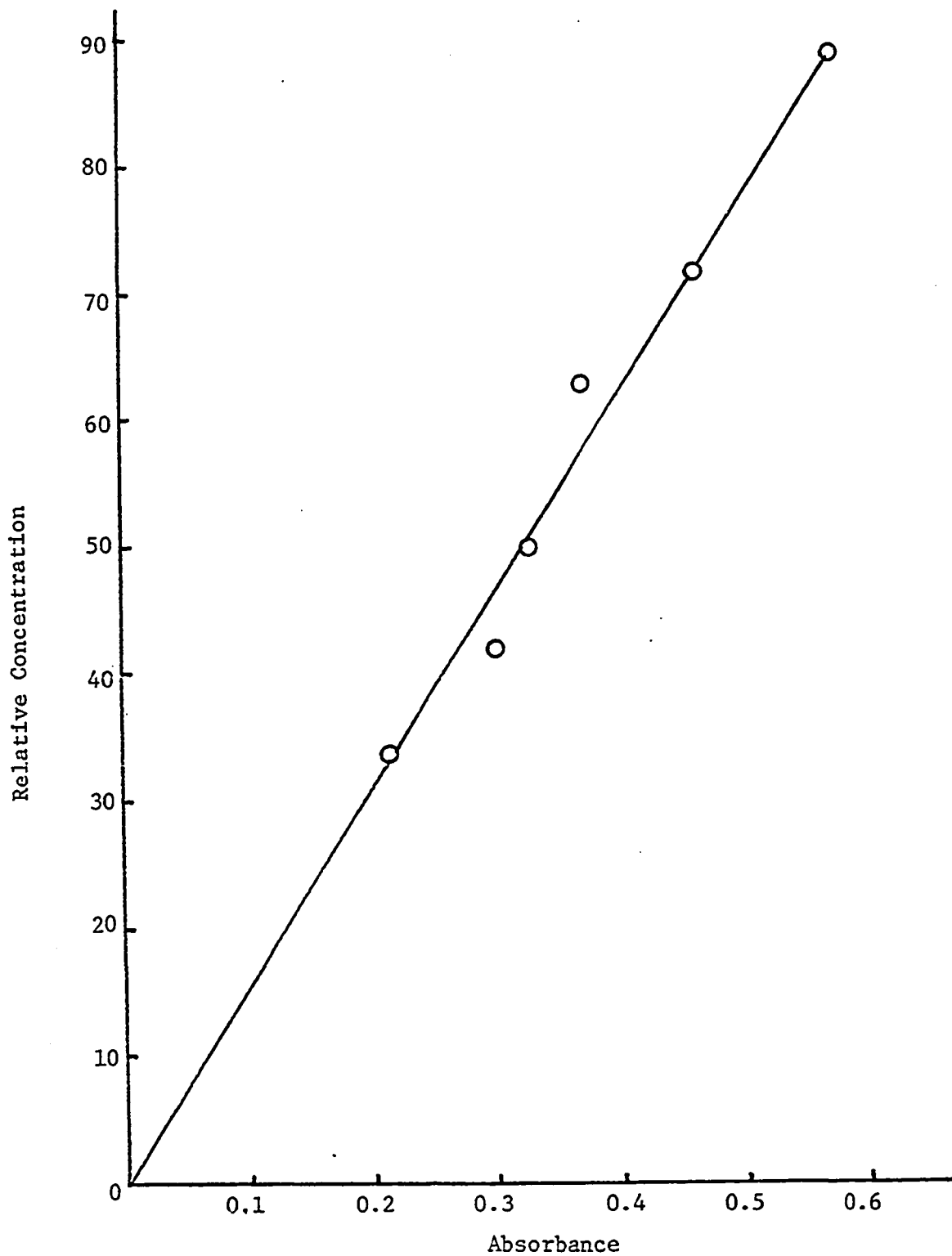


Fig. 12 - Lambert Beer Law and Extraction Procedure Control for α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfinate (100 = 0.0299 M).

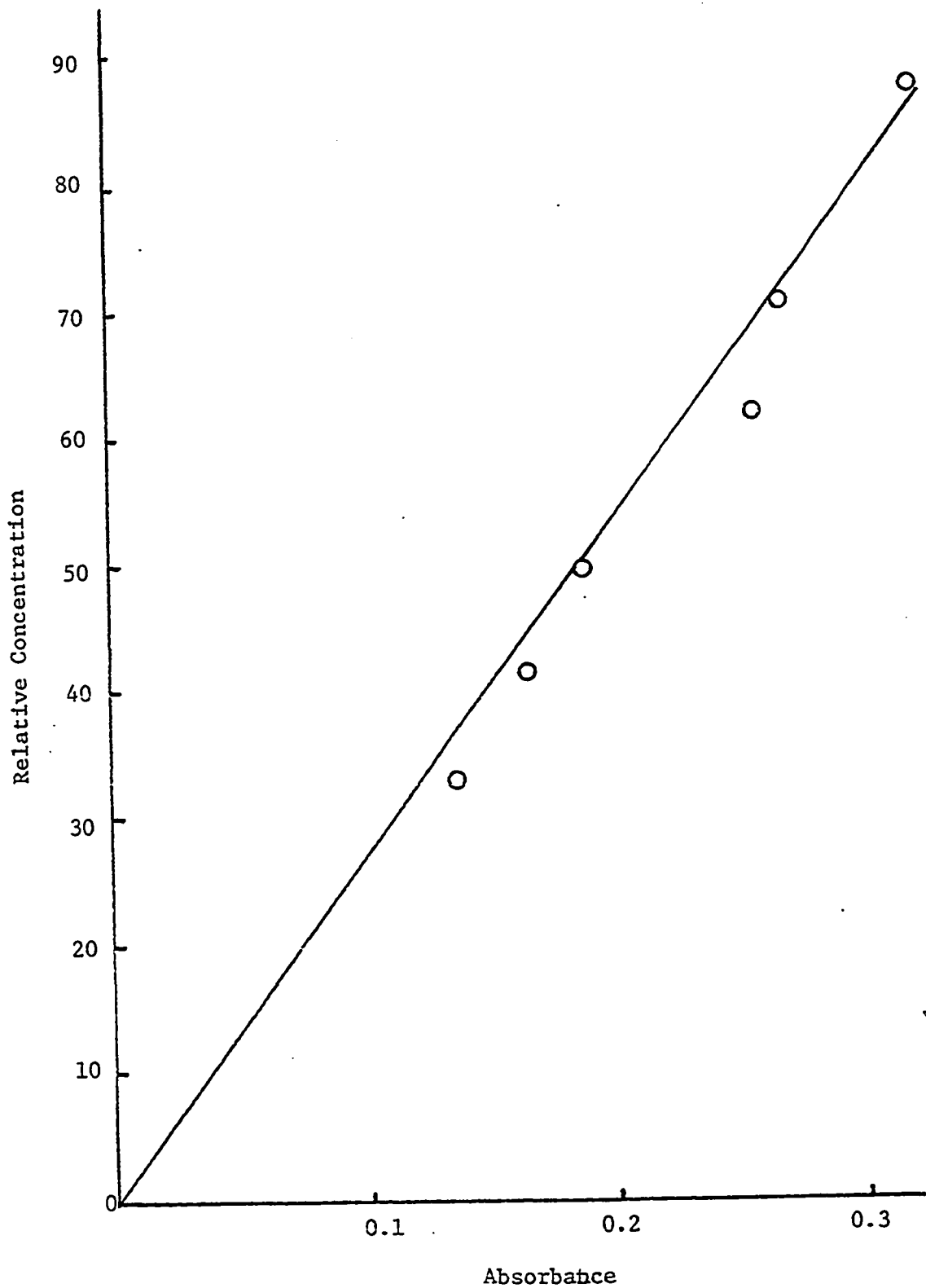


Fig. 13 - Lambert Beer Law and Extraction Procedure Control for α -Phenylallyl 2,6-Dimethylbenzenesulfinate (100 = 0.0295 M).

TABLE XXIX

Rate of Disappearance of Cinnamyl 2,6-Dimethylbenzenesulfinate (0.02833 M)
in Ethanol with Added 2,6-Lutidine (0.02835 M) at 90.0° by Infrared
Spectroscopy.

Time (sec.)	I_o/I	$\log \frac{I_o}{I} = A_{obs}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^4$ sec^{-1}	% reaction
0		0.2930	$\bar{1}.4680$	-	-	-
600	1.861	0.2697	$\bar{1}.4309$	0.037	1.42	8
1440	1.671	0.2230	$\bar{1}.3483$	0.092	1.47	18
2040	1.539	0.1872	$\bar{1}.2723$	0.196	2.21*	25
3000	1.524	0.1829	$\bar{1}.2622$	0.206	1.58	34
4080	1.465	0.1659	$\bar{1}.2198$	0.248	1.40	41
5400	1.361	0.1338	$\bar{1}.1266$	0.341	1.45	53
7200	1.272	0.1045	$\bar{1}.0191$	0.449	1.44	63
9600	1.209	0.0824	$\bar{2}.9159$	0.552	1.32	72

Average value of $k = (1.44 \pm 0.05) \times 10^{-4} \text{ sec}^{-1}$.

* Value not included in average

TABLE XXX

Rate of Disappearance of Cinnamyl 2,6-Dimethylbenzenesulfinate (0.01819 M) in 60% Ethanol with Added 2,6-Lutidine (0.03023 M) at 50.0° by Infrared Spectroscopy.

Time (sec.)	I_o/I	$\log \frac{I_o}{I} = A_{obs}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^5 \text{ sec}^{-1}$	% Reaction
0	1.9187	0.2828	$\bar{1}.4154$	-	-	-
1200	1.8788	0.2739	$\bar{1}.4376$	0.0138	2.65	3
2400	1.8500	0.2672	$\bar{1}.4268$	0.0246	2.36	6
4800	1.8004	0.2553	$\bar{1}.4070$	0.0554	2.66	10
7200	1.7112	0.2332	$\bar{1}.3678$	0.0836	2.67	18
14400	1.5605	0.1934	$\bar{1}.2865$	0.1649	2.69	32
18600	1.4969	0.1753	$\bar{1}.2437$	0.2077	2.57	38
24000	1.4080	0.1485	$\bar{1}.1718$	0.2796	2.68	48
32520	1.3373	0.1262	$\bar{1}.1011$	0.3503	2.48	56
Average value of $k = (2.60 \pm 0.09) \times 10^{-5} \text{ sec}^{-1}$						

TABLE XXXI

Rate of Disappearance of Cinnamyl 2,6-Dimethylbenzenesulfinate (0.02180 M) in Acetic Acid with Added Sodium Acetate (0.04382 M) at 50.0° by Infrared Spectroscopy.

Time (sec.)	I_o/I	$\log \frac{I_o}{I} = A_{obs}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^5 \text{ sec}^{-1}$	% reaction
0	2.452	0.3896	$\bar{1}.5906$	—	—	—
5400	2.277	0.3573	$\bar{1}.5531$	0.0375	1.34	12
16200	2.105	0.3232	$\bar{1}.5095$	0.0811	1.15	17
21600	2.032	0.3079	$\bar{1}.4884$	0.1022	1.09	21
28800	1.197	0.2825	$\bar{1}.4510$	0.1396	1.12	26
43200	1.734	0.2390	$\bar{1}.3784$	0.2122	1.16	39
61200	1.475	0.1688	$\bar{1}.2274$	0.3632	1.37	57
108000	1.277	0.1062	$\bar{1}.0261$	0.5645	1.20	73
144000	1.227	0.0889	$\bar{2}.9489$	0.5732	1.03	77
193500	1.104	0.0430	$\bar{2}.8338$	0.6568	1.02	89
Average value of $k = (1.16 \pm 0.09) \times 10^{-5} \text{ sec}^{-1}$.						

TABLE XXXII

Rate of Disappearance of α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfinate
(0.02601 M) in Ethanol with Added 2,6-Lutidine (0.03229 M) at 50.0⁰
by Infrared Spectroscopy.

Fast reacting diastereoisomer

Time (sec.)	$\log \frac{I_o}{I}$ = A_{obs}	A_{ext}	A_{calc}	$\log A_{calc}$	$\log \frac{A_o}{A_{calc}}$	$k \times 10^4$ sec ⁻¹	% reaction
0	0.6363	0.4343	0.2018	$\bar{1}.3049$	-	-	-
600	0.6200	0.4317	0.1983	$\bar{1}.2974$	0.0075	2.88*	11
1500	0.5508	0.4083	0.1425	$\bar{1}.1538$	0.1571	2.32	25
2400	0.4956	0.3981	0.0975	$\bar{2}.9890$	0.3059	2.94*	37
3600	0.4926	0.3811	0.1115	$\bar{1}.0472$	0.2577	1.65	49
5400	0.4235	0.3581	0.654	$\bar{2}.8156$	0.3893	1.66	63
7200	0.3887	0.3373	0.0514	$\bar{2}.7110$	0.5939	1.90	75
9900	0.3275	0.0255	0.0255	$\bar{2}.4065$	0.8984	2.09	83

Average value of $k = (1.92 \pm 0.23) \times 0.23) \times 10^{-4} \text{ sec}^{-1}$

Calculation of rate of disappearance of slow reacting diastereoisomer
overleaf.

* Value not included in average.

TABLE XXXII (Contd.)

Slow reacting diastereoisomer

Time (sec.)	I_o/I	$\log \frac{I_o}{I} = A_{obs}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^5$ sec^{-1}	% reaction
19200	1.673	0.2235	$\bar{1}.3493$	0.289	3.47	49
22620	1.587	0.2007	$\bar{1}.3025$	0.335	3.41	55
31080	1.424	0.1535	$\bar{0}.0861$	0.452	3.35	65
57900	1.138	0.0562	$\bar{2}.7497$	0.888	3.53	77
78060	1.063	0.0265	$\bar{2}.4232$	1.215	3.58	95
Average value of $k = (3.47 \pm 0.07) \times 10^{-5} \text{ sec}^{-1}$						

Ratio of fast to slow reacting diastereoisomer in starting ester = 0.46

TABLE XXXIII

Rate of Disappearance of α,γ -Dimethylallyl 2,6-Dimethylbenzene-sulfinate (0.0262 M) in 60% Ethanol with Added 2,6-Lutidine (0.0328 M) at 25.0° by Infrared Spectroscopy

Fast reacting diastereoisomer

Time (min.)	$\log \frac{I_o}{I_{=A_{obs}}}$	A_{ext}	A_{calc}	$\log A_{calc}$	$\log \frac{A_o}{A_{calc}}$	$k \times 10^4 \text{ sec}^{-1}$	% reaction
0	0.647	0.473	0.174	$\bar{1}.241$	-	-	-
12	0.596	0.462	0.134	$\bar{1}.127$	0.114	3.66	23
20	0.566	0.455	0.111	$\bar{1}.045$	0.196	3.78	35
45	0.499	0.434	0.065	$\bar{2}.813$	0.428	3.65	63
80	0.426	0.400	0.026	$\bar{2}.416$	0.826	3.98	81
Average value of $k = (3.77 \pm 0.11) \times 10^{-4} \text{ sec}^{-1}$							

Slow reacting diastereoisomer

Time (min.)	I_o/I	$\log \frac{I_o}{I_{=A_{obs}}}$	$\log A_{obs}$	$\log \frac{A_o}{A}$	$k \times 10^5 \text{ sec}^{-1}$	% reaction
180	2.140	0.330	$\bar{1}.519$	-	-	33
420	1.572	0.198	$\bar{1}.297$	0.222	3.54	59
660	1.308	0.116	$\bar{1}.065$	0.454	3.62	75
1065	1.115	0.047	$\bar{2}.672$	0.847	3.68	90
Average value of $k = (3.61 \pm 0.05) \times 10^{-5} \text{ sec}^{-1}$.						

Ratio of fast to slow reacting diastereoisomer in starting ester = 0.37

TABLE XXXIV

Rate of Disappearance of α, γ -Dimethylallyl 2,6-Dimethylbenzenesulfinate
(0.02276 M) in Acetic Acid with Added Sodium Acetate (0.02917 M) at 25.0°
by Infrared Spectroscopy.

Fast reacting diastereoisomer

Time (min.)	$\log \frac{I_o}{I}$ = A_{obs}	A_{ext}	A_{calc}	$\log A_{calc}$	$\log \frac{A_o}{A_{calc}}$	$k \times 10^5$ sec^{-1}	% reaction
0	0.489	0.348	0.141	$\bar{1}.149$	-	-	
20	0.474	0.346	0.128	$\bar{1}.107$	0.042	8.06	9
90	0.421	0.333	0.088	$\bar{2}.945$	0.204	8.70	38
180	0.379	0.317	0.062	$\bar{2}.792$	0.357	7.61	56
240	0.354	0.309	0.045	$\bar{2}.653$	0.496	7.94	68

Average value of $k = (8.08 \pm 0.31) \times 10^{-5} \text{ sec}^{-1}$

Calculation of rate of disappearance of slow reacting diastereoisomer
overleaf.

TABLE XXXIV (Contd.)

Slow reacting diastereoisomer

Time (min.)	I_o/I	$\log \frac{I_o}{I} / I_{=A_{obs}}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^5$ sec^{-1}	% reaction
300	2.094	0.321	$\bar{1}.507$	-	-	22
420	1.923	0.284	$\bar{1}.453$	0.054	1.72	28
800	1.698	0.230	$\bar{1}.362$	0.145	1.11	45
1140	1.466	0.166	$\bar{1}.220$	9.287	1.31	58
1440	1.324	0.122	$\bar{1}.085$	0.422	1.42	68
1800	1.262	0.101	$\bar{1}.005$	0.502	1.28	75
2400	1.172	0.069	$\bar{2}.839$	0.668	1.22	82
Average value of $k = (1.35 \pm 0.15) \times 10^{-5} \text{ sec}^{-1}$						

Ratio of fast to slow reacting diastereoisomer in starting ester = 0.40

TABLE XXXV

Rate of Disappearance of α -Phenylallyl 2,6-Dimethylbenzenesulfinate
(0.02873 M) in Ethanol with Added 2,6-Lutidine (0.02966 M) at 25.0°
by Infrared Spectroscopy.

Fast reacting diastereoisomer							
Time (min.)	$\log \frac{I_0}{I} = A_{\text{obs}}$	A_{ext}	A_{calc}	$\log A_{\text{calc}}$	$\log \frac{A_0}{A_{\text{calc}}}$	$k \times 10^5$ sec^{-1}	% reaction
0	0.474	0.216	0.258	$\bar{1}.411$	-	-	-
140	0.332	0.172	0.160	$\bar{1}.204$	0.206	5.65	39
190	0.275	0.155	0.120	$\bar{1}.079$	0.332	6.71	51
275	0.228	0.137	0.091	$\bar{2}.960$	0.451	6.29	62
340	0.209	0.122	0.087	$\bar{2}.941$	0.470	5.31	71
Average value of $k = (5.99 \pm 0.51) \times 10^{-5} \text{ sec}^{-1}$.							

Slow reacting diastereoisomer

Time (min.)	I_0/I	$\log \frac{I_0}{I} = A_{\text{obs}}$	$\log A_{\text{obs}}$	$\log \frac{A_0}{A}$	$K \times 10^5$ sec^{-1}	% reaction
510	1.233	0.0914	$\bar{2}.961$	-	-	55
650	1.211	0.0830	$\bar{2}.919$	0.416	2.46	65
780	1.148	0.0603	$\bar{2}.780$	0.555	2.73	71
900	1.096	0.0399	$\bar{2}.601$	0.734	3.13	78
1080	0.086	0.0361	$\bar{2}.558$	0.777	2.76	82
Average value of $k = (2.78 \pm 0.16) \times 10^{-5} \text{ sec}^{-1}$						

Ratio of fast to slow reacting diastereoisomer = 1.19

TABLE XXXVI

Rate of Disappearance of α -Phenylallyl 2,6-Dimethylbenzenesulfinate
(0.0232 M) in 60% Ethanol with Added 2,6-Lutidine (0.0298 M) at 25.0°
by Infrared Spectroscopy.

Fast reacting diastereoisomer

Time (sec.)	$\log \frac{I_o}{I} = A_{obs}$	A_{ext}	A_{calc}	$\log A_{calc}$	$\log \frac{A_o}{A_{calc}}$	$k \times 10^4$ sec^{-1}	% reaction
0	0.395	0.176	0.219	$\bar{1}.341$	-	-	-
300	0.314	0.163	0.151	$\bar{1}.178$	0.163	1.25	25
600	0.254	0.125	0.129	$\bar{1}.109$	0.232	0.89	45
900	0.191	0.083	0.108	$\bar{1}.035$	0.306	0.78	59
Average value of $k = (9.70 \pm 0.18) \times 10^{-4} \text{ sec}^{-1}$							

Slow reacting diastereoisomer

Time (sec.)	I_o/I	$\log \frac{I_o}{I} = A_{obs}$	$\log A_{obs}$	$\log \frac{A_o}{A}$	$k \times 10^4$ sec^{-1}	% reaction
1800	1.300	0.114	$\bar{1}.057$			
2400	1.252	0.098	$\bar{2}.992$	0.065	2.50	14
3000	1.223	0.087	$\bar{2}.940$	0.117	2.24	35
4500	1.155	0.062	$\bar{2}.793$	0.264	2.25	53
6300	1.100	0.040	$\bar{2}.602$	0.455	2.33	70
Average value of $k = (2.33 \pm 0.09) \times 10^{-4} \text{ sec}^{-1}$						

Ratio of fast to slow reacting diastereoisomer = 1.24

TABLE XXXVII

Rate of Disappearance of α -Phenylallyl 2,6-Dimethylbenzenesulfinate
(0.02900 M) in Acetic Acid with Added Sodium Acetate (0.04094 M) at
25.0° by Infrared Spectroscopy.

Time (sec.)	$\log I_o/I$ = A_{obs}	A_{ext}	A_{calc}	A_{calc}^{log}	$\log A_o/A_{calc}$	$k \times 10^4$ sec ⁻¹	% reaction
0	0.7186	0.3436	0.3750	$\bar{1}.5740$	-	-	
360	0.5753	0.3236	0.2517	$\bar{1}.4009$	0.1731	11.60	28
540	0.5394	0.2944	0.2415	$\bar{1}.3829$	0.1911	8.15	40
900	0.4338	0.2512	0.1826	$\bar{1}.2615$	0.3125	8.00	56
1200	0.3818	0.2399	0.1519	$\bar{1}.1815$	0.3925	7.53	61
1500	0.3104	0.2291	0.0813	$\bar{2}.9101$	0.6639	10.19	75
1800	0.2920	0.2188	0.0732	$\bar{2}.8645$	0.7095	9.09	80
Average value of $k = (9.00 \pm 1.11) \times 10^{-4}$ sec ⁻¹							

Calculation of rate of disappearance of slow reacting diastereoisomer
overleaf.

TABLE XXXVII (Contd.)

Slow reacting diastereoisomer

Time (sec.)	I_o/I	$\log \frac{I_o}{I} = A_{obs}$	$\log A_{obs}$	$\log A_o/A$	$k \times 10^4$ sec^{-1}	% reaction
2100	1.721	0.2357	$\bar{1}.3723$	0.163	1.79	31
2400	1.640	0.2148	$\bar{1}.3320$	0.203	1.95	35
3000	1.599	0.2037	$\bar{1}.3091$	0.226	0.73	42
3600	1.479	0.1700	$\bar{1}.2304$	0.305	0.95	49
6000	1.308	0.1165	$\bar{1}.0663$	0.469	0.80	66
7200	1.254	0.0973	$\bar{2}.988.$	0.547	0.75	73
9000	1.189	0.0752	$\bar{2}.8762$	0.659	0.69	80
Average value of $k = (1.81 \pm 0.08) \times 10^{-4} \text{ sec}^{-1}$						

Ratio of fast to slow reacting diastereoisomer in starting ester = 1.10

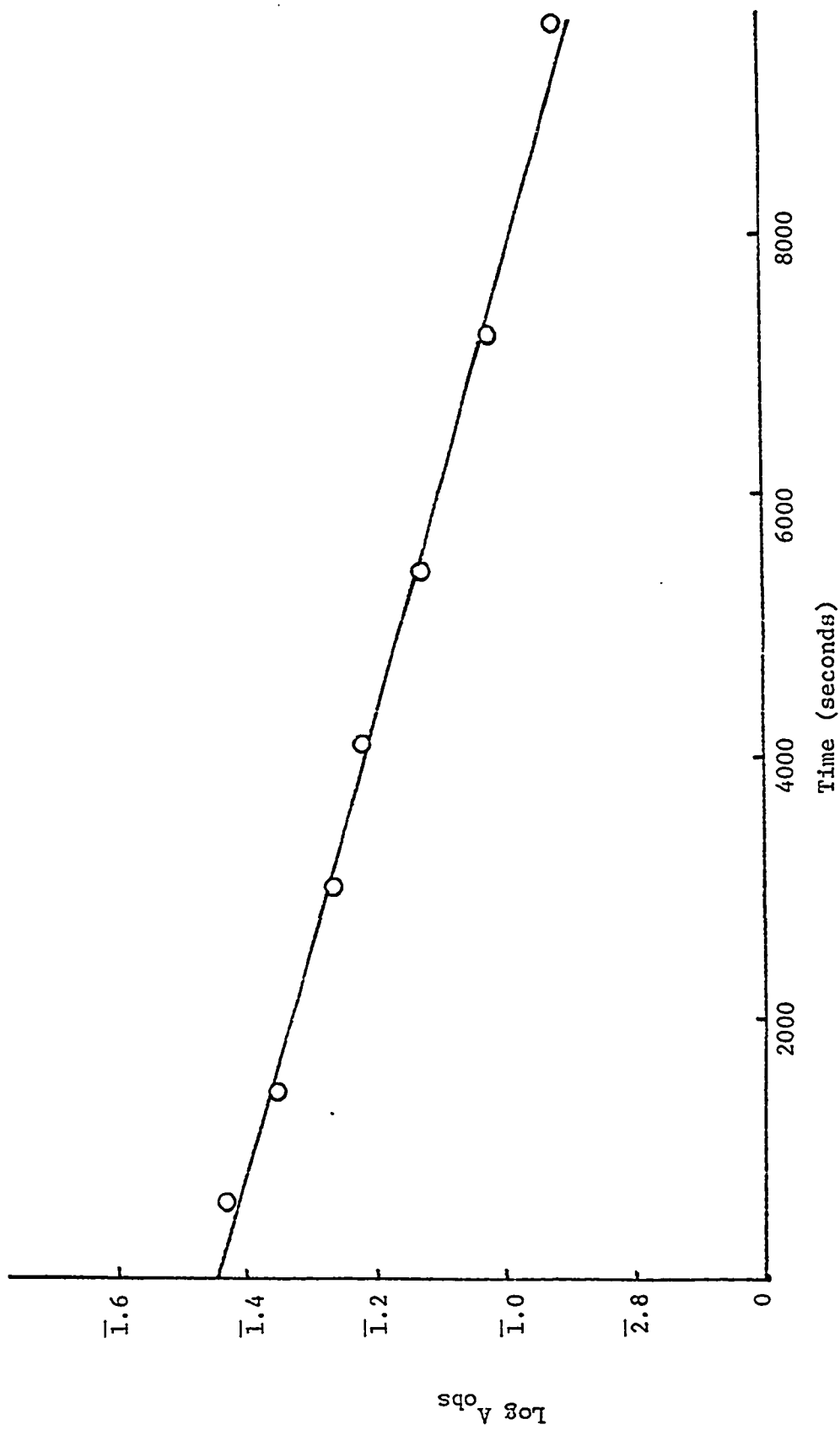


Fig. 14 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of Cinnamyl 2,6-Dimethylbenzenesulfinate in Ethanol at 90.0° (Table XXIX).

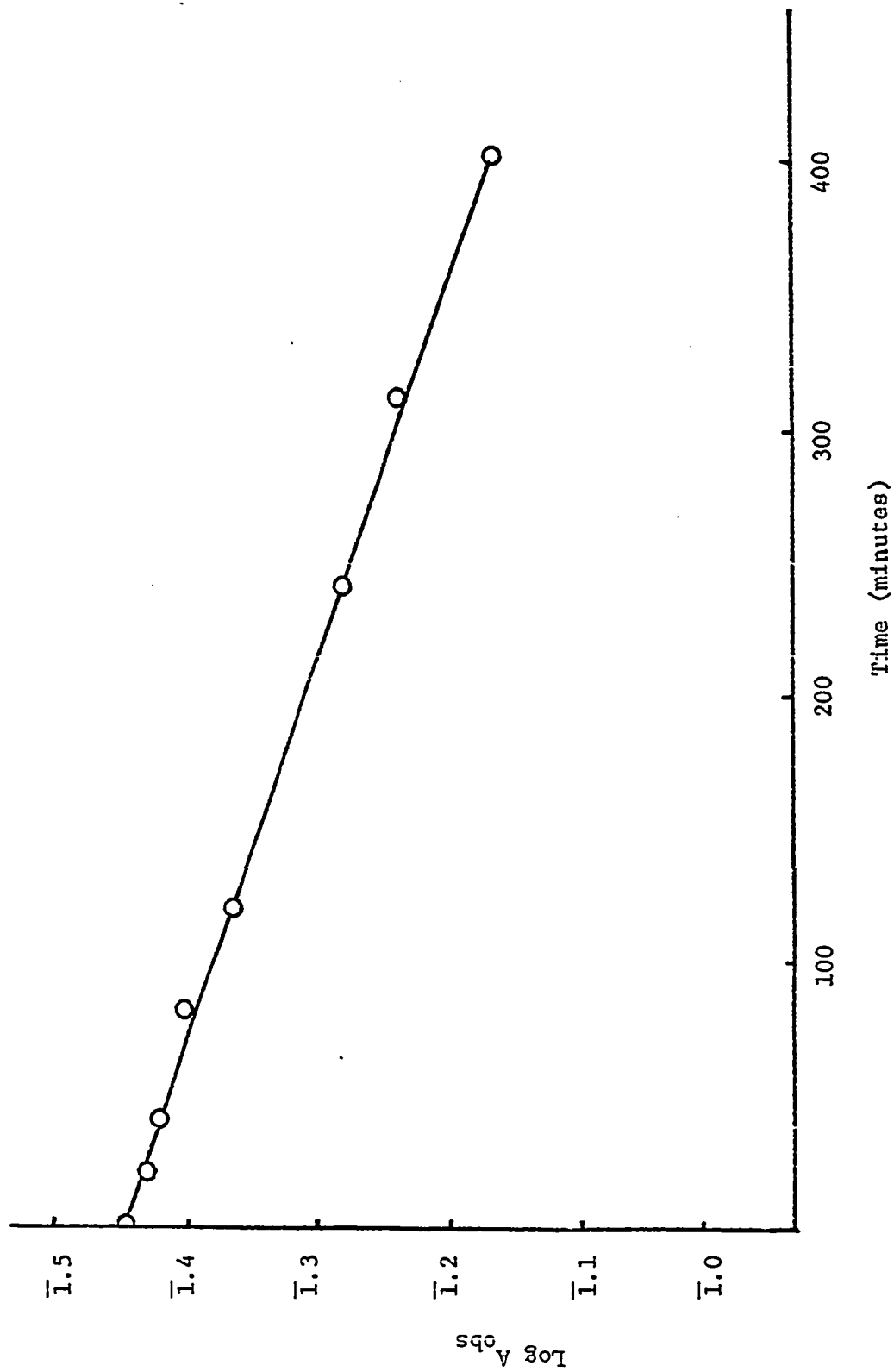


Fig. 15 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of Cinnamyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol at 50.0° (Table XXX)

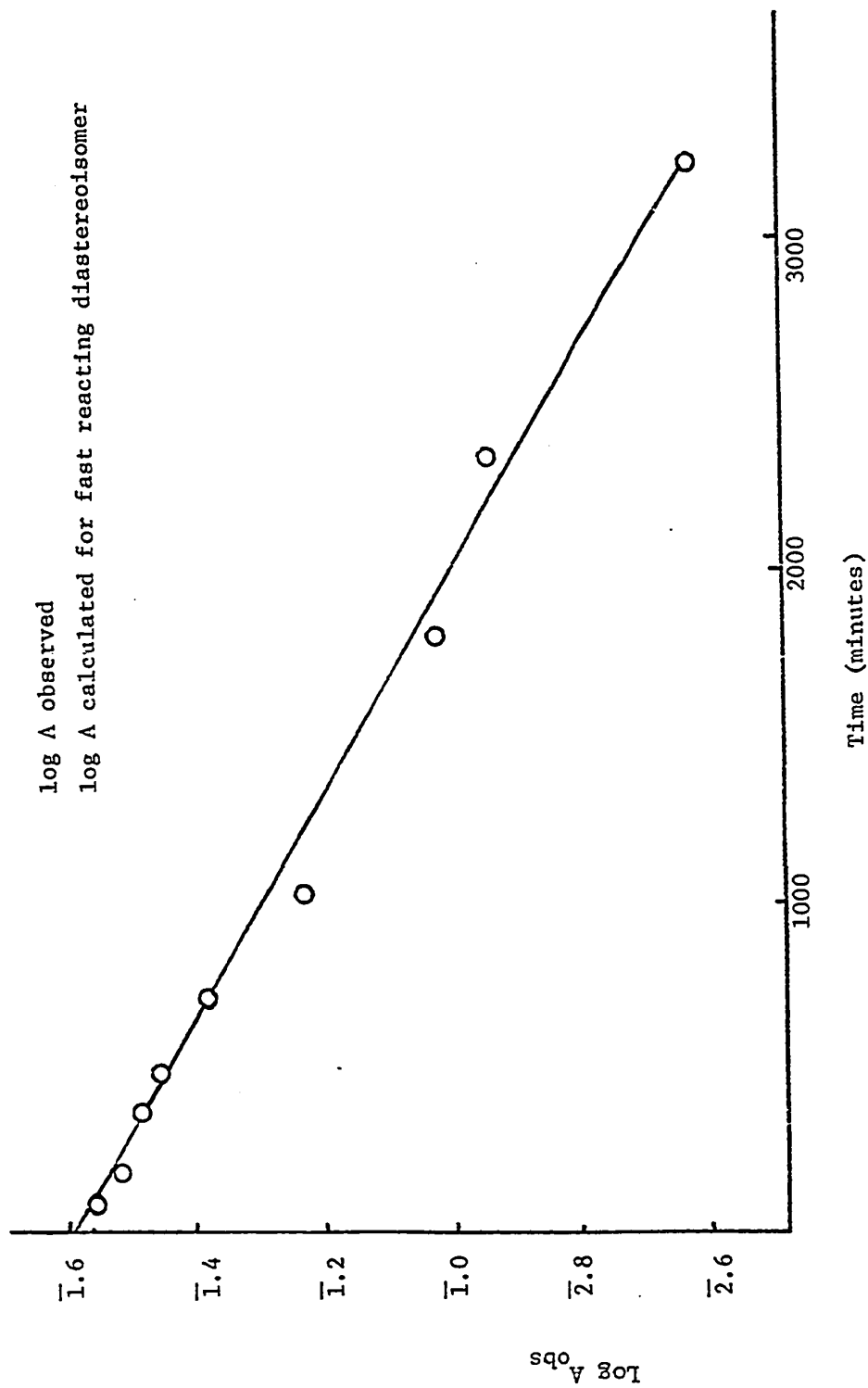


Fig. 16 → Plot of $\log A_{\text{obs}}$ Against Time for the Rearrangement of Cinnamyl 2,6-Dimethylbenzenesulfonate in Acetic Acid at 50.0° (Table XXXI)

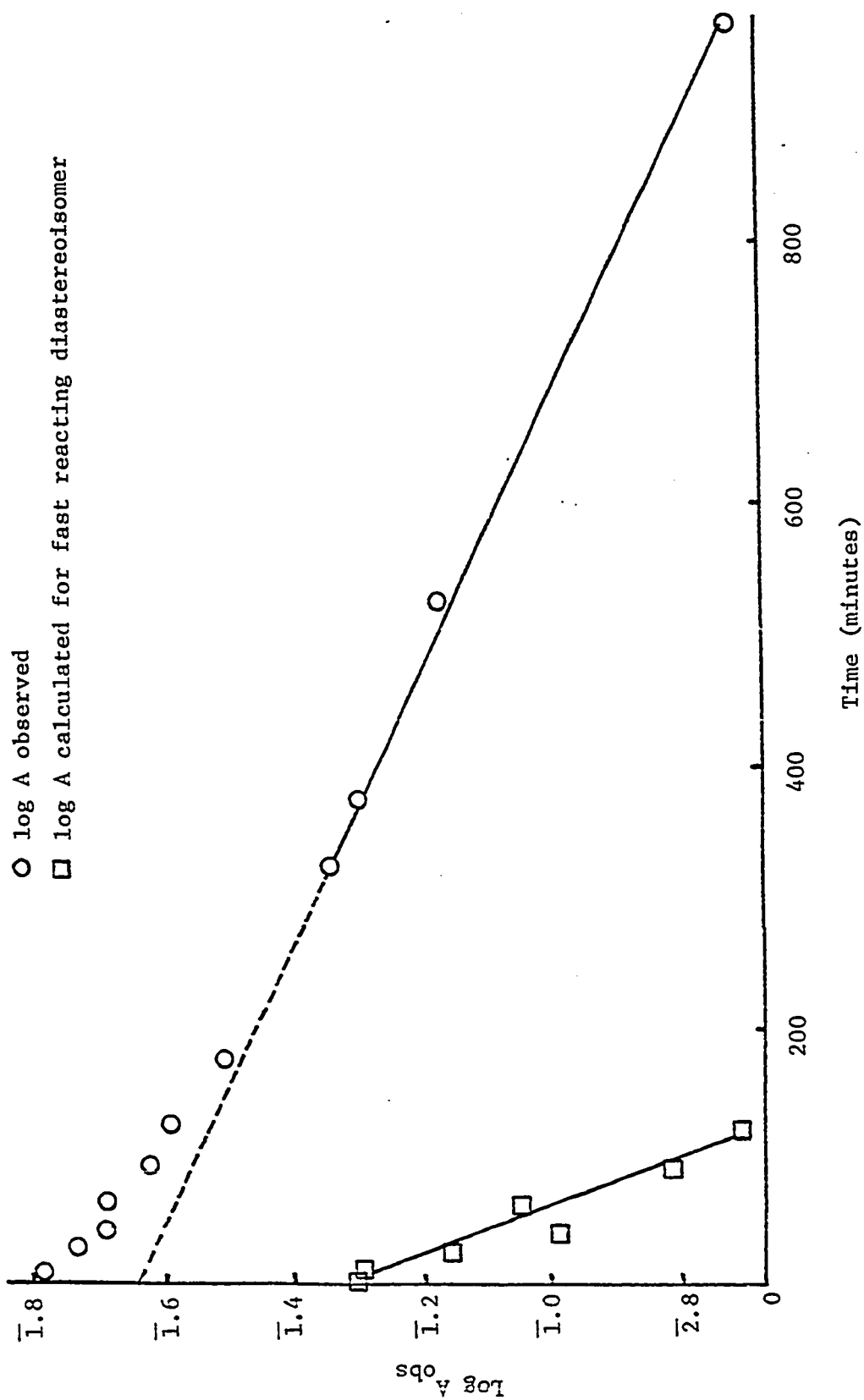


Fig. 17 - Plot of Log A_{obs} Against Time for the Rearrangement of α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfinate in Ethanol at 50.0° (Table XXXII)

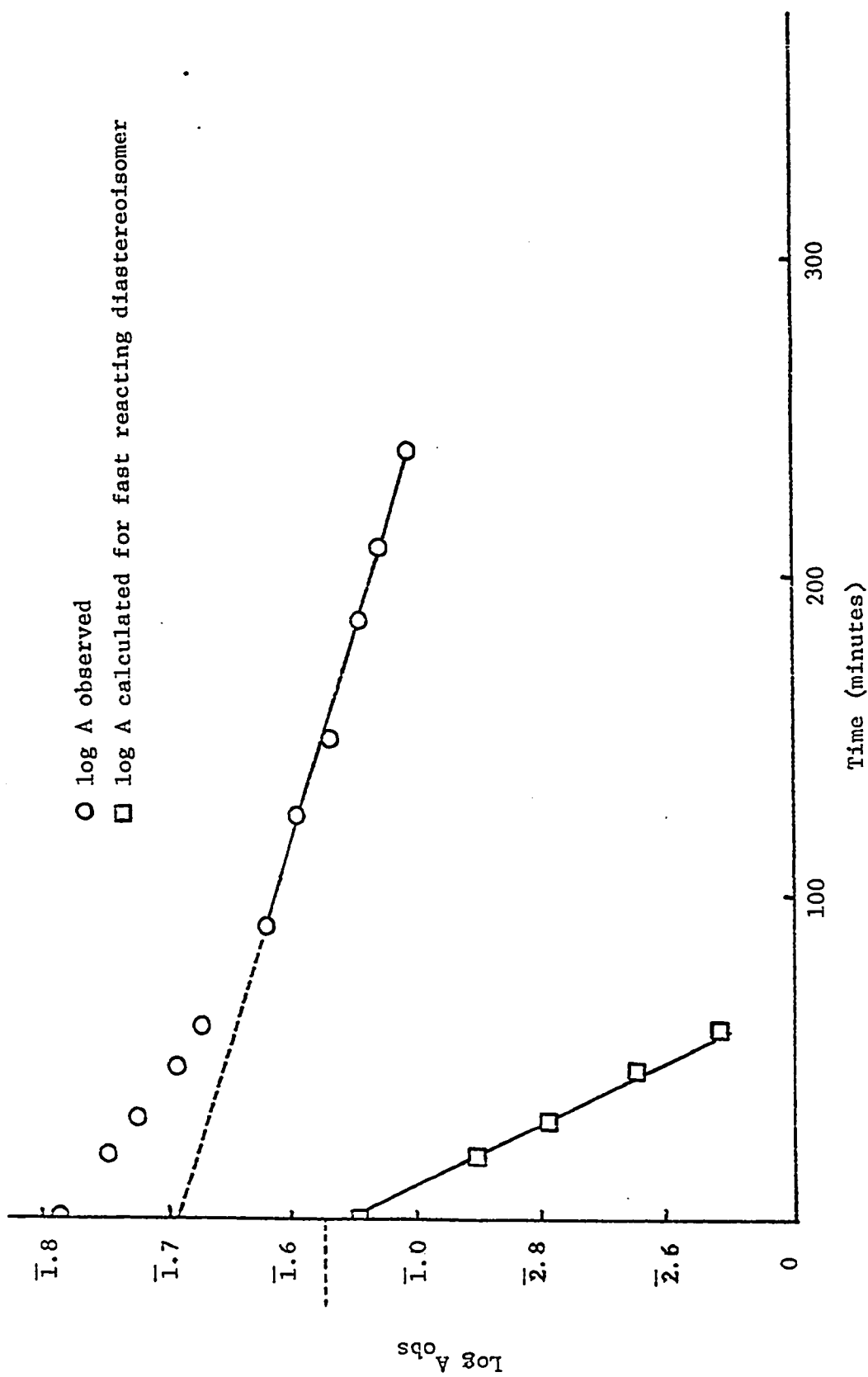


Fig. 18 - Plot of Log A_{obs} Against Time for the Rearrangement of α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfonate in 60% Ethanol at 25.0° (Table XXXIII).

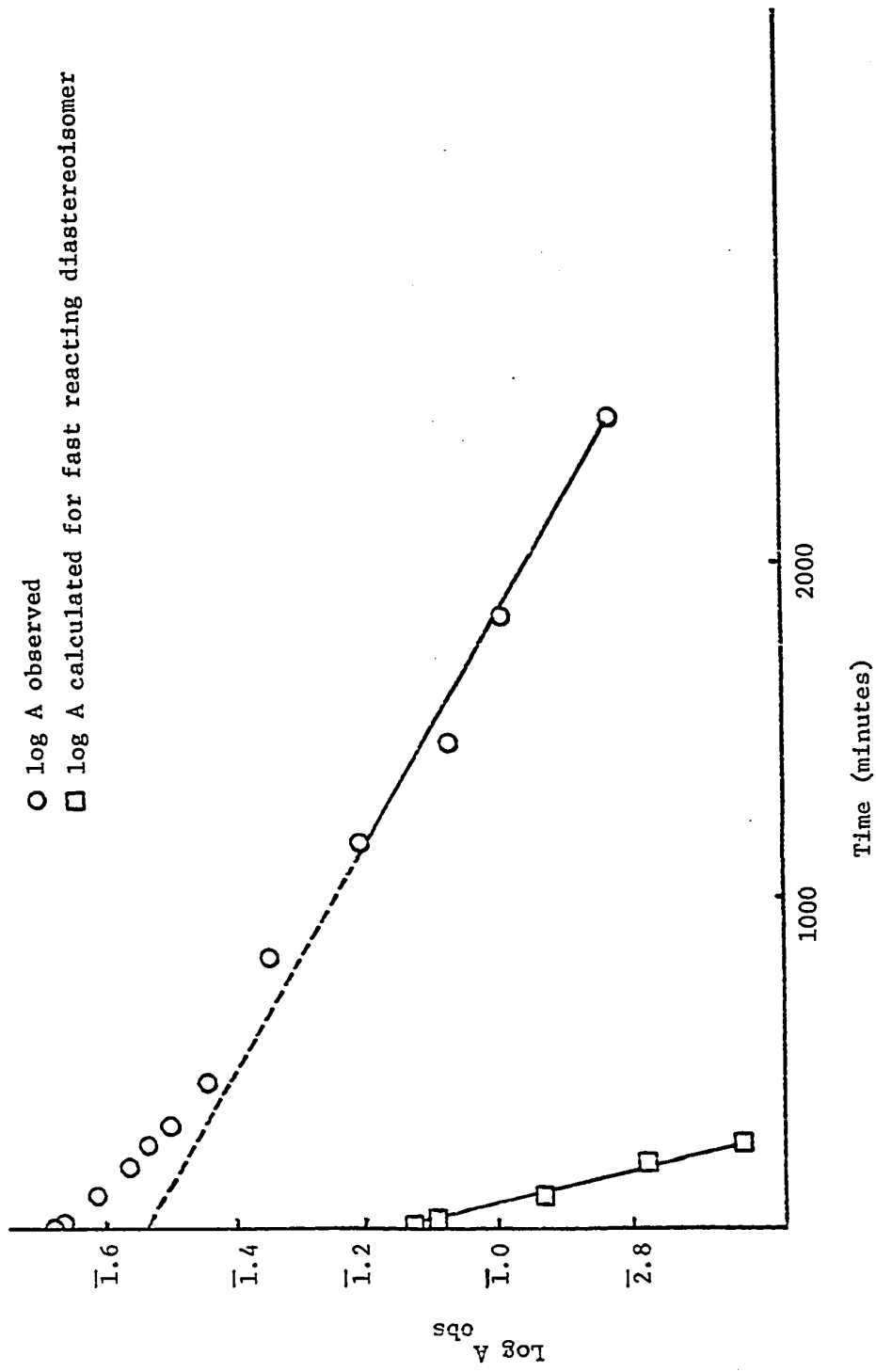


Fig. 19 - Plot of $\log A_{obs}$ Against Time for the Rearrangement of α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfonate in Acetic Acid at 25.0° (Table XXXIV)

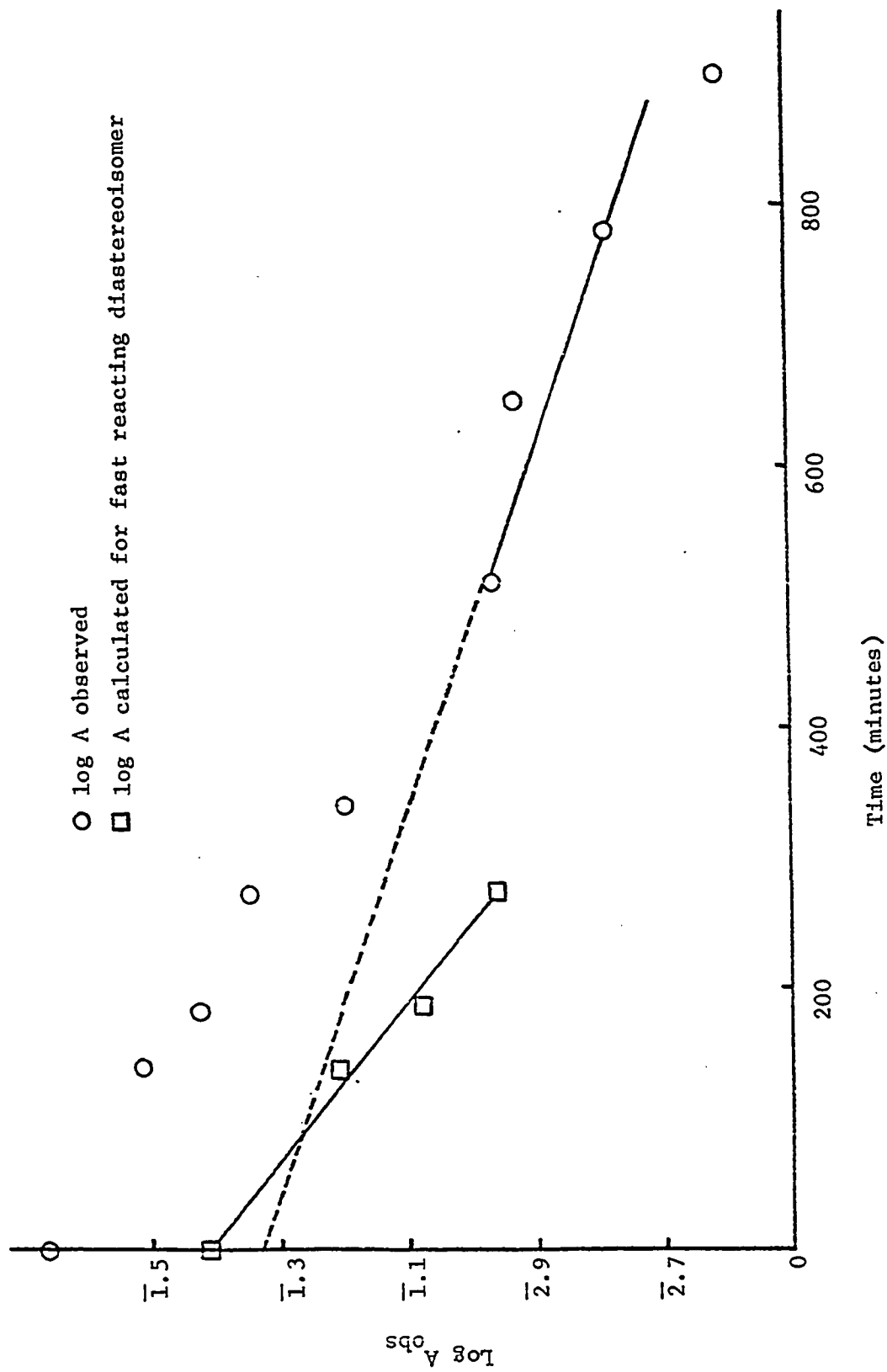


Fig. 20 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of α -Phenylallyl 2,6-Dimethylbenzenesulfinate in Ethanol at 25.0° (Table XXXV)

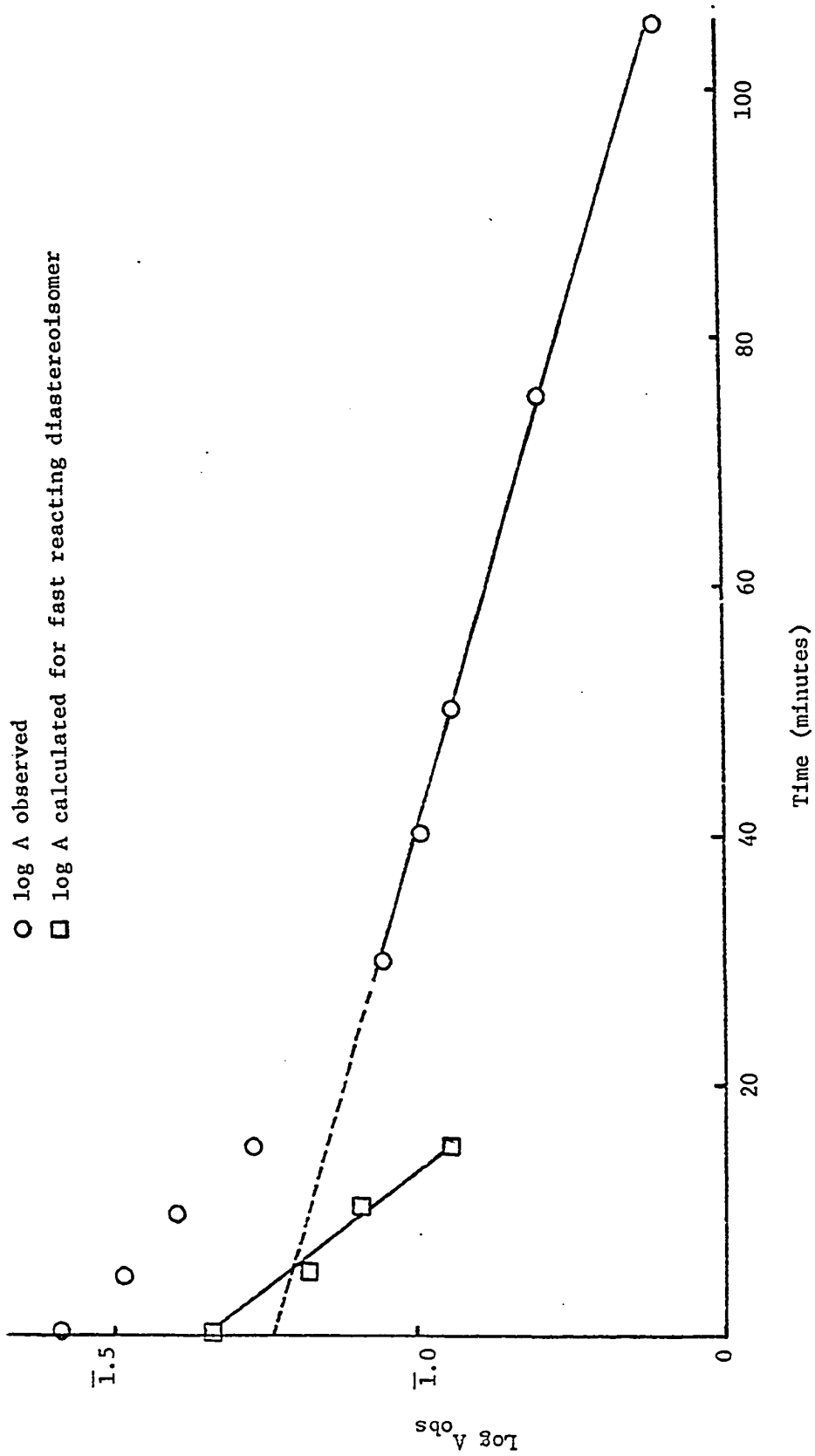


Fig. 21 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of α -Phenylallyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol at 25.0° (Table XXXVI)

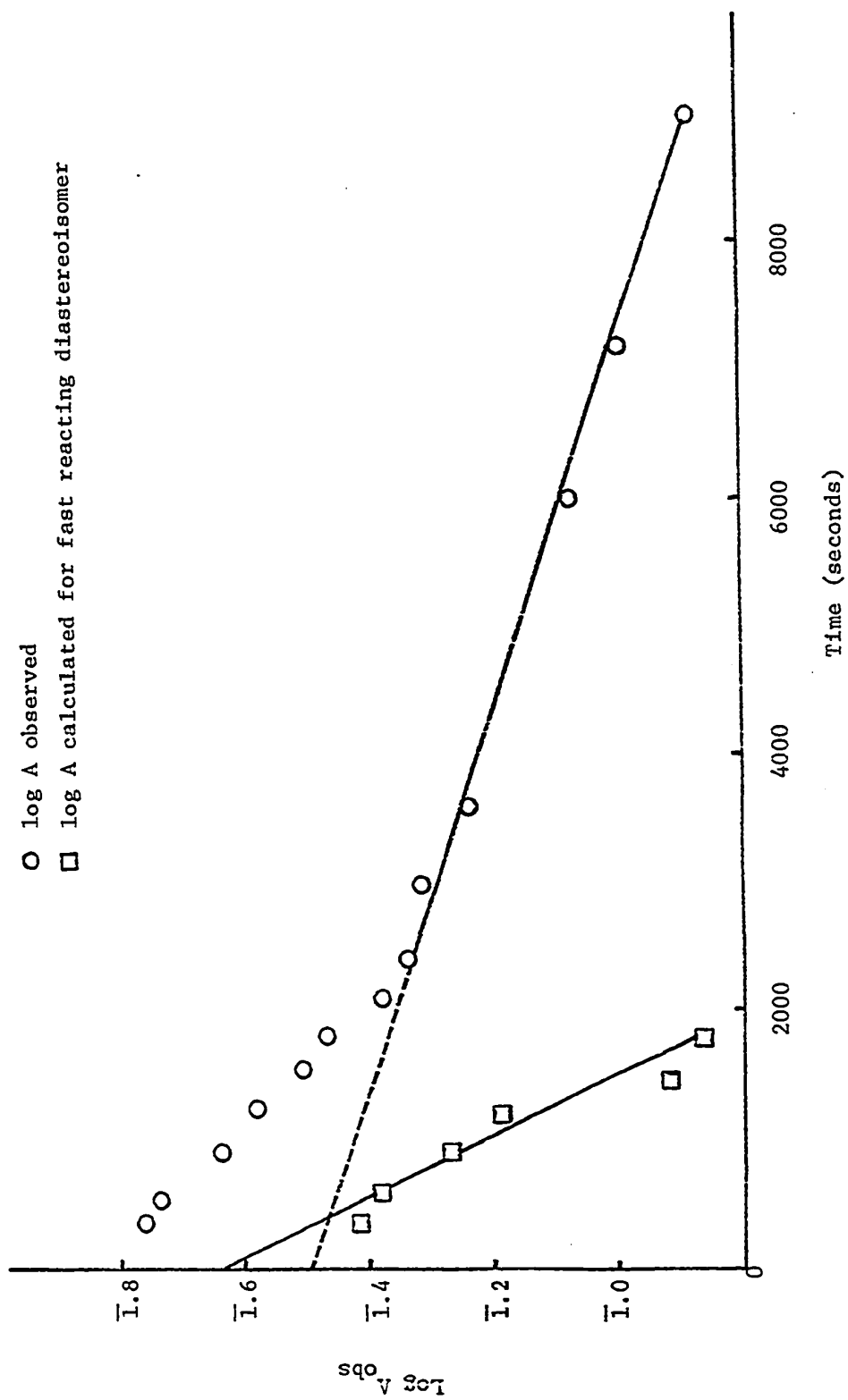


Fig. 22 - Plot of $\text{Log } A_{\text{obs}}$ Against Time for the Rearrangement of α -Phenylallyl 2,6-Dimethylbenzenesulfinate in Acetic Acid at 25.0° (Table XXXVII)

by Braverman (12) is presented in Table XXXVIII.

The signal in the nmr spectrum of α -phenylallyl 2,6-dimethylbenzenesulfinate, assigned to the aromatic methyl groups, is a pair of singlets at τ 7.46 and τ 7.58, each of which can be assigned to a pair of optical isomers. Two criteria were used to assign these signals to the diastereoisomers. The concentration of each diastereoisomer could be determined from the infrared measurements. In the graphs of the logarithm of the absorbance against time (Figures 20 to 22) the straight lines representing the logarithm of the absorbance due to the fast and slow reacting diastereoisomers were extrapolated to zero time allowing determination of the relative absorbances and hence the relative concentrations of the two diastereoisomers in the starting ester. The results suggested that, in all samples of ester on which measurements were made, the fast reacting diastereoisomer was present in greater concentration than the slow reacting diastereoisomer, the ratio being approximately 60:40. Since the nmr spectra of the same samples showed a more intense signal at τ 7.46 than at τ 7.58, it was assumed that the former signal was due to the fast reacting diastereoisomer. This was confirmed by allowing a sample of the ester to rearrange in 60% ethanol with 2,6-lutidine added and measuring its nmr spectrum after work-up at various stages of the reaction. After careful removal of the lutidine, it was found that the signal at τ 7.46 decreased more rapidly than that at τ 7.58. The nmr spectrum therefore gives a ready measure of the relative amounts of fast and slow reacting diastereoisomers present in any sample of the α -phenylallyl ester.

TABLE XXXVIII

Summary of Rate Constants for Rearrangement of Cinnamyl, α,γ -Dimethylallyl and α -Phenylallyl 2,6-Dimethylbenzenesulfonates.

Ester	Solvent	Base	Temp. °C	$k \times 10^5$ (sec ⁻¹)		
cinnamyl	EtOH	a	90.0°	14.4 ± 0.5		
cinnamyl	60% EtOH	a	50.0°	2.60 ± 0.09	101	± 6 ^f
cinnamyl	HOAc	b	50.0°	1.16 ± 0.09	42.4	± 1.9 ^f
α,γ -dimethylallyl	EtOH	a	50.0°	19.2 ± 2.3 ^c	347	± 0.07 ^d
α,γ -dimethylallyl	EtOH	a	70.0°	134 ± 15 ^{c,e}	23.8	± 2.4 ^{d,e}
α,γ -dimethylallyl	60% EtOH	a	25.0°	37.7 ± 1.1 ^c	3.61	± 0.05 ^d
α,γ -dimethylallyl	60% EtOH	a	70.0°	654 ± 116 ^{c,e}	265	± 16 ^{d,e}
α,γ -dimethylallyl	HOAc	b	25.0°	9.08 ± 0.31 ^c	1.35	± 0.15 ^d
α,γ -dimethylallyl	HOAc	a	70.0°	424 ± 119 ^{c,e}	148	± 17 ^{d,e}
α -phenylallyl	EtOH	a	25.0°	5.99 ± 0.51 ^c	2.78	± 0.16 ^d
α -phenylallyl	60% EtOH	a	25.0°	97.0 ± 1.8 ^c	23.3	± 0.9 ^d
α -phenylallyl	60% EtOH	a	25.0°	120 ^{c,e}	32.6	^{d,e}
α -phenylallyl	HOAc	b	25.0°	90.0 ± 11.1 ^c	18.1	± 0.8 ^d
α -phenylallyl	HOAc	a	25.0°	106 ± 6 ^{c,e}	18.8	± 0.7 ^{d,e}

a - 2,6-lutidine

b - sodium acetate

c - fast reacting diastereoisomer

d - slow reacting diastereoisomer

e - values taken from ref. 12

f - run at 90.0°, values taken from ref. 12

When the nmr spectrum of α -phenylallyl 2,6-dimethylbenzenesulfinate was run using a 100 Mc spectrophotometer, the two signals at τ 7.46 and τ 7.58 could be integrated cleanly. It was shown that the products of the rearrangement of the ester in any of the three solvents did not interfere with either of the signals. The rate of disappearance of these signals was measured when the ester was allowed to rearrange in acetic acid with sodium acetate added and in ethanol and 60% ethanol with pyridine added. This base was used in place of 2,6-lutidine since it gives no signal in the nmr which could overlap with those being measured. The residue after work-up of each sample was dissolved in 0.512 ml of carbon tetrachloride containing 5% tetramethylsilane and 1% cyclohexane. The integration was run twice on each spectrum and, using the cyclohexane signal as an internal standard, the separate rates of disappearance of the two diastereoisomers were calculated. The results are detailed in Tables XXXIX, XL and XLI. In the runs in 60% ethanol, no trace of the formation of ethyl 2,6-dimethylbenzenesulfinate could be detected. This is in agreement with the findings using 60 Mc spectra.

Initially, the values of the rates of rearrangement of the diastereoisomers measured by ir and by nmr spectroscopy did not agree with one another. In all three solvents, the rate of rearrangement of the slow reacting diastereoisomer is faster by nmr than by ir spectroscopy. However, it was found that there was potentially a very large experimental error in the rates measured by ir spectroscopy. The absorbances used to calculate the rate of disappearance of the slow reacting diastereoisomer were very low, ranging from 0.0914 to 0.0361 for the run in ethanol and from 0.114 to 0.040 for the run in 60% ethanol. The error in the rate constants could therefore be considerably larger than the scatter of the

TABLE XXXIX

Rate of Disappearance of α -Phenylallyl 2,6-Dimethylbenzenesulfinate
(0.02839 M) in Ethanol with Added Pyridine (0.03924 M) at 25.0° by
NMR Spectroscopy

Time sec	Integration		$\frac{a}{a-x}$		$\log \frac{a}{a-x}$		$k \times 10^5$ sec ⁻¹	
	FRD	SRD	FRD	SRD	FRD	SRD	FRD	SRD
	0	81.0	73.7	-	-	-	-	-
720	77.9	71.3	1.040	1.034	0.0170	0.0145	5.44	4.64
1200	75.7	69.8	1.070	1.056	0.0294	0.0236	5.64	4.53
2100	72.9	67.2	1.111	1.097	0.0457	0.0402	5.01	4.41
3600	67.7	63.0	1.196	1.170	0.0777	0.0682	4.97	4.36
6600	56.2	52.1	1.441	1.415	0.1587	0.2507	5.54	4.26

Average value of k for fast reacting diastereoisomer = $(5.32 \pm 0.26) \times 10^{-5} \text{ sec}^{-1}$

Average value for k for slow reacting diastereoisomer = $(4.49 \pm 0.08) \times 10^{-5} \text{ sec}^{-1}$

Table continued overleaf...

TABLE XXXIX (Contd.)

Second run

Time sec	Integration		$\frac{a}{a-x}$		$\log \frac{a}{a-x}$		$k \times 10^5$ sec^{-1}	
	FRD	SRD	FRD	SRD	FRD	SRD	FRD	SRD
0	82.5	70.2	-	-	-	-	-	-
4200	65.3	59.5	1.263	1.180	0.1014	0.0719	5.56	3.94
7080	55.5	50.6	1.486	1.387	0.1721	0.1421	5.60	4.62
11460	47.1	42.6	1.752	1.648	0.2432	0.2169	4.89	4.36

Average value of k for fast reacting diastereoisomer = $(5.35 \pm 0.30) \times 10^{-5} \text{ sec}^{-1}$

Average value of k for slow reacting diastereoisomer = $(4.31 \pm 0.15) \times 10^{-5} \text{ sec}^{-1}$

Ratio of fast to slow reacting diastereoisomer in starting ester = 1.14

TABLE XL

Rate of Disappearance of α -Phenylallyl 2,6-Dimethylbenzenesulfinate
(0.02936 M) in 60% Ethanol with Added Pyridine (0.03863 M) at 25.0°
by NMR Spectroscopy.

Time sec	Integration		$\frac{a}{a-x}$		$\log \frac{a}{a-x}$		$k \times 10^4$ sec ⁻¹	
	FRD	SRD	FRD	SRD	FRD	SRD	FRD	SRD
0	88.0	70.3	-	-	-	-	-	-
900	47.0	48.9	1.872	1.438	0.2723	0.1577	6.07	4.04
2040	22.9	29.4	3.843	2.391	0.5846	0.3786	6.60	4.27
3120	10.2	18.9	8.627	3.720	0.9359	0.5705	6.91	4.21

Average value of k for fast reacting diastereoisomer = $(6.83 \pm 0.15) \times 10^{-4} \text{ sec}^{-1}$

Average value of k for slow reacting diastereoisomer = $(4.17 \pm 0.06) \times 10^{-4} \text{ sec}^{-1}$

Ratio of fast to slow reacting diastereoisomer in starting ester = 1.25

TABLE XLI

Rate of Disappearance of α -Phenylallyl 2,6-Dimethylbenzenesulfinate
(0.02826 M) in Acetic Acid with Added Sodium Acetate (0.05140 M)
at 25.0° by NMR Spectroscopy.

Time sec	FRD		SRD		FRD		SRD	
	FRD	SRD	FRD	SRD	FRD	SRD	FRD	SRD
0	65.9	56.1	-	-	-	-	-	-
600	48.5	47.2	1.359	1.189	0.1332	0.0752	5.11	2.89
900	42.4	43.5	1.554	1.290	0.1914	0.1106	4.90	2.83
1200	36.4	37.2	1.810	1.508	0.2577	0.1783	4.95	3.42
2400	20.6	29.9	3.199	1.876	0.5050	0.2732	4.85	2.62
3240	14.4	21.7	4.576	2.585	0.6607	0.4125	4.70	2.93

Average value of k for fast reacting diastereoisomer = $(4.90 \pm 0.10) \times 10^{-4} \text{ sec}^{-1}$

Average value of k for slow reacting diastereoisomer = $(2.94 \pm 0.19) \times 10^{-4} \text{ sec}^{-1}$

Ratio of fast to slow reacting diastereoisomer in starting ester = 1.17

calculated values would suggest. The presence of this error was illustrated when the rate of rearrangement of the slow reacting diastereoisomer was run using a more concentrated bromoform solution to measure the absorbance. The results are presented in Table XLII and Figure 23. The rate constant obtained ($5.9 \times 10^{-4} \text{ sec}^{-1}$) is approximately midway between the rates of rearrangement of the fast and slow reacting diastereoisomers under the same conditions as measured by nmr spectroscopy and is in agreement with the nmr data above. Since the separate rates of rearrangement of the diastereoisomers could not be separated using the ir spectral data, the rates which were calculated from the nmr spectral data were used in subsequent calculations.

It was hoped that a similar determination of the rates of rearrangement of the diastereoisomers of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate by nmr spectroscopy would be possible. However, the signals due to the methyl groups on the allyl moiety are doublets and were not completely separated from one another even in a 100 Mc spectrum. No splitting of the signal due to the aromatic methyl groups was observed in the 60 Mc spectrum, and when run on a 100 Mc instrument, the difference in chemical shift of the signals due to the two isomers was seen to be only 1.5 Hertz. Separate integration of the signals was not possible and so an accurate value of the rate constants was not available by this method.

An oxygen-18 label was introduced into the sulfinyl-oxygen position of the cinnamyl, α,γ -dimethylallyl and α -phenylallyl esters using the same method as that described in Chapter II to introduce a label into the sulfinyl-oxygen position of the allyl, crotyl and

TABLE XLII

Rate of Disappearance of α -Phenylallyl 2,6-Dimethylbenzenesulfinate
(0.03719 M) in 60% Ethanol with Added 2,6-Lutidine (0.03250 M) at
25.0° by Infrared Spectroscopy.

Time (sec.)	I_o/I	$\log I_o/I$ = A_{obs}	$\log A_{obs}$	$\log A_o/A$	$k \times 10^4$ sec^{-1}	% reaction
1560	3.679	0.5658	$\bar{1}.7526$	-		60
1800	3.096	0.4908	$\bar{1}.6907$	0.0619	5.93	65
2100	2.606	0.4160	$\bar{1}.6191$	0.1335	5.69	70
2400	2.257	0.3535	$\bar{1}.5484$	0.2042	5.60	75
3000	1.815	0.2589	$\bar{1}.4131$	0.3395	5.43	81
3780	1.430	0.1553	$\bar{1}.1911$	0.5615	5.82	89
Average value of $k = (5.69 \pm 0.14) \times 10^{-4} \text{ sec}^{-1}$						

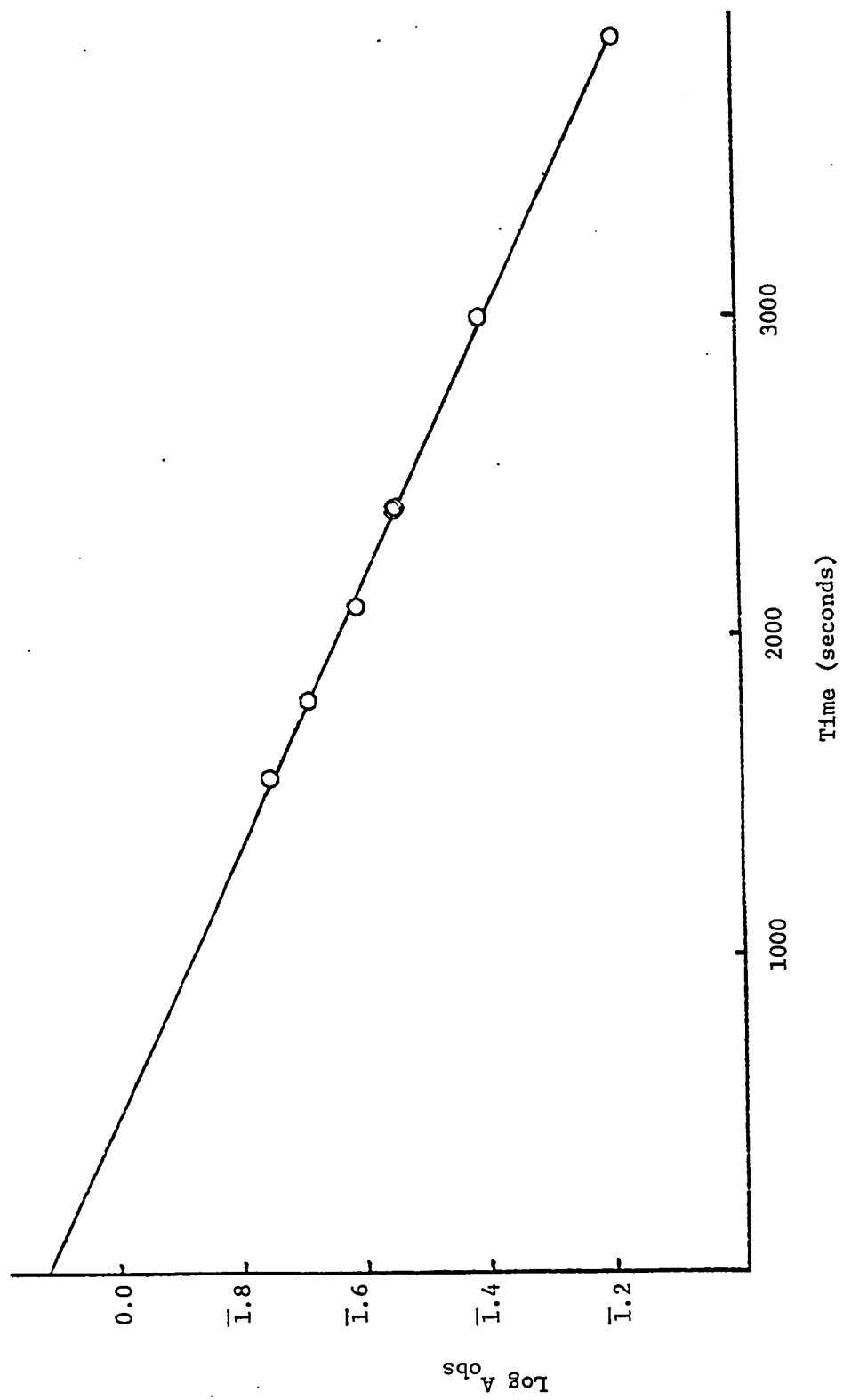


Fig. 23 - Plot of Log A_{obs} Against Time for the Rearrangement of α -Phenylallyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol at 25.0° (Table XLII).

α -methylallyl esters. The rate of equilibration of this label during the rearrangement of the esters in ethanol, 60% ethanol and acetic acid was measured. The ester remaining after partial rearrangement was hydrolyzed and the excess oxygen-18 in the resulting alcohol measured using the modified Unterzaucher apparatus. A brief description of the method of measuring the excess oxygen-18 and a sample calculation were presented in Chapter II.

Any α,γ -dimethylallyl alcohol which had been produced by solvolysis during the rearrangement of the α,γ -dimethylallyl ester was removed by warming the recovered ester under reduced pressure prior to hydrolyzing it. Since α -phenylallyl 2,6-dimethylbenzenesulfinate tended to rearrange on warming under vacuum and α -phenylallyl alcohol is considerably less volatile than α,γ -dimethylallyl alcohol, no attempt was made to remove it. The alcohol formed by a solvolysis reaction involving carbon-oxygen bond fission would not contain any excess oxygen-18 label and so the presence of this alcohol in the sample used to determine the excess oxygen-18 was allowed for in the calculation of the rate constant for scrambling. However, the correction was quite small, since, in the rearrangement of α -phenylallyl 2,6-dimethylbenzenesulfinate in 60% ethanol with 2,6-lutidine added, only 9.6% of 2,6-dimethylbenzenesulfonic acid was produced after 10 half lives, and this is the upper limit of the amount of solvolysis which is occurring. The method used to apply the correction is described below for a run using cinnamyl 2,6-dimethylbenzenesulfinate. Less than 2% of ethyl 2,6-dimethylbenzenesulfinate was detected in the products of the reaction of α -phenylallyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol and 2,6-lutidine and so no correction for the presence of unlabelled alcohol was applied to the calculation of the rate constant

in this solvent.

Braverman quotes a figure of 5.6% acid formed after 10 half lives in the rearrangement of cinnamyl 2,6-dimethylbenzenesulfinate in 60% ethanol and 2,6-lutidine and a repeat of this measurement gave a value of 6.4%. Small amounts of cinnamyl alcohol will therefore also be formed during the rearrangement of the cinnamyl ester and, like the α -phenylallyl alcohol it could not be removed during the work-up of the unrearranged ester. Consequently corrections were again applied to the atom excess oxygen-18 observed in the alcohol obtained after hydrolysis of the ester to allow for the fact that it contained alcohol produced from solvolysis. The application of this correction is outlined for the determination of the rate of oxygen-18 scrambling during the rearrangement of cinnamyl 2,6-dimethylbenzenesulfinate in 60% ethanol at 50.0° (Run II-142-G, Table XLV).

In the cinnamyl alcohol obtained after reaction has proceeded for 885 minutes,

$$\frac{\text{Peak at mass 46}}{\text{Peak at mass 44}} = 0.00507$$

In natural CO₂

$$\frac{\text{Peak at mass 46}}{\text{Peak at mass 44}} = 0.00392$$

The alcohol resulting from solvolysis of the ester (4.8% after 75% reaction) would have a 46/44 peak ratio of 0.00392. Of the alcohol which was recovered, 25% will have arisen from hydrolysis and 4.8% from carbon-oxygen bond fission of the ester, therefore,

$$0.00507 = \frac{25}{29.8} R_c + \frac{4.8}{29.8} 0.00392$$

where R_c is the 46/44 peak ratio of the alcohol resulting from hydrolysis of the ester.

$$R_c = 0.00517$$

This value was used to calculate the fraction of ester containing equilibrated oxygen-18, F_{scr} , presented in Table XLV.

During the rearrangement of these esters in acetic acid, minor quantities of the corresponding acetates are formed. For example from the reaction of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate in acetic acid at 25.0°, 9% of the product was identified as α,γ -dimethylallyl acetate. The acetate would be hydrolyzed along with the 2,6-dimethylbenzenesulfinate and the alcohol recovered would be derived from both sources. α,γ -Dimethylallyl acetate was sufficiently volatile that it could be removed along with any alcohol prior to hydrolysis. α -Phenylallyl acetate and cinnamyl acetate could not be removed in this way but were detected in trace quantities only and so the presence of unlabelled alcohol from these acetates was not taken into account in the calculation of the rate constants.

The conditions used to hydrolyze the esters are summarized in Table XLIII.

The α,γ -dimethylallyl alcohol formed by hydrolysis of the α,γ -dimethylallyl ester was recovered by preparative gas chromatography using a silicone grease packed column at 118° with a helium flow rate of 120 cc per minute. α -Phenylallyl alcohol decomposed on the chromatography column, however, it could be steam distilled (68) from the basic hydrolysis mixture and recovered by extraction of the aqueous distillate with ether. Cinnamyl alcohol is a low melting solid (m.p. 33°) which is slightly soluble in

TABLE XLIII

Conditions for Hydrolysis of Cinnamyl, α,γ -Dimethylallyl and α -Phenylallyl 2,6-Dimethylbenzenesulfinates.

Ester	Solvent	Base Concn.	Temp °C	Time
Cinnamyl	50% aqueous dioxane	0.2 M	25°	5 hours
α,γ -Dimethylallyl	50% aqueous dioxane	0.5 M	25°	12 hours
α -Phenylallyl	50% aqueous dioxane	0.5 M	25°	3 hours

warm water. Accordingly, the residue from the ether extract of the basic solution was shaken with hot water, filtered, and the solid which precipitated on cooling was recrystallized from ether-pentane. It was shown by the appropriate controls that the alcohols from esters which had been dissolved in solvent and immediately recovered and hydrolyzed did not contain excess oxygen-18. Therefore there was no incorporation of the oxygen-18 label into the ether-oxygen position of the ester during either work-up or hydrolysis. No impurities could be detected in the recovered alcohols.

The fraction of recovered ester which contained equilibrated oxygen-18 (F_{scr}), could be calculated from the excess oxygen-18 in the alcohol and the excess oxygen-18 in the sulfinyl oxygen position of the starting ester using equation 4.4.

$$F_{scr} = \frac{2 \times \text{atom percent oxygen-18 in alcohol}}{\text{atom percent oxygen-18 in sulfinyl oxygen position of starting ester.}} \quad \text{----- 4.4}$$

The values of F_{scr} obtained are detailed in Tables XLIV to LII.

TABLE XLIV

Rate of Scrambling of Oxygen-18 in Cinnamyl 2,6-Dimethylbenzenesulfinate-sulfinyl-¹⁸O (0.02833 M) in Ethanol with Added 2,6-Lutidine (0.02835 M) at 90.0°

Run No.	Time (sec.)	F _{scr}	k x 10 ⁵ sec ⁻¹	% reaction
III-96-A	1440	0.017	5.40*	18
III-96-B	2040	0.021	1.03	25
III-96-C	3000	0.031	1.05	34
III-96-D	4080	0.041	1.02	41
III-96-E	5400	0.045	0.86	53
III-96-F	7200	0.057	0.81	63
III-96-G	9600	0.078	0.85	72

Average value of k = (0.94 ± 0.09) x 10⁻⁵ sec⁻¹.

% Atom excess oxygen-18 in starting ester = 1.614

* Value not included in average

TABLE XLV

Rate of Scrambling of Oxygen-18 in Cinnamyl 2,6-Dimethylbenzenesulfinate-sulfinyl-¹⁸O (0.01688 M) in 60% Ethanol with Added 2,6-Lutidine (0.02816 M) at 50.0°.

Run No.	Time (min.)	F _{scr}	k x 10 ⁶ sec ⁻¹	% reaction
II- 142-A	105	0.01925	3.10	15
II- 142-B	195	0.02841	2.40	25
II- 142-C	300	0.0458	2.59	35
II- 142-D	435	0.0552	2.18	45
II- 142-E	556	0.0695	1.98	55
II- 142-F	730	0.0844	2.01	65
II- 142-G	885	0.103	2.05	75
II -142-H	1410	0.241	3.25	85
Average value of k = (2.45 ± 0.40) x 10 ⁻⁶ sec ⁻¹				

% Atom excess oxygen-18 in starting ester = 2.434

TABLE XLVI

Rate of Scrambling of Oxygen-18 in Cinnamyl 2,6-Dimethylbenzene-sulfinate-sulfinyl-¹⁸O (0.02803 M) in Acetic Acid with Added Sodium Acetate (0.05926 M) at 50.0°.

Run no.	Time (sec.)	F _{scr}	k × 10 ⁶ sec ⁻¹	% reaction
II-195-A	23400	0.0789	3.51	25
II-195-B	36600	0.132	3.88	35
II-195-C	54000	0.183	3.74	50
II-195-D	89400	0.209	3.22	65
II-195-E	108000	0.306	3.40	73

Average value of k = (3.55 ± 0.21) × 10⁻⁶ sec⁻¹.

% Atom excess oxygen-18 in starting ester = 2.356

TABLE XLVII

Results from Scrambling of Oxygen-18 in α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfinate-sulfinyl- ^{18}O , (0.03276 M) in Ethanol with Added 2,6-Lutidine (0.02793 M) at 50.0 $^{\circ}$

Run no.	Time (sec.)	% atom excess oxygen-18 in alcohol	% reaction	
			FRD	SRD
III-104-A	1800	0.00400	30	
III-104-B	3600	0.00401	49	
III-104-C	7200	0.00402	74	
III-104-D	10800	0.00404		32
III-104-E	14580	0.00397		40

% Atom excess oxygen-18 in starting ester - 1.878

Measured % atom excess oxygen-18 in natural carbon dioxide

= 0.00400.

TABLE XLVIII

Results from Scrambling of Oxygen-18 in α, γ -Dimethylallyl 2,6-Dimethylbenzenesulfinate-sulfinyl-¹⁸O in 60% Ethanol with Added 2,6-Lutidine at 25.0°.

Run no	[ester] M	[2,6-Lutidine] M	Time Sec.	% Atom excess oxygen-18 in alcohol	% reaction FRD SRD
I-130-A	0.0216	0.0244	870	0.00402	20
I-130-B	0.0213	0.0242	1200	0.00403	35
I-130-S	0.0212	0.0249	1830	0.00401	50
I-142-B	0.0221	0.0252	3600	0.00399	74
I-142-C	0.0212	0.0257	5400	0.00395	14
I-142-D	0.0225	0.0254	10800	0.00416	28
I-142-E	0.0214	0.0252	21600	0.00392	50

% Atom excess oxygen-18 in starting ester = 2.482

Measured % atom excess oxygen-18 in natural carbon dioxide
for runs I-130 = 0.00400

Measured % atom excess oxygen-18 in natural carbon dioxide
for runs I-142 = 0.00397

TABLE XLIX

Rate of Scrambling of Oxygen-18 in α, γ -Dimethallyl 2,6-Dimethyl-benzenesulfinate - sulfinyl- ^{18}O in Acetic Acid at 25.0°.

Fast reacting diastereoisomer

Run No.	[ester] M	[2,6-lutidine] M	Time (sec.)	F _{scr}	k x 10 ⁵ sec ⁻¹	% reaction
I-168-A	0.0211	0.0258	1560	0.01842	1.19	25
I-168-B	0.0216	0.0237	2700	0.04252	1.30	34
I-168-C	0.0215	0.0237	6900	0.1046	1.60	53

Average value of k = $(1.36 \pm 0.16) \times 10^{-5} \text{ sec}^{-1}$.

Slow reacting diastereoisomer

Run No.	[ester] M	[2,6-lutidine] M	Time (sec.)	F _{scr}	k x 10 ⁶ sec ⁻¹	% reaction
I-168-B	0.0216	0.0237	2700	0.0053	2.07	1.2
I-168-C	0.0215	0.0237	6900	0.0135	2.07	4.6
I-168-D	0.0231	0.0230	24000	0.0482	2.07	18.4
I-155-D	0.0216	0.0254	43200	0.08815	2.15	31
I-168-E	0.0216	0.0246	54000	0.1100	2.16	37.6
I-155-E	0.0220	0.0240	86400	0.1493	1.87	53.7
I-155-F	0.0222	0.0244	133560	0.2015	2.07	70.1

Average value of k = $(2.07 \pm 0.05) \times 10^{-6} \text{ sec}^{-1}$.

% Atom excess oxygen-18 in ester = 2.256

TABLE I

Rate of Scrambling of Oxygen-18 in α -Phenylallyl 2,6-Dimethylbenzenesulfinate-sulfinyl- ^{18}O (0.02818 M) in Ethanol with Added 2,6-Lutidine (0.02809 M) at 25.0°.

Fast reacting diastereoisomer

Run No.	Time (sec.)	F _{scr}	k x 10 ⁵ sec ⁻¹	% reaction
III-26-A	720	0.008	1.19	4
III-26-B	1200	0.015	1.20	6
III-26-C	2100	0.027	1.30	11
III-26-D	4200	0.041	1.01	20

Average value of k = (1.18 ± 0.08) x 10⁻⁵ sec⁻¹.

Slow reacting diastereoisomer

Run no.	Time (sec.)	F _{scr}	k x 10 ⁶ sec ⁻¹	% reaction
III-26-F	10200	0.032	3.25	36
III-26-G	16320	0.049	3.06	52
III-26-H	28020	0.079	2.94	70

Average value of k = (3.08 ± 0.10) x 10⁻⁶ sec⁻¹

% Atom excess oxygen-18 in starting ester = 1.996

TABLE LI

Rate of Scrambling of Oxygen-18 in α -Phenylallyl 2,6-Dimethylbenzenesulfinate-sulfinyl-¹⁸O in 60% Ethanol at 25.0°.

Fast reacting diastereoisomer

Run no.	[ester] M	[2,6-lutidine] M	Time (sec.)	F _{scr}	k x 10 ⁴ sec ⁻¹	% reaction
I-127-A	0.0193	0.0258	300	0.0423	1.54	18
I-127-B	0.0188	0.0245	600	0.0580	1.00	33
I-127-C	0.0187	0.0240	900	0.0849	1.00	45

Average value of k = (1.18 ± 0.24) x 10⁻⁴ sec⁻¹.

Slow reacting diastereoisomer

Run no.	[ester] M	[2,6-lutidine] M	Time (sec.)	F _{scr}	k x 10 ⁵ sec ⁻¹	% reaction
I-127-A	0.0193	0.0258	300	0.0085	2.75	12
I-127-B	0.0188	0.0245	600	0.0176	2.98	22
I-127-C	0.0187	0.0240	900	0.0271	3.00	32
I-127-D	0.0192	0.0243	1800	0.0451	2.56	54
I-127-E	0.0187	0.0241	2400	0.0568	2.44	64
I-127-F	0.0190	0.0244	3000	0.0786	2.74	71
I-127-G	0.0190	0.0240	4200	0.101	2.51	82
I-127-H	0.0190	0.0260	5820	0.132	2.43	91

Average value of k = (2.68 ± 0.19 x 10⁻⁵ sec⁻¹

% Atom excess oxygen-18 in ester = 1.778

Rate of Scrambling of Oxygen-18 in α -Phenylallyl 2,6-Dimethylbenzene-sulfinate-sulfinyl- ^{18}O (0.02833 M) in Acetic Acid with Added Sodium Acetate (0.03805 M) at 25 $^{\circ}$.

Fast reacting diastereoisomer

Run no.	Time (sec.)	F _{scr}	k x 10 ⁴ sec ⁻¹	% reaction
III-22- A	360	0.0133	3.8	15
III-22- B	900	0.0335	3.8	36
III-22- C	1500	0.043	2.9	52

Average value of k = $(3.5 \pm 0.40) \times 10^{-4} \text{ sec}^{-1}$.

Slow reacting diastereoisomer

Run no.	Time (sec.)	F _{scr}	k x 10 ⁵ sec ⁻¹	% reaction
III-22-A	360	0.0062	1.70	10
III-22-B	900	0.0160	1.78	22
III-22-C	1500	0.0250	1.67	35
III-22-D	2400	0.037	1.57	51
III-22-E	3300	0.050	1.54	61
III-22-F	4200	0.076	1.88	70
III-22-G	5400	0.116	1.71	79

Average value of k = $(1.69 \pm 0.09) \times 10^{-5} \text{ sec}^{-1}$

% Atom excess oxygen-18 in ester 1.996

In ethanol and 60% ethanol, the alcohol recovered after hydrolysis of the remaining α,γ -dimethylallyl ester did not contain excess oxygen-18. The results using these solvents are presented in Table XLVII and XLVIII; the calculated atom percent excess oxygen-18 in the alcohol is reported. The alcohol from the α,γ -dimethylallyl ester contained excess oxygen-18 when the rearrangement was carried out in acetic acid, while both the α -phenylallyl and the cinnamyl alcohols contained excess oxygen-18 in the three solvents used, ethanol, 60% ethanol and acetic acid.

Figures 24 to 30 show plots of the logarithm of the fraction of unreacted ester (F_{unscr}) against time. For cinnamyl 2,6-dimethylbenzenesulfinate these plots are reasonably linear and it was possible to calculate the rate of scrambling of the label in the following straightforward manner.

The concentration of the ester at any time t (C_t) was calculated from

$$\log C_t = \log C_0 - 2.303 (k_{\text{rearr}})t$$

where C_0 is the initial concentration of the ester, and k_{rearr} is the rate constant for rearrangement of the ester in the same solvent as that in which the scrambling was measured.

The concentration of unreacted ester (C_u) is give by

$$C_u = C_t - F_{\text{scr}} C_t$$

and the total rate constant for scrambling and rearrangement (k_{tot}) is

$$k_{\text{tot}} = \frac{2.303}{t} \log \frac{C_0}{C_u}$$

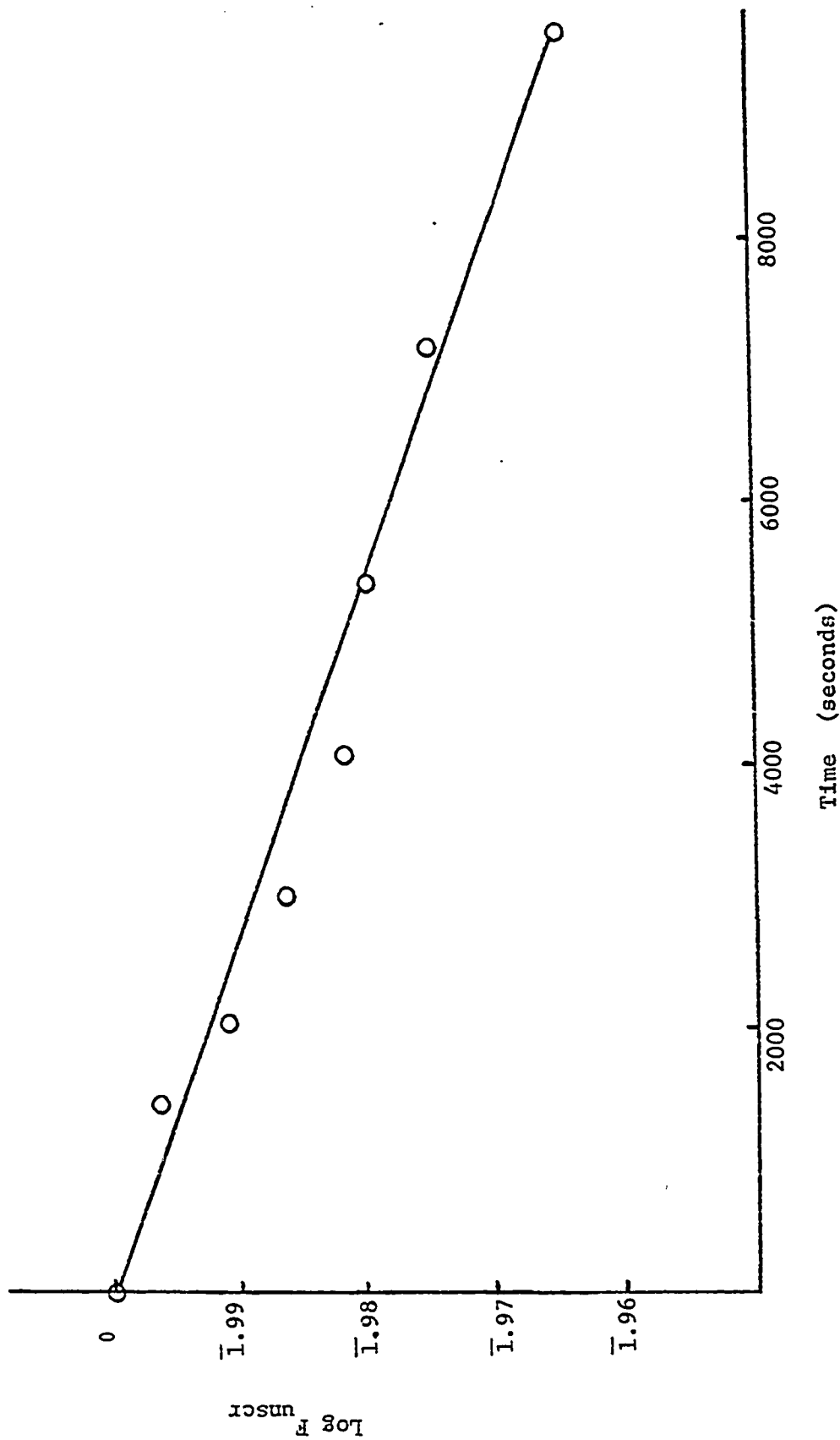


Fig. 24 - Plot of $\text{Log } F_{\text{unscr}}$ Against Time in the Reaction of Cinnamyl 2,6-Dimethylbenzenesulfinate in Ethanol at 90.0° (Table XLIV).

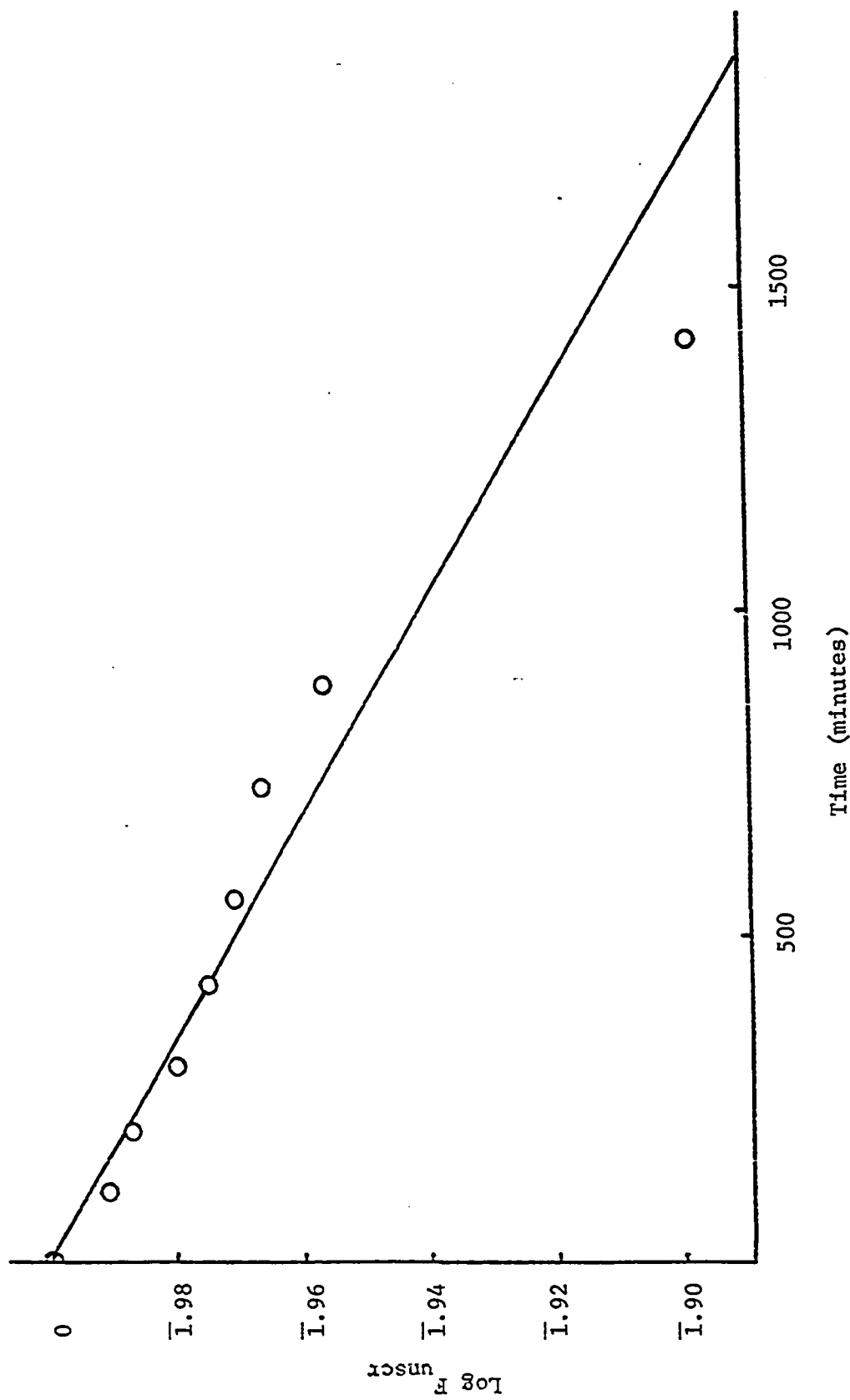


Fig. 25 - Plot of $\text{Log } F_{\text{unscr}}$ Against Time in the Reaction of Cinnamyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol at 50.0° (Table XLV)

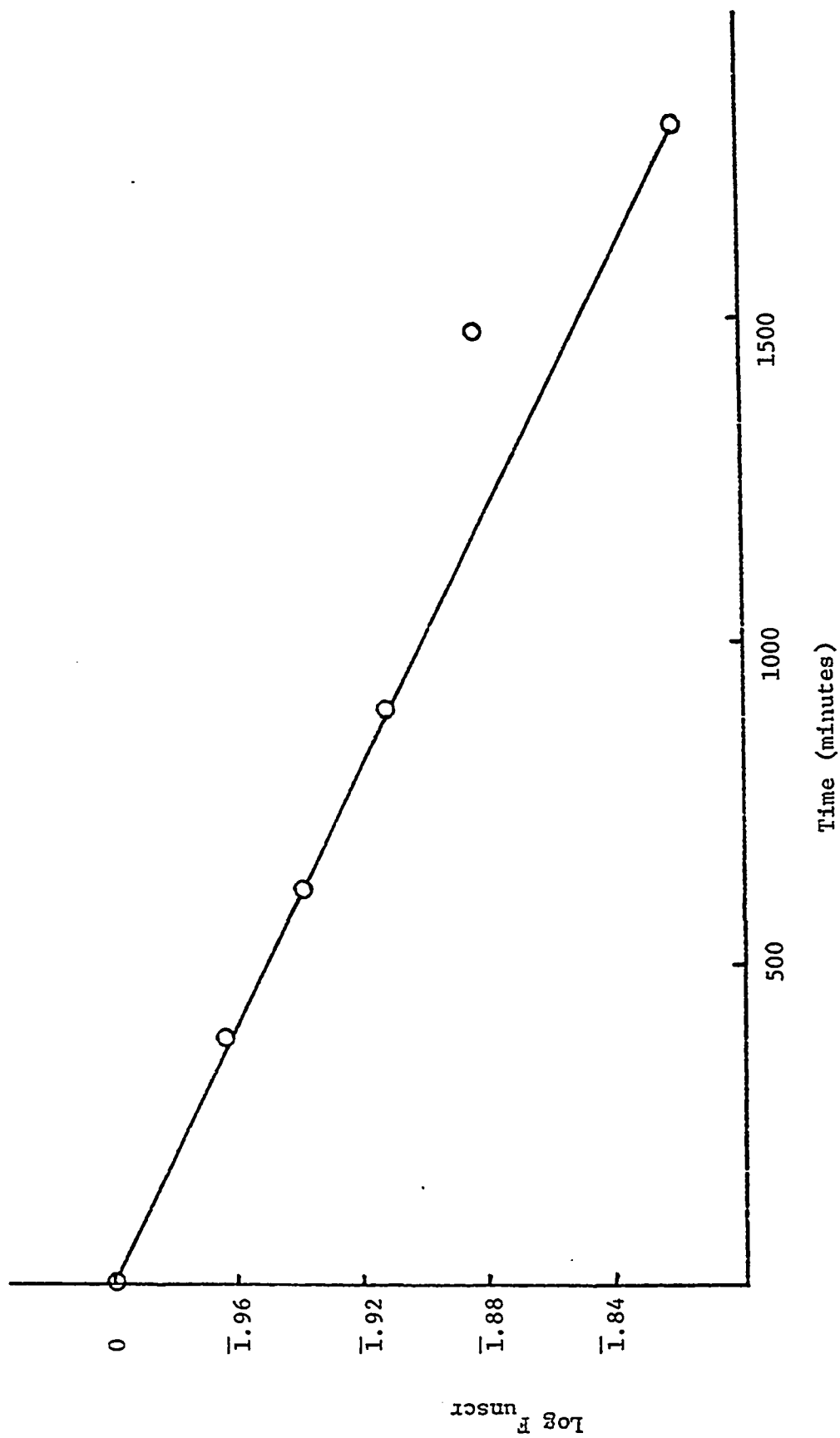


Fig. 26 - Plot of Log F_{unscr} Against Time in the Reaction of Cinnamyl
2,6-Dimethylbenzenesulfinate in Acetic Acid at 50.0° (Table XLVI)

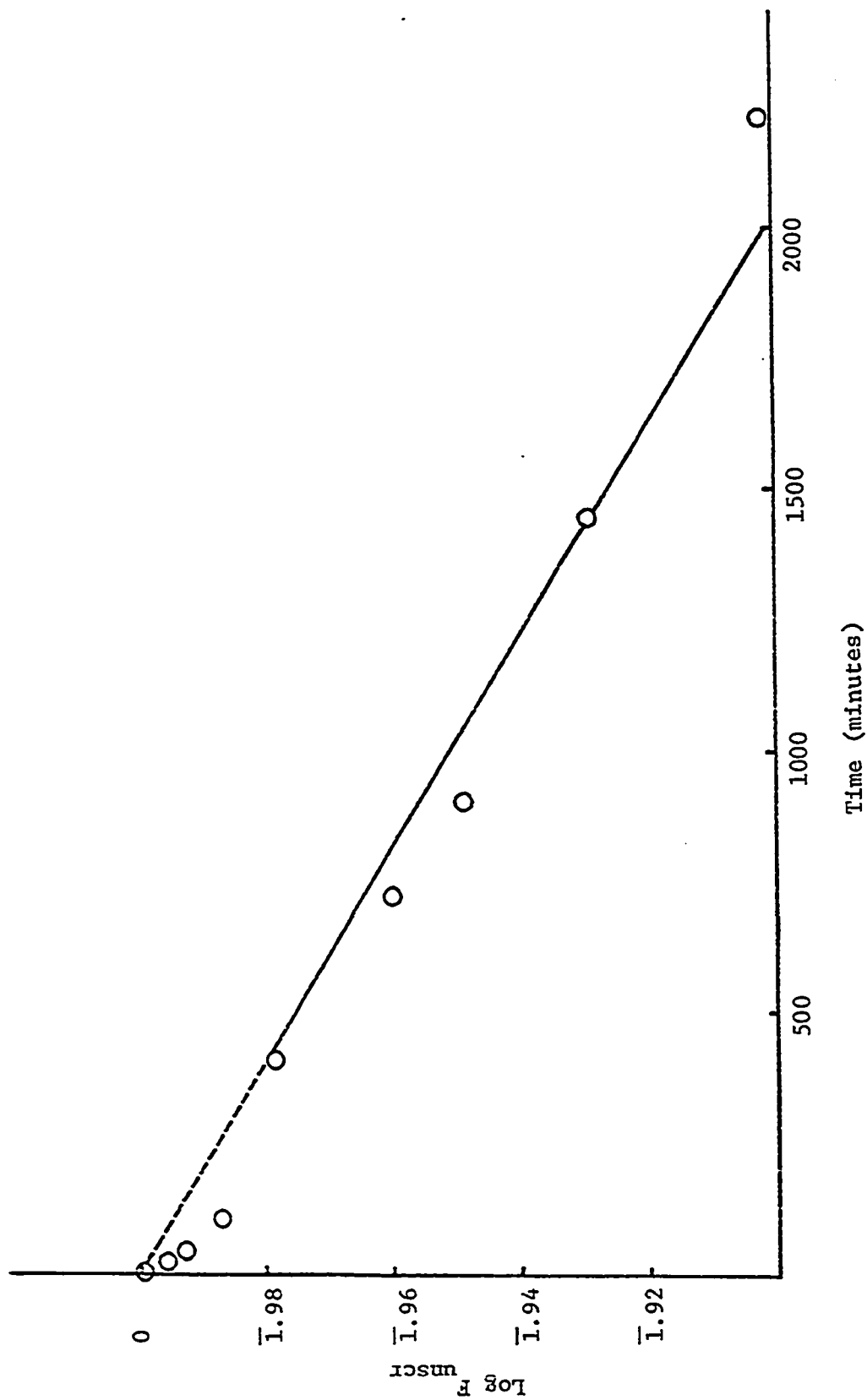


Fig. 27 - Plot of $\text{Log } F_{\text{unscr}}$ Against Time in the Reaction of α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfonate in Acetic Acid at 25.0° (Table XLIX)

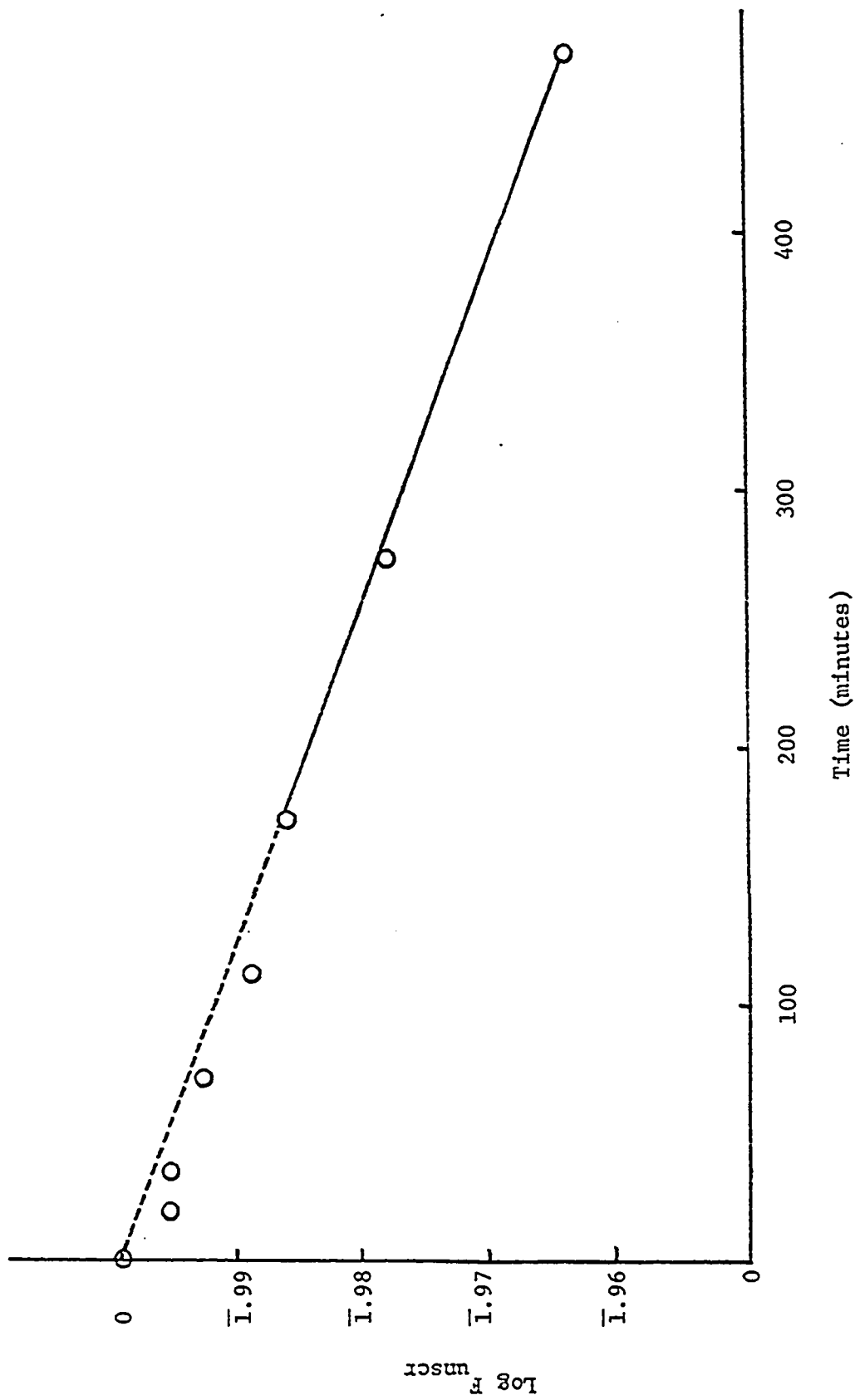


Fig 28 - Plot of $\text{Log } F_{\text{unscr}}$ Against Time in the Reaction of α -Phenylallyl
2,6-Dimethylbenzenesulfinate in Ethanol at 25.0° (Table L)

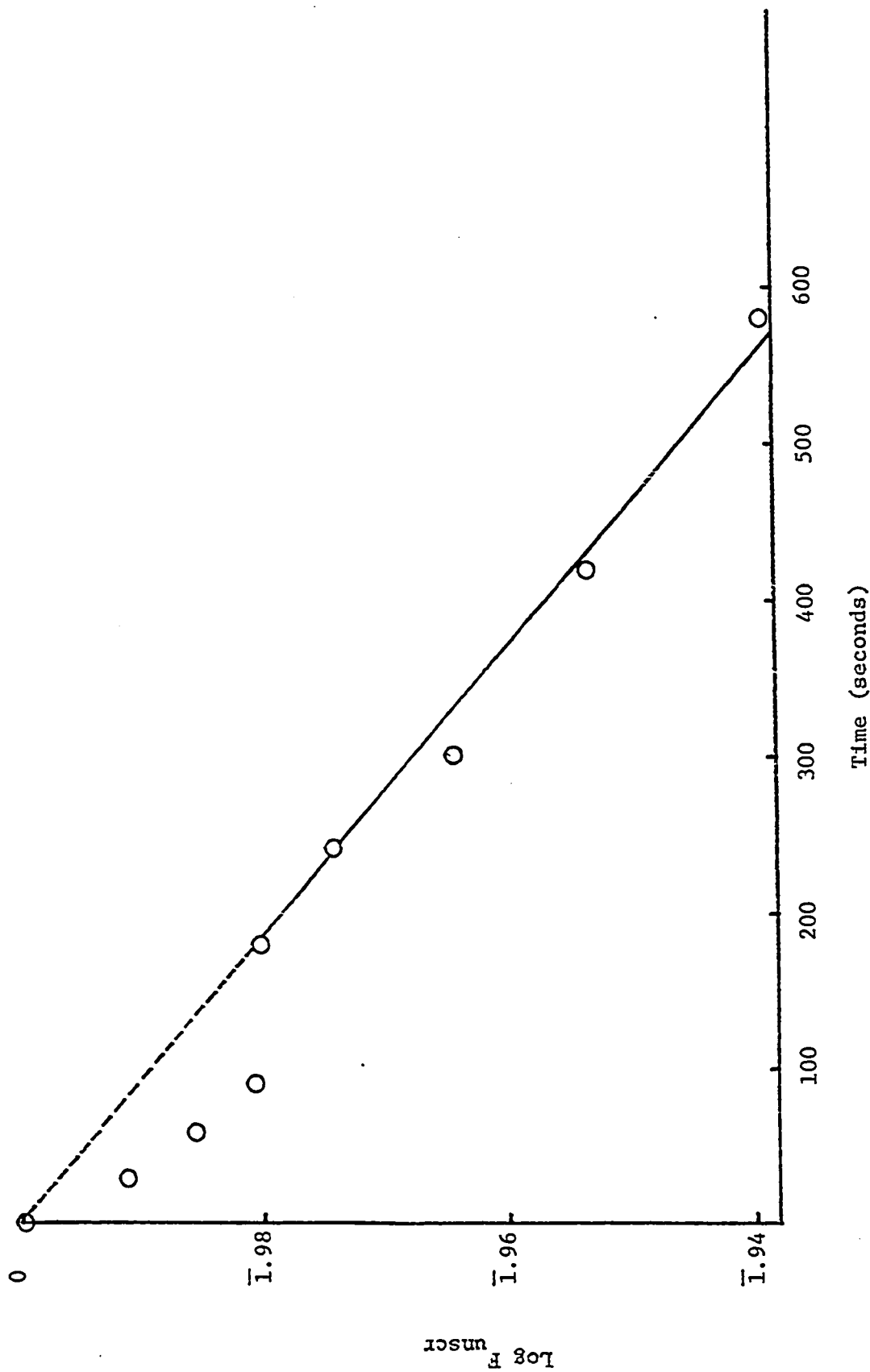


Fig. 29 - Plot of Log F_{unscr} Against Time in the Reaction of α -Phenylallyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol at 25.0° (Table LI)

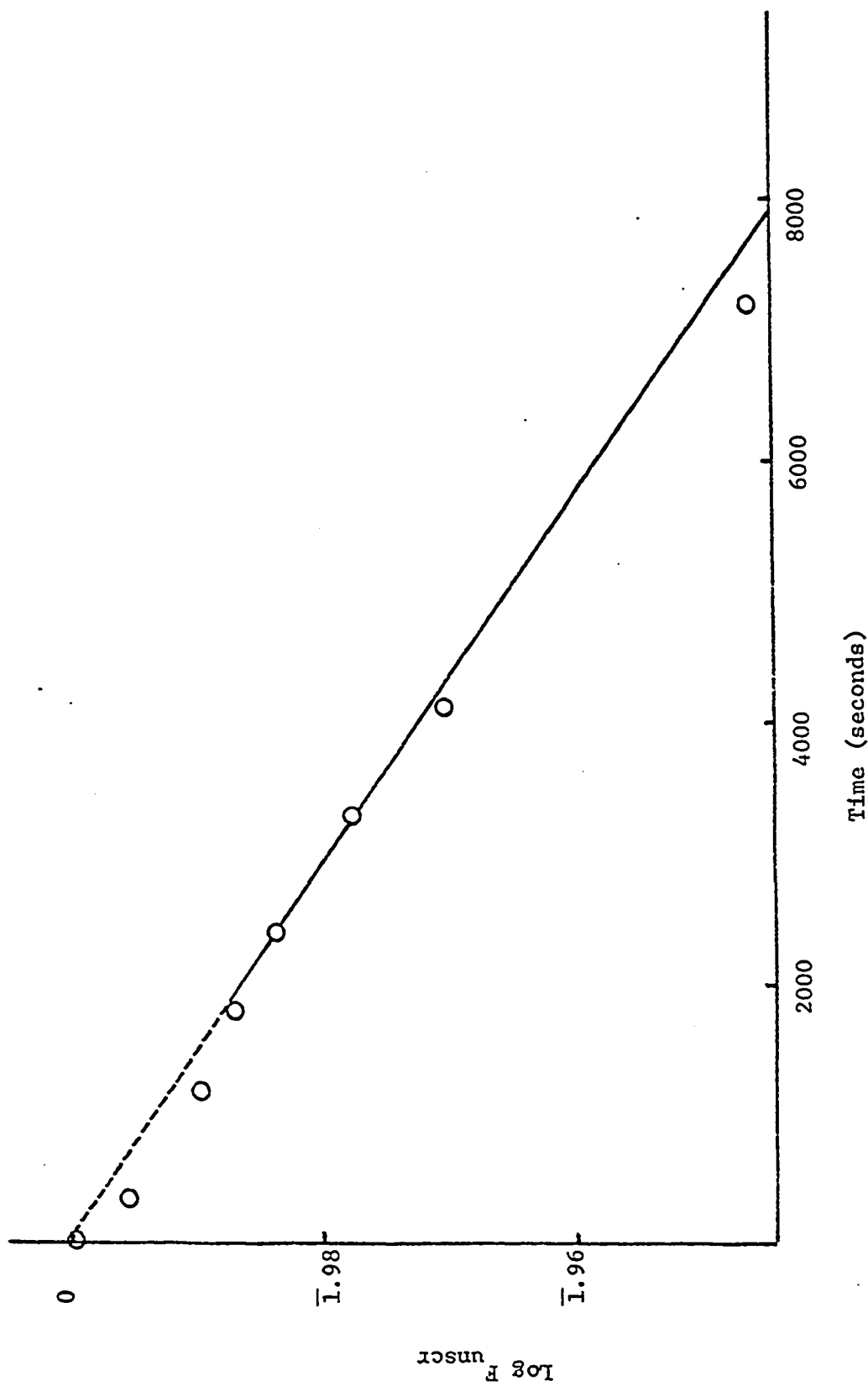


Fig. 30 - Plot of $\text{Log } F_{\text{unscr}}$ Against Time in the Reaction of α -Phenylallyl 2,6-Dimethylbenzenesulfinate in Acetic Acid at 25.0° (Table LII)

Since the rate constant for rearrangement is known, the rate constant for scrambling can be obtained from

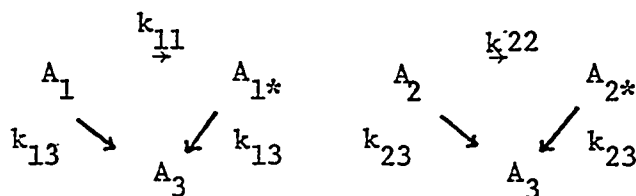
$$k_{\text{scr}} = k_{\text{tot}} - k_{\text{rearr}}$$

The rate constants obtained using this method are included in Tables XLIV to XLVI.

As has been mentioned α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate and α -phenylallyl 2,6-dimethylbenzenesulfinate are present in diastereoisomeric forms, and the graphs of the logarithm of the fraction of unreacted ester against time (Figures 27-30) show deviations from linearity. The initial concentration of each diastereoisomer in the α,γ -dimethylallyl ester was determined by infrared spectroscopy in the manner outlined for the α -phenylallyl ester. The concentrations of the diastereoisomers could be determined from both the nmr spectra and the ir spectra of the α -phenylallyl ester. These values were found to agree with one another within the experimental error and suggested an approximately 60:40 ratio of fast to slow reacting diastereoisomer, the ratio varying slightly with different preparations of ester.

In order to be able to calculate rate constants for scrambling for each of the diastereoisomers, it was necessary to be able to separate the total fraction of ester containing equilibrated oxygen-18 into a fraction of slow reacting diastereoisomer containing equilibrated oxygen-18 and a fraction of fast reacting diastereoisomer containing equilibrated oxygen-18. The graphs of the logarithm of the fraction of unreacted ester against time (Figures 27 to 30) became reasonably linear only after a sufficient time had elapsed for most of the fast

reacting diastereoisomer to have rearranged to sulfone. The points taken early in the reaction fell below the line. As will be shown below, points on this line represented the logarithm of the fraction of slow reacting diastereoisomer which did not contain oxygen-18 in the ether-oxygen position. The following scheme for scrambling of oxygen-18 in the ester can be set up:



where A is unreacted ester,

A* is ester containing equilibrated oxygen-18,

A₁ is fast reacting diastereoisomer,

A₂ is slow reacting diastereoisomer,

and A₃ is product sulfone.

After all A₁ and A_{1*} have rearranged to A₃, then there are only A₂ and A_{2*} present and so

$$\frac{A_2 + A_{2*}}{A_1 + A_{1*} + A_2 + A_{2*}} = 1$$

Then,

$$\begin{aligned}
 -\frac{d(A_2)}{dt} &= (k_{22} + k_{23}) (A_2) \\
 \therefore (A_2) &= A_2^0 e^{-(k_{22} + k_{23})t}
 \end{aligned}$$

and

$$\begin{aligned}
 - \frac{d(A_2 + A_{2*})}{dt} &= k_{23}(A_2 + A_{2*}) \\
 \therefore (A_2) + (A_{2*}) &= (A_2^0 + A_{2*}^0) e^{-k_{23}t} \\
 \therefore \frac{(A_2)}{(A_2) + (A_{2*})} &= \frac{(A_2^0)}{(A_2^0) + (A_{2*}^0)} e^{-k_{22}t} \\
 \therefore \ln \frac{(A_2)}{(A_2) + (A_{2*})} &= \ln F_2 = -k_{22}t + \ln \frac{(A_2^0)}{(A_2^0) + (A_{2*}^0)} \\
 \therefore -\ln F_2 &= k_{22}t
 \end{aligned}$$

Therefore, a plot of $\ln F_2$ against t should give a straight line of slope $-k_{22}$. Hence points on the straight line which was obtained were taken to represent the logarithm of the fraction of slow reacting diastereoisomer which contained oxygen-18 in the ether-oxygen position.

Since the fraction of ester labelled in the sulfinyl position at any time is

$$\begin{aligned}
 F &= \frac{A_1}{A_1 + A_1^*} \times \frac{A_1 + A_1^*}{A_1 + A_1^* + A_2 + A_2^*} + \frac{A_2}{A_2 + A_2^*} \times \frac{A_2 + A_2^*}{A_1 + A_1^* + A_2 + A_2^*} \\
 &= F_1 \times m_1 + F_2 \times m_2
 \end{aligned}$$

where F_1 is the fraction of the fast reacting diastereoisomer which has not reacted, m_1 is the mole fraction of all ester which is A_1 or A_1^* ,

F_2 is the fraction of the slow reacting diastereoisomer which has not reacted, m_2 is the mole fraction of all ester which is A_2 or A_{2*} , then,

$$F_1 = \frac{F - m_2 \times F_2}{m_1}$$

Since F , F_2 , m_1 and m_2 were known at any time t , the values of F_1 could be calculated.

Using these values of the fraction of each diastereoisomer which has not reacted and knowing the diastereoisomer concentrations, the rates of scrambling of oxygen-18 were calculated using the same method as that detailed for cinnamyl 2,6-dimethylbenzenesulfinate. The rate constants are in Tables XLIX to LII.

Attempts have been made to separate the diastereoisomers of α -phenylallyl 2,6-dimethylbenzenesulfinate. The nmr spectrum gives a ready measure of the relative amounts of fast and slow reacting diastereoisomers present in any sample of the ester. The separation of the diastereoisomers of α -phenylallyl 2,6-dimethylbenzenesulfinate was hampered by the instability of the ester at room temperature. It was hoped that it might be possible to separate the isomers by fractional crystallization. However, on cooling an ether-pentane solution of the ester to -70° , a viscous oil separated which could not be induced to crystallize, and on allowing the mixture to stand in the freezing compartment of the refrigerator, a slow rearrangement to cinnamyl 2,6-dimethylphenyl sulfone occurred. When the crystals of this sulfone were removed by filtration, the

F_2 is the fraction of the slow reacting diastereoisomer which has not reacted, m_2 is the mole fraction of all ester which is A_2 or A_{2*} , then,

$$F_1 = \frac{F - m_2 \times F_2}{m_1}$$

Since F , F_2 , m_1 and m_2 were known at any time t , the values of F_1 could be calculated.

Using these values of the fraction of each diastereoisomer which has not reacted and knowing the diastereoisomer concentrations, the rates of scrambling of oxygen-18 were calculated using the same method as that detailed for cinnamyl 2,6-dimethylbenzenesulfinate. The rate constants are in Tables XLIX . to LII.

Attempts have been made to separate the diastereoisomers of α -phenylallyl 2,6-dimethylbenzenesulfinate. The nmr spectrum gives a ready measure of the relative amounts of fast and slow reacting diastereoisomers present in any sample of the ester. The separation of the diastereoisomers of α -phenylallyl 2,6-dimethylbenzenesulfinate was hampered by the instability of the ester at room temperature. It was hoped that it might be possible to separate the isomers by fractional crystallization. However, on cooling an ether-pentane solution of the ester to -70° , a viscous oil separated which could not be induced to crystallize, and on allowing the mixture to stand in the freezing compartment of the refrigerator, a slow rearrangement to cinnamyl 2,6-dimethylphenyl sulfone occurred. When the crystals of this sulfone were removed by filtration, the

unrearranged ester remained as an oil.

Chromatography of the ester on Woelm alumina of activity grade I at room temperature and eluting with ether:pentane, resulted in almost complete rearrangement to sulfone. When the temperature of the column was reduced to -70° and 50:50 pentane:ether was used as eluent, the first 100 ml of solution from the column yielded a sample of ester in which the ratio of fast to slow reacting diastereoisomer, as judged from the nmr spectrum, was 2.7:1 rather than the 1.23:1 of the starting ester. However, this ratio could not be improved upon, and a considerable loss of material by rearrangement occurred.

The ester was treated with sodium methoxide and with sodium hydroxide for short periods of time in the hope that the base would react preferentially with one of the isomers. It was judged from the nmr spectra of the products of the reaction after various time intervals that hydrolysis of the diastereoisomers was not occurring at sufficiently different rates to allow of their separation by this method.

If interconversion of the diastereoisomers was not occurring it seemed possible that isolation of a sample of slow reacting diastereoisomer might be achieved by allowing the ester to react in 60% ethanol until most of the fast reacting diastereoisomer had been converted to sulfone. According to the results of the rate of rearrangement of the isomers measured by nmr spectroscopy, in 60% ethanol the fast reacting diastereoisomer rearranged approximately 1.6 times as rapidly as the slow reacting diastereoisomer. Samples of ester were allowed to react in 60% ethanol for various lengths of time and the nmr spectra of the residues after work-up

were measured. They indicated that both diastereoisomers were still present. Since 2,6-lutidine and ethyl 2,6-dimethylbenzenesulfinate, which show signals in the nmr at τ 7.59 and τ 7.42 respectively, would interfere with the assignment of signals to the diastereoisomers, the ester was allowed to rearrange in acetonitrile and in acetone. Pyridine was added to both solutions. Once again, all of the nmr spectra of the partially rearranged ester indicated the presence of both of the diastereoisomers.

Tests were carried out to see if diastereoisomer interconversion was taking place during reaction. A solution of α -phenylallyl 2,6-dimethylbenzenesulfinate (0.03812 M) and pyridine (0.05341 M) in 60% ethanol was allowed to stand at 25.0° for 20 minutes and then worked-up in the manner described for the rate determination by nmr spectroscopy. The nmr spectrum of the product indicated that the ester which was still present contained a larger proportion of slow than fast reacting diastereoisomer. The remaining portion of the product was dissolved in ether, potassium carbonate was added and the solution was placed in the freezing compartment of the refrigerator. After one week, the nmr spectrum of this portion was measured and indicated that the composition of the ester was now such that both diastereoisomers were present in almost equal amounts.

The formation of cinnamyl 2,6-dimethylbenzenesulfinate by a rearrangement having a 6-membered cyclic transition state from α -phenylallyl 2,6-dimethylbenzenesulfinate could conceivably account for the observed oxygen-18 scrambling, although as mentioned in Chapter II, such a rearrangement has been ruled out for the allyl, crotyl and α -methylallyl esters. Since the α -phenylallyl ester

rearranges to cinnamyl sulfone about 100 times more rapidly than the cinnamyl ester rearranges to α -phenylallyl sulfone, the presence of the cinnamyl ester should be detectable in the products after most or all of the α -phenylallyl ester has disappeared. Using this scheme, whose kinetics will be detailed in the discussion section of this chapter, it could be estimated that, after 3600 seconds in acetic acid at 25^o, the reaction product would have to contain cinnamyl ester, α -phenylallyl ester and cinnamyl sulfone in the ratio of 1:4.7:14 respectively to account for the oxygen-18 scrambling observed in this solvent. A mixture of this composition was prepared, dissolved in 30 ml of ether and worked-up in the manner which had been used in the measurement of the rearrangement rate. Cinnamyl ester could be readily detected in the nmr spectrum of the residue. The products after two and ten half lives, of the reaction of α -phenylallyl 2,6-dimethylbenzenesulfinate in all of the solvents employed were analyzed from their 100 Mc spectra, but no signals which could be assigned to cinnamyl 2,6-dimethylbenzenesulfinate or to α -phenylallyl 2,6-dimethylphenyl sulfone were detected. Any cinnamyl ester which is being formed from the α -phenylallyl ester is therefore present in too small a quantity to be seen in the nmr spectrum and its formation cannot account for the presence of all of the observed oxygen-18 scrambling.

If α -phenylallyl 2,6-dimethylbenzenesulfinate can rearrange to cinnamyl 2,6-dimethylbenzenesulfinate then the rearrangement of the cinnamyl ester to the α -phenylallyl ester via a 6-membered transition state might also be possible. An analysis of the products of rearrange-

ment of the cinnamyl ester similar to that of the products of rearrangement of the α -phenylallyl ester was undertaken. However, in this case, the α -phenylallyl ester formed will react 100 times more rapidly than the cinnamyl ester to yield cinnamyl 2,6-dimethylphenyl sulfone, and the analysis is complicated by the fact that α -phenylallyl 2,6-dimethylphenyl sulfone was found to rearrange slowly to cinnamyl 2,6-dimethylphenyl sulfone in 60% ethanol and in acetic acid under the reaction conditions. Within the limits of the experimental error, the cinnamyl sulfone present in the reaction products was the fraction expected from rearrangement of the first formed α -phenylallyl sulfone. In anhydrous ethanol, no cinnamyl 2,6-dimethylphenyl sulfone was detected.

DISCUSSION

The reaction of cinnamyl 2,6-dimethylbenzenesulfinate in the solvents studied yielded α -phenylallyl 2,6-dimethylphenyl sulfone as the major product. Similarly, the α,γ -dimethylallyl ester rearranged to the α,γ -dimethylallyl sulfone and the α -phenylallyl ester to the cinnamyl sulfone. The yields of 2,6-dimethylbenzenesulfonic acid formed by solvolysis during these reactions are tabulated in Table XXIV. The mode of formation of this acid will be discussed briefly.

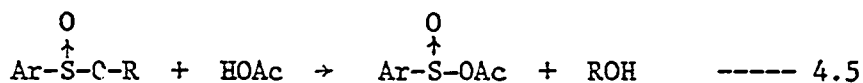
In the discussion of the allyl, crotyl and α -methylallyl esters, it was mentioned that in 60% ethanol, sulfur-oxygen bond fission is 6.5 times faster when the added base is acetate ion than when the added base is 2,6-lutidine (69). The quantity of acid produced during the reaction of cinnamyl 2,6-dimethylbenzenesulfinate varied little with the nature of the base: Braverman (12) quotes 5.8% acid formed in the presence of sodium acetate. In the course of the present work, it was found that 6.4% acid was formed in the presence of 2,6-lutidine. This suggests that most of the acid is being formed by carbon-oxygen bond fission. The 100 Mc nmr spectra of the products of the reaction of the cinnamyl ester in both 60% ethanol and anhydrous ethanol were carefully analyzed and no signals which could be assigned to ethyl 2,6-dimethylbenzenesulfinate were observed. Sulfur-oxygen bond fission in anhydrous ethanol must give rise to the ethyl ester. Noreyko (69) has shown that, in the reaction of *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate at

90.0°, sulfur-oxygen bond fission catalyzed by 2,6-lutidine is 12 times faster in 60% ethanol than in anhydrous ethanol. However, since no ethyl ester was detected in anhydrous ethanol, the rate of sulfur-oxygen bond fission must be very slow compared to the rate of carbon-oxygen bond fission. The rate of rearrangement of the cinnamyl ester in ethanol at 90.0° was found to be $14.4 \times 10^{-5} \text{ sec}^{-1}$ while Braverman (12) obtained a value of $10.1 \times 10^{-4} \text{ sec}^{-1}$ for the rate in 60% ethanol at 90.0°. From these values, the rate of carbon-oxygen bond fission is increased by a factor of ca. 7 in going from ethanol to 60% ethanol. Therefore, even in 60% ethanol where the rate of sulfur-oxygen bond fission will be speeded up by a factor of ca. 12, it seems likely that the acid produced arises largely from carbon-oxygen bond fission.

A similar argument can be applied in the case of the α -phenylallyl ester. Reaction of this ester in 60% ethanol with sodium acetate produced 10.4% acid; with 2,6-lutidine, 9.8% acid was formed. Thus the amount of acid produced is only slightly dependent on the nature of the base. Ethyl 2,6-dimethylbenzenesulfinate could not be detected in the products of the reaction of the α -phenylallyl ester in anhydrous ethanol with added 2,6-lutidine. Therefore less than 2% of the ethyl ester was formed during the reaction. It can be concluded that the acid produced in the reaction of the α -phenylallyl ester in 60% ethanol results mainly from carbon-oxygen bond fission.

Braverman found so little acid produced during the rearrangement of the α,γ -dimethylallyl ester in 60% ethanol in the presence of either acetate ion or 2,6-lutidine that he was unable to reach any conclusion

as to the mode of its formation. In acetic acid with added sodium acetate, it has been found that 9% of the reaction products from the rearrangement of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate were α,γ -dimethylallyl acetate, a product which may have arisen directly from carbon-oxygen bond fission or by reaction with the solvent of the alcohol formed by sulfur-oxygen bond fission. Braverman measured the amount of 2,6-dimethylbenzenesulfinic acid produced during the rearrangement of the α,γ -dimethylallyl ester in acetic acid by titrating the mixture with perchloric acid to the green end-point of p-naphtholbenzein and obtained a figure of 7.2%. Again this acid may have arisen either by carbon-oxygen bond fission or by sulfur-oxygen bond fission. The latter would lead initially to the formation of a mixed anhydride (equation 4.5)



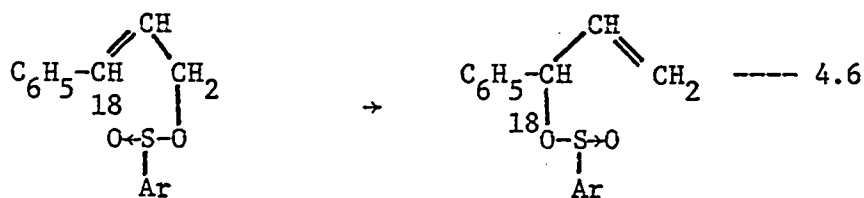
which would be unstable under the reaction conditions and would decompose to yield the sulfinic acid and acetic anhydride.

The rearrangement and oxygen-18 scrambling results are discussed under the heading of each ester.

Cinnamyl 2,6-Dimethylbenzenesulfinate

The rearrangement of this ester to α -phenylallyl 2,6-dimethylphenyl sulfone was measured in ethanol, 60% ethanol and acetic acid and it was found to react at a rate which was ca. 1.6 times as fast as the rearrangement of the slow reacting diastereoisomer of the α -methylallyl ester to crotyl sulfone.

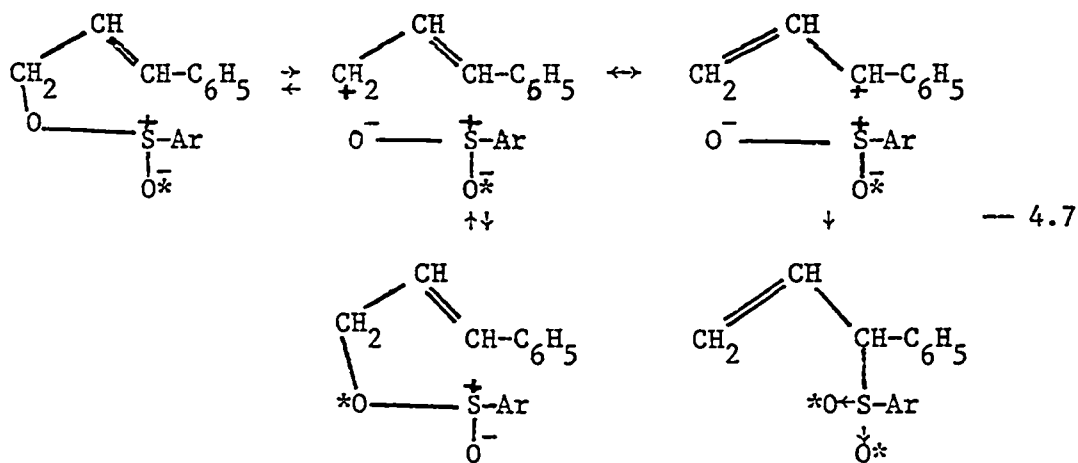
Scrambling of the oxygen-18 label was detected in the ester recovered after partial rearrangement in all three solvents. Since only one asymmetric centre is present in this molecule, it does not exist in diastereoisomeric forms and calculation of both the rates of rearrangement and of oxygen-scrambling was relatively straightforward. Since oxygen-18 scrambling is observed, an ion-pair intermediate which returns to starting material may be formed in the reaction. Alternatively, the possibility of a 6-membered transition state leading to the formation of the α -phenylallyl ester having an oxygen-18 label in the ether-oxygen position must be considered (equation 4.6).



Hydrolysis of the esters would result in the formation of a mixture of cinnamyl and α -phenylallyl alcohols and both would survive the work-up procedure. However, crystallization of the cinnamyl alcohol would have been expected to remove any α -phenylallyl alcohol impurity and since none could be detected in the spectra, less than 1% of the α -phenylallyl alcohol could have been present. An analysis of the products of the reaction can also be used to determine whether a fraction of the reaction proceeds via a 6-membered transition state. Since the α -phenylallyl ester will rearrange to yield cinnamyl sulfone

more rapidly than the cinnamyl ester will rearrange to α -phenylallyl sulfone, the products were analyzed for cinnamyl sulfone. In 60% ethanol and in acetic acid, cinnamyl sulfone was detected, while in ethanol it was not. It was shown that under the reaction conditions, in 60% ethanol and in acetic acid, α -phenylallyl sulfone slowly rearranged to cinnamyl sulfone and the amount of this latter sulfone detected was the amount to be expected from this reaction. Hence, rearrangement of cinnamyl 2,6-dimethylbenzenesulfinate to α -phenylallyl 2,6-dimethylbenzenesulfinate does not seem to occur under the reaction conditions.

The mechanism of oxygen-18 scrambling involving an ion-pair intermediate is illustrated in equation 4.7.

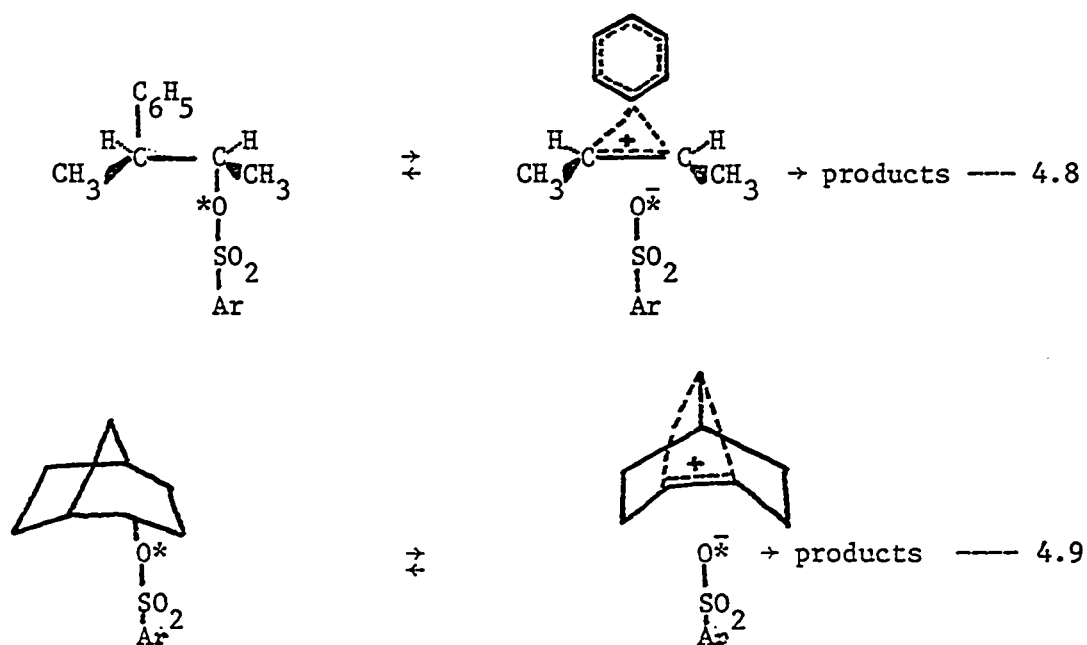


The asterisk denotes an oxygen-18 label.

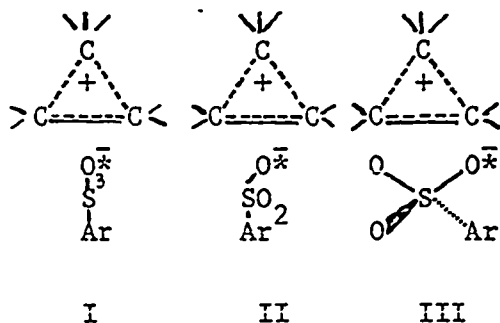
Two factors will influence the amount of oxygen-18 scrambling observed in a system such as this. Firstly, the degree of equilibration of the oxygen atoms of the ion-pair, and secondly,

the relative rates of product formation and return to covalent starting materials. These points will be discussed in turn.

Goering studied the oxygen-18 scrambling and racemization during the acetolysis of ether-oxygen labelled threo-3-phenyl-2-butyl p-toluenesulfonate (45) and endo-bicyclo(3,2,1)-octan-2-yl p-toluenesulfonate (44). The ionization of these esters is illustrated in equations 4.8 and 4.9 respectively.

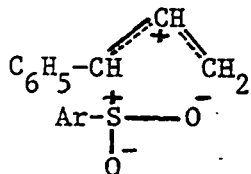


Goering drew three possible orientations for the ion-pair intermediate I, II and III, in which the asterisk denotes the oxygen which was the ether-oxygen of the starting ester.

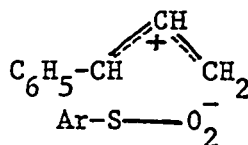


In I, the oxygens are completely equivalent; in II, the bond formed in return to covalent starting material is with the same oxygen as that which was broken, while in III, two equivalent oxygens are paired with two equivalent carbons. Using oxygen-18 labelled starting material return from each orientation will result in different amounts of scrambling of the label.

In the present system two possible orientations will be considered for the intermediate ion-pair, IV and V.



IV



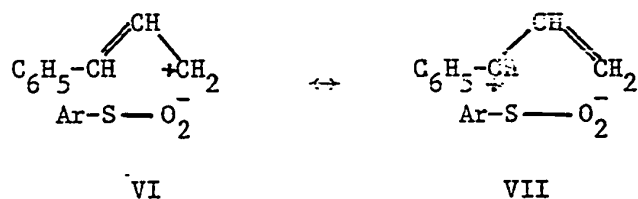
V

In IV, recombination of the ions occurs by reformation of the same carbon-oxygen bond as that which was broken and there would be no incorporation of the oxygen-18 label into the ether-oxygen position of the ester. In V, the two oxygen atoms are equivalent; the bond formed in the return of the ions to starting material is equally likely to be with either of the oxygens. This would give rise to 50% incorporation of the oxygen-18 label into the ether-oxygen position of the ester.

In his study of the systems mentioned above, Goering concluded that his results were best explained by having return occur from both intermediates I and II. It is therefore possible that return to form cinnamyl 2,6-dimethylbenzenesulfinate can occur from both species IV and V, in which case equilibration of the oxygen atoms would not be complete

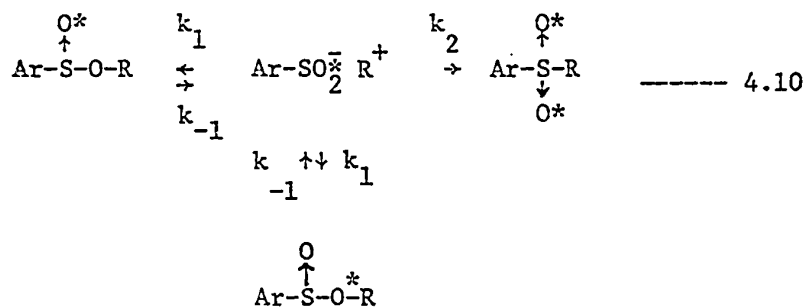
and the oxygen-18 scrambling would not detect all of the ion-pair return. It would be expected that the more stable the ion-pair formed, the more nearly orientation V would be the correct representation. The scrambling detected must therefore be a minimum measure of the ion-pair return to oxygen.

The second factor affecting the oxygen-18 scrambling observed is the partitioning of the ion-pair between return to covalent starting material and formation of products. The ion-pair structures IV and V imply resonance stabilization of the allylic cation. The discrete contributors to this resonance hybrid for ion-pair V will be structures VI and VII. Structure VII will be stabilized by the presence of the phenyl group on the carbon carrying the positive charge



and therefore would be expected to contribute to the resonance hybrid to a greater extent. This will facilitate ion-pair return to sulfur.

If the assumption is made that return to oxygen occurs from structure V only, then the kinetic scheme of equation 4.10 can be written where an asterisk denotes an oxygen-18 label.



Then, writing S for the concentration of the ester having the oxygen-18 label in the sulfinyl-oxygen position.

S* for the concentration of the ester having the oxygen-18 label in the ether-oxygen position.

P for the concentration of product sulfone,

and I for the concentration of the ionic intermediate, the following derivation of the significance of the relative values of the rate constants for rearrangement and scrambling of oxygen-18 can be made.

1) Rate of rearrangement.

$$\frac{dp}{dt} = - \frac{d(S + S^*)}{dt} = k_2 I \quad \text{-----} \quad 4.11$$

From steady state theory,

$$\frac{dI}{dt} = 0 = k_1 S + k_1 S^* - 2k_{-1} I - k_2 I$$

$$I = \frac{k_1(S + S^*)}{2k_{-1} + k_2} \quad \text{-----} \quad 4.12$$

Then substituting 4.12 into 4.11

$$\frac{dp}{dt} = \frac{k_1 k_2 (S + S^*)}{2k_{-1} + k_2}$$

2) Rate of scrambling.

$$S + S^* + P = \text{constant}$$

$$(S - S^*) + 2S^* + P = \text{constant}$$

$$(S - S^*) = \text{concentration of unreacted ester}$$

$$\frac{d(S - S^*)}{dt} + \frac{2dS^*}{dt} + \frac{dP}{dt} = 0$$

$\frac{d(S - S^*)}{dt}$ is the sum of the rate of scrambling and the rate of rearrangement.

$$\frac{-d(S - S^*)}{dt} = 2k_{-1}I - 2k_1S^* + k_2I \quad \text{----- 4.13}$$

Substituting 4.12 into 4.13

$$\begin{aligned} \frac{-d(S - S^*)}{dt} &= \frac{2k_1k_{-1}(S + S^*)}{2k_{-1} + k_2} - 2k_1S^* + \frac{k_1k_2(S + S^*)}{2k_{-1} + k_2} \\ &\quad + k_1(S - S^*) \end{aligned}$$

$$\begin{aligned} \frac{\text{Rate Constant for scrambling and rearrangement}}{\text{Rate constant for rearrangement}} &= \frac{2k_{-1} + k_2}{k_2} \\ &= \frac{2k_{-1}}{k_2} + 1 \end{aligned}$$

Hence the ratio of the total rate constant for scrambling and rearrangement to the rate constant for rearrangement provides a quantitative measure of the partitioning of the ion-pair between sulfone formation and return to covalent ester. The values of this ratio obtained for the cinnamyl system were 1.065, 1.088 and 1.30 when the reaction was in ethanol, 60% ethanol and acetic

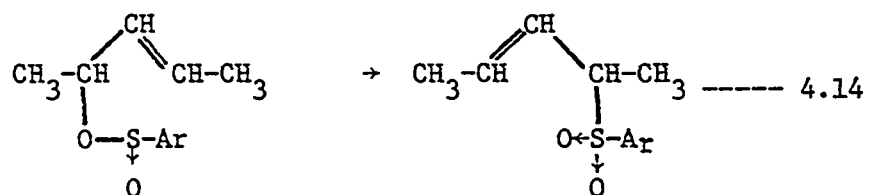
acid respectively. Therefore, the ratios of k_{-1} to k_2 are 0.03, in ethanol, 0.04 in 60% ethanol and 0.15 in acetic acid. These values reflect the ability of the solvent to facilitate ionization. Thus 60% ethanol is a better ionizing solvent than is anhydrous ethanol, while for sulfinate esters acetic acid, by its ability to hydrogen bond to the leaving group is still more effective. Further discussion of the role of acetic acid will be presented under the heading of the α,γ -dimethylallyl ester.

Ion-pair return to oxygen is less important for the cinnamyl ester in ethanol and 60% ethanol compared with the corresponding reactions of benzhydryl 2,6-dimethylbenzenesulfinate (15). The rate constant for solvolysis of the latter ester at 90.0° in anhydrous ethanol with added 2,6-lutidine was found to be $2.33 \times 10^{-5} \text{ sec}^{-1}$, while the rate constant for oxygen-18 scrambling in labelled ester was $0.67 \times 10^{-5} \text{ sec}^{-1}$. In acetic acid at 50.0° the rate constant for acetolysis was $1.63 \times 10^{-5} \text{ sec}^{-1}$, while the rate constant for oxygen-18 scrambling in the same solvent was $1.78 \times 10^{-5} \text{ sec}^{-1}$. Hence, ion-pair return is very much less extensive in the rearrangement of the cinnamyl ester than in the reactions of the benzhydryl ester. In the reactions of the latter ester, the presence of both intimate and solvent separated ion-pairs has been postulated. More complete oxygen equilibration appears to occur when solvent separated ions are involved in a reaction than when intimate ion-pairs are formed. For example, a special salt effect was observed (43) during the acetolysis of 2-*p*-methoxyneophyl-1-propyl *p*-toluenesulfonate. Therefore, solvent separated ion-pairs were proposed as intermediates in the reaction. From their study of oxygen-18

scrambling during the acetolysis of the ether-oxygen labelled ester, Denney and Goldstein (42) suggested that complete equilibration of the oxygen atoms had occurred. On the other hand, the reactions of threo-3-phenyl-2-butyl p-toluenesulfonate and endo-bicyclo-(3,2.1)-octan-2-yl p-toluenesulfonate in acetone have been proposed to involve intimate ion-pairs. Goering and his co-workers (44,45) have estimated that internal return involving rebonding of the p-toluenesulfonate ion to the original carbon atom is accompanied by about 50% randomization of the sulfonate oxygen atoms. Hence, it may be that intimate ion-pairs are involved in the rearrangement of the cinnamyl ester.

α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfinate

This ester exists in two diastereoisomeric forms, as was the case with the α -methylallyl ester. The rates of rearrangement of the diastereoisomers to the corresponding sulfone (equation 4.14)



were deduced from infrared spectral measurements in ethanol, 60% ethanol and acetic acid. The rate of rearrangement of the slow reacting diastereoisomer was found to be about ten times faster than that of the cinnamyl ester.

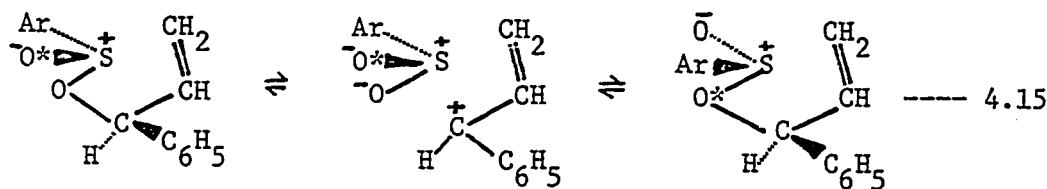
The α,γ -dimethylallyl ester recovered after partial rearrangement

in ethanol and 60% ethanol did not contain any excess oxygen-18 label in the ether-oxygen position, but scrambling of the label in the ester was detected during the rearrangement in acetic acid. The ratio of the total rate constant for scrambling and rearrangement to the rate constant for rearrangement was 1.168 for the fast reacting diastereoisomer and 1.156 for the slow reacting diastereoisomer. As with the allyl, crotyl and α -methylallyl esters, the lack of oxygen-18 scrambling during rearrangement of the α,γ -dimethylallyl ester in ethanol and 60% ethanol is consistent with the formation of a transition state in which bond-making and bond-breaking is sufficiently concerted that a discrete ionic intermediate is not formed.

Several factors may be important in the reaction in acetic acid. The rates of solvolysis of certain alkyl fluorides are enhanced in acetic acid (72, 73). For example, the solvolysis of benzhydryl fluoride is faster by 5 powers of ten in acetic acid than in ethanol solution, relative to the solvolysis of benzhydryl chloride (72). A similar acceleration of the ionization of arenesulfinates in acetic acid has been demonstrated (13, 15, 66). When the logarithm of the rate of solvolysis or rearrangement of benzhydryl 2,6-dimethylbenzenesulfinate was plotted against the logarithm of the rate of solvolysis of benzhydryl chloride in various solvents, straight line graphs were obtained. Only the acetic acid point deviated from the line and this by a factor of three powers of ten. Specific solvation of the leaving group has been proposed to account for this rate enhancement (13). However, when the logarithm of the rate of rearrangement of allyl 2,6-dimethylbenzenesulfinate is plotted against the logarithm of the rate of solvolysis of *p*-methoxy-

neophyl *p*-toluenesulfonate then the deviation of the acetic acid point is very small, ($\sqrt{10}^{0.5}$) (12). This may be fortuitous in that the rate of rearrangement of the allyl ester by a cyclic mechanism is so much faster than the rate of ionization that speeding up the ionization by a factor of 10^3 to 10^4 still has not made it important. However, it may be that for the α,γ -dimethylallyl ester, ionization is sufficiently fast to become important when acetic acid is used as solvent. It has been mentioned that the rate of rearrangement of the allyl ester has been calculated to be about three powers of ten faster than would be expected for a purely ionic mechanism, while the rate of rearrangement of the α,γ -dimethylallyl ester is only two powers of ten faster (12). Hence, the driving force attributed to the formation of a 5-membered cyclic transition state is of less importance relative to a reaction proceeding via an ionic transition state, for the α,γ -dimethylallyl ester than for the allyl ester. It has also been shown that in the acetolysis of *p*-chlorobenzhydryl chloride, ion-pair return is extensive (71). Thus, the ion-pair formed in this reaction has been estimated to return to covalent starting material 38 times as fast as it yields solvolysis products, while in 80% acetone the return is only 3 times as fast as the product formation. Hence, it may be that in the α,γ -dimethylallyl system, acetic acid is promoting ion-pair return. It has been noted that the ratio of rearrangement to oxygen-18 scrambling of the cinnamyl system in acetic acid is smaller than the ratio in either ethanol or 60% ethanol and this may be due to the same factor. However, if as has been proposed for cinnamyl 2,6-dimethylbenzenesulfinate, the oxygen-18

scrambling arises from recombination of the allylic cation with the labelled oxygen of the sulfinate anion, then this will bring about inversion of the groups about the sulfur atom. Thus, for the esters which have two asymmetric centres, ion-pair return to oxygen can lead to the diastereoisomer different from the starting material (equation 4.15).



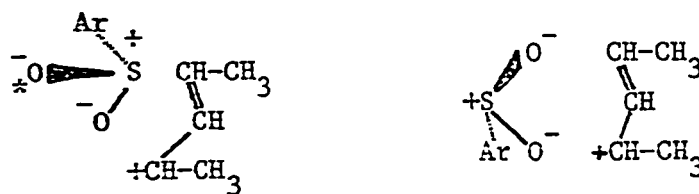
The asterisk denotes an oxygen-18 label.

For the ionic intermediate to return to the same diastereoisomer as the starting material with oxygen-18 scrambling, would require a double inversion, inversion occurring at both the sulfur and carbon centres. This can be accomplished in three ways. Firstly, it would result if migration of the anion to the opposite side of the cation occurred prior to recombination. Since it has been shown that the type of ionic intermediate which best fits the experimental evidence is an intimate ion-pair, it seems likely that this ion-pair would not have sufficient freedom of movement to allow such a migration path. If the ions were dissociated to such a degree that the migration were possible, the formation of solvolysis products would be expected. These are not observed to any extent.

Secondly, if pyramidal inversion of the groups about the sulfur

in the sulfinate anion were to occur faster than rotation and recombination then a mixture of diastereoisomers of the starting ester would be formed. Pyramidal inversion in sulfoxides and sulfonates has been found to be slow, so that it is probably also slow in the anion. Even if it is fast, it will still lead to some diastereoisomer interconversion.

The third scheme which could account for the incorporation of the oxygen-18 label into the ether-oxygen position of the ester and would not require diastereoisomer interconversion, is applicable only to esters having symmetric allylic groups. Two conformations, VIII and IX, of the ionic intermediate will be considered.



VIII

IX

The conformation VIII in which the carbon-oxygen bond is broken and the sulfur remains close to the carbon of the allylic group, will give rise to sulfone. In the second conformation, IX, the sulfur is remote from the carbons which are paired with the oxygen atoms. Return to form ester could occur by formation of either carbon-oxygen bond. Reformation of the original carbon will give rise to ester having the oxygen-18 label in the sulfinyl-oxygen position. Formation of the carbon-oxygen bond different from the original will result in ester having the oxygen-18 label in the ether-oxygen position.

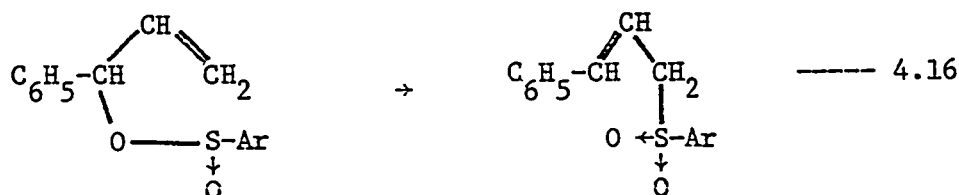
A good separation of the rates of the fast and slow reacting diastereoisomers of the α,γ -dimethylallyl ester in acetic acid appeared to have been achieved (Figure 19). The rates were found to differ by a factor of ca. 6, (Table XXXIV), and had half-lives of approximately 140 minutes for the fast reacting diastereoisomer and 14 hours for the slow reacting diastereoisomer, making them amenable to measurement. It therefore seems possible that the incorporation of oxygen-18 into the ether-oxygen position of the α,γ -dimethylallyl ester during reaction in acetic acid is occurring by the third process mentioned above. Such a process is formally similar to a rearrangement involving a 6-membered transition state. If this explanation is correct, the transition state must be more polar than the 5-membered cyclic transition state leading to sulfone formation otherwise oxygen-18 scrambling would have been observed during the reaction of the allyl, crotyl and α -methylallyl esters. Even in the case of the α,γ -dimethylallyl ester, it is only in acetic acid, the best ionizing solvent for these esters which has been studied in this work, that this process is detected. It is also possible that the 6-membered transition state may be less polar than that leading to oxygen-18 scrambling without allylic rearrangement. Since inversion will occur at the asymmetric carbon and sulfur atoms during rearrangement via a 6-membered transition state, racemization of optically active ester would result and so racemization should be faster than sulfone formation. The polarimetric rate constant for the rearrangement of the slow reacting diastereoisomer of optically active α,γ -dimethylallyl ester has been measured in ethanol but not in acetic

acid.

It is proposed that the process which leads to scrambling of the oxygen-18 label in this ester is quite separate from the process leading to rearrangement of the ester to sulfone.

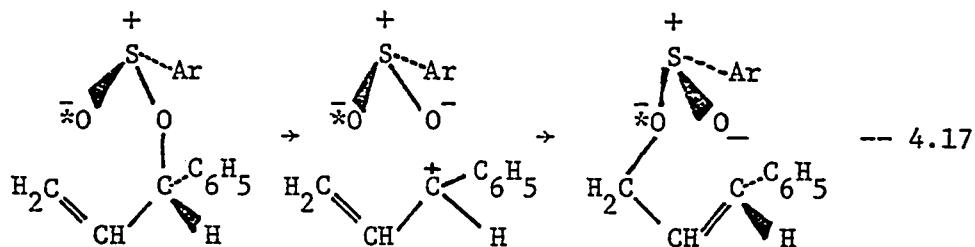
α -Phenylallyl 2,6-Dimethylbenzenesulfinate

The α -phenylallyl ester rearranges to cinnamyl sulfone (equation 4.16) approximately 10 times more rapidly than the rearrangement of the α,γ -dimethylallyl ester.



The presence of oxygen-18 scrambling in the ester recovered from partial reaction in ethanol, 60% ethanol and acetic acid has been detected. This could be due to the formation during the rearrangement of ion-pair intermediates which return to starting material.

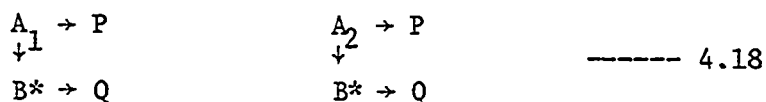
The type of rearrangement involving dissociation to an ion-pair and formation of a bond between what was the γ carbon of the starting ester and the sulfinyl-oxygen of the sulfinate group, which has been postulated to account for the oxygen-18 scrambling observed during the rearrangement of the α,γ -dimethylallyl ester, would lead to the formation of cinnamyl 2,6-dimethylbenzenesulfinate in this case. (equation 4.17)



If this ester, which is considerably more stable than the α -phenylallyl ester and would remain in the reaction mixture, were hydrolyzed along with the unrearranged α -phenylallyl ester then a mixture of cinnamyl and α -phenylallyl alcohols would be obtained and the oxygen-18 analysis would have been carried out on this mixture.

No cinnamyl alcohol was observed in the spectra of the hydrolysis product but less than 2% of it could have been missed.

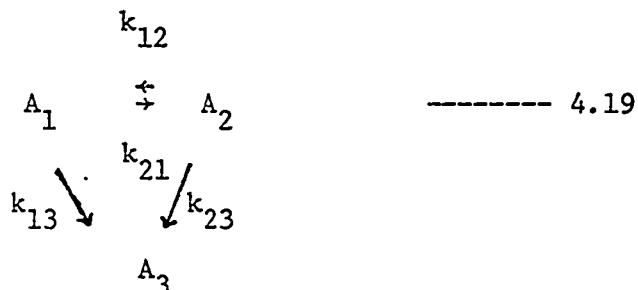
If it is assumed that cinnamyl ester can be formed from the α -phenylallyl ester, and that it is always produced having an oxygen-18 label in the ether-oxygen position, then the kinetics would be described by the scheme in equation 4.18.



where A_1 and A_2 are the fast and slow reacting diastereoisomers having an oxygen-18 label in the ether-oxygen position, B^* is cinnamyl 2,6-dimethylbenzenesulfinate having an oxygen-18 label in the ether-oxygen position, P is cinnamyl 2,6-dimethylphenyl sulfone and Q is α -phenylallyl 2,6-dimethylphenyl sulfone. The amount of cinnamyl ester which would have to be formed during the rearrangement of the α -phenylallyl ester to account for the observed scrambling was calculated using this scheme and

the observed rates of rearrangement of the cinnamyl ester and of the fast and slow reacting diastereoisomers of the α -phenylallyl ester. For example, after 3600 seconds in acetic acid, the products from rearrangement of the α -phenylallyl ester would have to contain cinnamyl ester, α -phenylallyl ester and cinnamyl sulfone in the ratio of 1:4.7:14 to account for the oxygen-18 scrambling observed in this solvent. Similar calculations were made for the products of the reactions in ethanol and 60% ethanol. These are minimum values since they are based on the assumption that all of the cinnamyl ester formed contains oxygen-18 in the ether-oxygen position. Since even these minimum amounts could not be detected in the products of the rearrangement it does not seem likely that this scheme is correct.

The oxygen-18 scrambling may arise by ion-pair return involving the formation of a bond between what was the α carbon and the ether-oxygen of the starting ester as was illustrated in equation 4.15. If this is the origin of the oxygen-18 scrambling, then there must be interconversion between the diastereoisomers and the reaction would proceed by the scheme in equation 4.19.



where A_1 is the fast reacting diastereoisomer, A_2 is the slow reacting diastereoisomer and A_3 is cinnamyl 2,6-dimethylphenyl sulfone, the product

of rearrangement of either A_1 or A_2 .

This is similar to the reaction scheme proposed by McLaren (14) for the solvolysis of α -(*p*-methoxyphenyl)ethyl 2,6-dimethylbenzenesulfinate. However, he was able to separate the diastereoisomers of the substrate and show that interconversion did occur.

The scheme of equation 4.19 leads to complicated kinetics, especially under present circumstances where it has not proved possible to separate the diastereoisomers and the rates of rearrangement and scrambling have had to be measured on mixtures of A_1 and A_2 .

Using the method of Frost and Pearson (74) as adapted by Lewis and Johnston (75) equations 4.20 and 4.21 can be developed for the concentrations of A_1 and A_2 at any time t . The derivations of these equations are given in the Appendix.

$$A_1 = -\frac{k_{21}b}{q} (e^{-\lambda_2 t} - e^{-\lambda_3 t}) + \frac{a(k_{12} + k_{13} - k_{21} - k_{23} + q)e^{-\lambda_2 t}}{2q} - \frac{a(k_{12} + k_{13} - k_{21} - k_{23} - q)e^{-\lambda_3 t}}{2q} \quad \text{----- 4.20}$$

$$A_2 = -\frac{k_{12}a}{q} (e^{-\lambda_2 t} - e^{-\lambda_3 t}) - \frac{b(k_{12} + k_{13} - k_{21} - k_{23} - q)e^{-\lambda_2 t}}{2q} + \frac{b(k_{12} + k_{13} - k_{21} - k_{23} + q)e^{-\lambda_3 t}}{2q} \quad \text{----- 4.21}$$

where a is the concentration of A_1 at $t = 0$, b is the concentration of A_2 at $t = 0$, $\lambda_2 = \frac{1}{2}(k_{12} + k_{13} + k_{21} + k_{23} + q)$, $\lambda_3 = \frac{1}{2}(k_{12} + k_{13} + k_{21} + k_{23} - q)$ and $q = [(k_{12} + k_{13} + k_{21} + k_{23})^2 - 4(k_{12}k_{23} + k_{13}k_{21} + k_{13}k_{23})]^{1/2}$.

The possible application of this scheme to the α -phenylallyl 2,6-dimethylbenzenesulfinate system could be tested by calculating the concentrations of A_1 and A_2 at various times t , and comparing them to the observed values.

The concentrations, a and b , of the fast and slow reacting diastereoisomers of the starting ester were obtained from the nmr spectra as has been described. Values for k_{12} , k_{13} , k_{21} and k_{23} were estimated from the existing calculations made on the nmr spectral data. As a starting point the values of k_{13} and k_{23} were assumed to be the values calculated from the nmr data less approximately 10%.

Since the rate constants for scrambling, calculated using the method described previously were about one-fifth as large as the rate constants for rearrangement, k_{12} and k_{21} were given values which were one-fifth of those of k_{13} and k_{23} respectively. The numbers were then altered until the best fit of the calculated concentrations of A_1 and A_2 to the nmr data were obtained. The calculated and observed values of the concentrations of A_1 and A_2 during rearrangement of the ester in ethanol, 60% ethanol and acetic acid are listed in Tables LIII, LIV and LV.

Having fixed values of the four rate constants which account for the observed rates of disappearance of the diastereoisomers, attention was turned to the scrambling process. If the oxygen-18 scrambling occurs by recombination of the ions, then every time the diastereoisomer of the starting material is formed by the recombination, oxygen-18 will appear in the ether-oxygen position of the ester. This process is symbolized in

TABLE LIII

Rearrangement and Scrambling of Oxygen-18 in Labelled α -Phenylallyl
2,6-Dimethylbenzenesulfonates in Ethanol at 25.0°. Comparison of
Calculated and Theoretical Values.

Values Assumed for Rate Constants:

$$k_{12} = 4.1 \times 10^{-6}, k_{21} = 2.2 \times 10^{-6}, k_{13} = 5.1 \times 10^{-5}, k_{23} = 4.5 \times 10^{-5}$$

Time (sec.)	Calculated concentrations		Observed concentrations		Fraction of Ester unreacted	
	FRD	SRD	FRD	SRD	calc.	observed.
720	0.01431	0.01311	0.01430	0.01308	0.998	
1200	0.01395	0.01285	0.01389	0.01281	0.996	0.994
2100	0.01329	0.01237	0.01338	0.01233	0.993	
3600	0.01228	0.01160	0.01242	0.01156	0.989	0.983
4200	0.01189	0.01130	-	-	0.987	
6600	0.01047	0.01020	0.01031	0.00956	0.979	0.974
6840	0.01034	0.01010	-	-	0.979	0.068
10200	0.00865	0.00873	-	-	0.968	0.951
16320	0.00626	0.00670	-	-	0.951	0.921
28020	0.00338	0.00403	-	-	0.918	

TABLE LIV

Rearrangement and Scrambling of Oxygen-18 in Labelled α -Phenylallyl
2,6-Dimethylbenzenesulfinate in 60% Ethanol at 25.0°. Comparison
of Calculated and Theoretical Values .

Values Assumed for Rate Constants:

$$k_{12} = 3.5 \times 10^{-5}, k_{21} = 1.5 \times 10^{-5}, k_{13} = 6.6 \times 10^{-4}, k_{23} = 4.2 \times 10^{-4}$$

Time (sec.)	Calculated concentrations		Observed concentrations		Fraction of Ester unreacted	
	FRD	SRD	FRD	SRD	calc.	observed.
900	0.00884	0.00913	0.00872	0.00910	0.977	0.977
1800	0.00481	0.00634	-	-	0.955	0.955
2040	0.00407	0.00575	0.00425	0.00505	0.949	-
2400	0.00321	0.00496	-	-	0.941	0.946
3000	0.00215	0.00387	-	-	0.928	0.921
3120	0.00197	0.00368	0.00189	0.00351	0.925	-
4200	0.000964	0.00234	-	-	0.904	0.899
5820	0.000336	0.00118	-	-	0.879	0.868

TABLE LV

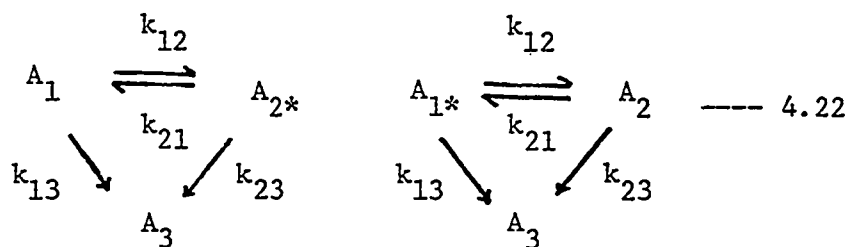
Rearrangement and Scrambling of Oxygen-18 in Labelled α -Phenylallyl
2,6-Dimethylbenzenesulfinate in Acetic Acid at 25.0°. Comparison
of Calculated and Theoretical Values.

Values assumed for Rate constants:

$$k_{12} = 2.1 \times 10^{-5}, k_{21} = 1.2 \times 10^{-5}, k_{13} = 4.9 \times 10^{-4}, k_{23} = 2.8 \times 10^{-4}$$

Time (sec.)	Calculated concentrations		Observed concentrations		Fraction of Ester unreacted	
	FRD	SRD	FRD	SRD	calc.	observed.
360	0.01275	0.01180	-	-	0.994	0.990
600	0.01118	0.01106	0.01123	0.01093	0.990	
900	0.00973	0.01019	0.00982	0.01008	0.985	
1200	0.00838	0.00940	0.00843	0.00862	0.980	0.977
1800	0.00622	0.00797	-	-	0.970	0.970
2400	0.00462	0.00675	0.00477	0.00693	0.961	0.963
3240	0.00306	0.00534	0.00336	0.00502	0.949	
3300	0.00297	0.00525	-	-	0.959	0.950
4200	0.00191	0.00408	-	-	0.936	0.934

equation 4.22.



where A_1 and A_2 are fast and slow reacting diastereoisomers respectively, having an oxygen-18 label in the sulfinyl-oxygen position, and A_{1*} and A_{2*} are the diastereoisomers having an oxygen-18 label in the ether-oxygen position.

Then at any time t , the total concentration of ester which is fast reacting diastereoisomer, $A_1 + A_{1*}$ is given by equation 4.20 and the total concentration of ester which is slow reacting diastereoisomer, $A_2 + A_{2*}$, is given by equation 4.21. Since the initial concentrations of A_{1*} and A_{2*} are zero, the concentration of A_{1*} at time t is given by equation 4.23, and that of A_{2*} at time t by equation 4.24.

$$A_{1*} = \frac{-k_{21}b}{q} (e^{-\lambda_2 t} - e^{-\lambda_3 t}) \quad \text{--- 4.23}$$

$$A_{2*} = \frac{-k_{12}a}{q} (e^{-\lambda_2 t} - e^{-\lambda_3 t}) \quad \text{--- 4.24}$$

where the symbols have the same significance as in equations 4.20 and 4.21.

The fraction of ester in which the oxygen atoms have equilibrated,

F_{scr} , is given by equation 4.25 and these fractions have been calculated

$$F_{scr} = \frac{2(A_1^* + A_2^*)}{A_1 + A_1^* + A_2 + A_2^*} \quad \text{----- 4.25}$$

using the values of the four rate constants which were found to give the best fit to the observed rates of disappearance of the α -phenylallyl ester in ethanol, 60% ethanol and acetic acid. The calculated and observed values are presented in Tables LIII, LIV and IV. The fact that the values are in reasonably good agreement with one another suggests that this mechanism is consistent with the data, but this is a passive and not a compelling argument.

This mechanism may also be used to rationalize the results of chromatography of the α -phenylallyl ester. After passage through the chromatography column, all samples of the ester were richer in the fast reacting diastereoisomer than was the starting material. No fractions were obtained which contained a greater proportion of the slow reacting diastereoisomer. Either it was destroyed or the equilibrium was being shifted. If the diastereoisomers can interconvert then equilibration may be taking place on the alumina and the observed ratio of fast to slow reacting diastereoisomer in ester which had been chromatographed would then be approaching the equilibrium ratio under these conditions.

EXPERIMENTAL

All melting and boiling points are uncorrected. Melting points were taken on a Hershberg melting point apparatus using a set of Anschutz thermometers.

Refractive indices were measured on a Bausch and Lomb Abbe-3L Refractometer which was thermostatted at 25°.

The infrared spectra were recorded on a Perkin Elmer infrared Spectrophotometer, Model 21 using sealed sodium chloride cells.

The nuclear magnetic resonance spectra were recorded on a Varian Analytical Spectrophotometer, Model A-60 or on a Varian HA-100 Spectrophotometer.

Solvents

Ethanol

Anhydrous ethanol was prepared according to the method of Lund and Bjerrum (77) as described by Fieser (78).

Ethanol (98%) was distilled through a column containing glass helices. The first and last few hundred millilitres of distillate were discarded. A 250 ml portion of the distillate was refluxed with magnesium turnings until reaction occurred. When the reaction had subsided, the remainder of the distillate was added, the mixture refluxed for one hour and distilled. The centre cut of the distillate was collected. The dried ethanol contained less than 0.006% of water as determined by Karl Fischer titration using the method of Winstein (79).

60% Ethanol

Using the same automatic pipette, three volumes of anhydrous ethanol at 25° were mixed with two volumes of boiled distilled water at 25°.

Dioxane

Reagent grade dioxane was purified using the method described by Fieser (81).

Reagent grade dioxane was refluxed with hydrochloric acid while bubbling nitrogen through the solution. Potassium hydroxide pellets were added to the cooled mixture; the aqueous layer was discarded and a second addition of potassium hydroxide pellets made. Again, the aqueous layer was discarded and the dioxane refluxed with sodium until the sodium was shiny, when the liquid was distilled. Karl Fischer titration indicated that the purified dioxane contained less than 0.006% of water.

Acetic Acid

Glacial acetic acid was dried using the method described by Fainberg and Winstein (80). The acid was refluxed for twelve hours with a quantity of acetic anhydride equivalent to the water present in the acid, as determined by Karl Fischer titration, and distilled. The water in the distillate was determined by Karl Fischer titration and the acid was refluxed again for twelve hours, this time with sufficient acetic anhydride to react with the water present and to make the solution 0.02 molar in acetic anhydride.

Pentane

Phillips Petroleum technical grade normal pentane was purified by shaking with concentrated sulfuric acid, washing with water and drying by distillation from phosphorous pentoxide.

Diethyl Ether

Mallinckrodt AR anhydrous ether was used without further purification.

Tetrahydrofuran

B.D.H. reagent grade tetrahydrofuran was purified by distillation from lithium aluminum hydride.

Toluene

Fisher toluene was allowed to stand over anhydrous calcium chloride for two days. It was decanted into a dry flask and freshly cut sodium added. After standing a further two days, more freshly cut sodium was added and the liquid distilled. The centre cut was collected.

Reagents

2,6-Lutidine

Eastman practical grade 2,6-lutidine was purified by the method of Brown (84).

After standing over 300 g. of potassium hydroxide pellets for two days, 1 kilogram of 2,6-lutidine was decanted and distilled from barium oxide through a helices column. Boron trifluoride gas was bubbled into the distillate until a concentration of 6.4 mole% was reached.

After heating, the 2,6-lutidine was distilled through a helices column; the fraction boiling between 141° and 143° was collected.

Benzenesulfinic Acid

Benzenesulfonyl chloride (100 g, 0.57 mole) was reduced (54) by stirring vigorously with a solution of sodium sulfite (300 g, 0.62 mole) in water (500 ml). Crushed ice (500 g) was added at the start of the reaction and at intervals during the 3 hour reaction period to maintain the temperature below 5° . The oily benzenesulfonyl chloride gradually disappeared. A precipitate formed when the solution was carefully acidified with concentrated hydrochloric acid. It was recovered by filtration at the water aspirator, washed with ice-cold water, air dried and recrystallized from water. The yield of benzenesulfinic acid was 63.5 g (0.45 mole, 79%), having m.p. $82.5-83^{\circ}$, (reported m.p. (7) $83-84^{\circ}$).

Benzenesulfinyl Chloride

Thionyl Chloride (46 g, 0.38 mole) in pentane (30 ml), was slowly added to a slurry of benzenesulfinic acid (26 g, 0.18 mole) in pentane (100 ml). When all of the solid had disappeared, the solution was carefully filtered through a glass wool plug. The pentane was removed by warming on the steam bath and the excess thionyl chloride by pumping under vacuum overnight. A 28.3 g (0.18 mole, 96.3%) quantity of benzenesulfinyl chloride was obtained.

2,6-Dimethylbenzenesulfinic Acid

The material was prepared using the method of Hanke (85) as

modified by Mermelstein (16).

2,6-Dimethylaniline (100 g, 0.83 mole) was dissolved in a cooled solution of concentrated sulfuric acid (80 ml) in water (600 ml) contained in a 3 litre 3-necked round bottom flask which was equipped with a Robinson stirrer, a dropping funnel and a thermometer. While maintaining the temperature of the solution below 5° using an ice-salt bath, a solution of sodium nitrite (60 g, 0.87 mole) in water (120 ml) was added dropwise with stirring. Sulfur dioxide was bubbled through the cold solution for 40 minutes before adding a cold solution of concentrated sulfuric acid (100 ml) in water (200 ml). The introduction of sulfur dioxide was stopped and copper powder (300 g, 4.72 mole) was added, still keeping the temperature of the mixture below 5° . Sulfur dioxide was again bubbled through the solution and the mixture was allowed to slowly warm up to room temperature, after which it was filtered and the filtrate discarded. The solid, a mixture of the desired acid, copper powder and possibly other salts, was washed with cold water (20 ml) and then the acid was dissolved by stirring into 1 litre of 10% aqueous sodium carbonate solution. The residual copper powder was removed by filtration at a water aspirator and the dark green filtrate treated with decolorising charcoal. After filtration, the acid was precipitated from the solution by the slow addition of cold 50% sulfuric acid. The product was recovered by filtration, washed with ice-cold water, air-dried and purified by recrystallization from wet alcohol. The pure acid was dried in a vacuum desiccator over Drierite and stored in a dark bottle in the refrigerator. 2,6-Dimethylbenzenesulfinic acid (124 g, 0.73 mole

88%) had a melting point of 98-99° (reported (16) m.p. 98-99°). The ir spectrum of the acid in chloroform showed strong peaks at 1030, 1070, 1122, 1150, 1325 and 1460 cm^{-1} while the nmr spectrum of the acid in deuteriochloroform showed signals at τ 2.7-3.0 (d, 3H) τ 3.72 (s, 1H), τ 7.32 (s, 6H).

2,6-Dimethylbenzenesulfinyl Chloride

2,6-Dimethylbenzenesulfinic acid (13 g, 0.08 mole), was placed in a flask containing pentane (40 ml). Thionyl chloride (23 g, 0.19 mole) in pentane (20 ml) was added as rapidly as possible, but such that the evolution of gas was not too vigorous. The contents of the flask were protected from moisture with a drying tube. When the reaction had subsided, the pale yellow liquid was filtered through a glass wool plug, the solvent was removed by warming on the steam bath and the excess thionyl chloride by pumping under vacuum overnight. The yield of 2,6-dimethylbenzenesulfinyl chloride was 13.9 g (0.075 mole, 98%).

2,6-Dimethylbenzenesulfinic Acid Labelled with Oxygen-18

2,6-Dimethylbenzenesulfinyl chloride (14 g, 0.075 mole) was cooled in an ice-methanol bath. Water containing either 5 or 10% atom excess oxygen-18 (1.6 g, 0.089 mole) in tetrahydrofuran (20 ml) was added slowly to the chloride. A few minutes after the addition was complete, precipitation commenced and soon a slurry of acid had formed. The solvent was removed using a rotary evaporator and the acid dried for 12 hours over Drierite. The yield of 2,6-dimethylbenzenesulfinic acid was 12.5 g (0.073 mole, 97.7%).

2,6-Dimethylbenzenesulfinyl Chloride Labelled with Oxygen-18

A solution of thionyl chloride (22 g, 0.18 mole) in pentane (20 ml) was slowly poured into a mixture of 2,6-dimethylbenzenesulfinic acid labelled with oxygen-18 (12.5 g, 0.074 mole) and pentane (40 ml). When the reaction was complete, the solution was decanted, the pentane was removed by warming on the steam bath and the excess thionyl chloride by distillation at low pressure. A pale yellow oil remained (13.2 g, 0.071 mole, 96%).

Allyl Alcohol

Fisher reagent grade allyl alcohol was purified by distillation through a Vigreux column; the fraction boiling between 92° and 95° was collected. The distillate had n_D^{25} 1.4130 (reported (82) n_D^{20} 1.4135).

Allyl 2,6-Dimethylbenzenesulfinate

A solution of 2,6-dimethylbenzenesulfinyl chloride (12.5 g, 0.067 mole) in pyridine (60 ml) was cooled in an ice-methanol bath. A similarly cooled solution of allyl alcohol (3.8 g, 0.065 mole) in pyridine (40 ml) was added dropwise to the chloride solution. The mixture, still in the cooling bath was allowed to stand in the refrigerator overnight. The solution was then poured into concentrated hydrochloric acid (100 ml) and ice and extracted with ether (400 ml). The extract was washed with 10% aqueous sodium carbonate until the aqueous layer was colourless (about 3 x 100 ml) and then with water until the washings were neutral to litmus. After drying over anhydrous granular potassium carbonate, the solvent was removed by distillation at low pressure to yield 10.0 g (0.048 mole, 73%) crude allyl 2,6-dimethylbenzenesulfinate. The ester was purified

by chromatography over alumina, eluting with 50:50 (v:v) pentane:ether. After evaporation of the solvent 8.4 g (0.04 mole, 61%) of a pale yellow oil remained. It had n_D^{25} 1.5456 (reported (12) n_D^{25} 1.5470); ir (CS_2), 765, 925, 966, 1132 cm^{-1} ; nmr (CCl_4), τ 3.8-4.4, (m, 3H), τ 4.6-4.9, (m, 2H), τ 5.52 (d, 2H), τ 7.4 (s, 6H).

α -Methylallyl Alcohol

Iodomethane (282 g, 2 mole) in ether (700 ml) was added dropwise to magnesium turnings (48.6 g, 2.0 mole) contained in a 3 litre 3-necked flask equipped with a dropping funnel, stirrer and condenser. The flask was cooled in an ice-water bath and the rate of addition regulated so that the ether refluxed gently. When the addition was complete the mixture was refluxed on the steam bath for one hour. Freshly distilled acrolein, (112 g, 2.0 mole, b.p. 50-52 $^{\circ}$) dissolved in ether (300 ml) was slowly added to the Grignard reagent with stirring and cooling. This was followed by the addition of a saturated aqueous solution of ammonium chloride (300 ml) also with stirring and cooling. The solution was decanted from the white plastic-like precipitate which formed towards the end of the addition. The precipitate was washed twice with ether and the washings combined with the main solution. The ether extract was dried and distilled. The fraction boiling between 92 and 94 $^{\circ}$ was collected, (reported (82) b.p. 96-97 $^{\circ}$). α -Methylallyl alcohol (35 g, 0.49 mole, 24%) was obtained having n_D^{25} 1.4009 (reported (86) n_D^{25} 1.4110).

α -Methylallyl alcohol was purified via the formation of the 3,5-dinitrobenzoate ester.

α -Methylallyl alcohol (8 g, 0.11 mole) was dissolved in pyridine (30 ml) and 3,5-dinitrobenzoyl chloride (32 g, 0.14 mole) added slowly with stirring and while cooling in an ice-water bath. After standing in the cooling bath for one hour and warming on the steam bath for a few minutes, the hot mixture was poured onto ice-water (100 ml) and filtered. The precipitate was stirred with 10% aqueous sodium carbonate solution (100 ml) and filtered again. It was dried and recrystallized from wet ethanol. A buff coloured solid (23.5 g, 0.09 mole, 80%) was obtained of m.p. 51° , (reported (7) m.p. 51.5° 52.5°).

α -Methylallyl 3,5,-dinitrobenzoate (23.5 g, 0.09 mole) was stirred on the steam bath with 0.5 molar aqueous sodium hydroxide. After 90 minutes the solution was allowed to cool and extracted with ether (5 x 100 ml). The extract was dried over anhydrous granular potassium carbonate and the ether was removed by distillation through a Vigreux column. Continued distillation through the same column, gave α -methylallyl alcohol which boiled between 92 and 94° , (5.9 g, 0.082 mole, 91%). Its ir and nmr spectra were superimposable on those described above.

α -Methylallyl Benzenesulfinate

Benzenesulfinyl chloride (5 g, 0.031 mole) in pyridine (20 ml) was cooled in an ice-methanol bath and a similarly cooled solution of α -methylallyl alcohol (2.0 g, 0.028 mole) in pyridine (10 ml) was added slowly with swirling. The mixture, still in the cooling bath was allowed to stand in the refrigerator overnight. It was poured into concentrated hydrochloric acid (35 ml) and ice and the aqueous emulsion was extracted with ether (200 ml). The extract was washed with water (2 x 100 ml) and dried over anhydrous granular potassium carbonate.

Removal of the solvent under reduced pressure yielded a very pale yellow oil which was purified by chromatography over alumina using pentane as eluent. The yield of pure ester was 3.38 g, (0.017 mole, 62%).

n_D^{25} 1.5322 (reported (7) n_D^{25} 1.5312); ir (CS_2) 839, 898, 901, 1140 cm^{-1} ; nmr (CCl_4), τ 2.05-2.75 (m, 5H), τ 3.80-4.50 (m, 1H), τ 4.52-5.09 (m, 2H), τ 5.09-5.45 (m, 1H), τ 8.69 (t, 3H).

α -Methylallyl 2,6-Dimethylbenzenesulfinate

2,6-Dimethylbenzenesulfinyl chloride (7.2 g, 0.039 mole) in pyridine (40 ml) was cooled in an ice-methanol bath. α -Methylallyl alcohol (2.7 g, 0.038 mole) in pyridine (10 ml) was similarly cooled and slowly added to the chloride solution. The mixture was left in the cold bath and transferred to the refrigerator where it was allowed to stand overnight before being poured into concentrated hydrochloric acid (75 ml) and ice. The aqueous mixture was extracted as described for α -methylallyl benzenesulfinate. It was purified by chromatography on alumina. Yield 4.9 g, (0.025 mole, 65%); n_D^{25} 1.5375 (reported (12) n_D^{25} 1.5370); ir (CS_2), 770, 895, 1134 cm^{-1} ; nmr (CCl_4), τ 2.68-3.19 (m, 3H), τ 4.05-5.37 (m, 4H), τ 7.41 (s, 6H), τ 8.62 (d of d, 3H).

Crotyl Alcohol

Freshly distilled crotonaldehyde (56 g, 0.8 mole, b.p. 96-98°) in ether (100 ml) was added to a suspension of lithium aluminum hydride (15.2 g, 0.4 mole) in ether (800 ml) with stirring, at such a rate that the ether refluxed gently. When the addition was complete the mixture was cooled in an ice bath. Water (15 ml), 15% aqueous sodium hydroxide (15 ml) and water (5 ml) were added in succession. Towards the end

of the addition of fine white precipitate formed. It was removed by filtration at a water aspirator, washed with ether and the solution and washings dried over anhydrous magnesium sulfate. The solvent was removed by distillation through a Vigreux column; the column was removed and the residue distilled. The fraction boiling between 115° and 117° was collected (reported (82) b.p. $121^{\circ}/754$ mm). The yield of crotyl alcohol was 23 g, (0.32 mole, 40%).

A sample of the alcohol was purified by formation of the 3,5-dinitrobenzoate.

Crotyl alcohol (8 g, 0.11 mole) was dissolved in pyridine (30 ml) and 3,5-dinitrobenzoyl chloride (32 g, 0.14 mole) was added with cooling and stirring. A brown precipitate formed rapidly. The slurry was allowed to stand for one hour at room temperature then was warmed on the steam bath for a few minutes and the hot mixture poured into ice-water (100 ml) while stirring vigorously. The precipitate was removed by filtration, stirred thoroughly with 10% aqueous sodium carbonate (100 ml) and filtered. After air-drying, it was recrystallized from ethanol-water and dried overnight in the air. Yield 24.5 g, (0.092 mole, 84%); m.p. 71° (reported (7) m.p. 71°).

Crotyl 3,5-dinitrobenzoate (24.5 g, 0.093 mole) was hydrolyzed by stirring on the steam bath with 0.5 M aqueous sodium hydroxide (250 ml) for one hour. The red-brown solution was extracted with ether (4 x 150 ml) the extract washed with water and after drying over anhydrous magnesium sulfate, the solvent was removed and the residue distilled, the fraction boiling between 115° and 117° being collected. The yield of crotyl alcohol was 5.5 g, (0.076 mole, 83%). The purified alcohol was found to

have n_D^{25} 1.4256 (reported (82) n_D^{25} 1.4262); ir, (CS_2) 962, 1075, 2850, 2910, 2935, 2960, 3010, 2200 cm^{-1} ; nmr (CCl_4) τ 4.25-4.58 (m, 2H), τ 5.59-6.25 (broad s, 3H), τ 8.34 (d of d, 3H).

Crotyl Benzenesulfinate

Solutions of benzenesulfinyl chloride (15.3 g, 0.095 mole) in pyridine (60 ml) and crotyl alcohol (6.5 g, 0.090 mole) in pyridine (20 ml) were cooled in an ice-methanol bath. The alcohol solution was slowly added to the chloride solution and the mixture, still in the cold bath was placed in the refrigerator. After standing overnight, it was worked up in the manner described under the preparation of the α -methylallyl benzenesulfinate. The ester was purified by chromatography on an alumina column, eluting with 50:50 (v:v) ether: pentane. The solvent was evaporated under reduced pressure to leave 12.3 g (0.063 mole, 70%) of a very pale yellow oil.

The ester was further purified by distillation in small quantity, (about 3 g) at low pressure, (b.p. 92-94 $^\circ$, 0.02 mm).

The ester had n_D^{25} 1.5390 (reported (7) n_D^{25} 1.5388); ir (CS_2), 700, 805, 900, 966, 1135 cm^{-1} ; nmr (CCl_4), τ 2.05-2.68 (m, 5H), τ 4.32-4.65 (m, 2H), τ 5.45-6.30 (m, 2H), τ 8.35 (d of d, 3H).

Crotyl 2,6-Dimethylbenzenesulfinate

A solution of crotyl alcohol (2.6 g, 0.036 mole) in pyridine (10 ml) was cooled in an ice-methanol bath and slowly added to a similarly cooled solution of 2,6-dimethylbenzenesulfinyl chloride (7.2 g, 0.038 mole) in pyridine (40 ml). The mixture was left in the cold bath and allowed

to stand in the refrigerator overnight. It was poured into concentrated hydrochloric acid (75 ml) and ice and work-up was similar to that described for α -methylallyl benzenesulfinate. The pale yellow liquid was purified by chromatography on alumina, eluting with pentane. On standing in pentane solution in the refrigerator, this ester solidified and was further purified by recrystallization from pentane-ether to yield 4.7 g (0.021 mole, 59%) of a low-melting white solid of m.p. 15-20°. The liquid had n_D^{25} 1.5448 (reported (12) n_D^{25} 1.5442); ir (CS₂), 767, 940, 959, 1130 cm⁻¹; nmr (CCl₄), τ 2.69-3.95 (m, 3H), τ 4.17-4.52 (m, 2H), τ 5.50-5.77 (m, 2H), τ 7.44 (s, 6H), τ 8.31 (d of d, 3H).

α,γ -Dimethylallyl Alcohol

Magnesium turnings (24.3 g, 1.0 mole) were placed in a 2 litre 3-necked flask equipped with a stirrer, dropping funnel and condenser. Methyl iodide (142 g, 1.0 mole) in ether (500 ml) was slowly added while stirring and cooling in an ice-water bath. The rate of addition was adjusted so that the ether refluxed gently. When the addition was complete, the mixture was refluxed on a steam bath for one hour and again cooled in an ice-water bath. Freshly distilled crotonaldehyde (70 g, 1.0 mole, b.p. 97-99.5°) in ether (150 ml) was added to the Grignard reagent with stirring. This addition was followed by that of a saturated aqueous solution of ammonium chloride (150 ml), again while cooling and stirring. The white precipitate which formed coagulated towards the end of the addition and the supernatant liquid could be decanted. The ether was removed by distillation under reduced pressure and the α,γ -dimethylallyl alcohol distilled at 2 mm, (b.p. 34-36°).

The receiver was cooled in a dry ice-acetone bath. Yield 61 g (0.71 mole, 71%); n_D^{25} 1.4264 (reported (12) n_D^{25} 1.4260); ir (CS_2), 908, 961, 1054, 1445, 2970 cm^{-1} ; nmr (CCl_4), τ 4.30-4.50 (q, 2H), τ 5.6-6.1 (t, 1H), τ 6.65 (s, 1H), τ 8.32 (d, 3H).

α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfinate

2,6-Dimethylbenzenesulfinyl chloride (8 g, 0.042 mole) in pyridine (46 ml) was cooled in an ice-methanol bath and a cold solution of α,γ -dimethylallyl alcohol (3.4 g, 0.040 mole) in pyridine (15 ml) was added dropwise while swirling the flask and cooling it. The mixture, still in the cold bath was left in the refrigerator overnight and poured into concentrated hydrochloric acid (60 ml) and ice. The ester was recovered using a method similar to that detailed under the preparation of α -methylallyl benzenesulfinate. It was purified by chromatography on alumina, eluting with 50:50 (v:v) ether : pentane. Yield 6.2 g (0.026 mole, 65%); n_D^{25} 1.5353 ; ir (CS_2), 735, 768, 848, 891, 959, 1028, 1130 cm^{-1} ; nmr (CCl_4), τ 2.72-3.25 (m, 3H), τ 4.23-4.55 (m, 2H), τ 5.05-5.68 (m, 1H), τ 7.45 (s, 6H), τ 8.30 (d, 3H), τ 8.62 (d, 3H).

Cinnamyl Alcohol

Eastman "white label" grade cinnamyl alcohol was used without further purification. It melted at 31°; ir (CS_2), 687, 726, 740, 960 cm^{-1} ; nmr (CCl_4), τ 2.83 (s, 5H), τ 3.57-3.82 (m, 2H), τ 5.83 (d, 2H), τ 6.18 (s, 1H).

Cinnamyl 2,6-Dimethylbenzenesulfinate

Solutions of 2,6-dimethylbenzenesulfinyl chloride (6.2 g, 0.033 mole)

in pyridine (30 ml) and cinnamyl alcohol (4.3 g, 0.032 mole) in pyridine (10 ml) were cooled in an ice-methanol bath. The alcohol solution was slowly added to the chloride solution while swirling. The mixture, still in the cold bath was left in the refrigerator overnight. It was poured into concentrated hydrochloric acid (40 ml) and ice, and the ester was recovered in the manner described under the preparation of α -methylallyl alcohol. The viscous liquid was stirred with ether (5 ml) and pentane (10 ml) and cooled in a dry ice-acetone bath. On stirring, solidification occurred. The solid was recrystallized twice from pentane-ether to yield 8 g (0.024 mole, 75%) of a shining white solid of m.p. 42.5-43° (reported (12) m.p. 41°); ir (CS_2), 693, 731, 760, 775, 948, 1140 cm^{-1} ; nmr (CCl_4), τ 2.48-3.25 (m, 8H), τ 3.42-3.81 (m, 2H), τ 5.39 (d, 2H), τ 7.40 (s, 6H).

α -Phenylallyl Alcohol

Magnesium turnings (41.5 g, 1.70 mole), were placed in a 3 litre 3-necked flask equipped with a stirrer, dropping funnel and condenser. A solution of bromobenzene (266 g, 1.70 mole) in ether (1 litre) was added at such a rate that the ether refluxed gently. After the addition had been completed, the mixture was refluxed for one hour on the steam bath. Freshly distilled acrolein (97 g, 1.17 mole, b.p. 50-52°) in ether (300 ml) was slowly added to the cooled, stirred Grignard solution followed by saturated aqueous ammonium chloride solution (350 ml). The pale yellow solution was decanted from the precipitate and the latter washed with ether. Evaporation of the ether from the combined solvent and washings yielded an orange-yellow oil which was distilled at 0.5 mm and the fraction boiling between 71° and 73° was collected. Yield 147 g (1.1 mole, 65%); n_D^{25} 1.5398

(reported (12) n_D^{25} 1.5401): ir (CS_2), 695, 982, 3380, 3590 cm^{-1} ; nmr (CCl_4), τ 2.5-3.4 (m, 6H), τ 3.9-4.5 (m, 1H), τ 4.7-5.2 (m, 2H), τ 6.65 (m, 1H).

α -Phenylallyl 2,6-Dimethylbenzenesulfinate

A solution of α -phenylallyl alcohol (7.7 g, 0.057 mole) in pyridine (5 ml) cooled in an ice-methanol bath, was slowly added to a similarly cooled solution of 2,6-dimethylbenzenesulfinyl chloride (11 g, 0.058 mole) in pyridine (26 ml). When the addition was complete the mixture, still in the cold bath, was allowed to stand in the refrigerator for one hour. The ester was recovered by pouring the mixture into concentrated hydrochloric acid (32 ml) and ice and extracting the aqueous emulsion with ether (500 ml). The extract was washed with ice-cold water (100 ml), cold 10% aqueous sodium carbonate solution (3 x 100 ml) and ice-cold water (2 x 100 ml). After drying over anhydrous potassium carbonate, the solvent was evaporated at reduced pressure. α -Phenylallyl 2,6-dimethylbenzenesulfinate (10 g, 0.035 mole, 60%) had n_D^{25} 1.5797 (reported (12) n_D^{25} 1.5795); ir (CS_2), 694, 769, 923, 1132 cm^{-1} ; nmr (CCl_4), τ 2.72 (s, 5H), τ 2.8-3.2 (m, 3H), τ 3.5-5.0 (m, 4H), τ 7.46 (s, 3H) τ 7.58 (s, 3H).

Allyl Alcohol Labelled with Oxygen-18

Freshly cut sodium (1.5 g, 0.065 mole) was cautiously added to water (3 ml, 0.10 mole) 5% of which was labelled with oxygen-18, while cooling the flask in ice-water. A condenser was attached to the flask to prevent loss of water by evaporation. When the addition was complete, allyl bromide (5 ml, 0.041 mole) was added and the mixture refluxed for 72 hours while stirring vigorously. The allyl alcohol was extracted into water and then

into ether. The ether extract was washed with water, 10% sodium carbonate solution and water before being dried over anhydrous granular potassium carbonate. The ether was removed by slow distillation through a Vigreux column to yield 0.8 g (0.014 mole, 34%) of allyl alcohol labelled with oxygen-18.

Allyl 2,6-Dimethylbenzenesulfinate Labelled with Oxygen-18 in the Ether Oxygen Position.

Allyl alcohol labelled with oxygen-18 (0.8 g, 0.014 mole) was dissolved in pyridine (5 ml) cooled in an ice-methanol bath and added slowly to a similarly cooled solution of 2,6-dimethylbenzenesulfinyl chloride (3.5 g, 0.019 mole) in pyridine (30 ml). After standing in the refrigerator overnight, the mixture was poured into concentrated hydrochloric acid (40 ml) and ice and the aqueous emulsion was extracted in the same manner as that described for allyl 2,6-dimethylbenzenesulfinate. The yield of ester was 1.2 g (0.0057 mole, 30%) after chromatography on alumina. The spectra of this ester were superimposable on those obtained from the unlabelled ester.

2,6-Dimethylbenzenesulfinate Esters with Oxygen-18 in the Sulfinyl Oxygen Position.

Allyl, α -methylallyl, crotyl, α,γ -dimethylallyl, cinnamyl, and α -phenylallyl 2,6-dimethylbenzenesulfinate esters labelled with oxygen-18 in the sulfinyl-oxygen position were prepared using the methods described above for each unlabelled ester, but using 2,6-dimethylbenzenesulfinyl chloride labelled with oxygen-18 in place of the unlabelled chloride. The physical data of the esters was identical to that detailed above.

α -Methylallyl Phenyl Sulfone

Crotyl benzenesulfinate (20 g, 0.10 mole) and 2,6-lutidine (5 g, 0.05 mole) were dissolved in 60% aqueous ethanol (1 litre). The solution was distributed among 6 pressure bottles which were sealed and suspended in an oil bath at 100° for 24 hours. The bottles were allowed to cool slowly to room temperature before their contents were poured into water (1 litre). The aqueous mixture was extracted with ether (500 ml) and the extract was washed with water (2 x 100 ml) 0.6 M hydrochloric acid (100 ml), 10% aqueous sodium carbonate (100 ml) and water (2 x 100 ml). The extract was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure to yield 11.0 g (0.06 mole, 55%) of a pale yellow oil. On stirring the oil with pentane while cooling in a dry ice-acetone bath, a solid formed. Recrystallization from ether-pentane gave colourless crystals. Yield 9.0 g (0.05 mole, 45%); m.p. 31-32°; ir (CS₂), 630, 689, 929, 1088, 1139, 1150, 1208, 1220 cm⁻¹; nmr (CCl₄), τ 2.0-2.68 (m, 5H), τ 3.85-4.50 (m, 1H), τ 4.68-5.21 (m, 2H), τ 6.40 (s, 1H), τ 8.62 (d, 3H); microanalysis, calculated for C₁₀H₁₂SO₂, C 61.20% H 6.17%, S 16.33%, found, C 61.19%, 61.03%, H 6.02%, 6.09%, S 15.91%, 15.96%.

 α -Methylpropenyl Phenyl Sulfone

Two methods of preparing this sulfone from α -methylallyl phenyl sulfone were adopted.

1. α -Methylallyl phenyl sulfone (1.0 g, 0.005 mole) was stirred with 0.1 M sodium hydroxide (100 ml) at room temperature for 24 hours. The emulsion was extracted with ether (50 ml), the ether dried over

anhydrous magnesium sulfate and removed under reduced pressure. The pale yellow oil was dissolved in a small amount of ether, and pentane was added to the cloud point. On standing in the refrigerator, crystals were deposited (0.7 g, 0.004 mole). They were recrystallized twice from ether-pentane and had m.p. 51° ; nmr (CCl_4), $\tau 2.09-2.59$ (m, 3H), $\tau 2.90-3.33$ (m, 1H), $\tau 8.15$ (d, 3H), $\tau 8.22$ (s, 3H).

2. α -Methylallyl phenyl sulfone (1.0 g, 0.005 mole) was stirred with 0.1 M aqueous sodium hydroxide (100 ml) on the steam bath for 2 hours. The emulsion was extracted with ether as described above and crystals (0.65 g, 0.003 mole) were obtained which were found to be identical to those from the above preparation.

2-Butyl Phenyl Sulfone from α -Methylpropenyl Phenyl Sulfone

α -Methylpropenyl phenyl sulfone (0.5 g, 0.0025 mole) was dissolved in ethanol (50 ml) and 10% palladium on powdered charcoal (0.1 g) added. The mixture was placed in a hydrogenation bottle which was fitted to a Parr hydrogenation apparatus no. 3911. The bottle was evacuated and hydrogen at a pressure of 34.3 lbs/sq. in. was introduced. The bottle was shaken for three hours and removed from the apparatus. The catalyst was removed by filtration and the ethanol evaporated under reduced pressure. A pale yellow oil was formed; nmr (CCl_4), $\tau 2.06-2.61$ (m, 5H), $\tau 6.82-7.45$ (m, 1H), $\tau 8.69-9.22$ (m, 6H).

2-Butyl m-(Di-3-bromobenzoylamino)-phenyl Sulfone.

The crude 2-butyl phenyl sulfone obtained from the hydrogenation was added to a nitrating mixture (3 ml) formed from 3 parts of concentrated sulfuric acid to 1 part of concentrated nitric acid, held at 50° while

stirring vigorously. The reaction mixture was maintained at 50° for 5 minutes while shaking continuously, then the hot solution was poured onto crushed ice (20 cc), and the aqueous emulsion extracted with ether (30 ml). After washing the extract with water, and drying it over anhydrous sodium sulfate, the ether was evaporated to leave a viscous yellow oil, (0.374 g, 0.0068 mole).

Iron powder (3.74 g, 0.07 mole) and water (10 ml) containing sulfuric acid (1 drop), and 2-butyl m-nitrophenyl sulfone (0.374 g, 0.0068 mole), the product of the above nitration, were shaken together and heated on the steam bath for 30 minutes, shaking at frequent intervals. Water was added as necessary to replace that lost by evaporation along with a further two drops of sulfuric acid. The slurry was filtered, the metal washed with dilute sulfuric acid and the filtrate made alkaline by the addition of sodium bicarbonate. The mixture (a deep blue-green precipitate had formed) was extracted with ether and the ether washed once with water (10 ml). The amine was extracted into dilute hydrochloric acid and the acid neutralized by the addition of 10% aqueous sodium carbonate solution. Ether (50 ml) was used to extract the basic solution and after drying the extract over anhydrous magnesium sulfate, it was reduced in volume to 10 ml and added to 10% aqueous potassium hydroxide solution (50 ml). Eastman m-bromobenzoyl bromide (0.5 g, 0.002 mole) was added and after shaking for 10 minutes precipitation occurred. The solid was removed by filtration, washed thoroughly with water and recrystallized from 95% ethanol; m.p. 173-174° (reported (7) m.p. 170-172°; nmr (CCl₄), τ 2.05-3.10 (m, 12H), τ 6.1-7.5 (broad m, 1H), τ 7.83-9.40 (m, 8H); microanalysis, calculated for C₂₄H₂₁O₄NBr₂S, C 49.76, H 3.65, N 2.42, Br 27.58, found, C 50.03, 49.89, H 3.44, 3.61, N 2.63, 2.32, Br 27.84.

2-Butyl Phenyl Sulfone from 2-Butyl Phenyl Sulfide

Matheson, Coleman and Bell benzenethiol (11 g, 0.1 mole) was added dropwise to a cooled solution of clean sodium metal (2.3 g, 0.1 mole) in absolute ethanol (60 ml). This was followed by the slow addition of Eastman 2-bromobutane (13.7 g, 0.1 mole) during which time sodium chloride separated out. The mixture was refluxed at 100° for 5 hours. The condenser was removed and the volume of the solution was reduced to 30 ml. The hot solution was poured onto ice (400 g), while stirring vigorously and the aqueous mixture was extracted with ether which was washed with water (2 x 50 ml) and dried. Evaporation of the ether left 12 g (0.07 mole, 72%) of 2-butyl phenyl sulfide.

Hydrogen peroxide (20 ml of 30%) was slowly added to 2-butyl phenyl sulfide (10 g, 0.06 mole) in glacial acetic acid (20 ml). The solution became hot as the addition proceeded. After standing overnight, the mixture was heated at 70° for two hours then most of the water and acid were evaporated and the residue extracted with ether. The extract was washed with water (2 x 20 ml), 10% aqueous sodium carbonate (2 x 20 ml) and water (2 x 10 ml). After drying over anhydrous magnesium sulfate, the solvent was evaporated and the residue distilled, b.p. 188°/5 mm: nmr (CCl₄), τ 2.00-2.60 (m, 5H), τ 6.81-7.62 (m, 1H), τ 7.62-9.25 (m, 8H).

Ethyl 2,6-Dimethylbenzenesulfinate

Solutions of 2,6-dimethylbenzenesulfinyl chloride (2.4 g, 0.013 mole) in pyridine (10 ml) and ethanol (0.6 g, 0.013 mole) in pyridine (5 ml) were cooled in an ice-methanol bath. The cold alcohol solution was slowly added to the chloride solution and the mixture, still in the cold

bath was left in the refrigerator overnight. The ethyl ester was recovered in the same manner as the allyl ester. It was recrystallized from pentane. Yield 1.7 g (0.0086 mole, 66%); m.p. 56° ; ir (CS_2), 768, 880, 1010, 1130, cm^{-1} ; nmr (CCl_4), τ 2.69-3.20 (m, 3H), τ 5.95 (q, 2H), τ 7.42 (s, 6H), τ 8.69 (t, 3H).

α,γ -Dimethylallyl Acetate

α,γ -Dimethylallyl alcohol (4 g, 0.046 mole) and acetic anhydride (4 g, 0.038 mole) in pyridine (30 ml) were heated on the steam bath for one hour. The pale yellow solution was poured into a mixture of concentrated hydrochloric acid (30 ml) and ice and the aqueous emulsion was extracted with ether (100 ml). The extract was washed with water (100 ml), 10% aqueous sodium carbonate (50 ml) and water (3 x 50 ml) and dried over potassium carbonate. The residue after removal of the solvent was distilled, h.p. $109-110^{\circ}$ (700 mm) and yielded 4.1 g (0.032 mole, 69%) of a colourless liquid.

Controls and Procedures

Thermal Rearrangement of α -Methylallyl and Crotyl Benzenesulfinates

1) Approximately 1.5 molar in toluene solution.

A 2 g (0.010 mole) quantity of the appropriate ester was dissolved in anhydrous toluene (5 ml). The solutions were sealed in ampoules which were suspended in oil baths for $6\frac{1}{2}$ hours, the α -methylallyl ester at 80° and the crotyl ester at 100° . At the end of the reaction time, the toluene was removed from the solution under reduced pressure. The nmr

spectrum of 0.1 g of the residue in carbon tetrachloride was measured and the remainder was refluxed for 1 hour with 80 ml of 0.1 N sodium hydroxide. The aqueous solution was washed twice with benzene (100 ml) and the combined benzene solutions were washed with water (50 ml) and dried over anhydrous magnesium sulfate. The solvent was evaporated and the nmr spectrum of the residue in carbon tetrachloride was measured.

2) Approximately 1.5 molar in toluene solution with 2,6-lutidine added.

A 2 g (0.010 mole) quantity of the appropriate ester and 2 ml of 2,6-lutidine were added to anhydrous toluene (5 ml). The solutions were sealed in ampoules which were heated for 6½ hours in oil baths, the α -methylallyl ester at 80° and the crotyl ester at 100°. The ampoules were cooled and the contents shaken with 0.3 M hydrochloric acid (2 x 50 ml). The organic layer was washed with 10% aqueous sodium carbonate (2 x 10 ml) and water (2 x 20 ml) and was dried over magnesium sulfate before the toluene was removed by warming under reduced pressure. The nmr spectra of the residual oils in carbon tetrachloride were measured and the remainder was stirred overnight with sodium hydroxide (100 ml of 0.1 M) at room temperature. The basic solution was shaken with benzene (100 ml), the benzene solution was washed with water (2 x 50 ml), dried over magnesium sulfate and the solvent removed under reduced pressure. The nmr spectra of the residues in carbon tetrachloride were measured.

3) Approximately 0.1 molar in toluene solution with 2,6-lutidine added.

Solutions of each ester which were approximately 0.1 molar, and 2,6-lutidine, also approximately 0.1 molar, in toluene were sealed in

pressure bottles which were heated for 6½ hours or 42 hours in oil baths, the α -methylallyl ester at 80° and the crotyl ester at 100°. The cooled solutions were shaken with hydrochloric acid (100 ml of 0.3 M) to remove the lutidine and then with water (50 ml), 10% aqueous sodium carbonate (100 ml) and water (2 x 50 ml). After drying over magnesium sulfate, the solvent was removed under reduced pressure. The residues, after measurement of the nmr spectra in carbon tetrachloride solution, were stirred with 100 ml of 0.1 M sodium hydroxide for 12 hours at room temperature. The aqueous emulsion was extracted with ether, the extract washed with water (2 x 50 ml), dried over anhydrous magnesium sulfate and the solvent evaporated. The nmr spectra of the residues in carbon tetrachloride were measured.

- 4) Approximately 0.1 molar in 60% ethanol solution with 2,6-lutidine added.

Solutions of each ester (0.1 molar) and 2,6-lutidine (0.1 molar) in 60% ethanol were sealed in pressure bottles which were heated in oil baths for 6½ hours, the α -methylallyl ester at 80° and the crotyl ester at 100°. The cooled solutions were extracted with ether (100 ml) and the extracts washed with water (5 x 50 ml), 0.3 M hydrochloric acid (2 x 50 ml), 10% aqueous sodium carbonate (2 x 50 ml) and water (2 x 50 ml) and dried over magnesium sulfate. The solvent was evaporated and the nmr spectra of the oily residues in carbon tetrachloride were measured. The remainder was stirred with 0.1 M sodium hydroxide (100 ml) for 12 hours at room temperature. The aqueous emulsion was extracted with ether (100 ml), the extract washed with water (2 x 50 ml) and the solvent evaporated at reduced pressure. The nmr spectra of the residues in carbon tetrachloride were measured.

Formation of α,γ -Dimethylallyl Acetate During the Acetolysis of α,γ -Dimethylallyl 2,6-Dimethylbenzenesulfinate.

Gas chromatography on a Ucon oil filled column at 134° was used to analyze the products of the acetolysis of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate. A series of standard solutions of α,γ -dimethylallyl acetate in ether with cyclohexane added as standard were prepared, extracted in the same manner as described below and analyzed by gas chromatography. A graph (Figure 31) was prepared of peak area against concentration of acetate.

A solution of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate (0.02389 molar) and sodium acetate (0.1198 molar) in acetic acid was maintained at 25° in a constant temperature bath. After the required time intervals, 10 ml aliquots were withdrawn using the same automatic pipette and were added to ether (100 ml) and ice. The aqueous layer was separated and the organic layer washed with 10% aqueous sodium carbonate (2 x 25 ml) and water (2 x 50 ml). After drying over potassium carbonate, the solvent was removed by slow distillation through a Vigreux column. The residue was dissolved in ether (1.0 ml), and cyclohexane (0.1 ml) was added and the solution was analyzed by gas chromatography using the same conditions under which the calibration graph had been prepared. After about 30% of the rearrangement had occurred 2.4% acetate was formed; after 60% 4.6% acetate and after 10 half lives for the reaction, 9% of the products were identified as α,γ -dimethylallyl acetate.

Formation of 2,6-Dimethylbenzenesulfinic Acid During the Rearrangement of α -Phenylallyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol.

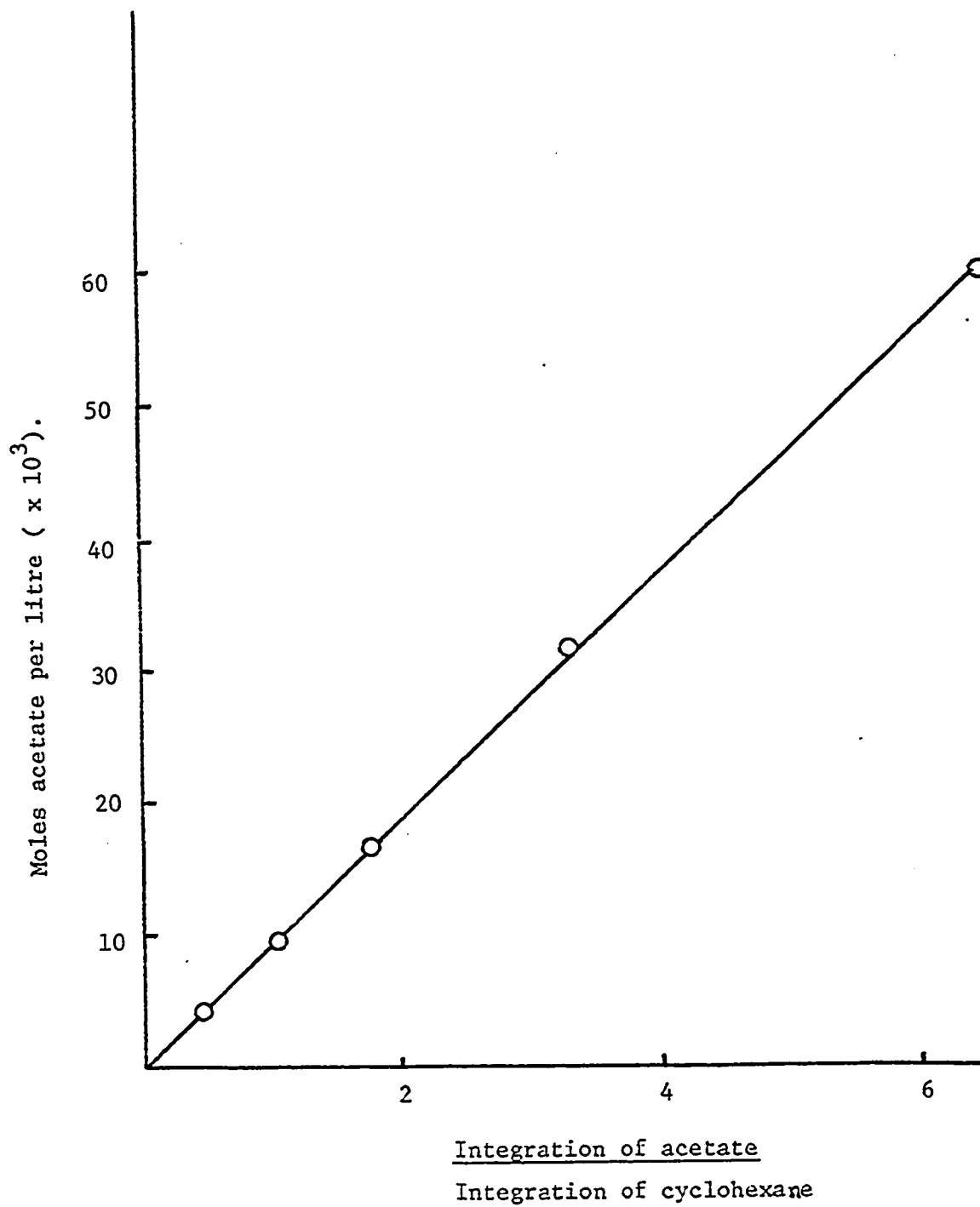


Fig. 31 - Calibration Graph for Gas Chromatography of α,γ -Dimethylallyl Acetate.

Two solutions of ester in 60% ethanol were prepared. One was 0.02414 M in ester and 0.04107 M in sodium acetate and the other was 0.02586 M in ester and 0.03004 M in 2,6-lutidine. Both solutions were placed in a constant temperature bath at 25° for 12 hours, which length of time was approximately ten half lives for the slow reacting diastereoisomer. Aliquots of the solutions (5 ml) were titrated with 0.0278 M sodium ethoxide in ethanol to the red endpoint of phenolphthalein. It was found that when the base was sodium acetate, 10.4% acid had been formed, while in the presence of 2,6-lutidine 9.8% acid was produced.

Formation of Ethyl 2,6-Dimethylbenzenesulfinate During the Rearrangement of α -Phenylallyl 2,6-Dimethylbenzenesulfinate in Anhydrous Ethanol.

As in the determination of the amount of acid formed during the rearrangement of the α -phenylallyl ester in 60% ethanol, the effect on the formation of ethyl ester, during the rearrangement in anhydrous ethanol, of both sodium acetate and 2,6-lutidine was investigated.

The solutions of the α -phenylallyl ester in ethanol were 0.02569 M in ester and 0.03856 M in sodium acetate, or 0.02683 M in ester and 0.02880 M in 2,6-lutidine. After 60 hours (ca. ten half lives for the slow reacting diastereoisomer) at 25° the solutions were poured into water (200 ml) and the emulsion allowed to stand at room temperature for one hour when flocculation occurred. The precipitate of cinnamyl 2,6-dimethylphenyl sulfone was removed by filtration, washed with ethanol (10 ml) and the filtrate extracted with ether (150 ml). The extract was washed with 0.1 M hydrochloric acid (100 ml), 10% aqueous sodium carbonate (2 x 50 ml) and water (2 x 100 ml). It was dried over potassium carbonate, the

solvent was removed and the nmr spectra of the residues were measured in carbon tetrachloride solution. The presence of signals due to ethyl 2,6-dimethylbenzenesulfinate was observed in the spectrum of the residue formed when sodium acetate was used as the base, but not when the base was 2,6-lutidine. From the integration of the nmr signals it was estimated that not more than 5% of the ethyl ester was formed in the presence of sodium acetate.

Formation of 2,6-Dimethylbenzenesulfinic Acid During the Rearrangement of Cinnamyl 2,6-Dimethylbenzenesulfinate in 60% Ethanol.

A solution of cinnamyl 2,6-dimethylbenzenesulfinate (0.01819 M) and 2,6-lutidine (0.03023 M) in 60% ethanol was prepared. Samples of the solution (about 6 ml) were sealed in ampoules and suspended in a constant temperature bath at 50° for 75 hours (ten half lives for the reaction.) Aliquots (5 ml) were titrated with 0.0289 M sodium ethoxide in ethanol to the red end-point of phenolphthalein. It was estimated that 6.4% of acid had been produced.

Measurement of the Rates of Rearrangement for the 2,6-Dimethylbenzenesulfinate Esters.

1) Procedure when ethanol or 60% ethanol used as solvent

Solutions of the esters in ethanol or 60% ethanol were prepared which were approximately 0.02 M in ester and 0.02 M in 2,6-lutidine. When the rates were run at 25.0° the solutions were placed in stoppered flasks which were suspended in a constant temperature bath at this temperature. After the appropriate time intervals, 5 ml aliquots were withdrawn using the same automatic pipette and were run into 60 ml

separating funnels containing 30 ml of ether. The ether extract was washed as rapidly as possible with ice-cold water (4 x 10 ml) shaking the funnel 40 times for each wash.

For rates run at higher temperatures, just over 5 ml portions of the solutions were sealed in ampoules which were immersed in constant temperature baths at 50.0°, 70.0° or 90.0°. The ampoules were removed from the baths when required and the reaction was quenched by plunging them into an ice slush. When they had equilibrated to room temperature, the ampoules were opened and 5 ml aliquots withdrawn using an automatic pipette, and added to 30 ml of pentane in the case of the allyl ester and to 30 ml of ether in the cases of the remaining esters. The solution was washed with water (4 x 10 ml), shaking 40 times for each wash.

The extracts from runs at both 25.0° and at higher temperatures were now treated similarly.

The solvent solution was poured into a 50 ml Erlenmeyer flask containing two spatulafuls of anhydrous granular potassium carbonate. The separating funnel was rinsed with 2 x 5 ml of solvent and the washings added to the main extract. The solution was dried for one hour and filtered through a glass wool plug into a 50 ml pear-shaped flask. The drying agent was rinsed with 5 ml of solvent and this was also poured through the filter. The solvent was removed by evaporation at low pressure and the residue was dissolved in 1 ml of bromoform, the infrared spectrum of this solution was measured over the appropriate wavelength range using a Perkin Elmer PE 21 infrared spectrophotometer and a 0.5 mm cell which had been balanced against a variable cell when both contained solvent.

2) Procedure when acetic acid used as solvent.

The rates of rearrangement of the esters in acetic acid were measured using solutions which were approximately 0.02 M in ester and 0.03 M in sodium acetate. The rates were run using a method similar to that described when ethanol or 60% ethanol was used as solvent, but the work-up procedure was modified.

Each 5 ml aliquot of solution was added to 30 ml of ether and ice (about 10 g) contained in a 60 ml separating funnel. The aqueous layer was separated and the organic layer was washed with water (2 x 10 ml), 10% aqueous sodium carbonate (2 x 10 ml) and water (2 x 10 ml) shaking 40 times for each wash. The extract was then dried, the solvent evaporated and the infrared spectrum of the residue measured as described in procedure 1) above.

Measurement of the Rate of Oxygen-18 Scrambling During the Rearrangement of 2,6-Dimethylbenzenesulfinate Esters Labelled in the Sulfinyl Oxygen Position.

Between 0.8 g and 1.0 g of ester and 0.3 g to 0.5 g of base were dissolved in 150 ml of solvent to yield a solution which was approximately 0.02 M in both ester and base. When the solvents were ethanol or 60% ethanol, the base was 2,6-lutidine; when the solvent was acetic acid, the base was sodium acetate.

The solutions were sealed in pressure bottles which were suspended in the appropriate constant temperature bath. The contents of the bottles at 25.0° were worked-up immediately after their removal from the bath; after removal from baths at higher temperatures, the bottles were placed

in the refrigerator where they were allowed to cool slowly. The work-up procedures differed slightly depending on the solvent.

1) Work-up of ethanol and 60% ethanol solutions.

The contents of the pressure bottles were poured into 300 ml of ether and the extract washed with water (400 ml), 0.5 M hydrochloric acid (50 ml), 10% aqueous sodium carbonate (2 x 50 ml) and water (3 x 50 ml). The acid wash was included to remove the 2,6-lutidine and was carried out as rapidly as possible. In the case of the α -phenylallyl and the α,γ -dimethylallyl esters, all of the wash liquids were cooled to about 5^o.

2) Work-up of acetic acid solutions.

The contents of the pressure bottles were poured into 300 ml of ether and 500 ml of water. The aqueous layer was separated and the organic layer washed with water (2 x 200 ml), 10% aqueous sodium carbonate (3 x 100 ml) and water (2 x 100 ml). In the case of the α -phenylallyl and the α,γ -dimethylallyl esters, all of the wash liquids were cooled to about 5^o.

The work-up procedure for all solvents now continues in the same manner.

For all the esters, except the α -phenylallyl, the extract was dried over potassium carbonate and the solvent was removed using a rotary evaporator while warming the solution to about 50^o. The ester remaining in the residue was hydrolyzed using the conditions detailed in Table XV and XLIII. In each case, 100 ml of the basic solution was used. Sodium hydroxide (100 ml of 0.5 M) in 50% aqueous dioxane was added to the washed extract containing the α -phenylallyl ester before the

ether was removed. The mixture was stirred at room temperature for 3 hours and the α -phenylallyl alcohol was recovered from this basic mixture as described in (c) below.

The basic mixtures containing all but the α -phenylallyl alcohol were extracted with ether (5 x 50 ml) and the extract dried over potassium carbonate. The method of isolation of the alcohol from the ether extract varied with the nature of the alcohol.

(a) Allyl, Crotyl, α -Methylallyl and α,γ -Dimethylallyl Alcohols.

The volume of the ether extract containing these alcohols was reduced to about 2 ml by warming in an oil bath at 60° and distilling the ether through a Vigreux column. The alcohol in the residue was recovered by preparative gas chromatography. The conditions of column temperature and gas flow rates for allyl, crotyl and α -methylallyl alcohols are in Tables XVI. A silicone grease packed column at 118° with a helium flow rate of 120 cc. per minute was used for the α,γ -dimethylallyl alcohol. The alcohols were collected in U-shaped tubes which were cooled in an ice-methanol bath.

(b) Cinnamyl Alcohol.

The solvent was removed from the ether extract containing this alcohol and the residue was shaken with hot water (100 ml), heated on the steam bath and shaken again. The undissolved material was removed by filtration while the liquid was still hot and the cooled aqueous solution was washed with ether (3 x 50 ml). The ether was dried over potassium carbonate, the solvent removed and the solid residue recrystallized from ether-pentane.

(c) α -Phenylallyl Alcohol.

The basic emulsion containing this alcohol was steam distilled.

About 500 ml of distillate was collected and washed with ether (3 x 100 ml). The ether extract was washed with water (5 x 50 ml) to remove as much as possible of the dioxane, dried over potassium carbonate and the solvent removed by distillation under reduced pressure. The residue was distilled at 25 mm using a microdistillation apparatus or, where the yield of alcohol was very low, using a molecular "cold-finger" type distillation apparatus, b.p. 112-114.

The excess oxygen-18 content of the alcohols was measured using an Unterzaucher apparatus as modified by Oita and Conway (64) and by Denney and Greenbaum (65). A diagram of this apparatus is provided in Figure 32 taken from reference 15 and a detailed description of its construction is also in this reference.

The Burrell Perma-Therm heater C maintains a tube containing copper powder at 550°. The copper powder reacts with any oxygen in the nitrogen to form copper oxide. The 1% hydrogen in the nitrogen gas used reduced this copper oxide back to copper. The water thus formed is removed in tube D which is filled with magnesium perchlorate and indicating Drierite. The furnace F at 900° surrounds a quartz combustion tube G containing platinized carbon held in place by rolls of platinum gauze. Any carbon oxysulfide formed during the combustion of these sulfur-containing compounds is reduced in the copper gauze packed tube H, heated to 900° by the furnace I. The resulting cuprous sulfide is reduced to copper and hydrogen sulfide by the hydrogen in the nitrogen. The hydrogen sulfide is absorbed by the Ascarite present together with Drierite in tube J. The carbon monoxide resulting from the combustion of the sample and the reduction of the carbon oxysulfide, is oxidized to carbon dioxide by iodine pentoxide at 120° in tube K. The iodine liberated is trapped in the U-tube M

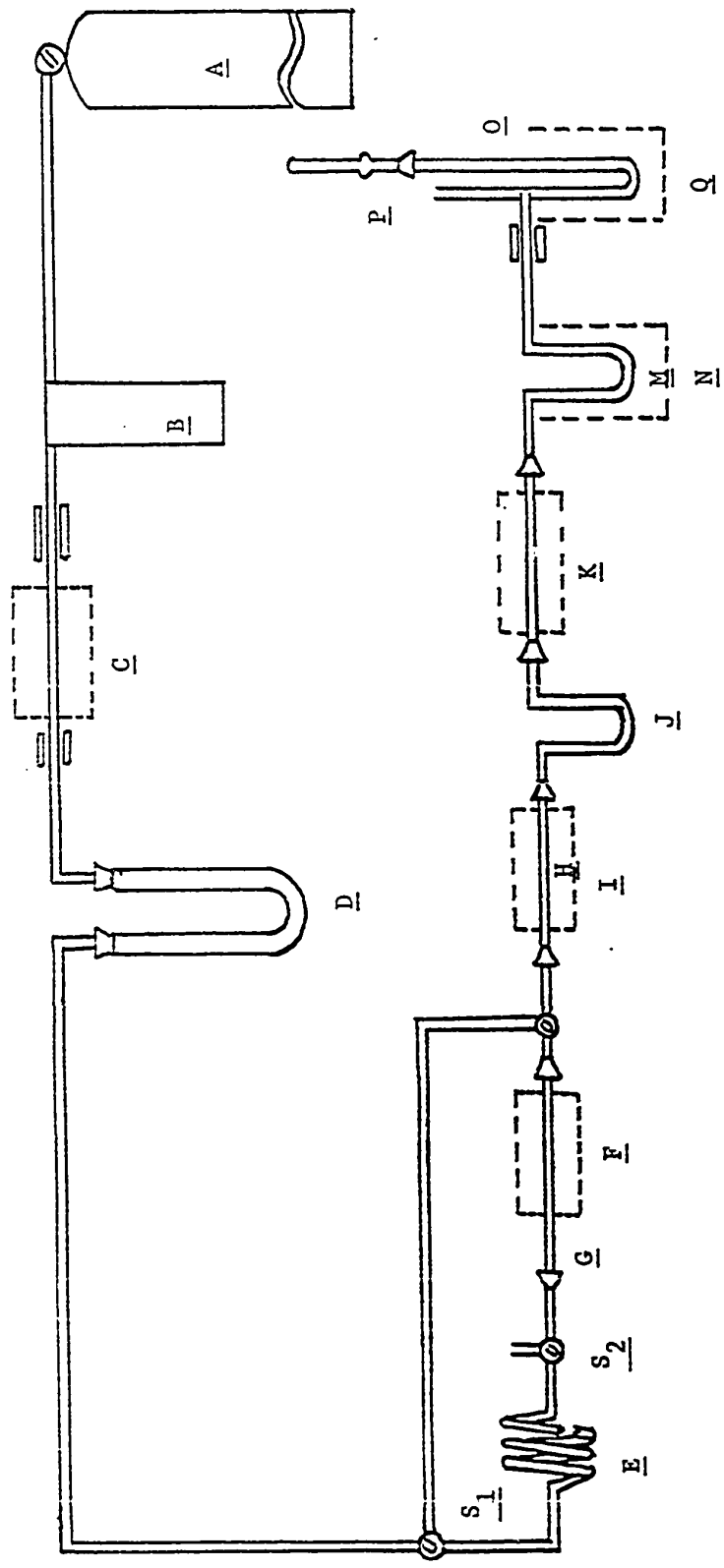


Figure 32 - Modified Unterzaucher apparatus.

- A. Nitrogen source
- B. Flow meter.
- C. Burrell Perma-Therm heater.
- D. Drying tube.
- E. Glass expansion coil.
- F. Furnace.
- G. Pyrolysis tube.
- H. Copper tube.
- I. Furnace
- J. Drying tube.
- K. Iodine pentoxide tube.
- M. Iodine collection tube.
- N. Dry ice-acetone bath
- O. Sample collection tube.
- P. Guard tube.
- Q. Liquid nitrogen bath.
- S₁, S₂, S₃ are stopcocks.

which is surrounded by a dry ice-acetone bath, while the carbon dioxide is solidified in the sample collection tube O by cooling it in liquid nitrogen. Moisture is prevented from condensing in the collection tube by the presence of a drying tube P filled with Ascarite and Drierite.

About 10 mg of alcohol was weighed into a platinum boat and with a 20 cc per minute reverse flow of nitrogen, the boat was inserted into the tube G. Dry ice was packed around this tube to prevent volatilization of the alcohol. After 5 minutes, the flow rate of the nitrogen was reduced to 10 cc per minute and the stopcocks S_1 , S_2 and S_3 were adjusted so that nitrogen flowed through the full length of the apparatus and a liquid nitrogen bath was placed around the sample collection tube O. A movable furnace was placed about 5 cm upstream from the boat and its temperature raised to 900° . When the sample had vaporized, the heater was slowly moved towards the boat and was allowed to stand around it for 5 minutes, before being moved towards the furnace F at a rate of about 2 cm per minute. When the furnace was reached, the heater was kept stationary for 5 minutes then switched off. The flow of nitrogen was continued for 20 minutes before the sample collection tube was removed, evacuated, sealed and the sample submitted for mass spectral analysis.

Measurement of the Rate of Rearrangement of α -Phenylallyl

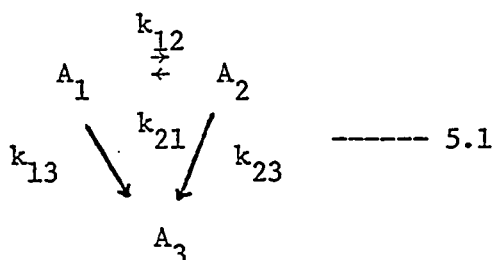
2,6-Dimethylbenzenesulfinate Using NMR Spectroscopy.

Solutions of ester (0.02839 M), and pyridine (0.03924 M) in ethanol, of ester (0.02936 M) and pyridine (0.03863 M) in 60% ethanol and of ester (0.02826 M) and sodium acetate (0.05140 M) in acetic acid were prepared. The flasks containing the solutions were suspended

in a constant temperature bath at 25°. After the appropriate time intervals, 10 ml aliquots were withdrawn using an automatic pipette and were run into 50 ml of ether contained in 100 ml separating funnels. Where ethanol or 60% ethanol had been used as solvent, the ether extracts were washed with water (4 x 20 ml). Where the solvent was acetic acid, each extract was washed with water (2 x 20 ml), 10% aqueous sodium carbonate (3 x 10 ml) and water (2 x 20 ml), shaking 40 times for each wash. All of the wash liquids were cooled to about 5°. Each extract was poured into a 100 ml Erlenmeyer flask containing 3 spatulafuls of potassium carbonate. The separating funnel was rinsed with ether (5 ml) and the washings added to the main extract. After drying for one hour, the solution was filtered through a glass wool plug into a 100 ml pear-shaped flask. The drying agent was washed with ether (5 ml) and this liquid was also poured through the filter. The solvent was removed under reduced pressure and the residue was thoroughly shaken with 0.512 ml of a 20:1:0.2 mixture of carbon tetrachloride:tetramethylsilane:cyclohexane. The solution was filtered through a glass wool plug into an nmr tube, type E. The nmr spectra were measured on a 100 Mc Spectrophotometer from τ 6.5 to τ 9.0.

APPENDIX

The kinetic treatment of the scheme outlined in equation 5.1 is detailed.



The symbols have the same connotations as described in Chapter III of the text.

$$-\frac{d(A_1)}{dt} = (k_{12} + k_{13})(A_1) - k_{21}(A_2)$$

$$-\frac{d(A_2)}{dt} = (k_{21} + k_{23})(A_2) - k_{12}(A_1)$$

$$\frac{d(A_3)}{dt} = k_{13}(A_1) + k_{23}(A_2)$$

The secular equation corresponding to these differential equations is

$$\begin{vmatrix}
 k_{12} + k_{13} - \lambda & -k_{21} & 0 \\
 -k_{12} & k_{21} + k_{23} - \lambda & 0 \\
 k_{13} & -k_{23} & -\lambda
 \end{vmatrix} = 0$$

which gives on expansion

$$(k_{12} + k_{13} - \lambda)(k_{21} + k_{23} - \lambda)(-\lambda) + k_{21}k_{12} = 0$$

$$\therefore \lambda^3 - \lambda^2(k_{12} + k_{13} + k_{21} + k_{23}) + (k_{12}k_{23} + k_{13}k_{21} + k_{13}k_{23}) = 0$$

whose roots are

$$\lambda_1 = 0$$

$$\lambda_2 = \frac{1}{2} (k_{12} + k_{13} + k_{21} + k_{23}) + \frac{1}{2} [(k_{12} + k_{13} + k_{21} + k_{23})^2 - 4(k_{13}k_{21} + k_{23}k_{12} + k_{13}k_{23})]^{1/2}$$

$$\lambda_3 = \frac{1}{2} (k_{12} + k_{13} + k_{21} + k_{23}) - \frac{1}{2} [(k_{12} + k_{13} + k_{21} + k_{23})^2 - 4(k_{13}k_{21} + k_{23}k_{12} + k_{13}k_{23})]^{1/2}$$

Corresponding to the roots λ_1 , λ_2 and λ_3 , there are particular solutions of the secular equation of the form

$$\sum_{j=1}^m (K_{ij} - \delta_{ij}) B_j = 0 \quad \text{----- 5.2}$$

where $i = 1, 2, \text{-----} m$.

$$K_{ij} = -k_{ji} \text{ where } i \neq j, \text{ and } k_{ii} = \sum_{p=1}^m k_{ip}$$

$$\delta_{ij} = 1, \text{ where } i = j \text{ and } 0 \text{ where } i \neq j$$

and B_j are the solutions.

B_{jr} are the sets of solutions corresponding to λ_r .

Arbitrarily, set all of the $B_{3r} = 1$.

Then from equation 5.2 three sets of simultaneous equations are obtained, any two of which are independent and can be solved

for B_{1r} and B_{2r} .

The equations are

$$(k_{12} + k_{13} - \lambda) B_{1r} - k_{21} B_{2r} = 0$$

$$-k_{12} B_{1r} + (k_{21} + k_{23} - \lambda) B_{2r} = 0$$

$$-k_{13} B_{1r} - k_{23} B_{2r} - \lambda = 0$$

These yield the following set of solutions:

$$B_{1r} = \frac{-k_{21}\lambda_r}{k_{12}k_{23} + k_{13}k_{23} + k_{21}k_{23} - k_{23}\lambda_r}$$

$$B_{2r} = \frac{-k_{12}\lambda_r}{k_{12}k_{23} + k_{12}k_{23} + k_{21}k_{13} + k_{13}\lambda_r}$$

These are not the desired solutions since they will not satisfy the initial conditions of concentration. The desired solutions can be derived by employing matrix algebra. They are represented by matrix equation

$$A = BEB^{-1}A_0$$

where

$$A = \begin{vmatrix} A_1 \\ A_2 \\ A_3 \end{vmatrix} \quad A_0 = \begin{vmatrix} a \\ b \\ 0 \end{vmatrix} \quad E = \begin{vmatrix} 1 & 0 & 0 \\ 0 & e^{-\lambda_2 t} & 0 \\ 0 & 0 & e^{-\lambda_3 t} \end{vmatrix}$$

a and b being the initial concentrations of A_1 and A_2

Then in simplified form

$$B = \begin{vmatrix} 0 & B_{12} & B_{13} \\ 0 & B_{22} & B_{23} \\ 1 & 1 & 1 \end{vmatrix}$$

Then $BEB^{-1}A_0$ is given by the following matrix

$$\frac{a(B_{12}B_{23}e^{-\lambda_2 t} - B_{13}B_{22}e^{-\lambda_3 t})}{B_{12}B_{23} - B_{13}B_{22}}$$

$$\frac{-bB_{12}B_{13}(e^{-\lambda_2 t} - e^{-\lambda_3 t})}{B_{12}B_{23} - B_{13}B_{22}}$$

$$\frac{aB_{22}B_{23}(e^{-\lambda_2 t} - e^{-\lambda_3 t})}{B_{12}B_{23} - B_{13}B_{22}}$$

$$\frac{-b(B_{22}B_{13}e^{-\lambda_2 t} - B_{23}B_{12}e^{-\lambda_3 t})}{B_{12}B_{23} - B_{13}B_{22}}$$

$$\frac{a(B_{22} - B_{23} + B_{23}e^{-\lambda_2 t} - B_{22}e^{-\lambda_3 t})}{B_{12}B_{23} - B_{13}B_{22}}$$

$$\frac{b(B_{13} - B_{12} - B_{13}e^{-\lambda_2 t} - B_{12}e^{-\lambda_3 t})}{B_{23}B_{12} - B_{13}B_{22}}$$

The equations for A_1 and A_2 then are

$$A_1 = \frac{a(B_{12}B_{23}e^{-\lambda_2 t} - B_{13}B_{22}e^{-\lambda_3 t})}{B_{12}B_{23} - B_{13}B_{22}} - \frac{bB_{12}B_{13}(e^{-\lambda_2 t} - e^{-\lambda_3 t})}{B_{12}B_{23} - B_{13}B_{22}}$$

$$A_2 = \frac{aB_{22}B_{23}(e^{-\lambda_2 t} - e^{-\lambda_3 t})}{B_{12}B_{23} - B_{13}B_{22}} - \frac{b(B_{22}B_{13}e^{-\lambda_2 t} - B_{23}B_{12}e^{-\lambda_3 t})}{B_{12}B_{23} - B_{13}B_{22}}$$

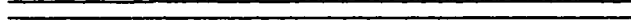
Substitution of the solutions for B_{ir} and simplification lead to

$$A_1 = -\frac{k_{21}b}{q}(e^{-\lambda_2 t} - e^{-\lambda_3 t}) + \frac{a(k_{12} + k_{13} - k_{21} - k_{23} + q)e^{-\lambda_2 t}}{2q} - \frac{a(k_{12} + k_{13} - k_{21} - k_{23} - q)e^{-\lambda_3 t}}{2q}$$

$$A_2 = -\frac{k_{12}a}{q}(e^{-\lambda_2 t} - e^{-\lambda_3 t}) - \frac{b(k_{12} + k_{13} - k_{21} - k_{23} - q)e^{-\lambda_2 t}}{2q} + \frac{b(k_{12} + k_{13} - k_{21} - k_{23} + q)e^{-\lambda_3 t}}{2q}$$

where $q = [(k_{12} + k_{13} + k_{21} + k_{23})^2 - 4(k_{13}k_{21} + k_{12}k_{23} + k_{13}k_{23})]^{1/2}$

and λ_2 and λ_3 are as previously defined.



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