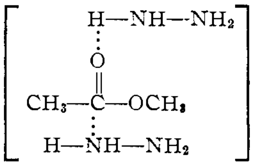
when the ratio of ester to hydrazine is 1:1 or 2:1. The fact that the reaction is second order with respect to the hydrazine when the ester is in excess is interesting. Whether this change from second order to third order is dependent only on the change in concentrations of the ester and hydrazine cannot be answered at present. There is some possibility that the methanol may play a role in the change in order. Unfortunately this could not be determined in the present work since it was not possible to study the various ratios of ester to hydrazine in benzene solution in the absence of methanol. The latter was necessary to maintain homogeneity.[4]

The simplest conceivable transition state for the third-order reaction would be



$$\left[\begin{array}{c} H\text{—}NH\text{—}NH_2 \\ \vdots \\ O \\ \| \\ CH_3\text{—}C\text{—}OCH_3 \\ \vdots \\ H\text{—}\dot{N}H\text{—}NH_2 \end{array}\right]$$

This picture disregards the fact that the ester is in excess. It should be more applicable in those systems where the hydrazine is in excess. In the latter cases, the reactions had second-order kinetics. In some way then it would appear that the methanol is partly responsible for the change in kinetic order. No amount of methanol, however, will cause the change to third-order kinetics when the ratio of ester to hydrazine is 1:2. The ratio of reactants is the most important single factor, although the methanol plays an important part at that point where the hydrazine is no longer in excess.

As the ester becomes equivalent to the hydrazine and finally is present in excess, it becomes apparent that some equilibrium, governing the availability of hydrazine or ester, is disturbed. This could account for the diminished reaction rate as the reaction becomes third order. This disturbance is not observed when the hydrazine is in excess. On the basis of the present data, it is reasonable to suppose that hydrogen bonding of one of the reactants with methanol is responsible for the disturbance. In view of the fact that it has not been possible to study the reaction in the absence of methanol it has been decided to postpone discussion of proposed mechanisms for the effects observed. Such discussion will be included in the next paper in the series. At that time data will be available from a study of aminolysis reactions also.

PHILADELPHIA, PENNA.

[4] Recent work in our laboratory on the aminolysis of methyl acetate gives a similar change in order from second to third. In this case methanol plays a definite role in the change.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE RADIOCARBON LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Allylic Rearrangements. XLIII. Some Studies of the Thermal Decomposition of Allyl Chlorosulfinate-1-C^{14} [1]

BY S. H. SHARMAN,[2a] F. F. CASERIO,[2b] R. F. NYSTROM, JOHN C. LEAK AND W. G. YOUNG

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Allyl chlorosulfinate-1-C^{14} has been decomposed thermally to allyl chloride and sulfur dioxide in a variety of solvents. Through the use of special experimental techniques, the chlorosulfinate ester has been decomposed with quantitative allylic rearrangement in the solvent *n*-decane and with varying degrees of preservation of structure in other solvents. Qualitative rate data for the reaction in several solvents also are presented. A mechanism involving a rate-determining alkyl–oxygen ionization is discussed.

Introduction

The reaction of thionyl chloride with various substituted allyl alcohols has been examined under a variety of conditions in these laboratories,[3] and the resulting data have indicated that the decomposition of the intermediate chlorosulfinate ester is extremely complex in nature. In order to study more thoroughly the reactions of this intermediate, attention recently has been focused upon the allyl system itself ($CH_2{=}CHCH_2$—). Aside from the reduction of the allylic system to its simplest form, the present investigation offers the added advantage, peculiar in the allylic field to this system, that the chlorosulfinate ester of allyl alcohol is a stable, isolable compound. The decomposition reaction may thus be examined directly without interference from the by-product of the reaction of thionyl chloride with alcohol, namely, hydrogen chloride. Due to the symmetry properties involved, radiocarbon labeling of the chlorosulfinate was required.

A preliminary experiment, reported in 1953,[4] suggested that allyl chlorosulfinate-1-C^{14} ($CH_2{=}CHC^{14}H_2OSOCl$) decomposes without added solvent at approximately 90° to give allyl chloride containing 51% 1-C^{14}. As a consequence of several subsequent experiments, summarized in Table I, it became evident that, in the absence of tertiary amine bases or their hydrochlorides, the results of such decomposition reactions could not be duplicated under the usual operating conditions. It also became clear that the addition of even trace

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[1] This work was supported in part by a grant to W. G. Young from the National Science Foundation.

[2] (a) Standard Oil Co. of California Research Fellow, 1956–1957; (b) Standard Oil Co. of California Research Fellow, 1952–1953.

[3] (a) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 813 (1956); (b) W. G. Young, F. F. Caserio and D. Brandon, *Science*, **117**, 473 (1953); (c) W. G. Young, F. F. Caserio, R. H. DeWolfe and G. Dennis, THIS JOURNAL, **77**, 4182 (1955); (d) W. G. Young and F. F. Caserio, unpublished work.

[4] R. F. Nystrom and J. C. Leak, THIS JOURNAL, **75**, 3039 (1953).

quantities of such amine compounds causes the decomposition to proceed with essentially quantitative preservation of allylic structure.

TABLE I

PRELIMINARY RESULTS OF THE DECOMPOSITION OF ALLYL CHLOROSULFINATE-1-C^{14}

Added amine or amine hydrochloride	Solvent	Temp., °C.	Allyl chloride % 3-C^{14}	% 1-C^{14}	Yield, %
None	None	61	62	38	81
None	None	61	28	72	90
$(C_4H_9)_3N$ (catalytic amt.)	None	61	2	98	92
Pyridine (catalytic amt.)	None	*ca.* 20	3	97	74
None	$EtOC_2H_4OEt$	63	9	91	..
$(C_4H_9)_3NHCl$	$EtOC_2H_4OEt$	25	2	98	..
$(C_4H_9)_3NHCl$	$EtOC_2H_4OEt$	25	2	98	..

On the basis of (1) the fact that the effect of added amine or amine hydrochloride was considerably more striking in the allyl than in the butenyl system,[3a,d] (2) the knowledge that the effects brought about by the addition of such compounds are the result of a bimolecular process of the SN2 type involving chloride ion[3d,5] and (3) the observation (to be discussed presently) that the rate of decomposition of allyl chlorosulfinate by processes other than those of the SN2 type is slower by a factor of at least four powers of ten than the decomposition of crotyl- or α-methylallyl chlorosulfinate, it was concluded that the allyl system is enormously more sensitive than the butenyl system to the SN2 type process by virtue of the relatively reduced rates of the other competing processes.

Dissolved hydrogen chloride gas has been shown to participate strongly in the decomposition of the butenyl chlorosulfinate esters *via* the SN2 process in solvents other than ether[3d] (a solvent known to form a stable, undissociated complex with hydrogen chloride[6]). Even in ether, the addition of copious quantities of the gas seriously affects the product composition, reducing the percentage of allylic rearrangement accompanying decomposition from 99 to 90%.[3d] It thus seemed clear that the unexpected behavior of the reaction of allyl chlorosulfinate-1-C^{14} in 1,2-diethoxyethane, a solvent which would be expected to display properties similar to those of diethyl ether with respect to its ability to complex hydrogen chloride effectively, was due to the intrusion of the bimolecular process involving the dissolved gas. Apparently the strength of the ether·HCl complex is not great enough to "deactivate" the hydrogen chloride gas with respect to its tendency to attack the extremely sensitive allyl system. The inability to duplicate results in the reactions performed without added solvent likewise was attributed to the action of trace quantities of hydrogen chloride not removed during the original purification of the ester or generated by the action of minute traces of water present in the reaction mixtures according to the scheme

$$\begin{tikzcd}
H_2O + ROSOCl \arrow[r] \arrow[d] & ROSO_2H + HCl \arrow[d, "H_2O"] \\
ROH + HOSOCl \arrow[dr, "H_2O"'] & ROH + SO_2 + H_2O \\
 & SO_2 + HCl + H_2O
\end{tikzcd}$$

Hydrogen chloride (or chloride ion) formed in this manner could be expected to participate in a chain reaction of the type

$$HCl + ROSOCl \longrightarrow ClR + SO_2 + HCl$$

or

$$Cl^- + ROSOCl \longrightarrow ClR + SO_2 + Cl^-$$

Consequently, minute traces of water in the reaction system could give rise to a chain of events which would be expected to have a striking effect upon the course of the decomposition of allyl chlorosulfinate-1-C^{14} if the SN2 process assumes control of the reaction to the extent that the results imply. This premise is supported by the observation that the chlorosulfinate ester is extremely sensitive to atmospheric moisture, decomposing immediately upon being exposed to the air of the laboratory.

Results

An experimental technique was developed for the decomposition of allyl chlorosulfinate-1-C^{14} with and without added solvent under completely anhydrous conditions. The elaborate, all-glass apparatus employed was designed in such a way that the careful purification of the ester and the subsequent handling and transfer of all liquid components (starting materials, products, solvents, etc.) could be accomplished within a carefully dried, closed system. The decomposition was, in most cases, effected by heating the anhydrous reaction mixture to the temperature required for decomposition at a "standard initial rate" equivalent to a first-order half-life of approximately 18 minutes. The radioactive allyl chloride product was purified and ozonized, and the dimedone derivative of the resulting formaldehyde was prepared for assay of activity. The results of such experiments are summarized in Table II.

The allyl alcohol-1-C^{14} employed was found to contain only 0.3% 3-C^{14} by methods described in the Experimental section. As indicated in Table II, analysis for 3-C^{14} of the diallyl sulfite produced as a by-product of the formation of the chlorosulfinate ester indicated that the percentage of rearrangement of the allyl group accompanying the preparation of the ester was small if not negligible. This conclusion was further supported by analysis of allyl *n*-amyl sulfite prepared from the chlorosulfinate compound. The mixed sulfite contained 0.6% 3-C^{14}.

Study of the mixed sulfite prepared from unreacted starting material in the reaction performed in thionyl chloride indicated that rearrangement of the allyl chlorosulfinate during the decomposition process was negligible. Due to the nature of the products of this reaction, however, it is clear that no generalizations may be drawn from this experiment. Similar attempts at isolation of unreacted ester from the reactions executed in liquid

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(5) E. S. Lewis and G. M. Coppinger, THIS JOURNAL, **76**, 796 (1954).

(6) (a) A. M. Buswell, W. H. Rodebush and M. F. Roy, *ibid.*, **60**, 2528 (1938); (b) D. R. Chesterman, *J. Chem. Soc.*, 906 (1935); (c) T. Mounajed, *Compt. rend.*, **197**, 44 (1933).

TABLE II

RESULTS OF THE DECOMPOSITION OF ALLYL CHLOROSULFINATE-1-C^{14} UNDER ANHYDROUS CONDITIONS

Solvent	Decompn. temp., °C.	Allyl chloride % 3-C^{14}	Allyl chloride % 1-C^{14}
None	78–80[a]	88.5	11.5
None	78–80[a]	89.9	10.1
Allyl-*n*-amyl sulfite prepared from allyl chlorosulfinate used in this reacn. contained 99.4% 1-C^{14}			
None[b]	78–80[a]	85.5	14.5
The diallyl sulfite produced in this expt. contained 98.9% 1-C^{14}			
n-Butyl ether	128–130	91.4	8.6
n-Butyl ether	128–130	93.2	6.8
n-Decane	138–141	99.1	0.8
Dioxane	98–100	34.1	65.9
Dioxane	98–100	34.2	65.8
Dimethylformamide	145–151	1.8	98.2
Sulfur dioxide	−15[a]	<8% reacn. in 11 hr.	
Sulfur dioxide	20[a]	84.7	15.3
Sulfur dioxide	35[a]	85.1	14.9
The diallyl sulfite produced in this expt. contained 96.0% 1-C^{14}			
Thionyl chloride	55–56	94.5	5.5
Thionyl chloride	57–59	98.2	1.8
The allyl-*n*-amyl sulfite prepared from unreacted allyl chlorosulfinate contained 98.2% 1-C^{14}			

[a] Decomposition not performed at the "standard initial rate." [b] In this reaction, a slight leak developed in the reaction system while under reduced pressure thus allowing atmospheric moisture to be drawn through the reaction mixture.

sulfur dioxide (the most powerful ionizing solvent of those employed) at 20 and 35° were unsuccessful because of the technical difficulties involved. In the rather extensive studies of the reaction of thionyl chloride with allylic alcohols performed in these laboratories, however, no evidence for rearrangement of starting materials during the decomposition process has appeared. Investigations of the reactions of *cis*-crotyl alcohol, to be published presently, strongly support our contention that rearrangement does not occur.

A control experiment, performed in liquid sulfur dioxide at 20°, demonstrated that allyl chloride remains completely unrearranged under the conditions of the decomposition reactions executed in this solvent. This appears to be good evidence that the product is stable under the conditions of all reactions performed, with the possible exception of the experiments effected in dioxane and dimethylformamide. It is clear, however, that the chloride product does not rearrange in the amide solvent to any significant extent. This statement is based upon the fact that any rearrangement of allyl chloride which occurs causes the ratio of 1-C^{14} to 3-C^{14} to approach a value of 1:1. Consequently, in any reaction which produces allyl chloride-1-C^{14} or 3-C^{14} of essentially 100% purity, no rearrangement can have occurred.

Discussion

Although the use of the solvent ether allows, under normal reaction conditions, the ready decomposition of the butenyl and pentenyl chlorosulfinate esters with quantitative allylic rearrangement,[3b,c] the results of the present investigation demonstrate that only under conditions meticulously controlled to avoid the initial presence and subsequent formation of hydrogen chloride or chloride ion may the decomposition of allyl chlorosulfinate be executed with the same results. Roberts, Young and Winstein,[7] in 1942, suggested a cyclic process, termed S_Ni', to explain allylic rearrangements of the general type encountered in the present work. Young[3c] recently stated that, in the reactions of thionyl chloride with allylic alcohols, the available data did not allow a choice to be made between a concerted cyclic process and a mechanism involving the formation of rigidly-oriented ion-pair intermediates followed by collapse to rearranged products. The results of the present investigation allow further scrutiny of the "S_Ni' type" process.

It is clear that in order for an ion-pair mechanism to be operative, an ionization stage must be important in the reaction. Generally speaking, there are two criteria which may be used to verify the presence or absence of such an ionization. If the rate of a reaction is shown to be extremely sensitive to variation of the ionizing power of the solvent, a rate-controlling ionization stage is strongly suggested. If it is also demonstrated that the rate is sensitive to changes in the structure of the substrate in such a way that an increase in rate is observed as more and more powerful electron-donating groups are attached to the carbon atom undergoing nucleophilic substitution, it is difficult to assign a mechanism which does not involve a rate-determining ionization. It is conceivable that a reaction adhering to the above principles would not involve ion-pair intermediates. This would be the case if the rate-determining step were not merely ionization, but complete dissociation without the intervening formation of relatively stable lower-energy ion-pair intermediates. Such a situation is unlikely, and, in most cases, would be detectable by various diagnostic techniques.

Table III presents qualitative rate data obtained in the decomposition reactions of allyl chlorosulfinate-1-C^{14}. Although these relative rate values are admittedly crude and cannot be considered accurate to better than 30% (except the ratio k_{SO_2}/k_{decane} which unquestionably has a value of at least 1000), they do indicate a definite trend. If one excludes the relative rate figures for the decompositions in dioxane and dimethylformamide because of the obvious operation of some specific solvent effect, it can be seen that the reaction rate varies over a range of at least three powers of ten and that it rises generally as the ionizing power of the solvent is increased. Sulfur dioxide is known to be a solvent of relatively high ionizing power, and it seems reasonable to assume that thionyl chloride, as well, should possess considerable ability to solvate ionic species. On this basis, one would expect allyl chlorosulfinate, which performs the function of a solvent in the reactions executed without added solvent, to exhibit an ionizing character smaller than, but not extremely dissimilar to, that

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(7) J. D. Roberts, W. G. Young and S. Winstein, THIS JOURNAL, **64**, 2157 (1942).

of thionyl chloride. Lewis and Boozer[8] have observed the same general rate dependence upon solvent character in the decomposition of secondary alkyl chlorosulfinates, although the effects did not appear to be as large.

TABLE III

RELATIVE RATES OF DECOMPOSITION OF ALLYL CHLOROSULFINATE-1-C^{14}

Solvent	$k_{solvent}/k_{decane}$
n-Decane	1^b
Dimethylformamide	0.5
n-Butyl ether	2
Dioxahe	16
None	100
Thionyl chloride	270
Sulfur dioxide[a]	>1000

[a] Calculated from the decomposition performed at 20°. [b] 6×10^{-4} sec.$^{-1}$ at 140°.

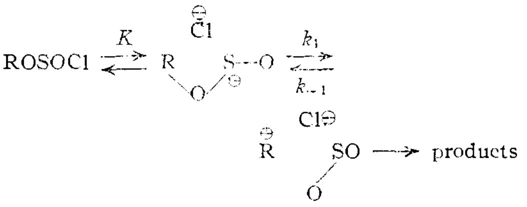
A much more striking feature of the chlorosulfinate decomposition is its sensitivity to changes in the structure of the substrate. For example, if one compares the reaction of crotyl alcohol with thionyl chloride in ether[3d] with the decomposition of allyl chlorosulfinate-1-C^{14} in n-butyl ether, he is able to estimate that the rates of decomposition of the esters differ by a factor of at least 10^4 and probably 10^5. This effect is of the order of magnitude one would expect a methyl group to exert upon a rate-controlling ionization stage. The choice of these particular reactions for comparison purposes is based upon the fact that in all the experiments performed using the butenyl system, hydrogen chloride was present during the decomposition reaction, but in the case of the reaction executed in ether, the dissolved gas had little or no effect upon the decomposition process as evidenced by the product composition. Consequently, since no hydrogen chloride was present in the decomposition of allyl chlorosulfinate-1-C^{14}, this is the fairest comparison that can be made using the available data.

Streitwieser[9] has shown that the composition of 1-butyl-1-*d* chlorosulfinate in dioxane is slower by a factor of approximately 42 than the corresponding reaction in the 2-butyl system.[8] He points out that this is not surprising since primary carbonium ions are known to be considerably less stable than their secondary counterparts. A rough calculation of the relative rates of decomposition of allyl and 1-butyl-1-*d* chlorosulfinates in dioxane indicates that the reaction of the allyl system is faster by a factor of about 6. As a basis of comparison, Vernon[10] has reported that allyl chloride is solvolyzed in slightly aqueous formic acid 25 times faster than is n-propyl chloride. Comparison of rough rate data from the reaction of α-methylallyl alcohol with thionyl chloride in ether[3d] with those obtained from the decomposition of 2-pentyl chlorosulfinate in n-butyl ether[8] indicates that the former is faster by a factor of approximately 10^5.

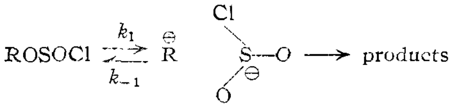
The rate-retarding deuterium isotope effects observed by Boozer and Lewis[11] present a rather striking indication of the effect of change of structure upon the rate of reaction. The substitution of deuterium for hydrogen of the β-carbon atoms of the 2-pentyl chlorosulfinate system led to a reduction of the rate of decomposition by a factor of 1.45 in dioxane and 3.34 in isoöctane.

The effect of change of structure upon the stability of the chlorosulfinate ester is worthy of examination. Survey of the reported investigations of the reaction of thionyl chloride with alcohols indicates that only in the cases of the saturated alkyl and the allyl systems have stable chlorosulfinate esters been isolated. Thus it appears that attachment to the carbinol carbon atom of electron-donating groups more powerful than one vinyl group renders the intermediate too unstable to permit isolation. Several attempts have been made in these laboratories to isolate crotyl chlorosulfinate, but it has been found that, even at very low temperatures, the compound decomposes as soon as it is formed. Similarly, no other substituted allyl or benzyl chlorosulfinates have been isolated.

Analysis of the foregoing data makes it clear that the behavior of chlorosulfinate esters generally satisfies the conditions of the criteria established for reactions involving a rate-determining ionization step. There are two possible ionization stages which might be rate-controlling: alkyl–oxygen ionization, or ionization of the S–Cl bond as originally suggested by Boozer and Lewis.[8] The sensitivity of the reaction to changes in solvent character allows no differentiation to be made between these two mechanisms; but the striking changes accompanying variation in the structure of the substrate make it appear that ionization of the C–O bond is the rate-controlling step. A process of this type might be either the initial step of the reaction or the second step, preceded by ionization and return of chloride in a rapid pre-equilibrium. The ionization of the alkyl–oxygen bond would be expected to be especially facilitated if such a pre-equilibrium were operative. Mechanisms of the type reflected above are presented in their simplest form in schemes A and B. In each case, k_1 represents the rate constant of the rate-controlling step, but no implications as to the relative values of the k_1's and k_{-1}'s or as to the detailed structure of the intermediates are intended. Furthermore, the lack of detail concerning the product-forming steps is not intended to imply that such processes are simple, for many sequences involving further ionization, dissociation, internal return, migration of ions within ion-pairs and exchange are possible.



(A)



(B)

It seems quite clear that the intermediate produced by the rate-determining step of the reaction

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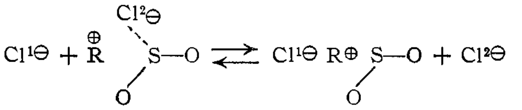
(8) C. E. Boozer and E. S. Lewis, THIS JOURNAL, **75**, 3182 (1952).

(9) A. Streitwieser and W. D. Schaeffer, *ibid.*, **79**, 379 (1957).

(10) C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

(11) C. E. Boozer and E. S. Lewis, THIS JOURNAL, **76**, 794 (1954).

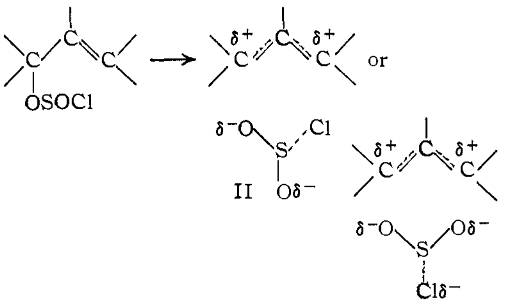
is an undissociated ion-pair of the type suggested by Kosower.[12] Experiments performed in liquid sulfur dioxide indicate that added chloride ion has absolutely no effect either upon the product composition or upon the stereochemical results of the reaction of optically active α-methylallyl alcohol with thionyl chloride in this most ionizing of solvents employed (products: 68% crotyl chloride, 32% α-methylallyl chloride—retention with 60% racemization).[3a] This fact suggests that the species which decomposes or collapses to give product is an ion-pair intermediate. It does not exclude the possibility of dissociation resulting in the formation of chloride ions, but it does indicate that, if such a process is operative, return to the product-forming ion-pair is extremely important, since chloride ions in solution clearly do not attack to give product. It is further worthy of note that these investigations in liquid sulfur dioxide show that the S$_N$2 process does not function in this solvent and that exchange of the type pictured in scheme C is not important in the product-forming stage. Such an exchange of ion-pair partners (Cl^1 for Cl^2), leading to a new ion-pair of different configuration, is not excluded by the facts, but a process of this type cannot be used to explain the inversion of configuration of asymmetric configuration, since the data indicate that such an ion-pair species as I does not lead to product. Exchange, then, may occur, but the reverse process must take place before the intermediate can collapse.



$$\mathrm{Cl^{1}}\ominus + \overset{\oplus}{\mathrm{R}}\ \ \mathrm{S(\cdots Cl^{2}\ominus)(=O)-O} \rightleftharpoons \mathrm{Cl^{1}}\ominus\ \mathrm{R}\oplus\ \mathrm{S(=O)-O} + \mathrm{Cl^{2}}\ominus \qquad (C)$$

I

It now becomes important to inquire as to what structures the intermediate ion-pairs of the type discussed might display in the allylic system. Examination of the results of the reactions of the butenyl alcohols[3b] and of α,α-dimethylallyl alcohol[3c] with thionyl chloride in ether and of the decomposition of allyl chlorosulfinate-1-C^{14} in *n*-decane make it appear that such an ion-pair intermediate possesses considerable structure as would be expected in such solvents, incapable as they are of supporting an extensive separation of charge. As was pointed out by Winstein and Robinson,[13] initial ionization of the alkyl–oxygen bond causes the development of positive charge on both the α- and γ-carbon atoms of the allylic system. It would not be surprising, then, if the energetically most stable arrangement of the ion-pair were one of the two conformations pictured in scheme D. One would expect structure II to be more favorable energetically than III due to the greater polarizability of chlorine relative to oxygen. This presumption is supported by the fact that no evidence for rearrangement of allylic chlorosulfinate esters has been reported. Collapse of II would lead to completely rearranged products as has been observed in the present investigation, and it would appear that a mechanism of the above type, a refinement of the S$_N$i′ process as it was originally proposed, can be assigned to account for these results.



II

III

(D)

It is worthy of note that the decomposition of allyl chlorosulfinate-1-C^{14} in dimethylformamide appears out of line with the other reactions both from the standpoint of rate of reaction and of the fraction of rearranged product obtained. Decomposition required the highest of all the temperatures employed, and it is possible that the product results can be attributed to a slight decomposition of the solvent at this temperature, giving rise to the formation of trace quantities of amine which would then be expected to affect the course of the reaction in the manner observed. It is also conceivable that at such high temperatures, a reaction involving the amide itself, functioning as a base, might have become important. In either case, however, it is difficult to explain why the processes which normally operate at lower temperatures in solvents of considerably lower ionizing power should not have functioned at temperatures somewhat lower than those actually required for decomposition.

The results of the reactions performed in dioxane indicate that some specific solvent effect was operative in this medium as well as in dimethylformamide. This is not surprising in view of the observations of Lewis and Boozer[8] that dioxane and tetrahydropyran appear to possess the somewhat unique quality of promoting retention of asymmetric configuration in the decomposition of optically active secondary alkyl chlorosulfinate esters. This phenomenon has been also observed in these laboratories in connection with studies of the α-methallyl system.[3d] An explanation of the general type proposed by the above authors to account for the unusual behavior in aliphatic systems may be applicable, with slight modification, to the allylic system as well.

Although it seems probable that alkyl–oxygen ionization to an intermediate ion-pair is the rate-determining step in all the reactions of decomposition of chlorosulfinate esters, and that the completely rearranged products obtained under certain conditions in the allylic system are generated by a process of the type described above, the details of the product-forming step or steps which lead to the formation of the unrearranged fraction of mixtures obtained under other conditions (in the absence of the specific solvent effects described earlier) are still unclear. Since the data present compelling evidence against the operation of a dissociation process in the decomposition of the butenyl chlorosulfinates even in liquid sulfur dioxide, it seems reasonable to assume that such a mechanism does not function in reactions of the

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(12) E. M. Kosower, Ph.D. Thesis, U.C.L.A., 1952.

(13) S. Winstein and G. Robinson, THIS JOURNAL, 80, 169 (1958).

unsubstituted allyl system, less prone as it is toward any ionization processes. All products, then, are most probably generated through the collapse of ion-pair intermediates or through the operation of mechanism involving SN2 type attack by chloride ion (or hydrogen chloride). The latter process undoubtedly contributes strongly to the reactions of the butenyl chlorosulfinates in solvents less polar than sulfur dioxide since the attacking chloride species cannot be removed from the reaction mixture; however it would seem that the SN2 type process cannot be employed to account for products of preserved allylic structure in the studies of the unsubstituted allyl system where extreme care has been taken to avoid HCl or chloride ion. There are several relatively unoriented ion-pairs which may be visualized as resulting from ionization stages proceeding from the rigidly oriented intermediate generated by the rate-determining step. Collapse of a fraction of such complex intermediates may account for the relatively small portions of unrearranged allylic chloride often obtained. A highly-oriented ion-pair intermediate displaying a geometry similar to that normally envisioned for the classical concerted SNi process must also be considered. At the present stage of the work, however, no convincing arguments can be presented to resolve the problem under discussion.

Experimental

Preparation and Purification of Materials. Thionyl Chloride.—Eastman Kodak Co. white label grade thionyl chloride was purified by the method of Cottle.[14]

***n*-Decane.**—Humphrey–Wilkinson *n*-decane was purified by shaking successively with several portions of concentrated sulfuric acid, water, dilute aqueous sodium carbonate and again with water. The product, after preliminary drying with anhydrous magnesium sulfate, was passed through a 4-foot column containing fine mesh silica gel, distilled through a fractionating column rated at 102 theoretical plates, and stored over sodium hydride. It boiled at 91.2° (51 mm.) and had n^{25}D 1.4094.

***n*-Butyl Ether.**—Braun technical grade *n*-butyl ether was purified by shaking successively with several portions of 5% aqueous ferrous sulfate solution, 1:1 sulfuric acid, water, aqueous sodium carbonate solution and again with water. After preliminary drying with anhydrous magnesium sulfate and flash distillation at reduced pressure, the product was refluxed for 8 hours with metallic sodium at a pressure of 300 mm. Fractionation was subsequently effected through the column referred to above. The anhydrous product, which gave a negative peroxide test by the method of O'Brien,[15] had a boiling point of 51.2° (29 mm.) and n^{25}D of 1.3971. It was stored in the dark over sodium hydride.

Dioxane.—Eastman Kodak Co. white label grade dioxane was purified by the method of Fieser.[16] Final distillation was effected through a 90-theoretical plate fractionating column. The product, which showed a negative peroxide test by the method of O'Brien,[15] had a boiling point of 102.2° and n^{25}D of 1.4199. It was stored in the dark over sodium hydride and in an atmosphere of nitrogen.

Dimethylformamide.—Matheson dimethylformamide was distilled at reduced pressure from Drierite through a 102-plate column. The middle fraction, which was retained, had a boiling point of 57.5° (24 mm.) and n^{25}D of 1.4281. It contained less than six parts per million of water as indicated by titration with Karl Fischer reagent.

Allyl Alcohol-1-C^{14}.—The samples of allyl alcohol-1-C^{14} used in this work, prepared[17] in the Radiocarbon Laboratory of the University of Illinois, possessed activities in the range 0.3 to 1.0 microcuries per millimole. The alcohol boiled over the range 96.3–96.6° and had n^{25}D 1.4103. The percentage of radioactive carbon in the 1-position was shown to be at least 99.7%.

Allyl chloride-1-C^{14} was prepared by the slow, dropwise addition of thionyl chloride to a solution of allyl alcohol-1-C^{14} and purified tri-*n*-butylamine in *n*-butyl ether at −10° (all reactants present in equimolar quantities). After addition was complete, the cooling bath was removed, and the mixture was stirred at room temperature for one hour. The low-boiling components were subsequently removed by reduced-pressure flash distillation, shaken with 2% aqueous sodium carbonate solution, and dried overnight with Drierite. Fractionation through an efficient single center rod column gave a product boiling at 44.5° and having n^{25}D 1.4110.

A sample of the allyl chloride was ozonized, and the resulting formaldehyde was converted to its dimedone derivative. Assay of this derivative indicated that product was contaminated with only 0.3% allyl chloride-3-C^{14}. These data indicate, on the basis of an argument presented in the text of this paper, (1) that the reaction employed for the preparation of allyl chloride-1-C^{14} leads to complete preservation of allylic structure and (2) that the starting alcohol used contained no more than 0.3% allyl alcohol-3-C^{14}.

Allyl Chlorosulfinate-1-C^{14}.—Ten grams (0.172 mole) of dry allyl alcohol-1-C^{14} was added dropwise over a period of 50 minutes to 60 g. (0.51 mole) of purified thionyl chloride which was cooled by a Dry Ice-acetone-bath and stirred with a magnetic stirring bar. A pressure of 80 mm. was maintained in the 50-ml. reaction flask but not in the adding funnel containing the alcohol. Two traps were situated between the reaction and vacuum pump systems. The first was immersed in a Dry Ice–acetone mixture, and the second was cooled by liquid nitrogen approximately −191–195°.

With the addition complete, the pressure was raised to 400 mm., and the Dry Ice–acetone-bath was removed from the reaction flask. Vigorous stirring was continued while the allyl chlorosulfinate–thionyl chloride mixture was allowed to reach room temperature (approximately 30 minutes), during which time the bulk of the hydrogen chloride was transferred to the liquid nitrogen trap. The pressure then was reduced gradually, over a period of 20 minutes, to 40 mm. in order to remove all but the last traces of the gas.

The reaction flask then was transferred quickly to a short distillation column fitted with a receiver system which included a fraction cutter. The two partially filled traps were replaced. It should be noted that subsequent to this point, in any of the procedures involving allyl chlorosulfinate, the system was never opened to the atmosphere.

With the reaction mixture maintained at 25° by an electrically heated oil-bath and the condenser system at approximately −10° by circulation of ice–salt water, the pressure was reduced gradually to 15 mm. over a period of two hours, and the bulk of the thionyl chloride was distilled into a receiver placed at the bottom of the fraction cutter. The temperature of the oil-bath was then increased slowly until it reached 50°. Shortly thereafter, a sharp rise from room temperature to 38° was observed by means of a thermometer placed in the head of the distillation apparatus. After this head temperature had become constant at the above reading, the stopcock at the bottom of the fraction cutter was closed, and the allyl chlorosulfinate-1-C^{14} was distilled into the fraction cutter (maintained at −10°). This procedure gave 10.0 ml. of crude product. Since the product was contained in an elaborate glass system and could not be weighed, calculation of the yield required the measurement of density described below. Using the value of $d^{-10}{}_4 = 1.28$, the yield was estimated at 53%.

Analysis of Allyl Chlorosulfinate-1-C^{14}.—The system was isolated by closing all stopcocks, and the two traps were replaced. The receiver flask containing thionyl chloride was removed, and the distillation system was fitted with a glass purification apparatus. This apparatus then was evacuated to a pressure of 0.8 mm. and heat was applied to the glass surfaces by means of a bunsen burner. A slow stream of pure nitrogen, which previously had been passed through a liquid nitrogen trap to remove all traces of moisture, was then swept through the system. The pressure was again

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(14) D. L. Cottle, This Journal, **68**, 1380 (1946).

(15) J. L. O'Brien, *Chem. Eng. News*, **33**, 2008 (1955).

(16) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 368.

(17) The barium carbonate-C^{14} used in this preparation was purchased under AEC Contract AT-(40-1)-282.

reduced to 0.8 mm. Heat now was applied to the entire system (exclusive of the isolated apparatus containing the chlorosulfinate), and dry nitrogen was allowed to flow into the apparatus until the pressure had reached 700 mm. After cooling of the glass surfaces, the stopcock at the bottom of the fraction cutter was opened, and the cold chlorosulfinate was allowed to drain into the super-dry purification apparatus. After the ester had reached room temperature, the pressure was reduced to 20 mm. and a slow stream of the super-dry nitrogen was bubbled through the liquid compound for 20 minutes in order to remove the last traces of hydrogen chloride gas and any allyl chloride which might have accumulated as a result of decomposition of the chlorosulfinate. The material remaining in the apparatus after this treatment was assumed to be pure allyl chlorosulfinate-1-C^{14}.

Small samples were removed from the purification apparatus under carefully controlled conditions for the various measurements; $n^{25}\text{D}$ 1.4761, d^{-10}_4 1.28, d^{28}_4 1.14.

Anal. Calcd. for $C_3H_5O_2SCl$: C, 25.62; H, 3.58; Cl, 25.22. Found: C, 25.76; H, 3.68; Cl, 25.20.

Preparation of Allyl *n*-Amyl Sulfite.—One and eight-tenths grams of the allyl chlorosulfinate collected in the manner described above was added dropwise to a magnetically stirred and Dry Ice–acetone cooled solution of 1 g. of *n*-amyl alcohol and 0.9 g. of pyridine in 30 ml. of dry pentane. After stirring for 45 minutes at room temperature, sufficient water was added to dissolve the precipitated pyridine hydrochloride. The layers were separated and washed successively with several portions of 0.5 *N* hydrochloric acid, dilute sodium carbonate and water; 20 ml. of pentane was added, and the mixture was dried with magnesium sulfate.

After removal of the drying agent, the solvent was removed by distillation through a one-foot Vigreux column, and the resulting residue was distilled through a simple micro distillation apparatus. The product had a boiling point of 86–88° (4 mm.) and $n^{25}\text{D}$ of 1.4110. Analysis by the technique described later indicated that the allyl portion of the mixed sulfite contained 99.4% 1-C^{14}.

Diallyl Sulfite.—The residue from the original distillation of allyl chlorosulfinate-1-C^{14} described earlier was dissolved in pentane and worked up in the same manner as allyl *n*-amyl sulfite. It boiled at 83° (16 mm.) and had $n^{25}\text{D}$ of 1.4528. Material isolated from two experiments contained 98.9 and 96.0% 1-C^{14}.

The Decomposition of Allyl Chlorosulfinate-1-C^{14}.—All pyrolytic decomposition reactions were carried out under completely anhydrous conditions. The technique described in the section on preparation of the chlorosulfinate ester was employed for removal of all traces of moisture from the decomposition system (attached to the fraction cutter in place of the purification apparatus). The chlorosulfinate then was introduced into the system, and the last traces of hydrogen chloride and allyl chloride were removed, as before, with the aid of super-dry nitrogen. The apparatus was protected by a series of traps identical with that outlined earlier. In most cases, the purified anhydrous solvent was distilled into the decomposition vessel through a pre-dried system. In the reaction performed in thionyl chloride, the solvent was subjected to the same final purification treatment normally executed upon the chlorosulfinate ester.

The decomposition was accomplished by heating the reaction mixture to the temperature at which products were delivered to the cold receiver system at a rate equivalent to a first-order half-life of approximately 18 minutes (the half-life of the reaction performed without added solvent was approximately 14 minutes). During this process, the pressure generally was maintained at such a value that the solvent refluxed gently from a vertical condenser kept at 50°. After decomposition was complete, the products, allyl chloride and sulfur dioxide, were fractionated (still within a closed system in order that traces of chlorosulfinate ester would not be decomposed by atmospheric moisture to contaminate the chloride product). The allyl chloride thus collected was subsequently ozonized and analyzed by the technique described later.

The reactions in liquid sulfur dioxide were performed in heavy-wall glass ampoules. After the chlorosulfinate ester had been purified by the above techniques and transferred to the super-dry ampoule, sulfur dioxide, passed successively through concentrated sulfuric acid and phosphorus pentoxide, was condensed in the ampoule at Dry Ice temperatures. A stopcock in the neck of the ampoule was turned, breaking the gas delivery tube, and the system was sealed with the use of a torch. In three experiments, the reaction systems were maintained at −15, 20 and 35° for 11, 11 and 13 hours, respectively.

After cooling to Dry Ice temperatures, the tip of the ampoule was sealed to the entrance of a fractionation system with DeKhotinsky cement. The entire apparatus, exclusive of the ampoule, then was subjected to the drying techniques described previously in order that traces of unreacted chlorosulfinate would not be decomposed under the influence of moisture and thus contaminate the product. The tip of the ampoule now was broken by the use of a glass striker arm incorporated within the closed system, and the contents of the ampoule were transferred to the fractionation apparatus. Sulfur dioxide was removed by slow fractional distillation. The allyl chloride product was removed similarly by distillation. The trace of allyl chlorosulfinate remaining as a final residue from the above procedure was isolated and converted to allyl *n*-amyl sulfite by techniques described earlier. The resulting quantity of the mixed sulfite was, however, insufficient for ozonization. Two hundred milliliters of solvent was employed in all experiments.

Test for Rearrangement of Allyl Chloride-1-C^{14} in Liquid Sulfur Dioxide.—Six and one-half grams of allyl chloride-1-C^{14} was subjected to the conditions of the decomposition reaction performed at 20°. The apparatus was the same as that described above. Analysis of the chloride isolated by the standard technique indicated that allylic structure had been preserved to the extent of 100%.

Ozonization Procedure.—A solution of 0.6 ml. of allyl chloride-C^{14} in 20 ml. of C.P. chloroform was placed in an ozonization tube and immersed in a mixture of Dry Ice and acetone. Oxygen, containing approximately 3% ozone, was passed through the cold solution for 30 minutes. The chloroform solution of ozonide was then poured into a 125-ml. flask containing 2.0 g. of powdered zinc; 20 ml. of water and 2.5 ml. of glacial acetic acid then were added, and the mixture was stirred by means of a glass-covered magnet for 0.5 hour. The mixture was subsequently filtered, and the filtrate was combined with 56 ml. of dimedone reagent containing 1.56 g. of dimedone per 20 ml. of 95% ethanol. The resulting solution was allowed to stand for 24 hours.

Approximately 100 ml. of water then was added to the slightly yellow solution. The chloroform appeared as a second phase and was boiled off on a steam-bath. The dimedone derivative which then precipitated was recrystallized three times from 95% ethanol. After drying, the white needles had a melting point of 192.6–193.0° (cor.). A mixed melting point with an authentic sample gave no depression whatever. Ozonization of other allylic compounds was executed in the same manner. Quantities equivalent in 0.008 mole of potential formaldehyde were employed.

Estimation of Relative Rates.—A first-order rate constant was calculated for each reaction from the estimated value of the half-life. All values thus obtained were extrapolated to a single temperature by assuming a twofold increase in rate per ten degree rise in temperature.

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