[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

1,3-Shifts. IV. The Kinetics of the Thermal Rearrangement of α-Phenethyl Chlorocarbonates[1]

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The rate of rearrangement of five α-phenethyl chlorocarbonates has been measured in both toluene and dioxane solution. The enthalpy and entropy of activation have been determined for each of the compounds. The stereochemistry of the rearrangement has been studied, and a much higher degree of retention of configuration was observed than had been reported for the rearrangement of the corresponding chlorosulfite esters. 1,3-Shifts are suggested to be of three types, and the special characteristics of each type are discussed.

Introduction

In 1937, Hughes, Ingold and co-workers[2] suggested a mechanism involving a four-membered cyclic transition state for certain replacement reactions which gave retention of configuration. There is comparatively little evidence for this type of reaction except for the stereochemical observation in the case of the rearrangement of chlorocarbonate esters,[3] chlorosulfite esters[4] and similar reactions. Recently Lewis and Boozer[5] have found evidence that chlorosulfites rearrange *via* initial dissociation to a carbonium ion followed by recombination to give the chloride and sulfur dioxide. However, their evidence was largely indirect, and was based on the effect of different solvents on the degree of retention of configuration and on the effect of deuterium substitution on a carbon adjacent to the reaction site. A similar suggestion was made by Cram[6] for the course of the reaction of 3-phenyl-2-butanol and similar compounds with thionyl chloride.

The rearrangement of alkyl chlorocarbonates has been studied by Choppin and co-workers.[7] The reactions were investigated in the gas phase, and they were found to be unimolecular and homogeneous. The activation energy was sufficiently low that a process involving initial dissociation into ions appeared unlikely. It is difficult to compare their results with other work since the reactions were carried out in the gas phase at a relatively high temperature.

In order to obtain evidence of a different type, we have chosen to investigate a rearrangement in which it would be possible to obtain a measure of the electrical effects which operate in these reactions. An attempt was made to study α-phenethylchlorosulfite. However it was not possible to obtain this compound in other than dilute solution, and it was found to rearrange at too low a temperature for a convenient kinetic study. Our attention was then directed toward the α-phenethyl chlorocarbonates. A satisfactory method for the preparation of these compounds was developed and the rates of rearrangement were determined in both toluene and dioxane solution. The stereochemistry of the reaction was investigated in both solvents.

Experimental

Preparation of α-Phenethyl Chlorocarbonates.—To a 120-ml. flask fitted with a nitrogen inlet tube and a drying tube was added 60 ml. of anhydrous ether and 1 g. (0.04 mole) of sodium hydride. After dry nitrogen had been passed through the solution for ten minutes to flush out any oxygen, 0.04 mole of the alcohol was added and the flow of nitrogen was continued for five minutes. The flask was allowed to stand for 10 to 24 hours, until all of the alcohol had reacted. The ether was then removed on a steam-bath leaving a dry residue to which was added 60 ml. of pentane giving a slurry.

To a 200-ml. three-necked flask equipped with a stirrer and an addition tube was added a solution of 15 g. (0.15 mole) of phosgene in 90 ml. of pentane. The flask was cooled to −60 to −78° and the slurry of the alkoxide in pentane was added with stirring over a one-half hour period. The mixture was stirred for an additional half-hour and then allowed to warm to 0°. After cooling to −60°, the solution was quickly filtered by gravity to remove the sodium chloride.

The solvent was removed under reduced pressure at 0°, and the residue (3-4 ml.) was placed in a freezer at −20° for storage. The product consisted of approximately equal amounts of the chlorocarbonate and the corresponding chloride. Several batches of material prepared in this way, and also by the use of pyridine as the base, were found to give identical rate constants for rearrangement.

The alcohols used were prepared by previously described procedures or by conventional methods, and were distilled through an 18-inch packed column. The properties of the materials are given in Table I.

TABLE I

PROPERTIES AND SYNTHESIS OF α-PHENETHYL ALCOHOLS

Substituent	B.p. °C.	B.p. Mm.	n^{25}_D	d^{25}	M.p., °C., der.	Ref.
H	91	15	1.5190	1.0123	91.4–92[b]	8
p-Cl[a]	125	15	1.5409	1.1707	93–93.6[b]	9
p-CH_3[a]	119	35	1.5192	0.9833	94.5–95[b]	10
p-F[a]	89	11	1.5032	1.1076	102.5–102.9[c]	11
m-Br	129	11	1.5668	1.4529	93–93.6[d]	12

[a] Prepared by the lithium aluminum hydride reduction of the corresponding acetophenone. [b] Phenylurethans. In all cases, the derivative was made by the treatment of the alcohol with the appropriate isocyanate, and also by the treatment of the chlorocarbonate with the appropriate amine. A mixed m.p. gave no depression in any case. [c] α-Naphthylurethan. *Anal.* Calcd. for $C_{19}H_{16}NO_2F$: C, 73.77; H, 5.21. Found: C, 73.88; H, 5.21. [d] α-Naphthylurethan. *Anal.* Calcd. for $C_{19}H_{16}NO_2Br$: C, 61.63; H, 4.36; N, 3.78. Found: C, 61.69; H, 4.14; N, 3.81.

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(1) This investigation was supported by a contract with the Office of Ordnance Research.

(2) W. A. Cowdrey, E. D. Hughes, E. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

(3) A. H. J. Houssa and H. Philips, *ibid.*, 1232 (1932).

(4) A. McKenzie and G. W. Clough, *ibid.*, **103**, 687 (1913).

(5) E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 308 (1952); C. E. Boozer and E. S. Lewis, *ibid.*, **75**, 3182 (1953); *ibid.*, **76**, 794 (1954).

(6) D. J. Cram, *ibid.*, **75**, 332 (1953).

(7) A. R. Choppin, H. A. Frediani and G. F. Kirby, Jr., *ibid.*, **61**, 3176 (1939); A. R. Choppin and G. F. Kirby, Jr., *ibid.*, **62**, 1592 (1940); A. R. Choppin and E. L. Compere, *ibid.*, **70**, 3797 (1948).

(8) F. Straus and H. Grindel, *Ann.*, **439**, 299 (1924).

(9) C. Gastaldi and F. Cherchi, *Gazz. chim. ital.*, **45II**, 272 (1915).

(10) A. Klages, *Ber.*, **35**, 2247 (1902).

(11) F. S. Florinski, *J. Gen. Chem.*, **21**, 1843 (1951).

(12) J. H. Brown and C. S. Marvel, THIS JOURNAL, **59**, 1176 (1937)

Kinetic Apparatus and the Method.—The apparatus was essentially that described by Schubert,[13] in which the volume of carbon dioxide liberated was determined volumetrically. The reaction vessel was a bulb with a volume of about 20 ml. During a run, it was shaken through an arc of about 5 inches at a rate of 200 swings a minute. To start a run, the solvent was introduced into the bulb which was then allowed to come into equilibrium with the bath. A sample of the chlorocarbonate (0.45 to 0.75 ml.) was then introduced through a serum bottle stopper on a side arm of the reaction vessel using a hypodermic syringe. Shaking was started and the volume was read at regular intervals. The thermostat would maintain a constant temperature ±0.03°.

The rate constants were determined by plotting ln (V_∞ − V) against time, and a straight line was obtained to 90% reaction in the case of reasonably fast runs. With some of the slower runs, it was difficult to obtain a value of V_∞ and thus the method of Guggenheim[14] was used. All of the rate constants given were calculated by this method, and a typical rate plot is shown in Fig. 1. In all runs, powdered glass was added to the reaction vessel in order to prevent supersaturation by carbon dioxide. The quantity of glass added had no effect on the rate constants, and thus the reaction is homogeneous.

Rearrangement of (−)α-Phenethyl Chlorocarbonate.—α-Phenethyl chlorocarbonate was prepared from (−)α-phenethyl alcohol and then rearranged under the standard kinetic conditions using both toluene and dioxane. Using toluene, alcohol having $[\alpha]^{25}\text{D}$ −8.14° (neat, l = 1) gave the chloride having $[\alpha]^{25}\text{D}$ −17.00° (neat, l = 0.5), b.p. 74° at 13 mm., $n^{25}\text{D}$ 1.5242, d^{25} 1.0652. Using dioxane, alcohol having $[\alpha]^{25}\text{D}$ −9.95° (neat, l = 1) gave the chloride having $[\alpha]^{25}\text{D}$ −23.70° (neat, l = 0.5), b.p. 74–75° at 14 mm., $n^{25}\text{D}$ 1.5241.

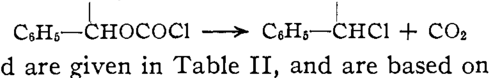
Reaction of α-Phenethyl Alcohol with Thionyl Chloride.—To a solution of 2.6 ml. of α-phenethyl alcohol ($[\alpha]^{25}\text{D}$ −10.62°, neat, l = 1) in 15 ml. of toluene was added 2.8 g. of thionyl chloride (about a 10% excess). Vigorous gas evolution occurred immediately and slight warming was noted. After warming on a steam-bath for 15 minutes, the solution was distilled giving 1.9 ml. of α-phenethyl chloride, b.p. 84° at 23 mm., $[\alpha]^{25}\text{D}$ −8.73°.

The above procedure was repeated using 15 ml. of purified dioxane instead of the toluene. No gas evolution was noted after the addition of the thionyl chloride although the solution became somewhat warm. The solution was heated on a steam-bath for one-half hour, and then was distilled giving 1.5 ml. of α-phenethyl chloride, b.p. 84° at 23 mm., $[\alpha]^{25}\text{D}$ −13.90°.

Neopentyl Chloroformate.—An excess of phosgene was passed into a solution of 4 g. of neopentyl alcohol in 85 ml. of pentane at −20 to −30°. Distillation of the solution gave 5.9 g. (86%) of neopentyl chloroformate, b.p. 54–56° at 36 mm., $n^{25}\text{D}$ 1.4073. The phenylurethan was prepared and had m.p. 111–112°, which was not depressed by admixture with authentic neopentyl phenylurethan, m.p. 111–112°,[15] prepared from neopentyl alcohol and phenyl isocyanate. Neopentyl chloroformate was found to decompose very slowly at its boiling point, and gave only a small amount of hydrogen chloride and olefin.

Results

The rates of rearrangement of a number of substituted α-phenethyl chlorocarbonates were determined in both toluene and dioxane solution by measuring the rate of carbon dioxide formation. In all cases, excellent first-order rate plots were obtained to over 90% reaction. The constants obtained are given in Table II, and are based on the natural logarithm. The rate of rearrangement of benzyl chlorocarbonate also was determined, the constant being 3.5 × 10^{-5} sec.$^{-1}$ at 90.0° in dioxane. The enthalpy and entropy of activation were calculated from these data using the method of least squares. The values obtained are given in Table III.



$$C_6H_5\text{—}\underset{}{\overset{\displaystyle CH_3}{\overset{|}{C}}}HOCOCl \longrightarrow C_6H_5\text{—}\overset{\displaystyle CH_3}{\overset{|}{C}}HCl + CO_2$$

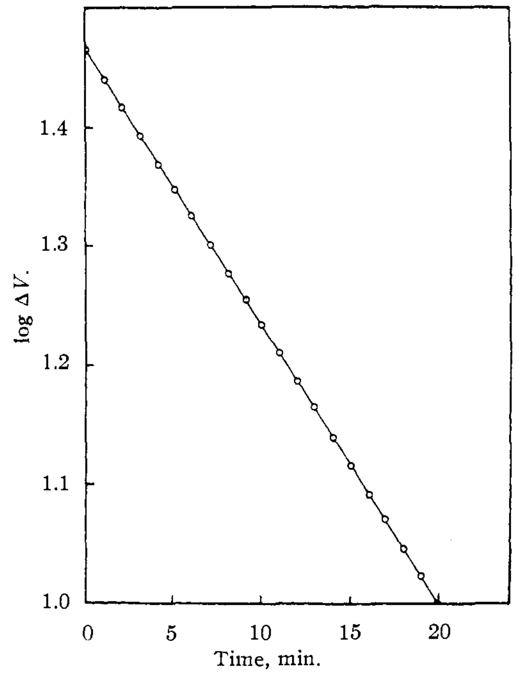


Fig. 1.—Rate plot for the rearrangement of α-phenethyl chlorocarbonate at 80° in toluene.

TABLE II

RATES OF REARRANGEMENT OF SUBSTITUTED β-PHENETHYL CHLOROCARBONATES

	Dioxane		Toluene	
Subst.	t(°C.)[a]	k(sec.$^{-1}$)[b] × 10^3	t(°C.)	k(sec.$^{-1}$) × 10^3
H	60	0.743	60	0.122
	70	2.03	70	0.348
	80	5.87	80	0.881
			90	2.11
p-Cl	60	0.380	70	0.177
	70	1.01	80	0.455
	80	2.53	90	1.15
p-F	60	1.29	70	0.783
	70	3.87	80	1.69
	80	9.72	90	3.48
m-Br	70	0.154	80	0.110
	80	.390	90	.211
	90	.858	100	.410
p-CH$_3$	30	.550	40	.434
	40	1.58	50	.933
	50	4.08	60	2.36

[a] The corrected temperatures are as follows: 30° = 29.89°; 40° = 39.92°; 50° = 49.95°; 60° = 59.89°; 70° = 69.98°; 80° = 80.25°; 90° = 90.43°; 100° = 100.61°. [b] The average error is ±3%.

A Hammett[16] plot of log k against σ is shown in Fig. 2. It is interesting to note that all of the points fall on a straight line with the exception of that for hydrogen. It would have been of value to

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(13) W. M. Schubert, THIS JOURNAL, **71**, 2639 (1949).

(14) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(15) A. Richard, *Ann. chim. phys.*, [8] **21**, 339 (1910), reported m.p. 114°.

(16) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, Book Co., New York, N. Y., 1940, pp. 184–193.

TABLE III

ENTHALPY AND ENTROPY OF ACTIVATION

Subst.	Dioxane $\Delta H^{\ddagger}$	Dioxane $\Delta S^{\ddagger}$	Toluene $\Delta H^{\ddagger}$	Toluene $\Delta S^{\ddagger}$
H	23.1	− 3.9	21.7	−11.6
p-Cl	21.1	−11.2	22.2	−11.9
p-CH_3	18.8	−11.4	17.3	−19.1
m-Br	20.1	−17.6	16.3	−31.0
p-F	22.5	− 4.3	17.4	−22.4

have data for substituents with smaller and larger values of σ than those which were used. However, the *m*-bromo compound reacted at about as slow a rate as could be accurately measured, and the *p*-methyl compound was so reactive that it was difficult to prepare and handle.

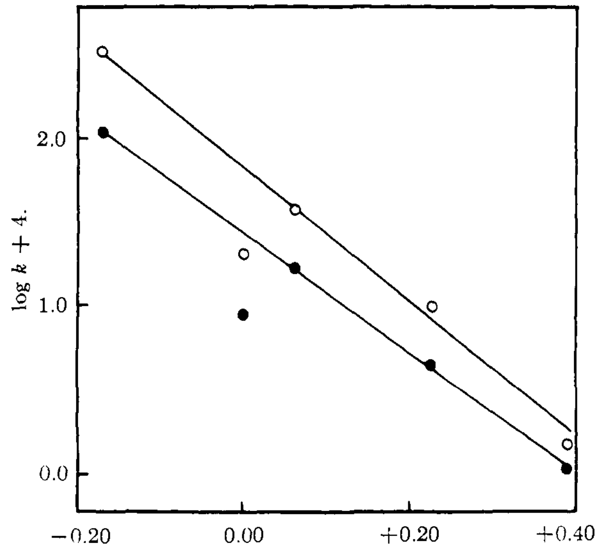


Fig. 2.—Hammett plot for the rearrangement of α-phenethyl chlorocarbonates in dioxane (upper line, open circles) and in toluene (lower line, closed circles).

The slope of the line (ρ) for dioxane solution was −3.86, and that for toluene solution was −3.56, neglecting the point for the unsubstituted compound. The similarity of these values indicates that the solvent does not greatly alter the effect of substituents, although the reactions in dioxane solution were considerably faster than those in toluene solution. A plot of $\Delta H^{\ddagger}$ against σ (Fig. 3) illustrates the importance of the entropy effect in this reaction.

In order to demonstrate that the reaction studied actually involved a frontside displacement, optically α-phenethyl alcohol was converted to the chlorocarbonate and then to the chloride using both toluene and dioxane as the solvent. In each case, the rotation of the chloride formed was about twice as high as that reported for the reaction of α-phenethyl alcohol with thionyl chloride,[17] and corresponded to retention of configuration.

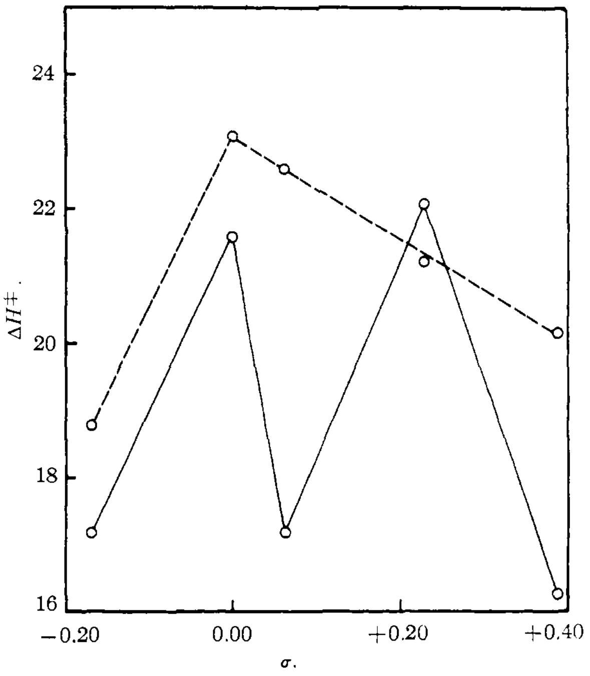
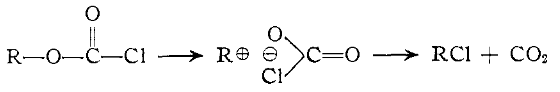


Fig. 3.—Effect of substituents on the enthalpy of activation. The upper (dashed) curve is for dioxane solution, and the lower curve is for toluene solution.

Discussion

The large positive value of ρ indicates that the migrating group is electron deficient in the transition state, and further suggests a carbonium ion intermediate. The fact that benzyl chlorocarbonate rearranged at a very much slower rate than α-phenethyl chlorocarbonate is in agreement with this view. The mechanism of this reaction is then similar to that suggested by Lewis and Boozer[5] for the rearrangement of chlorosulfites, involving initial dissociation into a carbonium ion solvated by the leaving group, followed by "rearrangement" and recombination with the loss of carbon dioxide.



$$\mathrm{R{-}O{-}\overset{\overset{O}{\|}}{C}{-}Cl \longrightarrow R^{\oplus}\ \ {}^{\ominus}\!\!\begin{smallmatrix}O\\ Cl\end{smallmatrix}\!\!>\!C{=}O \longrightarrow RCl + CO_2}$$

An attempt was made to effect the rearrangement of neopentyl chlorocarbonate in order to see if skeletal rearrangement of the neopentyl group would occur. The chlorocarbonate was found to be very unreactive, and the only products were a small amount of olefin and hydrogen chloride.

Lewis and Boozer[5] in their study of the stereochemistry of the rearrangement of *sec*-alkyl chlorosulfites found that complete retention of configuration was obtained in dioxane solution, whereas complete inversion was found using toluene as the solvent. In dioxane, it was suggested that the carbonium ion is solvated as it is formed, thus facili-

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(17) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **103**, 687 (1913) reported that the alcohol gave the chloride having 1.17 times the rotation of the starting alcohol in each of two experiments. Later, E. Ott, *Ber.*, **61**, 2124 (1928), reported values of 1.23, 1.14, 1.30 and 1.14 for this ratio in four experiments. In the present work, the observed ratios were 2.38 in dioxane and 2.08 in toluene. It is interesting to note that R. L. Burwell, Jr., A. D. Shields and H. Hart, THIS JOURNAL, **76**, 908 (1954), found that the reaction of α-phenethyl alcohol with phosphorus oxychloride and pyridine gave the chloride having a rotation 2.39 times as great as the starting alcohol, but of opposite sign (using specific rotations). This rotation, which is in good agreement with that obtained in this work, represents the highest rotation thus far obtained for α-phenethyl chloride.

tating the dissociation. The chloride ion then combined with the carbonium ion on the front side giving the chloride with the same configuration as the starting alcohol. It was also suggested that toluene would not solvate the carbonium ion, and that the sulfur–chlorine bond would ionize without the formation of the carbonium ion. This chloride ion then migrated to the rear of the molecule and effected a displacement of sulfur dioxide.

In the present work, it was found that retention of configuration was obtained in both toluene and in dioxane. Furthermore, the reaction of α-phenethyl alcohol with thionyl chloride, which presumably proceeds *via* the chlorosulfite ester, gave retention of configuration in either solvent. If the difficulty in forming a carbonium ion is the cause for inversion in toluene solution with the *sec*-alkyl chlorosulfites, then the difference between that case and the present one becomes clear. A carbonium ion derived from α-phenethyl alcohol has the possibility for resonance stabilization which is denied to the secondary alkyl groups. Thus, it should be possible to obtain the carbonium ion in either solvent in the α-phenethyl series since it would have a smaller requirement for specific external solvation, and this would then lead to the reaction giving retention of configuration.

The effect of substituents on the enthalpy of activation is somewhat unusual as is shown by Fig. 3. Unfortunately, there are few data with which this may be compared since there does not appear to be a previous investigation of the temperature dependence of the rate of reaction for several substituted benzene derivatives giving an ionic transition state using a solvent of low dielectric constant.[18]

In dioxane, the enthalpy of activation was proportional to the sigma value in all cases except *p*-methyl. It is commonly assumed that the sigma value represents the electrical effects operating in the system, and that it would parallel the change in enthalpy of activation.[19] If the entropy were constant, then log k would be proportional to $-\Delta H^{\ddagger}/2.3RT$, and the slope of a plot of $-\Delta H^{\ddagger}/2.3RT$ against σ would also give the value of ρ. If the value of the enthalpy of activation did indeed reflect the electrical effects operating in the system, then the rho value obtained from a plot of $-\Delta H^{\ddagger}/2.3RT$ against σ would in all cases indicate the nature and magnitude of the electrical effects. In the present case, a plot of this type gives a slope of $+1.9$! This value is both large, and of the opposite sign to that obtained in a plot of log k against σ.

The reaction certainly involves a carbonium ion intermediate as indicated by the effect of substituents, and by the observation that benzyl chlorocarbonate rearranges at a very much smaller rate than does α-phenethyl chlorocarbonate. Thus, it is apparent that the electrical effects enter into the entropy of activation, and in the present case the effect on the entropy is greater than that on the enthalpy of activation.

The much lower enthalpy of activation for the *p*-methyl substituted compound is perhaps not surprising since Kochi and Hammond[20] found that in the solvolysis of benzyl tosylates, the *p*-methyl substituted compound had a higher rate of reaction than expected on the basis of its sigma value. This was attributed to the additional resonance contribution of the methyl group in a reaction which had a large electron demand. In the present case, the rho value is over one unit more negative than observed in the solvolysis of benzyl tosylates, and thus one would expect an even greater effect. It was not expected, however, that this effect should show up only in the enthalpy of activation, and not in the rate reaction.

In toluene, no consistent pattern was found for the variation of enthalpy or entropy of activation with sigma values, although the net effect on the rate of reaction was essentially the same as in dioxane solution (*cf.* Fig. 2). The entropy and enthalpy of activation are certainly not independent of each other for an increase in solvation will lower the enthalpy of activation but will at the same time lower the entropy of activation since more solvent molecules will be frozen out. This will be particularly noticeable in solvents which are not associated, since they have more entropy to lose in solvation than do associated solvents like water. Thus, if a reaction shows a considerable change in degree of solvation with a change in substituent, one might well find a large change in both enthalpy and entropy. Furthermore, if one is using a solvent which will solvate poorly, but which is very disordered (*i.e.*, not associated), these two effects might well cancel each other and lead to a comparatively small effect on the rate of reaction. Toluene is a poor solvating solvent and solvation by this compound might then be strongly affected by the electron density distribution in the molecule, such as would be produced by different substituents.

It may also be noted that the enthalpy and entropy of activation are in general lower in toluene than in dioxane. This effect is commonly observed in reactions which have relatively ionic transition states, such as the reaction of alkyl halides with amines.[21] In summary, evidence has been found for a carbonium ion intermediate, and the results indicate that our knowledge of the effects of solvation in solvents of low dielectric constants leaves much to be desired.

It is now possible to consider the relationship between this rearrangement and other 1,3-shifts. There appear to be three types of intramolecular 1,3-shifts. The first is characterized by initial carbonium ion formation, followed by recombination. The second has an electron rich migrating group in the transition state, and the third has an electron deficient migrating group in the transition state, although initial dissociation is not involved.

The rearrangement of the chlorosulfites and the chlorocarbonates is of the first type. In this reaction, the order of reactivity is proportional to the stability of the carbonium ion derived from the migrating group. Thus, for example, *n*-alkyl chlorocarbonates are very stable compounds, whereas the

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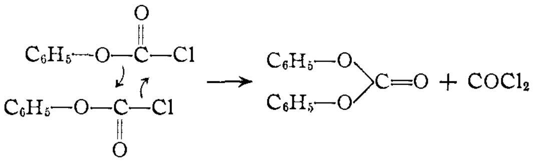
[18] H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

[19] Ref. 16, p. 227.

[20] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

[21] *Cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 128.

α-phenethyl chlorocarbonates rearrange readily. Groups such as phenyl would be expected not to rearrange, and this is borne out by the observation that phenyl chlorocarbonate will not rearrange, but rather gives diphenyl carbonate and phosgene on heating.[22]



$$2\,C_6H_5{-}O{-}C(=O){-}Cl \longrightarrow (C_6H_5{-}O)_2C{=}O + COCl_2$$

Similarly, although rearrangements with electron deficient transition states will proceed at the bridgehead of apocamphane, the reaction of apocamphanol with thionyl chloride did not lead to the chloride.[23] This is expected since this system does not appear to be capable of supporting a carbonium ion at the bridgehead.

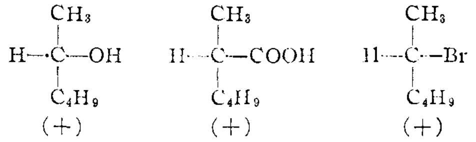
An example of the second type of 1,3-shift may be found in the rearrangement of aryl benzanilimino ethers to the corresponding diarylbenzamides.[24] In this reaction, only aryl groups appear to be capable of migrating in an intramolecular reaction, and the effect of substituents clearly indicates that the migrating group is electron rich in the transition state.

The third type is not as well established as the other two, but the silver salt–halogen reaction appears to be an example. This mechanism was first suggested by Rottenberg[25] on the basis of the observations that *t*-butylacetic acid gave neopentyl bromide without rearrangement in the migrating group,[26] and that the reaction could be effected at the bridgehead of a bicyclic system.[27] These data may be accommodated by either a 1,3-shift, or by a free radical process.

At that time, the only stereochemical evidence concerning this reaction was that of Arcus, Campbell and Kenyon,[28] who converted silver (+)α-phenylpropionate to (+)α-phenethyl bromide, presumably with inversion of configuration. Later, Abbott and Arcus[29] reported that they were unable to repeat this former work, only racemic material being obtained. However, they did find that silver (+)-2-ethylhexanoate on treatment with bromine gave (+)3-bromoheptane if the silver halide were removed before the rearrangement was allowed to occur. They were unable to determine whether inversion or retention of configuration had occurred, since the relative configurations of the acid and the bromide were not known.

Sufficient data are available for one to make a tentative assignment of configuration. It is reasonable to assume that the relationship between (+)2-methylhexanoic acid and (+)2-bromohexane will be the same as that between (+)2-ethylhexanoic acid and (+)3-bromoheptane.[30] The relationship between the former two may be adduced from the data available in the literature.

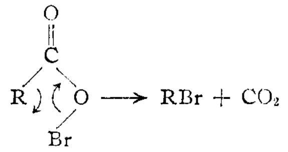
The relative configurations of (+)2-hexanol and (+)2-methylhexanoic acid are as shown below.[30,31]



$$\begin{array}{ccc} CH_3 & CH_3 & CH_3 \\ | & | & | \\ H{-}C{-}OH & H{-}C{-}COOH & H{-}C{-}Br \\ | & | & | \\ C_4H_9 & C_4H_9 & C_4H_9 \\ (+) & (+) & (+) \end{array}$$

It has been found that (+)2-butanol gives (−)2-bromobutane[32] and (+)2-pentanol gives (−)2-bromopentane[33] on treatment with hydrogen bromide. Since this reaction undoubtedly gives inversion of configuration, the (+) alcohols are related to the (+) bromides. Thus it would appear that the silver salt reaction gave retention of configurations.

Since free radical reactions have been shown usually to give racemic products when the asymmetric center is involved,[34] it is then unlikely that the silver salt–halogen reaction involved a free radical mechanism, at least in the aliphatic cases. The only type of mechanism which would be expected to give retention of configuration in this system is an intramolecular 1,3-shift.



$$R{-}C(=O){-}O{-}Br \longrightarrow RBr + CO_2$$

The characteristics of this reaction should then be similar to those of the majority of the 1,2-shifts, which have electron deficient transition states. Thus, both alkyl and aryl groups should migrate with reasonable facility, and one would not expect skeletal rearrangement in the reaction of neopentyl compounds. This is in good accord with the observed characteristics of this reaction.

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(22) S. T. Bowden, *J. Chem. Soc.*, 310 (1939).

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