Acid Catalysed *ortho*-Claisen Rearrangement of Allyl Aryl Ethers in Trifluoroacetic Acid

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The rearrangement of allyl aryl ethers in trifluoroacetic acid (TFA) has been examined by kinetic and product studies. The addition of a co-solvent dramatically decreases the rate of rearrangement at 60°. In $CDCl_3$–TFA mixtures, the first-order rate constant was found to increase exponentially with the fraction of TFA present. The presence of a small amount of water (optimum 5%) accelerates while greater concentrations decrease the rate. Electron-donating substituents *para* to the ether group, and to the *ortho*-position at which new bond formation takes place affect the rate to nearly equal extents and a linear Hammett plot was obtained by plotting $(\sigma_p + \sigma_m)/2$ *versus* log *k*. A large salt effect with an order of magnitude increase in *k* in the presence of $LiClO_4$ (0·05M) and a deuterium solvent kinetic isotope effect of 1·4 were observed. It was concluded that the mechanism of the rearrangement involves a highly polar transition state with the degree of proton transfer depending upon the conditions, presence of salt, H_2O concentration, *etc.* A complication which can lower yields if care is not exercised, is the addition of TFA to the side chain double bond of the rearrangement product.

THE *ortho*-Claisen rearrangement of allyl aryl ethers has played an important role in the development of classical organic chemistry [1-4] and has recently been of renewed interest in connection with the application of the Woodward–Hoffmann rules.[5,6] Owing to difficulties in classifying the reaction as homolytic or heterolytic, the *ortho*-Claisen rearrangement has been described as a ' no mechanism ' reaction.[2]

In our preliminary communication [7] we presented rate data for the rearrangement of a number of *para*- and *meta*-substituted allyl aryl ethers in trifluoroacetic acid (TFA) and indicated the utility of the medium for synthetic applications of the *ortho*-Claisen rearrangement.

An early indication that the *ortho*-Claisen rearrangement might be subject to acid catalysis was the observation that extent of rearrangement of allyl *p*-tolyl ether increased with time, presumably due to catalysis by the phenolic reaction product.[8] The effect of solvent on the rate of rearrangement has been found not to be very great [3,9] but is most noticeable in going to hydroxylic or phenolic solvents. The latter has been attributed to partial protonation of the ethereal oxygen by hydrogen bonding to the solvent.[9,10] More recent studies on the effect of solvent,[11] led to the conclusion that the sensitivity of the rearrangement to the solvent can be attributed either to the hydrogen bonding ability or the polar character of the solvent with the latter probably fitting the data best.

It has been pointed out that at low temperatures rearrangement in the presence of strong acids more closely resembles an acid catalysed rearrangement than an *ortho*-Claisen rearrangement.[3] For example, the boron trichloride catalysed rearrangement of allyl *p*-tolyl ether at 7° was accompanied by allyl transfer as well as rearrangement.[12] However, only the normal Claisen product was obtained from the reaction of boron trichloride with allyl phenyl ether at −80°.[13]

In this paper we show the effect of substituents, solvent composition, the presence of salts, deuteriated solvent, and the temperature on the *ortho*-Claisen rearrangement in TFA which provide strong evidence for general acid catalysis and the heterolytic nature of the reaction.

RESULTS

Substituent Effects.—The effect of *para*- and *meta*-substituents on the rate of rearrangement of allyl aryl ethers in TFA at 60° is summarized in Table 1. A plot of log *k versus* $(\sigma_m + \sigma_p)/2$ gave a linear plot with slope of −4·0 with only the compounds containing electron-withdrawing Cl deviating significantly from the line.

TABLE 1

First-order rate constants for the rearrangement of allyl aryl ethers in TFA at 60°

Aryl substituent	$10^4k/s^{-1}$	$(\sigma_m + \sigma_p)/2$ [a]
p-Cl	0·22	+0·30
m-Cl	0·32	+0·30
H	1·1	0·0
p-OMe	2·0	−0·077
m-OMe	2·0	−0·077
p-Me	3·4	−0·12
m-Me	3·3	−0·12
m,p-Me_2	11·0	−0·24

[a] Hammett σ constants taken from K. B. Wiberg, ' Physical Organic Chemistry,' Wiley, New York, 1964.

Effect of a Co-solvent.—For practical purposes, it was desirable to determine whether or not the large rate enhancement of the *ortho*-Claisen rearrangement when conducted in TFA would be retained upon dilution with more common solvents. Rate constants obtained in TFA–$CDCl_3$ as well as acetonitrile are given in Table 2. The dramatic effect of the presence of a co-solvent is further illustrated by the plots of *k* and log *k versus* % TFA

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[1] D. S. Tarbell, ' Organic Reactions,' ed. R. Adams, Wiley, New York, 1944, vol. II, p. 1.

[2] S. J. Rhoads, ' Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, 1963, vol. I, p. 655.

[3] H. J. Shine, ' Aromatic Rearrangements,' Elsevier, Amsterdam, 1967.

[4] A. Jefferson and F. Scheinmann, *Quart. Rev.*, 1968, **22**, 391.

[5] H. J. Hansen and H. Schmid, *Chem. in Britain*, 1968, **5**, 111.

[6] H. J. Hansen and H. Schmid, *Chemica*, 1970, **24**, 89.

[7] U. Svanholm and V. D. Parker, *J.C.S. Chem. Comm.*, 1972, 645.

[8] J. F. Kincaid and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1939, **61**, 3085.

[9] H. L. Goering and R. R. Jacobsen, *J. Amer. Chem. Soc.*, 1958, **80**, 3277.

[10] W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Amer. Chem. Soc.*, 1958, **80**, 3271.

[11] W. N. White and E. F. Wolfarth, *J. Org. Chem.*, 1970, **35**, 2196, 3585.

[12] P. Farhni, A. Habich, and H. Schmid, *Helv. Chim. Acta*, 1960, **43**, 448.

[13] W. Gerrard, M. F. Lappert, and H. B. Silver, *Proc. Chem. Soc.*, 1957, 19.

in $CDCl_3$ (Figure 1). It is seen that the rate constant increases in exponential fashion with the fraction of TFA present.

TABLE 2

Rate constants for the rearrangement of allyl *p*-tolyl ethers in solvent mixtures at 60°

Co-solvent	TFA : co-solvent (v/v)	$10^4k/s^{-1}$
None	100 : 0	3·4
$CDCl_3$	90 : 10	2·2
$CDCl_3$	83 : 17	1·5
$CDCl_3$	67 : 33	0·68
$CDCl_3$	50 : 50	0·35
$CDCl_3$	33 : 67	0·19
CD_3CN	67 : 33	0·44

TABLE 3

Rate constanst for the rearrangement of allyl *p*-tolyl ether in TFA containing water at 60°

H_2O (%)	0 ^{a}	0·5 ^{b}	3·0 ^{c}	5·0 ^{c}	7·5 ^{c}	10 ^{c}	17 ^{c}
$10^4k/s^{-1}$	1·7	3·4	6·2	7·0	5·8	3·3	0·94

^{a} Calculated amount of trifluoroacetic anhydride necessary to react with 0·5% water added. ^{b} Estimated nominal water content. ^{c} Water added to solvent containing 0·5% water.

Effect of the Presence of Water.—The presence of water in TFA allows a definite possibility of catalysis by H_3O^+ of the rearrangement of allyl aryl ethers. Reagent grade TFA contains as much as 0·5% water. TFA essentially free of water can be obtained by the addition of trifluoroacetic anhydride.[14] Rate constants as a function of the water content of TFA are tabulated for the rearrangement of allyl *p*-tolyl ether at 60° in Table 3. The variation of the first-order rate constant with the water content is illustrated by Figure 2.

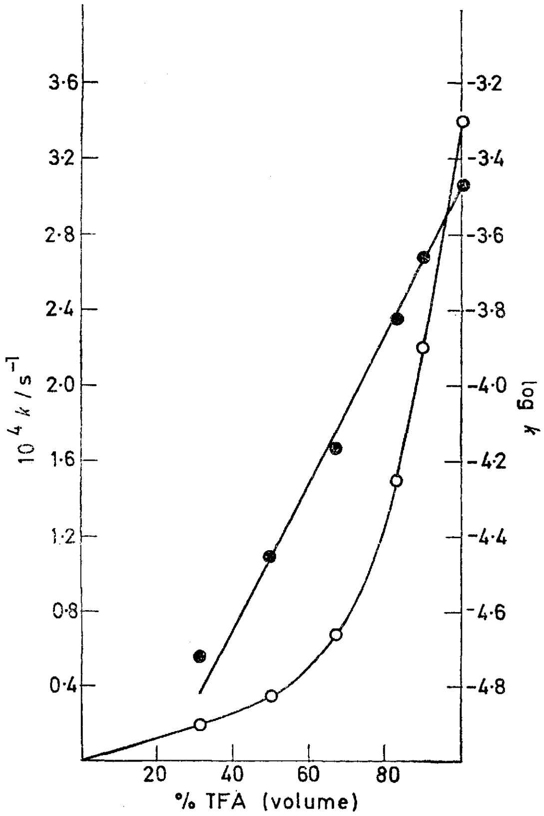

FIGURE 1 First-order rate constants for the *ortho*-Claisen rearrangement of allyl *p*-tolyl ether in TFA–$CDCl_3$ mixtures at 60°. Open circles refer to *k* (left scale) and filled circles to log *k* (right scale)

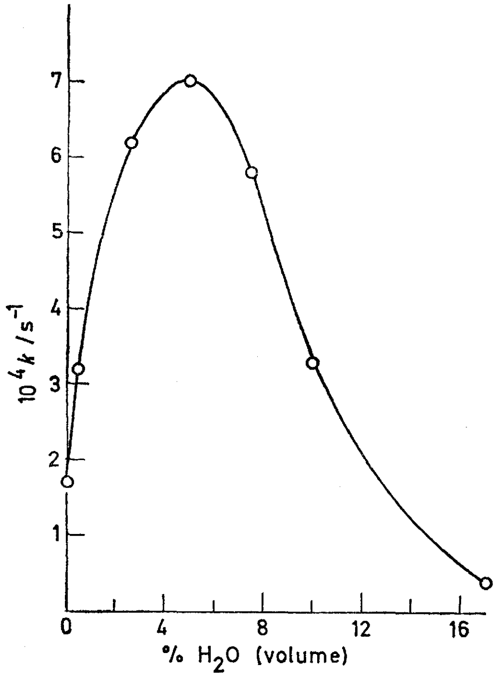

FIGURE 2 First-order rate constants for the *ortho*-Claisen rearangement of allyl *p*-tolyl ether in TFA–H_2O mixtures at 60°

Temperature Effects.—First-order rate constants for the rearrangement of allyl *p*-tolyl ether in TFA and in TFA containing $LiClO_4$ (0·01M) are given as a function of temperature in Table 4. A plot of log *k versus* $1/T$ for the rearrangement of allyl *p*-tolyl ether was linear throughout the temperature range investigated. The activation energy for the rearrangement was determined to be 17·8 kcal mol^{-1} and the entropy of activation was calculated[15] as −23 cal mol^{-1} K^{-1}.

TABLE 4

Rate constants for the rearrangement of allyl *p*-tolyl ether in TFA at various temperatures

$[LiClO_4]$/M	T/°C	$10^4k/s^{-1}$
0	20	0·12
0	31	0·29
0	42	0·59
0	50	1·3
0	60	3·4
0·01	36	4·2
0·01	50	8·0
0·01	60	19

Salt Effects.—The rate of the rearrangement of allyl *p*-tolyl ether in TFA was found to be greatly accelerated by the presence of salts which do not otherwise interfere with the reaction. First-order rate constants are tabulated for the reaction in the presence of several different salts at different temperatures in Table 5.

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[14] M. G. Harriss and J. B. Milne, *Canad. J. Chem.*, 1971, **49**, 2937, 3612.

[15] J. F. Bunnett, in 'Technique in Organic Chemistry,' eds. S. L. Friess, E. S. Lewis, and A. Weissberger, Interscience, New York, 1961, vol. VIII, part 1, p. 201.

Deuterium Kinetic Isotope Effect.—The kinetic solvent isotope effect for the rearrangement of allyl *p*-tolyl ether in TFA was determined under differing conditions of water content, temperature, and in the presence of salts. Rate data are summarized in Table 6.

TABLE 5

Rate constants for the rearrangement of allyl *p*-tolyl ether in TFA containing salts

Salt	T/°C	10^4k/s^{-1}
None	36	0·31 [a]
0·01M-$LiClO_4$	36	4·2
0·025M-$LiClO_4$	36	8·9
0·05M-$LiClO_4$	36	15
0·01M-$LiClO_4$	50	8·0
0·01M-$LiClO_4$	60	19
0·025M-Me_4NBF_4	36	2·5
0·1M-Me_4NBF_4	36	8·3
0·05M-CF_3CO_2K	60	2·6
0·05M-CF_3CO_2Na	60	2·6
0·05M-CF_3CO_2Li	60	3·6
None	60	3·4

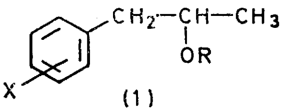
[a] Extrapolated value from Table 4.

TABLE 6

Rate constants for the rearrangement of allyl *p*-tolyl ether in TFA and [^{2}H]TFA

Solvent	Salt	T/°C	10^4k/s^{-1}	k_-/k_D
TFA	None	60	3·4	1·4
[^{2}H]TFA	None	60	2·5	
TFA (dry)	None	60	1·7	1·4
[^{2}H]TFA (dry)	None	60	1·2	
TFA	0·01M-$LiClO_4$	60	19	1·1
[^{2}H]TFA	0·01M-$LiClO_4$	60	17	
TFA	0·1M-Me_4NBF_4	36	8·3	1·2
[^{2}H]TFA	0·1M-Me_4NBF_4	36	6·8	

Products of the Rearrangement.—Since the main objective of this study was not the optimization of conditions for high yield isolation of rearrangement products, only a limited number of product isolations were carried out. The best procedure for achieving high yields of the initial rearranged product appears to be interrupting the reaction after *ca.* 50% conversion and then separating the phenolic product from the starting ether. For example, a 90% yield of rearrangement product from allyl *p*-tolyl ether was obtained after 30% conversion. A complication which accompanies higher conversions is the addition of TFA to the double bond of the product to give compounds (1a). The latter are readily detected from the ^{1}H n.m.r. spectra of



(1)

a; R = CF_3CO
b; R = H

the reaction mixtures by the appearance of a doublet due to the methyl group of (1a). Addition to the double bond is slow compared to the rate of rearrangement and this is not a serious complication if the reaction is interrupted before complete conversion. The alcohol (1b; X = *p*-Me) * was isolated in 65% yield after leaving allyl *p*-tolyl ether at room temperature in TFA for about two weeks.

DISCUSSION

The low sensitivity of the *ortho*-Claisen rearrangement to substituent effects has previously been pointed out [2] and was used as a basis for the classification of the reaction as one going by way of a 'no mechanism' pathway. Kinetic investigations in two different solvents, diphenyl ether [9] and carbitol,[10] revealed that satisfactory correlations could not be obtained using either σ_p or σ_m in the Hammett equation. However, good correlations were obtained using σ_p^+ constants and in both cases small negative values of ρ were found, $-0{\cdot}510$ and $-0{\cdot}609$ for diphenyl ether and carbitol, respectively. That the rearrangement in TFA is much more sensitive to substituent effects is brought out by the data in Table 1 and the Hammett plot where a reasonable large value of $-4{\cdot}0$ was found for ρ. It is of interest to note that satisfactory correlations were not obtained using σ_p, σ_m, or σ_p^+ but a reasonably good correlation was obtained by averaging σ_p and σ_m and the value thus obtained was equally valid when the substituent was either *para* or *meta* to the ether group. In contrast to the previous kinetic studies,[9,10] we found that electron-withdrawing groups greatly retard the rate of rearrangement in TFA. In fact, the rearrangement of allyl *p*-nitrophenyl ether was immeasurably slow in TFA at 60° while in diphenyl ether [9] it rearranged *ca.* 60% as fast as the unsubstituted compound. Another significant difference in substituent effects in TFA and the other solvents is that allyl *p*-cresyl ether rearranged nearly two times as fast as allyl *p*-methoxyphenyl ether in TFA while the opposite result was obtained in the other solvents.[9,10] The latter result is completely consistent with the $(\sigma_p + \sigma_m)/2$ correlation since methoxy activates the *para*-position and simultaneously deactivates the *meta*-position while methyl has an activating influence at both positions. Thus, the substituent effect observed for the rearrangement in TFA strongly indicates that positive charge is developing at the position of the ether group and at the position where new bond formation is occurring to nearly equal extents in the transition state.

Perhaps the most pertinent mechanistic question is, 'What is the role of TFA that provides for such a large rate enhancement of the rearrangement?' † An obvious and probable possibility is that TFA serves as a proton donor or acidic catalyst. Two alternative possibilities of acid catalysis exist, (a) a pre-equilibrium involving protonation of the substrate followed by rate-determining rearrangement [equations (1) and (2)] or (b) a proton transfer from TFA concerted with rearrangement [equation (3)]. The solvent kinetic isotope effect serves as an illuminating probe in distinguishing between mechanisms of type (a) and (b). In general, when a pre-equilibrium protonation such as equation (1) is involved in a reaction, the value of the solvent kinetic isotope effect is governed by the ratio, K_{SD^+}/K_{SH^+},‡ and the normal value of the deuterium kinetic isotope effect

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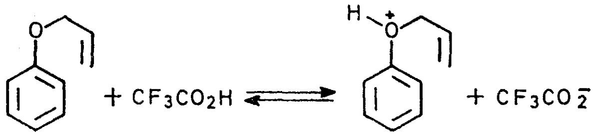
* Hydrolysis of the trifluoroacetate occurred during work-up.

† Extrapolation of a log k *vs.* $1/T$ plot to 185° gave a rate constant of 0·52 which is 10^5 greater than the gas-phase rate constant.[11]

‡ K_{SH^+} Is the dissociation constant of the conjugate acid of the substrate.

is expected to be of the order 0·3—0·5.[16] On the other hand, in a reaction such as equation (3), where the transfer of the proton from donor to acceptor is incomplete in the transition state, a solvent kinetic isotope effect, k_H/k_D, of $>1{\cdot}0$ is to be expected.[17] The data for the rearrangement of allyl *p*-tolyl ether in TFA reveal that under all conditions examined, a deuterium kinetic isotope effect of $>1{\cdot}0$ was observed (Table 6). These data can be taken as strong evidence that mechanism (a), if it occurs at all, is not the sole reaction pathway for the rearrangement.



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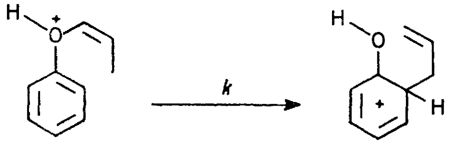

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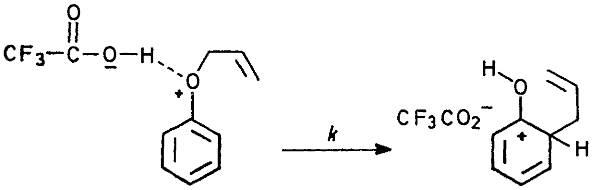

(3)

However, here we must exercise some caution since the presence of the non-interfering salts, $LiClO_4$ and Me_4NBF_4, while greatly enhancing the rate of the reaction brought about a lowering of k_H/k_D from 1·4 to *ca.* 1·1 (Table 6). The salt effect could be due to an alteration of the polar character of the medium or due to the specific enhancement of some ionic equilibrium.* The fact that in the presence of these salts the value of k_H/k_D decreased suggested that perhaps equilibrium (1) was being affected. The data (Table 5) show that the presence of potassium and sodium trifluoroacetate brought about a decrease in the rate as compared to the absence of salt while in the presence of lithium trifluoroacetate, an increase in the value of the first-order rate constant was observed. The difference in behaviour between the lithium and the other two trifluoroacetates is readily explained from conductivity data of the salts in TFA.[19] Lithium trifluoroacetate is an electrolyte in TFA; however, it is highly associated and the conductivity appears to be due to triple ions and the increase in trifluoroacetate ion concentration is small.[19] On the other hand, both the sodium and potassium salts produce significant concentrations of trifluoroacetate ion upon dissolving in TFA.[19] Thus, the origin of the large salt effect in the presence of the indifferent salts and its absence in the presence of trifluoroacetate salts must be due to the enhancement of equilibria involving trifluoroacetate ion. Then it follows that the lowering of the kinetic solvent isotope effect in the presence of lithium perchlorate and tetramethylammonium fluoroborate is most likely due to the enhancement of a pre-equilibrium such as equation (1). The fact that in the absence of salt, the isotope effect is closer to that expected for a concerted proton transfer [equation (3)] is indicative that both mechanisms (a) and (b) are operative, *i.e.*, the rearrangement is subject to general acid catalysis. Thus, the importance of mechanism (a) is not very great in the absence of the non-interfering salts but becomes important in their presence.

Turning now to the effect of the addition of either $CDCl_3$ or MeCN as a co-solvent, it is apparent that the decrease in the rate of rearrangement cannot be due to a change in the polarity of the medium. The dielectric constant of TFA is *ca.* 8,[20] while that for chloroform [21] and acetonitrile [22] are 5 and 37, respectively. In TFA–co-solvent (2 : 1), the rate in the presence of $CDCl_3$ was reduced to 1/5 and in the presence of MeCN to 1/8 of the rate in pure TFA (Table 2). Thus, the effect of $CDCl_3$ and MeCN are comparable although they differ significantly in dielectric constant. What the two solvents have in common is that they are aprotic.

An analogy to the effect of the co-solvent can be drawn from the effect of aprotic solvents on the rates of S_N2 reactions. For example, in mixtures of water and dimethyl sulphoxide (DMSO), the rate of solvolysis of bromoacetic acid increased by a factor of as high as 50 in going from pure water to 80% DMSO.[23] The rate enhancement was attributed to decreased solvation, hence increased reactivity, of the neighbouring carboxylate anion in the presence of the aprotic solvent. The latter, an increase in the reactivity of anions on going to aprotic media where hydrogen bonding solvation is not possible, appears to be a general phenomenon and has recently been reviewed.[24,25] A similar effect on the *ortho*-Claisen rearrangement in TFA would be expected to be accompanied by a rate decrease rather than enhancement since the anionic centre ($CF_3CO_2^-$) is forming in the transition state [according to mechanism (b)] and decreased solvation of the anion would be expected to have a destabilizing effect on the transition state and hence decrease the rate. Although not conclusive, the above argument explains the effect of the presence of the co-solvent.

The effect of water on the rate of rearrangement of allyl *p*-tolyl ether in TFA is not immediately apparent.

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* For a discussion of salt effects see ref. 18.

[16] P. M. Laughton and R. E. Robertson, in 'Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Dekker, New York, 1969, ch. 7, pp. 435—442.

[17] Ref. 16, pp. 454—458.

[18] B. K. Morse, in ref. 15, pp. 519—520.

[19] G. Harriss and J. B. Milne, *Canad. J. Chem.*, 1971, **49**, 1888.

[20] J. Bessiere, *Bull. Soc. chim. France*, 1969, 3353.

[21] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, Chemical Rubber Company, Cleveland, 1966, p. E-56.

[22] C. K. Mann, in 'Electroanalytical Chemistry,' ed. A. J. Bard, Dekker, New York, 1969, vol. 3, ch. 2.

[23] C. A. Kingsbury, *J. Amer. Chem. Soc.*, 1965, **87**, 5409.

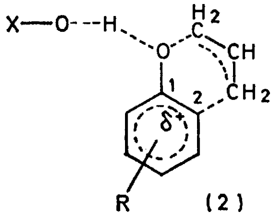
[24] A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.

[25] C. D. Ritchie, in ref. 16, ch. 4.

Since TFA is a strong acid in aqueous solution (pK_a +0·3) [26] and a weak acid in the pure state,[14] the effect of the addition of water to TFA would be expected to be a shift in equilibrium (1) to the right and thus increase the catalytic activity. It seems probable that this is the effect observed in going from 0 to 5% water (Table 3 and Figure 2). The fact that the rate decreases on further addition of water could be due to a specific solvent effect of TFA on the transition state and dilution with water decreases this stabilization.

The energy of activation, $\Delta H^{\ddagger}$ 17·8 kcal mol^{-1}, follows the trend previously found [11] for the rearrangement of allyl *p*-tolyl ether, *i.e.*, a decrease in $\Delta H^{\ddagger}$ with increasing acidity was found in going from the gas phase ($\Delta H^{\ddagger}$ 35·1 kcal mol^{-1}) to benzene ($\Delta H^{\ddagger}$ 26·3 kcal mol^{-1}) to *p*-chlorobenzene ($\Delta H^{\ddagger}$ 22·9 kcal mol^{-1}) as solvent.

In order to account for the substituent effect, the kinetic isotope effect, and the kinetic salt effect, we propose that the mechanism of the *ortho*-Claisen rearrangement in TFA involves a highly polar transition state in which the positive charge is spread over the aromatic ring in such a way that charge densities in the 1- and 2-positions are of nearly equal magnitude [structure (2)]. The degree of transfer of the proton to the etheral oxygen atom in the transition state is dependent upon the reaction conditions. In TFA in the absence of non-interfering salts or in the presence of trifluoroacetate ion, only partial transfer of the proton appears to occur in the transition state and reaction path (b) is favoured. Under conditions which favour the dissociation of TFA (*i.e.*, in the presence of non-interfering salts) it appears that at least a portion of the reaction occurs by a pre-protonation mechanism [path (a)] *i.e.*, complete transfer of the proton occurs in the transition state. In addition to the acidic nature of TFA, the mixed solvent data indicate that specific solvation by TFA is involved, probably solvation of a developing anionic centre.



(2)

EXPERIMENTAL

Reagents.—TFA (Schuchardt), containing <0·5% water was used without further purification. [^{2}H]Chloroform and [$^2H_3$]acetonitrile were spectral grade and used without further purification. The allyl aryl ethers were all prepared by published procedures.

Spectra.—^{1}H N.m.r. spectra were recorded at 60 MHz with tetramethylsilane as internal standard on a Varian A-60A spectrometer equipped with a variable temperature controller (V6040).

Kinetic Measurements.—Substrate (50 μl) was placed in an n.m.r. tube which was equilibrated in a bath at the temperature of the kinetic run. Solvent (0·5 ml) was pipetted from a container, also kept in the bath, onto the substrate. Immediately after mixing, the tube was placed in the spectrometer probe and the measurements were started. First-order rate constants were determined graphically from the decrease in the intensity of the signals from the *O*-methylene protons. Good straight line plots were obtained for more than one half-life in all cases. Identical results could also be obtained by following the appearance of initial rearrangement product from the increase in the intensity of the signals due to the *C*-methylene protons. In general the data reported are the average of two or more runs in which agreement within 5% was observed.

Spectral Changes during Reactions.—Allyl *p*-tolyl ether, immediately after dissolving in TFA (*ca.* 10% solution), showed τ 7·75 (3H, s, Me), 5·38 (2H, d, OCH_2), 4·87—3·63 (3H, complex, olefinic protons), and 3·05 (4H, AA′BB′, ArH). On standing, the signal at τ 5·38 decreased in intensity accompanied by the appearance of a new doublet centred at 6·65, due to the *C*-methylene protons of the rearrangement product. The aromatic region gradually changed to a broad signal with decreased intensity. On prolonged standing, the signals due to both substrate and primary product disappeared and new signals at τ 5·00, 7·00, and 8·50 appeared which are due to the product of addition of TFA to the double bond of the rearrangement product.

o-*Allyl*-p-*cresol from Allyl* p-*Tolyl Ether.*—The ether (1·0 g) was allowed to dissolve in TFA (10 ml). After *ca.* 30% conversion, determined by following the changes in the n.m.r. spectrum, TFA was evaporated under reduced pressure. The residue was dissolved in dichloromethane, the solution was extracted with dilute NaOH solution, the basic aqueous phase was acidified with dilute HCl, and the resulting solution was extracted with dichloromethane. Evaporation of dichloromethane left *o*-allyl-*p*-cresol (702 mg, 86% based on ether consumed). The dichloromethane solution from the basic extraction contained substrate (690 mg). The isolated *o*-allyl-*p*-cresol gave τ ($CDCl_3$) 7·77 (3H, s, Me), 6·67 (2H, d, CCH_2), 3·35 (1H, OH), 5·00—3·67 (3H, olefinic), 3·37 (1H, d, ArH), and 3·13 (2H, *m*-ArH).

Hydration Product.—A solution, identical with that of the previous experiment, was allowed to stand for two weeks at room temperature. Work-up in the same manner yielded *o*-(2-hydroxypropyl)-*p*-cresol (740 mg, 66%), τ ($CDCl_3$) 8·87 (3H, d, aliphatic Me), 7·83 (3H, s, ArMe), 7·33 (2H, d, CCH_2), 5·90 (1H, sextet, *C*H*OH*), 3·78 (2H, 2 × OH), and 3·25 (3H, ArH).

[3/1431 *Received, 9th July,* 1973]

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[26] A. L. Henne and C. F. Fox, *J. Amer. Chem. Soc.*, 1951, **73**, 2323.