The *ortho*-Claisen Rearrangement of Phenyl Allyl Ethers in Trifluoroacetic Acid

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Summary Phenyl allyl ethers spontaneously rearrange when dissolved in trifluoroacetic acid; rate constants for several *para*-substituted compounds are estimated to be *ca.* 10^5 times as great as those observed in the thermal rearrangement.

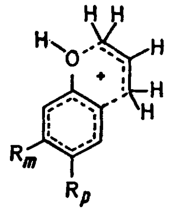
The Claisen rearrangement of allyl phenyl ethers can be achieved under mild conditions, by dissolving the appropriate ether in trifluoroacetic acid (TFA) at room temperature. A unique substituent effect is associated with this reaction. Electron-donating substituents in either the *para*- or *meta*-positions of the phenyl group enhance the rate to about the same extent, implicating a cyclic transition state in which the positive charge is equally distributed over several atoms. We estimate that the rate in TFA exceeds that of the same compounds in carbitol[1] by a factor of *ca.* 10^5.

On being dissolved in TFA, the allyl phenyl ethers (see Table) are converted into the corresponding *o*-alkyl-phenols. No mono-rearranged product could be detected in the case of 1,4-diallyloxybenzene. Rate constants obtained at 60° are tabulated.

Rate constants for the acid catalysed Claisen rearrangement o allyl phenyl ethers in trifluoroacetic acid

Phenyl substituent	10^4k (s^{-1})	Relative rate
m-Cl	0·32	0·34
H	1·1	1·0
p-OMe	2·0	1·8
m-OMe	2·0	1·8
p-$O{\cdot}CH_2{\cdot}CH{:}CH_2$	2·7	2·5
p-Me	3·0	2·7
m-Me	3·3	3·0

The data show that either Me or OMe has the same effect irrespective of whether it is in the *meta*- or *para*-position and must indicate that electron release to the ether oxygen and the position undergoing attack by the incoming group are of nearly equal importance. This is further substantiated by the fact that greater rate enhancement is observed for Me than for OMe since Me simultaneously activates both sites while resonance and inductive effects of OMe counteract one another, activating one site while de-activating the other. Thus, we arrive at the conclusion that a transition state such as (I), in which the positive charge is spread over several atoms, best describes the acid catalysed Claisen rearrangement. The fact that OMe is less effective than Me in rate enhancement could be due to association of the OMe group with TFA in that it is well known that TFA undergoes complex formation with ethers.



(I)

A recent evaluation of solvent effects on the *ortho*-Claisen rearrangement concluded that enhancement of rates by phenols and carboxylic acids probably is not due to acid catalysis but either to the hydrogen-bonding abilities or the polar character of the solvent.[2] In connection with the latter study,[3] it is of interest to compare the effect of *para*-substituents to that observed in this work. In tetradecane, carbitol, and aqueous ethanol, the rate of rearrangement of *p*-methoxyphenyl allyl ether exceeds that of the *p*-methyl compound by a factor of 2—4, while we observe that the *p*-methyl compound reacts about 1·5 times as fast as the *p*-methoxy-compound. This suggests that the transition state may be different when TFA is the solvent.

The Claisen rearrangement in TFA is also suitable for synthetic purposes. For example, 2,5-diallylhydroquinone was isolated in about 70% yield after allowing the ether to react at 50° for 1 h. The reactions described in this communication further demonstrate the utility of solvents of intermediate acidity. For example, stronger acids such as sulphuric or fluorosulphuric acid are totally unsuitable for the study of reactions of phenols or alkyl aryl ethers due to the sulphonation reactions[4] which take place very rapidly even at low temperature.

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