

weighting function was used, where z is the titer for unreacted acetate and z_1 is this value for the first point. This weighting

$$w = \frac{1}{(2/z_1) + (1/z)}$$

function was chosen arbitrarily so that the contribution from errors linear in time and errors linear in the titer would become equal at 1 half-life. Calculations of the rate constant and its standard deviation were performed on a Burroughs 220 computer, and are recorded in Table I.

Product Recovery from Hydrolysis.—A sample of methylferrocenylcarbinyl acetate (0.153 g., 0.56 mmole) was solvolyzed in 100 ml. of 80% acetone at 45° for 10 half-lives. The solution was diluted with water and the product was extracted into methylene chloride. The organic solution was washed several times with water, an equal volume of benzene was added to the extract, and the solvent was removed at reduced pressure and temperatures not exceeding 50° to yield a yellow solid, m.p. 75.5–77.5°. Recrystallization produced 0.67 g. (52%) of alcohol melting at 77.5–78.5°. The crude product accounted for at least 75% of the starting acetate, and no other product was detected by chromatography. A sample of solvolysis solution had an extinction coefficient at 440 m μ which was nearly identical with that of a solution made up with an equivalent amount of the carbinol, and gave no evidence of a shift in the maximum.

Ethanolysis of Methylferrocenylcarbinyl Acetate.—The ethyl ether of the carbinol was prepared by slowly bubbling dry hydrogen chloride for 20 sec. into a solution of 1.65 g. of methylferrocenylcarbinol in 35 ml. of absolute ethanol. After standing 1 hour the mixture was poured into an excess

of dilute aqueous sodium acetate, the product extracted into methylene chloride and washed with water. The solution was evaporated to an oil, and the product was chromatographed on neutral alumina with 50:50 benzene-ether. After the solvent had been removed, the product was distilled in a molecular still at 50° and 10 m μ pressure to yield a red-orange oil, n_D^{20} 1.5739.

Anal. Calcd. for $C_{14}H_{10}OFe$: C, 65.14; H, 6.98. Found (E): C, 65.12; H, 7.06.

Refluxing a solution of 1.5 g. of methylferrocenylcarbinyl acetate in 300 ml. of absolute ethanol for 3.5 hr. and isolating the product as before produced an oil with n_D^{20} 1.5741 and an infrared spectrum identical with that of the ether, which lacked carbonyl or hydroxyl absorption.

Methylferrocenylcarbinol (10.5 g., 2 mmoles) in 150 ml. of absolute ethanol with 0.06 ml. (1 mmole) of acetic acid added was refluxed for 3.5 hr. When the product was chromatographed, it was found that most of the carbinol had been converted to the ether.

A sample of methylferrocenylcarbinyl acetate (0.101 g., 0.37 mmole) was refluxed in absolute ethanol. Samples were removed after 1.5 and 6 hr., and titrated with standard sodium hydroxide. Both aliquots required about 5% in excess of the predicted volume of base. A control containing 0.1 g. (0.39 mmole) of the carbinol and 0.04 g. (0.45 mmole) of ethyl acetate required an amount of base equal to the indicator blank after 6 hr. reflux.

A sample of methylferrocenylcarbinol was refluxed in the presence of ethyl acetate with a trace of added acetic acid in ethanol solution. No further acetic acid was produced.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

The *ortho*-Claisen Rearrangement. IV. The Rearrangement of X-Cinnamyl *p*-Tolyl Ethers¹

BY WILLIAM N. WHITE AND WILMER K. FIFE^{2,3}

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The rates of rearrangement of ten X-cinnamyl *p*-tolyl ethers were determined with the object of obtaining information to define the electronic character of the transition state of the Claisen rearrangement. The rates were best correlated by σ^+ -constants and a ρ -value of -0.40 . Since the rates of rearrangement of allyl *p*-X-phenyl ethers are similarly correlated by negative ρ - and σ^+ -constants, the transition state must involve a depletion of electrons in both the aryl and allyl portions of the molecule. This might result from simultaneous homolysis of the allyl-oxygen bond and homogenesis of the allyl-*ortho*-carbon bond to give a highly electronegative, electron-deficient oxygen capable of withdrawing electrons from both the allyl and aryl groups.

Introduction

Although the over-all course of the Claisen rearrangement, in terms of the structural restrictions on reactants, intermediates and products, is well understood^{4,5} the conformation and electrical character of the transition state have until recently escaped elucidation. The conformation of the transition state is now known,⁶ but available experimental results^{7,8} do not permit an unambiguous description of its electrical character.

(1) This investigation was supported by research grant NSF-G7345 from the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow, 1955–1956; Sinclair Oil Co. Fellow, 1959–1960.

(3) From the thesis submitted by Wilmer K. Fife in partial fulfillment of the requirements for the Doctor of Philosophy Degree at The Ohio State University.

(4) D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1945, pp. 1–48.

(5) D. J. Cram in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 295–303.

(6) (a) E. N. Marvell and J. L. Stephenson, *J. Org. Chem.*, **25**, 676 (1960); (b) A. W. Burgstahler, *J. Am. Chem. Soc.*, **82**, 468 (1960); (c) L. D. Huestis and L. J. Andrews, *ibid.*, **83**, 1963 (1961); and (d) W. N. White and B. E. Norcross, *ibid.*, **83**, 1968 (1961).

(7) H. L. Goering and R. R. Jacobson, *ibid.*, **80**, 3277 (1958).

(8) W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, *ibid.*, **80**, 3271 (1958).

An understanding of the electronic nature of the transition state is required to complete the description of the mechanism of the Claisen rearrangement. This can be studied by determining the effect of solvent and of substituents of varying electrical character on the rate of reaction. Some information concerning the electrical nature of the transition state is available from studies of the rates of rearrangement of allyl *p*-X-phenyl ethers.^{7,8} The substituent effects on the rates of rearrangement of the allyl *p*-X-phenyl ethers are best correlated by σ^+ -substituent constants⁹ and a negative value of ρ in Hammett's equation.¹⁰

If the transition state involves a charge separation, then there should be polar effects of substituents in the allyl group also. Very little information is available which concerns the polar effects of substituents in the allyl group. It is known that α - and γ -allyl substituents affect the rate of rearrangement while β -substituents have no significance influence.^{7,11} However, these results

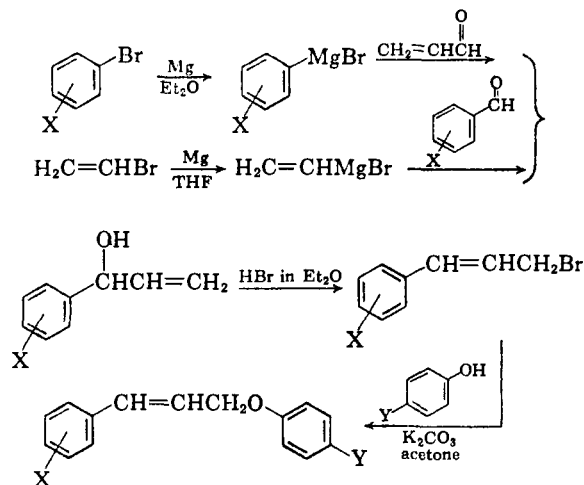
(9) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4980 (1958).

(10) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 184–198; and (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

need considerable amplification. A systematic study of the effect of substituents in the allyl group should provide further insight into the nature of the rearrangement because electronic changes occurring in the aromatic portion of the molecule during the reaction process should also be reflected in the allyl group. To provide this information, a series of *m*- and *p*-X-cinnamyl *p*-X-phenyl ethers were prepared and their rearrangement was studied kinetically.

Results

The desired *m*- and *p*-X-cinnamyl *p*-Y-phenyl ethers were prepared from substituted bromobenzenes and benzaldehydes by the sequences



The *m*- and *p*-methoxycinnamyl bromides could not be prepared in this way because of polymerization of the α -(methoxyphenyl)-allyl alcohols in the presence of acids. However, the *m*- and *p*-methoxycinnamyl chlorides could be prepared by using thionyl chloride in dilute ether solution. All of the substituted cinnamyl halides reacted with substituted phenols in the presence of potassium carbonate in acetone to give in good yields the desired *m*- and *p*-X-cinnamyl aryl ethers as crystalline solids.

Although most of the cinnamyl aryl ethers prepared in this investigation were new compounds, rigorous structure proofs were unnecessary because the literature contains reports of analogous syntheses of cinnamyl aryl ethers.¹² In addition, correct chemical analyses, and infrared¹³ and ultraviolet¹⁴ absorption spectra furnished evidence to confirm the structures in question.

Rearrangement of the ethers to the corresponding α -arylallylphenols in Carbitol solution went smoothly and in excellent yield. The rearrangement product was found to be free of starting material and to contain only the expected 4-Y-2-

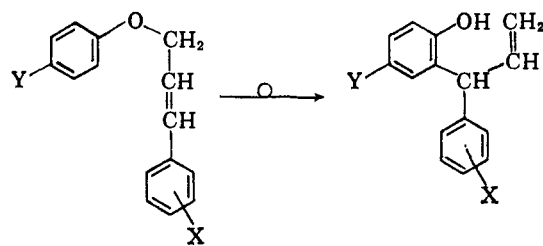
(11) S. J. Rhoads and R. L. Crecelius, *J. Am. Chem. Soc.*, **77**, 5057 (1955).

(12) (a) L. Claisen, F. Roth, F. Kremers and E. Tietze, *Ann.*, **442**, 232 (1925); (b) C. D. Hurd and L. Schmerling, *J. Am. Chem. Soc.*, **59**, 107 (1937); (c) L. Claisen and E. Tietze, *Ber.*, **58**, 275 (1925).

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34.

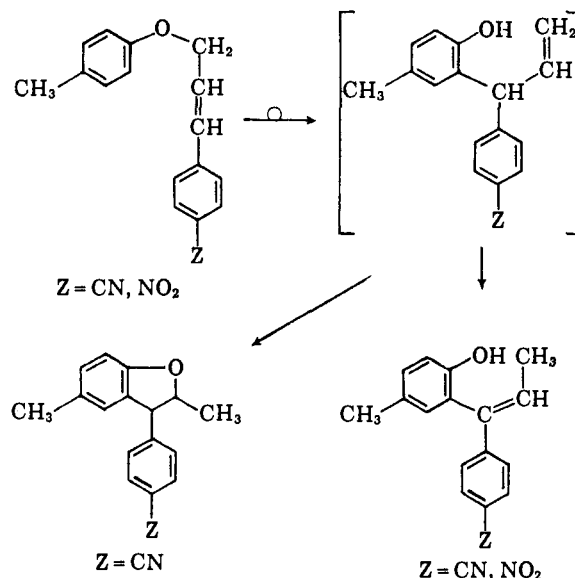
(14) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Ex. 18, 24.

(α -(X-phenyl)-allyl)-phenols except when X was *p*-cyano or *p*-nitro. The structural conclusions were



again based on literature analogies,¹² infrared¹³ and ultraviolet¹⁴ spectra, and the chemical properties of these substances.

p-Cyanocinnamyl *p*-tolyl ether rearranged to give equal amounts of two products, a white, crystalline solid and a yellow, viscous oil. The solid, a neutral material, was tentatively assigned the structure of 2,5-dimethyl-3-(*p*-cyanophenyl)-coumaran; and the oil, a weakly acidic material, the structure of 4-methyl-2-(1-(*p*-cyanophenyl)-1-propenyl)-phenol. These assignments were based



on the composition, infrared¹³ and ultraviolet¹⁴ spectral analyses, and analogies in the literature.^{12a} The formation of a coumaran is not too surprising because *o*-allylphenols are known to cyclize to coumarans in the presence of acids.^{12a} The propenyl substituted phenol would result if the carbon-carbon double bond of the allyl side-chain shifted into conjugation with the two benzene rings. This tendency to extend conjugation is enhanced by the strongly electron-deficient cyano group.

Only a yellow solid product, a phenol, was isolated from the rearrangement of *p*-nitrocinnamyl *p*-tolyl ether. The product's structural data were analogous to those for 4-methyl-2-(1(*p*-cyanophenyl)-1-propenyl)-phenol, and therefore it was presumed to be 4-methyl-2-(1(*p*-nitrophenyl)-1-propenyl)-phenol.

The specific rate constants of 14 substituted cinnamyl aryl ethers were determined spectrophotometrically at several temperatures with Carbitol as solvent (Table I). In all cases, the

TABLE I
 RATE CONSTANTS FOR REARRANGEMENT OF X-CINNAMYL Y-PHENYL ETHERS IN CARBITOL

X	Y	$140.04 \pm 0.06^{\circ}$	$150.01 \pm 0.03^{\circ}$	$159.98 \pm 0.15^{\circ}$	$180.01 \pm 0.03^{\circ}$
H	H	1.10 \pm 0.00	5.29 \pm 0.06
<i>m</i> -Cl	H	0.75 \pm .01	3.09 \pm .03
H	<i>p</i> -CH ₃ O	9.66 \pm .19	34.6 \pm .4
H	<i>p</i> -CH ₃	..	1.75 ^c	3.41 \pm .17	15.1 \pm .2
<i>p</i> -CH ₃ O	<i>p</i> -CH ₃	..	4.87 \pm 0.11	9.61 \pm .39	32.6 \pm .1
<i>m</i> -CH ₃ O	<i>p</i> -CH ₃	..	1.90 ^c	3.62 \pm .06	16.0 \pm .7
<i>p</i> -CH ₃	<i>p</i> -CH ₃	..	2.40 ^c	6.08 \pm .05	21.4 \pm .4
<i>m</i> -CH ₃	<i>p</i> -CH ₃	0.63 ^b	2.04 ^c	4.04 \pm .19	17.6 \pm .9
<i>p</i> -Cl	<i>p</i> -CH ₃	.54 ^b	1.21 \pm 0.11	3.39 \pm .37	13.4 \pm .3
<i>m</i> -Cl	<i>p</i> -CH ₃	.52 \pm 0.03	1.22 ^c	3.00 ^b	11.0 \pm .4
<i>p</i> -CN	<i>p</i> -CH ₃	.38 ^{a,b}	0.92 ^{a,b}	2.14 \pm 0.32 ^a	8.75 ^{a,b}
<i>m</i> -CN	<i>p</i> -CH ₃	.28 ^b	0.99 ^c	1.99 \pm 0.07	9.84 \pm 0.11
<i>p</i> -NO ₂	<i>p</i> -CH ₃	1.19 ^{a,b}	..
<i>m</i> -NO ₂	<i>p</i> -CH ₃	0.27 ^b	0.68 ^c	1.90 \pm 0.01	8.36 \pm 0.13

^a Rearrangement does not follow normal course. ^b Value calculated from a decay curve which represents average of two runs. ^c Value of a single run.

reaction was followed to eight reaction half-lives which was taken as the point of infinite reaction. These infinity absorptions compared favorably with the measured absorptions of the pure phenolic products. Six points, each corresponding to a different fraction of reaction, were determined in each run and these generally determined a smooth decay curve which reached a minimum at infinite reaction time. At least ten points were taken from the decay curve and used to calculate the logarithm of the fraction of reaction, which gave an excellent straight line when plotted against time. The average percentage deviation of all these rate constants from their individual means is 4.4%.

The measurements on the rearrangement of *p*-cyanocinnamyl *p*-tolyl ether followed a first-order kinetic plot only to about 50% of reaction and the reproducibility of experimental data was very poor. However, since neither of two products isolated from the rearrangement was the normal product expected from the Claisen rearrangement, the results are ambiguous. In addition, the data obtained for the rearrangement of *p*-nitrocinnamyl *p*-tolyl ether did not conform to a first-order kinetic plot at all. The calculated first-order rate constant gradually decreased to zero as the reaction progressed. Since the reaction was followed by measuring the decrease in absorption due to the conjugated carbon-carbon double bond and both the reactant and final product in the rearrangement of *p*-nitrocinnamyl *p*-tolyl ether contained such a bond, it was not surprising that the measured kinetics were complicated. The experimental results for both the *p*-nitro and *p*-cyano substituted ethers are consistent with a consecutive reaction sequence in which the normal rearrangement product isomerized to the more stable conjugated phenol. This explanation requires that the rates of rearrangement and isomerization be nearly equal.

The temperature dependence of the rate constants were determined and the activation parameters were calculated by standard methods.¹⁵ The activation parameters are summarized in Table II. The activation energy generally in-

creased as the substituent became more electron deficient. The entropies of activation were large and negative, consistent with the picture of the reaction as involving a "loose" initial state and a highly oriented transition state. The activation parameters determined in this investigation agree with those reported previously^{7,8,11} and support the proposed conformation of the transition state.¹⁶

 TABLE II
 ACTIVATION PARAMETERS FOR REARRANGEMENT OF X-CINNAMYL Y-PHENYL ETHERS AT 180.01°

X	Y	E_a^a	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger a}$
H	H	30.6	29.8	-13.1
<i>m</i> -Cl	H	27.6	26.6	-21.1
H	<i>p</i> -CH ₃ O	25.0	23.9	-22.5
H	<i>p</i> -CH ₃	26.9	26.2	-18.2
<i>p</i> -CH ₃ O	<i>p</i> -CH ₃	24.2	23.2	-24.0
<i>m</i> -CH ₃ O	<i>p</i> -CH ₃	27.9	26.2	-18.9
<i>p</i> -CH ₃	<i>p</i> -CH ₃	26.4	26.3	-18.1
<i>m</i> -CH ₃	<i>p</i> -CH ₃	29.2	28.9	-12.7
<i>p</i> -Cl	<i>p</i> -CH ₃	29.0	29.0	-13.3
<i>m</i> -Cl	<i>p</i> -CH ₃	27.5	27.0	-17.9
<i>p</i> -CN ^c	<i>p</i> -CH ₃	28.9 ^c	27.9 ^c	-16.4 ^c
<i>m</i> -CN	<i>p</i> -CH ₃	33.2	30.4	-10.6
<i>m</i> -NO ₂	<i>p</i> -CH ₃	31.6	30.8	-9.9

^a Kcal./mole. ^b Cal./deg./mole. ^c Rearrangement did not yield the normal product.

Discussion

The immediate purpose of this investigation was to obtain information concerning the electronic nature of the transition state in the Claisen rearrangement. The ultimate goal was to apply the results of this investigation together with those of other studies toward the establishment of a precise, detailed mechanism for the reaction. Information concerning the polar nature of reactions can be obtained by studying the effects of solvent and certain structural changes on reactivity.

The experimental rate constants for the rearrangement of *m*- and *p*-X-cinnamyl *p*-tolyl ethers were treated by making use of the σ^{-16} and σ^+ substituent⁹ constants and the following form of

(15) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 94-98.

(16) H. C. Brown and D. H. McDaniel, *J. Org. Chem.*, **23**, 420 (1958).

Hammett's equation

$$\log k_x = \rho\sigma_x + b$$

This form of the equation, which includes the empirical constant b (the theoretical value of $\log k_0$), was used because it prevents undue weight being given to the reaction rate of the unsubstituted compound. The least squares method¹⁷ was used to fit the experimental data to the equation. Correlation coefficients (r) and standard deviations (s) from the regression line also were calculated. The results of the Hammett treatment are listed in Table III and illustrated in Fig. 1.

TABLE III

APPLICATION OF HAMMETT'S EQUATION					
σ^a	ρ^b	b^b	r^c	s^c	% ^d
σ	-0.517	-3.742	0.952	0.108	9.06
σ^+	-0.402	-3.798	0.995	0.047	3.16

^a Type of substituent constant used for fitting equation. ^b Values of ρ and b obtained by least squares method. ^c r = correlation coefficient, s = standard deviation. ^d Percentage mean deviation in estimation of rate constant, k , from equation.

The best correlation of the experimental rates of rearrangement was obtained with the σ^+ -substituent constants. This is indicated by visual inspection of the plots and by the facts that the correlation coefficient for the σ^+ -correlation is much closer to 1.00 and the standard deviation is less than when σ -constants are used. σ^+ -Constants appear to apply to reactions in which an electron deficiency that can interact by direct resonance with the substituent is created or destroyed at some stage of the reaction preceding the rate-determining transition state.⁹ Thus, the change from initial to transition state in the reaction under study must involve the formation or dissipation of an electron deficiency capable of resonance stabilization by the substituent.

The sign of the reaction constant (ρ) is diagnostic of whether electron deficiencies or excesses are created or are destroyed during the forward progress of the reaction, provided the experimental temperature is below the isokinetic temperature for the reaction.¹⁸ The isokinetic temperature (β) may be found from the relation

$$\Delta H \approx \Delta H_0 + \beta \Delta S$$

An isokinetic temperature of 522°K. is obtained when the activation parameters for the rearrangement of *m*- and *p*-X-cinnamyl *p*-tolyl ethers are fitted to the isokinetic relationship (Fig. 2) by application of the least squares method.¹⁷ The correlation coefficient is 0.992 and the standard deviation is 1.65. The experimental temperature (453°K. or less) was well below the isokinetic temperature. Therefore, the sign of ρ is mechanistically significant. Since ρ is negative and the reaction is correlated by σ^+ , an electron deficiency that can interact directly with the substituent by resonance must occur in the allyl chain as the molecule goes from the initial state to the transition state.

(17) G. W. Snedecor, "Statistical Methods," The Iowa State College Press, Ames, Iowa, 1946.

(18) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

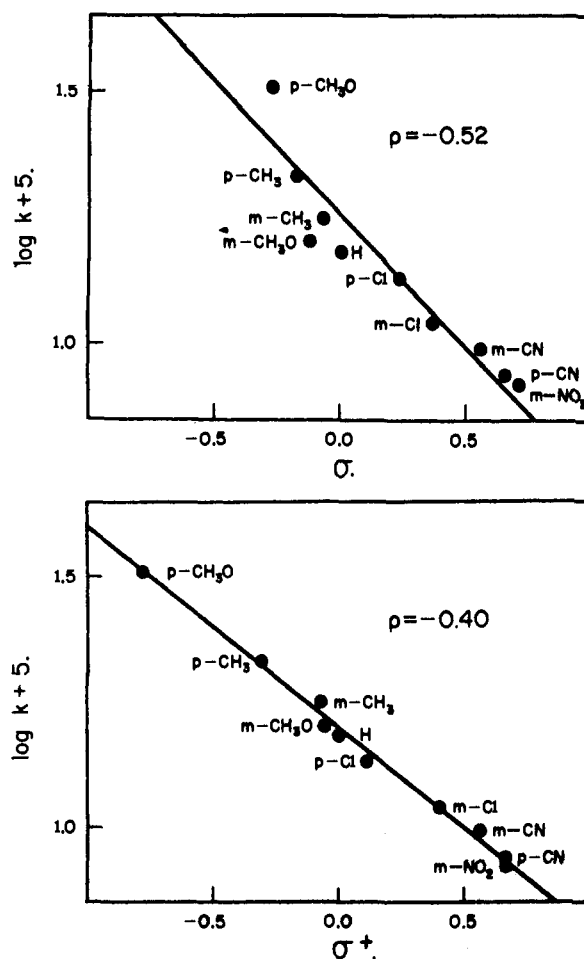


Fig. 1.—Hammett plots of rates of rearrangement of X-cinnamyl *p*-tolyl ethers.

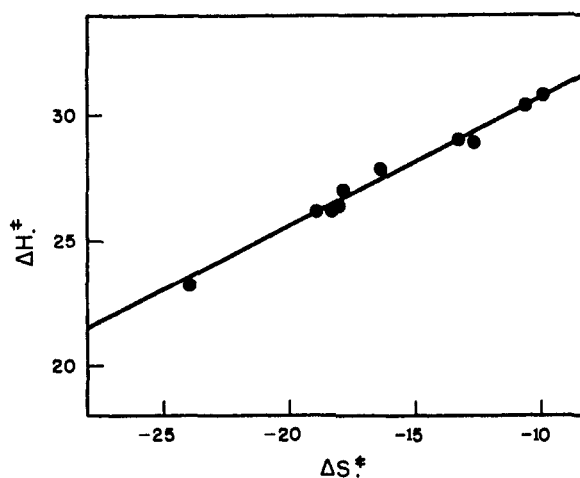
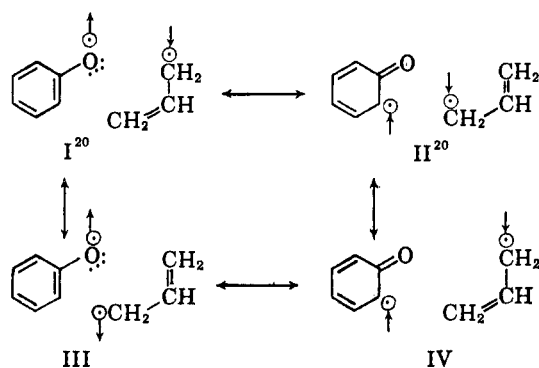


Fig. 2.—Isokinetic plot of activation parameters for rearrangement of X-cinnamyl *p*-tolyl ethers.

A similar result was obtained in a study of the rearrangement of allyl *p*-X-phenyl ethers (negative ρ and correlation by σ^+).^{7,8} This means that electron donation in both the allyl and the phenyl group of an allyl phenyl ether aids the reaction. This rather unusual result completely rules out

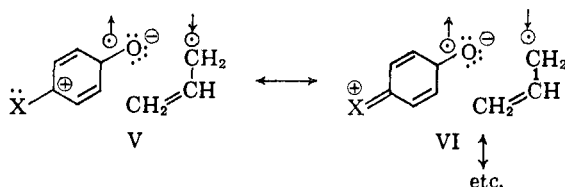
any transition state in which the allyl group and the aryloxy moiety attain charges of opposing types.

The transition state can be pictured as involving a conformation of the molecule in which the p -orbital on the γ -carbon atom of the allyl group has become situated directly over the p -orbital of the *ortho* carbon atom. Interaction between these p -orbitals would begin the formation of a carbon-carbon bond at the same time as the allyl carbon-oxygen bond commences to lengthen and break. The extent of formation of the carbon-carbon bond and cleavage of the carbon-oxygen bond in the transition state is probably dependent on the substitution in the allyl and aryloxy portions of the molecule. The transition state involves contributions from structures such as I, II, III and IV.¹⁹



This transition state proceeds to the normal intermediate 6-allyl-2,4-cyclohexadienone by the completion of the severance of the carbon-oxygen bond and the formation of the allyl- σ -carbon bond. This intermediate then rapidly enolizes to form the σ -allylphenol.

If this mechanism is correct, the observed substituent effects should be interpretable in terms of it. Oxygen has been found to have a high electron affinity²¹ and electronegativity.²² Thus, additional structures in which the oxygen withdraws electrons from the ring or its substituents may contribute. Since the electron-donating capabilities



(by resonance) of the substituent become involved here just as they are in the reaction defining σ^+ , it seems likely that the substituent effect would be correlated by σ^+ -constants which, of course, is the experimental finding. This mechanism also involves the creation of an electron deficiency on the ring during the forward course of the reaction which

(19) Many other contributors having different positions of the double bonds and electrons can be written—there are 20 non-polar structures in all.

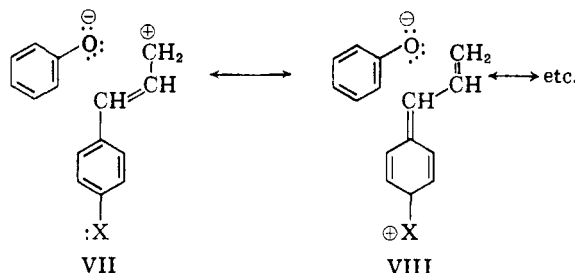
(20) Structure I is simply an alternate representation of an allyl aryl ether with a stretched carbon-oxygen bond and II is a 6-allyl-2,4-cyclohexadienone with a long carbon-carbon bond.

(21) H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953).

(22) J. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1953.

interprets the observed negative value of the reaction constant (ρ).²³⁻²⁶

The relative rates of reaction of X-cinnamyl *p*-tolyl ethers also can be interpreted in terms of the postulated transition state electron distribution. These rates, as mentioned previously, are also interrelated by σ^+ constants and a negative ρ . This might result if resonance structures such as VII and VIII also contributed to stabilization of the transition state.



Again the high electron affinity²¹ of the phenoxy radical must be responsible for the observed result. The electronegative oxygen must be capable not only of attracting electrons from the ring to which it is attached, but also from the allyl (or cinnamyl) chain. Once more the creation, in a forward step of the reaction, of an electron deficiency that can interact with the substituent by resonance demands the use of σ^+ -constants and a negative value of ρ .²⁷⁻²⁹

This representation of the Claisen rearrangement transition state also explains the rates of reaction and isomer distributions observed in the rearrangement of allyl *m*-X-phenyl ethers³⁰ and the rates of isomerization of α - and γ -alkylallyl aryl ethers.^{7,11} The latter compounds rearrange faster than the corresponding simple allyl aryl ethers. This may be the result of stabilization of the tran-

(23) An alternate explanation of the negative ρ observed is that the reactant may be stabilized when resonance can occur between the ether oxygen and electron-withdrawing substituents. This stabilization would cause compounds with electron-withdrawing groups to react more slowly than those with electron-releasing substituents. However, if this explanation was valid, the substituent effects would be correlated by σ^- or σ^+ -constants rather than σ^+ -constants.

(24) Thermal cleavage of *t*-butyl X-phenyl peracetates (P. D. Bartlett and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960)) required σ^+ -constants for correlation purportedly because of the electronegativity of the oxygen in the *t*-butoxy radical.

(25) A somewhat similar explanation must be required to account for the relative stabilities of 2,4,6-tri-*t*-butylphenoxy and 4-methoxy-2,6-di-*t*-butylphenoxy radicals (C. D. Cook, D. A. Kuhn and P. Flann, *J. Am. Chem. Soc.*, **78**, 2002 (1956)).

(26) It is reported that inhibition of autoxidation by substituted phenols is correlated by σ^+ -constants and a negative ρ (C. D. Cook and D. C. Lane and R. S. Stone, private communication).

(27) A negative ρ might also result from stabilization of the cinnamyl double bond in reactant by resonance with electron-attracting substituents in the cinnamyl ring. However, this would not satisfactorily account for correlation by σ^+ -constants since this type of interaction probably would require σ^- or σ^+ -constants.

(28) This interpretation resembles in some respects that given for the relative reactivities of substituted X-methylstyrenes toward the electron-demanding maleic anhydride radical. The observed substituent effects in this copolymerization reaction are also better correlated by σ^+ - than by σ^- -constants. For an excellent summary of this work and its interpretation see C. Walling, "Free Radicals in Solution," J. Wiley and Sons, Inc., New York, N. Y., 1957.

(29) The σ^+ -correlation of the thermal decomposition rates of *t*-butyl X-phenylperacetates (see footnote 24) is interpreted on the basis of a very similar mechanism.

(30) C. Slater, Ph.D. Dissertation, The Ohio State University, 1960.

sition state by electron donation from the alkyl groups at the ends of the allyl group.

In summary, it appears that the observed substituent effects in both the aromatic ring and the allyl group require a mechanism for the Claisen rearrangement in which the transition state must receive contributions from a variety of resonance structures, such as I-VIII.³¹

Experimental

***p*-Nitrocinnamoyl Chloride.**—A mixture of 15 g. of *p*-nitrocinnamic acid, 113 g. of thionyl chloride and 100 ml. of benzene was refluxed for 4 hours during which the reaction mixture became homogeneous. Evaporation of the benzene yielded a tan colored solid which was crystallized from 1:3 benzene-cyclohexane to give 14.2 g. (87%) of *p*-nitrocinnamoyl chloride, m.p. 147–150° (lit.³² m.p. 150.5–152.5°).

***p*-Nitrocinnamyl Alcohol.**—To a suspension of 2.06 g. (0.054 mole) of lithium aluminum hydride in 100 ml. of diglyme (diethylene glycol dimethyl ether) was added during 2 hours with stirring a solution which contained 12 g. (0.16 mole) of *t*-butyl alcohol and 50 ml. of diglyme. The resulting solution was slowly stirred into a solution of 11.4 g. (0.054 mole) of *p*-nitrocinnamoyl chloride in 100 ml. of diglyme at –50° under nitrogen. After warming to room temperature, the reaction mixture was poured onto 200 g. of crushed ice. The crude solid product was collected by filtration and taken up in 150 ml. of ether. This solution was washed with 50 ml. of 5% aqueous sodium hydroxide and 25 ml. of saturated salt solution, and dried over anhydrous magnesium sulfate. Evaporation of the ether gave 8 g. (84%) of crude *p*-nitrocinnamaldehyde which was dissolved in 100 ml. of absolute methanol. To this solution was added slowly with stirring a solution of 3 g. (0.08 mole) of sodium borohydride in 50 ml. of absolute methanol. During the hydride addition, the temperature rose to 41° and then returned to 25° when the reaction was complete. The reaction mixture was acidified with dilute sulfuric acid and filtered to remove inorganic salts. The filtrate was evaporated to obtain a dark brown solid which was dissolved in 75 ml. of ether, washed with 25 ml. of 5% aqueous sodium carbonate, and dried over anhydrous magnesium sulfate. Evaporation of the ether and crystallization of the crude product from cyclohexane-benzene gave 8 g. (84%) of *p*-nitrocinnamyl alcohol, m.p. 124.5–126° (lit.³³ m.p. 127–128°).

Preparation of α -Arylallyl Alcohols. Method A.—To 6.3 g. (0.26 mole) of magnesium turnings and 75 ml. of anhydrous ether under nitrogen was added with stirring a solution of 0.25 mole of aryl bromide and 250 ml. of anhydrous ether at such a rate as to just maintain refluxing. After the reaction was complete, as shown by the disappearance of magnesium, the resulting dark brown solution was cooled to –10° and a solution of 14 g. (0.25 mole) of freshly distilled acrolein and 50 ml. of anhydrous ether was added dropwise. Stirring was continued for 1 hour before the reaction product was hydrolyzed with 50 ml. of saturated aqueous ammonium chloride. The organic layer was decanted from the inorganic salts and dried over anhydrous potassium carbonate. The crude product obtained by evaporating the dried ethereal solution was distilled under reduced pressure in the presence of a small quantity of solid potassium carbonate (to lessen isomerization of the α -arylallyl alcohol). The infrared spectra of the products so obtained indicated they were never completely pure but contained some of the corresponding cinnamyl alcohols which were equally useful in the preparation of cinnamyl halides. The α -arylallyl alcohols prepared by method A are listed in Table IV.

Method B.—A solution containing 0.25 mole of substituted benzaldehyde and 200 ml. of anhydrous tetrahydrofuran was cooled to –10° under nitrogen and 0.25 mole of vinyl-

magnesium bromide³⁴ dissolved in 500 ml. of anhydrous tetrahydrofuran was added slowly with stirring over a period of 2 hours. The reaction mixture was stirred while it warmed to 15° during 1 hour. Following hydrolysis of the reaction product with 50 ml. of saturated aqueous ammonium chloride, the organic layer was decanted and dried over anhydrous potassium carbonate. The crude product obtained by evaporating the dried solution was distilled under reduced pressure in the presence of a small quantity of solid potassium carbonate to give the desired α -arylallyl alcohol contaminated with trace amounts of unreacted substituted benzaldehyde and the corresponding aryl vinyl ketone. The α -arylallyl alcohols prepared by method B are also listed in Table IV.

TABLE IV
 α -(X-PHENYL)-ALLYL ALCOHOLS

X	Method	Yield, %	B.p. °C.	Mm.	B.p. (lit.) °C.	Mm.
H	A	66	78	2	106–107	15 ^b
<i>p</i> -CH ₃ O	A	46	105	2	129–130	12 ^c
	B	52				
<i>m</i> -CH ₃ O	B	75	92–96	1		
<i>p</i> -CH ₃	A	46	120–125	10	120–122 ^d	10 ^e
<i>m</i> -CH ₃	A	53	76–78	1	115–117	11 ^f
<i>p</i> -Cl	A	66	85–88	1	122–123	10 ^g
	B	52				
<i>m</i> -Cl	A	62	82	1	^h	
<i>p</i> -CN	B	55	117–122	1	ⁱ	
<i>m</i> -CN	B	70				
<i>m</i> -NO ₂	B	40	134.5 ^g	1	^j	

^a Distillation halted by decomposition. ^b C. Moureu and P. Gallagher, *Bull. soc. chim. France*, [4] 29, 1009 (1921). ^c M. Lora Tomayo and J. Leon, *Anales real soc. españ. fis. quim.*, 44B, 963 (1948). ^d Fractional distillation did not yield a pure compound. ^e H. Burton and C. K. Ingold, *J. Chem. Soc.*, 915 (1928). ^f H. Burton, *ibid.*, 1656 (1928). ^g H. Burton, *J. Chem. Soc.*, 1655 (1928). ^h *Anal.* Calcd. for C₉H₉ClO: C, 64.10; H, 5.38. Found: C, 63.90; H, 5.63. ⁱ *Anal.* Calcd. for C₉H₇NO₂: C, 60.33; H, 5.06. Found: C, 60.24; H, 5.32.

Preparation of *m*- and *p*-X-Cinnamyl Bromides.—A solution containing 0.10 mole of α - or γ -arylallyl alcohol and 100 ml. of anhydrous ether was saturated with anhydrous hydrogen bromide. After standing for 3 hours, the resulting yellow solution was dried over anhydrous magnesium sulfate and evaporated to give the crude substituted cinnamyl bromide. The crude product was distilled under reduced pressure or crystallized from cyclohexane to obtain the pure substituted cinnamyl bromide. The substituted cinnamyl bromides obtained in this way are listed in Table V.

TABLE V
m- AND *p*-X-CINNAMYL BROMIDES

X	Yield, %	M.p. or b.p. (mm.). °C.	M.p. or b.p. (lit.) °C.
H	72	88–90 (1)	132 (17) ^a
<i>p</i> -CH ₃	75	61–63	64–65 ^b
<i>m</i> -CH ₃	70	94–96 (1)	138–140 (11) ^c
<i>p</i> -Cl	86	60–62	62–63 ^d
<i>m</i> -Cl	83	100 (1)	^e
<i>p</i> -CN	42	76–77.5	^f
<i>m</i> -CN	43	122–127 (1)	^g
<i>p</i> -NO ₂	60	52–55	58–62 ^h
<i>m</i> -NO ₂	74	85.7–86.5	ⁱ

^a C. Moureu and P. Gallagher, *Bull. soc. chim. France*, [4] 29, 1010 (1921). ^b H. Burton and C. K. Ingold, *J. Chem. Soc.*, 915 (1928). ^c H. Burton, *ibid.*, 1656 (1928). ^d H. Burton, *ibid.*, 1655 (1928). ^e *Anal.* Calcd. for C₉H₇BrCl: C, 46.68; H, 3.48. Found: C, 46.82; H, 3.74. ^f *Anal.* Calcd. for C₁₀H₉NO: C, 54.08; H, 3.63. Found: C, 53.93; H, 3.82. ^g Fractional distillation did not yield a pure compound. ^h B. Elperin, *et al.*, *J. Am. Chem. Soc.*, 79, 1954 (1957). ⁱ *Anal.* Calcd. for C₉H₇BrNO₂: C, 44.65; H, 3.33. Found: C, 44.86; H, 3.56.

(34) H. Normant, *Compt. rend.*, 239, 1510 (1954).

(31) Contributions from structures V and VI and structures VII and VIII must be fairly evenly balanced to result in the similarity of substituent effects for the *m*- and *p*-X-cinnamyl *p*-tolyl ethers and allyl *p*-X-phenyl ethers.

(32) V. Izmailski and A. Belostvetov, *J. Gen. Chem. (U. S. S. R.)*, 11, 691 (1941).

(33) G. Carrara, R. Ettorre, P. Fava, G. Rollard, E. Testa and A. Vecchi, *J. Am. Chem. Soc.*, 76, 4394 (1954).

TABLE VI

X-CINNAMYL Y-PHENYL ETHERS

X	Y	Yield, %	Recrystn. ^a solvent	M.p., °C.	Carbon, %		Hydrogen, %	
					Calcd.	Found	Calcd.	Found
H	H	86	Sk B	68-69.7 ^b				
<i>m</i> -Cl	H	55	Sk B	69-70.5	73.62	73.43	5.35	5.17
H	<i>p</i> -CH ₃ O	62	Cyc	107-108	79.97	79.98	6.71	6.52
H	<i>p</i> -CH ₃	86	Sk B	79-80.6 ^c				
<i>p</i> -CH ₃ O	<i>p</i> -CH ₃	42	Cyc	123.5-125	80.28	79.98	7.13	7.06
<i>m</i> -CH ₃ O	<i>p</i> -CH ₃	58	Sk B	54-55.8	80.28	80.06	7.13	7.36
<i>p</i> -CH ₃	<i>p</i> -CH ₃	57	Cyc	119-122.7	85.67	85.51	7.61	7.86
<i>m</i> -CH ₃	<i>p</i> -CH ₃	73	Sk B	60-61	85.67	85.81	7.61	7.52
<i>p</i> -Cl	<i>p</i> -CH ₃	71	Cyc	124.5-125.7	74.27	74.23	5.84	5.63
<i>m</i> -Cl	<i>p</i> -CH ₃	88	Sk B	74-76.5	74.27	74.14	5.84	5.97
<i>p</i> -CN	<i>p</i> -CH ₃	67	Cyc	98-99.1	81.90	81.82	6.06	5.92
<i>m</i> -CN	<i>p</i> -CH ₃	75	Sk B	92.5-93.7	81.90	81.75	6.06	6.08
<i>p</i> -NO ₂	<i>p</i> -CH ₃	63	Cyc	97.5-99	71.36	71.10	5.61	5.53
<i>m</i> -NO ₂	<i>p</i> -CH ₃	83	Cyc	91-92	71.36	71.56	5.61	5.48

^a Sk B = Skellysolve B, Cyc = Cyclohexane. ^b L. Claisen and E. Tietze, *Ber.*, 58, 279 (1925), reported m.p. 66-66.5°. Lit. m.p. 78-79° (note *b*).

TABLE VII

4-Y-2-[α-(X-PHENYL)-ALLYL]-PHENOLS

X	Y	Yield, %	°C.	B.p.	Mm.	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
H	H	90	139-140		2 ^b				
<i>m</i> -Cl	H	75 ^a	"			73.62	73.93	5.35	5.06
H	CH ₃ O	55 ^a	81-82.3 ^d			79.97	80.08	6.71	6.84
H	CH ₃	80 ^a	145		2 ^c				
<i>p</i> -CH ₃ O	CH ₃	95	"			80.28	80.17	7.13	7.28
<i>m</i> -CH ₃ O	CH ₃	95	165		1	80.28	80.28	7.13	7.42
<i>p</i> -CH ₃	CH ₃	95	147.5		1	85.67	85.96	7.61	7.70
<i>m</i> -CH ₃	CH ₃	95	143.5		1	85.67	85.85	7.61	7.62
<i>p</i> -Cl	CH ₃	90	157.5		1	74.27	74.50	5.84	5.85
<i>m</i> -Cl	CH ₃	90	158		1	74.27	74.47	5.84	6.01
<i>m</i> -CN	CH ₃	80	178		1	81.90	81.73	6.06	5.90
<i>m</i> -NO ₂	CH ₃	75	186		1	71.36	71.18	5.61	5.88

^a Isolation procedure described by L. Claisen, *Ber.*, 58, 275 (1925). ^b L. Claisen, *ibid.*, 58, 275 (1925), reported b.p. 183-185° (12 mm.). ^c Insufficient material for b.p. determination. ^d M.p.; crystallized from Skellysolve B. ^e L. Claisen, *Ber.*, 58, 275 (1925), reported b.p. 191° (12.5 mm.).

Preparation of *m*- and *p*-Methoxycinnamyl Chlorides.—To a solution containing 11.9 g. (0.10 mole) of thionyl chloride and 100 ml. of anhydrous ether was added with swirling 16.4 g. (0.10 mole) of α-(methoxyphenyl)-allyl alcohol dissolved in 100 ml. of anhydrous ether. The solution was immediately evaporated by a stream of air to obtain the crude *p*-substituted isomer as a white crystalline solid and the *m*-isomer as a pale yellow oil.

The crude *p*-isomer was purified by crystallization from petroleum ether (b. p. 30-60°) to obtain *p*-methoxycinnamyl chloride, m.p. 71.5-73°, in 83% yield.

Anal. Calcd. for C₁₀H₁₁ClO: C, 65.76; H, 6.07. Found: C, 65.77; H, 5.90.

The *m*-isomer was purified by dissolving the crude material in boiling petroleum ether (b.p. 30-60°), separating the petroleum ether layer from the residue by decantation, and evaporating the solution with a stream of air. Further purification was impossible since *m*-methoxycinnamyl chloride decomposed when distilled at 1 mm. or when allowed to stand for more than an hour.

Preparation of Substituted Cinnamyl Aryl Ethers.—A mixture of 0.10 mole of substituted cinnamyl halide, 0.10 mole of substituted phenol, 14 g. (0.10 mole) of powdered anhydrous potassium carbonate and 75 ml. of anhydrous acetone was stirred and refluxed under nitrogen for 6-10 hours. After adding 250 ml. of water, the reaction mixture was extracted with two 75-ml. portions of 1:1 ether-benzene. The combined extracts were washed with five 25-ml. portions of Claisen alkali³⁵ and 50 ml. of saturated salt solution. The washed ethereal solution was dried over an-

hydrous potassium carbonate. Evaporation of the dried solution yielded a white or yellow crystalline solid which was chromatographed through Grade I Woelm alumina with benzene as eluent. The chromatographed ether was crystallized several times from cyclohexane or Skellysolve B to obtain a pure sample for kinetic measurements. The substituted cinnamyl aryl ethers are listed in Table VI.

Preparation of Rearrangement Products.—A solution of 1-2 g. of substituted cinnamyl aryl ether in 10 ml. of Carbitol (diethylene glycol monoethyl ether) was heated in a sealed Pyrex tube at 150° for a period of time corresponding to ten reaction half-lives (based on rearrangement rates). The tube was opened and the contents were dissolved in 50 ml. of 1:2 ether-Skellysolve B. After washing the ethereal solution with three 20-ml. portions of water and 25 ml. of saturated salt solution, it was dried over anhydrous magnesium sulfate. The crude phenols obtained as lightly colored oils by evaporating the dried solutions were purified by chromatography using Grade I Woelm alumina and 1:99 methanol-ether as eluent. The chromatographed phenols were distilled under reduced pressure to obtain samples for analysis and infinity-point checks.

The structural assignments for the rearrangement products have in all cases been based on ultraviolet and infrared spectral analysis, and chemical analysis except for the two phenols previously prepared and characterized. The products were those expected in all cases except for the rearrangement of *p*-cyanocinnamyl *p*-tolyl ether and *p*-nitrocinnamyl *p*-tolyl ether. The normal rearrangement products are listed in Table VII.

The crude product obtained from the rearrangement of *p*-cyanocinnamyl *p*-tolyl ether yielded about equal amounts of two products when chromatographed on Grade I Woelm

(35) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 310.

TABLE VIII

COMPARISON OF ULTRAVIOLET LIGHT ABSORPTION OF X-CINNAMYL Y-PHENYL ETHERS AND THEIR REARRANGEMENT PRODUCTS

X	Y	λ^a	ϵ (ether) ^a	ϵ (phenol) ^a
H	H	252	21,500	1160
<i>m</i> -Cl	H	252	20,400	655
H	<i>p</i> -CH ₃ O	250	22,600	860
H	<i>p</i> -CH ₃	251	22,200	1435
<i>p</i> -CH ₃ O	<i>p</i> -CH ₃	264	26,000	2930
<i>m</i> -CH ₃ O	<i>p</i> -CH ₃	254	17,250	1100
<i>p</i> -CH ₃	<i>p</i> -CH ₃	256	23,900	805
<i>m</i> -CH ₃	<i>p</i> -CH ₃	254	20,000	900
<i>p</i> -Cl	<i>p</i> -CH ₃	257	26,000	1270
<i>m</i> -Cl	<i>p</i> -CH ₃	252	20,700	895
<i>p</i> -CN	<i>p</i> -CH ₃	271	29,000	16,000 ^b
			2930 ^c	
<i>m</i> -CN	<i>p</i> -CH ₃	254	18,800	1920
<i>p</i> -NO ₂	<i>p</i> -CH ₃	308	16,800	13,500 ^d
<i>m</i> -NO ₂	<i>p</i> -CH ₃	244	31,300	6150

^a λ = wave length in millimicrons, ϵ (ether) = molar extinction coefficient of substituted cinnamyl aryl ether, ϵ (phenol) = molar extinction coefficient of reaction product. ^b Rearrangement product in which carbon-carbon double bond has shifted into conjugation with phenyl rings. ^c Cyclic ether assumed to be 2,5-dimethyl-3-(*p*-cyanophenyl)-coumaran.

alumina with 1:99 methanol-ether as eluent. The first fraction was a white crystalline solid which was crystallized from cyclohexane to obtain in 50% yield 2,5-dimethyl-3-(*p*-cyanophenyl)-coumaran, m.p. 100.5-101.5°.

Anal. Calcd. for C₁₇H₁₅NO: C, 81.90; H, 6.06. Found: C, 81.87; H, 5.86.

The second fraction was a yellow, weakly acidic oil which was distilled under reduced pressure to obtain in 50% yield 4-methyl-2-(1-(*p*-cyanophenyl)-1-propenyl)-phenol. (There was insufficient material for a b.p. determination.)

Anal. Calcd. for C₁₇H₁₅NO: C, 81.90; H, 6.06. Found: C, 81.70; H, 6.08.

The chromatographed phenol resulting from the rearrangement of *p*-nitrocinnamyl *p*-tolyl ether was recrystallized from cyclohexane to obtain in 50% yield 4-methyl-2-(1-(*p*-nitrophenyl)-1-propenyl)-phenol, m.p. 122-125°.

Anal. Calcd. for C₁₆H₁₅NO₂: C, 71.36; H, 5.36. Found: C, 71.49; H, 5.85.

Purification of Carbitol.—Commercial Carbitol (diethylene glycol monoethyl ether) was dried over calcium hydride at 150° for 12 hours. The dry solvent was twice fractionated under reduced pressure using a 12-inch Vigreux column to obtain "kinetic-grade" Carbitol, b.p. 101° (20 mm.).

TABLE IX

EXPERIMENTAL DATA FOR CALCULATION OF RATE CONSTANT

Run 2, cinnamyl *p*-tolyl ether; $T = 180.01 \pm 0.03^\circ$, $k = 1.54 \times 10^{-5} \text{ sec.}^{-1}$; concn. = 0.027 *M*

Time, min.	Wt., g. ^a	D_{251}^a	$D_{251} \text{ (st.)}^a$
0	0.0420	0.935	0.890
2	.0425	.815	.767
7	.0383	.648	.677
20	.0386	.489	.508
45	.0390	.303	.311
75	.0408	.194	.190
120	.0430	.117	.109
180	.0395	.061	.062
720	.0367	.046	.050

^a Wt. = weight of aliquot of heated sample diluted to 25 ml. with 95% ethanol, D_{251} = optical density of diluted solution at 251 m μ , $D_{251} \text{ (st.)}$ = optical density of diluted solution corrected to standard concentration of 0.0400 g. per 25 ml.

Kinetic Procedure.—Samples of the substituted cinnamyl aryl ethers were dissolved in sufficient dry, purified Carbitol to yield 0.001 *M* or 0.025 *M* solutions. Portions of these solutions were sealed in small Pyrex tubes which were immersed in a constant temperature bath ($\pm 0.05^\circ$) for various timed intervals. The reaction was stopped by removing the tubes from the bath and allowing them to cool rapidly to room temperature.

The contents of the tubes were analyzed by taking advantage of the difference in ultraviolet light absorption of the starting material, which has a conjugated carbon-carbon double bond in the cinnamyl group, and the product in which the carbon-carbon double bond has moved out of conjugation with the aryl ring.³⁶ The relevant spectra data are summarized in Table VIII.

For the kinetic determinations, the sealed Pyrex tubes containing the heated samples were opened and an aliquot was taken from each one and diluted with 95% ethanol to yield a final solution which had easily measurable optical densities. Graphical application of the first-order rate expression

$$kt = 2.303 \log \frac{D - D_0}{D - D_t}$$

where k = specific rate constant, t = time (sec.), D = optical density at infinite time, D_0 = optical density at zero time and D_t = optical density at time t , gave good straight lines and excellent agreement between individual runs. The optical density at infinite time was taken to be that of a sample heated for eight reaction half-lives. A typical kinetic run is summarized in Table IX.

Rate constants for the rearrangement of the substituted cinnamyl aryl ethers were determined in this way at several temperatures. The results are summarized in Table I.

(36) E. A. Braude, D. W. Turner and H. S. Waight, *J. Chem. Soc.* 2396 (1958).