olic hydrogen chloride. The substance decomposed slowly when heated on the Fisher-Johns apparatus.

Anal. Calcd. for $C_{10}H_{14}ClNO_4S$: C, 42.9; H, 5.04; Cl, 12.7; S, 11.5. Found: C, 43.4; H, 4.93; Cl, 12.7; S, 11.6.

Methyl {*p*-[Bis(2-hydroxyethyl)amino]benzylsulfonyl}-acetate (XVIII).—A solution of 9.15 g. (0.0376 mole) of the recrystallized amine (XVII) in 70 ml. of methanol containing 0.65 g. (0.0030 mole) of *p*-toluenesulfonic acid was treated at 5° with 60 ml. of liquefied ethylene oxide. The mixture was stirred in a stoppered flask at room temperature for 7 days, treated again at 0° with 10 ml. of ethylene oxide in 15 ml. of methanol, and stirred as before for 2 more days, then was concentrated *in vacuo* to a residual sirup. A solution of the sirup in 200 ml. of dichloromethane was washed with saturated aqueous sodium bicarbonate (150 ml.) and water (150 ml.), dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residual solid (11.2 g., 91% yield) was recrystallized from a chloroform–benzene mixture to give a 37% yield of product, m.p. 106–109°. Further recrystallization afforded an analytically pure sample, m.p. 108–109°, R_f identical to that of XVII in solvent system A and 0.39 in solvent system B.[8]

Anal. Calcd. for $C_{14}H_{21}NO_6S$: C, 50.7; H, 6.39; S, 9.68. Found: C, 50.8; H, 6.37; S, 9.87.

Methyl {*p*-[Bis(2-chloroethyl)amino]benzylsulfonyl}acetate (VIII).—Recrystallized XVIII (10.0 g., 0.0300 mole) was heated with 50 ml. of phosphoryl chloride on a steam bath for 25 min. The dark solution was poured (with precautions described for IV) into 750 ml. of stirred ice and water. When hydrolysis was complete, the gummy product that separated was dissolved by addition of dichloromethane (200 ml.). Stirring was continued for 15 hr. while the mixture warmed to room temperature. The organic layer was separated and the aqueous layer was washed with dichloromethane (250 ml.); the combined dichloromethane solutions were washed with water (300 ml.) and saturated aqueous sodium bicarbonate, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The solid residue was stirred and ground under a layer of ether and then collected on a filter, yielding 8.80 g. (79%) of product, m.p. 97–98°. Recrystallization from aqueous acetone afforded 6.80 g. (61%) of the analytical sample, m.p. 101.5–102°, $R_f{}^8$ 0.77 in solvent system A and 0.06 in solvent system B.

Anal. Calcd. for $C_{14}H_{19}Cl_2NO_4S$: C, 45.6; H, 5.20; Cl, 19.2; O, 17.4; S, 8.70. Found: C, 45.6; H, 5.52; Cl, 19.0; O, 17.5; S, 8.66.

Acknowledgment.—The authors wish to thank Dr. Peter Lim for interpretation of the infrared spectra and his staff for the paper chromatographic data, and Mr. O. P. Crews and staff for large-scale preparation of certain intermediates.

The *ortho*-Claisen Rearrangement. VI. The Rates of Rearrangement of Allyl *m*-*X*-Phenyl Ethers to 2-Allyl-5-*X*-phenols[1]

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Received April 3, 1961

The rates of rearrangement of seven allyl *m*-*X*-phenyl ethers to the corresponding 2-allyl-5-*X*-phenols are correlated most satisfactorily using $\sigma_p{}^+$ (*not* $\sigma_m{}^+$) constants and a ρ value of -0.66 in Hammett's equation. This unusual result can be explained best on the basis of simultaneous homolysis of the allyl-oxygen bond and homogenesis of the *ortho* carbon-allyl bond in a transition state involving a highly electronegative oxygen atom.

The electrical nature of the transition state of the Claisen rearrangement has been the subject of several recent investigations. To obtain information on this problem, the rates of rearrangement of a series of allyl *p*-*X*-phenyl ethers[4,5] and a series of *X*-cinnamyl *p*-tolyl ethers[6] have been determined.

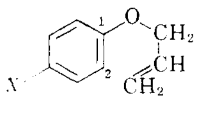
It was found[4,5] that a good correlation of substituent effects on the rate of reaction of allyl *p*-*X*-phenyl ethers was obtained when $\sigma_p{}^+$ constants[7] and a negative value of ρ were used in the ordinary form of Hammett's equation,[8,9]

$$\log \frac{k}{k_0} = \rho^+\sigma_p{}^+$$

However, a further satisfactory correlation of the data[4] was obtained by application of the two-parameter equation,[9]

$$\log \frac{k}{k_0} = \rho_1\sigma_p + \rho_2\sigma_m$$

in which ρ_1 and ρ_2 define the effect of the substituent on the reaction occurring at the 1- and 2-positions of the ring.



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

[2] Monsanto Fellow, 1959–1960; Ethyl Corp. Fellow, 1958–59.

[3] From the thesis submitted by Carl D. Slater in partial fulfillment of the requirements for the Degree of Doctor of Philosophy at the Ohio State University.

[4] W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

[5] H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3278 (1958).

[6] W. N. White and W. K. Fife, *J. Am. Chem. Soc.*, **83**, 3846 (1961).

[7] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[8] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, Inc. New York, 1940, pp. 184–198.

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

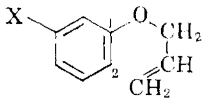
It may be that one of these methods of treating the experimental data provides spurious correlation.

Kinetic data for the rearrangement of *X*-cinnamyl *p*-tolyl ethers also required the use of σ^+ constants and a negative ρ in Hammett's equation. This correlation coupled with that for the rearrangement of allyl *p*-*X*-phenyl ethers, was taken to mean that opposing charges could not be developed on the allyl and aryloxy moieties in the transition state. The transition state was pictured as involving lengthening of the allyl-oxygen bond and simultaneous formation of the *ortho* carbon-allyl bond in such a way that the electrons constituting these bonds are about equally divided between the two portions of the molecule. The geometry is preserved by interaction of *p*-orbitals of the oxygen and *ortho* carbon atoms of the aryloxy group with those of the α- and γ-carbon atoms of the allyl group, respectively.

Quantitative data concerning the rates of rearrangement of allyl *m*-*X*-phenyl ethers, as well as the relative amounts of 3- and 5-isomers formed, could be utilized to gain a more detailed knowledge of the electrical nature of the transition state of the *o*-Claisen rearrangement. In particular, these data could be used to decide upon the validity of the two-parameter Hammett equation. The ρ's obtained by application of this equation to the rates of rearrangement of allyl *p*-*X*-phenyl ethers indicate that reaction is facilitated by electron donation toward the position of bond breaking, and by electron withdrawal from the position of bond making. If the two-parameter equation is to be applicable then it must assume the form

$$\log \frac{k}{k_0} = \rho_1\sigma_m + \rho_2\sigma_p$$

for the rearrangement of allyl *m*-*X*-phenyl ethers to 2-allyl-5-*X*-phenols, and the values of ρ_1 and ρ_2



in this equation must be identical to those in the previous equation.

Therefore, the rate of isomerization of each member of a series of allyl *m*-*X*-phenyl ethers was determined and factored into the rates of rearrangement to 2-allyl-5-*X*-phenol and 2-allyl-3-*X*-phenol by multiplying the total rate by the fraction of each of these isomers formed.[10]

Experimental

Kinetic measurements. The extent of rearrangement of allyl *m*-*X*-phenyl ethers was determined by taking advantage of the difference in ultraviolet absorption of the phenyl ethers and the phenolic rearrangement products in aqueous base.

To determine the wave length at which measurements were to be made, a small sample (1.0 to 5.0 g.) of the appropriate allyl aryl ether was refluxed for 3 to 6 hr. in carbitol or diphenyl ether solution and the product was isolated by distillation (crystallization in the case of allyl *m*-cyanophenyl ether). The ultraviolet spectrum of a small sample of the rearrangement product dissolved in sodium hydroxide solution was scanned, and the wave length of maximum absorption was located. These results are listed in Table I

TABLE I

WAVE LENGTHS OF MAXIMUM ABSORPTION IN AQUEOUS BASE OF REARRANGEMENT PRODUCTS OF ALLYL *m*-*X*-PHENYL ETHERS

X	λ(mμ)
OCH_3	290
CH_3	294
Br	296
Cl	295
COC_6H_5	370
CN	329

The solvent employed in all runs was Carbitol (monoethyl ether of diethylene glycol) that had been distilled through a 13-in. fractioning column. It boiled at 88° at 12 mm.

Freshly distilled allyl *m*-*X*-phenyl ether[10] (0.1000 to 0.4500 g.) was weighed into a 25-ml. volumetric flask and the flask was diluted to the mark with Carbitol (monoethyl ether of diethylene glycol). Approximately 1.4-ml. portions of this solution were aliquoted into 10 × 75 mm. Pyrex test tubes and the tubes were sealed. The tubes were immersed in a constant temperature bath for various time intervals. Upon removal from the bath, the tubes were rapidly cooled, opened and 1.00-ml. aliquots were transferred to 25-ml. volumetric flasks and diluted with 96% ethanol. Aliquots (5.00 ml.) of these alcoholic solutions were diluted to 25.00 ml. with 0.1*N* sodium hydroxide solution (addition of 5.00 ml. of 96% ethanol to the 5.00 ml. aliquot before dilution with base was necessary with the samples from allyl *m*-benzoylphenyl ether to prevent precipitation). The optical densities of these solutions were determined at the appropriate wave length in matched 1.000 cm. silica cells against a water blank by means of a Beckman Model DU spectrophotometer.

The optical densities at infinite times were obtained by allowing two to four samples to react for eight or more half-lives at 200° (at least 99.6% completion). The average optical density of the diluted solutions was employed as the infinity point.

Calculations were made by application of the integrated first-order rate expression

$$kt = \ln \frac{D_\infty - D_0}{D_\infty - D_t}$$

k = specific rate constant
t = time in seconds
D_∞ = optical density at infinite time
D_0 = optical density at zero time
D_t = optical density at time t

Data from a typical run are shown in Table II.

Results

The specific rate constants for the rearrangement of six allyl *m*-*X*-phenyl ethers were determined at temperatures of 160.0 ± 0.1°, 181.1 ± 0.1°, and 200.0 ± 0.1° using Carbitol (monoethyl ether of diethylene glycol) as solvent. A procedure utilizing

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(10) W. N. White and C. D. Slater, *J. Org. Chem.*, **26**, 3631 (1961).

TABLE II

REARRANGEMENT OF ALLYL *m*-BROMOPHENYL ETHER AT 181.1 ± 0.1°

Sample Number	t (Min.)	D_t	$\ln \frac{D_\infty - D_0}{D_\infty - D}$
0	0	0.008	0.000
1	30	0.248	0.160
2	60	0.353	0.239
3	120	0.553	0.410
4	180	0.749	0.612
5	240	0.848	0.731
6	360	1.066	1.061
7	480	1.226	1.398
8	660	1.367	1.834
9	2000	1.625	—

the differences in ultraviolet absorption of basic solutions of starting materials and products was employed. The results are shown in Table III.

TABLE III

RATE CONSTANTS FOR THE REARRANGEMENT OF ALLYL *m*-X-PHENYL ETHERS

X	160.0 ± 0.1°	181.1 ± 0.1°	200.0 ± 0.1°
CH_3O	16.5 ± 0.10	82.3 ± 4.6	333 ± 10
CH_3	9.19 ± 0.02	50.7 ± 0.5	203 ± 2
Br	7.07 ± 0.12	45.5 ± 0.2	183 ± 2
Cl	7.36 ± 0.19	39.0 ± 0.1	168 ± 7
H	4.54 ± 0.20^{a,b}	25.6 ± 0.1^{a}	124 ± 3
C_6H_5CO	4.66 ± 0.03	26.5 ± 2.4	113 ± 1
CN	3.54 ± 0.04	21.6 ± 1.1	75 ± 2
F	—	33.6 ± 1.0	—
CF_3	—	16.3 ± 0.1	—

[a] Data from Ref. 4. [b] At 159.77 ± 0.04°.

The reaction was followed to at least 59% completion in all cases except that of allyl *m*-cyanophenyl ether at 160°, which was run to 46% completion. From six to nine points were determined in each run, and these defined a good, straight line when the logarithm of fraction of reaction was plotted against reaction time. The results in Table III are the average of duplicate runs, with the exception of allyl *m*-methylphenyl ether at 181° (four runs) and allyl *m*-benzoylphenyl ether at 181° (three runs). The average percentage deviation of the rate constants from their individual means was 2.1%.

By utilizing the percentages of the isomers formed in these rearrangements,[10] it is possible to separate the over-all rate constants into those for the formation of 2-allyl-5-X-phenols and 2-allyl-3-X-phenols. These values are tabulated in Tables IV and V.

The values given for X = H are those obtained experimentally divided by the statistical factor of two. To obtain the rate constants listed for 181.1°, the averages of the isomer distributions[10] observed at 200.0° and 160.0° were used.

TABLE IV

RATE CONSTANTS FOR THE FORMATION OF 2-ALLYL-5-X-PHENOLS

$k \times 10^6$ (sec.$^{-1}$)

X	160.0°	181.1°	200.0°
CH_3O	11.4	56.0	220
CH_3	3.68	20.3	81
Br	2.05	14.6	64
Cl	2.50	13.3	57
H	2.27^{a-c}	12.8^{a,c}	62^{c}
C_6H_5CO	0.98	5.8	26
CN	1.10	6.7	23

[a] Data from Ref. 4. [b] At 159.77 ± 0.04°. [c] Actual rate constant has been divided by statistical factor of two.

TABLE V

RATE CONSTANTS FOR THE FORMATION OF 2-ALLYL-3-X-PHENOLS

$k \times 10^6$ (sec.$^{-1}$)

X	160.0°	181.1°	200.0°
CH_3O	5.1	26.3	113
CH_3	5.51	30.4	122
Br	5.02	30.9	119
Cl	4.86	25.7	111
H	2.27^{a-c}	12.8^{a,c}	62^{c}
C_6H_5CO	3.68	20.7	87
CN	2.24	14.9	52

[a] Data from Ref. 4. [b] At 159.77 ± 0.04°. [c] Actual rate constant has been divided by a statistical factor of two.

For each reaction a plot of logarithm of the rate constant against the reciprocal of the absolute temperature gave a straight line, the slope of which defined the energy of activation, E_a.[11] From these values $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated by standard methods[11] for each reaction. These parameters are compiled in Tables VI and VII.

TABLE VI

ACTIVATION PARAMETERS FOR THE FORMATION OF 2-ALLYL-5-X-PHENOLS

X	E_a^{a}	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$
CH_3O	30.0	29.1	−14.7
CH_3	31.6	30.7	−13.2
Br	34.4	33.5	− 7.7
Cl	34.6	33.7	− 7.5
H	33.3	32.4	−10.3
C_6H_5CO	33.6	32.7	−11.4
CN	34.1	33.2	− 9.9

[a] Kcal./mole. [b] Cal./deg./mole; computed for 181.1°.

Application of the equations of Purlee, Taft, and DeFazio[12] to the combined average deviations observed in the kinetic runs and isomer distribution determinations indicates that the statistical error in $\Delta H^\ddagger$ is ±0.7 kcal./mole and that in $\Delta S^\ddagger$ is ±1.6 cal./deg./mole.

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(11) A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1953, Chapter 5.

(12) E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *J. Am. Chem. Soc.*, **77**, 837 (1955).

TABLE VII

ACTIVATION PARAMETERS FOR THE FORMATION OF 2-ALLYL-3-X-PHENOLS

X	E_a[a]	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]
CH_3O	31.5	30.6	−13.0
CH_3	31.6	30.7	−12.5
Br	32.6	31.7	−10.1
Cl	31.5	30.6	−13.0
H	33.3	32.4	−10.3
C_6H_5CO	32.1	31.2	−12.1
CN	29.9	29.0	−17.6

[a] Kcal./mole. [b] Cal./deg./mole; computed for 181.1°.

Discussion

Unambiguous deductions about the electrical nature of a reaction based on the sign and magnitude of ρ in Hammett's equation can be made only after the relationship of the temperature at which the reaction was studied to the isokinetic temperature[13] has been established. The isokinetic temperature is determined by use of the equation

$$\Delta H^{\ddagger} = \beta \Delta S^{\ddagger} + \Delta H_0^{\ddagger} \qquad (3)$$

in which β is the isokinetic temperature and $\Delta H_0^{\ddagger}$ is a constant.

The data for the rearrangement of allyl m-X-phenyl ethers to 2-allyl-5-X-phenols were fitted to this equation by the least squares method,[14] to obtain $\Delta H^{\ddagger} = 593\ \Delta S^{\ddagger} + 38518$, with $r = 0.939$ (correlation coefficient, and $s = 636$ (standard deviation). The isokinetic temperature for this reaction is therefore 593°K, which is well above the experimental temperature of 454°K. Thus, the sign of ρ will be a valid basis for mechanistic considerations.

An attempt was first made to correlate the corrected rates of rearrangement[15] of both allyl m-X-phenyl ethers and allyl p-X-phenyl ethers ing Hammett's equation in the ordinary way.[16] The least squares method was employed and the correlation coefficient, r, and standard deviation, s, were calculated. The results of these computations are shown in Table VIII.

TABLE VIII

HAMMETT CORRELATION OF CORRECTED RATES[a] OF REARRANGEMENT OF ALLYL X-PHENYL ETHERS

Subst. Const.	ρ	r[b]	s[c]
σ	−0.870	−0.893	0.167
σ^+	−0.577	−0.881	0.176
σ^-	−0.616	−0.854	0.193

[a] Rates of rearrangement of allyl m-X-phenyl ethers were corrected so that the constant used applies only to the formation of 2-allyl-5-X-phenols and the rates of isomerization of the allyl p-X-phenyl ethers were divided by two to account for the availability of two equivalent ortho positions. [b] Correlation coefficient. [c] Standard deviation.

The Hammett plot using ordinary σ constants is shown in Figure 1. It is obvious that this relationship is poor. However, those obtained by means of the other two sets of constants (σ^+ and σ^-) are worse. This can be seen by comparing the correlation coefficients and the standard deviations for these fits (Table VIII). It is thus apparent that the application of Hammett's equation in the usual way to the rates of reaction of allyl X-phenyl ethers results in severe incongruities.

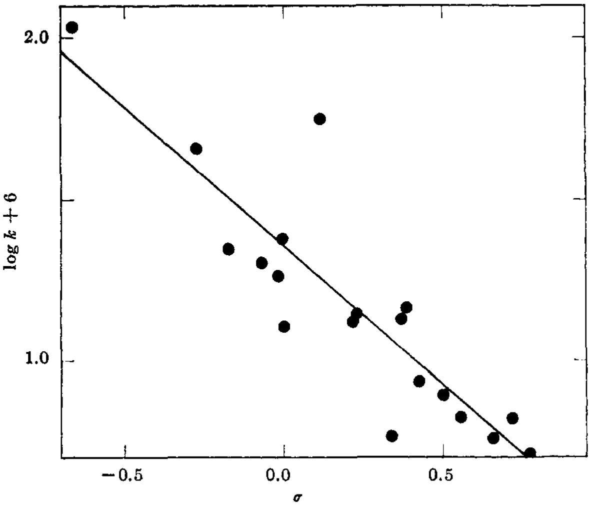

Fig. 1.—Hammett correlation of rates of rearrangement of allyl m-X-phenyl ethers to 2-allyl-5-X-phenols using σ constants.

The two-parameter equation was also applied to the rate constants for the *meta* and *para* substituted allyl phenyl ethers separately. The calculated values of ρ_1 and ρ_2, the correlation coefficient R, and the standard deviation S, are shown in Table IX.

The values of R and S indicate that both treatments of the data are quite satisfactory. As has been mentioned in the introduction, however, a meaningful mechanistic interpretation of the Claisen rearrangement in terms of the two-parameter equation is possible only if the values of ρ_1 and ρ_2 obtained by separate application of the equation to the rate constants of the allyl p-X-phenyl ethers and to the rate data for the allyl m-X-phenyl ethers are equal. As this is not the case (Table IX), the correlation of the rate results for the allyl X-phenyl

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

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

(15) Corrections were applied to the rates of isomerization of both the allyl m-X-phenyl ethers and the allyl p-X-phenyl ethers. The rates of reaction of the *meta* isomers were multiplied by the fraction of 2-allyl-5-X-phenyl formed in order to obtain the rate of rearrangement into the unhindered *ortho* position. Since there are two equivalent *ortho* positions in allyl p-X-phenyl ethers, the rates of rearrangement of these substances were divided by two to obtain the partial rate factor for rearrangement into one *ortho* position. These latter rates were taken from ref. 4.

(16) The values of σ_m and σ_p used were those recommended by D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); σ^+ values were obtained from H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958); and the values of σ_p^- from H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953). It was assumed that σ_m^- was the same as σ_m. All values for the benzoyl substituent are from ref. 4.

TABLE IX

HAMMETT CORRELATION OF CORRECTED RATES[a] OF REARRANGEMENT OF ALLYL *X*-PHENYL ETHERS WITH EQUATION 2

Location of Substituent	ρ_1	ρ_2	R[b]	S[c]
meta	1.77	−1.64	0.979	0.082
para	−1.37	0.88	0.988	0.064

[a] See footnote *a* to Table VIII. [b] Correlation coefficient. [c] Standard deviation.

ethers by means of the two-parameter equation is a spurious correlation.

The rates of formation of 2-allyl-5-*X*-phenols alone were dealt with using σ_m, σ_p, $\sigma_p{}^+$, and $\sigma_p{}^-$ separately. The results are summarized in Table X.

TABLE X

HAMMETT CORRELATION OF CORRECTED RATES[a] OF REARRANGEMENT OF ALLYL *m*-*X*-PHENYL ETHERS

Subst. Const.	ρ	r[b]	s[c]
σ_m	−0.801	−0.568	0.291
σ_p	−0.874	−0.881	0.169
$\sigma_p{}^+$	−0.664	−0.964	0.096
$\sigma_p{}^-$	−0.610	−0.870	0.177

[a] See footnote *a* to Table VIII. [b] Correlation coefficient. [c] Standard deviation.

It can be seen from the values of *r* and *s*, that the best correlation is afforded by use of $\sigma_p{}^+$, whereas those obtained with the other constants are poor.

The similarity of this result to that obtained for allyl *p*-*X*-phenyl ethers[4] suggested the possibility that all the data on the isomerization of allyl *X*-phenyl ethers could be interrelated by using the $\sigma_p{}^+$ constants for both *meta* and *para* isomers. In order to test this, the corrected rates[15] of reaction for all the allyl *X*-phenyl ethers were fitted to the Hammett equation using $\sigma_p{}^+$ constants only. The data for both the allyl *m*-*X*-phenyl ethers and the allyl *p*-*X*-phenyl ethers are correlated with a high degree of precision using a value of ρ of -0.609 ($r = 0.989$, $s = 0.057$). Fig. 2 illustrates the closeness of fit obtained. This is simply the result of the near identity of effect of a substituent regardless of whether it appears in the *meta* or *para* position. This must signify that the *meta* substituents interact with the reactive site in the transition state of the Claisen rearrangement in about the same way as the *para* substituents.

The findings of the present investigation appear anomalous when compared to the usual results obtained by variation of *meta* and *para* substituents in aromatic molecules. In the "usual reactions" *meta* and *para* substituents differ in their effect on rates and equilibria. However, in the Claisen rearrangement a substituent in either the *meta* or *para* position has an identical effect upon the rate. The "usual reaction" is heterolytic in character. This implies that the bond-breaking and bond-making in the Claisen rearrangement are of an alternate class.

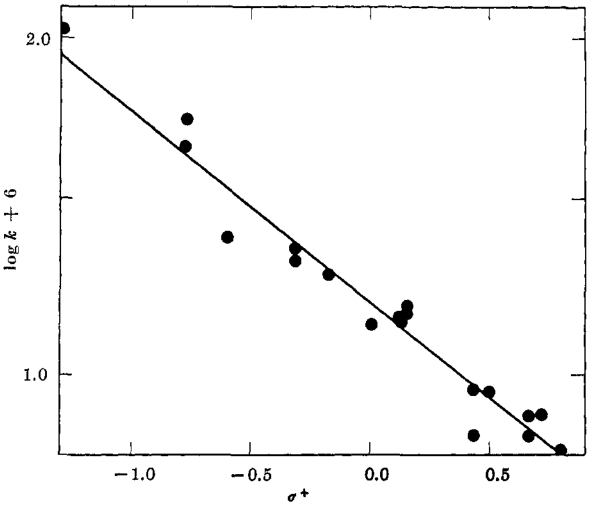
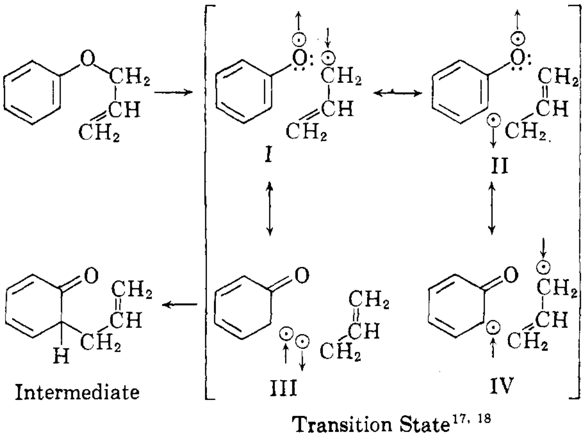


Fig. 2.—Hammett correlation of rates of rearrangement of allyl *m*-*X*-phenyl ethers to 2-allyl-5-*X*-phenols using σ^+ constants.

These results can best be interpreted in terms of a previously postulated mechanism[6] which can be represented by the following sequence:



The intermediate 6-allyl-2,4-cyclohexadienone rapidly enolizes to the product. This mechanism satisfactorily accounted for the substituent effects observed in the rearrangement of allyl *p*-*X*-phenyl ethers and *X*-cinnamyl *p*-tolyl ethers.[6]

If this mechanism is operative, a $\sigma_p{}^+$ correlation of the rates of rearrangement of allyl *m*-*X*-phenyl ethers would be plausible if structures of the following types (V and VI) contributed to the stabilization of the transition state as the substituent is making electrons available by direct resonance just as it does in the defining reactions for $\sigma_p{}^+$. These structures would be expected to be

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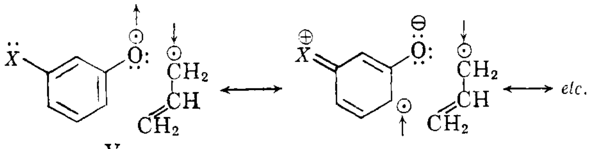
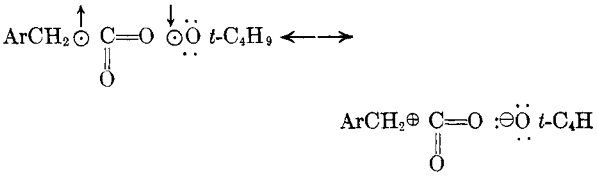
(17) Many other contributors that have different positions of the double bonds and electrons can be written—there are twenty nonpolar structures in all.

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



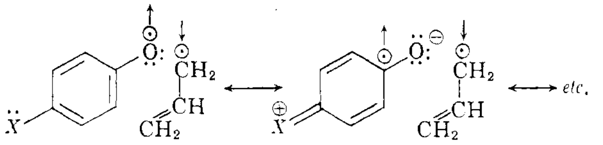
V VI

important contributors because the oxygen atom is highly electronegative and thus would tend to withdraw electrons from the ring by resonance, just as the oxygen atom in a carbonyl group usurps the π-electrons associated with the carbon atom. Moreover, the effect might be larger in the case of the phenoxy radical as the π-electron system of the aromatic ring is more mobile than that associated with the single carbon atom of a carbonyl group. This electron-withdrawing ability of oxygen with an unpaired electron is also implied by the σ^+ correlation of the rates of decomposition of *t*-butyl *X*-phenylperacetates and by the explanation given for this result[19]—*i.e.*, the transition state involved is stabilized as shown:



$$\mathrm{ArCH_2}\overset{\uparrow}{\odot}\ \underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}{=}\mathrm{O}\ \overset{\downarrow}{\odot}\ddot{\mathrm{O}}\ t\text{-}\mathrm{C_4H_9} \longleftrightarrow \mathrm{ArCH_2}^{\oplus}\ \underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}{=}\mathrm{O}\ :\ominus\ddot{\mathrm{O}}\ t\text{-}\mathrm{C_4H}$$

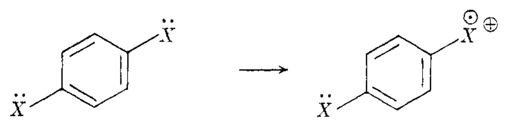
As the rates of rearrangement of allyl *p*-*X*-phenyl ethers are nearly the same as those of the corresponding substituted allyl *m*-*X*-phenyl ethers, a further requirement is that the following structures (VII and VIII) must stabilize the transition state for rearrangement of the *para* isomers to almost the same extent as structures V and VI stabilize the activated complex in the case of the *meta* isomers.



VII VIII

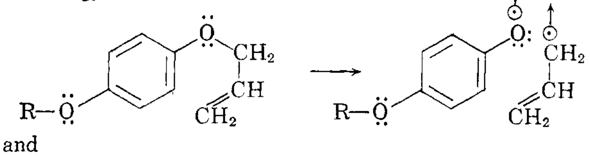
The question of the equivalence of contributions of structures VI and VIII is fairly difficult. It should be pointed out in this connection, however, that numerous resonance structures of the type of VI and VIII can be written for both series of substituents. These structures involve the same number of bonds and nearly equidistant formal charge separations. If anything, the charge separations in the structures for the *meta* series are less than those for their *para* isomers, so that the charged structures in the *meta* series should be more stable electrostatically. It thus appears, at least superficially, that there is no obvious reason why resonance stabilization should not be equal for the *meta* and *para* substituted series.

Molecular orbital calculations tend to support this conclusion. It was assumed that the electronic changes occurring as the reactant proceeded to transition state could be represented as

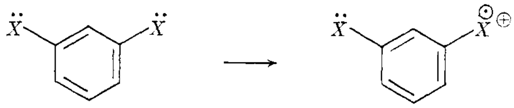


IX XI

in analogy to



and



XII XIII

in analogy to the change from the initial state to the activated complex for allyl *m*-*X*-phenyl ethers. Several calculations were made utilizing different values for the matrix element associated with the coulomb integral, H_{xx}, of the heteroatom *X*. A decrease in this term is associated with a "tightening" of the atomic orbital concerned, and is thus inversely related to the electronegativity of the atom—*i.e.*, as the electronegativity increases, the value of the matrix element decreases.

The m.o. calculations indicate that the presence of an electronegative, electron-rich substituent, X, in the molecule C_6H_5X facilitates the ionization (IX → XI or XII → XIII) regardless of whether the substituent is in the *meta* or the *para* position, although the effect is greater in the *para* position (Table XI). Values of the coulomb integral (H_{xx}) for oxygen used in the past vary from $\alpha + 0.5\beta$ to $\alpha + 4\beta$.[20] These computations, although only qualitative and suggestive, tend to support the possibility of resonance stabilization in these hy-

TABLE XI

CALCULATED IONIZATION ENERGIES

H_{xx}[a]	$-\Delta E$ (C_6H_5X)	$-\Delta E$ (m-$C_6H_4X_2$)	$-\Delta E$ (p-$C_6H_4X_2$)
α	$\alpha + 0.00\beta$	$\alpha + 0.00\beta$	$\alpha - 0.31\beta$
$\alpha + 0.5\beta$	$\alpha + .28\beta$	$\alpha + .24\beta$	$\alpha + .00\beta$
$\alpha + 1.0\beta$	$\alpha + .50\beta$	$\alpha + .45\beta$	$\alpha + .25\beta$
$\alpha + 1.5\beta$	$\alpha + .66\beta$	$\alpha + .59\beta$	$\alpha + .44\beta$
$\alpha + 2.0\beta$	$\alpha + .76\beta$	$\alpha + .69\beta$	$\alpha + .57\beta$
$\alpha + 2.5\beta$	$\alpha + .81\beta$	$\alpha + .75\beta$	$\alpha + .66\beta$

[a] H_{xx} = coulomb integral for the heteroatom, α = coulomb integral for carbon, and β = resonance integral for the carbon-carbon bond.

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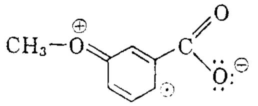
(20) A. Streitwieser, Jr., *J. Am. Chem.* Soc., **82**, 4123 (1960).

pothetical reactions from a *meta* substituent as well as from a *para* substituent. By analogy, *meta* substituents in allyl *X*-phenyl ethers may have a similar effect upon the Claisen rearrangement as *para* substituents.

Unfortunately, no similar substituent effects in mechanistically well defined situations have been reported, but systems that might be expected to show effects of this type have not yet been studied. However, the decompositions of substituted benzoyl peroxides[21,22] exhibit substituent effects similar in some respects to those found in the Claisen rearrangement. Thus, it is found that *m*-methoxybenzoyl peroxide is abnormally reactive, pyrolyzing several times faster than the unsubstituted compound. Its Hammett σ constant indicates it should be less reactive. This might be caused by stabilization of the incipient radical by structures such as



XIV

which are analogous to those postulated for the transition state of the rearrangement of allyl *m*-methoxyphenyl ether.

In summary, the kinetic and isomer distribution data on the Claisen rearrangement of allyl *m*-*X*-phenyl ethers are interpretable in terms of a transition state involving contributions from structures such as I, II, III, IV, V, and VI.

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Notes

Stereochemistry of Hydroboration

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Received February 19, 1962

The recent discovery by H. C. Brown and coworkers[2-4] of the anti-Markownikoff hydration of olefins, by hydroboration with subsequent oxidation, has already found many and significant applications in organic syntheses. Brown and Zweifel[5] have shown that the process involves stereospecific *cis* addition of diborane to the olefin followed by peroxidation to a borate ester with retention of configuration, so that the net result after hydrolysis of the latter is *cis* addition of water to the olefin. While the least substituted alcohols are always formed from aliphatic or alicyclic unsymmetrical olefins, polar effects seem to influence the direction of diborane addition in substituted styrenes.[6]

Steroid olefins represent ideal substrates to test conformational and steric effects in hydroboration. Addition of diborane to Δ^5-steroids took place predominately from the α-side,[7] suggesting that steric factors may be important in the reaction. In that case, however, the major product (a 6α-hydroxy-5α-steroid) was also the thermodynamically more stable one. We therefore decided to study the hydroboration of symmetrically substituted steroid olefins, where polarity effects are largely absent, in order to evaluate steric versus conformational effects. A recent description of similar work[8] prompts us to submit our results, which represent a more complete picture of the reaction of 2-cholestene.

From hydrolysis experiments on cholestanol acetates it is known that the 3-position is less hindered than the 2-position[9] in such compounds. If conformational factors were controlling the hydroboration of 2-cholestene, the products should be largely the equatorial 3β- and 2α-cholestanol with the former predominating. If steric factors were in control, one would expect mainly the α-cholestanols (predominantly 3α-cholestanol). Addition of diborane to 2-cholestene followed by alka-

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