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The *ortho*-Claisen Rearrangement. I. The Effect of Substituents on the Rearrangement of Allyl *p*-X-Phenyl Ethers[1,2]

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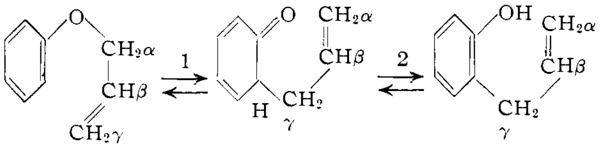
The rates of rearrangement of 13 allyl *p*-X-phenyl ethers have been determined. These rates can be correlated by using the ordinary form of Hammett's equation ($\log k/k_0 = \rho\sigma$) and σ^+ values or an expanded form of this equation ($\log k/k_0 = \rho_m\sigma_m + \rho_p\sigma_p$). The values of ρ thus determined are interpreted in terms of possible polar mechanisms for the *ortho*-Claisen rearrangement. This polar character of the reaction is also supported by preliminary observations on solvent effects.

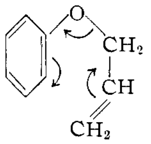
Introduction

A fairly large number of studies during the past two decades[4] have been concerned with the mechanism of the Claisen rearrangement, especially in regard to intramolecularity, steps, and the determination of which carbon of the allyl group becomes attached to the aromatic ring. These studies have proved that the reaction is intramolecular, and that while the γ-carbon of the allyl group becomes attached to the aromatic ring in the *ortho*-Claisen rearrangement, the α-carbon becomes attached in the *para* rearrangement. It also has been shown that the *para* rearrangement involves a dienone intermediate, and by analogy it is assumed that the *ortho* rearrangement involves a similar intermediate.[5] The current understanding of the *ortho*-Claisen rearrangement can therefore be summarized as



It has been intimated that neither step 1 nor step 2 is reversible and that step 1 is rate determining,[5] although Curtin and Crawford[6] have found that if enolization is blocked, a 6-allyl-2,4-cyclohexadienone will in part revert to the allyl ether.

Although the over-all details of the Claisen rearrangement are fairly well established, there has been no systematic study of the electrical, polar or electronic nature of the reaction. Differences in reaction velocity of variously substituted compounds have, however, been noted and interpreted in a qualitative way.[5,7] Thus, Schmid[5] explains the difference in reactivity as due to a difference in bond order of the 1,2-bond in the aromatic portion of the allyl aryl ether, while Tarbell and Wilson[7] postulate a directional flow of electrons during the rearrangement step



The polar nature of the reaction implied by a substituent effect is supported by the observation of Kincaid and Tarbell[8] that the rate of rearrangement of allyl *p*-tolyl ether in the absence of solvent gradually increased to about four times the initial rate as the medium changed from ether to phenol.

The investigation to be described was undertaken in an attempt to clarify and define polar influences on the *ortho*-Claisen rearrangement and to determine the electrical nature of the reaction.

Experimental

Preparation of Allyl *p*-X-Phenyl Ethers.—A mixture of 0.2 mole of *p*-X-phenol, 24.2 g. (0.23 mole) of allyl bromide, 28.0 g. (0.20 mole) of dry, powdered potassium carbonate, and sufficient dry acetone (about 50 cc.) to give an easily stirred mass was stirred and refluxed for eight hours. Then 150 cc. of water was added, and the mixture was extracted with two 75-cc. portions of ether. The combined ether solutions were washed with two 75-cc. portions of 10% sodium hydroxide solution and twice with 100-cc. portions of saturated brine. The washed ether solution was dried over potassium carbonate. The ether was decanted and evaporated. The residue was distilled under reduced pressure or crystallized several times to obtain samples for kinetic measurements.

All of the phenols, except *p*-cyanophenol, *p*-acetaminophenol and *p*-methylsulfonylphenol, were commercial products. These were purified by several crystallizations or distillations prior to use in synthesis so that the physical constants were in close accord with those in the literature.

p-Cyanophenol, m.p. 111.6–112.7° (lit.[9] m.p. 113°), was prepared in 53% yield by the von Braun reaction[10] on *p*-bromophenol.

p-Acetaminophenol, m.p. 168.5–169.5° (lit.[11] m.p. 168–169°), was obtained in 56% yield by acetylation of *p*-aminophenol with acetic anhydride.[12]

p-Methylsulfonylphenol, m.p. 94.8–95.6° (lit.[13] m.p. 95.5–96.5°), was synthesized from *p*-methoxybenzenesulfonyl chloride, m.p. 42.8–43.4° (lit.[14] m.p. 42–43°), by reduction to the sulfinic acid.[15] The salt of the sulfinic acid was refluxed with a solution of chloroacetic acid to yield *p*-methylsulfonylanisole, m.p. 120.3–120.8° (lit.[16] m.p. 121°), which was cleaved with hydrobromic acid[13] to obtain the desired product.

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[2] Given in part at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 11, 1957.

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[4] For an excellent summary of the recent studies of the mechanism of the Claisen rearrangement see D. J. Cram in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 5, pp. 295–303.

[5] H. Schmid, *Helv. Chim. Acta*, **20**, 13 (1957).

[6] D. Y. Curtin and R. J. Crawford, THIS JOURNAL, **79**, 3156 (1957).

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[8] J. F. Kincaid and D. S. Tarbell, *ibid.*, **61**, 3085 (1939).

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[10] M. S. Newman, *Org. Syntheses*, **21**, 89 (1941).

[11] L. Claisen, *Ann.*, **418**, 69 (1919).

[12] A. Lumière, L. Lumière and H. Barbier, *Bull. soc. chim. France*, [3] **33**, 783 (1905).

[13] F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).

[14] F. Fichter and W. Tamm, *Ber.*, **43**, 3032 (1910).

[15] F. C. Whitmore and F. H. Hamilton, *Org. Syntheses*, **2**, 89 (1922).

[16] M. E. Heppenstall and S. Smiles, *J. Chem. Soc.*, 899 (1938).

Allyl *p*-aminophenyl ether was obtained by hydrolysis of allyl *p*-acetaminophenyl ether.[11]

TABLE I

PREPARATION OF ALLYL *p*-X-PHENYL ETHERS

X	Yield, %	Crystn. solvent[a]	M.p. or b.p.,[b] °C. (mm.)	Reported, °C. (mm.)
NO_2	93	Distd.	124.5–126.0 (2.0)	160 (12)[c]
CN	77	Et. or bz.	47.3–48.7[d]	
CH_3SO_2	47	Bz. + cy.	72.0–73.4[e]	
CH_3CO	79	Distd.	116.0–117.5 (2.0)	147 (10)[f]
C_6H_5CO	89	Et.	78.0–78.7[g]	
H	82	Distd.	93.0–93.7 (29.0)	192 (760)[h]
Cl	75	Distd.	109.0–110.0 (15.0)	107 (12)[c]
Br	93	Distd.	110.5–111.5 (7.5)	126 (14)[c]
C_6H_5	82	Et.	83.7–84.8[i]	
CH_3	81	Distd.	97.5–98.5 (17.2)	91 (12)[c]
$NHCOCH_3$	87	Bz. + cy.	93.3–93.7	93[h]
CH_3O	84	Distd.	116.5–117.5 (11.5)	120 (13)[j]
NH_2	83	Distd.	111.0–112.5 (2.5)	136 (11)[h]

[a] et. = ethanol, bz. = benzene, cy. = cyclohexane, distd. = liquid product, distilled. [b] The entry in this column is a m.p. unless the previous column indicates the product was distilled in which case the entry is a b.p. [c] L. Claisen and O. Eisleb, *Ann.*, **401**, 21 (1913). [d] Calcd. for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.69; H, 5.89; N, 8.73. [e] Calcd. for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70. Found: C, 56.59; H, 5.85. [f] R. T. Arnold and J. C. McCool, THIS JOURNAL, **64**, 1315 (1942). [g] Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.66: H, 6.14. [h] L. Claisen, *Ann.*, **418**, 78 (1919). [i] Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.58; H, 6.81. [j] F. Mauthner, *J. prakt. Chem.*, **102**, 41 (1921).

TABLE II

PREPARATION OF 2-ALLYL-4-X-PHENOLS

X	Conditions Solvent[a]	Hr.	%	Crystn. solvent[b]	M.p. or b.p.,[c] °C. (mm.)	Reported °C. (mm.)
NO_2	DCB	6.0	59	Tet.	79.0–79.6	79[d]
CN	None	0.1	56	Tet.	83.1–84.3[e]	
CH_3SO_2	DPE	1.0	50	Tet.	80.8–81.4[f]	
CH_3CO	DPE	1.0	76	Bz.	115.9–116.7	115–116[g]
C_6H_5CO	DPE	1.0	73	Bz.	129.0–130.6[h]	
H	None	6.0	77	Distd.	119.5–120.5 (30.2)	220 (760)[i]
Cl	None	0.3	55	Distd.	130.0–132.0 (15.0)	125 (12)[d]
Br	None	0.1	51	Liq.	58.1–59.6	50[d]
C_6H_5	DPE	1.0	60	Cy.	74.9–75.6[j]	
CH_3	DPE	1.0	55	Distd.	112.5–113.5 (12.5)	112 (12)[d]
$NHCOCH_3$	DPE	0.1	63	Bz.	87.9–90.2	93[i]
CH_3O	DPE	1.0	62	Distd.	130.0–131.5 (6.0)	145 (13)[k]
NH_2	DPE	0.1	53	Bz.	112.3–114.0	112.5–113.5[l]

[a] DCB = *o*-dichlorobenzene, DPE = diphenyl ether. [b] tet. = carbon tetrachloride, bz. = benzene, lig. = ligroin, b.p. 30–60°, cy. = cyclohexane, distd. = liquid product, distilled. [c] The entry in this column is a m.p. unless the previous column indicates the product was distilled in which case the entry is a b.p. [d] L. Claisen and O. Eisleb, *Ann.*, **401**, 21 (1913). [e] Calcd. for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.59; H, 5.90; N, 8.87. [f] Calcd. for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70. Found: C, 56.78; H, 5.74. [g] R. T. Arnold and J. C. McCool, THIS JOURNAL, **64**, 1315 (1942). [h] Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.85; H, 6.07. [i] L. Claisen, *Ann.*, **418**, 79 (1919). [j] Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.47; H, 6.92. [k] F. Mauthner, *J. prakt. Chem.*, **102**, 41 (1921). [l] W. A. Jacobs and M. Heidelberger, THIS JOURNAL, **39**, 2188 (1917).

Preparation of 2-Allyl-4-X-phenols.—The allyl *p*-X-phenyl ether (0.05 mole) was refluxed either alone or in 10–20 cc. of solvent for a short period. The reaction mixture was cooled, dissolved in 50 cc. of ligroin, b.p. 65–110°, and extracted with two 25-cc. portions of 20% sodium hydroxide solution. The combined basic solutions were washed twice with 25 cc. of petroleum ether, b.p. 30–60°, and then acidified with 30 cc. of concd. hydrochloric acid. The resulting mixture was extracted three times with 50-cc. portions of ether. The combined ether solutions were dried over calcium chloride. The ether was decanted and evaporated, and the residue was distilled or crystallized several times to effect purification.

Kinetics of the Rearrangement Reaction.—Samples of the allyl *p*-X-phenyl ethers were dissolved in sufficient dry, purified solvent to yield solutions varying in concentration from 0.05 to 0.10 molar. Portions (about 1.5 cc.) of these solutions were sealed in small Pyrex test-tubes which were immersed in a constant temperature paraffin bath for various timed intervals.

TABLE III

COMPARISON OF LIGHT ABSORPTION OF ALLYL *p*-X-PHENYL ETHERS AND SODIUM 2-ALLYL-4-X-PHENOXIDES

X	λ[a]	ϵ_E[a]	ϵ_p[a]	X	λ[a]	ϵ_E[a]	ϵ_p[a]
NO_2	314	10500	830	Cl	247	220	9570
	415	40	19000		302	0	3400
CN	248	19500	2540	Br	246	980	10100
	283	480	20300		302	10	3260
CH_3SO_2	240	17000	1990	C_6H_5	260	20100	4060
	271	880	17200		300	740	18900
CH_3CO	243	2550	7660	CH_3	239	320	7290
	276	15700	2110		299	0	3310
	334	110	23100	$NHCOCH_3$	245	11900	7270
C_6H_5CO	294	16700	2410		300	240	4940
	355	300	21300	CH_3O	238	1480	7610
H	240	90	8170		308	30	3880
	291	0	3580	NH_2	236	9860	[b]
					300	2300	[b]

[a] λ = wave length in millimicrons, ϵ_E = molar extinction coefficient of allyl *p*-X-phenyl ether, ϵ_p = molar extinction coefficient of sodium 2-allyl-4-X-phenoxide. [b] 2-Allyl-4-aminophenol oxidized too rapidly in alkaline solution to have its extinction coefficient determined.

The contents of the tubes were analyzed by taking advantage of the difference in ultraviolet and visible light absorption of the starting material (a phenyl ether) and the sodium salt of the product (a phenol). Table III lists the relevant data.

These were not the only maxima observed for these compounds, but were the only ones for which there was a considerable difference between the absorption of the ether and the corresponding phenoxide and, therefore, were the only peaks useful for analytical purposes. In order to take advantage of this difference of absorption, it was necessary to convert the rearrangement product to its sodium salt. This was done by using 0.1 *M* aqueous or alcoholic sodium hydroxide solutions as solvent for the spectral determinations.

In particular, for the kinetic determinations, the sealed Pyrex test-tubes containing the sample were broken open and a 1.00-cc. aliquot removed and diluted in successive steps in volumetric flasks with 0.1 *M* sodium hydroxide solution in 95% ethanol or water to yield a final solution having an easily measurable optical density.

Graphical application of the integrated first-order rate expression

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

where

k = specific rate constant
t = time (sec.)
D_∞ = optical density at infinite time
D_0 = optical density at zero time
D_t = optical density at time t

gave excellent straight lines and close correlation between individual runs. This equation was applied to at least two wave lengths in each run, and the correspondence between these independently calculated rate constants was very close. The optical density at infinite time was taken to be that of the pure phenol.

This procedure was applicable to all of the ether rearrangements except that of allyl *p*-aminophenyl ether. In this case the alkaline solutions of the 2-allyl-4-aminophenol became oxidized at such a rate that the optical density could not be determined easily. For this reason a slightly different procedure was developed. A 1.00-cc. aliquot of the reaction mixture was added to 10.0 cc. of 1 *M* sodium hydroxide solution and the resulting mixture was extracted five times with 9-cc. portions of cyclohexane. The cyclohexane was collected in a 50.00-cc. volumetric flask and made up to volume with cyclohexane. An aliquot of this solution was further diluted with 95% ethanol to yield a solution with an easily determinable optical density. This method also resulted in excellent first-order kinetics.

Results

The specific rate constants of 13 allyl *p*-X-phenyl ethers were determined at 181.1 ± 0.1° using Carbitol (ethyl ether of diethylene glycol) as solvent (Table IV). The reaction was followed to at least 60% completion in all cases and for most of the runs to 70–90%. From 6 to 12 points were determined in each run and these generally lay neatly along a straight line when t was plotted against log $(D_\infty - D_t)$. The average percentage deviation of all these rate constants from their individual means is 3.2%. The experiments with allyl *p*-cyanophenyl ether and allyl *p*-acetaminophenyl ether require some comment since these two compounds have substituents subject to alcoholysis, and Carbitol is an alcohol. In neither case was it apparent that this side reaction was seriously interfering—excellent straight kinetic plots were obtained. Furthermore, it was found possible to preparatively rearrange these ethers in refluxing Carbitol to obtain good yields of the expected phenol (84% 2-allyl-4-acetaminophenol and 73% 2-allyl-4-cyanophenol). Finally, the usual analytical procedure was applicable to allyl *p*-acetaminophenyl ether rearranged in Carbitol indicating the easily oxidizable 2-allyl-4-aminophenol was not present. However, some broadening of the absorption bands was noted when the rearrangement of the allyl *p*-cyanophenyl ether was carried to 85% completion. These results can be explained, on one hand, by the relatively rapid rearrangement of the allyl *p*-acetaminophenyl ether and, on the other, by the inertness of nitriles to alcoholysis in the absence of acid or basic catalysts.

TABLE V

TEMPERATURE DEPENDENCE OF RATE AND ACTIVATION PARAMETERS FOR REARRANGEMENT OF ALLYL *p*-X-PHENYL ETHERS

X	$k_1 \times 10^6$(sec.$^{-1}$) at temp. (°C.) 159.77 ± 0.04°	 180.92 ± 0.03°	 199.75 ± 0.06°	Ea[a]	ΔH^*[b]	ΔS^*[c]
C_6H_5CO	2.30 ± 0.07	15.7 ± 0.5	67.9 ± 2.0	34.5	33.6	− 7.3
Br	4.66 ± .12	24.8 ± .6	94.6 ± 3.0	30.7	29.8	−14.8
H	4.54 ± .20	25.9 ± .6	108.0 ± 2.0	32.2	31.3	−11.5
CH_3	8.71 ± .08	47.1 ± .4	187.6 ± 2.4	31.2	30.3	−12.6
CH_3O	17.3 ± .3	86.6 ± .9	357.2 ± 1.0	30.8	29.9	−12.1

[a] Kcal./mole. [b] Kcal./mole. [c] Cal./deg./mole.

TABLE IV

RATE CONSTANTS FOR REARRANGEMENT OF ALLYL *p*-X-PHENYL ETHERS AT 181.1 ± 0.1° IN CARBITOL

X	n[a]	$k_1 \times 10^5$, sec.$^{-1}$	X	n[a]	$k_1 \times 10^5$, sec.$^{-1}$
NO_2	3	1.03 ± 0.09	Br	3	2.77 ± 0.05
CN	3	1.13 ± .03	C_6H_5	2	3.68 ± .08
CH_3SO_2	2	1.34 ± .04	CH_3	8	4.42 ± .01
CH_3CO	2	1.58 ± .02	$NHCOCH_3$	1	5.79
C_6H_5CO	2	1.60 ± .07	CH_3O	3	9.16 ± 0.12
H	3	2.56 ± .01	NH_2	1	21.3
Cl	2	2.63 ± .01			

[a] n = number of runs.

The temperature dependence of the rate of rearrangement of five allyl *p*-X-phenyl ethers was investigated and from the results, the thermodynamic quantities of activation were computed by standard procedures[17] (Table V).

Finally, the influence of solvent on the kinetics of rearrangement was investigated using allyl *p*-tolyl ether (Table VI).

Discussion

The purpose of this investigation was to obtain information regarding the fundamental nature of the *ortho*-Claisen rearrangement and, in particular, information about any possible electrical effects on the reaction. Knowledge of this latter type is usually secured by studying the influence of substituents on the reaction and comparing the results with the effect of the same substituents on another reaction, the electrical nature of which is purportedly well-understood. Although this comparison is often done qualitatively, a quantitative or semi-quantitative comparison can be achieved by application of Hammett's equation.[18,19] Through this equation it is possible to relate the electrical effects in the reaction being studied with that in the dissociation of substituted benzoic acids,[18,19] or substituted anilines or phenols,[18,19] or substituted di- or triphenylmethanols in sulfuric acid.[20]

TABLE VI

SOLVENT INFLUENCE ON RATE OF REARRANGEMENT OF ALLYL *p*-TOLYL ETHER IN CARBITOL AT 181.1 ± 0.1°

Solvent	$k_1 \times 10^5$, sec.$^{-1}$
n-Octane	0.80
Adiponitrile	2.47
Tetrahydrothiophene dioxide	3.14
Carbitol	4.39
Carbitol + 10% LiCl	5.96

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(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 95–97.

(18) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 184–198.

(19) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(20) N. C. Deno and W. L. Evans, THIS JOURNAL, **79**, 5804 (1957).

With the aim of defining the electrical nature of the *ortho*-Claisen rearrangement, Hammett's equation ($\log k_X/k_H = \rho\sigma$) was applied to the experimental rate constants for the rearrangement of the 13 allyl *p*-X-phenyl ethers. Actually, the slightly modified equation

$$\log k_x = \rho\sigma + b \qquad (1)$$

was used in order not to give undue weight to the rate constant for the unsubstituted compound (k_H); b is therefore the intercept of the line defined by this equation on the $\log k_x$ axis or the calculated value of $\log k_H$. To apply this equation it is necessary to have values of σ, the variable that describes the effect of the substituent on the standard reaction. The values of σ employed in this study are summarized, and their source indicated in Table VII.

TABLE VII

SUBSTITUENT CONSTANTS (σ)

X	σp[a]	σm[a]	σ^{-}[a]	σ^{-}[b]
NO_2	0.778	0.710	1.270	0.778
CN	.628	.678	1.000	.628
CH_3SO_2	.728	.647	1.049	.728
CH_3CO	.516	.306	0.874	.516
C_6H_5CO	.429[c]	.343[c]	(.727)[d]	.429[c]
H	.000	.000	.000	.000
Cl	.227	.373	.227	.06
Br	.232	.391	.232	.09
C_6H_5	.009	.06[c]	.009	− .157[f]
CH_3	− .170	− .069	− .170	− .31
$NHCOCH_3$	− .086[e]	.102[b]	− .086[e]	− .48
CH_3CO	− .268	.115	− .268	− .76
NH_2	− .660	− .161	− .660	−1.33

[a] Ref. 19 unless otherwise indicated by a footnote to this table. [b] Ref. 20 unless otherwise indicated by a footnote to this table. [c] From unpublished work by W. N. White, R. C. Schlitt and D. Gwynn on dissociation constants of substituted benzoic acids. [d] From the assumption $\sigma^{-}(C_6H_5CO) = \sigma^{-}(CH_3CO) \times \sigma(C_6H_5CO)/\sigma(CH_3CO)$. [e] N. Lichtin, THIS JOURNAL, **74**, 4207 (1952). [f] From the data of N. Lichtin and P. D. Bartlett, THIS JOURNAL, **73**, 5530, 5537 (1951), concerning the dissociation constants of triarylmethyl chlorides in sulfur dioxide by application of σ^{+} values.

The experimental data were fitted to the modified form of Hammett's equation using the least squares method.[21] Correlation coefficients (r) and standard deviations (s) from the regression line were calculated by standard procedures.[21] This treatment leads to the results tabulated in the first four rows of Table VIII and illustrated in Figs. 1, 2, 3 and 4.

TABLE VIII

APPLICATION OF HAMMETT'S EQUATION

σ[a]	ρ[b]	b[b]	r[c]	s[c]	%[d]
σ_p	−0.862	+0.628	0.964	0.106	18.6
σ_m	−1.093	+ .765	.826	.225	41.5
σ^{-}	−0.597	+ .665	.934	.143	25.5
σ^{+}	−0.609	+ .480	.994	.043	7.1
σ_m and	$\rho_m = +0.593$	+ .536	.979	.085	15.6
σ_p	$\rho_p = -1.232$				
σ_m and	$\rho_m = +0.103$	+ .453	.995	.041	6.0
σ^{+}	$\rho^{+} = -0.649$				

[a] Type of σ constant (Table VII) used for fitting equation. [b] Value of σ and b obtained by least squares method. [c] r = correlation coefficient, s = standard deviation (ref. 21). [d] Percentage mean deviation in estimation of rate constant (not $\log k$) from equation.

An inspection of these figures and the first four rows in the table reveals that the best correlation of the experimental data is obtained using the set of σ^{+} constants (for perfect correlation, $r = 1$ and $s = 0$), while the poorest fit of the kinetics results from application of the σ_m constants. This may indicate that reactivity is mainly determined by breaking of the allyl–oxygen bond which takes place at the position *para* to the substituent rather than by the formation of the new allyl–carbon bond which occurs *meta* to the substituent. The fact that in the over-all rearrangement, reaction occurs both at the position *para* to the substituent and also at the position *meta* to it suggests that the form of Hammett's equation that has been employed is too simple and that a modified equation taking account of this dual effect of the substituent should be used.

$$\log k_x = \rho_m\sigma_m + \rho_p\sigma_p + b \qquad (2)$$

An equation of this form has been suggested by Jaffe[19] for reactions involving two positions on an aromatic ring. When this equation is made to conform to the kinetic results the correlation of the data is improved (last two rows of Table VIII and Figs. 5 and 6) but this would be anticipated for an increase in the number of variables. Therefore, it is not necessarily significant that this equation more faithfully reproduces the experimental data.

The electrical nature of a reaction is often deduced from the sign and magnitude of its ρ value by comparison with the ρ of a standard reaction, such an aromatic acid dissociation, in which the electrical effects are clearly delineated. However, this procedure is not without its dangers since it must be shown that the reaction under consideration was measured below its isokinetic temperature[22] so $\Delta H^{\ddagger}$ is dominant in the determination of $\Delta F^{\ddagger}$. For most reactions which have been studied sufficiently to allow the isokinetic temperature to be determined, the isokinetic temperature is above the temperatures at which the reaction was studied. Thus, most simple correlations of reactivity by substituent effects have proved to be valid. The isokinetic temperature for the *ortho*-Claisen rearrangement was determined by application of the equation[22]

$$\Delta H^{\ddagger} = \beta\Delta S^{\ddagger} + \Delta H^{\ddagger}_0$$

(β = isokinetic temperature, $\Delta H_0^{\ddagger}$ = a constant) to the data in Table V. The equation calculated is

$$\Delta H^{\ddagger} = 540\ \Delta S^{\ddagger} + 37{,}320$$

($r = 0.942$, $s = 614$). The isokinetic temperature is, therefore, 540°K. The experimental temperature was lower than this (454°K.). Thus, the values of ρ found by use of equations 1 and 2 can be utilized to define the electrical nature of the Claisen rearrangement by comparison with ρ values of reactions in which the polar character is more apparent.

The usual standard of comparison is the aqueous ionization reaction of aromatic acids for which ρ is defined as + 1. All the ρ values estimated by use

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[21] G. W. Snedecor, "Statistical Methods," The Iowa State College Press, Ames, Iowa, 1946.

[22] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

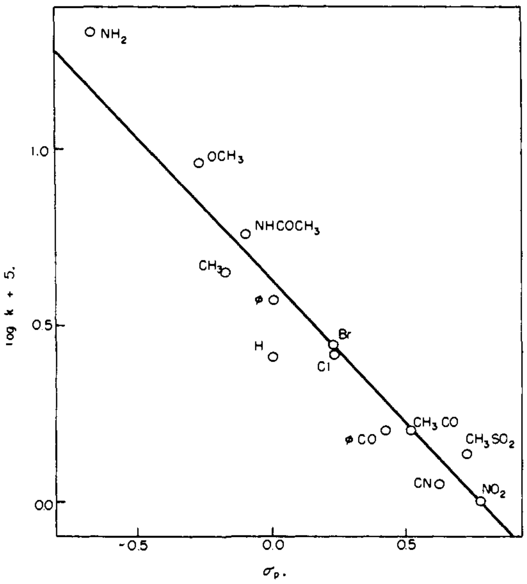


Fig. 1.—Hammett plot utilizing equation 1 and the set of σ_p values ($\rho = -0.862$).

of equation 1 are, on the other hand, negative, and about -1 as are the ρ_p values from equation 2, although the ρ_m values are small and positive. Since dissociation of the acids is aided by electron withdrawal and hindered by electron donation to the reactive center, the opposite must be true of the Claisen rearrangement—electron withdrawal from the ring by the substituent hinders the reaction; electron donation aids it. If equation 2 really applies, then the slightly modified conclusion must be that the reaction is aided greatly by electron donation to the *p*-position and slightly by electron attraction from the *m*-position by the substituent. This conclusion about the importance in the Claisen rearrangement of electron donation by the substituent is supported by the improvement observed when the sets of σ^+ values are utilized. These normally are useful only for strongly electron-demanding reactions.[23]

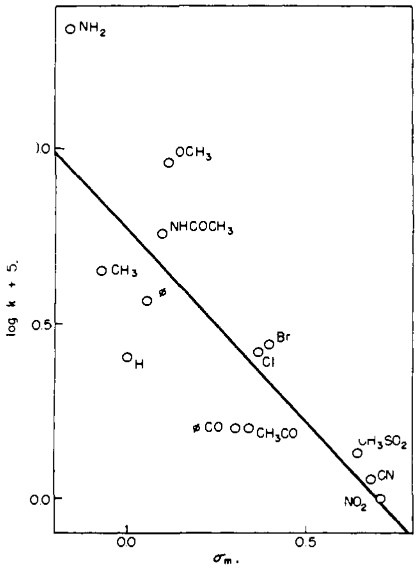


Fig. 2.—Hammett plot utilizing equation 1 and the set of σ_m values ($\rho = -1.093$).

The interpretation of these conclusions is by no means unambiguous or definite, especially since there is some question as to whether equation 1 utilizing σ^+ values or equation 2 most nearly correctly reflects the molecular action. Several possibilities present themselves, and at least one of these may be readily ruled out.

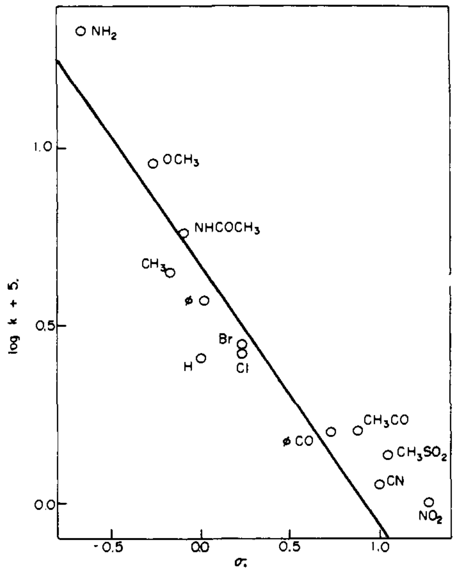


Fig. 3.—Hammett plot utilizing equation 1 and the set of σ^- values ($\rho = -0.597$).

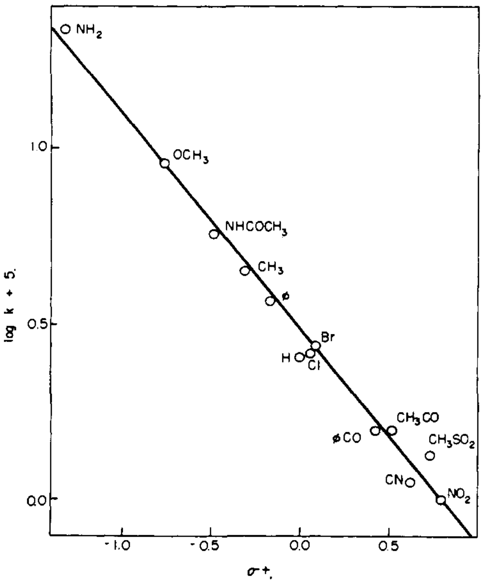


Fig. 4.—Hammett plot utilizing equation 1 and the set of σ^+ values ($\rho = -0.609$).

If equation 2 represents the true physical phenomenon of the Claisen rearrangement, the observed ρ values are very neatly explained by assuming that the enolization of the intermediate cyclohexadienone is involved in the determination of the rate. This seems unlikely, however, since the

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

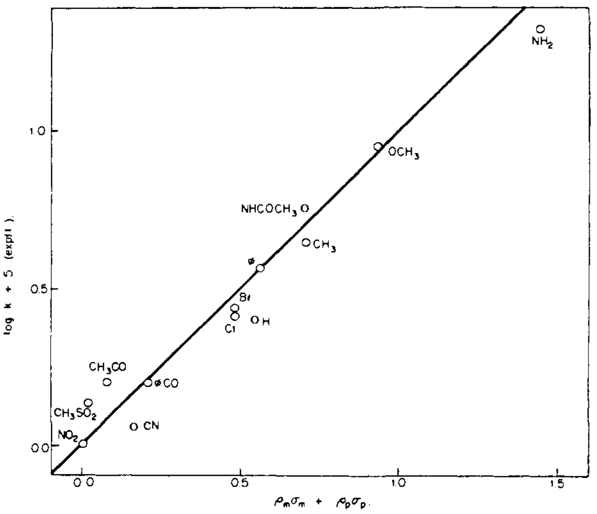


Fig. 5.—Plot of logarithms of rate constants calculated from equation 2, the parameters in Table VIII, and the sets of σ_m and σ_p values against the logarithms of the experimental rate constants ($\rho_m = +0.593$, $\rho_p = -1.232$).

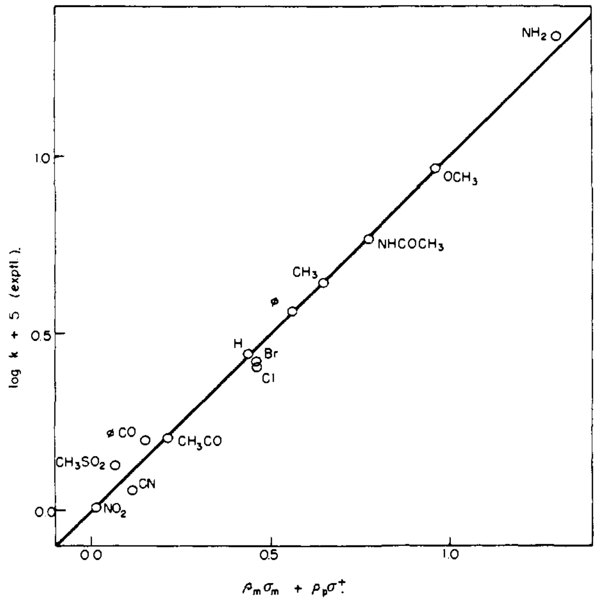
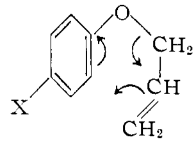


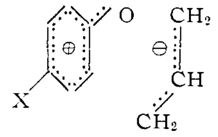
Fig. 6.—Plot of logarithms of rate constants calculated from equation 2, the parameters in Table VIII, and the sets of σ_m and σ^+ values against the logarithms of the experimental rate constants ($\rho_m = +0.103$, $\rho^+ = -0.649$).

Claisen rearrangement apparently is insensitive to the presence of acids or bases.[8] The enolization of other ketones *is* subject to acid and base catalysis.[24,25]

If the enolization step is not important in the determination of rate of rearrangement, then the rate effect of substituents must be interpreted in terms of the rearrangement step. There are several possibilities. If the concerted Hurd–Pollack mechanism[26] is accepted, then equation 2 would be followed since reaction is occurring simultaneously or almost simultaneously both at the position *para* to the substituent and at the position *meta* to it. The experimental ρ values would demand that bond-making and bond-breaking be somewhat polar in nature and not of equal importance in the activated complex and that the *over-all* electronic change be able to be summarized as

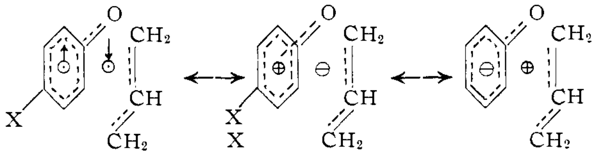


Another potential mechanism, probably first suggested by Cram,[27] is that "ion-pairs (of a highly oriented character)" may possibly intervene between the allyl aryl ether and the dienone intermediate. It seems improbable that ion-pairs of the classical type envisaged by Bjerrum could maintain at the usual rearrangement temperatures the relationship of the two ends of the allyl group to the oxygen and *ortho*-carbon of the phenol ring required by the radioactive tracer results of Ryan and O'Connor[28] and Schmid and Schmid[28] or the stereospecificity found by Alexander and Kluiber.[29] For an ion-pair mechanism the values of ρ determined by either equation 1 or 2 would require the allyl group to ionize as an anion and the aromatic moiety as a cation.



although at first sight unusual, theoretical considerations lead one to expect this mode of ionization (*vide infra*).[30]

A final possibility is that a transition state or intermediate is of the nature of a charge transfer complex[31]—that is, the two molecular fragments (allyl and aryloxy groups) are held together by electronic interaction which might be represented by the resonance structures



I II III

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(24) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. X, p. 529.

(25) However, if the proton was transferred intramolecularly, acid or base catalysis might not be observed. This appears improbable. Furthermore, unpublished work from this Laboratory has shown that there is no observable isotope effect in the rearrangement of allyl 2-deutero-4-methylphenyl ether ruling out this possibility.

(26) C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

(27) Reference 1, Chapt. 5, p. 302, and This Journal, **74**, 2129 (1952).

(28) J. P. Ryan and P. R. O'Connor, *ibid.*, **74**, 5866 (1952); H. Schmid and K. Schmid, *Helv. Chim. Acta*, **35**, 1879 (1952); **36**, 489 (1953).

(29) E. R. Alexander and R. W. Kluiber, This Journal, **73**, 4304 (1951).

(30) The fact that γ-methallyl aryl ethers rearrange 2.5 times as fast as the corresponding allyl aryl ethers (unpublished work of the authors) is difficult, but not impossible, to explain on the basis of the ion-pair mechanism since it would be expected that the inductive effect of the γ-methyl group would destabilize the allyl anion moiety of the intermediate ion-pair, and thus hinder its formation, although it would probably aid its collapse to covalent species.

(31) R. S. Mulliken, This Journal, **74**, 811 (1952).

Strong interaction of this nature is possible since the carbons of the allyl group may lie in a plane directly over the aryloxy grouping so that the α-carbon of the allyl group is over the oxygen of the aryloxy moiety, the β-carbon is over the 1-position of the ring, and the γ-carbon over the 2-position. This places one terminal carbon of the allyl group over the oxygen from which it breaks away and the other over the *o*-carbon to which it becomes bonded. This complex must be very short-lived if it is to maintain its orientation. The substituent data are explained if structure II contributes more to the resonance hybrid than III—a positive charge which is stabilized by electron donation is placed on the aromatic ring during reaction and as a final stage, if equation 2 is to apply, a negative charge is cancelled at the position *meta* to the substituent requiring electron withdrawal. That II actually would contribute more than III is indicated by the fact that the difference between the ionization potential of the benzyl radical[32] and the electron affinity of the allyl radical[33] is about 17 kcal./mole greater than the difference between the ionization potential[32] of the allyl radical and the electron affinity of the benzyl radical.[33] Although this comparison is not precise because the actual system involves a phenoxy radical rather than a benzyl radical, it is likely that the comparison is justified since the electron affinity of phenoxy radical[34] is even less positive than that of benzyl radical by 14 kcal./mole. Finally, this latter mechanism is supported by an analogy to the Diels–Alder reaction for which a charge transfer complex mechanism has been postulated by Woodward.[35] Like the Claisen rearrangement, the effect of substituents on the Diels–Alder reaction of 1-(*p*-X-phenyl)-1,3-butadienes and maleic anhydride has been found to be most suitably correlated by use of the σ^+ constants and a small, negative ρ.[23,36]

The existence of a polar intermediate or transition state in the Claisen rearrangement is demonstrated not only by the substituent effects but also by the preliminary results on the effect of solvent (Table VI). A semi-quantitative treatment of the data is not possible since the dielectric constants of these solvents have not been measured at the temperature of rearrangement, and the change of dielectric constant with temperature is different for different solvents. However, it is encouraging that the solvent of lowest dielectric constant at ordinary temperatures (*n*-octane) yields a rate one-third to one-seventh that obtained with the other solvents, and that the addition of a salt to Carbitol (which should increase the dielectric constant) increases the rate. The solvent rate effect observed for the Claisen rearrangement is similar in magnitude to that for the Menschutkin reactions of methyl iodide in benzene–nitrobenzene mixtures,[37] a reaction which is most definitely polar in nature.

There are, therefore, at least three reasonable mechanistic explanations for the substituent and solvent effects observed in the Claisen rearrangement. Unfortunately, at present, there is not enough experimental information available to decide among these possibilities.

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(32) D. P. Stevenson quoted by A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(33) N. S. Hush and K. B. Oldham quoted by H. O. Pritchard, *ibid.*, **52**, 529 (1953).

(34) N. S. Hush quoted in H. O. Pritchard, *ibid.*, **52**, 529 (1953).

(35) R. B. Woodward, THIS JOURNAL, **62**, 3058 (1942); R. B. Woodward and H. Baer, *ibid.*, **66**, 645 (1944).

(36) The effect of a γ-methyl group in the allyl portion of the ether (footnote 30) can be explained as being due to a larger contribution by structure III to the hybrid. The additional methyl group should tend to stabilize III.

(37) H. C. Raine and C. N. Hinshelwood, *J. Chem. Soc.*, 1378 (1939); K. J. Laidler and C. N. Hinshelwood, *ibid.*, 858 (1938).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A Kinetic Study of the *ortho*-Claisen Rearrangement[1]

BY HARLAN L. GOERING AND ROBERT R. JACOBSON

RECEIVED JANUARY 27, 1958

The relative rates of the *ortho*-Claisen rearrangement of allyl phenyl ether, fifteen *m*- and *p*-substituted allyl phenyl ethers and α-, β- and γ-methyallyl phenyl ether at 185 and 197° in diphenyl ether have been determined. A dilatometric method for following the reaction accurately using low concentrations (about 0.1 *M*) of substrate was developed. The relative rates of rearrangement of allyl *p*-cresyl ether in twelve solvents also have been determined. The relative reactivities of the series of *p*-substituted allyl phenyl ethers can be correlated by the σ^+ substituent constants.

Introduction

In many respects the *ortho*-Claisen rearrangement[2] is similar to the intramolecular (SNi′) rearrangement of allylic esters.[3] Both of these reactions are first-order intramolecular processes.[2,3] The relative positions of the atoms in the reactants and products are the same for the two reactions and in each case the over-all reaction can be summarized as a six-membered cyclic process as illustrated by I and II.[4] In the Claisen rearrangement

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(1) This work was supported in part by the Office of Ordnance Research, U. S. Army, and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, Chapt. 1.

(3) (a) H. L. Goering and R. W. Greiner, THIS JOURNAL, **79**, 3464 (1957); (b) H. L. Goering, J. P. Blanchard and E. F. Silversmith, *ibid.*, **76**, 5409 (1954); H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 1129 (1955); (c) unpublished work of R. H. Jagow and M. M. Pombo.

(4) It recently has been shown with O^{18}-labeled esters that in the SNi′ rearrangement of allylic esters the carbonyl oxygen atom in the reactant becomes the alkyl oxygen atom in the product as illustrated by II; W. E. Doering, private communication (1955); E. A. Braude and D. W. Turner, *Chemistry & Industry*, 1223 (1955).