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).

COLUMBUS 10, OHIO

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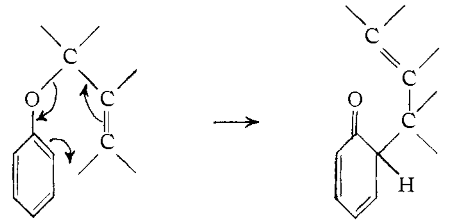
[1] This work was supported in part by the Office of Ordnance Research, U. S. Army, and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

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

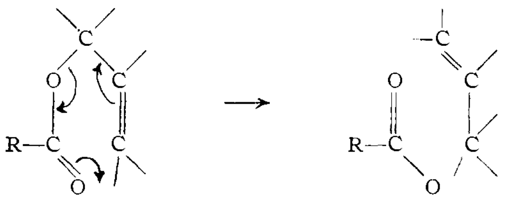
[3] (a) H. L. Goering and R. W. Greiner, THIS JOURNAL, **79**, 3464 (1957); (b) H. L. Goering, J. P. Blanchard and E. F. Silversmith, *ibid.*, **76**, 5409 (1954); H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 1129 (1955); (c) unpublished work of R. H. Jagow and M. M. Pombo.

[4] It recently has been shown with O^{18}-labeled esters that in the S$_N$i′ 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).

(I) the initially formed dienone is converted to the corresponding phenol.

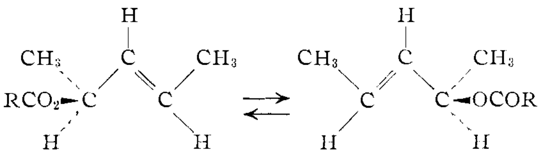


I

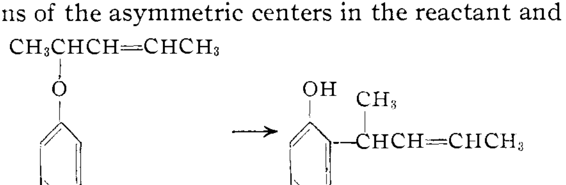


II

It would appear that the stereochemical relationship between reactant and product should be the same for the two reactions, however, there is evidence that this may not be the case. It has been demonstrated[3a,3c] that in the rearrangement of *trans*-α,γ-dimethylallyl esters (III), the configuration of the asymmetric carbon in the product is opposite that of the asymmetric carbon in the reactant, *i.e.*, in this system the product and reactant are enantiomers as illustrated below. On the other hand, it has been concluded[5] that in the Claisen rearrangement of optically active *trans*-α,γ-dimethylallyl phenyl ether (IV),[6] the configurations of the asymmetric centers in the reactant and product (V) are the same. If this conclusion is correct, the stereochemical relationship between reactant and product differs for the two cases. In another problem the relative configurations of IV and V are being re-examined to determine whether this apparent discrepancy is real.

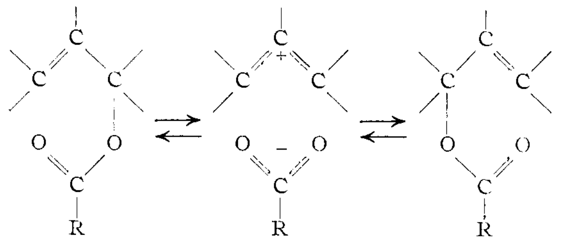


IIIa IIIb



IV V

Considerable information concerning the timing and nature of the electronic shifts in the S_Ni' rearrangement summarized by II has been presented in earlier papers.[3] It appears that an intermediate VI (an "internal ion-pair" intermediate according to Winstein's classification[7]) is involved in this reaction as follows. As indicated previously[3a] there is evidence that there is some covalent bonding between the allylic carbon atoms and the oxygen atoms in VI. It has been suggested[8] that similar intermediates may be involved in other intramolecular processes including the Claisen rearrangement. In order to obtain information concerning mechanistic details of the *ortho*-Claisen rearrangement (I) we have examined the effects of substituents and variation of solvent on the rate of rearrangement. The results of this investigation are presented in this paper.



VI

The rates of the *ortho*-Claisen rearrangement of a few aryl allyl ethers in the absence of solvent have been reported previously.[9,10] Kinetic studies of the rearrangement of allyl *p*-cresyl ether in diphenyl ether[10] and allyl 2,4-dimethylphenyl ether in diethylaniline[11] also have been described. In the latter two cases rather high concentrations of substrate were used (5–33% by weight of the reaction mixture) and the reactions were followed by determination of the amount of phenol formed by quantitative acetylation. This method is limited to non-hydroxylic solvents and probably could not be used with low concentrations of substrate.

In the present work a dilatometric method was developed which can be used to follow reactions at temperatures up to 200°. Previously dilatometry has been used to follow reactions only at temperatures near room temperature.[12] Details of this method are included in the Experimental section. With it the *ortho*-Claisen rearrangement can be followed with a high degree of accuracy at temperatures of 185–200° using low concentrations of substrate (about 0.1 *M*). We have used this method to determine (a) the relative reactivities of allyl phenyl ether and eighteen substituted allyl phenyl ethers and (b) the relative rates of rearrangement in twelve solvents.

Experimental

Allyl Phenyl Ethers.—Except as noted below all of the ethers were prepared by the following method which is a modification of the method used by Claisen.[13] A solution of 0.2 mole of phenol, 0.22 mole of allyl bromide and 0.22 mole of potassium carbonate in 50 ml. of dry acetone was refluxed for 8 hours. After cooling, the reaction mixture was diluted with 250 ml. of water and extracted with three 35-ml. portions of ether. The organic layer was washed first with 10% aqueous sodium hydroxide and then with water and dried over magnesium sulfate. After removal of the solvent the residue was fractionated under reduced

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[5] H. Hart, THIS JOURNAL, **76**, 4033 (1954).

[6] E. R. Alexander and R. W. Kluiber, *ibid.*, **73**, 4304 (1951).

[7] S. Winstein, E. Clippinger, A. Fainberg, R. Heck and G. Robinson, *ibid.*, **78**, 328 (1956).

[8] D. J. Cram, *ibid.*, **74**, 2129 (1952); **75**, 332 (1953).

[9] H. Schmid and K. Schmid, *Helv. Chim. Acta*, **35**, 1879 (1952).

[10] J. F. Kincaid and D. S. Tarbell, THIS JOURNAL, **61**, 3085 (1939).

[11] F. Kalberer and H. Schmid, *Helv. Chim. Acta*, **40**, 13 (1957).

[12] (a) J. N. Brönsted, *et al.*, THIS JOURNAL, **49**, 2554 (1927); **51**, 428 (1929); (b) L. K. J. Tong and A. R. Olson, *ibid.*, **65**, 1704 (1943).

[13] L. Claisen and O. Eisleb, *Ann.*, **401**, 21 (1913).

TABLE I

PHYSICAL PROPERTIES OF SUBSTITUTED ALLYL PHENYL ETHERS

Substituent	Obs. b.p. °C.	Mm.	Obs. n^{25}_{D}	Lit. b.p. °C.	Mm.	Lit. n^{t}_{D}	Ref.
p-NH_2	97.2–97.4	1	1.5679	136	11		16
p-OC_2H_5	119	11	M.p. 44.2–45.0°	.....	..	M.p. 39–40°	[a]
p-OCH_3	70.0–70.5	0.1	1.5249	119–120	13		35
p-CH_3	100.0–100.5	9	1.5157	65	4	1.5199 (20°)	9, 10
p-Cl	97.0–97.3	10	1.5348	106–107	12		13
p-Br	110.0–110.1	10	1.5583	126	14		13
None	67.5–67.6	10	1.5196	73	11	1.5190 (26°)	16, [b]
p-$COOC_2H_5$	100.0–100.1	0.6	1.5258	156	10		13
p-CHO	106.0–106.5	2	1.5669	142	10		13
p-$COCH_3$	89–90	0.6	1.5525	146–147	10	1.5432 (45°)	9, [c]
p-CN	94.0–94.5	.3	M.p. 43.6–44.4°	.....	..	M.p. 43°	[d]
p-NO_2	105–106	.4	1.5789	160	12		13
m-OCH_3	66.0–66.1	.5	1.5263	125–126	15		35
m-NO_2	92.2–92.3	.6	M.p. 32–33°	136–137	8	M.p. 31.5–32°	[e]
β-CH_3	75.2–75.8	10	1.5136	70	8	1.5168 (20°)	[f]
γ-CH_3	87.1–87.5	8	1.5183	95–98	12	1.5187 (19°)	[g]
α,γ-Dimethyl	59.8–60.0	0.4	1.5060	72	0.8	1.5110 (20°)	6

[a] S. M. McElvain and E. L. Engelhardt, THIS JOURNAL, **66**, 1077 (1944). [b] C. D. Hurd and L. Schmerling, *ibid.*, **59**, 107 (1937). [c] R. T. Arnold and J. C. McCool, *ibid.*, **64**, 1315 (1942). [d] M. W. Partridge, *J. Chem. Soc.*, 3043 (1949). [e] W. C. Wilson and R. Adams, THIS JOURNAL, **45**, 528 (1923). [f] Q. R. Bartz, R. F. Miller and R. Adams, *ibid.*, **57**, 371 (1935). [g] J. v. Braun and W. Schirmacher, *Ber.*, **56**, 538 (1923).

TABLE II

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR ARYL ALLYL ETHERS AND SUBSTITUTED 2-ALLYLPHENOLS

Substituted phenyl allyl ether	B.p. °C.	Mm.	n^{25}_{D}	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-$N(CH_3)_2$	88.1–88.2	0.5	1.5500	$C_{11}H_{15}NO$	74.55	74.89	8.53	8.24
p-C_2H_5	96.0–96.8	9	1.5124	$C_{11}H_{14}O$	81.45	81.26	8.70	8.78
m-$COOC_2H_5$	88.0–88.1	0.2	1.5169	$C_{12}H_{14}O_3$	69.89	69.80	6.84	6.71
α-CH_3	42.9–43.0	0.8	1.5078	$C_{10}H_{12}O$	81.04	80.70	8.16	8.10
Substituted 2-allylphenols								
4-$N(CH_3)_2$	85	0.1	1.5684	$C_{11}H_{15}NO$	74.55	74.67	8.53	8.60
4-C_2H_5	63.0–63.5	0.2	1.5301	$C_{11}H_{14}O$	81.45	81.43	8.70	8.58
4-CN	M.p. 83.0–84.0			$C_{10}H_9NO$	75.39	75.55	5.69	5.48
5(or 3)-$COOC_2H_5$	M.p. 151–152			$C_{12}H_{14}O_3$	69.89	69.95	6.84	7.00

pressure with a short Vigreux column. The main fraction was refractionated prior to use in the kinetic experiments.

The phenols were purified by distillation or recrystallization. *m*-Carbethoxyphenol and *p*-carbethoxyphenol were prepared by esterification of the corresponding hydroxybenzoic acids. *p*-Ethoxyphenol was prepared from hydroquinone and diethyl sulfate by the method used to prepare anisole from phenol and dimethyl sulfate.[14] *p*-Cyanophenol was prepared from *p*-aminophenol by the method used previously to convert *p*-toluidine to *p*-toluonitrile.[15] The rest of the phenols are available commercially. Allyl *p*-aminophenyl ether was prepared by hydrolysis of allyl *p*-acetamidophenyl ether.[16]

Allylic chlorides were used for preparing α- and γ-methylallyl and α,γ-dimethylallyl phenyl ether. These chlorides had the following physical properties: γ-methylallyl chloride, b.p. 83–83.7°, n^{25}_{D} 1.4325 (lit.[17] b.p. 83°, n^{20}_{D} 1.4351); α-methylallyl chloride, b.p. 62.5–63.5°, n^{25}_{D} 1.4125 (lit.[17] b.p. 63.5°, n^{20}_{D} 1.4150); α,γ-dimethylallyl chloride, b.p. 27° (30 mm.), n^{25}_{D} 1.4306 (lit.[17] b.p. 18–20° (12–13 mm.), n^{25}_{D} 1.4311). Commercially available β-methylallyl chloride was used to prepare β-methylallyl phenyl ether. Ethanol was used as the solvent instead of acetone for preparing allyl *p*-formylphenyl ether.[13]

Most of the allyl phenyl ethers used in the present work have been described previously. These are given in Table I together with the observed and reported physical properties. That the samples were homogeneous was indicated by the fact that fractionation gave fractions having the same physical properties. All of the samples had the correct chemical composition (carbon–hydrogen analysis) and the infrared spectra showed the samples to be free of phenol. The structures of these several substituted allyl phenyl ethers reported in Table I were confirmed by oxidation[18] to the corresponding aryloxyacetic acids—*p*-NH_2 (as its acetyl derivative), *p*-OC_2H_5, *p*-OCH_3, *p*-Cl, *p*-Br, *p*-NO_2, *m*-OCH_3, *m*-NO_2 and γ-CH_3. α,γ-Dimethylallyl phenyl ether (presumably the *trans* isomer[6]), was oxidized to α-phenoxypropionic acid, m.p. 115–116° (lit.[19] m.p. 115–116°) in good yield. The structures of the *p*-$CO_2C_2H_5$, *p*-CHO and *p*-CN phenyl allyl ethers were verified by conversion to *p*-allyloxybenzoic acid.[13]

The new allyl phenyl ethers are shown in the upper half of Table II. The structure of α-methylallyl phenyl ether was established by reduction (palladium-on-charcoal) to *sec*-butyl phenyl ether. The physical properties and infrared spectrum of this product were the same as for an authentic sample.[20] The unsaturated ether also was oxidized to α-phenoxypropionic acid, m.p. 115–116°.[19] When heated the ether rearranged to *o*-crotylphenol (isolated in 94% yield), b.p. 67–68° (0.6 mm.), phenylurethan m.p. 66–67° (lit.[21] phenylurethan m.p. 65–66°).

The structure of allyl *p*-ethylphenyl ether was established

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[14] G. S. Hiers and F. D. Hager, "Organic Syntheses," Coll. Vol. I, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 58.

[15] H. T. Clarke and R. R. Read, *ibid.*, p. 514.

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

[17] E. H. Huntress and E. E. Toops, Jr., "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[18] W. M. Lauer and W. F. Filbert, THIS JOURNAL, **58**, 1388 (1936).

[19] C. A. Bischoff, *Ber.*, **33**, 925 (1900).

[20] M. M. Sprung and E. S. Wallis, THIS JOURNAL, **56**, 1715 (1934).

[21] L. Claisen and E. Tietze, *Ber.*, **59**, 2344 (1926).

by oxidation to *p*-ethylphenoxyacetic acid, m.p. 96.3–96.5° (lit.[22] m.p. 97°).

The structure of *m*-carbethoxyphenyl allyl ether was established by hydrolysis to *m*-allyloxybenzoic acid, m.p. 80.0–80.5°.[23]

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.62; H, 5.59.

The structure of the latter compound was established by oxidation to *m*-carboxyphenoxyacetic acid, m.p. 207–208° (lit.[24] m.p. 206–207°).

Allyl *p*-dimethylaminophenyl ether was prepared in 33% yield by alkylation of the *p*-amino ether by a method that has been used previously for alkylating aromatic amines.[25] The structure of this compound was established by conversion to *p*-dimethylaminophenol, m.p. 77.5–78.0° (lit.[26] m.p. 78°) by refluxing 1 g. of the dimethylamino ether in 7 ml. of 48% hydrobromic acid for 5 hours. The amino phenol was isolated in 75% yield.

Rearrangement of Allyl Phenyl Ethers.—Four of the allyl phenyl ethers listed in Tables I and II rearrange to phenols that have not been described in the literature. These new phenols are included in Table II. The phenols were obtained from the ethers by the procedure given below for the conversion of allyl *m*-carbethoxyphenyl ether to rearrangement product. This is one of the two cases where two rearrangement products are possible and the only case in which two products are formed. A solution of 3.0 g. of allyl *m*-carbethoxyphenyl ether in 6 g. of diphenyl ether was heated under nitrogen for 9 hours at 220°. After cooling, the solution was extracted with 10% sodium hydroxide and the aqueous layer was saturated with carbon dioxide and extracted with ether. Removal of the ether gave a residue, 2.95 g. (98%), which apparently was a mixture of the two possible rearrangement products, *i.e.*, 2-allyl-5-carbethoxyphenol and 2-allyl-3-carbethoxyphenol. The higher melting component of the mixture was purified by several recrystallizations. This material is included in Table II. The lower melting component was not purified.

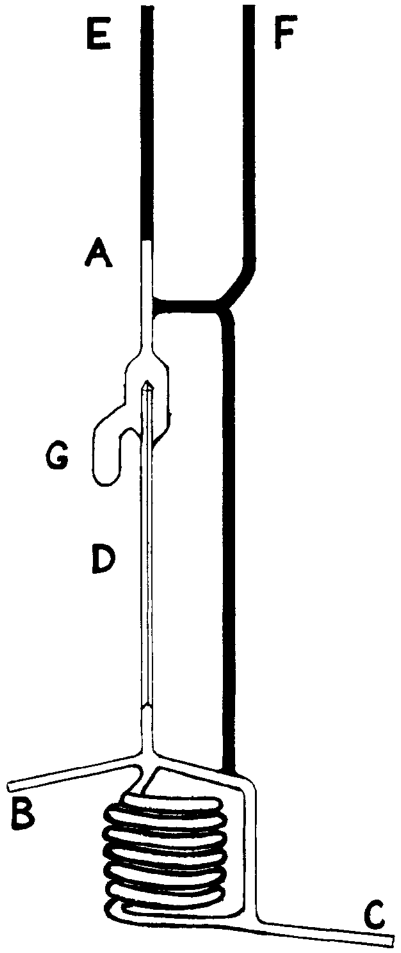

Fig. 1.—Dilatometer used in kinetic experiments.

Kinetic Experiments.—The dilatometer used to follow the reactions at temperatures of 185 and 197° is illustrated by Fig. 1. This dilatometer, which was designed for use at high temperatures, differs substantially from those used previously for following reactions at much lower temperatures (near room temperature).[12,27] The important features of this design are: (a) The coiled tube provides a high surface to volume ratio and thus temperature equilibration is rapid. This coil was constructed of 7 mm. thin walled Pyrex tubing and had a capacity of about 30 ml. (b) The level of the reaction mixture (sealed in the dilatometer at or near room temperature) in the capillary (D) can be adjusted so as to be on scale at the reaction temperature. The capillary (D) was 10 inches long and had a precision bore 0.0224 inch in diameter. The length of the dilatometer from the bottom of the coil to the top of the capillary was about 14 inches. During the kinetic experiments the sealed portion of the apparatus (from A to C) was immersed in the constant temperature bath and held in place by clamps attached to the two glass rods (E and F) which extended through its cover.

The constant temperature bath consisted of a Pyrex jar in a well insulated box. The box had a double paned window for observing the scale on the dilatometer. Except when in use the window was covered by a well insulated door. The Pyrex jar (12″ in diameter and 18″ deep) contained 6 gallons of Dow No. 550 silicone oil. The bath was heated by two 500 watt heaters. One of these served as a constant heater and the other as the intermittent heater. The latter was connected in series with a 50-watt light bulb. The constant heater was connected to a variable voltage control and the current for this heater was controlled by a Raytheon line voltage regulator. The temperature of the bath was controlled by a carefully selected Philadelphia type SW 912 thermoregulator. The bath was also provided with an efficient stirrer and a tight-fitting cover. The temperature fluctuations of the bath were less than 0.003° during a rate run and during the period of its use the absolute temperature varied less than 0.05°.

In the kinetic experiments the dilatometer was filled as follows. Both A and C were sealed and the reaction mixture was added through B at room temperature. After filling to the top of the coil, B was sealed and a scale with 2 mm. divisions was attached to the capillary tube. For emptying and cleaning the dilatometer A, B and C were opened.

The level of the liquid in the capillary at the reaction temperature was adjusted as follows. The sealed dilatometer was placed in the bath which had previously been heated a few tenths of a degree above the operating temperature. After the excess liquid had overflowed into the reservoir (G) the temperature was lowered to normal and the level of the liquid dropped to the top end of the scale. This operation required about 5 minutes. After equilibration for 10 minutes at the reaction temperature the zero-time reading (R_0) was taken and the rate of decrease in volume was determined. The total drop during a kinetic experiment varied from 50 to 90 mm. and the readings were recorded to 0.2 mm. The readings were always taken at the same time during the heating cycle (*i.e.*, when the intermittent heater shut off) to minimize errors resulting from the temperature fluctuation of the bath. When the dilatometer was filled with pure solvent the level fluctuated about 0.4 mm. However, when readings were taken at the same time during the heating cycle they agreed to within 0.2 mm. Thus it appears that the readings in the kinetic experiments are good to about ±0.2 mm.

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(22) S. M. McElvain, "The Characterization of Organic Compounds," revised edition, The Macmillan Co., New York, N. Y., 1953, p. 268.

(23) Evidently the melting point of 148° reported for this compound by Scichilone, *Gazz. chim. ital.*, **12**, 453 (1882), is incorrect.

(24) R. Meyer and C. D. Duxzmal, *Ber.*, **46**, 3366 (1913).

(25) W. L. Borkowski and E. C. Wagner, *J. Org. Chem.*, **17**, 1128 (1952).

(26) H. Wieland, *Ber.*, **43**, 712 (1910).

(27) R. Livingston in A. Weissberger's "Technique of Organic Chemistry," Vol VIII, Interscience Publishers, Inc., New York, N. Y., 1953, Chapt. 2

In the kinetic experiments the amount of substrate used was 1.5% by weight of the reaction mixture. This corresponds to a concentration of about 0.1 molar. The allyl aryl ethers were freshly distilled and the solvents were purified as follows. Diphenyl ether was purified according to the method of Kincaid and Tarbell.[10] N,N-Dimethylaniline was dried over fused potassium hydroxide prior to distillation and diphenylmethane was purified by fractionation. The other solvents (see Table V) were purified by standard methods.[28]

The specific first-order rate constants for the decrease in volume of the reaction mixtures were calculated by use of equation 1 in which R_0, R_t and R_∞ correspond to the readings at zero time, time t and "infinity" time (*i.e.*, after ten half-lives). Since with dilute solutions the change in volume is a

$$k = (1/t)\ \ln\ (R_0 - R_\infty)/(R_t - R_\infty) \qquad (1)$$

linear function of the percentage completion of the reaction,[28] k is the first-order rate constant for the reaction. Usually about 25 readings were taken during a kinetic experiment and values of k were calculated for each of these readings. These values did not show any trends over the range that the reactions were followed (to about 80% completion) and the average deviation was usually <2% of the value of k. In duplicate experiments the values of k agreed within the combined average deviations. A typical kinetic experiment is summarized in Table III. In this table only every third reading is recorded and thus the average value and average deviation may differ slightly from the value recorded in Table IV.

TABLE III

RATE OF REARRANGEMENT OF ALLYL *p*-CRESYL ETHER IN DIPHENYL ETHER AT 184.85°[a]

Time, 10^{-3} sec.	Dilatometer reading	$k \times 10^5$ sec.$^{-1}$
0	67.2	..
2.70	65.2	2.05
5.40	63.3	2.05
9.00	61.0	2.05
14.4	57.8	2.05
19.8	54.9	2.06
25.2	52.3	2.07
30.6	49.9	2.08
36.0	47.8	2.09
57.6	41.6	2.09
72.0	38.8	2.08
∞	30.6	..
	Average	2.07 ± 0.02

[a] The reaction mixture consisted of 1.5% by weight of the substrate in diphenyl ether.

First-order rate constants for the rearrangement of all but two of the ethers listed in Tables I and II were determined by this method. Allyl *m*-nitrophenyl ether decomposes in diphenyl ether at the reaction temperature and thus the rate of rearrangement of this compound could not be determined. For some unknown reason α,γ-dimethylallyl phenyl ether showed erratic behavior and the rate of decrease in volume of the reaction mixture was not reproducible.

Results

The results of the kinetic experiments are presented in Tables IV and V. In these experiments the concentration of substrate was 1.5% by weight of the reaction mixture (approximately 0.1 *M*). First-order rate constants for the rearrangement of nineteen ethers in diphenyl ether at 184.85 and 197.29° are given in Table IV together with the Arrhenius activation energies, E_a, and entropies of activation, $\Delta S^{\ddagger}$. Similar data for the rearrangement of allyl *p*-cresyl ether in benzonitrile are included in this table. Several of the constants in this table are average values (and average deviations) of more than one independent kinetic experiment. As indicated by the magnitudes of these deviations the rate constants are generally reproducible to within 1%. The rest of the constants are average values (and average deviations) of about twenty-five values determined during the course of the reaction. Judging from the reproducility of the rate constants the activation energies are probably reliable to within 1 kcal. The entropies of activation (calculated from the frequency factor,

TABLE IV

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REARRANGEMENT OF SUBSTITUTED ALLYL PHENYL ETHERS IN DIPHENYL ETHER

Substituent in aromatic ring or allyl portion	$k \times 10^5$, sec.$^{-1}$ 184.85 ± 0.05°	$k \times 10^5$, sec.$^{-1}$ 197.29 ± 0.02°	E_a, kcal./mole	$\Delta S^{\ddagger}$,[a] cal./degree
p-$N(CH_3)_2$	14.3 ± 0.2	38.7 ± 0.5	34.3	−2
p-NH_2	10.0 ± .2	27.4 ± .2	34.7	−2
p-OC_2H_5	4.77 ± .04	12.5 ± .1	33.1	−7
p-OCH_3	4.58 ± .01[b]	12.2 ± .1	33.6	−6
p-CH_3	2.08 ± .01[c]	5.58 ± .05	34.0	−7
p-C_2H_5	2.00 ± .03	5.51 ± .04	34.8	−5
p-Cl	1.70 ± .02	4.21 ± .04	31.2	−13
p-Br	1.58 ± .03	3.92 ± .02	31.2	−13
None	1.52 ± .02[b]	3.86 ± .03	31.6	−12
p-$COOC_2H_5$	1.115 ± .005[b]	2.80 ± .04	31.5	−13
p-CHO	1.07 ± .01	2.72 ± .03	32.2	−12
p-$COCH_3$	0.994 ± .007	2.54 ± .03	32.2	−12
p-CN	0.903 ± .007	2.285 ± .005[b]	32.0	−13
p-NO_2	0.892 ± .004[b]	2.26 ± .02	31.9	−13
m-OCH_3	4.92 ± .05	11.9 ± .02	30.4	−13
m-$COOC_2H_5$	1.48 ± .02	3.51 ± .04	29.8	−16
α-CH_3	21.1 ± .2	52.5 ± .7	31.4	−8
β-CH_3	1.32 ± .02	3.29 ± .03	31.5	−13
γ-CH_3	1.61 ± .02	4.05 ± .04	31.7	−12
p-CH_3	2.49 ± .03[d]	6.80 ± .08[d]	34.6[d]	−5[d]

[a] Calculated for T = 184.85°. [b] Average value (and average deviation) of two independent kinetic experiments. [c] Average value (and average deviation) of four independent kinetic experiments. Reference 5 reports $k = 2.69 \times 10^{-5}$ sec.$^{-1}$ at 185.8°, E_a = 33.1 (14.2% solution). [d] These data are for the rearrangement of the *p*-methyl ether in benzonitrile.

TABLE V

RATE CONSTANTS FOR THE REARRANGEMENT OF ALLYL *p*-CRESYL ETHER IN SEVERAL SOLVENTS AND ALLYL *p*-CARBETHOXYPHENYL ETHER IN ETHYLENE GLYCOL AT 184.85°

Solvent	$k \times 10^5$, sec.$^{-1}$
A. Allyl *p*-cresyl ether	
Ethylene glycol	18 ± 1[a]
Benzyl alcohol	9.7 ± 1.0
1-Octanol	9 ± 2
Phenol	45 ± 1[b]
Carbitol	3.6 ± 0.3
Methyl salicylate	2.45 ± .01
Benzonitrile	2.49 ± .03
N,N-Dimethylaniline	2.46 ± .04
Acetophenone	2.41 ± .12
Diphenyl ether	2.08 ± .01[a]
Diphenylmethane	2.12 ± .02
Decalin	1.56 ± .01
B. Allyl *p*-carbethoxyphenyl ether	
Ethylene glycol	6.4 ± 0.6

[a] Average of four independent determinations. [b] Average of two independent determinations.

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[28] J. A. Riddick and E. A. Troops in A. Weissberger's "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, Inc., New York, N. Y., 1958.

A) are probably good to within 2 or 3 entropy units.

Comparison of the rate constants in Table IV for the series of *p*-substituted allyl phenyl ethers shows that the rate of rearrangement is increased by electron-supplying substituents and decreased by electron-withdrawing substituents. However, the reaction is rather insensitive to these structural changes and at 185° there is only a sixteenfold variation within the series. Moreover, the activation energies are higher with electron-supplying substituents than with electron-withdrawing substituents and thus the spread in the rate constants decreases with temperature. For example, the extrapolated rate constants for the most and least reactive members of the series differ by only a factor of 5 at 50°.

The data presented in Table IV also show the effects of methyl substituents in the allyl part of the ether. As in the case of the *para*-Claisen rearrangement[29] substitution of a γ-hydrogen atom by a methyl group has essentially no effect on the rate or activation energy of the rearrangement. Similarly the effect of a β-methyl substituent is small as might be expected. On the other hand, as has been predicted,[29] an α-methyl substituent has a relatively large effect and increases the rate by a factor of 14. The thermodynamic data are not accurate enough to tell whether this increase in rate is due to an increase in entropy of activation or decrease in activation energy.

Rate constants for the rearrangement of allyl *p*-cresyl ether in several solvents and allyl *p*-carbethoxyphenyl ether in ethylene glycol at 184.85° are given in Table V. All of the non-hydroxylic solvents except acetophenone were stable at the reaction temperature, *i.e.*, when the pure solvents were heated in the dilatometer no volume changes were observed. Furthermore the rearrangement product was stable in these solvents and no changes in volume were observed after the reactions were complete. On the other hand, acetophenone and the hydroxylic solvents except phenol and methyl salicylate showed a slow decrease in volume when heated at the reaction temperature. Moreover, in the hydroxylic solvents the rearrangement product apparently undergoes a change subsequent to its formation which results in a slow volume contraction. When a pure sample of the rearrangement product, a 2-allyl-4-methylphenol, was heated in ethylene glycol the volume contracted at a somewhat greater rate than when the pure solvent was heated. Similarly, when the rearrangement product was heated in phenol the volume contracted slowly, whereas with the pure solvent no contraction was observed. This may be due to the conversion of the rearrangement product to dihydrobenzofuran. The rate of the contraction resulting from these side reactions was much slower than that due to the Claisen rearrangement. In these experiments the infinity readings (at ten half-lives) were corrected—the magnitude of the rather small correction was estimated from the rate of contraction of a solution of the rearrangement product—and the rate constants were computed in the usual manner. The constants obtained in this way were within the combined average deviations of the constants determined by the Guggenheim[30] method. Because of these complications the rate constants for the hydroxylic solvents and acetophenone are not as reliable as those for the non-hydroxylic solvents. For this reason activation energies for the rearrangement in hydroxylic solvents were not determined. As illustrated in Table V rate constants for duplicate experiments in ethylene glycol and phenol showed average deviation of about 5 and 2%, respectively. Glycerol, nitrobenzene and caproic acid contracted too rapidly at the reaction temperatures to be used in the kinetic experiments.

The data presented in Table V show that the rate of rearrangement is remarkably insensitive to variation of the medium. Rate constants for the rearrangement in the six non-hydroxylic solvents and methyl salicylate differ by less than a factor of 2, and 4 of the constants are essentially the same. The reaction is somewhat faster in hydroxylic solvents. The 18-fold difference in the rate in phenol and methyl salicylate suggests that the greater rate in the hydroxylic solvents may in some way be connected with hydrogen bonding between the solvent and substrate. The greater rate in phenol than in non-hydroxylic solvents is consistent with the observation[10] that the apparent first-order rate constant for the rearrangement of allyl *p*-cresyl ether in the absence of solvent increases as the medium changes from allyl *p*-cresyl ether to 2-allyl-4-methylphenol. Although the solvents were only compared at one temperature it appears that the relative rates would not change appreciably with temperature. The last entry in Table IV shows that the activation energy for the reaction in benzonitrile is within experimental error of that for the rearrangement in diphenyl ether. Comparison of the relative rates of rearrangement of the *p*-methyl and *p*-carbethoxy substituted ethers in ethylene glycol (Table V) and diphenyl ether (Table IV) shows that the reaction is more sensitive to variation of the substituent in the former solvent.

Discussion

It is apparent from the relative reactivities of the *p*-substituted allyl phenyl ethers (Table IV) that there is a qualitative relationship between reactivity and the substituent constants, σ, *i.e.*, reactivity decreases as σ increases. It was of interest to determine whether these rate data could be correlated quantitatively by the substituent constants.

A complicating factor in treating the data is that there are two reaction sites. One of these is *para* to the substituents (carbon–oxygen bond cleavage) and the other is *meta* to the substituents (carbon–carbon bond formation). It appeared that the nature of the correlation might provide information concerning the relative effects of the substituents at the two reaction sites. For example, if the substituents have a much greater effect on bond breaking than bond making, a linear relationship between the reactivities and the σ_p constants might be expected. On the other hand, if the substituents have an effect on both bond making and bond breaking one might expect a correlation between

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[29] S. J. Rhoads and R. L. Crecelius, THIS JOURNAL, **77**, 5057 (1955).

[30] See reference 12a.

the rates and a linear combination of the σ_p and σ_m constants. Because of these complications the data were treated in several ways. The substituent constants used in the various correlations are shown in Table VI.

TABLE VI

SUBSTITUENT CONSTANTS USED FOR CORRELATING REACTIVITIES OF *p*-SUBSTITUTED ALLYL PHENYL ETHERS

p-Substituent	$\sigma_p{}^a$	$\sigma_m{}^a$	$\sigma_p{}^{+b}$	$\sigma_m{}^{+c}$
$N(CH_3)_2$	−0.600	−0.211	−1.67	−0.211
NH_2	− .660	− .161	−1.33	− .161
OC_2H_5	− .250	.150	−0.76[d]	.047[d]
OCH_3	− .268	.115	− .76	.047
CH_3	− .170	− .069	− .31	− .069
C_2H_5	− .151	− .043	− .29	− .063
Cl	.227	.373	.11	.373
Br	.232	.391	.15	.391
None	.000	.000	.00	.000
$COOC_2H_5$	.522	.398	....	.....
$COCH_3$	.516	.306	....	.....
CN	.628	.678	....	.....
NO_2	.778	.710	....	.....

[a] These values were taken from ref. 32. [b] These values were taken from ref. 33a except the values for *p*-$N(CH_3)_2$ and *p*-NH_2 which were taken from ref. 33b. The σ^+ values for electron-withdrawing substituents are similar to the σ values. Since $\sigma_p{}^+$ values were not available for all of these substituents, σ_p values were used. [c] These values were taken from ref. 33a except for the values for NH_2 and $N(CH_3)_2$ for which σ values were used because σ^+ values were not available. Since $\sigma_m{}^+$ values were not available for all of the electron-withdrawing substituents σ_m values were used. [d] This value was assumed to be the same as that for OCH_3.

The data are not correlated well by the Hammett relationship,[31,32] (eq. 2) if σ_p substituent constants are used. As illustrated by the upper plot in Fig. 2 the relationship between log k/k^0 and the Hammett σ_p values is not linear. For those *p*-substituents which have two σ values, depending on the nature of the reaction, σ_p values rather than $\sigma_p{}^*$ values[32] were used in this plot. It is apparent that the $\sigma_p{}^*$ values would show larger deviations than the σ_p values. In this treatment the effect of the substituents at the *m*-position (where the allyl group becomes attached to the aromatic ring) has been neglected. A substantially poorer correlation (not shown) is obtained using σ_m constants instead of σ_p constants.

$$\log k/k^\circ = \rho\sigma_p \qquad (2)$$

As illustrated by the lower plot in Fig. 2 the data are correlated very well by the Hammett relationship (eq. 2) using Brown's $\sigma_p{}^+$ values.[33] The equation for the least-squares fit is

$$\log k/k^0 = -0.510\sigma_p{}^+ + 0.078 \qquad (3)$$

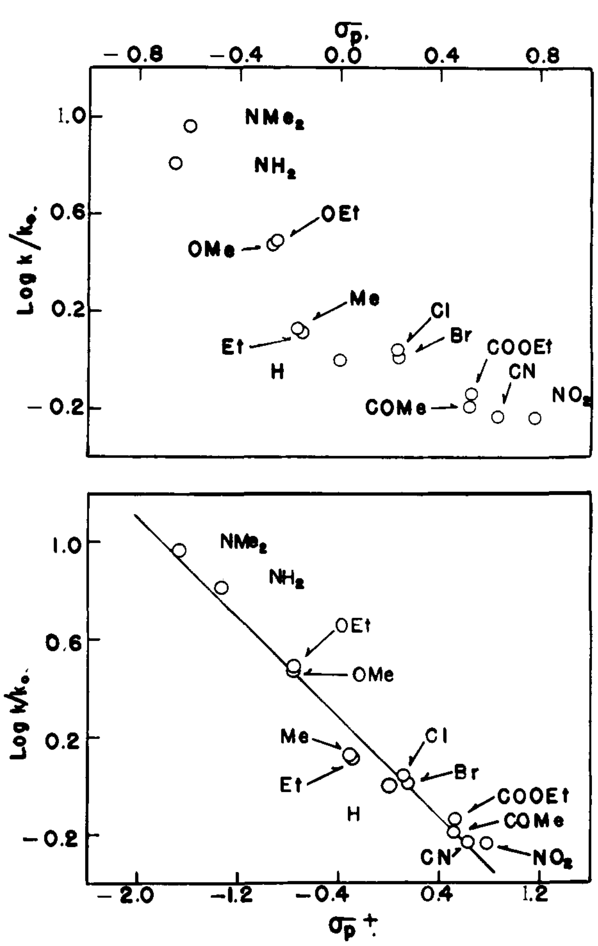

Fig. 2.—Plots of log k/k^0 *versus* σ_p and $\sigma_p{}^+$.

The standard deviation from the least-square line (s) is 0.064 and the correlation coefficient (r) is 0.988.[34] Rate data for allyl *p*-formylphenyl ether have not been included in this or the other plots because the $\sigma_p{}^+$ constant has not been reported and it seems evident that the σ_p value (based on one reaction[32]) is much too low. The $\sigma_p{}^+$ constant for *p*-formyl calculated from the rate data in Table IV by use of equation 3 is 0.465. The data for the two *m*-substituted allyl phenyl ethers included in Table IV show positive deviations from this plot and have not been included. The deviation is especially serious for the *m*-methoxy ether. In this case the observed rate is about three times greater than that calculated from the $\sigma_m{}^+$ value.[33] The failure of the correlation for the *m*-substituted ethers apparently is not due to the fact that the substituent is *ortho* to one of the two possible positions to which the allyl group can migrate. The *m*-methoxy ether, which shows the largest deviation, is reported to give only the product resulting from rearrangement of the allyl group to the position *para* to the substituent,[35] *i.e.*, 2-allyl-5-methoxyphenol. Thus it appears that in this case the position *ortho* to the substituent is not involved in the reaction.

As shown in Table VI there is little difference between the σ_m and $\sigma_m{}^+$ values. As indicated above, the correlation is very poor using σ_m values and it is thus apparent that $\sigma_m{}^+$ would also give a poor correlation.

Jaffé has suggested[32] that in cases (such as the present) where the substituents are both *meta* and

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(31) L. P. Hammett "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. VII.

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

(33) (a) H. C. Brown and Y. Okamoto, THIS JOURNAL, **79**, 1913 (1957); *J. Org. Chem.*, **22**, 485 (1957); (b) N. C. Deno and W. L. Evans, THIS JOURNAL, **79**, 5804 (1957).

(34) These quantities were calculated by the methods described in reference 32.

(35) F. Mauthner, *J. prakt. Chem.*, **102**, 41 (1921).

para to centers involved in the reaction the data should be treated using a four parameter equation[36]

$$\log k/k^0 = \rho_p\sigma_p + \rho_m\sigma_m \qquad (4a)$$

If this relationship is expressed in the form shown by equation 4b it becomes apparent that if this relationship holds a plot of log k/k^0 *versus* $[\sigma_p + (\rho_m/\rho_p)\sigma_m]$ will be linear.

$$\log k/k^0 = \rho_p[\sigma_p + (\rho_m/\rho_p)\sigma_m] \qquad (4b)$$

The value of (ρ_m/ρ_p) was estimated by substituting rate constants for two substituted ethers in equation 4b and solving the resulting simultaneous equations. This process was repeated using different combinations of rate constants and the average value for this parameter was found to be -1. The plot of log k/k^0 *versus* $(\sigma_p - \sigma_m)$ is shown in Fig. 3. The correlation is not much different from that obtained with the σ_p values and is considerably poorer than that obtained with the $\sigma_p{}^+$ constants. The least-squares equation for this plot is

$$\log k/k^0 = -1.61(\sigma_p - \sigma_m) - 0.054$$

The standard deviation is 0.18 and $r = 0.898$.

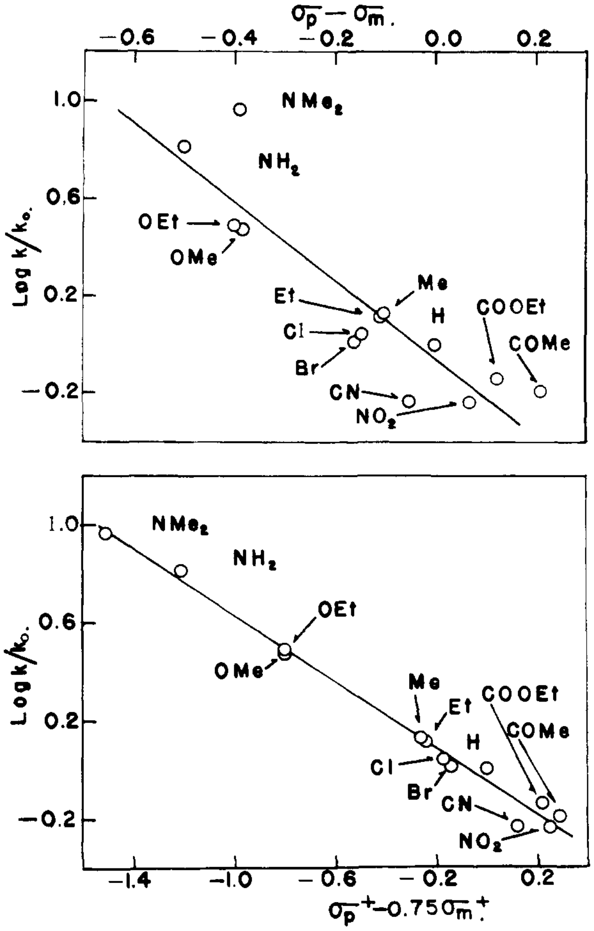

Fig. 3.—Plots of log k/k^0 *versus* $(\sigma_p - \sigma_m)$ and $(\sigma_p{}^+ - 0.75\sigma_m{}^+)$.

The data also were treated by equation 4 using σ^+ constants instead of σ constants. In this case $\rho_m/\rho_p = -0.75$ and thus log k/k^0 was plotted against $(\sigma_p{}^+ - 0.75\sigma_m{}^+)$. As illustrated by the lower plot in Fig. 3 this relationship is indeed linear. This correlation is slightly better than that obtained using $\sigma_p{}^+$ constant; $s = 0.046$ and $r = 0.994$. The least-squares equation is

$$\log k/k^0 = -0.678(\sigma_p{}^+ - 0.75\,\sigma_m{}^+) - 0.049$$

In the latter correlation $\rho_p = -0.678$ and $\rho_m = 0.508$. This implies that the reaction is facilitated by electron supply to the *p*-position (the ether linkage) and electron removal from the *m*-position. However, this is clearly an illusion. This is shown by the fact that the data are correlated by both equation 2 and equation 4 if σ^+ constants are used. These two linear relationships are shown by equations 5 and 6.

$$\log k/k^0 = \rho\sigma_p{}^+ \qquad (5)$$

$$\log k/k^0 = \rho_p[\sigma_p{}^+ + (\rho_m/\rho_p)\sigma_m{}^+] \qquad (6)$$

Since these two equations hold, the relationship shown by equation 7 must also hold for the substituents used in the present work.

$$\sigma_p{}^+ = \rho'(\sigma_p{}^+ + C\sigma_m{}^+) \qquad (7)$$

In the latter equation ρ' and C are ρ_p/ρ (equations 5 and 6) and ρ_m/ρ_p (equation 6), respectively. Conversely, if the linear relationship shown by equation 7 holds it becomes apparent that any reaction series that can be correlated by the Hammett equation will also be correlated by the four parameter equation. Thus the significance of the two parameters designated as ρ_p and ρ_m in the four parameter equation (4 and 6) is obscure.

The relationship shown by equation 7 was tested using both σ^+ and σ constants. With each type of constant the relationship was found to be linear. A plot of $\sigma_p{}^+$ *versus* $\sigma_p{}^+ - 0.75\sigma_m{}^+$ $(C = -0.75)$ using constants for 23 substituents was linear, $\rho' = 1.28$, $r = 0.972$, $s = 0.15$. A plot of σ_p *versus* $\sigma_p - \sigma_m$ $(C = -1)$ using the values given in Table VI was also linear, $\rho' = 1.78$, $r = 0.930$, $s = 0.16$. This clearly shows that equation 7 holds and consequently it appears that equation 4 cannot be used for its intended purpose.

The theoretical significance of the correlation of the rate data by the σ^+ constants is not obvious. Perhaps the most important observation in this connection is that the data for the *p*-substituted ethers are correlated by $\sigma_p{}^+$ rather than $\sigma_m{}^+$. The reaction is electron demanding, *i.e.*, ρ is negative, and presumably the substituent effect is transmitted primarily through the *p*- carbon–oxygen bond. The dependence of the rate on $\sigma_p{}^+$ rather than $\sigma_m{}^+$ implies that the transition state resembles the reactant more closely than the product. It is not clear why in the present case the data are correlated by σ^+ constants instead of σ constants. There are a number of other reactions which are correlated better by σ^+ than by σ constants.[33] However, for the most part these are cases where ρ is large and negative, *i.e.*, the reaction is sensitive to substituent effects. The present reaction is relatively insensitive to substituent effects.

The rather small effect of substituents is not sur-

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(36) This equation recently has been applied to the *ortho*-Claisen rearrangement of *p*-substituted allyl phenyl ethers by W. N. White, *et al.*, Abstracts of the 132nd Meeting of the American Chemical Society, September, 1957, New York, N. Y., p. 66 P. See also W. N. White, D. Gwynn, R. Schlitt, C. Gerard and W. Fife, THIS JOURNAL, 80, 3271 (1958).

prising. If the reaction is considered to involve simultaneous homolytic electron displacements ρ would be expected to be small. If simultaneous heterolytic displacements were involved the substituent effects at the *m*- and *p*-positions would be large but opposite in sign. Because of this cancellation the over-all effect would be small.[37]

The present data do not rule out the possibility that an intermediate may be involved in the rearrangement.[38] However, there do not seem to be any reasons for suspecting that this is the case. It appears that the data are consistent with a concerted one-step cyclic mechanism. The geometry of the transition state for such a mechanism has been discussed previously.[5,29]

[37] Ambiguities concerning the nature, *i.e.*, homolytic or heterolytic, and direction of electron displacements in concerted cyclic processes have been discussed by C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 597, 637 and 644.

[38] If an intermediate is involved the apparent first-order rate constant is a composite of three rate constants. The substituent and solvent effects can be predicted for the individual steps but not for the composite.

MADISON 6, WISCONSIN

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

Deuterium Isotope Effects in Some Acid-catalyzed Cyclizations of 2-Deuterio-2'-carboxybiphenyl

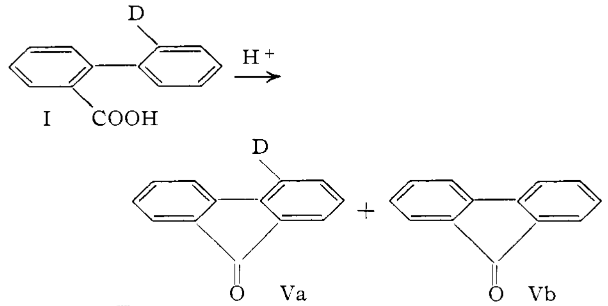
BY DONALD B. DENNEY AND PETER P. KLEMCHUK[1]

RECEIVED DECEMBER 23, 1957

2-Deuterio-2'-carboxybiphenyl has been cyclized to fluorenone with sulfuric acid, polyphosphoric acid and anhydrous hydrogen fluoride. The isotope effects for these reactions have been determined. Hydrogen fluoride cyclization exhibited a k_H/k_D of 3.02, whereas the other acid-catalyzed cyclizations had isotope effects in the range 1.13–1.46. The significance of these results is discussed with respect to possible mechanisms for these substitutions.

Melander's[2] pioneering studies on hydrogen isotope effects in aromatic nitration and bromination are now classics. Since his work was published many papers have appeared in which deuterium and tritium isotope effects have been measured during aromatic substitutions.[3] These studies have led in general to a greater understanding of the mechanisms of these reactions and have specifically provided information concerning intermediates in the reaction sequence as well as to whether or not loss of hydrogen is involved in the rate-determining step.

We wish to report at this time some measurements of deuterium isotope effects obtained during the acid-catalyzed cyclization of 2-deuterio-2'-carboxybiphenyl (I) to 4-deuteriofluorenone (Va) and fluorenone (Vb). As it can be seen, the isotope effects being measured here are those which have been termed intramolecular.[4] This system was chosen because it provides a degree of flexibility not easily obtained when intermolecular isotope effects are measured. For example, it has been possible to measure isotope effects of very fast reactions by this technique, since the isotope effect is obtained simply by analyzing the mixture of Va and Vb for deuterium. We also have been able to measure isotope effects in heterogeneous reactions such as the Friedel–Crafts reaction by the use of this technique.[5] The isotope effects which we have observed can be found in Table I. It is apparent that all of the reactions studied exhibit some isotope effect. The range is considerable from a k_H/k_D of 3.02 in anhydrous hydrogen fluoride to 1.13 in 86.54% sulfuric acid. In order to accept these values as being meaningful, it was necessary to prove that exchange was not taking place during the reaction. This sort of analysis has been accomplished for the sulfuric acid-catalyzed reaction. At various time intervals aliquots of the reaction mixture were removed and the fluorenone was isolated and analyzed for deuterium. All of the samples of fluorenone had the same deuterium content. If exchange was taking place with either the starting acid or the product, fluorenone, then there would be a steady decrease in the deuterium content of the fluorenone. Since this was not observed one knows that the isotope effects ob-



I

Va

Vb

TABLE I

Catalyst	Time, min.	Temp., °C.	k_H/k_D
Concd. sulfuric acid	2-60	1	1.31 ± 0.03
96.63% sulfuric acid	15	1	1.34 ± .03
86.54% sulfuric acid	90	1	1.13 ± .02
Polyphosphoric acid	15	95	1.31 ± .03
Polyphosphoric acid	24 hr.	25	1.46 ± .04
Hydrogen fluoride	30	19	3.02 ± .14

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[1] Alfred P. Sloan Fellow in Chemistry, 1956-1957.

[2] L. Melander, *Arkiv. Kemi*, **2**, 213 (1950).

[3] (a) W. M. Lauer and W. E. Noland, THIS JOURNAL, **75**, 3689 (1953); (b) T. G. Bonner, F. Bowyer and G. Williams, *J. Chem. Soc.*, 2650 (1953); (c) P. B. D. de la Mare, T. M. Dunn and J. T. Harvey, *ibid.*, 923 (1957); (d) H. Zollinger, *Helv. Chim. Acta*, **38**, 1597 (1955); (e) U. Berglund-Larsson and L. Melander, *Arkiv. Kemi*, **6**, 21 (1953); (f) T. G. Bonner and J. M. Wilkins, *J. Chem. Soc.*, 2358 (1955); (g) E. Grovenstein, Jr., and D. C. Kilby, THIS JOURNAL, **79**, 2972 (1957).

[4] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[5] Unpublished work.