This suggestion makes sense. It should be noted, though, that Goldberg's chelate ring with its principally covalent bonds is rather different from the electrostatic interactions ("built-in solvation") which we have proposed in this and the preceding paper.

Experimental

Materials.—4-Chloro-3-nitrobenzoic acid and 2-chloro-5-nitrobenzoic acid were prepared by nitration of, respectively, *p*- and *o*-chlorobenzoic acid. Each of the chloronitrobenzoic acids was allowed to react with piperidine (by dissolving the acid in excess piperidine and warming to reflux for about two minutes). The products, recrystallized from 95% ethanol, were 3-nitro-4-piperidinobenzoic acid, m.p. 207–208° (lit.[16] 202–203°), and 5-nitro-2-piperidinobenzoic acid, m.p. 199–200° (lit.[16] 201–202°). These authentic products were used in preparing solutions of the composition expected at the completion of reaction in the kinetic runs. Such solutions are useful in standardizing the analytical procedure. These nitropiperidinobenzoic acids also were isolated in high yield from reactions of piperidine with the corresponding chloronitrobenzoic acids under the conditions of the rate studies.

Piperidine and 93% ethanol for the rate studies were prepared as previously described.[2]

Rate Measurements.—The spectrophotometric technique previously described[2] was used. Piperidine and the two chloronitrobenzoic acids have negligible absorption in the visible range while the nitropiperidinobenzoic acids absorb strongly. 3-Nitro-4-piperidinobenzoic acid was determined by optical density measurements at 415 mμ, and 5-nitro-2-piperidinobenzoic acid by measurements at 390 mμ.

Our first runs were set up so as to provide second-order kinetics, the initial concentration of the sodium chloronitrobenzoate being about 0.015 *M* and that of the piperidine about 0.03 *M*. However, plots of $1/(a - x)$ *vs.* t (valid if the stoichiometry is: $ArCl + 2R_2NH \rightarrow ArNR_2 + R_2NH_2Cl$) showed an upward curvature, while plots of an appropriate log term *vs.* t (valid if the stoichiometry is: $C_6H_3NO_2ClCOO^- + R_2NH \rightarrow C_6H_3NO_2NR_2COOH + Cl^-$) showed a downward curvature. This indicated intermediate stoichiometry, not unreasonable considering that the basicity of an amine decreases while that of an acylate ion increases as the solvent changes from water to 93% ethanol.

Our principal runs were set up with piperidine in 40-fold excess, the initial concentrations being about 0.06 *M* (for piperidine) and 1.5×10^{-3} *M* (for the sodium chloronitrobenzoate). These runs provided clean-cut first-order kinetics. The first-order rate coefficients were divided by the piperidine concentration (in the reacting solution), and thus converted to second-order rate coefficients. As a check on this conversion, we determined the first-order rate coefficient for the reaction of piperidine with *o*-chloronitrobenzene in 93% ethanol, and then converted it to a second-order rate coefficient. The resulting value, 3.52×10^{-3} l. mole^{-1} min.$^{-1}$ at 101.8°, compares with Bunnett and Morath's[2] 3.88×10^{-3} l. mole^{-1} min.$^{-1}$ at 101.5°.

Infinity optical densities for a run with sodium 4-chloro-3-nitrobenzoate (I) at 119.3° and for a run with sodium 2-chloro-5-nitrobenzoate (II) at 101.8° were within 1% of the theoretical value for 100% conversion to the corresponding nitropiperidinobenzoic acids. This shows that no significant side reactions took place.

Since the reaction of II with piperidine at 46.0° was moderately slow, some quenched samples of the reaction solution had to stand for days before they could be analyzed as a group with other samples from the same run. A slight drift in optical density was observed to occur. It was established that 5-nitro-2-piperidinobenzoic acid undergoes some esterification under the conditions existing in the quenched solution. A small amount of the ethyl ester was isolated, by chromatography, and was identified by comparison of its infrared spectrum with that of an authentic sample. This complication was avoided, in later runs, by chilling the ampoules removed from the thermostat and storing them in a "deep freeze" until the run was completed, at which time they were all opened, quenched in the usual way, and analyzed directly.

Following are the second-order rate coefficients we determined, in units of l. mole^{-1} min.$^{-1}$. Each is the average value from two to four supposedly identical runs. The average deviation was about 2.5% for runs with I and less than 1% for runs with II.

Sodium 4-chloro-3-nitrobenzoate (I) at 101.8°, 1.39×10^{-2}; at 119.3°, 4.12×10^{-2}.

Sodium 2-chloro-5-nitrobenzoate (II): at 101.8°, 5.63×10^{-2}; at 46.0°, 9.62×10^{-4}.

Arrhenius activation energies and entropies of activation were calculated from standard expressions. ΔE values are uncertain by about ±1.0 kcal. in the case of I and by about ±0.1 kcal. in the case of II. The uncertainty in $\Delta S^{\ddagger}$ values is about ±3.0 cal./deg. in the case of I and about ±0.2 cal./deg. in the case of II.

Acknowledgments.—We thank the Office of Ordnance Research, U. S. Army, for financial assistance. A Fulbright travel grant to one of us is also appreciated.

CHAPEL HILL, N. C.

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(16) R. J. W. Le Fevre and E. E. Turner, *J. Chem. Soc.*, 1113 (1927).

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

The *para*-Claisen Rearrangement. III. Kinetics of the Rearrangement of Some γ-Substituted Allyl Ethers of Methyl *o*-Cresotinate[1]

BY SARA JANE RHOADS AND ROBERT L. CRECELIUS[2]

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Rates of rearrangement of the allyl (Ia), the γ-methylallyl (Ib), and the γ-ethylallyl (Ic) ethers of methyl *o*-cresotinate have been measured at several temperatures. Activation energies and entropies have been calculated and are discussed in terms of the structures of the compounds and the mechanism of the rearrangement.

The kinetics of the *para*-Claisen rearrangement of the allyl ether of 2,6-dimethylphenol have been studied by Tarbell and Kincaid[3] and constitute the only detailed kinetic examination of this rearrangement reported to date.[4] It seemed desirable to collect more rate data on this rearrangement and especially to extend such studies to a series of substituted allylic ethers in which the γ-substituent was systematically varied. This paper reports the results of such an investigation.

Rates of rearrangement in the pure liquid have been measured for the allyl (Ia), the γ-methylallyl (Ib) and the γ-ethylallyl (Ic) ethers of methyl *o*-cresotinate. The reactions were followed by the change in refractive index and showed good first-order rate dependence up to 80–90% completion.

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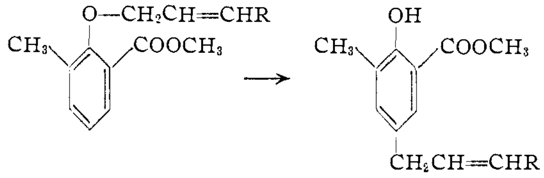
(1) Taken from the Ph.D. dissertation of R. L. Crecelius, University of Wyoming, June, 1954.

(2) Research Corporation Fellow, 1952–1953.

(3) D. S. Tarbell and J. F. Kincaid, THIS JOURNAL, **62**, 728 (1940).

(4) H. Schmid and K. Schmid, *Helv. Chim. Acta*, **36**, 489 (1953), report rate data for the allyl ether of methyl *o*-cresotinate at one temperature. Their value of $k_1 = 2.62 \times 10^{-1}$ sec.$^{-1}$ at 167.7° agrees well with ours (Table I).



Ia, R = H
b, R = CH_3
c, R = C_2H_5

IIa, R = H
b, R = CH_3
c, R = C_2H_5

The allyl and γ-methylallyl compounds were studied at five temperatures, the γ-ethylallyl compound at four (*cf.* Table I).

TABLE I[a]

FIRST-ORDER RATE CONSTANTS

T, °C.	$k \times 10^5$ sec.$^{-1}$ R = H	R = CH_3	R = C_2H_5
140.0		0.494 ± 0.008	
149.2	0.549 ± 0.004	1.07 ± .01	0.460 ± 0.002
158.4	1.22 ± .01	2.49 ± .03	1.01 ± .01
167.4	2.66 ± .02	4.90 ± .04	2.01 ± .02
178.6	6.19 ± .04	9.63 ± .08	4.66 ± .04
187.7	12.2 ± .10		

[a] In most cases the errors given represent average deviations on duplicate runs. In the few cases in which single runs are reported, the errors are the probable errors in *k* determined from the corresponding errors of individual points. The maximum error in *k* judged by average deviations is ± 1.2%; the maximum probable error in *k* within an individual run is ±1.6%. Both errors are safely less than ±2% assumed in the calculation of thermodynamic quantities.

After it was determined that a plot of log c/c_0 against time gave a good straight line, the best value of the slope was calculated by the method of least squares. The first-order rate constants so evaluated are given in Table I. In the same manner the best values of the Arrhenius activation energy, E_a, and the frequency factor, *A*, were computed by least squares. The entropy of activation, $\Delta S^{\ddagger}$, was obtained from the Arrhenius parameter *A* in the usual manner. These quantities are recorded in Table II.

TABLE II[a]

ENERGIES AND ENTROPIES OF ACTIVATION

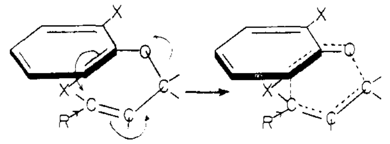
R =	H	CH_3	C_2H_5
E_a, kcal./m.	31.1 ± 0.3	30.4 ± 0.3	29.8 ± 0.4
ΔE_a	(0)	−0.7	−1.3
$\Delta S,^{\ddagger b}$ cal./deg.	−9.6 ± 0.6	−9.9 ± 0.6	−13.1 ± 0.8
$\Delta\Delta S^{\ddagger}$	(0)	−0.3	−3.5

[a] Errors given are the probable errors, assessed by assuming an error of ±2% in the values of *k*. [b] Calculated for *T* = 168.2°.

Comparison of the rate constants at a given temperature for the series of ethers shows that the effect of a γ-alkyl substituent on the rate is rather small, the rates of rearrangement showing little more than a twofold variation within the series. More importantly, the effect of γ-substitution is not predictable in any simple manner. Substitution of H by methyl approximately doubles the rate, but with the ethyl substituent a decrease in rate is observed, the rate of rearrangement of Ic being slightly slower than that of the simple allyl ether Ia. The statement[5] that γ-alkyl substituents in the allylic system facilitate rearrangement is apparently not generally true for the *para* rearrangement.

Deeper insight into the cause of this irregular rate variation is furnished by the thermodynamic data. The acceleration of the rearrangement observed with the methyl compound may be attributed largely to a decrease in activation energy, the entropy of activation being sensibly constant for the change R = H to R = CH_3. Introduction of a γ-ethyl substituent produces little change in E_a from that of the methyl compound, but a significant decrease in the entropy of activation is noted. This change in $\Delta S^{\ddagger}$ approximately cancels the effect of the lower activation energy with the result that the γ-ethylallyl ether and the allyl ether rearrange at nearly the same rate and both are slower than the γ-methyl compound.

Although the changes in E_a through the series are just within the limits of the significance of the data, it is perhaps more than fortuitous that the trend in E_a is what would be expected on a basis of the relative order of inductive electron release of alkyl groups, *i.e.*, H < CH_3 < C_2H_5.[6] According to the proposed mechanism for this rearrangement,[7,8] which involves as a rate-determining step a concerted electron reorganization of carbon–oxygen bond cleavage and carbon–carbon bond formation, an α- or γ-substituent in the allylic system would be expected to lower the potential energy component of the activation energy through its capacity for electron release.[9]



Consideration of the cyclic transition state immediately suggests steric complications arising from the interactions of the groups R and X. Manifestation of these steric effects could be expected in both E_a and $\Delta S^{\ddagger}$.[10,11] Within the limited series reported here, however, compressional energies of steric origin would be expected to be small[10,11]; on the other hand, differences in the entropy of activation may become important and rate-decisive.

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[5] D. S. Tarbell in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 25.

[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 316.

[7] C. D. Hurd and M. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

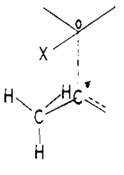
[8] S. J. Rhoads, R. Raulins and R. D. Reynolds, THIS JOURNAL, **76**, 3456 (1954).

[9] I. D. Webb and W. G. Young, *ibid.*, **73**, 777 (1951), and, later, C. A. Vernon, *J. Chem. Soc.*, 423, 4462 (1954), have demonstrated the activating effect of γ-alkyl substituents for both S_N1 and S_N2 displacement reactions of allylic halides, reactions which bear certain resemblances to the rearrangement discussed here, but which are free of the added complications arising from reaction at the (already substituted) γ-carbon. For the latter reason, the Claisen rearrangements might better be compared with the S_N2' reactions; data directly pertinent to the problem at hand are not available for these, although P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3555 (1953), have found an accelerating effect in S_N2' reactions for α-alkyl substituents.

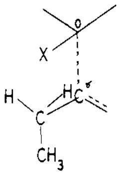
[10] I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946).

[11] Reference 6, p. 400*ff*.

Recently, Magat and Ivanoff[12] have given a semiquantitative interpretation of steric retardation of reaction rate for selected reaction series which show a relative constancy of activation energy but a regular diminution in $\Delta S^{\ddagger}$. Their calculations are based on the assumption that some of the possible conformations of the reacting molecules are forbidden in the activated complex; other things being equal, this reduction in permitted conformations may be related directly to a decrease in entropy of activation. The observed difference in $\Delta S^{\ddagger}$ for the γ-methyl and γ-ethylallyl ethers reported in this paper can be interpreted in the same manner. Thus, in the γ-methyl case, three staggered conformations of equal energy are possible in the transition state (A); for the γ-ethyl case, only one such conformation (B) is permitted, the other two being excluded by steric pressures.[13] It is noteworthy that the ratio of rates for these two ethers agrees with that reported by Magat[12] for comparable reaction series, *i.e.*, *ca.* 2:1. The present case, then, appears to be another example of steric retardation of reaction rate expressed largely through the entropy factor.[14]



A



B

It is unfortunate that pure samples of α-substituted allylic ethers of this series have not been available and thus could not be included in this study. Such compounds might be expected to derive activation from the alkyl substituents without the opposing steric complications. Qualitative evidence of the validity of this prediction is available, however, in the success of the preferential rearrangement of the α-isomers in this series.[8,15] Work is continuing on this general problem.

Acknowledgments.—Financial aid from the Research Corporation and the Research Council of the University of Wyoming is gratefully acknowledged. We are indebted also to Dr. Rebecca Raulins for technical advice and assistance with the calculations.

Experimental

Materials.—The three ether–phenol pairs were prepared and purified by methods already described.[8,15] Refractive indices of the purified ether samples employed: Ia, $n^{20}\text{D}$ 1.5180; Ib, $n^{20}\text{D}$ 1.5178; Ic, $n^{20}\text{D}$ 1.5140. Refractive indices of the corresponding purified phenols: IIa, $n^{20}\text{D}$ 1.5367; IIb, $n^{20}\text{D}$ 1.5351; IIc, $n^{20}\text{D}$ 1.5297.

Rate Measurements.—Rates of rearrangement were followed by change in refractive index by the technique of Foster, Cope and Daniels.[16] Five-drop samples of ether were sealed under vacuum in scrupulously cleaned Pyrex tubes (6 mm. o.d., 10-cm. length). Eight such tubes were immersed simultaneously in a stirred oil-bath thermostatically regulated to ±0.04°. At intervals of time chosen so that the range of 5 to 80% rearrangement was covered, the samples were withdrawn and plunged into ice-water to quench the reaction. The refractive indices of the samples were determined at 20.0 ± 0.01° with an Abbe-type Spencer refractometer with an estimated accuracy of ±0.0001. All runs contained 6–8 experimental points and, with a few exceptions, were made in duplicate.

The direct relationship between composition and refractive index was checked by known mixtures of ether and phenol. In all cases there was excellent agreement between calculated and observed values. The % rearrangement then could be calculated from the relationship, % rearranged $= 100(n_t - n_E)/(n_P - n_E)$, where n_t = refractive index of reaction mixture at time t, n_E = refractive index of pure ether and n_P = refractive index of pure phenol. Data for typical runs are given in Table III.

TABLE III

ALLYL ETHER OF METHYL *o*-CRESOTINATE AT 178.6°

t, sec.	$n^{20}\text{D}$	Rearranged, %	*t*, sec.	$n^{20}\text{D}$	Rearranged, %
	Run 1			Run 2	
0	1.5180	0	0	1.5180	0
3600	1.5217	19.8	3660	1.5215	18.7
7200	1.5246	35.3	7260	1.5246	35.3
10800	1.5270	48.1	10980	1.5270	48.1
14400	1.5289	58.3	14460	1.5289	58.3
17880	1.5304	66.3	18180	1.5306	67.4
21480	1.5317	73.3	21660	1.5318	73.8
25080	1.5327	78.6	25270	1.5327	78.6

$k = 6.22 \times 10^{-5}$ sec.$^{-1}$ $k = 6.16 \times 10^{-5}$ sec.$^{-1}$

Average $k = 6.19 \pm 0.04 \times 10^{-5}$ sec.$^{-1}$

The best values of k were determined by the least squares treatment of the rate data from the equation $\log c/c_0 = -kt/2.303$, where c/c_0 = fraction of ether unrearranged.

The energy of activation E_a and frequency factor $\log A$ were evaluated by the least squares method from the Arrhenius relationship

$$\log k = \log A - \frac{E_a}{2.303\ R}\left(\frac{1}{T}\right)$$

$\log A$ was converted to the entropy of activation at 441.3°K. by the relationship

$$\Delta S^{\ddagger} = 2.303R \log A - 2.2303R \log (k'T/h)$$

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[12] N. Ivanoff and M. Magat, *J. chim. phys.*, **47**, 914 (1950).

[13] Stuart–Briegleb molecular models for these compounds convincingly demonstrate this steric interference.

[14] *Cf.* also L. P. Hammett and T. I. Crowell, THIS JOURNAL, **70**, 3444 (1948); L. P. Hammett and P. M. Dunbar, *ibid.*, **72**, 109 (1950).

[15] S. J. Rhoads and R. L. Crecelius, *ibid.*, **77**, 5060 (1955).

[16] E. G. Foster, A. C. Cope and F. Daniels, *ibid.*, **69**, 1893 (1947).