TABLE IV

MOLECULAR TERMINATION CONSTANTS OF REPRESENTATIVE AROMATIC COMPOUNDS

Compound	k_r/k_p [a]
Anisole	1.62 ± 0.02
Thiophene	$0.98 \pm .07$
p-Xylene	$(1.05 \pm .01) \times 10^{-2}$
p-Chloroanisole	$(8.2 \pm .2) \times 10^{-3}$

[a] The precision is taken as the indeterminate error of the mean of the values of k_r/k_p calculated for each concentration (Table III), A.D. $= \pm \Sigma(d)/n\sqrt{n}$, where n is the number of values.

The method used to maintain the dielectric constant of the medium in this work resulted in a corresponding decrease of the concentration of carbon tetrachloride as the concentration of added compound or monomer was increased. If carbon tetrachloride itself were a fairly active molecular terminator, this would complicate the effects on degree of polymerization and the observed molecular termination constants might have to be corrected.[24] However, analysis for chlorine[25] of polymers prepared at high ratios of carbon tetrachloride to styrene and comparison of the degree of polymerization obtained in carbon tetrachloride with that obtained in the presumably inert solvent cyclohexane have demonstrated that the molecular termination constant of carbon tetrachloride cannot be greater than 2×10^{-4}.[26] The corresponding correction would be of the order of magnitude of the experimental error of the lowest constants.

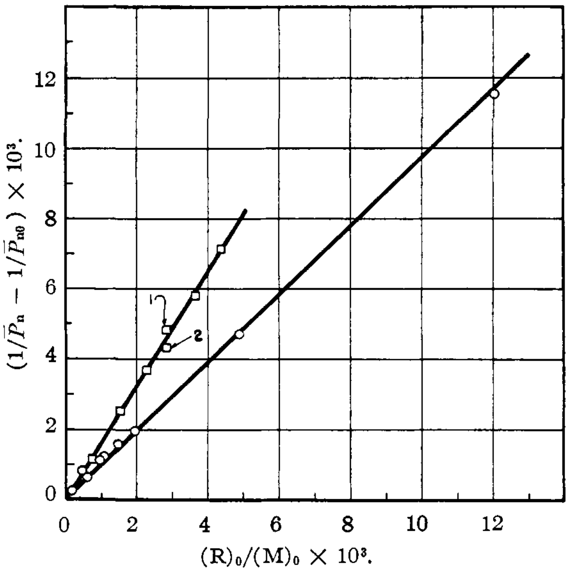

Fig. 3.—Plots according to equation 6: □, anisole, (1) 9% conversion, (2) 16% conversion; O, thiophene.

Acknowledgment.—The authors gratefully acknowledge the support of this work by the Office of Naval Research, Contract No. Nonr 343(00), Project NR356-262.

BROOKLYN, N. Y.

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(24) It can be shown readily that in this case equation 6 would have to be modified to:

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_{n0}} + \frac{(R)}{(M)}\left[\frac{k_r}{k_p} - \frac{V_r}{V_s} \times \frac{k_s}{k_p}\right]$$

where k_s/k_p is the molecular termination constant of carbon tetrachloride and V_r and V_s are the molar volumes of the respective substances.

(25) Analyses by Clark Microanalytical Laboratories, Urbana, Ill.

(26) Detailed data may be obtained upon request from the senior author.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

1,3-Shifts. III. The Kinetics of the Thermal Rearrangement of Phenyl Benzanilimino Ethers[1]

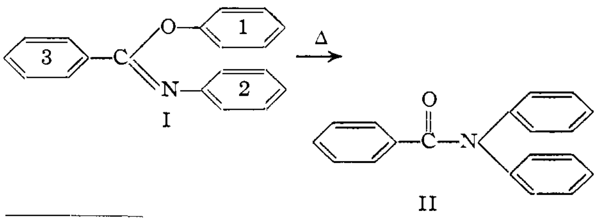
BY KENNETH B. WIBERG AND BERTRAM I. ROWLAND

RECEIVED OCTOBER 20, 1954

The rate of thermal rearrangement of a number of substituted phenyl benzanilimino ethers was determined in diphenyl ether solution. The rates of reaction for the *para* substituted compounds were found to parallel the rates of a nucleophilic displacement by piperidine on *p*-substituted *o*-nitrochlorobenzenes. It was found that the *ortho* substituted compounds in general gave a higher rate of reaction than the corresponding *para* substituted compounds, and this was shown to be largely an entropy effect by determining the entropy and enthalpy of activation for several compounds. The rearrangement of a mixture of phenyl benzanilimino ether and *p*-chlorophenyl benz-*p*-chloroanilimino ether was found to give no mixed products, indicating the reaction to be intramolecular.

Introduction

The number of rearrangements which appear to involve a cyclic four-membered transition state is very small in comparison to the number of intramolecular 1,2-shifts. In continuing a study of 1,3-shifts, we have chosen to investigate a reaction which is probably of this type, the thermal rearrangement of phenyl benzanilimino ether (I) to N-phenylbenzanilide (II). This reaction was investigated by Chapman[2] who measured the rate of reaction by the comparison of the melting



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(1) Taken from part of a thesis submitted by Bertram I. Rowland to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1954.

(2) A. W. Chapman, *J. Chem. Soc.*, 1992 (1925); 2296 (1926); 1749 (1927).

TABLE I

Substituent	Yield, %	Melting point, °C. Found	Melting point, °C. Reptd.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	$\lambda_{max.}$	Spectrum $\epsilon_{max.} \times 10^{-3}$	Ref.
Unsubst.	64	104.2–105.0	105	$C_{19}H_{15}ON$							224	21.5	8
o-CH_3	46	73.4–73.8		$C_{20}H_{17}ON$	83.59	83.72	5.96	5.72	4.88	4.53	224	21.1	
m-CH_3	60	62.7–63.2	65	$C_{20}H_{17}ON$							234	27.6	2
p-CH_3	64	58.8–59.8		$C_{20}H_{17}ON$	83.59	83.41	5.96	5.92	4.88	4.74	223	23.5	
o-C_2H_5[c]													
p-C_2H_5	15	42.7–43.3		$C_{21}H_{19}ON$	83.69	83.40	6.35	6.55	4.65	4.45	222	25.3	
o-*i*-C_3H_7[b]	58	76.2–76.7		$C_{22}H_{21}ON$	83.77	83.99	6.71	7.00	4.44	4.24	223	20.7	
p-*i*-C_3H_7	39	65.3–65.8		$C_{22}H_{21}ON$	83.77	83.68	6.71	6.40	4.44	4.39	222	25.7	
o-*t*-C_4H_9	40	90.7–91.1		$C_{23}H_{23}ON$	83.85	83.53	7.04	7.17	4.25	4.11	224	23.5	
p-*t*-C_4H_9	57	97.2–97.6		$C_{23}H_{23}ON$	83.85	83.79	7.04	6.72	4.25	4.15	223	24.3	
o-Cl	37	85.7–86.1	88	$C_{19}H_{14}ONCl$							224	22.3	2
p-Cl	57	90.0–90.6	92–93	$C_{19}H_{14}ONCl$							227	32.6	2
p-Br	51	83.0–83.8		$C_{19}H_{14}ONBr$	64.78	64.91	4.01	4.23	3.98	4.06	230	30.4	
p-CH_3CO	45	94.4–94.9	94–95	$C_{21}H_{17}O_2N$							250	25.6	2
o-NO_2[a,b,d]	54	109.6–112	116	$C_{19}H_{14}O_3N_2$							227	27.0	8
p-NO_2[a,b,d]	30	73.0–73.8	76–77	$C_{19}H_{14}O_3N_2$							224 263	20.6 20.7	2
o-CH_3O	20	112.6–112.8	113	$C_{20}H_{17}O_2N$							226	24.5	2
p-CH_3O	66	77.4–78.4	79–80	$C_{20}H_{17}O_2N$							227	25.3	2
p,p'-diCl	60	65.7–66.5	68–69	$C_{19}H_{13}ONCl_2$					4.09	4.03			9

[a] The substituted phenol was added after all of the sodium had reacted. [b] *t*-Butyl alcohol was used as the solvent instead of absolute ethanol. [c] It was not possible to obtain this compound in crystalline form. [d] These compounds were found not to give clean reactions, and thus were not studied further.

points of reaction mixtures after heating for various times with the melting points of synthetic mixtures of the imino ether and the amide. He concluded from these experiments that the reaction followed first-order kinetics. Similarly, by comparing the melting point of a heated mixture of equal amounts of I and *p*-tolyl benz-*p*-methylanilimino ether with that of equal amounts of II and N,N-di-*p*-tolylbenzamide, he concluded that the reaction was intramolecular.

He later determined the percentage reaction in 90 minutes for a number of substituted phenyl benzanilimino ethers. He found that electron-withdrawing groups on ring 1 facilitated the reaction, indicating an electron-rich migrating group. Electron-withdrawing groups on ring 2 weakly retarded the reaction, whereas substituents on ring 3 had little effect on the rate. He also observed that compounds with *ortho* substituents on ring 1 rearranged at a faster rate than those with the corresponding *para* substituent.

Chapman's rate data were unfortunately rather crude and were obtained using the pure substance rather than a solution. The determinations which were made on the basis of melting points are subject to much uncertainty. Therefore, we have determined the rate of reaction for a number of phenyl benzanilimino ethers substituted in ring 1 using diphenyl ether as a solvent. The entropy and enthalpy of activation were determined for several compounds, and a more convincing piece of evidence for the intramolecular character of the rearrangement was obtained.

Experimental[3]

Preparation of Benzanilimino Ethers.—To a 500-ml. flask fitted with a condenser, a drying tube and a nitrogen inlet tube was added 250 ml. of absolute ethanol and 0.3 mole of the phenol. Sodium (6.0 g., 0.25 atom) was added in small portions while nitrogen was bubbled through the mixture. A solution of 50 g. (0.24 mole) of benzanilimino chloride[4] in 50 ml. of absolute ether was added slowly to the solution after the sodium had dissolved. After 15 hours, the solution was distilled until about 175 ml. of distillate had been collected. The residue was poured into 500 ml. of ice-water and it was allowed to stand in an ice-chest overnight. After the ice had melted, the solid was filtered and recrystallized from absolute ethanol to a constant melting point. The compounds prepared in this manner are shown in Table I.

***sec*-Butyl Benzanilimino Ether.**—Sodium (6.0 g., 0.25 mole) was dissolved in 200 ml. of *sec*-butyl alcohol while nitrogen was bubbled through the solution. The procedure described above then was followed up to the distillation of the solvent. The reaction mixture was washed with water, dried over anhydrous potassium carbonate and distilled giving 25.0 g. (40%) of *sec*-butyl benzanilimino ether, b.p. 125–126° at 1 mm., n^{25}D 1.5623, d^{25} 1.022.

Phenols.—All the phenols which were used in the above preparation were purified commercial samples with the exception of *p*-ethylphenol, *o*-*t*-butylphenol and *o*-isopropylphenol. The first two compounds were prepared by published procedures[5,6] and *o*-isopropylphenol was prepared as follows.[7] To a solution of methylmagnesium bromide in 500 ml. of ether prepared from 79 g. (3.3 g. atoms) of magnesium was added with stirring a solution of 152 g. (1.0 mole) of methyl salicylate in 500 ml. of dry ether. After several hours, the solution was poured onto ice and acidified with dilute sulfuric acid. The phenol was extracted from the ether solution with 20% sodium hydroxide solution which was then heated to hydrolyze any unreacted ester. After acidification with carbon dioxide, the oil was dissolved in benzene, separated and distilled giving 84 g. (63%) of *o*-isopropenylphenol, b.p. 90–91° at 17 mm., n^{25}D 1.5496. Hydrogenation of 54 g. of *o*-isopropenylphenol in 100 ml. of dry ethanol at room temperature and 60 p.s.i.g. using about 200 mg. of Adams catalyst required 1.03 equivalents of hydrogen. Distillation of the solution gave 52.5 g. of *o*-isopropropylphenol, b.p. 97–98° at 13 mm.

Rearrangement of *o*-*t*-Butylphenyl Benzanilimino Ether.—The rearrangement of 0.8 g. of *o*-*t*-butylphenyl benzanil-

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[3] All melting points are corrected, whereas boiling points are not. The analyses were performed by B. Nist and by A. Elek.

[4] O. Wallach, *Ann.*, **184**, 79 (1877).

[5] J. P. Lambooy, THIS JOURNAL, **72**, 5327 (1950).

[6] H. Hart, *ibid.*, **71**, 1966 (1949).

[7] This is an adaptation of the procedure of A. Behal and M. Tiffeneau, *Bull. soc. chim. France*, [4] **3**, 315 (1908).

[8] O. Mumm, H. Hesse and H. Volquartz, *Ber.*, **48**, 385 (1915).

[9] A. W. Chapman, *J. Chem. Soc.*, 2458 (1930).

imino ether was carried out at 230° for nine hours. The product was recrystallized from ethanol and washed with ethanol and dilute hydrochloric acid. N-(*o*-*t*-Butylphenyl)-benzanilide (0.32 g., 40%) was obtained having m.p. 168–169°. The ultraviolet and infrared spectra of the anilide were sufficiently similar to that of N-phenylbenzanilide to indicate a compound of similar structure.

Anal. Calcd. for $C_{23}H_{23}ON$: N, 4.25. Found: N, 4.27.

Analytical Method.—The analytical procedure made use of the known difference in basicity between the benzanilimino ether and the anilide, the former being the stronger base. One milliliter of the reaction solution was transferred to a 30-ml. beaker and diluted with 8 ml. of glacial acetic acid. The solution was titrated potentiometrically with 0.1 *M* perchloric acid in glacial acetic acid, using a glass electrode, a silver–silver chloride electrode,[10] and a Beckman model H *p*H meter. It was found that the perchloric acid–glacial acetic acid solution quickly dissolved all stopcock greases and, therefore, the glass stopcock from a 5-ml. Pyrex buret was replaced with the Teflon stopcock arrangement from a 50-ml. Fisher and Porter "Ultramax" buret. The titrant was slowly and continuously run into the beaker with mechanical stirring, the *p*H meter being read at 0.2-ml. intervals. As the end-point was approached, 0.1-ml. portions were added and an interval of time was allowed after each addition till the *p*H meter gave a constant reading. The amide was shown not to interfere with the analysis, and the initial observed ether concentration was found to agree with that calculated from the quantity used with an average error of 1.4% and a maximum error of 3%. A typical titration curve is shown in Fig. 1.

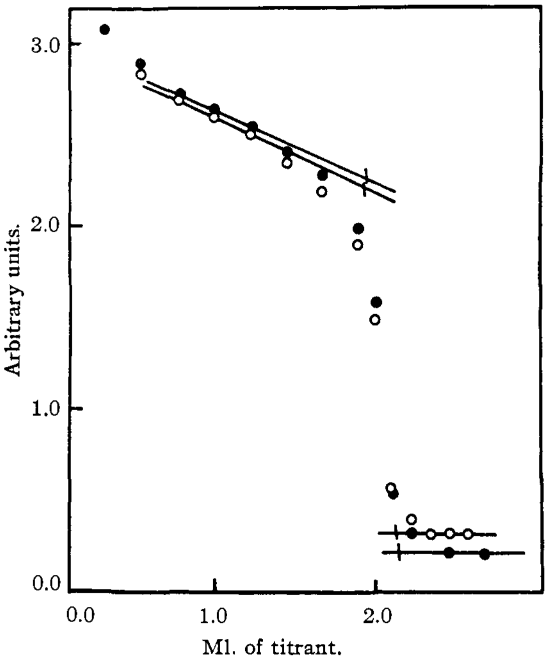

Fig. 1.—Titration curve for titration of phenyl benzanilimino ether with perchloric acid in glacial acetic acid.

Kinetic Method.—Approximately 2.5 g. of the benzanilimino ether was carefully weighed and dissolved in diphenyl ether (Eastman Kodak Co. white label, redistilled, b.p. 130–131° at 14 mm., $n^{25}D$ 1.5794) giving a final volume of 25 ml. This corresponds to about a 0.3 *M* solution. About 3 ml. of this solution was added to each of eight 10-mm. tubes about 4" long, which had been cleaned with dichromate solution, ammonium hydroxide solution and distilled water. The tubes were evacuated and sealed, and then immersed in the thermostat liquid. At regular intervals, a tube was removed, opened, and two 1-ml. aliquots were analyzed by the method described above. The agreement between the two aliquots was always very good. In all cases, a plot of the logarithm of the benzanilimino ether concentration against time gave a straight line, indicating the reaction to be first order. The runs usually were carried to better than 50% completion, and a typical rate plot is shown in Fig. 2. In one case, a run was repeated and a 4% deviation between the two results was obtained.

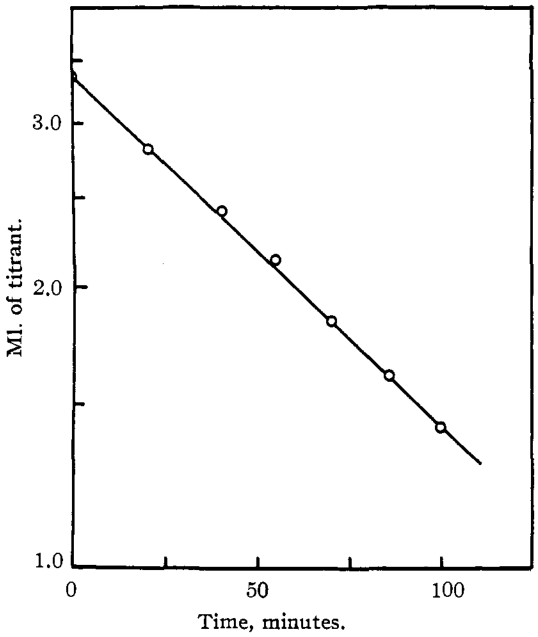

Fig. 2.—Rate plot for the rearrangement of *p*-chlorophenyl benzanilimino ether at 255.1°.

Thermostat.—The thermostat was constructed from a 12" × 12" Pyrex animal jar which was insulated with 6" of "Vermiculite." The thermostat liquid was du Pont "Hi-tec" (a eutectic mixture of potassium nitrate, sodium nitrate and sodium nitrite) which was heated with a 1 kw. fixed stainless steel clad heater and a 0.5 kw. regulated heater, both being connected through variable voltage transformers. The stirrer was a 4" by 1.5" hollow perforated stainless steel cylinder, partially open at each end, and attached to a $^1/_4$" stainless steel shaft. It was driven by a 0.25 h.p., 1725 r.p.m. motor *via* a flexible shaft. The temperature was regulated by a mercury contactor operating through a thyratron relay, and it could be operated conveniently as low as 180°. The temperature could be maintained at a constant value ±0.1°.

Results

In order to establish the mechanism of the rearrangement of benzanilimino ethers, it first was necessary to determine whether the reaction is intermolecular or intramolecular. The experiment of Chapman mentioned above, using the melting point of a mixture as the criterion, is hardly satisfactory. Therefore, a mixture of phenyl benzanilimino ether and *p*-chlorophenyl benz-*p*-chloroanilimino ether was heated until completely rearranged. Since the two compounds should rearrange at approximately the same rate, the mixed products should be formed if the reaction were intermolecular. The mixture of amides obtained was compared with a mixture of amides formed by heating each of the two ethers separately under the same conditions as the mixed rearrangement. Both the X-ray powder patterns and the infrared spectra of the two mixtures were identical, thus demonstrating the absence of mixed products and indicating the reaction to be intramolecular.

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[10] J. S. Fritz, *Anal. Chem.*, **22**, 1028 (1950).

The rate of rearrangement in diphenyl ether solution then was determined by following the disappearance of the benzanilimino ether by titrating with perchloric acid in glacial acetic acid solution. The rate constants are given in Table II, and are based on the natural logarithm. From these data, the entropy and enthalpy of activation may be calculated for several benzanilimino ethers. The values are given in Table III.

TABLE II

RATE OF REARRANGEMENT OF BENZANILIMINO ETHERS

Substituent	t, °C.	$k \times 10^5$, sec.$^{-1}$	$k_{255} \times 10^5$	k/k_0
o-*t*-Butyl	248.9	1.57		
	255.0	2.27	2.30[a]	0.30
	264.2	4.15		
	279.3	11.4		
p-Methyl	248.6	2.34		
	255.2	3.42	3.55[a]	0.46
	270.5	12.3		
	275.2	13.4		
H	233.6	1.62		
	245.3	3.67		
	255.1	7.72	7.66[a]	1.00
	264.2	14.2		
o-Methyl	233.6	1.75		
	246.1	4.53		
	254.9	8.48	8.87[a]	1.16
	255.5	9.56		
p-Chloro	233.6	3.04		
	246.1	7.07		
	249.0	9.02		
	255.1	14.3	13.8	1.80
p-Methoxy	255.3	1.63	1.60	0.21
p-Ethyl	255.2	3.74	3.69	.48
p-*i*-Propyl	255.2	3.84	3.79	.49
p-*t*-Butyl	255.0	3.82	3.82	.50
o-*i*-Propyl	255.2	6.84	6.75	.88
m-Methyl	255.6	7.41	7.11	.93
o-Methoxy	255.1	8.60	8.54	1.11
p-Bromo	255.2	18.4	18.1	2.36
o-Chloro	255.0	64.5	64.5	8.42
p-Aceto	203.3	5.84	...	..

[a] These values were obtained from the enthalpy and entropy of activation determined by the method of least squares.

TABLE III

ENTHALPY AND ENTROPY OF ACTIVATION

Substituent	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
p-Methyl	37.2 ± 0.9	− 9.7 ± 2
H	37.7	− 7.2
p-Chloro	37.4	− 6.7
o-Methyl	39.5	− 3.6
o-*t*-Butyl	36.7	−11.6

The ratio of rates for corresponding *ortho* and *para* substituted compounds is also of interest, and these values are given in Table IV.

TABLE IV

EFFECT OF POSITION OF SUBSTITUTION ON RATE OF REACTION

Substituent	k_{ortho}/k_{para}(255°)	Substituent	k_{ortho}/k_{para}(255°)
t-Butyl	0.60	Methyl	2.50
H	1.00	Chloro	4.67
i-Propyl	1.78	Methoxy	5.34

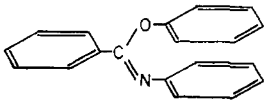
Discussion

Since electron-withdrawing substituents attached to the migrating group were found to accelerate the reaction, it is apparent that the rearrangement proceeds with an electron-rich migrating group. Thus, the mechanism appears to involve an attack of the electron pair of the nitrogen on the migrating group, and the reaction is essentially a nucleophilic displacement on an aromatic ring. A Hammett[11] plot of log k against σ (Fig. 3) showed a considerable scatter of points, which is not unexpected since this reaction involves the aromatic nucleus. The best straight line had a slope (ρ) of +1.75.

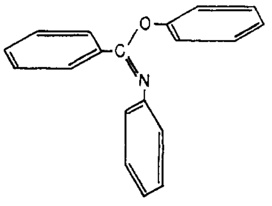
Very few nucleophilic displacements have been studied. However, Berliner and Monack[12] recently measured the rate of the reaction between piperidine and a series of *p*-substituted *o*-nitrobromobenzenes. If the log of their rate constants are plotted against the log of the rate constants for the rearrangement, a very good correlation is obtained (Fig. 4). This is additional evidence for a nucleophilic aromatic displacement. The low entropy of activation for the *p*-substituted compounds is also in accord with a mechanism involving a cyclic transition state.

It may be noted (Table III) that the rates of rearrangement for the *o*-substituted compounds were greater than those for the corresponding *p*-substituted compounds in all cases except *t*-butyl. This is unusual, since *o*-substituents usually retard reactions to a marked degree. Before considering the reason for this effect, the question of isomerism in the phenyl benzanilimino ethers must be considered first.

Two isomers are possible (Ia and Ib), corresponding to the *syn* and *anti* forms of an oxime. The *para* substituted compounds would be expected to be of the same series for several reasons. They were recrystallized repeatedly and had quite sharp melting points and thus are probably not mixtures of isomers. The good first-order plots which were obtained are also in agreement with this conclusion. Since they were prepared by the same method and had quite similar spectra, they are probably of the same series, and since no anomalies were found in the order of reactivity, this conclusion appears to be well founded. Similarly, it is likely that all of the *o*-substituted compounds are of the same series.



Ia



Ib

Unfortunately, there is no obvious way of determining whether the *para* and *ortho* compounds correspond to the same isomer. An examination of the Fisher–Hirshfelder models of the compounds suggests that the *o*-substituents would have an

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(11) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 184–193.

(12) E. Berliner and L. C. Monack, THIS JOURNAL, **74**, 1574 (1952).

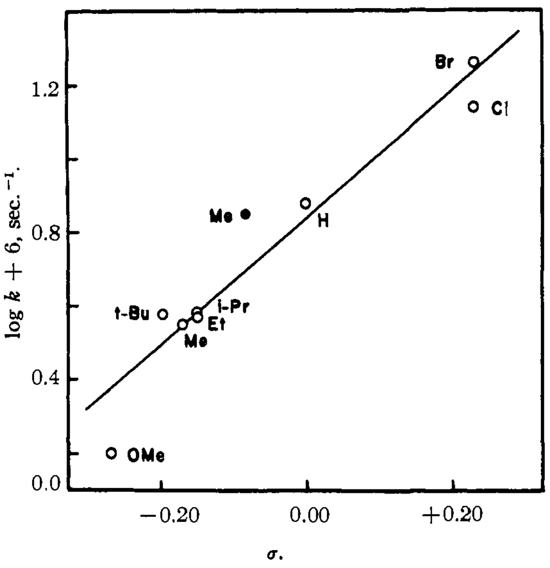

Fig. 3.—Hammett plot for rate of rearrangement of p-substituted phenyl benzanilimino ethers, except the solid circle which is a m-substituent.

equal effect on the formation of either isomer and, thus, it will be assumed that they are of the same series.

If this is the case, an explanation of the increased reactivity of the o-substituted compounds becomes apparent. In the benzanilimino ether, the o-substituent prevents free rotation of the phenyl to which it is attached. Since the formation of the four-membered cyclic transition state requires the restriction of this mode of rotation, the introduction of an o-substituent would lessen the entropy decrease in going from the reactants to the transition state. The data in Table III are in agreement with this conclusion, since there is a considerable increase in the entropy of activation in going from the p-methyl to the o-methyl substituted compound. The chloro group would be expected to reinforce the effect by virtue of the inductive effect operating close to the reaction site, and steric inhibition of resonance will account for much of the effect noted with the methoxy compounds. When the *ortho* substituent is a bulky group, steric compressibility becomes an important factor, and this should be reflected in a decrease in the entropy of activation, as was found in the case of the o-t-butylphenyl benzanilimino ether.

The above evidence would appear sufficient to establish a four-membered cyclic mechanism for the rearrangement of these ethers. It is known that in contrast to the phenyl ethers, the alkyl benzanilimino ethers give very poor yields of rearrangement product, and the reaction requires a higher temperature.[13] This is in marked contrast to the 1,2-shifts in which both alkyl and aryl groups usually rearrange with considerable facility. The difference in behavior may be found in the nature of the reaction.

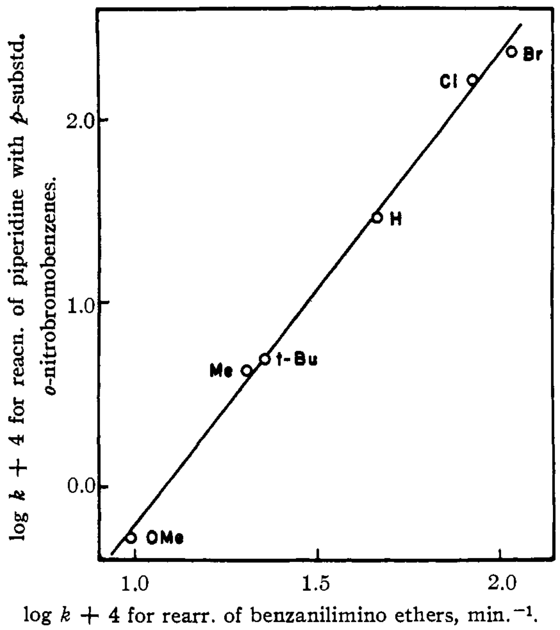

Fig. 4.—Comparison of the rates of rearrangement and the rates of a nucleophilic displacement on an aromatic ring.

The 1,2-shifts usually have an electron-deficient migrating group in the transition state, whereas the benzanilimino ethers have an electron-rich migrating group. An aryl group can accommodate the latter because of its unsaturation electrons, whereas an alkyl group can accommodate only an electron-deficient transition state. There are two reasons for the difficulty in effecting a frontside nucleophilic displacement on a saturated carbon. First, no type of hybridization similar to that suggested for an S$_N$2 type displacement is possible for a frontside reaction. Also, in many displacement reactions, a partial negative charge is found on both the entering and leaving groups in the transition state, and the electrostatic repulsion of these groups would increase the energy of activation. The latter reason cannot be overly important since neopentyl chloride does not react with aniline, a reaction which would involve partial positive and negative charges in the transition state, and thus should lower the energy of activation.

It is now believed that the n-alkyl benzanilimino ethers may rearrange *via* a free radical process, and this would account for many of the observed differences between the rearrangement of the alkyl and aryl ethers. The *sec*-butyl benzanilimino ether was found to undergo elimination rather than rearrangement and gave 2-butene and benzanilide as products. This reaction is probably typical of the *sec*-alkyl benzanilimino ethers, and may prove to be a convenient method for the dehydration of some *sec*-alcohols.

Acknowledgment.—We wish to thank the Research Corporation for financial support of this work, and also Dr. E. Lingafelter for his assistance in obtaining the X-ray powder patterns.

SEATTLE, WASHINGTON

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(13) G. D. Lander, *J. Chem. Soc.*, 406 (1903); A. W. Chapman, *ibid.*, 1750 (1927).