ORGANIC AND BIOLOGICAL CHEMISTRY

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A Kinetic Investigation of the Acid-catalyzed Rearrangement of Benzhydryl Azides and 1,1-Diarylethyl Azides[1]

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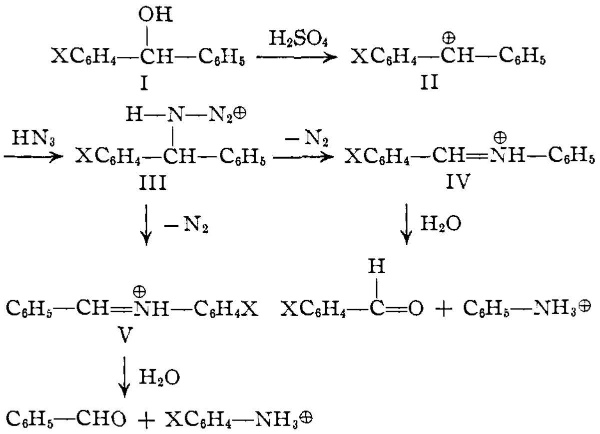
It has been demonstrated that the acid-catalyzed rearrangement of benzhydryl azides and 1,1-diarylethyl azides follows the kinetic law $-d(\text{azide})/dt = k(\text{azide})h_0$. Acetic acid was used as the solvent and sulfuric acid as the catalyst. The azides subjected to the kinetic study and the values of $k \times 10^8$(l./mole-sec.) at 25° are: benzhydryl azide, 2.38; *p*-bromobenzhydryl azide, 0.679; *p*-chlorobenzhydryl azide, 0.663; *m*-chlorobenzhydryl azide, 0.426; *p*-fluorobenzhydryl azide, 1.65; *p*-methylbenzhydryl azide, 5.41; *p*-methoxybenzhydryl azide, 21.6 (extrapolated value); 1,1-diphenylethyl azide, 0.663; 1-phenyl-1-*p*-chlorophenylethyl azide, 0.151; 1-phenyl-1-*p*-fluorophenylethyl azide, 0.525; 1-phenyl-1-*p*-tolylethyl azide, 1.35. Based in part on these data, arguments are presented to show that evolution of nitrogen and migration of an aryl group are not synchronous processes.

The present study was undertaken in an effort to elucidate more thoroughly the mechanism of the Schmidt rearrangement, particularly as applied to alcohols and olefins. Specifically, since product ratios have been determined previously for the Schmidt rearrangement of a series of *m*- and *p*-substituted benzhydrols[2] and 1,1-diphenylethylenes,[3] it was felt that a study of the kinetics of these reactions would furnish useful additional information pertaining to their mechanisms.

Treatment of a *m*- or *p*-substituted benzhydrol (I) with sulfuric acid and hydrogen azide gives, after hydrolysis of the reaction mixture, benzaldehyde, a *m*- or *p*-substituted benzaldehyde, the anilinium ion and a *m*- or *p*-substituted anilinium ion. It has been suggested[2] that I reacts with concentrated sulfuric acid to form the carbonium ion II which then combines with hydrogen azide to give the conjugate acid III of the *m*- or *p*-substituted benzhydryl azide. Rearrangement of III, with evolution of nitrogen, affords the conjugate acids IV and V of two isomeric Schiff bases. Upon subsequent hydrolysis IV and V give the ultimate products of the reaction. Upon analysis of the aldehyde fractions resulting from Schmidt reactions of *p*-methoxybenzhydrol, *p*-methylbenzhydrol, *p*-chlorobenzhydrol, *p*-bromobenzhydrol, *m*-chlorobenzhydrol and *p*-nitrobenzhydrol, it was found that the results could be correlated by a suitable adaptation of the Hammett equation. The equation of the line was found[2] to be

$$\log \text{product ratio} \frac{\text{benzaldehyde}}{m\text{- or }p\text{-subst. benzaldehyde}} = -2.03\sigma + 0.237$$

For study of the kinetics of each of the reactions, it was decided that prior preparation of the desired benzhydryl azide, followed by addition of the azide to an acetic acid solution of sulfuric acid,[4] would represent a convenient procedure. The method of Ege and Sherk[3d] was used to convert the various benzhydrols to the corresponding benzhydryl azides. The azides were purified by chromatography or by distillation (Table III).



$$\underset{\text{I}}{XC_6H_4-\overset{OH}{\overset{|}{C}}H-C_6H_5} \xrightarrow{H_2SO_4} \underset{\text{II}}{XC_6H_4-\overset{\oplus}{C}H-C_6H_5}$$

$$\xrightarrow{HN_3} \underset{\text{III}}{XC_6H_4-\overset{H-N-N_2^{\oplus}}{\overset{|}{C}}H-C_6H_5} \xrightarrow{-N_2} \underset{\text{IV}}{XC_6H_4-CH=\overset{\oplus}{N}H-C_6H_5}$$

$$\text{III} \xrightarrow{-N_2} \underset{\text{V}}{C_6H_5-CH=\overset{\oplus}{N}H-C_6H_4X} \xrightarrow{H_2O} C_6H_5-CHO + XC_6H_4-NH_3^{\oplus}$$

$$\text{IV} \xrightarrow{H_2O} XC_6H_4-\overset{H}{\overset{|}{C}}=O + C_6H_5-NH_3^{\oplus}$$

Pseudo-first-order rate constants, as determined by nitrogen evolution, were obtained from plots of $\log V_\infty/V_\infty - V_t$ *vs.* time. In the initial runs the reaction medium consisted of approximately a 5 *M* solution of sulfuric acid in acetic acid. The best straight line was drawn through the points representing the early stages of the reaction (up to about 50% of completion in most cases). The data are summarized in Table I. No significant change in the rate of nitrogen evolution was caused by the introduction of small amounts (15% of the weight of the azide employed) of benzalaniline or benzhydrol into the reaction mixture of benzhydryl azide, sulfuric acid and acetic acid. It was also determined that the presence of powdered glass had no effect on the rate of nitrogen evolution.

In order to determine the dependence of rate on the acidity of the medium, the rates of nitrogen evolution were measured at various sulfuric acid concentrations for a representative number of azides. The available data are summarized in Table I. Plots of pseudo-first-order rate constants *vs.* the negative of the acidity function, $-H_0$,[5] were linear, having a slope of +1. This

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[1] Abstracted from a thesis submitted by Cathryn H. Gudmundsen in partial fulfillment of the requirements for the Ph.D. degree, Kansas University, 1956.

[2] R. F. Tietz and W. E. McEwen, THIS JOURNAL, **77**, 4007 (1955).

[3] (a) W. E. McEwen, M. Gilliland and B. I. Sparr, *ibid.*, **72**, 3212 (1950); (b) L. P. Kuhn and J. Di Domenico, *ibid.*, **72**, 5777 (1950); (c) W. E. McEwen and N. B. Mehta, *ibid.*, **74**, 526 (1952); (d) S. H. Ege and K. W. Sherk, *ibid.*, **75**, 354 (1953); (e) D. R. Nielsen and W. E. McEwen, *ibid.*, **76**, 4042 (1954).

[4] We are indebted to Dr. G. P. Haight, Department of Chemistry, Swarthmore College, for the suggestion to use acetic acid as the solvent in these kinetic studies.

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 267.

TABLE I

SUMMARY OF KINETIC DATA FOR THE SCHMIDT REACTION OF BENZHYDRYL AZIDES

Azide	c H_2SO_4, moles/l.	T, °C.	k_1, hr.$^{-1}$	$h_0 \times 10^{-4}$	$k_2 \times 10^8$, l./mole sec.	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
Benzhydryl	4.82 ± 0.06	25.0	5.05 ± 0.03	5.89	2.38	21.2	−22.3
	4.82 ± .06	35.0	17.4 ± 0.4	5.89	8.21		
	4.82 ± .06	45.0	48.2 ± 1.0	5.89	22.7		
	4.82 ± .06	25.0	4.88[a]	5.89	2.30		
	5.13 ± .05	25.0	5.07 ± .06[a]	8.32	1.69		
	4.82 ± .06	25.0	5.67[b]	5.89	2.68		
	5.13 ± .05	25.0	5.77[b]	8.32	1.93		
	3.86 ± .01	25.0	1.46	2.19	1.85		
	4.42 ± .02	25.0	2.83	3.72	2.12		
	5.42 ± .09	25.0	11.4	11.0	2.89		
	5.90 ± .00	25.0	16.6	18.2	2.53		
	6.44 ± .02	25.0	30.3	32.4	2.60		
	7.19 ± .04	25.0	45.7	70.8	1.79		
p-Bromobenzhydryl	4.82 ± .06	25.0	1.44 ± .03	5.89	0.079	20.5	−27.0
	4.82 ± .06	35.0	4.92 ± .01	5.89	2.32		
	4.82 ± .06	45.0	14.3 ± .4	5.89	6.75		
p-Chlorobenzhydryl	5.02 ± .05	25.0	1.73 ± .03	7.24	0.663	22.8	−19.5
	5.02 ± .05	35.0	5.80 ± .09	7.24	2.22		
	4.82 ± .06	45.0	17.0 ± .1	5.89	8.02		
m-Chlorobenzhydryl	4.82 ± .06	25.0	0.902 ± .005	5.89	0.426	20.4	−28.3
	4.82 ± .06	35.0	2.83 ± .04	5.89	1.34		
	4.82 ± .06	45.0	8.54 ± .10	5.89	4.03		
	4.00 ± .04	25.0	0.333	2.51	0.368		
	5.90 ± .00	25.0	2.62	18.2	.400		
	7.19 ± .04	25.0	8.83	70.8	.347		
p-Fluorobenzhydryl	4.83 ± .05	25.0	3.49 ± .05	5.89	1.65	21.3	−22.5
	4.83 ± .05	35.0	11.4 ± .00	5.89	5.38		
	4.83 ± .05	45.0	34.7 ± .7	5.89	16.4		
p-Methoxybenzhydryl	5.13 ± .05	5.0	6.29 ± .16	8.32	2.10	19.5	−23.4
	5.13 ± .05	10.0	11.9 ± .1	8.32	3.97		
	5.13 ± .05	15.0	22.4 ± .5	8.32	7.48		
	4.00 ± .04	5.0	2.09	2.51	2.31		
	5.90 ± .00	5.0	13.7	18.2	2.09		
	7.19 ± .04	5.0	28.7	70.8	1.13		
	5.13 ± .05	25.0			21.6[c]		
p-Methylbenzhydryl	5.09 ± .04	20.0	9.26	7.77	3.31	22.5	−16.0
	5.02 ± .05	25.0	14.1 ± 0.1	7.24	5.41		
	4.82 ± .06	30.0	29.3 ± 0.3	5.89	13.8		
	4.82 ± .06	35.0	50.9 ± 1.1	5.89	24.0		
	2.96 ± .02	25.0	1.45	0.851	4.73		
	4.00 ± .04	25.0	4.67	2.51	5.16		
	5.90 ± .00	25.0	32.6	18.2	4.98		

[a] With 15 mole % benzalaniline added. [b] With 15 mole % benzhydrol added. [c] Extrapolated value.

demonstrates[6] that the reactions are second order, following the rate law

$$-\mathrm{d}(\text{azide})/\mathrm{d}t = k_2(\text{azide})h_0$$

Rates of nitrogen evolution were measured for the various benzhydryl azides at three or four different temperatures. From plots of $R \times 2.303 \times \log k_2h/kT$ *vs.* $10^3/T$ it was possible to calculate enthalpies and entropies of activation. The data are summarized in Table I.

Finally, a plot of $\log k_2/k_2^{\circ}$ *vs.* σ, shown in Fig. 1, was constructed. Although the complete data can best be fitted to a curve having a slight upward concavity, all of the points with the exception of that for *p*-methoxybenzhydryl azide are also reasonably well defined by a straight line having a slope of −2.26. In the argument which follows it will be convenient to make use of the linear portion of the curve.

The work described above not only establishes the kinetic order of the Schmidt rearrangement of benzhydryl azides, but, combined with previous work,[2] permits one more important conclusion to be reached about the detailed mechanism of the rearrangement: *viz., the evolution of nitrogen and rearrangement steps are not synchronous.* This conclusion may be reached by the following formal argument:

Let us make the (incorrect) assumption that a synchronous evolution of nitrogen and migration

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(6) A. A. Frost and R. D. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 276.

of an aryl group occurs in the Schmidt rearrangement of $\mathrm{XC_6H_4CH(N_3)C_6H_5}$. Let

k_2 = specific rate constant for nitrogen evolution
k_P = specific rate constant for $\mathrm{C_6H_5}$ migration
k_A = specific rate constant for $\mathrm{XC_6H_4}$ migration

Then

$$\mathrm{d(N_2)/d}t = k_2(\mathrm{XC_6H_4{-}\overset{\overset{\displaystyle N_3}{|}}{C}H{-}C_6H_5})h_0$$

$$\mathrm{d(XC_6H_4{-}CH{=}\overset{\oplus}{N}H{-}C_6H_5)/d}t = k_P(\mathrm{XC_6H_4{-}\overset{\overset{\displaystyle N_3}{|}}{C}H{-}C_6H_5})h_0$$

$$\mathrm{d(C_6H_5{-}CH{=}\overset{\oplus}{N}H{-}C_6H_4X)/d}t = k_A(\mathrm{XC_6H_4{-}\overset{\overset{\displaystyle N_3}{|}}{C}H{-}C_6H_5})h_0$$

Provided that $\mathrm{XC_6H_4\text{-}CH{=}\overset{\oplus}{N}H\text{-}C_6H_5}$, $\mathrm{C_6H_5\text{-}CH{=}\overset{\oplus}{N}H\text{-}C_6H_4X}$ and nitrogen are the only primary products of reaction[7]

$$\mathrm{d(N_2)/d}t = \mathrm{d(XC_6H_4{-}CH{=}\overset{\oplus}{N}H{-}C_6H_5)/d}t + \mathrm{d(C_6H_5{-}CH{=}\overset{\oplus}{N}H{-}C_6H_4X)/d}t$$

Therefore

$$k_2 = k_P + k_A$$

It is also clear that

$$k_A/k_P = \text{product ratio},$$
$$\mathrm{C_6H_5{-}CH{=}\overset{\oplus}{N}H{-}C_6H_4X/XC_6H_4{-}CH{=}\overset{\oplus}{N}H{-}C_6H_5} = \text{P.R. and } k_2 = k_P(1 + \text{P.R.})$$

This last equation may be related to the terms used in the various plots based on the Hammett equation as

$$\log k_2/k_2^\circ = \log k_P/k_2^\circ + \log(1 + \text{P.R.})$$

If the evolution of nitrogen and migration of the aryl group are synchronous processes, then a plot of log k_2/k_2° *vs.* log (1 + P.R.) should be linear (provided that only those values corresponding to the linear portion of Fig. 1 are chosen) and the slope should be +1. However, the slope actually turns out to be about two, and therefore the reactions are not synchronous (see discussion of errors following the Experimental section). Loss of nitrogen precedes migration of the aryl group, and the cation $\mathrm{C_6H_5CH(\overset{\oplus}{N}H)C_6H_4X}$ more nearly represents the transition state than does a bridged cation.

The same conclusion could have been reached on the basis of two other observations. (1) Whereas the point for *p*-methoxybenzhydrol falls on the straight line defined by the other five points in the plot of log molar product ratio, benzaldehyde/*m*- or *p*-substituted benzaldehyde, *vs.* σ,[2] the point for *p*-methoxybenzhydrol azide deviates markedly from the straight line defined by six other points in the plot of log k_2/k_2° *vs.* σ (Fig. 1). In other words, the product ratio plot is truly linear over the entire range of σ-values, whereas the kinetic plot is actually a shallow curve having positive curvature over the entire range of σ-values. (2) Whereas the straight line in the plot of log product ratio *vs.* σ has an intercept of 0.237, the plot shown in Fig. 1 passes through the origin. Neither of these observations is consistent with a synchronous loss of nitrogen and migration of an aryl group.

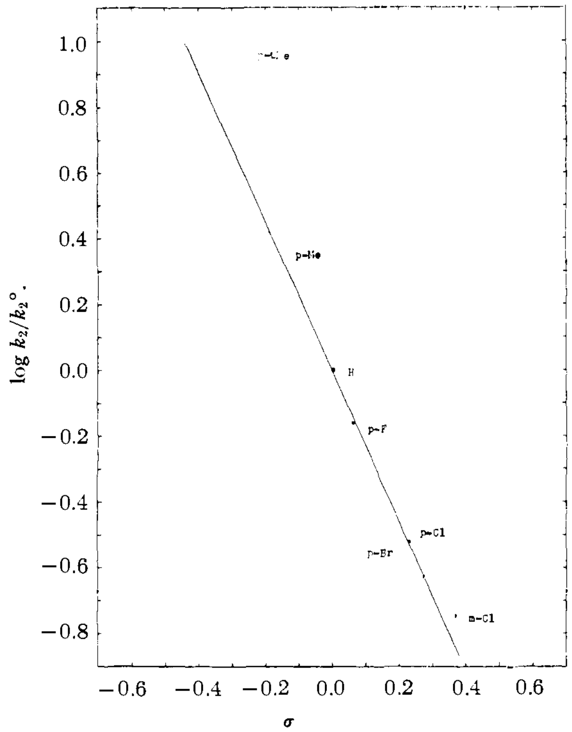

Fig. 1.—The Hammett equation applied to the Schmidt rearrangement of *m*- and *p*-substituted benzhydryl azides.

Treatment of a *m*- or *p*-substituted 1,1-diphenylethylene (VI) with sulfuric acid and hydrogen azide gives, after hydrolysis of the reaction mixture, acetophenone, a *m*- or *p*-substituted acetophenone, the anilinium ion and a *m*- or *p*-substituted anilinium ion. It has been assumed[3a] that VI reacts with sulfuric acid to form the carbonium ion VII which then combines with hydrogen azide to give the conjugate acid VIII of the *m*- or *p*-substituted 1,1-diphenylethyl azide. Rearrangement of VIII provides the conjugate acids IX and X of two isomeric anils. Upon subsequent hydrolysis IX and X give the ultimate products of the reaction. After analysis of the ketone fractions resulting from the Schmidt reactions of ten different *m*- or *p*-substituted 1,1-diphenylethylenes, it was found[3] that the results could be correlated by a suitable adaptation of the Hammett equation. The equation of the line is

$$\text{log molar product ratio, acetophenone}/m\text{- or }p\text{-substituted acetophenone} = -2.11\sigma + 0.293$$

The kinetics of a representative number of acid-catalyzed rearrangement reactions of 1,1-diarylethyl azides were measured in the same manner as for the benzhydryl azide series. It was demonstrated in the case of 1,1-diphenylethyl azide that the rate of rearrangement is proportional to the acidity of the medium, as measured by h_0. From

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(7) No products corresponding to hydrogen migration or to any other side reactions have ever been isolated from the reaction mixtures of any of the Schmidt reactions of benzhydrols. Furthermore, product ratios obtained in acetic acid as solvent are the same as those obtained in chloroform.

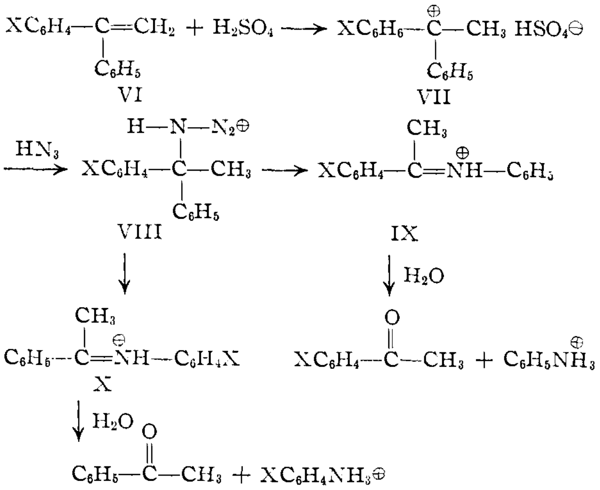
TABLE II

SUMMARY OF KINETIC DATA FOR THE SCHMIDT REACTION OF 1,1-DIPHENYLETHYL AZIDES

Azide	c H_2SO_4, moles/l.	T, °C.	k_1, hr.$^{-1}$	$h_0 \times 10^{-4}$	$k_2 \times 10^8$, l./mole sec.
1,1-Diphenylethyl	5.02 ± 0.05	25.0	1.73 ± 0.02	7.24	0.663[a]
	5.13 ± .05	35.0	4.54 ± .06	8.32	1.52
	5.13 ± .05	45.0	10.7 ± .3	8.32	3.57
	4.00 ± .04	25.0	0.803	2.51	0.888
	5.90 ± .00	25.0	5.08	18.2	.775
	7.19 ± .04	25.0	12.4	70.8	.487
1,1-Di-*p*-chlorophenylethyl	5.02 ± .05	25.0	0.113 ± 0.012	7.24	.0433
1-Phenyl-1-*p*-chlorophenylethyl	5.02 ± .05	25.0	0.393 ± .002	7.24	.151
1-Phenyl-1-*p*-fluorophenylethyl	5.02 ± .05	25.0	1.37 ± .14	7.24	.525
1-Phenyl-*p*-tolylethyl	5.02 ± .05	25.0	3.52 ± .07	7.24	1.35
1,1-Di-*p*-tolylethyl	5.02 ± .05	25.0	5.22 ± .16	7.24	2.00

[a] $\Delta H^{\ddagger}$ 15.2 kcal./mole; $\Delta S^{\ddagger}$ − 45.1 e.u.

measurements of the rate at three different temperatures it was possible to calculate the enthalpy and entropy of activation for the reaction of 1,1-diphenylethyl azide. All the data are summarized in Table II.



Although the number of cases studied was decidedly limited, a plot of log k_2/k_2° *vs.* σ, shown in Fig. 2, indicates a linear relationship over the range of σ-values, -0.17 to $+0.23$. The value of ρ is -3.16. Precisely the same arguments can be used for this series of reactions as for the benzhydryl azide series to demonstrate that the evolution of nitrogen and migration of an aryl group are not synchronous processes.

A comparison of the kinetic data obtained for the benzhydryl azide series (Table I) with the kinetic data obtained for the 1,1-diarylethyl azide series (Table II) reveals a striking fact. Although 1,1-diphenylethyl azide evolves nitrogen at a slower rate than benzhydryl azide, the enthalpy of activation of the 1,1-diphenylethyl azide reaction is markedly lower than that of the benzhydryl azide reaction. In other words, the fact that 1,1-diphenylethyl azide reacts more slowly is due to a relatively unfavorable entropy of activation. It is noteworthy that triphenylmethyl azide does not evolve nitrogen at all in contact with concentrated sulfuric acid at or near room temperature.[8] Perhaps a similar but more pronounced effect is operative in this case.

Acknowledgment.—The authors are indebted to the National Science Foundation for a research grant which made this investigation possible.

Experimental[9]

Preparation of Azides.—A modification of the procedure of Ege and Sherk[3d] was used to prepare the azides. The preparation of *p*-chlorobenzhydryl azide may be cited as a typical example of the method employed. To 125 ml. of anhydrous benzene was added 18.0 g. (0.115 mole) of trichloroacetic acid and 10.9 g. (0.05 mole) of *p*-chlorobenzhydrol.[2] A total of 75 ml. of a 1.76 *M* solution of hydrogen azide in benzene (0.15 mole) was then added in portions. The resulting pale yellow solution was allowed to stand at room temperature for 10 days, then poured into water. The benzene solution was washed with water until the washings no longer gave an acid reaction with litmus paper. The benzene layer was dried over anhydrous magnesium sulfate, then the solvent was distilled. The residue consisted of 13.4 g. of a cloudy, pale yellow oil. An equal volume of petroleum ether (b.p. 30–40°) was added to the oil and the resulting solution passed through a column of alumina (1 × 32 cm.). Evaporation of the solvent from the eluate gave a slightly turbid, pale yellow oil which was filtered through glass wool. The final product consisted of 8.5 g. of clear, pale yellow oil, which analyzed for 95% of the theoretical nitrogen content.

The azides of the 1,1-diphenylethyl series were prepared from the appropriate olefins by addition of hydrogen azide to the double bond, the reaction being catalyzed by trichloroacetic acid and carried out in benzene solution.

In Table III are listed the pertinent analytical data for the various azides employed in the kinetic runs.

Description of Kinetic Measurements.—The apparatus consisted of a 50-ml. flask immersed in a water-bath maintained at the desired temperature ±0.05°. This was fitted with a glass tube, containing a stopcock-regulated support for the sample vial. The glass tube was connected by Tygon tubing to a gas buret. The flask and tube were attached to a shaking device capable of causing vigorous agitation of the mixture.

All of the azides used in these studies were colorless or pale yellow oils. In each case 0.002 mole of the azide was weighed out in a small vial and added to 10 ml. of a solution of sulfuric acid in acetic acid of known molarity which had previously been maintained at the desired temperature for at least 20 minutes. Shaking was commenced immediately after introduction of the sample. The rate of nitrogen evolution was measured by the displacement of mercury in the gas buret, which was calibrated in tenths of a ml.

Slight adjustments in the values of zero time were necessary in a few cases due to a mixing effect. This effect was most pronounced in the runs with *p*-methoxybenzhydryl azide, which was to be expected because of its rapid rate of reaction.

Table IV gives the H_0 values for sulfuric acid–acetic acid mixtures reported by Hall and Spengeman.[10] Since these

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(8) C. L. Arcus and R. J. Mesley, *J. Chem. Soc.*, 178 (1953).

(9) All m.p.'s are corrected and all b.p.'s are uncorrected. Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(10) N. F. Hall and W. F. Spengeman, THIS JOURNAL, **62**, 2489 (1940).

TABLE III

PREPARATION AND PURIFICATION OF AZIDES

Azide	Method of purification	Molecular formula	Nitrogen, % Calcd.	Found (Dumas)	Found[a] (acid decompn.)
Benzhydryl	Distillation[b]	$C_{13}H_{11}N_3$	20.1	19.3	19.7
p-Bromobenzhydryl	Chromatography	$C_{13}H_{10}N_3Br$	14.6	12.3	12.5
p-Chlorobenzhydryl	Chromatography	$C_{13}H_{10}N_3Cl$	17.2	16.2	16.4
m-Chlorobenzhydryl[c]	Distillation[d]	$C_{13}H_{10}N_3Cl$	17.2	17.2	14.9[e]
p-Fluorobenzhydryl[f]	Chromatography	$C_{13}H_{10}N_3F$	18.5	18.9	18.7
p-Methoxybenzhydryl	Chromatography	$C_{14}H_{13}N_3O$	17.6	17.4	17.2
p-Methylbenzhydryl	Chromatography	$C_{14}H_{13}N_3$	18.8	18.2	18.4
1,1-Diphenylethyl	Chromatography[g]	$C_{14}H_{13}N_3$	18.8	18.0	18.3
1-Phenyl-1-*p*-chlorophenylethyl	Chromatography	$C_{14}H_{12}N_3Cl$	16.3	13.2	14.6
1-Phenyl-1-*p*-fluorophenylethyl	Chromatography	$C_{14}H_{12}N_3F$	17.4	17.7	16.9
1-Phenyl-1-*p*-tolylethyl	Chromatography	$C_{15}H_{15}N_3$	17.7	16.6	17.7

[a] Average of values based on the amount of N_2 evolved in the kinetic runs. [b] B.p. 122–123° (1.7 mm.), $n^{32}D$ 1.5851, reported[10] b.p. 134° (4 mm.). [c] *Anal.* Calcd. for $C_{10}H_{13}N_3Cl$: C, 64.07; H, 4.14; N, 17.25; Cl, 14.55. Found: C, 64.26; H, 3.97; N, 17.24; Cl, 14.40. [d] B.p. 145–146° (1.8 mm.). [e] There is no apparent explanation for the fact that only 87% of the expected nitrogen is evolved. [f] *Anal.* Calcd. for $C_{13}H_{10}N_3F$: F, 8.36. Found: F, 8.20. [g] Also purified by distillation, b.p. 112–115° (1 mm.), reported,[3] b.p. 118° (1.5 mm.). However, the distilled product turned deep yellow a short time after completion of the distillation.

TABLE IV

H_0 VALUES OF SOLUTIONS OF SULFURIC ACID IN ACETIC ACID

H_2SO_4, *M*	H_0	H_2SO_4, *M*	H_0
3.33	−3.95	5.29	−4.99
3.60	−4.28	5.66	−5.07
4.16	−4.53	6.10	−5.35
4.28	−4.57	6.61	−5.64
4.60	−4.71	7.14	−5.91
4.87	−4.75	7.81	−6.03

workers reported that H_0 is a linear function of molarity from 1 to 8 *M*, a plot of the data in Table IV was made by the method of least squares. The concentrations of the sulfuric acid–acetic acid solutions used in the kinetic measurements were determined by titration with a standard solution of sodium acetate in acetic acid, brom phenol blue being used as indicator,[11] and the corresponding values of H_0 obtained from the graph.

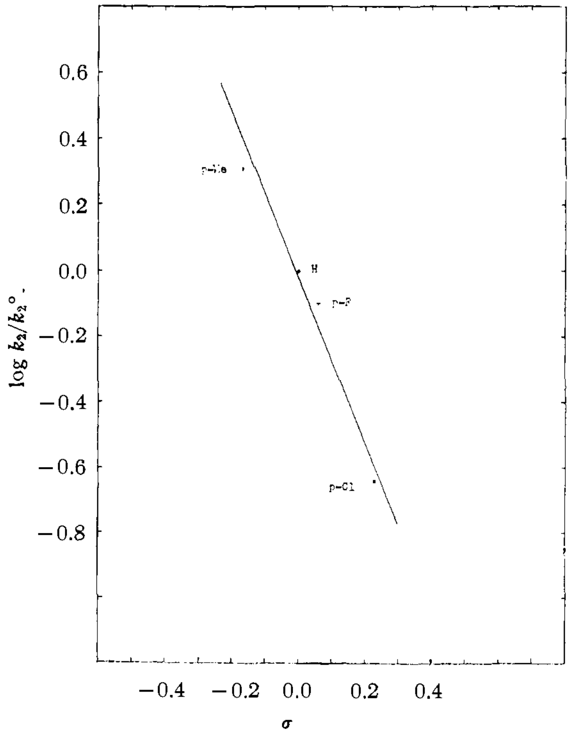

Fig. 2.—The Hammett equation applied to the Schmidt rearrangement of *p*-substituted 1.1-diphenylethyl azides.

Examination of Table I reveals that deviations in the values of k_2 for the various azides are due mainly to uncertainties in the values of H_0 (or h_0). For example, the value of k_2 for benzhydryl azide at 25° varies from 1.69 × 10^{-8} to 2.89 × 10^{-8}. The average value of k_2 based on 12 runs measured at different sulfuric acid concentrations, including 6 runs in which benzalaniline, benzhydrol or powdered glass was added to the reaction mixture, is 2.22 ± 0.34 (*i.e.*, ±16%). Yet the average deviation in values of k_1 is only about ±1.5%, and the average deviation in the measurements of the molarity of the sulfuric acid solutions is only about ±0.7%.

Comparison of Acetic Acid with Chloroform as the Solvent.—The theoretical section included an argument in which the combination of product ratio determinations and kinetic results was used to draw an important conclusion about the mechanism of the reaction. However, since the kinetic studies were carried out in acetic acid solution, whereas the product ratio determinations were made after rearrangement reactions carried out in chloroform solution, it seemed necessary to obtain some data on possible solvent effects. Specifically, it was necessary to determine whether relative rates of reaction or product ratios would change with change of solvent.

When attempts were made to measure pseudo-first-order rate constants for the benzhydryl and *p*-chlorobenzhydryl azide reactions in solutions of sulfuric acid in chloroform, it became apparent that the absolute rates of nitrogen evolution were much faster in chloroform than in acetic acid. This can only mean that, for a given concentration of sulfuric acid, the acidity of the chloroform medium, as measured by h_0, is much greater than the acidity of the acetic acid medium. The rates of nitrogen evolution were so fast in chloroform solution that the usual sulfuric acid concentrations and reaction temperatures could not be employed. However, by use of a 0.7 molal solution of sulfuric acid in chloroform and a reaction temperature of 5.0°, it was possible to obtain moderately reliable pseudo-first-order rate constants. The values were 41.4 hr.$^{-1}$ for benzhydryl azide and 9.72 hr.$^{-1}$ for *p*-chlorobenzhydryl azide. Within the limits of experimental error, which are undoubtedly much larger for the measurements in chloroform than for those in acetic acid, the relative rates of reaction of the two compounds are the same in both solvents.

The molar product ratio, benzaldehyde/*p*-chlorobenzaldehyde, obtained from the Schmidt rearrangement of *p*-chlorobenzhydrol in chloroform solution was reported to be 0.67 ± 0.07.[2] In order to determine the molar product ratio of aldehydes formed from the rearrangement reaction in acetic acid, the solutions from five kinetic runs, originally

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[11] S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

containing a total of 2.44 g. of *p*-chlorobenzhydryl azide of 95% purity (0.0095 mole), were combined and mixed with an equal volume of water. The resulting solution was extracted with ether in a continuous extraction apparatus. Distillation of the ether solvent through a Vigreux column left an acetic acid solution of the neutral and acidic reaction products. To this solution was added a solution of 14.0 g. (0.083 mole) of silver nitrate in 25 ml. of water. The resulting mixture was cooled in an ice-bath, and 90 ml. of an aqueous solution containing 35 g. of sodium hydroxide was added in the course of 30 minutes with mechanical stirring. The procedure for isolation of the aromatic acids was identical with that described previously under the heading, "Modified Schmidt Reaction of *p*-Chlorobenzhydrol, Run No. 2."[2] There was obtained 0.7730 g. (0.00493 mole) of *p*-chlorobenzoic acid and 0.3902 g. (0.0032 mole) of benzoic acid (86% combined yield). The molar product ratio, benzoic acid/*p*-chlorobenzoic acid (benzaldehyde/*p*-chlorobenzaldehyde) is therefore 0.65.

Thus both kinetic studies and product ratio determinations indicated that neither relative rates of reaction nor product ratios varied significantly on change of solvent from chloroform to acetic acid.

Discussion of Errors in the Use of the Equation

$$\log k_2/k_2^\circ = \log k_P/k_2^\circ + \log (1 + \text{P.R.})$$

It is clear that the specific rate constant, k_P, probably does not represent precisely the same value for each of the monosubstituted benzhydryl azides. However, there is evidence to support the assumption that variations among k_P values for the different compounds are small. For example, the individual points for each of the Hammett plots of log P.R. *vs.* σ do not deviate to any marked degree from a linear relationship.[2,3c,12] This would probably not be the case if the variations among k_P values for the different monosubstituted benzhydryl azides were large.[13]

It is critical for the mechanism considerations given in the theoretical section that the slope of the plot of log k_2/k_2° *vs.* log (1 + P.R.) be distinctly not equal to +1. In a previous paper[2] an estimate was made that product ratio determinations were probably accurate to within about ±10% of the true values. It is instructive to estimate what effect this deviation would have on the slope of the plot of log k_2/k_2° *vs.* log (1 + P.R.). The only values which may be used in the benzhydryl azide series are those for the substituents, *p*-CH_3, *p*-Br, *p*-Cl and *m*-Cl. A plot of log k_2/k_2° *vs.* log (1 + P.R.) gives a straight line having a slope of +2.06. If the P.R. value for *p*-methylbenzhydryl azide is increased 10% and that for *m*-chlorobenzhydryl azide decreased 10%, the most drastic direction of deviation in each case, and a new plot made, the slope is decreased to +1.91. In order to reduce the slope to +1.0, the theoretical value for the synchronous process, it would be necessary to increase the value of P.R. for the *p*-methylbenzhydryl case to about 14 and decrease the value of P.R. for the *m*-chlorobenzhydryl azide case to about 0.01, the observed value for the *p*-chlorobenzhydryl azide case remaining unchanged and this point serving as the "fulcrum" as the line is tilted. Therefore it can be concluded that the deviation of about ±10% in the analytical data does not invalidate the theoretical treatment.

In the 1,1-diarylethyl azide series the only values which may be used to construct a plot of log k_2/k_2° *vs.* log (1 + P.R.) are those for 1-phenyl-1-*p*-tolylethyl azide, 1-phenyl-1-*p*-fluorophenylethyl azide and 1-phenyl-1-*p*-chlorophenylethyl azide.[3a,c,d] The slope of the line is found to be 2.0 ± 0.3.[14]

The mathematical treatment leading to the mechanism conclusions cited above was in principle first used in the controversy over the solvolysis of tertiary alkyl halides as to whether ionization preceded union with a solvent molecule or was synchronous with it.[15,16]

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[12] J. H. Scherrer and W. E. McEwen, unpublished results.

[13] Perhaps a crude estimate of the variation in k_P may be obtained by consideration of the work of A. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 448 (1936). These workers measured the kinetics of the Beckmann rearrangement of several stereochemically pure ketoxime picryl ethers in carbon tetrachloride solution. They found with the picryl ethers of benzophenone oxime, *p*-chlorobenzophenone oxime and *p*-methylbenzophenone oxime about a fourfold variation in the term that would correspond to k_P in the equation under consideration. Inasmuch as the departure of molecular nitrogen in the acid-catalyzed rearrangement of benzhydryl azides is undoubtedly a much more facile process than the ionization and rearrangement of a ketoxime picryl ether in carbon tetrachloride solution, there is reason to believe that the variation in k_P values for the azide series would be distinctly less than the variation for the ketoxime picryl ether series.

[14] The value of 4.0, found by Ege and Sherk[3l] for the product ratio in the acid-catalyzed rearrangement of 1-phenyl-1-*p*-tolylethyl azide, was found to be more suitable for construction of the plot than the value of 5.0 found by McEwen, Gilliland and Sparr.[3a]

[15] A. R. Olson and R. S. Halford, THIS JOURNAL, **59**, 2644 (1937).

[16] L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 881 (1938).