acidified potassium iodide solution. The mixture was poured into 75 ml. of water, heated 15–20 min. on a steam-bath and neutralized with 15% sodium hydroxide. Addition of 0.5 g. of methone in 10 ml. of 95% ethanol precipitated 0.1576 g. (5.390×10^{-4} mole, 89%) of formaldehyde methone derivative m.p. 187.5–188.5°.

A 0.39-g. sample of S-*p*-chlorobenzylthiuronium 2,2,3-trimethyl-3-butene-1-sulfonate was dissolved in methanol and passed over Dow-X-50 cation exchange resin to liberate the free sulfonic acid. The column was eluted with methanol. Bromide–bromate titration gave an unsaturation value of 103%.

4-Methyl-4-hydroxy-2-pentanesulfonic Acid Sultone (X).—Evaporation of the solvent from the organic layer (separated from the aqueous layer after hydrolysis of the sulfonation of 4-methyl-2-pentene) with gentle heat gave only decomposition products. Evaporation without heat gave a residual amber oil. This was dissolved in ether and saturated at 0° with pentane. Cooling to −78° produced colorless crystals melting at about −48 to −44°. Carbon and hydrogen analyses on two different samples gave C, 46.76 and 46.83; H, 8.24 and 7.72. The theoretical values are: C, 43.89; H, 7.37. Neutral equivalents on different samples ranged from 270–311 (calcd. 164). The molecular weight, determined cryoscopically in acetic acid, was 141. The sultone decomposed at room temperature within a few hours.

3,4-Dimethyl-4-hydroxy-2-pentanesulfonic Acid Sultone (XI).—The two crops of crystals of crude sultone as precipitated from ether solution with pentane melted at 50–53° and 50–58°. Recrystallization of the first crop gave material melting at 42–43°. After standing for five months the solid melted at 74–76°. The 42–43° melting material on recrystallization from ether–pentane melted at 43–43.5°, but a second crystallization raised the m.p. to 70–73°, and a final crystallization gave material, m.p. 76–77°. Recrystallization of the initial material, m.p. 50–58°, gave the higher melting form. The infrared spectra of the 42–43° and 76–77° materials were identical except for two additional weak absorption bands at 10.95 and 12.5 μ present in the lower melting form. These appear to be dimorphic forms of the sultone, rather than *cis–trans* isomers.

Hydrolysis of 2,3-Dimethyl-2-phenyl-3-hydroxy-1-butanesulfonic Acid Sultone (XII).—Four grams (0.0167 mole) of XII was hydrolyzed in 400 ml. of water at steam-bath temperature, and the solution diluted to 500 ml. Titration of a 20-ml. aliquot with standard base showed the presence of a theoretical quantity of sulfonic acid. Bromide–bromate titration of a 50-ml. aliquot gave an unsaturation value of 147% (a small amount of solid precipitated).

Repetition of this experiment using 10% potassium hydroxide gave a solution an aliquot of which showed 190% unsaturation on bromide–bromate titration (high unsaturation values are typical of unsaturated sulfonic acids with a branch at the double bond; see ref. 8). Neutralization of the major portion of this solution with hydrochloric acid and evaporation gave 3.0 g. of potassium salts (84%). Coulometric titration[17] of a sample gave 71% unsaturation. S-*p*-Chlorobenzylthiuronium 2,3-dimethyl-3-phenyl-1-butene-1-sulfonate, m.p. 171–172°, was obtained in 62% yield (after three crystallizations, assuming 71% initial unsaturation) from the potassium salts.

Anal. Calcd. for $C_{20}H_{25}O_3N_2S_2Cl$: C, 54.47; H, 5.72. Found: C, 54.25; H, 5.51.

An identical derivative was obtained from the potassium salt isolated from the "neutral" hydrolysis.

The infrared spectrum of the potassium salt from the basic hydrolysis showed no absorption in the 11.2 μ region. The ultraviolet absorption spectrum of an aqueous solution showed a maximum at 258 mμ (ϵ_{max} 210), typical of an alkylbenzene, and no high intensity absorption at 244 mμ, characteristic of styrenes.

2,3-Dimethyl-4-hydroxy-2-butene-1-sulfonic Acid Sultone (XVIII).—The sulfonation was carried out using 12.0 g. (0.146 mole) of 2,3-dimethyl-1,3-butadiene, 11.4 g. (0.142 mole) of sulfur trioxide, 13 ml. of dioxane and 200 ml. of ethylene chloride. After hydrolysis, the organic layer was concentrated under vacuum at room temperature to give a sizable quantity of oil. Distillation in a Hickman still at 100° and 0.3 mm. gave 1.5 g. (6.5%) of XVIII, m.p. 40–41°. Crystallization from ether failed to raise the melting point.

Anal. Calcd. for $C_6H_{10}O_3S$: C, 44.44; H, 6.22. Found: C, 44.95; H, 6.37.

The aqueous layer contained only 30% of the sulfur trioxide used (3% as sulfate and 27% as sulfonic acid), suggesting that the yield of sultone was much higher than was isolated.

Repetition of this experiment using pentane to precipitate the sultone from the organic layer gave a 16% yield of sultone.

These experiments were performed at an early stage of the work and the precautions later adapted for the hydrolysis stage were not employed. It seems likely that the yield could be improved substantially over that realized.

EVANSTON, ILL.

[CONTRIBUTION FROM THE INSTITUTE OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OSAKA UNIVERSITY]

The Curtius Rearrangement. III. The Decomposition of Substituted Benzazides in Acidic Solvents, the Acid Catalysis

BY YASUHIDE YUKAWA AND YUHO TSUNO

RECEIVED MAY 26, 1958

Kinetic study of the Curtius rearrangement of various substituted benzazides was carried out in acidic solvents such as acetic acid, aqueous acetic acid and acetic acid containing sulfuric acid. The rate for a given substituent was increased by the changes of solvents in the order: toluene, acetic anhydride, AcOH, aq. AcOH and AcOH containing H_2SO_4. In acetic acid containing sulfuric acid, a linear Hammett correlation was observed. This result on the substituent effect was similar to that of the Schmidt reaction and was different from that of the Curtius rearrangement in toluene. However, in acetic acid without H_2SO_4, the linear Hammett plot was not given; the rates of the derivatives containing *para* electron releasing groups were nearly equal to that of parent compound. The analogous shape of Hammett plot was obtained in aqueous acetic acid and acetic acid containing lithium chloride. The energy of activation varied considerably by the change of substituent. In acetic acid without sulfuric acid, the change of log *PZ* was parallel with that of activation energy, whereas the log *PZ* was constant in the presence of sulfuric acid.

A previous paper[1] reported the substituent effect of the Curtius rearrangement of the various substituted benzazides in toluene; in the *meta*-substituted benzazides, the polar nature of the substituents controlled the rate, whereas, in the *para*-substituted one both electron releasing and attracting substituents in any case retarded the rate as compared with the unsubstituted. These results are somewhat unusual and differ from the Lossen,[2]

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(1) Y. Yukawa and Y. Tsuno, THIS JOURNAL, **79**, 5530 (1957).

(2) T. F. Bright and C. R. Hauser, *ibid.*, **61**, 618 (1939); W. B. Renfrow, Jr., and C. R. Hauser, *ibid.*, **59**, 2308 (1939).

Hofmann[3] and Schmidt[4] rearrangements. These facts would indicate that the effect of the bond energy of the breaking N–N bond predominates over that of the polar contribution of the substituent, as in the case of the decompositions of the benzenediazonium salts[5] and the arylazotriphenylmethanes.[6] The difference from the results obtained in the Lossen and Hofmann rearrangements may be elucidated in terms of the diminished double bond character of their breaking bonds, N–O–Acyl and N–halogen. However, the Schmidt rearrangement, the thermal decomposition of the adduct of benzoyl residue with hydrazoic acid in the presence of sulfuric acid, does not differ from the Curtius rearrangement as far as the breaking bond is concerned. It is apparent, therefore, that the dissimilarity of the substituent effect in both reactions must be attributed only to the effect of the sulfuric acid in the former as an acid catalyst, to which our attention was directed.

Recently, Newman and co-workers[7] demonstrated that the Curtius rearrangement was sensitive to an acid catalysis, whereas the influence of the acid catalysis on the substituent effect of this reaction has not yet been clarified. In this respect, kinetic study of the Curtius rearrangement was carried out in acidic solvents for the purpose of obtaining some information of the substituent effect or the mechanism of the Curtius rearrangement by the comparison of the acid-catalyzed Curtius with the Schmidt rearrangements.

Results and Discussion

The rates of the decomposition of a number of substituted benzazides were determined in acetic acid, acetic anhydride and acetic acid containing water, sulfuric acid and lithium chloride. In all runs excellent first-order plots were obtained covering over a period of 80% reaction. The rate constants obtained are listed in Tables I, II and III. From these constants the energies of activation and log PZ were calculated using the method of least squares, and the values are given also in Tables I and II.

As the solvent varied, the rate for a given substituent was reduced in the order; acetic acid containing sulfuric acid, aqueous acetic acid, acetic acid containing lithium chloride, pure acetic acid and acetic anhydride. In these solvents the rate was much higher than that in toluene.

In acetic acid containing sulfuric acid (20% vol.), electron releasing groups accelerated and electron attracting groups retarded the rate. A plot of the logarithms of the rate constants at 44.70° against sigma constants gives a straight line, as shown in Fig 1. The regression line is obtained by the sta-

TABLE I

KINETIC RESULTS FOR THE DECOMPOSITION OF SUBSTITUTED BENZAZIDES IN ACETIC ACID CONTAINING SULFURIC ACID (20% VOL.)

Substituent	Temp., °C.	$10^4 \times k_1$[a]	$\Delta E^\ddagger$[b]	log PZ[c]
p-HO	29.75	1.56 ± 0.01	24.5	14.88
	44.70	10.6 ± .08		
	45.02	11.0 ± .1		
p-C_2H_5O	44.70	8.22 ± .10		
p-CH_3O	24.75	0.567 ± .002	24.8	14.96
	29.75	1.100 ± .006		
	45.02	8.13 ± .05		
p-t-C_4H_9	29.75	0.707 ± .006	24.9	14.82
	44.70	4.95 ± .04		
None	34.75	1.095 ± .005	24.9	14.73
	44.70	3.93 ± .02		
	54.75	13.13 ± .06		
p-Cl	44.70	1.995 ± .008		
p-NO_2	44.70	0.991 ± .007	25.8	14.75
	65.20	11.8 ± .02		
m-NO_2	45.02	0.740 ± .006	26.1	14.80
	65.20	8.68 ± .08		

[a] The averaged rate constant in reciprocal min. and the averaged standard deviation of rate constants. [b] Arrhenius activation energy in kcal. mole^{-1}. [c] In reciprocal min.

TABLE II

KINETIC RESULTS FOR THE DECOMPOSITION OF SUBSTITUTED BENZAZIDES IN ACETIC ACID

Substituent	Temp., °C.	$10^3 \times k_1$[a]	$\Delta E^\ddagger$[b]	log PZ[c]
p-HO	55.60	2.405 ± 0.01	25.6	14.43
	65.20	7.35 ± .05		
	70.20	12.56 ± .04		
	74.50	20.8 ± 1		
	75.00	21.2 ± .2		
p-CH_3O	54.85	2.054 ± .004	25.5	14.27
	59.50	3.41 ± .03		
	65.20	6.634 ± .016		
	75.50	21.0 ± .1		
	76.00	21.2 ± .3		
p-t-C_4H_9	55.00	2.57 ± .02	25.7	14.50
	65.20	8.29 ± .02		
	70.00	13.93 ± .062		
	75.50	26.26 ± .014		
None	55.60	2.452 ± .013	25.9	14.59
	62.00	5.20 ± .026		
	65.20	7.68 ± .05		
	65.90	8.13 ± .026		
	70.00	12.55 ± .04		
	74.50	21.57 ± .04		
	79.98	37.5 ± .3		
p-Cl	65.20	6.052 ± .012	26.1	14.64
	81.00	34.2 ± .2		
p-NO_2	55.00	1.471 ± .0064	27.0	15.16
	65.20	5.15 ± .02		
	70.00	8.60 ± .06		
	74.77	15.83 ± .05		
m-NO_2	65.20	3.55 ± .02	28.6	16.01
	70.00	6.243 ± .006		
	76.10	13.39 ± .02		
	80.00	21.0 ± .17		

[a] The averaged rate constant in reciprocal min. and the averaged standard deviation of rate constants. [b] Arrhenius activation energy in kcal. mole^{-1}. [c] In reciprocal min.

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[3] C. R. Hauser and W. B. Renfrow, Jr., THIS JOURNAL, **59**, 121 (1937).

[4] L. H. Briggs and J. W. Lyttletone, *J. Chem. Soc.*, 421 (1943).

[5] M. L. Crossley, R. H. Kienle and C. H. Benbrook, THIS JOURNAL, **62**, 1400 (1940); C. K. Ingold, "Structure and Mechanism of Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 800–802; E. S. Lewis and E. B. Miller, THIS JOURNAL, **75**, 429 (1953).

[6] S. G. Cohen and C. H. Wang, *ibid.*, **75**, 5504 (1953); G. L. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 4397 (1956).

[7] M. S. Newman and H. L. Gildenhorn, THIS JOURNAL, **70**, 317 (1948); R. A. Coleman, M. S. Newman and A. B. Garrett, *ibid.*, **76**, 4534 (1954).

TABLE III

THE RATES OF THE DECOMPOSITION OF THE SUBSTITUTED BENZAZIDES AT 65.20°

Substituent	Solvent	$10^3 \times k_1$ (min.$^{-1}$)
p-HO	AcOH–H_2O (20% vol.)	14.2 ± 0.1
p-CH_3O		13.1 ± .1
p-t-C_4H_9		15.68 ± .03
None		13.44 ± .06
p-Cl		9.45 ± .04
p-NO_2		7.90 ± .06
m-NO_2		5.44 ± .02
p-HO	AcOH–LiCl (0.25 M)	9.82 ± .20
p-CH_3O		8.776 ± .013
p-t-C_4H_9		10.30 ± .08
None		9.41 ± .02
p-Cl		6.81 ± .06
p-NO_2		5.37 ± .03
m-NO_2		3.867 ± .012
p-HO	Ac_2O	3.92 ± .02
p-CH_3O		3.10 ± .02
p-t-C_4H_9		4.694 ± .012
None		4.42 ± .03
p-Cl		3.72 ± .02
p-NO_2		3.79 ± .02
m-NO_2		2.70 ± .02

tistical treatment[8] excluding the point for *para*-nitro derivative. This correlation line is represented by the equation

$$\log k_1 = -1.09\sigma - 2.399$$

The slope of this regression line, rho value, is -1.090 ± 0.068; the standard deviation from the regression line is 0.020 and the correlation coefficient is 0.990. The value of rho, -1.09, is much higher (more negative value) than that for the reaction in toluene[1] (-0.33 concerning the *meta*-substituents only).

In acetic acid without sulfuric acid, the rate for a given substituent was markedly increased relative to the rate in toluene. The Hammett plot gave a straight line except strongly electron releasing *para* groups and *para* nitro group. The rate of *para*-hydroxy and *para*-methoxy groups are nearly equal to that of the parent compound. The rho of this reaction is -0.46, which is slightly higher than the value in the solution of toluene. By the addition of lithium chloride and water to this solvent, the rate was slightly increased, but the consistent pattern of the Hammett plot in pure acetic acid was revealed (Fig. 2). The rho-value was slightly increased, $-0.53 \sim -0.55$.

In acetic anhydride, *para* electron-releasing groups showed a remarkable retardation of rate as compared with that of the parent compound. The shape of the Hammett plot in this case is the same as that in toluene. This plot is also given by shifting the shape of plot obtained in toluene along the vertical ordinate. Both reactions are correlated by the equation

$$\log k_{\text{acetic anhydride}} = \log k_{\text{toluene}} + 0.315$$

It would be of considerable interest to compare with the patterns of these Hammett plots in various solvents.

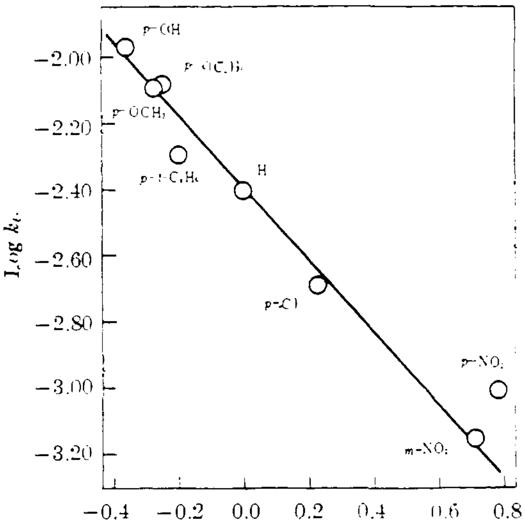

Fig. 1.—The Hammett plot of rate constants of the rearrangement of benzazides in acetic acid containing sulfuric acid at 44.70°.

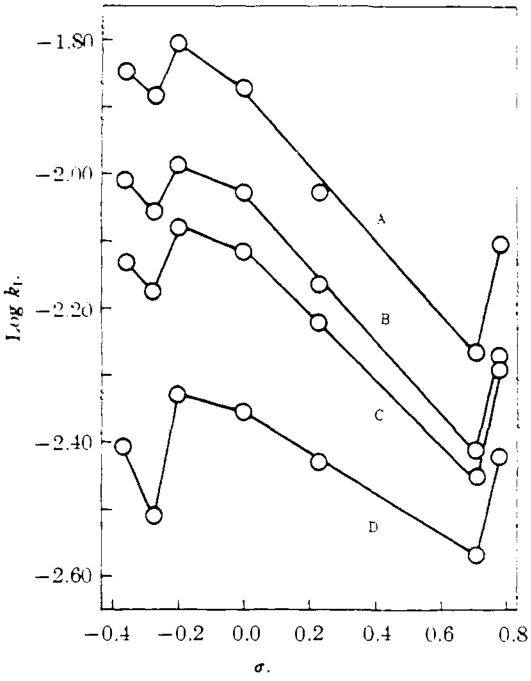

Fig. 2.—The Hammett correlations of the rearrangement of the benzazides at 65.20°; (A) in 80% aqueous acetic acid; (B) in acetic acid containing LiCl (1/4 M); (C) in pure acetic acid; (D) in acetic anhydride.

Concerning the substituent effect of the Schmidt rearrangement, Briggs and Lyttletone[4] reported about the half-lives for the reaction of various substituted benzoic acids with hydrazoic acid in the presence of sulfuric acid. According to their results, the rate was favored by electron releasing groups. The reciprocal logarithms of the half-lives are found to be almost linear against the Hammett sigma constants. A plausible mechanism proposed[7,9] could be represented as

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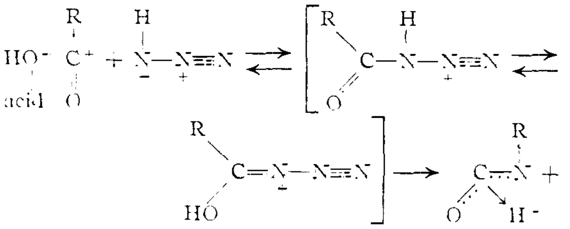
(8) H. H. Jaffe, *Chem. Revs.*, 53, 191 (1953).

(9) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 321.



The addition of the hydrazoic acid with the oxocarbonium cation, R–CO$^+$, may be a fast step and the decomposition of this intermediate adduct seems to be the rate determining step.

An azide is converted into its conjugate acid by a strong acid such as sulfuric acid. This conjugate acid may be formally identical with the adduct of hydrazoic acid with oxocarbonium cation. The acid-catalyzed Curtius rearrangement should be, therefore, similar to the Schmidt rearrangement in their rate-determining process and also presumably in their transition state. This leads us to assume that the effect of the substituents on the rate in both cases must be close together.

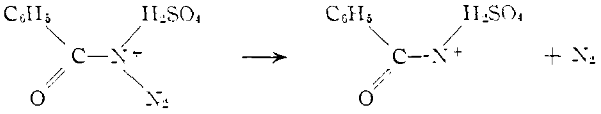
The above assumption is justified by the rate sequence, as shown in Table I and Fig 1, of the rearrangement in acetic acid containing sulfuric acid (20% vol.). This is the comparable condition with that of the Schmidt rearrangement. The rate of each substituent in this solvent increased to 50 ~ 100 folds of that in toluene. Moreover, a straight Hammett correlation line was obtained only in this solvent. This fact does suggest that in this solvent the effect of the polar contribution of substituents to the rate predominates over that of the resonance contribution to the bond energy of the breaking N–N bond. It is similar to the result of the Schmidt rearrangement, in contrast to that of the uncatalyzed Curtius rearrangement in toluene.

On the other hand, the rate in acetic acid without sulfuric acid, is found to be increased considerably as compared with that in toluene. The higher rho value than that in toluene appears to be an evidence of some increase in polar contribution of substituents. However, the failure of the Hammett relation (Fig. 2) shows that the increased polar contribution of substituent in this solvent is not sufficient to give a regular polar sequence. The same is true of the results in aqueous acetic acid and acetic acid containing lithium chloride (Fig. 2).

Sulfuric acid in acetic acid may produce acetic anhydride, which could be expected to influence on the rate by accelerating the rate or increasing the polar contribution of the substituents. In this situation, the effect may be significant in acetic anhydride. The result in acetic anhydride showed no individuality of the anhydride on the substituent effect to the rate. Another possible effect of the sulfuric acid may be a salt effect. This effect is also excluded by the experimental evidence that the addition of lithium chloride to the solution did not exert any remarkable effect on the polar contribution of the substituent to the rate. Furthermore, the salt effect of the strong acid or strongly solvated proton would be considered to be smaller than that of lithium salt.[10]

In general, as the polarity of solvent is varied, the contribution of the substituent is changed.[11] Therefore, it is important to ascertain whether the similar substituent effect given in toluene prevails in the other solvent of high polarity or not. The result in acetic anhydride provides an evidence of this. The rates in other higher solvating solvents were found to be higher than that in toluene or acetic anhydride;[12] furthermore, in several solvents, such as phenol and aniline, higher than in acetic acid. The substituent effect in them, however, is closely similar to that in toluene.[12] Hence the polarity of solvent does not appear to affect the nature of the substituent contribution in this reaction. The participation of the solvent, which has higher solvating power, is presumably distinguished from that of sulfuric acid.

The addition complex of an azide with sulfuric acid or the protonated azide undergoes decomposition to give a positively charged intermediate, whereas the usual Curtius rearrangement of azide involves an electrically neutral intermediate containing an electron deficient nitrogen atom



The rate of reaction involving the charged reaction center of transition complex must be influenced by the polar nature of substituent, as would presumably fit the Hammett equation.[13] In the acid-catalyzed rearrangement, the rate of decomposition would be influenced by the electrical nature of substituents, if the reaction center becomes more positive at the transition state than the initial state. Hence, the substituent effect of the acid-catalyzed reaction may differ markedly from that of uncatalyzed reaction.

The decomposition of benzazides, however, failed to give a regular Hammett sequence in 25% aqueous acetic acid solution containing sulfuric acid (25%), or in aqueous dioxane solution containing sulfuric acid or hydrochloric acid.[14] The linear Hammett relationship was obtained only in the presence of anhydrous acid (10 ~ 35%). Thus the contribution of sulfuric acid as Lewis acid appears to be effective to give a regular Hammett sequence, and in the protonated azide, substituents influence the rate in the same manner as they influence the rate of rearrangement in toluene.

On the energies of activation (Table I and II), there is a clear contrast between the acetic acid containing sulfuric acid and that without sulfuric acid. In acetic acid without sulfuric acid the energies of activation and log *PZ* are varied in parallel over a range of 25 ~ 29 kcal. mole^{-1} and 14 ~ 16 min.$^{-1}$ This phenomenon has been observed in various rate processes,[15] especially in the Curtius

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(10) J. E. Leffler and Shin-Kung Liu, THIS JOURNAL, **78**, 1949 (1956).

(11) D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 883 (1953).

(12) Y. Yukawa and Y. Tsuno, unpublished.

(13) This is suggested essentially by a Referee. He suggests also that the *p*-hydroxy and *p*-methoxy groups would show greater electron-release than described by the normal sigma constant, in the electrophilic reaction. However, the deviations of these groups from Hammett relation appears to be involved within experimental uncertainty.

(14) Y. Yukawa and Y. Tsuno, to be published.

(15) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

rearrangement, by both solvent change[16] and substituent change in toluene.[1,17] The plots of activation energies against log PZ for the Curtius reactions in acetic acid gave a straight line lying below those in toluene. On the other hand, in the presence of sulfuric acid, the energy of activation is considerably changed, whereas the log PZ is remained nearly constant (14.8 min.$^{-1}$). For a given substituent, the energy of activation in this solvent is slightly less (about 1 kcal. mole^{-1}) than that in acetic acid without sulfuric acid. Sulfuric acid might rather freeze out the entropy (to give a constant log PZ) than lower the energy of activation.

Then, it is reasonable to conclude that the rate sequence obtained in acetic acid containing sulfuric acid is attributed to the effect of Lewis acid catalysis by the sulfuric acid, thereby, the dissimilarity in the substituent contribution of the Curtius rearrangement and the Schmidt rearrangement would be caused by no intrinsic difference of their transition states but the change in the condition of reaction.

Experimental

Materials.—All azides were prepared by the methods previously reported.[1] Lithium chloride used were a reagent grade and dried over phosphorus pentoxide to a constant weight.

Solvents.—Acetic acid, which had been partially frozen and distilled, was heated under reflux with phosphorus pentoxide for 15 hours and carefully fractionated. The middle fraction, b.p. 117.5–8.3°, n^{25}D 1.3700, was collected.

Acetic anhydride was purified by refluxing with calcium carbide for 12 hours and fractionally distilled. The middle fraction, b.p. 139–40°, was collected.

The stock solvents, 20% aqueous acetic acid, was prepared by diluting 200 ml. of water with acetic acid to 1000 ml. (at 20°).

The acetic acid containing sulfuric acid was prepared by an addition of 200 ml. of 100% sulfuric acid into 500 ml. of acetic acid at 0° and the dilution with acetic acid to 1000 ml. at 20°. The accurate content of sulfuric acid was determined gravimetrically as barium sulfate. It was found to be 4 moles per liter, $f = 0.9898$. The acetic acid used for this solution was prepared by refluxing and fractionating the mixture of commercial acetic acid (1500 ml.), acetic anhydride (100 ml.) and concd. sulfuric acid (10 ml.), middle fraction, b.p. 117–118.5°, being collected.

A solution of lithium chloride in acetic acid was prepared as follows: lithium chloride (0.5 mole) was dissolved into 500 ml. of acetic acid, the insoluble salt was filtered off and 250 ml. of this solution was diluted to 1000 ml. The accurate content of the chloride was determined as silver chloride: 0.25 mole per liter, $f = 0.9826$.

Rate Determinations.—The rate measurements were carried out by the same procedure as the previous one.[1]

The temperatures of the reaction bath were maintained to a constancy of ±0.01°, and the uncertainty of temperature would be within ±0.03°.

The reaction mixture was not stirred, but the powdered glass was added to the reaction flask in order to prevent supersaturation by nitrogen gas evolved. All reactions were followed over a period of at least three half-lives of azide decomposition. The infinity reading, V_∞, was taken after an interval of time equal to 9~10 times as much as the half-life of reaction. The volume of nitrogen was obtained quantitatively (close to the theoretical amount). A plot of the log ($V_\infty - V$) against time gave an excellent straight line covering over a period of three half-lives of the reaction (Fig. 3), and the rate constants were evaluated from an equation

$$k_1 t = 2.303 \, [\log V_\infty - \log (V_\infty - V)]$$

In the cases of solvents, acetic acid, aqueous acetic acid and acetic acid containing lithium chloride, the measurements were made in 100 ml. of them. The initial concentration of azides were about 0.05 mole per liter. For all runs the duplicated measurements, differed in initial concentrations within 0.1~0.03 mole per liter, were made at the same time. The results showed that the initial concentration did not give any significant effect on the rate without ones in an aqueous acetic acid. The values listed in the tables and discussed above are the mean values of the duplicated results. The reproducibilities of these rate constants appear to be within 2%, which is demonstrated in Fig. 3.

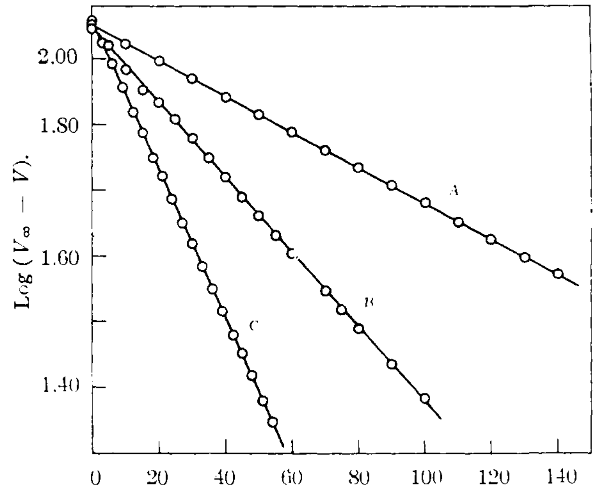

Fig. 3.—The plots of log ($V_\infty - V$) *vs.* time; (A) *m*-$NO_2C_6H_4CON_3$ at 70.00° in AcOH; (B) $C_6H_5CON_3$ at 54.75° in AcOH–H_2SO_4; (C) *p*-*t*-$C_4H_9C_6H_4CON_3$ at 75.50° in AcOH.

In acetic acid, the rates were measured at several different temperatures. From these values, the linear Arrhenius plots were obtained. Newman[16] reported the rates for unsubstituted benzazide as follows: 0.002245 (min.$^{-1}$) at 55°, 0.00828 at 65° and 0.0217 at 75°. These are in good agreement with the values in Table II, but the value at 65° is somewhat higher. From the Arrhenius plot obtained by combining the rate constant in Table II with Newman's, the value of the rate constant of the present study, 0.00768 at 65.20°, is more preferable. The small content of an acetic anhydride in acetic acid did not affect on the rate.

The reactions in an aqueous acetic acid solution the rate constants were fluctuated sensitively by those initial concentrations. The preliminary experiments in 50 ml. of this solvent (azide, 0.005 mole) gave the following results: (subst., k_1 in min.$^{-1}$ at 65.20°) *p*-HO, 0.0180; *p*-CH_3O, 0.015; *p*-*t*-C_4H_9, 0.0185; non., 0.0175; *p*-NO_2, 0.00871 and *m*-NO_2, 0.00638. These are slightly higher than those in 100 ml. of an aqueous acetic acid solution. However, the effect of small difference in initial concentration was negligible.

The measurements, in acetic acid containing sulfuric acid and in acetic anhydride, were carried out in 50 ml. of solvents. The initial concentrations were about 0.1 mole per liter. The rates for several substituents in 100 ml. of the latter solvent did not deviate from the values in 50 ml. solvent. The duplicated runs of double concentration gave an identical rate constant within an experimental uncertainty. In the case of the former solvent, the slight change in the initial concentration of azides did not affect the rate. All runs in this solvent were of pseudo first order, but at low temperature, 25–35°, the lower initial rates were observed over 30-60 minutes, which is somewhat longer as compared with other solvents. This would be attributed to the slower dissolution of azides to this solvent. The dissolution of *p*-*t*-C_4H_9 derivative was markedly slow and this showed the longest period of the decrease of the initial rate constant. Avoiding this effect, the solution of azides was shaken vigorously for about ten minutes before the measurement was started.

The reaction products were detected as acetanilides.

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[16] M. S. Newman, S. H. Lee, Jr., and A. B. Garrett, This Journal, **69**, 113 (1947).

[17] Y. Yukawa and Y. Tsuno, *ibid.*, **80**, 6346 (1958).

Acknowledgment.—The authors wish to express their sincere appreciation to Professor M. Murakami and Dr. I. Moritani for their invaluable suggestions in this work, and they are also indebted to the Ministry of Education for the partial financial support of this research.

[Contribution from Baker Laboratory of Chemistry, Cornell University]

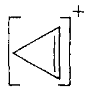
Synthesis of Cyclopropane Derivatives. Precursors for Dimethylenecyclopropane and Trimethylenecyclopropane

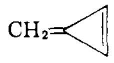
By A. T. Blomquist and Daniel T. Longone[1]

Received October 11, 1958

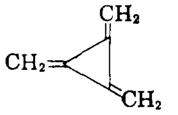
Two diamines, *trans*-1,2-bis-(dimethylaminomethyl)-cyclopropane and *trans*-2,3-bis-(dimethylaminomethyl)-1-methylenecyclopropane, desired as precursors for projected syntheses of dimethylenecyclopropane and trimethylenecyclopropane, respectively, have been obtained *via* the reaction sequence $R(CO_2H)_2 \rightarrow R(COCl)_2 \rightarrow R(CONMe_2)_2 \rightarrow R(CH_2NMe_2)_2$. The various transformations were effected in good yields starting from *trans*-1,2-cyclopropanedicarboxylic acid and *trans*-1-methylenecyclopropane-2,3-dicarboxylic acid (Feist's acid). Examination of the infrared spectra of some fourteen cyclopropane derivatives confirmed the view that absorption bands in the 9.8–10.0 and 11.5–11.7μ regions are not reliable for indicating the presence of a cyclopropane system in a molecule.

The increasing interest in the chemistry of cyclopropane derivatives is due in part to the prediction of non-classical aromatic character for certain unsaturated cyclopropyl compounds. Application of the molecular orbital (LCAO) method in the calculation of the electron delocalization energies, bond orders and free valence indices of a number of small ring compounds predicts delocalization (resonance) energies of about 34, 16 and 29 kcal. for the cyclopropene cation (I), methylenecyclopropene (II) and trimethylenecyclopropane (III), respectively.[2]


I



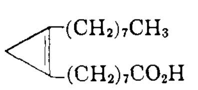
II



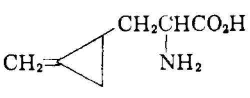
III

Since the results of these calculations are essentially qualitative due to the known limitations of the method used and the approximations introduced, the only true test of their reliability must eventually lie in the synthesis and study of the compounds in question. A derivative of I, the triphenylcyclopropenyl cation, has recently been synthesized.[3] The success in obtaining this relatively stable cation not only supports experimentally the reliability of the theoretical conclusions cited above but also stimulates synthetic effort toward other non-classical aromatic compounds in the cyclopropane series.

The cyclopropane compounds of particular interest are those which contain *exo* or *endo* double bonds. Besides the naturally occurring cyclopropene sterculic acid[4] and the methylenecyclopropane Hypoglycin A[5] the number of, and routes to, such cyclopropyl compounds are meager. For this reason, a careful study of the applicability to cyclopropane systems of standard classical transformations utilized successfully in the larger, strainless-ring homologs to convert dicarboxylic acids to diolefins would be valuable.[6] This paper describes the synthesis and characterization of intermediates to be used for such a study. They are derived from two of the more readily accessible cyclopropanedicarboxylic acids, *trans*-1,2-cyclopropanedicarboxylic acid (XII) and Feist's acid (XX).

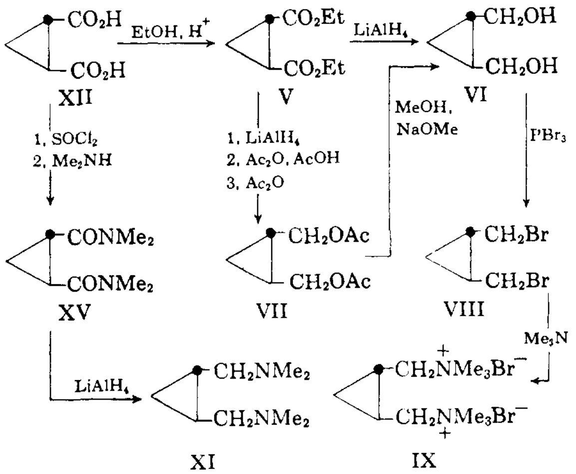


sterculic acid



Hypoglycin A

Derivatives of *trans*-1,2-Cyclopropanedicarboxylic Acid (XII).—The dicarboxylic acid XII, obtained from α-bromoglutaric ester (IV) by the method described by Ingold,[7] served as the starting material for synthesis of the cyclopropane derivatives given below.



Cyclization of the bromoester IV *via* intramolecular dehydrobromination with methanolic potas-

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[1] U. S. Rubber Research Fellow, 1957–1958. The work reported here was abstracted from part of the dissertation presented by Daniel T. Longone in September, 1958, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, This Journal, **74**, 4579 (1952).

[3] R. Breslow, *ibid.*, **79**, 5318 (1957).

[4] K. L. Rinehart, Jr., W. A. Nilsson and H. A. Whaley, *ibid.*, **80**, 503 (1958).

[5] J. A. Carbon, W. B. Martin and L. R. Swett, *ibid.*, **80**, 1002 (1958); R. S. deRopp, *et al.*, *ibid.*, **80**, 1004 (1958).

[6] (a) A. T. Blomquist and D. T. Longone, *ibid.*, **79**, 3916 (1957); (b) A. T. Blomquist, J. Wolinsky, Y. C. Meinwald and D. T. Longone, *ibid.*, **78**, 6057 (1956).

[7] C. K. Ingold, *J. Chem. Soc.*, **119**, 305 (1921).