semicarbazone, after three crystallizations from water, melted[31] at 184–185.5°.

α-Chloroacetyl-α-methyl-γ-butyrolactone (XI).—To a solution of 10.0 g. of α-acetyl-α-methyl-γ-butyrolactone (X) in 20 ml. of dry benzene was added 9.6 g. of sulfuryl chloride, and the resulting solution was allowed to stand at room temperature until gas evolution had ceased. After gently warming on the steam-bath for 15 min., the solvent was removed at reduced pressure, leaving a pale yellow oil which crystallized on standing overnight in the refrigerator. The yield of crude product was 12.4 g. (100%), m.p. 34–38°. One recrystallization from chloroform–petroleum ether at −50° gave 9.9 g. (80%) of white crystals, m.p. 37–42°. Three further recrystallizations from chloroform–petroleum ether raised the m.p. of an analytical sample to 45.5–47°.

Anal. Calcd. for $C_7H_9ClO_3$: C, 47.60; H, 5.14. Found: C, 47.82; H, 5.26.

Conversion to the **phenyl sulfone XIa** was effected by refluxing for 1 hr. a solution of 0.9 g. of the chloro compound and 1.0 g. of sodium benzenesulfinate in 10 ml. of 50% ethanol. Two recrystallizations from ethanol gave white prisms, m.p. 90.5–91.5°.

Anal. Calcd. for $C_{13}H_{14}O_5S$: C, 55.32; H, 5.00. Found: C, 55.16; H, 5.17.

Acid Hydrolysis of α-Chloroacetyl-α-methyl-γ-butyrolactone (XI) to 2,3-Dihydroxy-2,3-dimethyltetrahydrofuran (XXIa).—A mixture of 31.0 g. of the crude chlorolactone XI and 100 ml. of 1% hydrochloric acid was heated on the steam-bath for 2.5 hr. until carbon dioxide was no longer evolved. The resulting dark brown solution was neutralized with solid sodium bicarbonate and then extracted three times with ether to remove all of the deeply colored material, which was discarded. The remaining clear aqueous solution was continuously extracted with ether for 96 hr., the ether extract was dried over sodium sulfate and the ether was removed at the steam-bath, leaving a colorless oil which crystallized on cooling in the refrigerator for several hours. One recrystallization from ether gave 9.3 g. (40%) of white crystals of compound XXIa, m.p. 62.5–67.5°. Two further recrystallizations from ether gave an analytical sample, m.p. 63.5–65°. The infrared spectrum in a potassium bromide pellet showed a double hydroxyl band at 3356 and 3226 cm.$^{-1}$ with no absorption in the carbonyl region. In chloroform solution, however, the spectrum was radically different, a single hydroxyl band at 3401 and a strong carbonyl band at 1706 cm.$^{-1}$ being observed.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.23; H, 9.16.

Preparation of the following derivatives was attempted without success: phenylhydrazone, 2,4-dinitrophenylhydrazone, semicarbazone, 3,5-dinitrobenzoate, phenylurethan, benzilidene acetal and trityl ether.

In a periodate titration by the method of Jackson,[32] a 253-mg. sample of XI consumed 409 mg. (1.00 equiv.) of sodium metaperiodate, after a reaction time of two hours. The calculated value, based on a molecular weight of 132, is 410 mg.

Reaction of 2,3-Dihydroxy-2,3-dimethyltetrahydrofuran (XXIa) with Sodium Metaperiodate.—A solution of 4.6 g. of the diol XXIa and 7.5 g. of sodium metaperiodate in 150 ml. of water was allowed to stand at room temperature for 4 hr. and then continuously extracted with ether for 24 hr. The ether extract was dried and the solvent was removed leaving a colorless liquid, which was distilled. Two fractions were collected.

Fraction 1 (0.4 g.) was collected at 52–55° (80 mm.). It was identified as acetic acid by preparation of the *p*-bromophenacyl ester, m.p. and mixed m.p. 84.5–85.5°.

Fraction 2, 1.6 g., b.p. 72–73° (9 mm.), was identified as a mixture of 4-hydroxy-2-butanone and 4-acetoxy-2-butanone by comparison of the properties shown in Table I with synthetic samples and by mixed m.p.'s of derivatives.

TABLE I

	4-Hydroxybutanone[a]	4-Acetoxybutanone[b]	Product
Compn., %	C, 54.53	C, 55.37	C, 54.67
	H, 9.15	H, 7.75	H, 8.26
B.p., °C. (mm.)	61–62.5 (8)	69–70 (9)	72–73 (9)
n^t_D	1.4280	1.4143[c]	1.4211
t, °C.	26	25	20
Main infrared bands, cm.$^{-1}$	3356, 1709	1733, 1715, 1236	3390, 1733 1715–1709, 1236

[a] J. T. Hays, G. F. Hager, H. M. Engelmann and H. M. Spurlin, THIS JOURNAL, **73**, 5369 (1951). The reported values are: b.p. 73–76° (12 mm.), n^{20}_D 1.4290. [b] E. R. Buchman and H. Sargent, *ibid.*, **67**, 400 (1945), report b.p. 76–78° (8 mm.). [c] C. H. Hoffman, *et al.*, *ibid.*, **79**, 2316 (1957), give n^{25}_D 1.4148.

Treatment of the mixture with 2,4-dinitrophenylhydrazine gave the derivative of methyl vinyl ketone, m.p. 212–213° dec., after four recrystallizations from aqueous pyridine. A mixed m.p. with the same derivative prepared either from authentic 4-hydroxy-1-butanone or methyl vinyl ketone was undepressed. The reported m.p. is 217°.[33]

Fraction 2 gave a **3,5-dinitrobenzoate**, which after three recrystallizations from ethanol–water had m.p. 101–102°. It did not depress the m.p. of the same derivative prepared from authentic 4-hydroxy-2-butanone.

Anal. Calcd. for $C_{11}H_{10}N_2O_7$: C, 46.81; H, 3.57. Found: C, 47.00; H, 3.67.

ROCHESTER, N. Y.

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(31) While the present work was in progress, F. N. Stepanov and O. K. Smirnov, *Zhur. Obshchei Khim.*, **27**, 1042 (1957) (*C. A.*, **52**, 2747 (1958)), reported the following properties: for the lactone X, b.p. 125–126° (18 mm.), n^{20}_D 1.4561; for the semicarbazone, m.p. 190°.

(32) E. L. Jackson, in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 361.

(33) I. N. Nazarov, L. A. Kazitsyna and I. I. Zaretskaya, *Zhur. Obshchei Khim.*, **27**, 606 (1957) (*C. A.*, **51**, 16383 (1957)).

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

The Curtius Rearrangement. II. The Decomposition of *o*-Substituted Benzazides in Toluene

BY YASUHIDE YUKAWA AND YUHO TSUNO

RECEIVED MAY 26, 1958

The rates of decomposition of six *o*-substituted benzazides were determined volumetrically by collecting the nitrogen evolved. The rates of *o*-substituted derivatives were much higher than those of *m*- and *p*-derivatives. The relative reactivities followed the order of the bulkiness of *o*-substituents, although the changes were relatively small compared to the divergence between *o*-isomers and *m*-, *p*-isomers. These results are attributed to the increase in the steric requirement of the migrating group, and discussed in terms of the steric restriction of resonance of the benzene ring with the azidocarbonyl residue, and the steric compression of migrating group.

In an earlier paper,[1] the effect of *m*- and *p*-substituents on the rate of the Curtius rearrangement of benzazides was reported and discussed. The kinetic study of this rearrangement has now been extended to *o*-substituted benzazides.

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

Experimental

Materials.—The method of preparation of *o*-substituted benzazides was essentially the same as that of Curtius and others.[2] All azides were prepared from the corresponding esters in satisfactory yields.

o-Hydroxybenzazide was prepared by the usual method[3] from the hydrazide (m.p. 147°). Colorless plates (m.p. 27–8°, in 80% yield) were obtained on recrystallizations from aq. alcohol and ether. *o*-Nitrobenzazide was obtained from the hydrazide (m.p. 124–125°) in 85% yield by the Curtius method.[4] Recrystallizations from ether gave pale yellow needles having m.p. 36–38°.

o-Bromobenzazide was prepared by the following procedure. The hydrazide (m.p. 152–153°) was obtained from the ethyl ester (b.p. 131° (12 mm.)) quantitatively. Four grams of the hydrazide was dissolved in 4 ml. of concd. hydrochloric acid and 100 ml. of water. This solution was covered with 50 ml. of ether. An aq. solution of sodium nitrite (4 g. in 30 ml.) then was added dropwise to this solution with stirring at $-5 \sim 0°$. Stirring was continued for 30 min. at the same temperature. Then the ethereal layer was separated, washed with cold water and dried over calcium chloride with cooling. The solvent was removed as completely as possible under reduced pressure yielding colorless liquid, 3.5–3.7 g. When the reaction was carried out with high concentrations of hydrochloric acid, a red-brown liquid resulted. The colorless liquid product was taken up into 10 ml. of anhydrous toluene and dried again over calcium chloride. One-third of this solution which was separated from drying agent was used for a rate measurement without further purification. Nitrogen gas was evolved quantitatively on decomposition of this sample. When the decomposition product was treated with a small amount of water and allowed to stand for several days, *syn*-di-*o*-bromophenylurea was obtained; m.p. 220–222° from alcohol. The above procedure for azide preparation should be undertaken carefully with cooling lower than 0°, to avoid an occasional explosion or a vigorous evolution of gas. This appears to be the most appropriate procedure in terms of purity of the product and safety, and was employed as a general procedure for the preparation of other azides.

o-Toluylazide was prepared from the corresponding hydrazide (m.p. 124.3–5.0° from toluene), by the general procedure.[5]

o-Chlorobenzazide was obtained in the same manner from *o*-chlorobenzhydrazide. The hydrazide was obtained in 80% yield by refluxing (10 hr.) the alcoholic solution (75 ml.) of 20 g. of the ethyl ester (b.p. 116.5–117.0° (12 mm.)) and 15 g. of 85% hydrazine hydrate. Recrystallizations from anhydrous toluene gave white needles, m.p. 114–116.5° (reported[6] 109–110°).

Anal. Calcd. for $C_7H_7ON_2Cl$: C, 49.30; H, 4.10; N, 16.41. Found: C, 49.11; H, 4.13; N, 16.50.

The decomposition of *o*-chlorobenzazide yielded di-*o*-chlorophenylurea (m.p. 234–237°) quantitatively.

o-Methoxybenzazide was prepared by the general method. *o*-Methoxybenzhydrazide was obtained by refluxing the alcoholic solution (75 ml.) of 25 g. of the ester (b.p. 129° (12 mm.)) and 15 g. of 80% hydrazine hydrate for 10 hours. The solvent was evaporated as completely as possible and the crude material having m.p. 73–78° was separated. Recrystallization from anhydrous benzene and toluene gave the pure hydrazide, m.p. 100–101° (reported[7] 83–86°).

Anal. Calcd. for $C_8H_{10}O_2N_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.68; H, 6.06; N, 17.07.

When the above alcoholic solution was refluxed for only 2 hr., a product having m.p. 78–81° was obtained in low yield. The melting point was not changed by further recrystallizations from benzene, toluene or alcohol.[8]

Solvent.—Toluene purified by the usual method was heated under reflux with sodium metal for five days under protection from atmospheric humidity by a drying tube containing phosphorus pentoxide. It was carefully fractionated and stored over sodium, b.p. 110.3–110.5°.

Kinetic Runs.—The rates of the reaction were followed by the rate of the evolution of nitrogen gas. The apparatus and the procedure of the rate determination were described previously.[1] The temperature of the reaction bath was maintained constant within 0.01°. Stirring of the reaction mixture was not undertaken but the powdered glass was added to the reaction flask to prevent the supersaturation of nitrogen.

In the case of the solid azides, *o*-nitro- and *o*-hydroxybenzazides, about 5 mmoles of sample was decomposed in 75 ml. of toluene and the rates were measured by collecting the nitrogen evolved. The other *o*-derivatives are liquid and their further purification is impossible. Hence the liquids obtained were used directly for the rate measurements. The toluene solution of an azide, one-third of the sample prepared from 20 mmoles of the corresponding hydrazide, was transferred into 75 ml. of toluene at a constant temperature with shaking, and the volumes of nitrogen were followed to $75 \sim 90\%$ completion of the reaction. For each run of *o*-nitro- and *o*-hydroxybenzazides, the final volume of nitrogen evolved was close to the theoretical amount. For the liquid azides, the final volume of nitrogen indicated that the content of an azide in a sample solution was always about $80 \sim 90\%$ of the amount calculated from the starting hydrazide; therefore the content in a sample was about $5 \sim 6$ mmoles.

The preparation of an azide and the rate measurement were repeated for several times, to avoid the effect of impurities due to the incomplete purification of sample.

With *o*-bromobenzazide, the addition of the hydrazide (less than 100 mg.) to the reacting solution did not affect the rate. When the preparation of a liquid azide was carried out with a high concentration of hydrochloric acid, somewhat higher initial rates were observed and the first-order plot was concave upward. The use of excess aqueous sodium nitrite solution to hydrochloric acid appeared to be necessary to obtain satisfactory kinetics. Duplicate runs at different concentration of azide ($3 \sim 10$ mmoles) gave strictly the same rate constant.

The reaction products were detected as *syn*-diphenylureas by treating with a small amount of water, except for *o*-hydroxybenzazide, which gave a benzoxazolone, m.p. 132°, as a sole product.

Results

The decomposition of *o*-substituted benzazides in all cases followed first-order kinetics accurately

$$-0.4343\, k_1 \times t = \log (V_\infty - V) - \log V_\infty$$

Some typical runs are shown in Fig. 1. The rate constants obtained are listed in Table I. In all runs but those of the *o*-methoxy derivative, the average deviation from the mean value of the rate constants is less than 1% and the reproducibility of the constants obtained from the two or three experiments is within 2%, as shown in Fig. 1. Although the liquid azides followed first-order kinetics satisfactorily within a precision of 1% or less, they appeared to be slightly inferior in their reproducibilities (2% or less) than those of the crystalline azides (less than 1%). This presumably can be attributed to incomplete purification of the liquid azides. Other effects, such as those of the concentration of azide and of the supersaturation, were not observed.

Decomposition of *o*-methoxybenzazide gave a quantitative amount of nitrogen, although in four runs no linear first-order plot except a run at 47.60° was obtained. The run at 47.60° gave a straight plot and nearly the same rate constant as that of

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(2) P. A. S. Smith, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 337; Houben-Weyl, "Methoden der Organischen Chemie," Band VIII, Georg Thieme Verlag, Stuttgart, 1952, p. 676.

(3) A. Strauve and R. Radenhausen, *J. prakt. Chem.*, [2] **52**, 239 (1895).

(4) T. Curtius and O. Trachmann, *ibid.*, [2] **51**, 168 (1895); A. Strauve and R. Radenhausen, *ibid.*, [2] **52**, 231 (1895).

(5) Y. Tsuno, *Memoirs Inst. Sci. Ind. Res., Osaka Univ. (Japan)*, **15**, 183 (1958); R. Stolle and H. P. Stevens, *J. prakt. Chem.*, [2] **69**, 366 (1904).

(6) L. Kalb and O. Gross, *Ber.*, **58B**, 727 (1926).

(7) P. A. S. Smith, THIS JOURNAL, **76**, 436 (1954).

(8) H. H. Fox and John T. Gibas, *J. Org. Chem.*, **17**, 1653 (1952).

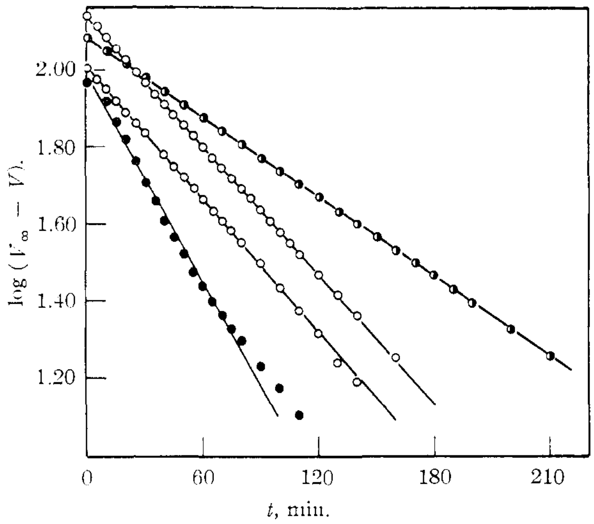

Fig. 1.—Plots of log (V_∞ − V) against time t of the decompositions of o-substituted benzazides: —◑—, o-nitrobenzazide at 54.80°; —○—, o-methylbenzazide at 44.50°; —●—, o-methoxybenzazide at 47.60°.

the o-methyl derivative. It seems likely that the reactivity of the o-methoxy derivative is approximately the same as that of o-methyl compound.

The temperature coefficients of rate constant were determined over 20°. Plots of log *k* *vs.* 1/*T* are linear. Activation energies and log *PZ* were calculated from the rate constants using the method of least squares. They are given also in Table I. The least square treatment indicates that the average deviations of the experimental log *k* from the regression line of the Arrhenius equation are ±0.002 for the crystalline azides and ±0.005 for the liquid azides. They are somewhat larger than those of the *p*-derivatives (less than ±0.001).[1] The uncertainty in the activation energy is estimated to be in all cases less than ±0.5 kcal. and in the log *PZ* less than ±0.20 reciprocal minute. Therefore, the variation of activation energy and log *PZ* with the o-substituents may be entirely significant with respect to the experimental uncertainty.

Discussion

It may be noted that the rates of the rearrangement for the o-substituted benzazides were much greater (50~200 fold) than that for the unsubstituted compound except in the case of o-hydroxybenzazide. The unexpectedly high stability of the o-hydroxy derivative presumably was due to chelation or hydrogen bonding of the hydroxy and the azidocarbonyl groups. Thus, the reactivity of this compound will not be considered in the following discussion.

The rates of decomposition of o-substituted benzazides at 35.00°, the relative rates to the unsubstituted benzazide and the *ortho/para* rate ratios of corresponding substituted compounds are listed in Table II. As the polar effect (inductive and resonance polar) is assumed to be approximately the same in the o-position as in the *p*-position, the *ortho/para* rate ratios may be a rough function of any other factor than polar factor.[9] It may be plausible to assume that the most decisive factor in the present reaction is a steric one. The relative rate also appears to be a rough function of the steric factor, since the relative rate parallels the *ortho/para* rate ratios. This leads us reasonably to a further assumption that the role of the polar factor is not large in the reactivities of o-substituted benzazides, as seen in the case of *m*- and *p*-derivatives.[1]

TABLE I

KINETIC RESULTS OF THE CURTIUS REARRANGEMENT OF THE o-SUBSTITUTED BENZAZIDES

Substituent	Temp., °C.	$k_1 \times 10^{2\,a}$	$\Delta E^{*\,b}$	log PZ^c
HO	78.60	0.0819 ± 0.0006	32.3	16.89
	84.70	.1802 ± .0015		
	90.70	.383 ± .003		
	94.20	.587 ± .002		
	99.00	1.027 ± .0085		
CH_3O	30.00	0.20~0.24		
	47.60	2.03 ± 0.04		
CH_3	24.50	0.1073 ± .0002	23.5	14.32
	30.00	.225 ± .0008		
	35.00	.427 ± .003		
	44.50	1.306 ± .011		
	48.50	2.13 ± .016		
Br	25.00	0.260 ± .0015	22.0	13.57
	30.00	.476 ± .002		
	35.00	.871 ± .007		
	40.00	1.501 ± .006		
	45.00	2.72 ± .02		
Cl	25.00	0.1904 ± .0008	22.2	13.53
	30.00	.340 ± .004		
	35.00	.629 ± .0020		
	37.70	.851 ± .003		
	40.05	1.148 ± .003		
	44.50	1.87 ± .012		
NO_2	35.20	0.2318 ± .00095	24.7	14.85
	44.70	.765 ± .007		
	45.02	.798 ± .0035		
	54.80	2.57 ± .01		

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

TABLE II

THE EFFECT OF THE o-SUBSTITUENTS

Subst.	$k_{35.00}{}^a$	Rel. rate[b]	$k_o/k_p{}^c$	k_o/k_p (Lossen)[d]
H	$4.28 \times 10^{-5\,e}$	1	1	1.0
o-CH_3	4.27×10^{-3}	100	131	10.0
o-CH_3O	$4.3 \times 10^{-3\,f}$	100[f]	150[f]	8.5
o-Br	8.71×10^{-3}	203	277	8.0
o-Cl	6.29×10^{-3}	147	208	5.6
o-NO_2	2.25×10^{-3}	53	70	2.2
o-HO	$1.2 \times 10^{-6\,g}$	0.025	0.044	..

[a] Rate in reciprocal min. [b] Relative rate at 35.00° to the unsubstituted benzazide. [c] The *ortho/para* rate ratio at 35.00°, the rates of *p*-substituted benzazides at 35.00° are calculated using the Arrhenius equation from the data of ref. 1. [d] The *ortho/para* rate ratio at 30° for the Lossen rearrangement, data from ref. 9. [e] Calculated from the data of ref. 1. [f] An expected value, see Result. [g] Extrapolated using the Arrhenius equation.

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(9) Activity may become somewhat less than one in the concentrated solutions. However, it appears to be negligible in the concentration range used in the present study.

A point of interest is that the introduction of an *o*-substituent, an electron-releasing as well as an electron-attracting group, increases the rate to a great extent as compared with the parent compound. The distinct divergence in rates of all *o*-substituted from the unsubstituted derivatives and the high *ortho/para* rate ratios of the corresponding substituents are undoubtedly to be attributed to the steric effect of *ortho* groups. A similar divergence was not found in the Lossen rearrangement,[10] as shown in Table II. The contribution of *o*-groups to the rate is expected to result either from the steric restriction of resonance of aryl with azidocarbonyl residues in the initial state or the steric compression by an increased bulkiness of the migrating group, or from both.

As previously reported,[1] unsubstituted and *m*- and *p*-substituted benzazides appear to be stabilized by resonance of the benzene ring with the azidocarbonyl residue, and consequently their reactivities were determined mainly by changes of the bond energy of the $N-N_2$ bond. Therefore, inhibition of this resonance interaction would be expected to accelerate the reaction remarkably.

In the rearrangement of saturated aliphatic acylazides, in which the resonance effect of the migrating group on the breaking $N-N_2$ bond may be negligible, the rate was much higher than that of benzazide.[11] For instance, hexahydrobenzazide and diethylacetazide exhibited comparable rates to those of the *o*-substituted benzazides ($C_6H_{11}-$, 5.95×10^{-3} and $(C_2H_5)_2CH-$, 16.5×10^{-3} min.$^{-1}$ at 34.75°, respectively).[11] Furthermore, the rates of saturated acylazides were found to be favored by an increased bulkiness of the migrating group, while rate changes with structural changes were not so large as the *ortho/para* rate ratios (*e.g.*, the rate ratio, $(C_2H_5)_2CH-/n\text{-}C_3H_7-$, is only 5.56 at 34.75°).[11] Thus the rate enhancement of *o*-isomers appears too large to attribute only to the effect of steric compression of the migrating group. In contrast, the difference of reactivity between cinnamoylazide and phenylpropionylazide (and phenylacetazide) was found to be about one hundred fold.[11] It may be reasonable to consider that the inhibition of resonance may be sufficient to cause a rate acceleration of some hundred fold. These facts suggest that the difference in reactivity between *o*- and *p*-isomers of benzazide depends largely on the effect of the steric restriction of resonance in the initial state, and only slightly on the steric compression of the migrating group.

In an arylcarbonyl azide, the resonance contribution of the benzene ring brings an increase in the degree of the double bond character of the breaking bond, $N-N_2$ bond, and stabilizes the molecule in the initial state. When the substituent is in the *o*-position, the resonance interaction of the benzene ring with the azidocarbonyl residue would be reduced by the restriction of the coplanarity and as a result, the resonance stabilization of the initial molecule would be lost and the bond energy of breaking $N-N_2$ bond, therefore, the activation energy of the decomposition, would be decreased.[12]

However, the role of steric compression also should not be neglected, because this is one of the important rate-determining factors in the rearrangement of aliphatic acylazides.[13,14] The dual effect of the steric factor would be, more or less, operative in an acceleration of the reaction rate. As the polar factor appears to be less effective than the steric factor in this reaction, the rate may follow the order of a steric parameter or that of the effective bulkiness of substituents. But the effect of substituent change is far smaller than the divergence of the *o*-isomers from the other isomers.

Recently, Taft[15] has proposed a measure, *Es*, of the steric factor of substituent in aliphatic and *o*-substituted benzoic acid derivatives from ester hydrolysis. The *Es* value decreases in the order $NO_2 > Br, CH_2 > Cl > CH_3O$ in *o*-substituted benzoic acid, but $Br > Cl > CH_3O > CH_3$ in α-substituted acetic acid. In the racemization of optically active biphenyls,[16] two series of steric effectiveness were obtained; $NO_2 > Br > Cl > CH_3 > CH_3O$ and $Br > CH_3 > Cl > NO_2 > CH_3O$. These are insufficient to permit a definite estimation of the steric effectiveness of each substituent in the present reaction, because the relative effectiveness of the steric factor was varied by changes of position to which the substituent group attached. The relative reactivity and the *ortho/para* rate ratio of this reaction appear to follow roughly the sequence of *Es* values for α-substituted acetic acid, or the former sequence of biphenyls, except for the nitro group. The relatively low reactivity of the *o*-nitro derivative presumably is to be attributed to the polar contribution of the strongly electron-attracting nature of this group. The same result in the *ortho/para* rate ratio as in the relative rate may not be restricted to what was mentioned above, since the *ortho/para* rate ratio appears to be not sufficiently free from the polar effect of substituents. This is true in the case of the Beckmann rearrangement of acetophenone oximes.[17]

Another point of interest is that the enhancement by *o*-substituent is much greater in the Curtius rearrangement than in the Lossen[10] (Table II) and the Beckmann rearrangements, of which the *ortho/para* rate ratios were reported to be 107 for CH_3, 15 for Cl and 6 for NO_2.[17] This may be explained in terms of resonance interaction of the

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[10] R. D. Bright and C. R. Hauser, THIS JOURNAL, **61**, 618 (1939); W. B. Renfrow, Jr., and C. R. Hauser, *ibid.*, **59**, 2308 (1937).

[11] Y. Yukawa and Y. Tsuno, unpublished.

[12] A Referee suggests that the electron deficient nitrogen atom is brought closer to the π-electron cloud of the ring by the proximity of *o*-group. This situation might be accompanied with the steric restriction of resonance.

[13] Observed also in other rearrangements; see Y. Yukawa and T. Yokoyama, *Memoirs Inst. Sci. Ind. Res., Osaka Univ.*, **13**, 171 (1956).

[14] The steric compression appears to suggest the existence of a backside-participation of the migrating group. Since the driving force of this reaction usually has been considered to be the process of $N-N_2$ bond fission, the contribution of the steric compression would be less effective to the rate than that of the restriction of resonance, which directly favors the process of the $N-N_2$ bond fission.

[15] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13, pp. 556–675.

[16] R. L. Shriner, R. Adams and C. S. Marvel in H. Gilman, "Organic Chemistry," 2nd ed., Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 362–368.

[17] D. E. Pearson and W. E. Cole, *J. Org. Chem.*, **20**, 488, 494 (1955).

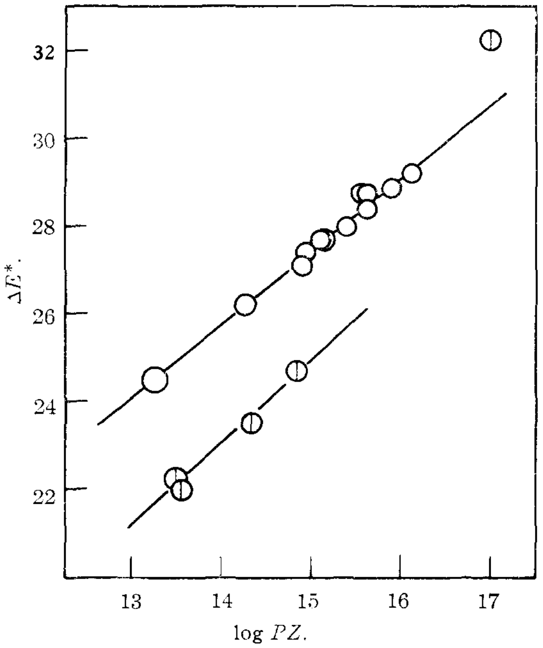

Fig. 2.—The correlation between activation energy and log PZ of the decompositions of various substituted benzazides: upper line, O, *m*- and *p*-substituted benzazides; lower line, ⦶, *o*-substituted benzazides.

benzene ring with the breaking bond in each parent compound. The double bond character of the breaking bonds in oximes and hydroxamic acids is negligible as compared with that of azides; hence the above resonance is less effective in oximes and hydroxamic acids than in azides. Data indicate that the rate ratios of cyclohexyl to phenyl derivatives are 12 in the Lossen,[10] 25 in the Beckmann[18] and 140 in the Curtius rearrangements. The ratios appear to correspond to the acceleration attributable mainly to the loss of the resonance stabilization of phenyl derivatives and presumably parallel to the acceleration due to the steric restriction of resonance by the *o*-group.

In view of these facts, the resonance stabilization would be expected to play a more important role in the Curtius rearrangement than in the others, and the steric restriction of resonance by the *o*-group would accelerate the reaction to a greater extent in the Curtius than the other rearrangements.

A further point of interest is found in the Arrhenius parameters obtained (given in Table I). *o*-Substituted compounds provide much lower energies of activation and slightly lower log PZ factors than those of the *m*- and *p*-isomers, except for the *o*-hydroxy compound. The more bulky the group in the *o*-position, the faster the rate and the lower the energy of activation. The restriction of the resonance or an increase in steric effect attributable to the *o*-substitution would be reflected primarily in the energy of activation and only slightly in the log PZ factor. Moreover, the activation energy parallels the log PZ factor and both are correlated linearly.[1,19] The plots of ΔE^* *vs.* log PZ in *ortho* series are ranged below the line of *m* and *p*-substituted derivatives, as shown in Fig. 2. Only the *o*-hydroxy compound falls above the *m*-,*p*-correlation line. The vertical displacement of the *ortho* correlation line from that of *m*-,*p*-derivatives may refer mainly to the contribution of the steric restriction of resonance between the benzene ring and the azidocarbonyl residue, except the *o*-hydroxy derivative. It is, therefore, reasonable to consider that the difference of about 3 kcal. between both lines would be equal to the additional conjugation energy of the *m*-,*p*-substituted phenyl groups to that of the azidocarbonyl residue in the initial state. The effect reflected in the log PZ term is difficult to understand in terms of the restriction of resonance. The decrease in log PZ with the bulky group may presumably be attributed to the other terms, such as the steric restriction of solvation and the changes in the degree of the freedom of motions.

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[18] Y. Yukawa and M. Kawakami, unpublished data.

[19] C. N. Hinshelwood, "Kinetics of Chemical Change," The Clarendon Press, Oxford, 1940, pp. 257–261; J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936).

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Kinetic and Equilibrium Studies of Cyclic Ketal Formation and Hydrolysis[1,2]

BY MELVIN S. NEWMAN AND ROBERT J. HARPER, JR.[3]

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The work herein reported was undertaken to obtain information about the hydrolytic stability of cyclic ketals derived from 1,3-propanediol and its 2,2-dialkylated analogs. We thought that from a study concerned with rate and equilibrium features of the reactions valuable information concerning the use and preparation of cyclic ketals as blocking agents for ketonic functions would be obtained. We also foresaw that further knowledge of the *gem*-dialkyl effect might be gained. For comparative purposes ketals of ethylene glycol were included since such ketals are commonly in use.

To this end ketals were prepared from cyclohexanone, cyclopentanone and 2-methylcyclopentanone and ethylene glycol, 1,3-propanediol, 2,2-dimethyl-

[1] This work reported was abstracted from the Ph.D. thesis of R.J.H., The Ohio State University, 1957.

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[3] Holder of the Standard Oil Co. of Indiana Fellowship, 1956–1957.