added 5.00 ml. of 0.05 *M* sodium metaperiodate in 50% methanol. At various times 1-ml. aliquots were analyzed by adding 2 ml. of water, 0.4 ml. of 20% sulfuric acid, 1 ml. of 20% potassium iodide, and titrating the liberated iodine with standard thiosulfate. The periodate uptake in moles per mole of phenylhydrazone at room temperature was: at 0.5 hr., 2.05; at 1.5 hr., 1.96; at 21 hr., 2.09.

(−)-**Bornesitol (VI).**—Approximately 1.2 g. of sirupy 3-*O*-methyl-D-*myo*-inosose-1 (II), obtained by the chromatography of a solution of oxidized quebrachitol,[2] was dissolved in 20 ml. of water and 0.1 g. of sodium borohydride was added. The solution, which became slightly alkaline (*p*H 8), was allowed to stand at room temperature for 1 hr., after which time it no longer reduced Benedict reagent. The excess sodium borohydride was destroyed with acetic acid and the sodium ions were removed by passing the solution through a Dowex-50 column. Paper chromatography showed the presence of quebrachitol and a compound with the mobility of bornesitol (R_p 0.59), and concentration of the solution precipitated 0.82 g. of material melting from 167–177°. The mother liquors were concentrated to 1 ml. and, together with the crystalline material, chromatographed on a cellulose column with acetone–water 8:1. Two bands were obtained, the first of which yielded 0.61 g. of quebrachitol (I), m.p. 191.5–192°. The second band, on concentration and the addition of ethanol, yielded 0.30 g. of substance melting at 205–205.5° and showing $[\alpha]_D$ −32.6° (*c* 1.0 and 1.4 in water). By comparison, the reported physical constants of (−)-bornesitol are m.p. 203–204° and $[\alpha]_D$ −32° (water),[19] and of (+)-bornesitol m.p. 199–203° and $[\alpha]_D$ +31° (water).[20,21] We found that chromatography (cellulose column) of authentic (+)-bornesitol raised its m.p. to 205–205.5°.

Twenty-three mg. of the material of the second band was refluxed for 1 hr. with 2 ml. of acetic anhydride and 24 mg. of anhydrous sodium acetate. Water was added and the resulting solution concentrated to give a white precipitate weighing 27.3 mg., m.p. 140°; reported for (−)-bornesitol pentaacetate,[19] m.p. 142°, 157°; for (+)-bornesitol pentaacetate,[21] m.p. 138–139°, 157°; the acetates are dimorphic. The infrared spectrum (chloroform solution) was essentially identical with that of an authentic sample of (+)-bornesitol pentaacetate.

Further confirmation that the material of band 2 was (−)-bornesitol was obtained by demethylating it to *myo*-inositol, identified by m.p., mixed m.p., chromatographic mobility and conversion to the hexaacetate.

(+)-**Ononitol (VIII).**—One gram of *O*-isopropylidenequebrachitol (IV), prepared by the procedure of Angyal and Macdonald,[10] was treated for 44.5 hours with oxygen over platinum (procedure B, preceding paper). The product, 2,3-*O*-isopropylidene-6-*O*-methyl-D-*myo*-inosose-1 [2,3-*O*-isopropylidene-6-*O*-methyl-(−)-*vibo*-inosose, V], was not isolated. Instead, the oxidized solution was filtered, 104 mg. of sodium borohydride was added, and the solution was allowed to stand at room temperature for 2 hr. The excess reducing agent was destroyed with acetic acid and the sodium ions removed with Dowex - 50 (H^+). The concentration of acetic acid was increased to approximately 10% and the solution was refluxed for 10 minutes, after which the acetic acid and boric acid were removed by repeated concentrations and additions of water and methanol. The products were then separated by cellulose column chromatography with acetone–water 9:1. The major product consisted of 0.50 g. of quebrachitol (I), m.p. 190–191°.

After the quebrachitol was eluted, an additional band was detected. This band contained 40 mg. of material which crystallized from aqueous ethanol as a hydrate, m.p. 167–168°. Heating the substance overnight *in vacuo* at 100° caused the loss of one molar portion of water, but did not change the melting point; $[\alpha]_D^{23}$ (anhydrous basis) +5.5° (*c* 11.2, water); reported[19] for (+)-ononitol are m.p. 172° and $[\alpha]_D$ +6.6° (water).

The synthetic methyl ether was acetylated by refluxing 22 mg. of it with 3 ml. of acetic anhydride and 25 mg. of anhydrous sodium acetate for 0.5 hour. After cooling, water was added and on concentration 24.3 mg. of crystals precipitated. The melting point was 121°, $[\alpha]_D^{23}$ −11.14° (*c* 0.83, $CHCl_3$); lit.[19] for (+)-ononitol pentaacetate: m.p.'s 122°, 131° (dimorphic), $[\alpha]_D$ −12° ($CHCl_3$).

On demethylation with refluxing HI, the synthetic ononitol yielded *myo*-inositol, identified by m.p., mixed m.p., chromatographic mobility and conversion to the hexaacetate.

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(18) For general statements pertaining to experimental procedure, and for the methods used for paper chromatography, cellulose column chromatography, demethylation and catalytic oxidation, see the relevant paragraphs of the Experimental section of the preceding paper.

(19) V. Plouvier, *Compt. rend.*, **241**, 983 (1955).

(20) E. R. Flint and B. Tollens, *Ann.*, **272**, 288 (1893).

(21) F. E. King and L. Jurd, *J. Chem. Soc.*, 1192 (1953); our authentic sample was from Prof. King.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

Kinetic Evidence for the Formation of Azene (Electron-deficient Nitrogen) Intermediates from Aryl Azides(1)

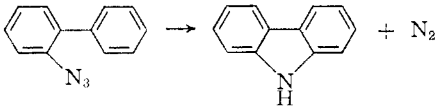
BY PETER A. S. SMITH AND J. HERBERT HALL

RECEIVED JULY 11, 1961

The kinetics of the thermal decomposition of a group of phenyl and 2-biphenylyl azides bearing halogen, nitro, methyl or methoxy substituents have been measured at several temperatures and in different solvents. The variation of rate with substitution is small; the enthalpies and entropies of activation show a linear relation. None of these functions can be correlated satisfactorily by the Hammett equation; *m*-substituents have little effect on the activation enthalpies, but *p*-substituents have an effect that follows the order of the values of $\Delta\sigma$ ($= \sigma p - \sigma m$). There is little effect of solvent on the rates other than a weak acceleration by hydroxylic solvents. The over-all behavior is best accounted for by initial cleavage to an aryl azene intermediate, $Ar\text{-}\ddot{N}$:

The thermal decomposition of azides usually leads to the loss of two-thirds of the azide nitrogen and the formation of products derived from rearrangement (eq. 1), cyclization (eq. 2) or hydrogen abstraction (eq. 3).(2) These results may be interpreted as coming about by a concerted reaction path, by initial formation of an adduct, such as a triazoline or triazene, or by initial formation of an azene,(3) $R\text{-}\ddot{N}$: Many attempts have been made to inter-

$$R_3C{-}N_3 \longrightarrow R_2C{=}N{-}R + N_2 \qquad (1)$$



(2)

$$Ar{-}N_3 \xrightarrow{(H)} Ar{-}NH_2 + N_2 \qquad (3)$$

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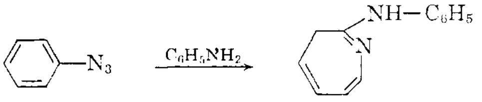
(1) From the doctoral thesis of J. H. H. Supported in part by the Office of Ordnance Research, U. S. Army.

(2) J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 1 (1954).

(3) The term "azene" is used in this paper to denote derivatives of NH, also known as "imine radical" and "univalent nitrogen." The shorter term, apparently introduced by Huisgen, has obvious advantages. The word "nitrene," seen occasionally in recent literature, is inadmissible, inasmuch as it has long been the accepted term for the ylides of Schiff's bases (*cf. C. A.*, Decennial Indices).

cept azene intermediates, but they have led for the most part to ambiguous results. Certain reactions of sulfonyl azides[4] provide the best case for the formation of azenes.

Simple aryl azides decompose thermally by mixed paths that vary with the environment. One type of compound that may form is an azepine, a rearrangement product resulting from expansion of the benzene ring, but its formation has never been found to be the major reaction[5] except in extreme dilution; reported yields range from 7 to 54%. Appl and Huisgen[6] have measured the kinetics of *m*-nitro-, *m*-methoxy- and *m*-methylphenyl azides in aniline solution, in which azepine formation has been demonstrated only for phenyl and *p*-tolyl azides. They found little variation in rate of nitrogen evolution, and concluded that the rearrangement is not a concerted process, since the electronic effects of substituents should be considerable if participation by the *o*-carbon in the loss of nitrogen is involved. However, since the products of decomposition under these conditions are mixtures, in which the anilino azepines are usually minor constituents, it is not completely certain that the measured kinetics are really those of a single reaction. If different rate-determining steps are involved for competing paths of decomposition, then it is not valid to ascribe the lack of variation of the collective rate to a lack of a concerted process in just one of them. It was our purpose to investigate the effect of substitution on the decomposition of aryl azides under conditions where only one principal reaction path is involved, as indicated by the formation of only a single product in essentially quantitative yields.



(4)

Two aryl azides, phenyl[7] and *o*-nitrophenyl,[8] have previously been investigated kinetically as individuals; both obey first-order kinetics, but, of course, give no information on substituent effects. The case of *o*-nitrophenyl azide is a special one, not really part of the present problem, for it appears from its far larger rate constant and the absence of ordinary solvation effects that loss of nitrogen is concerted with bond formation from azide nitrogen to the continuously adjacent oxygen of the nitro group.

We first considered the decomposition of aryl azides in decalin solution, where one might reasonably expect hydrogen abstraction from the solvent to be especially favored (eq. 3). Table I lists the products obtained with a series of phenyl azides. Hydrogen abstraction varied from near quantitative to zero, and the quantity of nitrogen evolved was in some cases much more than two-thirds of that present in the azido group. Furthermore, drifts from strictly first-order kinetics were observed in all cases, perhaps resulting from interaction between azide and unsaturation in the solvent generated by hydrogen abstraction. This reaction therefore cannot be used for an accurate comparison of substituent effects on rates. We were, however, able to confirm Appl and Huisgen's observations that nitrogen evolution is first order, and that the effect of *m*-substitution on the rate constant is very small. However, with *p*-substituents, we observed an eightfold increase from the slowest to the fastest. All substituents increased the rate constant, in the order *p*-NO$_2$ < *p*-C$_6$H$_5$ < *p*-Br < *p*-CH$_3$O < 2,4-Cl$_2$. The results are recorded in Table II. The source of the excess nitrogen is not clear, but it cannot arise from intermediate formation of azobenzene, since an experiment in which phenyl azide was decomposed in the presence of azobenzene gave essentially the same result, 1.32 moles, as it did alone. The gas evolved from *m*-nitrophenyl azide was examined in the mass spectrometer, and found to contain less than 1% of any gas other than nitrogen that would give rise to peaks in the region of mass 2 to 44.

TABLE I

YIELDS OF PRODUCTS FROM THE DECOMPOSITION OF ARYL AZIDES

Phenyl azide	Moles N$_2$ per mole of azide	Arylamine, %
m-Bromo	1.03,[a] 1.06[b]	85[a]
m-Methoxy	1.04[a]	97[a]
2,4-Dichloro	1.10[a]	41[a]
m-Nitro	1.30,[a] 1.27[b]	1[a]
p-Bromo	....	78[a]
p-Nitro	1.30[b]	Small[a]
Unsubstituted	1.20,[b] 1.34[b]	44[a]

[a] In decalin at 141.3°. [b] In bis-(2-ethoxyethyl) ether at 163.6°.

TABLE II

APPROXIMATE RATE CONSTANTS FOR THE LOSS OF NITROGEN FROM PHENYL AZIDES OTHER THAN 2-AZIDOBIPHENYLS[a]

Substituents	$k \times 10^3$, min.$^{-1}$ 141.3°	161.2°
None	1.7 (D)	15 (D)
		22.9 (A)[b]
		18.4 (N)[b]
p-Methoxy	8.4 (D)	67 (D)
p-Nitro	3.9 (D)	21 (D)
p-Phenyl	......	34 (D)
p-Bromo	6.0 (D)	......
2,4-Dichloro	15 (D)	96 (D)
o-Arsonic acid	......	70 (D)
o-Benzenesulfinyl	7 (D)	51 (D)
m-Methoxy	2.0 (D)	24.5 (A)[b]
m-Methyl	1.1 (D)	24.1 (A)[b]
m-Nitro	1.7 (D)	18.4 (A)[b]

[a] Solvents: D = decalin; A = aniline; N = nitrobenzene
[b] Results of Appl and Huisgen[6] at T = 159.86–160.28°.

We then turned to the *o*-azidobiphenyl system, which generally gives carbazoles in high yields.[9] This system has the advantage of allowing the investigation of the effects of substituents on both the ring bearing the azide and the ring to which cyclization takes place, but it has the disadvantage

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[4] J. F. Heacock and M. T. Edmison, *J. Am. Chem. Soc.*, **82**, 3460 (1960); J. N. Ashley, G. L. Buchanan and A. P. T. Eason, *J. Chem. Soc.*, 60 (1947).

[5] R. Huisgen, D. Vossius and M. Appl, *Chem. Ber.*, **91**, 1 (1958).

[6] M. Appl and R. Huisgen, *ibid.*, **92**, 2961 (1959).

[7] K. E. Russell, *J. Am. Chem. Soc.*, **77**, 3487 (1955).

[8] T. F. Fagley, J. R. Sutter and R. L. Oglukian, *ibid.*, **78**, 5567 (1956).

[9] P. A. S. Smith and B. B. Brown, *ibid.*, **73**, 2435 (1951).

TABLE III

YIELDS AND PROPERTIES OF 2-AMINO- AND 2-AZIDO-BIPHENYLS

	2-Amino		2-Azido	
Substituents	Yield, %	M.p. or b.p., °C. (mm.)	Yield, %	M.p. or b.p., °C. (μ)
5-Methoxy	89	117–120 (0.2)[a]	58	50–60 (50)[b]
4-Methoxy	75	143–146 (0.6)[c]	77	38.9–39.5[d]
4-Methyl	88	100–103 (0.2)[e]	79	50–60 (50)[f]
5-Methyl	88	116 (0.6)[g]	85	50–60 (50)[h]
4-Bromo	91	123–142 (0.2)[i]	90	43.2–43.8[j]
4-Nitro	71[k]	71.7–72.1[l]	60	68.8–69.9[m]

[a] Contaminated with chlorine; *Anal.* Calcd. for $C_{13}H_{13}NO$: C, 78.36; H, 6.57. Found: C, 77.31; H, 6.31. [b] Purified by chromatography before evaporative distillation. *Anal.* Calcd. for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92. Found: C, 69.06; H, 5.03. [c] Reported b.p. 128–130° (0.08 mm.) by F. C. Copp and L. P. Walls, *J. Chem. Soc.*, 311 (1950). [d] *Anal.* Calcd. for $C_{13}H_{11}N_3$: C, 69.32; H, 4.92. Found: C, 69.25; H, 5.04. [e] Reported b.p. 193–194° (29 mm.) by E. Ritchie, *J. Proc. Roy. Soc. N. S. Wales*, **78**, 169 (1945). [f] *Anal.* Calcd. for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30. Found: C, 74.71; H. 5.55. [g] *Anal.* Calcd. for $C_{13}H_{13}N$: C, 85.26; H, 7.15. Found: C, 85.38; H, 7.14. [h] *Anal.* Calcd. for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30. Found: C, 74.57; H, 5.39. [i] *Anal.* Calcd. for $C_{12}H_{10}NBr$: C, 58.08; H, 4.06. Found: C, 58.11; H, 4.05. [j] *Anal.* Calcd. for $C_{12}H_8N_3Br$: C, 52.57; H, 2.94. Found: C, 52.49; H, 2.93. [k] From carboxylic acid by Curtius degradation. [l] *Anal.* Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71. Found: C, 67.18; H, 4.60. [m] *Anal.* Calcd. for $C_{12}H_8N_4O$: C, 60.00; H, 3.34. Found: C, 60.04; H, 3.46.

that the synthesis of some of the compounds that might be desired is difficult. Some were prepared by reduction of the nitro compound prepared by the Gomberg–Bachmann biaryl synthesis with the appropriate 2-nitro-N-nitrosoacetanilide and benzene, and then converting the amino group to an azido group through its diazonium salt; others were prepared from amines obtained by the Curtius degradation of *o*-arylbenzoic acids, obtained by the Gomberg–Bachmann biaryl synthesis with N-nitroso-N-acetylanthranilic esters. The properties of the new compounds are given in Table III.

Thermal decomposition in decalin solution led to quantitative nitrogen evolution in all cases. The carbazoles formed have all been reported previously. Yields were estimated by the ultraviolet absorption spectra of the solutions, and confirmed by actual isolation; they were mostly quantitative, and in no case less than 75%. The rates were in all cases strictly first order, except for small deviations at the very beginning and end. The rate constants were determined by the Guggenheim method, in the range from 10 to 80% of completion. In addition, *o*-azidobiphenyl was examined at four initial concentrations covering a 4.5-fold range; the same value was found for the rate constant within experimental error.

The rate constants obtained are reported in Table IV. Each value is the average of two or more separate experiments, except in the examples noted, which are for azides reported in a previous paper.[10] The three temperatures at which the measurements were made are confined to a somewhat narrow range, as were those used by Appl and Huisgen, owing to the high sensitivity of the rates to changes in temperature. The enthalpies and entropies of activation are recorded in Table V.

TABLE IV

FIRST-ORDER RATE CONSTANTS FOR THE LOSS OF NITROGEN FROM 2-AZIDOBIPHENYLS

2-Azidobiphenyl	$k \times 10^3$, min.$^{-1a}$ 148°	155.3°	163.6°
Unsubstd.	7.65 ± 0.09	14.55 ± 0.05	30.3 ± 0.05
5-Methoxy	63.3 ± .2	107.3 ± 1.3	194.2 ± .6
5-Methyl	15.27 ± .26	27.3 ± 0.6	54.0 ± .1
5-Bromo	16.14 ± .56	29.5 ± 1.1	55.8 ± .05
5-Nitro	13.13 ± .06	25.0 ± 0.1	52.4 ± .4
4-Methoxy	8.33 ± .4	15.81 ± .18	33.2 ± .1
4-Methyl	7.82 ± .07	15.18 ± .11	31.6 ± .05
4-Bromo	10.41 ± .11	20.8 ± .05	42.0 ± .6
4-Nitro	6.45 ± .16	12.81 ± .07	28.0 ± .5
2′,5′-Dimethoxy	4.62 ± .01	11.78 ± .04[b]	23.5 ± .3[c]
2′,3′-Benzo	5.50[d]	12.72[b,d]	27.4[c,d]
3,4-Benzo	107.3[e]		
3′,4′-Benzo	10[d]	18[b,d]	36[c,d]
4′-Nitro			27[d,f]
3,5-Dibromo			35[d,f]
6,2′-Methylene (4-fluorenyl azide)			30[d,f]

[a] ± average deviation. [b] 156.7°. [c] 163.9°. [d] Single determination only. [e] 24.2 at 127.3°. [f] 161.2°.

TABLE V

ENTROPIES AND ENTHALPIES OF ACTIVATION FOR DECOMPOSITION OF 2-AZIDOBIPHENYLS

2-Azidobiphenyl	$\Delta H^{\ddagger}$, kcal./mole[a]	$\Delta S^{\ddagger}$, cal./deg. mole, 156°
Unsubstd.	31.4 ± 0.5	−2.5 ± 1.1
5-Methoxy	25.5 ± .2	−12.3 ± 0.4
5-Methyl	29.0 ± .4	−6.8 ± 1.0
5-Bromo	28.2 ± .8	−8.6 ± 1.9
5-Nitro	41.6 ± .3	−1.0 ± 0.7
4-Methoxy	31.7 ± .2	−2.7 ± .4
4-Methyl	31.8 ± .2	−1.3 ± .6
4-Bromo	31.8 ± .7	−0.9 ± 1.5
4-Nitro	33.6 ± 1.1	2.4 ± 2.6
2′,5′-Dimethoxy	36.7 ± 0.3	9.0 ± 0.7
2′,3′-Benzo	36.0 ± 2.5	8.0 ± 8
3′,4′-Benzo	29 ± 6	
3,4-Benzo	30.8 ± 2.5	2.1 ± 8

[a] Derived from mean slope of log k/T *vs.* $1/T$, ± maximum deviation.

The effect of changes in solvent was investigated with *o*-azidobiphenyl. The rate constant for its decomposition at 173.9° remained essentially unchanged in decalin (k = 0.08 min.$^{-1}$) and nitrobenzene (k = 0.09 min.$^{-1}$), but was approximately doubled in ethylene glycol (k = 0.16 min.$^{-1}$) and tripled in benzyl alcohol (k = 0.25 min.$^{-1}$). The acceleration in these hydroxylic solvents may be related to the known sensitivity of nitrogen evolution to acids.[11] The results of Appl and Huisgen and ourselves (Table II) also suggest a small acceleration in aniline.

Discussion

The effect of substitution on the rates is moderate, the extremes differing by a factor of seventeen. As with simple phenyl azides, *m*-substituents have hardly any effect and *p*-substituents give rise to variation by a factor of 8.3 from one extreme to the other. All *p*-substituents studied accelerate the reaction, and there is no simple correlation with Hammett's substituent constants. Changes in the ring to which cyclization occurs apparently have little effect on the rate, although the examples are few and ambiguous. These observations strongly

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(10) P. A. S. Smith, J. M. Clegg and J. H. Hall, *J. Org. Chem.*, **23**, 524 (1958).

(11) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2438 (1951).

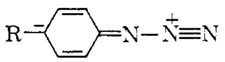
suggest that the rate-determining step is the same in the azidobiphenyl system as with simple phenyl azides, and is not concerned with the formation of the various types of products isolated, but with a common initial step. If so, this must be direct cleavage of the azide to an azene, without prior cyclization or addition, and, in view of the insensitivity to *m*-substituents, probably without anchimeric assistance, as concluded by Appl and Huisgen.

The sensitivities of the rate constants to temperature vary in such a way as to give rise to an isokinetic temperature at about 250°, considerably above the temperature of our measurements. Both the enthalpies and entropies of activation vary widely, but they are approximately linear with each other, and so act to counteract each other's effect on the rate. This phenomenon has been encountered in many reactions, and specifically in the decomposition of triarylmethyl azides, in which a rearrangement reaction predominates. Saunders and Ware[12] have attributed this to charge separation in the transition state, resulting from

$$Ar_3C{-}N_3 \longrightarrow Ar_2C{=}N{-}Ar + N_2$$

assistance by the migrating phenyl group in the loss of nitrogen. This effect should orient solvent molecules in proportion to its magnitude, causing a more negative entropy effect.

Because of the widely varying entropy of activation and the existence of the isokinetic temperature, an attempt to interpret the effects of substitution would be more fruitful in terms of activation enthalpies than rate constants. The considerable variation of the enthalpies of activation with *para* substitution (*i.e.*, at 5-position), but not with *meta*, indicates a predominantly mesomeric electronic effect. It is not in the expected order for Hammett substituent constants, for *p*-bromo is out of position, giving the order $p\text{-}NO_2 > H > p\text{-}CH_3 > p\text{-}Br > p\text{-}CH_3O$. This is, however, qualitatively the same as the order of the values of $\Delta\sigma$ ($\sigma_p - \sigma_m$), which Price[13] has considered, and the related $\sigma_R{}^\circ$ values of Taft, Ehrenson, Lewis and Glick,[14] which are a measure of the extent to which these groups take part in conjugation. In contrast, Saunders and Ware observed the normal order for the effect of substitution on the enthalpy of activation for their reaction, and a much compressed range of magnitudes. They did not examine *m*-substituted compounds, however, which in our reaction showed little variation of enthalpy of activation. Furthermore, in their compounds the azido group is separated from the benzene rings by a carbon atom, and conjugation effects would be less important.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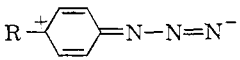
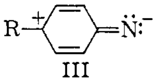

II

The fact that $\Delta H^{\ddagger}$ is sensitive to *para* substituents but not to *meta* indicates that changes in the degree of conjugation involving the azido group and the benzene ring are probably the determining factor. We have described evidence in an accompanying paper[15] that such conjugation has the character represented by I, rather than II. Interaction of structure I with a *p*-nitro group would lead to increased stability, but would not with a *p*-methoxy group, which would seek to impose an opposite polarity. The best we can do at present to estimate the effects of substituents on the stability of the transition state is to consider the effects on the presumed initial product, an aryl azene, which the transition state must resemble to some extent. The conjugation shown in I is presumably largely lost; conjugation of the developing azene (shown in the singlet state) with the benzene ring can be described by the polar form III. This would be stabilized by interaction with a *p*-methoxy group and destabilized by a *p*-nitro group, precisely opposite to the situation with the aryl azide structure. (If, however, the azene should be in a triplet state, conjugation would not be possible, but the over-all argument would not be affected.) The result of *p*-substitution by a nitro group should therefore be to lower the energy of the ground state and possibly raise the energy of the transition state, thereby increasing the activation enthalpy, which indeed it does by 10 kcal./mole. *p*-Substitution by a methoxyl group should have the reverse effect, decreasing the activation enthalpy, as observed to the extent of 6 kcal. The effects of *p*-methyl and *p*-bromo groups are in concord with this interpretation, if conjugation involving *p*-electrons of the bromo group is more important than a simple inductive effect. This is a reasonable assumption in view of the insensitivity of the activation enthalpy to the inductive influence of *m*-substituents.


III

It should be noted that electron-releasing substitution on the ring to which cyclization ultimately occurs noticeably raises the activation enthalpy. Although it is not clear how this result comes about, it cannot be the results of electrophilic attack by the azido group prior to loss of nitrogen, for such a process would have its activation enthalpy lowered, rather than raised, by electron-releasing substitution. The unexceptional rate constant for 4′-nitro-2-azidobiphenyl (of which there was unfortunately not enough material to determine $\Delta H^{\ddagger}$) is further evidence that nitrogen evolution may not require incipient formation of a new N–C bond.

It is significant that the entropy of activation is nearly constant with 2-azidobiphenyl and derivatives substituted *meta* to the azido group, but variable and negative with *p*-substitution. This may be considered to result from changes in conjugative restriction of the rotation of the azido group, and in the effect of the azido group on rotation about the aryl–aryl bond of the biphenyl system, caused by conjugation with substituents *para* to the azido group. Alternatively, changes

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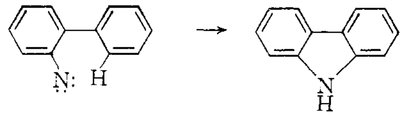
in solvation[10] attending changes in charge separation on approaching the transition state would be expected to vary with *p*-substituents but not appreciably with *m*-substituents, leading to entropy effects of the sort observed.

The rate constants for loss of nitrogen from triarylmethyl azides, from simple phenyl azides and from 2-azidobiphenyls are all of the same order of magnitude, the triarylmethyl azides being, however, generally slower. The enthalpies of activation for all three types of compounds are also of the same order of magnitude, falling in the range 24–36 kcal./mole. In view of these similarities as well as similarities in the effects of substituents in equivalent positions, it is tempting to conclude that these compounds decompose by a path having a common type of intermediate, an azene. However, the rearrangement of triarylmethyl azides may nevertheless be a concerted process not involving an azene, for it would otherwise be more difficult to rationalize the observed substituent effects. Whether azenes that might be formed from aryl azides would be in a singlet or triplet state cannot be determined from present information. The formation of the carbazole system (eq. 5) can be formulated as an initial attack by the azene on either the 2′-hydrogen, the 2′-carbon or the bond joining them. When cyclization is not possible, the alternative reactions of rearrangement, hydrogen abstraction and dimerization come into play.



(5)

Experimental[16]

2-Nitro-5-methoxyacetanilide.—Although this compound has been reported before,[17] the reported preparations are almost useless for synthesis. This procedure, although poor, is a marked improvement. A solution of acetyl nitrate was prepared by the cautious addition of 60 ml. of concd. nitric acid to 300 ml. of acetic anhydride at 0–15°. This mixture was then added slowly to a solution of 115 g. of *m*-methoxyacetanilide[18] in 400 ml. of glacial acetic acid at 0–15°, and the resulting mixture was allowed to come to room temperature over a period of 4 hr. Pouring into ten volumes of water precipitated a solid, which was collected and dried. The solid was extracted repeatedly with hot ligroin (b.p. 90–100°) by decantation until solid no longer precipitated from the cooled extract. Concentration and filtration gave 28 g. (19%) of 2-nitro-5-methoxyacetanilide, m.p. 123–127°, raised to 127–128° by recrystallization from ethanol (reported[17] m.p. 125°).

2-Nitro-5-methoxybiphenyl.—To a solution of 9.2 g. of nitrogen tetroxide in 100 ml. of acetic acid and 75 ml. of acetic anhydride at 0–10° was added 12.3 g. of sodium acetate and 10.5 g. of 2-nitro-5-methoxyacetanilide, and the mixture was stirred for 7 hr. at 0–10°. The mixture was then poured into ice-water and the solid that separated was extracted into 600 ml. of benzene. The benzene solution was washed with water and then allowed to stand at 35° for 15 hr., after which it was refluxed for 2 hr. and then concentrated to an oil. Distillation of the residue gave 8.5 g., b.p. 120–147° (0.3 mm.). This material was purified by chromatography on alumina, the first band, a light yellow oil, being collected. Distillation gave 5.9 g. (52%) of 2-nitro-5-methoxybiphenyl, b.p. 136–138° (0.2 mm.), which was crystallized with considerable difficulty from methanol, and then had m.p. 50.6–51.3°.

Anal. Calcd. for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.88. Found: C, 68.19; H, 4.89.

The following biphenyls were prepared from the appropriate N-nitrosoacetanilide and purified in a similar manner: 2-nitro-4-methoxybiphenyl, 16% yield, m.p. 71–73° (reported[19] m.p. 75–76°); 2-nitro-4-methylbiphenyl, 46% yield, m.p. 49–50° (reported[20] to be an oil); 2-nitro-5-methylbiphenyl, 53% yield, m.p. 82–85° (reported[21] m.p. 86–87°).

2-Nitro-4-bromobiphenyl was prepared from 2-nitro-4-bromoacetanilide and purified in a similar manner. The crude oil, distilled at 140–150° (0.7 mm.), gave a 28% yield of crystalline product after chromatography on alumina; m.p. 61.8–62.4°.

Anal. Calcd. for $C_{12}H_8BrNO_2$: C, 51.82; H, 2.89. Found: C, 51.90; H, 2.98.

2-Amino-4-nitrobiphenyl.—4-Nitrobiphenyl-2-carbonyl chloride was prepared by the action of 100 ml. of thionyl chloride on 18.4 g. of 4-nitrobiphenyl-2-carboxylic acid (m.p. 184.8–185.4°, reported[22] m.p. 173°) which had been prepared by the hydrolysis of its methyl ester, obtained from methyl 2-acetamido-5-nitrobenzoate by nitrosation and coupling to benzene in the manner described for 2-nitro-5-methoxybiphenyl. The crude acid chloride was converted to azide by reaction with sodium azide in wet acetone, and the dried azide, m.p. 74° dec., was converted to the corresponding isocyanate, m.p. 101–102.5°, which was hydrolyzed with warm, 50% potassium hydroxide. The resulting solution was acidified to decompose the carbamate salt, made basic again, and the crude amine which precipitated was separated from a small amount of the corresponding urea by solution in 20 ml. of methanol. Dilution of the methanol solution with water and chilling produced 1.47 g. (71%) of 2-amino-4-nitrobiphenyl, m.p. 70–72° (see Table II). This amine was also prepared by the Hofmann degradation of 4-nitrobiphenyl-2-carboxamide with aqueous potassium hypochlorite solution; the yield was only 7% and the product was less pure.

2-Phenyl-5-nitrobenzamide (4-Nitrobiphenyl-2-carboxamide).—Treatment of the crude acid chloride from 5.89 g. of 2-phenyl-5-nitrobenzoic acid with concd. ammonium hydroxide gave 5.36 g. (93%) of the amide, m.p. 184–185°.

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.45; H, 4.16. Found: C, 64.46; H, 4.14.

2-Azidobiphenyls were prepared by diazotizing the amines in cold hydrochloric acid solution and adding a slight excess of sodium azide in water[23]; the crude products that separated were purified by crystallization from methanol or ethanol, or by shortpath distillation under high vacuum. In some cases the very low solubility of the common amine salts in water made the use of isethionic acid instead of hydrochloric acid much more satisfactory. Some of the azides used, not listed in Table II, have been described earlier.[11]

Carbazoles.—Separately from the kinetic experiments, approximately 1% solutions of the 2-azidobiphenyls in decalin were refluxed for about 1 hr., and then chilled to −15° overnight. The carbazoles that crystallized were reasonably pure, as shown by melting point, and were obtained in yields of 65–79%. The decalin solutions of carbazoles resulting from the kinetic experiments were assayed for total carbazole by comparing the intensity of the long wave-length maxima with those of standard solutions; the assays were mostly above 97% of the initial azide. Most of the carbazoles have been prepared by this reaction before,[7,8] but the following carbazoles have not: 3-methoxy-, m.p. 148–149° (reported[23,24] 138–139°, 151–152°); 2-

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[16] Melting point temperatures are uncorrected. Analyses are by Spang Microanalytical Laboratory, Ann Arbor, Mich.

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methyl-, m.p. 258–260° (reported[23] 259°); 3-methyl-, m.p. 205–206° (reported[25] 207°); and 2-bromo-, m.p. 249–250° (reported[26] 250–251°).

Phenyl Azides.—All of the phenyl azides used in this work are known compounds, and all were prepared by the reaction of diazonium salts with aqueous sodium azide. The decalin solutions resulting from the thermal decomposition experiments were assayed for the corresponding aniline by extraction with aqueous acid, neutralization, treatment with acetic anhydride or benzoyl chloride, and isolation of the solid anilide. *p*-Nitroaniline, however, precipitated with much other material from the cold reaction mixture, and was isolated with some difficulty by extractions and crystallizations with benzene, petroleum ether, and charcoal. The major product was a non-basic, insoluble, high-melting, dark brown solid. The results are given in Table I.

Phenyl azide was also decomposed in decalin solution containing an equivalent amount of azobenzene. The volume of nitrogen evolved, 1.32 moles per mole of azide, was not significantly different from that from phenyl azide in decalin alone; however, the rate was approximately half that in the absence of azobenzene. 2-Azidobiphenyl, which normally gives only 1 mole of nitrogen per mole of azide, gave 1.11 moles when an equivalent amount of azobenzene was present, but the rate was unchanged within experimental error.

Kinetic Measurements.—Standard solutions of the various azides were prepared in resorcinol dimethyl ether in concentrations about 1 M. The reaction vessel, charged with 110 ml. of decalin for each experiment, was immersed in a thermostat bath and connected to a water-jacketed gas buret by a capillary tube. The gas buret was kept at constant temperature by circulating water of controlled temperature through the jacket. Temperatures were controlled to ±0.1°. The apparatus was allowed to come to temperature equilibrium for 2 hours before each experiment. At time zero, 0.050 ml. of the standard azide solution was introduced by inserting a syringe through a capillary tube that opened into the reaction vessel beneath the liquid surface; this tube was closed by a serum cap at other times. Violent stirring was maintained with a magnetic stirrer. Volume readings were made at intervals appropriate to the rate being measured.

First-order rate constants were determined by the method of Guggenheim,[27] using a graphic plot of log ΔV *vs.* time, and a reference time corresponding to approximately two half-lives. The enthalpies of activation were determined graphically from log k/T *vs.* $1/T$, and the entropies of activation were calculated from the Eyring equation for the temperature of 156°.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

The Electronic Character of the Azido Group Attached to Benzene Rings[1]

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Bromination of phenyl azide produces *p*-bromophenyl azide, and of 2-naphthyl azide, 1-bromo-2-naphthyl azide. Bromination of equimolar mixtures of phenyl azide with benzene, toluene or anisole gives results that place the azido group midway between methyl and methoxy in activation toward electrophilic aromatic substitution. The three azidobenzoic acids and the three azidoanilines have been prepared and their dissociation constants have been measured. The azido group is acid-strengthening to about the same extent as fluoro. The electronic spectra of the azidoanilines, their hydrochlorides, and some other aryl azides are recorded.

The azido group has been the object of relatively little investigation with respect to its influence on the benzene ring and on other ring-attached substituents. We know only that nitration is directed *ortho* and *para* to the azido group in phenyl azide[2] and the naphthyl azides.[3] The question of the effect of the azido group on the susceptibility of aromatic rings to electrophilic attack has not been explicitly answered, although one can infer that it is ring-activating from the fact that an azido group allows three nitro groups to be introduced onto a benzene ring by direct nitration,[4] and that nitration of either α- or β-naphthyl azide takes place on the ring bearing the azido group. In addition, the effect of *p*-substituents on the ultraviolet absorption spectra of phenyl azides has been investigated, and from this a value of 0.27 has been deduced for σ_p, the Hammett substituent constant, for the azido group.[5]

We have studied the bromination of phenyl and β-naphthyl azides. Phenyl azide reacts readily with bromine at room temperature, with and without ferric bromide catalyst, and the product is *p*-bromophenyl azide in a high state of purity. When an equimolar mixture of benzene and phenyl azide was treated with a half equivalent of bromine, no bromobenzene was found, but only *p*-bromophenyl azide, apparently free from isomers. At the same time, bromoaniline hydrobromide was formed in a side reaction by the action of hydrogen bromide on phenyl azide.[6]

Because of the sensitivity of azides to strong acids, we did not try to evaluate the substituent constant,[7] σ_{p^+}, by direct measurement of the rate of electrophilic substitution, but instead approached it by competition experiments by brominating an equimolar mixture of anisole and phenyl azide, with one-half molar equivalent each of bromine and sodium acetate in glacial acetic acid. There resulted 13 times as much *p*-bromoanisole as *p*-bromophenyl azide. The composition of the product was determined by first reducing the azides to anilines with sodium borohydride, a process that was demonstrated to be essentially quantitative with phenyl azide (and may be the method

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