

methyl-, m.p. 258–260° (reported²³ 259°); 3-methyl-, m.p. 205–206° (reported²⁵ 207°); and 2-bromo-, m.p. 249–250° (reported²⁶ 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 $\pm 0.1^\circ$. 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 $\log \Delta V$ 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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(26) B. M. Barclay and N. Campbell, *ibid.*, 530 (1945).

(27) E. A. Guggenheim, *Phil. Mag.*, **2**, 238 (1926).

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The Electronic Character of the Azido Group Attached to Benzene Rings¹

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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 azide² 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

(1) Partly from the doctoral dissertation of J. H. H., University of Michigan, 1959. Supported in part by Allegany Ballistics Laboratories, Hercules Powder Co.

(2) P. Drost, *Ann.*, **307**, 49 (1899).

(3) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **91**, 1942 (1907).

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(5) C. N. R. Rao and C. W. W. Hoffman, *Sci. and Culture (Calcutta)*, **22**, 463 (1957).

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

(7) (a) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); (b) N. C. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957); (c) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

of choice). Vapor phase chromatography and ultraviolet absorption spectra gave mutually consistent results, the former being apparently more reliable. Bromination of a toluene-phenyl azide mixture resulted in 12 times as much *p*-bromophenyl azide as *p*-bromotoluene. From these ratios and the reported^{7c} values of σ_p^+ , -0.76 for methoxy and -0.31 for methyl, one can calculate σ_p^+ for the azido group to be -0.54 . This value is obtained by first determining the rate constant ratios, $k_{\text{CH}_3}/k_{\text{N}_3}$ and $k_{\text{CH}_3\text{O}}/k_{\text{N}_3}$, from the integrated bimolecular rate equations, which yield the relation

$$\log \frac{A_0}{A} = \frac{k_A}{k_B} \log \frac{B_0}{B}$$

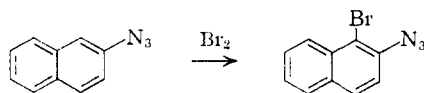
Since in our experiments $(\text{Br}_2)_0 = A_0 = B_0$ (the initial substrate concentrations), and $B = A_0 - A$ is a consequence of complete consumption of the bromine, the expression

$$\frac{k_A}{k_B} = \frac{\log (A_0/A)}{\log [A_0/(A_0 - A)]}$$

can also be used to calculate the rate-constant ratios. The results by either method were in acceptable agreement; $k_{\text{CH}_3}/k_{\text{N}_3} = 0.018-0.040$, and $k_{\text{CH}_3\text{O}}/k_{\text{N}_3} = 30.5-37.1$. The value of σ_p^+ is then obtained from the Hammett equation in the form $\log (k_A/k_B) = \rho(\sigma_A^+ - \sigma_B^+)$. The two independent experiments allow σ_p^+ to be evaluated without assuming a value for the reaction constant, ρ . From the value of σ_p^+ , ρ can then be calculated to have the value -7.0 for the reaction conditions used, a value considerably lower than that most recently determined for bromination in acetic acid in the absence of sodium acetate, -12.14 , but close to values for other bromination conditions^{7c} (use of the higher value of ρ leads to values of -0.44 and to -0.64 for σ_p^+ from the separate experiments).

The value -0.54 for σ_p^+ is also consistent with the position of the carbonyl stretching frequency of *p*-azido-acetophenone, near 1680 cm^{-1} . While our instruments do not permit the frequency to be measured with the necessary precision to evaluate σ_p^+ quantitatively,^{7c,8} the carbonyl band can be stated to be of lower frequency than that of acetophenone, slightly higher than *p*-acetanidoacetophenone ($\sigma_{\text{AcNH}^+} = -0.6$), and markedly higher than *p*-aminoacetophenone ($\sigma_{\text{NH}_2^+} = -1.3$).

Bromination of β -naphthyl azide produced but a single bromo azide, whose structure was established as 1-bromo-2-naphthyl azide by conversion to the known 1-bromo-2-acetnaphthalide.



o-, *m*- and *p*-azidobenzoic acids were prepared from the corresponding aminobenzoic acids, and their apparent K_a values were determined by potentiometric titration in aqueous methanol (45.4% by volume). The figures obtained are given in Table I.

The three azidoanilines were prepared from the corresponding nitrophenylphthalimides by way of the amino and the azidophenylphthalimides.

(8) R. N. Jones, W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 504 (1957).

TABLE I

APPARENT IONIZATION CONSTANTS OF AZIDOBENZOIC ACIDS IN 45.4% AQUEOUS METHANOL AT 25°

Benzoic acid	Unsubstd.	<i>o</i> -Azido	<i>m</i> -Azido	<i>p</i> -Azido
$K_a \times 10^6$	5.76	29.5	13.5	6.92

Their K_b values were determined by potentiometric titration in aqueous methanol. The constants obtained are reported in Table II.

TABLE II

IONIZATION CONSTANTS FOR AZIDOANILINES IN 45.4% METHANOL AT 25°

Aniline	Unsubstd.	<i>o</i> -Azido	<i>m</i> -Azido	<i>p</i> -Azido
$K_b \times 10^{11}$	25.7	2.30	3.31	12.6

The ultraviolet absorption spectra of the azidoanilines were measured in isoöctane and in methanol, and the spectra of their hydrochlorides were measured in 0.1 *N* hydrogen chloride in methanol. The absorption maxima and extinction coefficients are reported in Table III.

TABLE III

ULTRAVIOLET SPECTRA OF PHENYL AZIDES

Substituent	Solvent ^a	λ_{max} , m μ	Molar extinction coefficient, ϵ
<i>o</i> -Amino	I	310	6,450
		252	9,880
		225	21,500
	M	309	4,800
		252	9,210
		225	17,600
<i>m</i> -Amino	I	301	2,790
		230	23,500
	M	302	2,660
		233	23,000
<i>p</i> -Amino	I	307	3,100
		260	18,100
	M	267	16,100
		249	13,300
<i>m</i> -Amino, HCl	M	250	13,600
<i>p</i> -Amino, HCl	M	249	14,400
<i>p</i> -Nitro	I	299	17,000
		220	14,000
<i>m</i> -Nitro	I	315	1,600
		242	20,500
<i>p</i> -Bromo	I	297	2,100
		285	3,000
		255	17,800
<i>m</i> -Bromo	I	293	1,500
		283	2,000
		251	12,000

^a I = isoöctane, M = methanol.

Discussion

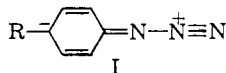
The azido group behaves as an electron-withdrawing group in azido aliphatic acids,⁹ and dipole moment measurements of substituted phenyl azides show the dipole to be directed with the negative pole away from the ring.¹⁰ Our measurements of the effect of the azido group on the dissociation con-

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

(10) E. Bergmann and W. Schutz, *Z. physik. Chem.*, **19B**, 389 (1932); L. E. Sutton, *Nature*, **128**, 639 (1934); G. Favini, *Gazz. chim. ital.*, **91**, 270 (1961).

stants of benzoic acid and aniline are qualitatively in agreement with the foregoing observations; the azido group is acid strengthening in all positions on the ring, albeit to a considerably different degree. Comparison with the effect of fluorine or acylamino substitution shows that the inductive electron-withdrawing effect of the azido group is very similar. The currently accepted value^{7a} for the Hammett substituent constant, σ_m , for the fluoro group, 0.337, is bracketed by the values for the azido group calculated from our measurements: 0.37 from the benzoic acids, and 0.33 from the anilines. Conjugative electron release is of the same sign for both groups, but may be very slightly greater for the fluoro group, the value for σ_p , 0.062, being just under the values 0.08 and 0.11 calculated for the azido group from our measurements on benzoic acids and anilines, respectively. The corresponding values¹¹ for the benzamido group are $\sigma_m = 0.217$, $\sigma_p = 0.078$.

The electromeric influence of the azido group on a benzene ring must be strongly electron donating to account for its *ortho-para* orienting character and its marked activating influence on electrophilic substitution. The large value, -0.54 , of σ_p^+ shows that in this respect the effect is much greater than for the fluoro substituent ($\sigma_p^+ = -0.073$), and is more like that for acetamido¹¹ (-0.6). This implies that the structure I is of considerable importance in describing the influence of the *p*-azido group. As a result of the strong electromeric effect,



the azido group thus resembles acylamino somewhat more than halogen in its interaction with the benzene ring and other substituents on it.

The aliphatic azido group has been reported to absorb ultraviolet radiation weakly in the region 2800–2900 Å.¹² The ultraviolet spectra of a number of aryl azides have been reported^{8,13,14}; all show strong absorption in the near ultraviolet, at wave lengths similar to those of the corresponding acetanilides, as Grammaticakis has pointed out.¹³ An empirical relationship between substituent-induced wave-length shifts and Hammett substituent constants has been described by Doub and Vandenbelt,¹⁵ and we were interested to see if it could be applied to the azido group. Unfortunately, a marked discrepancy between the two reported determinations of the spectrum of *m*-nitrophenyl azide exists, and we felt it desirable first to redetermine some of the reported examples while determining certain new ones. Our results for *m*-nitrophenyl azide as well as the others listed in Table III confirm those of Grammaticakis, insofar as one can interpret them from the small-scale, graphic form in which all his results are presented. It is of in-

terest that the three azidoanilines have quite different spectra, but those of their salts are superimposable, and very similar to phenyl azide.

Rao and Hoffman⁸ have applied the Doub and Vandenbelt correlation of the value of $\Delta\sigma$ ($\sigma_p - \sigma_m$) with the shift of the primary absorption band, and calculated a value of 0.5 for $\Delta\sigma$ from the spectra of *p*-tolyl and *p*-anisyl azides. This value is nearly double that obtained from our equilibrium constant measurements. Their value, however, is incorrectly obtained, for they utilized compounds in which the *ortho-para*-directing azido group is opposed to other groups of the same directional type; Doub and Vandenbelt pointed out that their correlation is reliable only when *p*-substituents are of different directional types. The value of the wave-length shift, $\Delta\lambda$, obtainable from the spectrum of *p*-azidobenzoic acid illustrated by Grammaticakis (λ_{\max} 268 m μ) allows the magnitude of $\Delta\sigma$ to be estimated as 0.25, in good agreement with our measurements (0.29). The value of 0.27 for σ_p for the azido group calculated by Rao and Hoffman is also probably unreliable for similar reasons; it is clearly in disagreement with the value 0.08 obtained from our equilibrium measurements on *p*-azidobenzoic acid.

Experimental¹⁶

Bromination of Phenyl Azide. A. In the Absence of Iron Salts.—A solution of 11.9 g. (0.1 mole) of phenyl azide in 60 ml. of carbon tetrachloride was cooled to 0–10° and a solution of 19.2 g. (0.12 mole) of bromine in 20 ml. of carbon tetrachloride added dropwise with stirring over a period of 10 hours. After stirring an additional hour, the mixture was filtered and the solid washed thoroughly with carbon tetrachloride. The filtrate was washed with 10% hydrochloric acid, 10% sodium hydroxide solution and finally with water. It was dried over magnesium sulfate and the solvent removed. The residual oil was distilled, giving two fractions. The first fraction (0.54 g., b.p. 30–62° (1.0 mm.)) was recovered phenyl azide. The second fraction (10.62 g., b.p. 62–63° (1.0 mm.), m.p. 21.0–21.8°) was *p*-bromophenyl azide (54%), as shown by a mixed melting point with material prepared from *p*-bromoaniline.

The solid insoluble in carbon tetrachloride was stirred with sodium hydroxide solution and the liberated amines extracted into ether. Evaporation of the ether gave 3.89 g. of a mixture of bromoanilines.

B. In the Presence of Iron.—The foregoing procedure was repeated with the addition of 0.56 g. (0.01 mole) of powdered iron. After a total reaction time of 2 hours, the mixture was worked up as before, to give 8.94 g. (45%) of *p*-bromophenyl azide and a small amount of recovered phenyl azide.

Bromination of Phenyl Azide in the Presence of Benzene.—To a solution of 11.9 g. (0.1 mole) of phenyl azide and 7.8 g. (0.1 mole) of benzene in 60 ml. of carbon tetrachloride was added dropwise a solution of 16.0 g. (0.1 mole) of bromine in 20 ml. of carbon tetrachloride over a period of 6 hours, with stirring and cooling to 0–10°. After an additional 2 hours, the solution was filtered and the solid washed with carbon tetrachloride. The solid bromoaniline hydrobromides (8.25 g.) were discarded. The filtrate was extracted twice with 10% hydrochloric acid, then twice with 10% sodium hydroxide, dried over magnesium sulfate and then distilled. The residue after removal of carbon tetrachloride and benzene was distilled under vacuum, giving three fractions: I, 1.04 g., b.p. 66–68° (20 mm.); II, 1.25 g., b.p. room temperature (1.0 mm.); and III, 8.25 g., b.p. 63–64° (1.0 mm.). The infrared spectra of I and II were identical and contained bands at 4.75 μ characteristic of the azido group. Fraction I contained no bromine, and its boiling point is in agreement with that re-

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(13) P. Grammaticakis, *Compt. rend.*, **244**, 1517 (1957).

(14) E. B. Lieber, C. N. R. Rao, T. S. Chao and W. H. Wahl, *J. Sci. Ind. Research (India)*, **16B**, 95 (1957).

(15) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(16) Melting and boiling points are uncorrected. Analyses by Spang Microanalytical Lab., Ann Arbor, Mich.

ported¹⁷ for phenyl azide (66–68° (21 min.)). No bromobenzene could be detected. Fraction III was *p*-bromophenyl azide (42%).

1-Bromo-2-azidonaphthalene.—A solution of 7.04 g. (0.044 mole) of bromine in 10 ml. of carbon tetrachloride was added dropwise with stirring to a solution of 6.76 g. (0.04 mole) of 2-azidonaphthalene in 40 ml. of carbon tetrachloride chilled in an ice-bath. The addition was complete after 3 hours. After stirring for another hour, the solvent was removed under vacuum at room temperature. The residue was heated with 100 ml. of petroleum ether (b.p. 90–100°) and the solution filtered hot. On cooling to 5°, 4.83 g. of 1-bromo-2-azidonaphthalene separated, m.p. 110.5–111.5°. Concentration of the filtrate to 15 ml. gave an additional 0.80 g., m.p. 108–111°, giving a total yield of 5.63 g. (57%). An analytical sample, prepared by recrystallization from 95% ethanol, melted at 111.0–111.5°, undepressed by mixture with a sample of 1-bromo-2-azidonaphthalene prepared from 1-bromo-2-naphthylamine by diazotization and treatment with sodium azide.

Anal. Calcd. for C₁₀H₆BrN₃: C, 48.38; H, 2.44. Found: C, 48.34; H, 2.45.

Bromination of Phenyl Azide in the Presence of Toluene or Anisole.—Equimolar mixtures of phenyl azide and toluene or anisole were dissolved in glacial acetic acid containing a half-equivalent of sodium acetate (prepared by adding the calculated amount of sodium bicarbonate). A half-equivalent of bromine was added, and the mixtures were allowed to stand at room temperature for 16 hours; a trace of bromine still remained in the toluene reaction mixture. The reaction mixtures were then diluted with water, a little potassium pyrosulfite was added to destroy residual bromine, and the mixtures were extracted with several portions of petroleum ether (b.p. 30–40°). The solvent was removed through a fractionating column, and the residue was refluxed with excess sodium borohydride in isopropyl alcohol for 2 hours. The resulting mixture was diluted with water and acidified, and extracted with four portions of petroleum ether (b.p. 30–40°). The acidic aqueous solution was made strongly basic with potassium hydroxide and extracted with five portions of petroleum ether. The separated extracts were dried over potassium hydroxide or alumina and analyzed both by vapor phase chromatography and by ultraviolet spectroscopy, using both the primary and secondary absorption bands of each component. The spectroscopic method gave results which vary considerably from one reference wave length to another, and are believed to be of qualitative value only. For the toluene-phenyl azide reaction, the proportion of *p*-bromoaniline in the aniline-*p*-bromoaniline mixture was 88% (v.p.c.), or 76 ± 18% (ultraviolet); the proportion of bromotoluenes (assumed to be 2/3 *p*-isomer) in the toluene-bromotoluene mixture was 7% (v.p.c.) or 21 ± 8% (ultraviolet); v.p.c. ratio bromotoluene: bromophenyl azide, 1:12. For the anisole-phenyl azide reaction, the proportion of *p*-bromoaniline in the bases was 7% (v.p.c.) or 6 ± 5% (ultraviolet); the proportion of bromoanisoles in the neutral fraction was 92% (v.p.c.) or 85 ± 4% (ultraviolet); v.p.c. ratio bromoanisole: bromophenyl azide, 13:1.

Reduction of Phenyl Azide by Sodium Borohydride.—A mixture of 1.10 g. of phenyl azide and 0.25 g. of sodium borohydride in 10 ml. of isopropyl alcohol was refluxed for 2 hours, cooled, diluted with concentrated aqueous potassium hydroxide, and treated with 1.5 ml. of benzoyl chloride. The white, crystalline precipitate of benzanilide weighed 1.77 g. (97.5%), m.p. 162–163° (reported¹⁸ m.p. 163°); a small second crop was obtained from the filtrate.

In methanol solution very little reduction was obtained. It appears from the present results and the reported failure of reduction in aqueous dioxane¹⁹ that reduction is too slow to compete effectively with protolytic destruction of borohydride unless the proton-donating power of the solvent is kept low.

Reduction of 1-Bromo-2-azidonaphthalene.—1-Bromo-2-azidonaphthalene (1.24 g., 0.005 mole) and phenol (1.0 g.) were placed in 15 ml. of benzene. To this mixture

was added 15 ml. of hydrobromic acid (48% aqueous solution) and the mixture was refluxed for 3 hours. The mixture was cooled and the precipitated solid filtered off. The benzene layer was separated from the aqueous layer and discarded. The solid was suspended in the aqueous layer and the mixture made basic with sodium hydroxide. The resulting solid was filtered off and recrystallized from 80% ethanol. The first crop was found to be the original azide, m.p. 106–109°. Addition of water to the filtrate precipitated crude 1-bromo-2-naphthylamine, m.p. 58–59°, reported²⁰ m.p. 63–64°. Acetylation with acetic anhydride in acetic acid gave 1-bromo-2-acetamidonaphthalene, m.p. 139–140°, reported²¹ m.p. 140°.

Repetition of the above procedure using ethanol in place of benzene to give a homogeneous solution resulted only in the formation of 2-naphthylamine. Attempts to use stannous chloride in aqueous ethanol gave the same result, in agreement with the reported²² loss of the bromo group from 1-bromo-2-naphthylamine by reduction.

Ultraviolet Spectra of Azidoanilines and Azidoaniline Hydrochlorides.—The ultraviolet spectra of *o*-, *m*- and *p*-azidoanilines were determined in isoöctane and methanol. The ultraviolet spectra of *o*-, *m*- and *p*-azidoaniline hydrochlorides were determined in methanol which was approximately 0.1 *N* in hydrogen chloride. A Cary recording spectrophotometer, model 11, was used.

Aminophthalimides.—The preparation of the three aminophthalimides has been described by Meyer and Maier²³ by the reduction of the nitrophthalimides by iron and acetic acid. However, owing to the sensitivity of the reactions to changes in the amounts of acetic acid, iron and water, their directions are inadequate for reliable repetition. Our experience has led to the following method as being optimum for the reduction of *p*-nitrophenylphthalimide.

To a solution of 13.4 g. (0.05 mole) of *p*-nitrophenylphthalimide in 2 l. of boiling acetone was added 200 ml. of water, 200 ml. of acetic acid and 34 g. (0.6 mole) of powdered iron, and the mixture was stirred rapidly while being refluxed for 3 hours. The hot solution was filtered, and a saturated aqueous solution of sodium carbonate was added slowly until the acetic acid was neutralized. The upper layer that resulted was separated from the lower aqueous slurry of iron hydroxides and then diluted with 12 l. of water. Upon chilling for 2 hours in ice and filtering there was obtained 11.8 g. (99%) of *N*-(*p*-aminophenyl)-phthalimide, m.p. 248–249.5° (reported²³ m.p. 250°). By a precisely similar procedure, *m*-nitrophenylphthalimide gave an 87% yield of *N*-(*m*-aminophenyl)-phthalimide, m.p. 188–189° (reported²³ m.p. 188–189°).

In a procedure similar except for quantities, 23.8 g. (0.089 mole) of *o*-nitrophenylphthalimide in 1.5 l. of acetone with 150 ml. of acetic acid, 150 ml. of water and 58 g. (1.07 mole) of powdered iron, refluxed for 1 hour, gave a 90% yield of *N*-(*o*-aminophenyl)-phthalimide, m.p. 190–193° (reported²³ m.p. 184–186°).

***N*-(*o*-Azidophenyl)-phthalimide.**—To a suspension of 18.8 g. (0.079 mole) of *N*-(*o*-aminophenyl)-phthalimide in 1 l. of water was added 100 ml. of concd. hydrochloric acid all at once. The resulting slurry was chilled to 0–5° and diazotized by the addition of 6 g. of sodium nitrite in 25 ml. of water; after 3 hours of stirring nearly all solid had dissolved. The solution was filtered, a small amount of ether was added to reduce foaming, and a solution of 5.7 g. of sodium azide in 25 ml. of water was added dropwise. When gas evolution had ceased, the residual ether was evaporated in an air stream, the mixture was stirred for an hour, and the precipitated azide (19.6 g., 96%) was filtered off and washed with water. It melted with decomposition at 191°, both crude and after repeated recrystallization from benzene.

Anal. Calcd. for C₁₄H₈N₄O₂: C, 63.63; H, 3.05. Found: C, 63.57; H, 3.13.

***N*-(*m*-Azidophenyl)-phthalimide.**—By an essentially similar procedure, 12.9 g. of *N*-(*m*-aminophenyl)-phthalimide was converted to 19.9 g. (82%) of *N*-(*m*-azidophenyl)-phthalimide, m.p. 145–146°. Repeated recrystallization

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from ethanol or benzene gave a product that softened at 133° and melted at 142–144°. When the melt was allowed to solidify, the new m.p. was 146–147°. These interconversions were reproducible.

Anal. Calcd. for $C_{14}H_8N_4O_2$: C, 63.63; H, 3.05. Found: C, 63.59; H, 3.26.

N-(*p*-Azidophenyl)-phthalimide.—Owing to the insolubility of the salts of N-(*p*-aminophenyl)-phthalimide with common acids, resort was made to isethionic acid (2-hydroxyethanesulfonic acid) in the diazotization procedure. A solution of this acid was prepared from 51 g. of commercial sodium isethionate, which was first freed from sulfate by filtering its hot solution in 400 ml. of 95% ethanol and 50 ml. of water through a layer of Celite. The addition of 700 ml. of absolute ethanol to the ice-cooled filtrate precipitated 44 g. of product which did not give a precipitate with barium chloride. A water solution of the sulfate-free salt was then passed through a column containing 150 g. of 20–30 mesh Dowex ion-exchange resin in the acid form. The effluent solution, approximately 0.29 *N*, was used directly in the diazotization.

To a slurry prepared from 16.9 g. (0.0712 mole) of finely powdered N-(*p*-aminophenyl)-phthalimide and 500 ml. of water was added 365 ml. of 0.29 *N* isethionic acid; much of the salt formed precipitated. After 15 minutes of stirring, the mixture was cooled to 0–5° and diazotized by the addition of 5.4 g. of sodium nitrite in water. After 5 hours of stirring at 0–5° the salt had dissolved, leaving only a small amount of a finely divided solid. The filtered solution was treated with a solution of 5.1 g. of sodium azide, in the presence of a little ether to reduce foaming. When gas evolution ceased, the ether was evaporated in an air stream, and after a further 20 minutes the precipitated azide was collected and washed with water; wt. 17.0 g. (90%), m.p. 187° dec. An analytical sample recrystallized from benzene had m.p. 190° dec.

Anal. Calcd. for $C_{14}H_8N_4O_2$: C, 63.63; H, 3.05. Found: C, 63.61; H, 3.11.

***o*-Azidoaniline.**—A slurry of 19.6 g. (0.0742 mole) of powdered N-(*o*-azidophenyl)-phthalimide in 200 ml. of 95% ethanol was stirred with 3.72 g. (0.0742 mole) of hydrazine hydrate for 90 minutes, whereupon 100 ml. of water followed by 30 ml. of 20% sodium hydroxide solution was added. Most of the solid dissolved in a few minutes; filtration gave 0.35 g. of unreacted starting material. Dilution of the filtrate with 2 l. of water and chilling in ice precipitated 4.4 g. of *o*-azidoaniline, m.p. 61–63°. The mother liquors yielded a further 1.3 g., m.p. 56–69°, by extraction

with ether; total yield 57%. Several recrystallizations from aqueous methanol gave an analytical sample, m.p. 63–63.5°. *o*-Azidoaniline decomposes to an intensely red substance at about 65°; consequently, all operations in its preparation and purification must be carried out at mild temperatures.

Anal. Calcd. for $C_6H_5N_3$: C, 53.72; H, 4.51. Found: C, 53.79; H, 4.58.

***m*- and *p*-azidoanilines** were prepared from the corresponding azidophenylphthalimides by procedures essentially similar to that described for the *o*-isomer. *p*-Azidoaniline was obtained in 46% yield and had m.p. 65–66° (reported²⁴ m.p. 65°); it turns dark red at its melting point. *m*-Azidoaniline was obtained as an oil from its ether solution in 47% yield, b.p. 76° (0.6 mm.), 70° (0.4 mm.), n_D^{25} 1.6251. Its preparation has been reported,²⁵ but neither properties nor analysis were given.

Anal. Calcd. for $C_6H_5N_3$: C, 53.72; H, 4.51. Found: C, 53.79; H, 4.56.

Azidobenzoic Acids.—*o*-, *m*- and *p*-azidobenzoic acid were prepared from the corresponding aminobenzoic acids by diazotization and coupling to sodium azide²⁶; the samples used were purified by repeated recrystallization from aqueous ethanol.

Ionization Constants of Azidoanilines and Azidobenzoic Acids.—Samples of approximately 0.0015 mole of the benzoic acids were accurately weighed, dissolved in a mixture of 100 ml. of methanol and 100 ml. of water, and titrated with 0.03721 *N* aqueous sodium hydroxide, using a Beckman model G pH meter. The apparent ionization constants were determined from the pH at the half-neutralization points, at which the solvent composition was 45.4 ± 0.2% methanol by volume, taking $pK_w = 14.00$. Three determinations were made for each acid, and the average for each is reported in Table I; the average deviations of pK_a were 0.03 or less. The neutralization equivalents were from 163.3 to 164.3 (calcd. 164.1).

Samples of approximately 0.0017 mole of the anilines were treated similarly, using 0.04429 *N* hydrochloric acid for titration. The solvent composition at the half neutralization point was 45.4 ± 0.4%, and the average deviation of pK_b among determinations was 0.02 or less. The average value for each compound is given in Table II.

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A Crystalline Hexamer from Acrylonitrile

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In the presence of several alcohols, triphenylphosphine has been found to catalyze the conversion of acrylonitrile to a crystalline hexamer, m.p. 240°, which has been shown to be identical with the cyanoethylation product of 1,4-dicyano-*trans*-2-butene and is assigned the structure of 1,1,4,4-tetra-(2-cyanoethyl)-1,4-dicyano-*trans*-2-butene (I). The corresponding acid and methyl and ethyl esters have been prepared and characterized.

In view of the stereoregular polymerization of vinylic compounds containing electron-donating groups by a wide variety of Lewis acids, the corresponding possibility of stereoregular coordination polymerization of vinylic compounds containing electron-withdrawing groups by hindered Lewis bases seemed worthy of investigation. While this objective has not been achieved in experiments described herein, we have obtained a new crystalline hexamer of acrylonitrile.

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Experimental²

1,1,4,4-Tetracyanoethyl-1,4-dicyano-*trans*-2-butene (I).
A. From Acrylonitrile Polymerization.—A mixture of 16 g. of acrylonitrile, 0.4 g. of triphenylphosphine and 5 ml. of ethanol was sealed under nitrogen and heated in the dark at 80° for 2–4 weeks. The resulting mixture of crystals and viscous brown oil was extracted with acetone. The insoluble crystals were recrystallized from dimethylformamide (DMF)-ethanol (or acetonitrile); 4.5 g. (28%), m.p. 240°.

Anal. Calcd. for $C_8H_8N_4$: C, 67.90; H, 5.69; N, 26.40. Found: C, 68.04; H, 6.17; N, 26.36.

(2) Analyses by Midwest Microlab, Inc., Indianapolis, Ind., and Galbraith Laboratories, Knoxville, Tenn. All m.p.'s are uncorrected.