

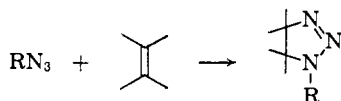
The Addition of Aryl Azides to Norbornene. A Kinetic Investigation

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The addition of a series of *meta*- and *para*-substituted aryl azides to norbornene has been kinetically investigated. The reaction is insensitive to solvent polarity and is characterized by a large negative entropy of activation. A sizable substituent effect ($\rho = +0.84$) has been observed. These results are discussed in terms of a concerted mechanism involving a charge imbalance in the transition state.

The reaction of organic azides and olefinic bonds, leading to the formation of 1,2,3- Δ^2 -triazolines, was first reported by Wolff in 1912.² Subsequently, the



work of several investigators demonstrated the generality and limitations of the addition.³⁻⁵ In particular, Alder and Stein's extensive study delineated the scope and provided information regarding the stereochemical course of the reaction.⁶ More recently the azide-olefin addition has received considerable attention from a number of investigators.⁷ This interest stems, in part, from the potential use of the reaction, *via* decomposition of the triazoline adducts, as a route to substituted aziridines.⁸

A variety of organic azides (aryl, alkyl, acyl, and sulfonyl) have been employed. Although the conditions necessary for the addition process have in some instances⁹ caused destruction of the initially formed adduct, it has generally been possible to isolate the triazoline product. Alder first pointed out the exceptional susceptibility to azide addition of strained double bonds in bicyclic compounds.⁶ Since then the reaction has been used as a diagnostic test for such strained bonds, and the crystalline triazolines have served as analytical derivatives.

(1) To whom inquiries should be directed: Socony Mobil Oil Co., Princeton, N. J.

(2) L. Wolff, *Ann.*, **394**, 23, 59, 68 (1912).

(3) F. D. Chattaway and G. D. Parkes, *J. Chem. Soc.*, 127, 1307 (1925); 113 (1926).

(4) L. Fieser and J. L. Hartwell, *J. Am. Chem. Soc.*, **57**, 1479 (1935).

(5) L. Wolff, *Ann.*, **399**, 274 (1913).

(6) K. Alder and G. Stein, *ibid.*, **485**, 211 (1931); **501**, 1 (1933).

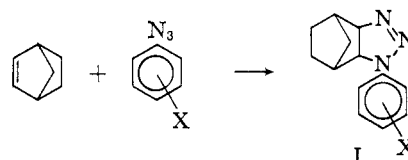
(7) (a) G. D. Buckley, *J. Chem. Soc.*, 1850 (1954); (b) S. J. Davis and C. S. Rondestvedt, *Chem. Ind. (London)*, 845 (1956); (c) A. Mustafa, S. M. A. D. Zayed, and S. Khattab, *J. Am. Chem. Soc.*, **78**, 145 (1956); (d) S. M. Gurvich and A. P. Terent'ev, *Sb. Statei Obsch. Khim. Akad. Nauk SSSR*, **1**, 401 (1953); (e) E. A. Chandross and G. Smolinsky, *Tetrahedron Letters*, No. 13, 19 (1960); (f) L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, **28**, 3309 (1963).

(8) (a) P. K. Kadaba and J. O. Edwards, *ibid.*, **26**, 2331 (1961); (b) P. Scheiner and W. R. Vaughan, *ibid.*, **26**, 1923 (1961); (c) P. Scheiner, *ibid.*, **30**, 7 (1965).

(9) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962); (b) T. Curtius and W. Dorr, *J. prakt. Chem.*, **125**, 425 (1930); (c) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963).

Apart from angular strain, however, the factors activating the olefinic component for addition have not been systematically examined.¹⁰ Recent reports indicate that the olefinic bond of cyclic enamines is particularly reactive,¹¹⁻¹³ and the generally activating influence of conjugated groups has been suggested¹⁴ but not experimentally established. Substituent effects in the azide component have not been reported.

The azide-olefin reaction falls within the reaction type termed "1,3-dipolar addition" by Huisgen and his associates.¹⁵ These additions, resulting in the formation of five-membered rings, appear to be mechanistically related to the Diels-Alder reaction; both may be considered multicenter cycloaddition processes. In common with the Diels-Alder reaction, ambiguity exists in our knowledge of the mechanism of 1,3-dipolar additions. Although a highly ordered, cyclic transition state (concerted addition) has been proposed,¹⁵ the extent of simultaneity of bond formation and the charge distribution in the transition state remain unknown. To provide data relevant to these questions, and to determine the electronic factors that activate azides for 1,3-dipolar addition, we have undertaken a kinetic investigation of the addition of *meta*- and *para*-substituted phenyl azides to norbornene.



Experimental

Materials. Aryl Azides. All of the azides used in this work have been previously reported. They were prepared from the corresponding anilines, *via* the reaction of the diazonium salts with sodium azide.¹⁶ Prior to kinetic measurements the azides were redistilled (reduced pressure) through a short Vigreux column. Purification of *p*-nitro-, *m*-nitro-, *p*-bromo-, and *p*-methoxyphenyl azides was accomplished by recrystallization from a suitable solvent. The azides were found to be indefinitely stable when stored in dark brown bottles at -20° .

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

(11) M. E. Munk and Y. K. Kim, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963, p. 29Q.

(12) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Ber.*, **96**, 802 (1963).

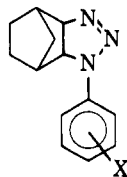
(13) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Gazz. chim. ital.*, **91**, 849, 933 (1961); **92**, 1040 (1962).

(14) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).

(15) R. Huisgen, *Proc. Chem. Soc.*, 357 (1961).

(16) P. A. S. Smith and J. H. Boyer, *Org. Syn.*, **31**, 14 (1951).

Table I. Substituted Triazoline Adducts



X	Yield, %	M.p., ^a °C.	Recrystn. solvent ^b	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
H	64	101–102 ^c	A	C ₁₃ H ₁₅ N ₃
<i>p</i> -CH ₃	69	79–80	A	C ₁₄ H ₁₇ N ₃	73.97	74.01	7.54	7.40	18.49	18.46
<i>m</i> -CH ₃	66	89–90	A	C ₁₄ H ₁₇ N ₃	73.97	73.96	7.54	7.48	18.49	18.73
<i>p</i> -CH ₃ O	58	90–91	A	C ₁₄ H ₁₇ N ₃ O	69.11	69.15	7.04	7.04	17.28	17.25
<i>m</i> -CH ₃ O	51	48–49	D	C ₁₄ H ₁₇ N ₃ O	69.11	69.35	7.04	7.28	17.28	17.50
<i>p</i> -Br	88	123–124	B	C ₁₃ H ₁₄ BrN ₃	53.43	53.39	4.83	4.92	14.38	14.32
<i>m</i> -Br	93	98–99	A	C ₁₃ H ₁₄ BrN ₃	53.43	53.32	4.83	4.72	14.38	14.41
<i>p</i> -NO ₂	92	164–165	C	C ₁₃ H ₁₄ N ₄ O ₂	60.45	60.60	5.46	5.32	21.69	21.40
<i>m</i> -NO ₂	83	101–102	C	C ₁₃ H ₁₄ N ₄ O ₂	60.45	60.60	5.46	5.47	21.69	21.68

^a Fisher-Johns block, uncorrected. ^b Solvents: A, *n*-hexane; B, *n*-heptane; C, methanol; D, pentane–diethyl ether (1:1). ^c Lit.¹⁷ 101–102°.

Norbornene was used as supplied (Aldrich) without further purification.

Norbornene–Aryl Azide Adducts. 3-Phenyl-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene (I, X = H) was prepared as previously described,¹⁷ m.p. 101–102° from *n*-hexane.

Except as noted below, the new adducts were prepared by treating 0.15-mole portions of norbornene and aryl azide in 125 ml. of refluxing petroleum ether (60–90°) for 3–4 hr. After cooling in the refrigerator, the well formed crystals were collected by filtration. No attempt was made to collect second crops from the filtrates. Yields, melting points, recrystallization solvents, and analytical data are presented in Table I.

The reaction solvent for the preparation of the *p*-nitro adduct consisted of 100 ml. of ethyl acetate and 100 ml. of petroleum ether (b.p. 60–90°). In this case heating was terminated after 20 min.; much solid product had separated. Solvent consisting of 50 ml. of ethyl acetate and 75 ml. of petroleum ether was used in the preparation of the *m*-nitro adduct.

The ethyl acetate solvent for the kinetic runs was reagent grade, redistilled through a 1.5-m. column packed with glass helices, b.p. 76.5–77.0°. The acetonitrile and cyclohexane solvents were similarly distilled before use.

Ultraviolet Absorption Measurements. A Cary Model 15 spectrophotometer was used. Solutions were measured in a 1.00-cm. quartz cell (3-ml. capacity) fitted with a ground-glass stopper. The spectrophotometer cell compartment was thermostated by means of a circulating water jacket.

Temperature Measurement and Control. Within the cell compartment temperature measurements were made with a calibrated thermistor.¹⁸ Observations of the closed compartment over prolonged periods showed that temperature variation was less than ±0.04° at the temperatures employed: 20.40, 25.10, and 35.87°.

Kinetic Method. The ultraviolet spectra of the azides and triazoline adducts in ethyl acetate solutions were de-

termined, and suitable wave lengths were chosen for following the reaction. The wave length used in each case was determined on the basis of the following criteria: (1) minimum slope in the adduct spectrum and (2) maximum difference in the magnitude of the extinction coefficients of the adduct and the corresponding azide. These criteria serve to enhance the reliability of the kinetic data (see eq. 1).

The extinction coefficients of the azide, triazoline, and norbornene were then evaluated at the appropriate wave lengths. These values were accurately determined at 20, 25, and 35°.

The concentration of product (triazoline adduct, [P]) may be related to the observed absorbance (A_{obsd}) by eq. 1, where A, N, and P refer to azide, norbornene, and product, respectively. A_{blank} is the absorbance of the pure solvent.

$$[P] = \frac{A_{\text{obsd}} - A_{\text{blank}} - \epsilon_{\text{N}}[N]_0 - \epsilon_{\text{A}}[A]_0}{\epsilon_{\text{P}} - \epsilon_{\text{A}}} \quad (1)$$

Determination of Rates of Addition. Samples of norbornene and the aryl azides were accurately weighed into volumetric flasks, and the solutions were made up with ethyl acetate; norbornene solutions were in the range 0.24–0.47 *M*, azides, 0.001–0.024 *M*. The azide solutions were prepared immediately before use. One-half hour before each run, the reactant solutions were placed in a water bath thermostated at the reaction temperature. At time zero, a 2.00-ml. portion of the azide solution was pipetted into 10.00 ml. of norbornene solution, and time measurement was begun. Mixing was carried out in a flask maintained at the reaction temperature. A portion of the reaction mixture was transferred to the quartz cell, placed in the thermostated cell compartment, and the absorbance was measured at appropriate time intervals. The reactions were followed to less than 3% completion. A typical run lasted 80 min. and involved an observed absorbance change of 0.5 absorbance unit.

Rate constants were determined by the method of initial rates.¹⁹ Plots of concentration of product (tri-

(17) G. Komppa and S. Beckman, *Ann.*, **512**, 172 (1934).

(18) H. C. Wolfe, "Temperature, Its Measurement and Control," Reinhold Publishing Corp., New York, N. Y., 1955, p. 307.

(19) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 45.

azole) vs. time were constructed; the specific rate constants were calculated directly from the slope and the initial reactant concentrations. The concentration vs. time plots were linear to 3% reaction, based on initial azide concentration. Rate constants presented in Table III are average values of two or more determinations, using different initial norbornene and azide concentrations for each run. The average deviations show the method to be satisfactorily precise.

As a check on the accuracy of the initial rate method, the rate constant for phenyl azide-norbornene addition (25°) was also determined by the pseudo-first-order technique. Using a large initial norbornene concentration (2.827 *M*) and a low initial phenyl azide concentration (1.996×10^{-4} *M*), the reaction was followed at 320 *mμ* to more than 85% completion. A plot of $-\log [\text{PhN}_3]$ vs. time was linear, and allowed calculation of a pseudo-first-order rate constant from the slope. Evaluation of the actual rate constant from the norbornene concentration and the pseudo-constant gave a value 1.03×10^{-3} l. mole⁻¹ min.⁻¹. The values obtained by the initial rate method (1.02×10^{-3} and 1.04×10^{-3} l. mole⁻¹ min.⁻¹) are in excellent agreement with the pseudo-first-order value.

Preliminary studies established the first-order kinetic dependence with respect to norbornene and phenyl azide at 25.10°. Using eq. 2,¹⁹ where dx/dt refers to the slope of the product concentration vs. time plot and [B] refers to the initial concentration B for two runs (subscripts 1 and 2) in which the other reactant is at a constant initial concentration, the rate expression exponent *n* may be evaluated. Subsequent variation of

$$n_B = \frac{\log (dx/dt)_1 - \log (dx/dt)_2}{\log [B]_1 - \log [B]_2} \quad (2)$$

the initial concentrations of the other component while $[B]_{\text{initial}}$ is constant permits calculation of the second exponent. Applying this method to the norbornene-phenyl azide system, the expected kinetic dependence was found. Table II presents the pertinent data. First-order dependence on reactants was then assumed for the addition of the other aryl azides to norbornene.

Table II. Kinetic Order Determination of Norbornene + Phenyl Azide in Ethyl Acetate at 25.10°

Run	[PhN ₃] ₀ , <i>M</i> × 10 ³	[NB] ₀ , <i>M</i> ^a	dx/dt , mole l. ⁻¹ min. ^{-1b}	<i>n</i> ^c
1	3.14	0.328	1.07×10^{-6}	1.01
2	3.14	0.164	5.33×10^{-7}	
3	1.54	0.314	0.497×10^{-6}	1.00
4	3.08	0.314	0.997×10^{-6}	

^a Initial norbornene concentration. ^b Slope of concentration of product vs. time plot (3% reaction). ^c Rate expression exponent calculated from eq. 2.

Calculations. The Hammett ρ -values were calculated from least-squares plots of $\log k_x/k_0$ vs. σ^0 , according to the procedure of Taft.²⁰⁻²² Because of possible direct resonance interaction between the *p*-NO₂ substituent and the reaction center, the data for this substituent were omitted from the ρ -calculation. The cor-

(20) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).
(21) R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959).

(22) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

relation coefficients (*r*) were calculated in the usual manner.²³ Enthalpies of activation were determined graphically from $\log k$ vs. $1/T$, and the entropies of activation were calculated from the Eyring equation for the temperature of 25.10°.

Results

The strongly chromophoric properties of the triazole adducts in the 390–310-*mμ* region suggested the applicability of a spectrophotometric technique for following the reaction. Previous work²⁴ had shown that substituted phenyl azides absorb only moderately in this spectral region. It therefore appeared quite practicable to observe accurately the increase in the product concentration during the early stages of reaction (<3%), and thus to evaluate directly the initial rate ($d[\text{product}]/dt$) from the slope of the essentially linear $[\text{product}]$ vs. time plot. The specific rate constant was then calculated from the initial reactant concentrations and the initial rate. In practice, this "approximate" method gave reproducible results, in ac-

$$k = \frac{d[\text{product}]/dt}{[\text{azide}]_0[\text{norbornene}]_0}$$

cord with a rate constant determined from an integrated expression (see Experimental).

The spectrophotometric method requires an accurate knowledge of the molar extinction coefficients of the aryl azides and the triazole products. Although the ϵ -values for the azides were found to be invariant (within experimental error) over the temperature range of this investigation, the triazole absorptions exhibited a marked temperature dependence. In several instances changes in ϵ amounting to *ca.* 15% were observed between 20 and 35°. The extinction coefficients and wave lengths used in this study are presented in Table III.

Preliminary studies with phenyl azide established the first-order kinetic dependence on azide and norbornene. Subsequently, this relationship was assumed to hold throughout the work. The essential irreversibility of the addition reaction was demonstrated during the determination of the triazole extinction coefficients. Solutions of the triazole adducts were stable over prolonged periods (2–3 days), when protected from the light. (1,2,3-Triazolines are known to undergo facile photodecomposition.^{8c}) Thus adduct dissociation does not appear to be kinetically significant under the conditions of this investigation. No indication of alternative reaction paths was detected; it has therefore been assumed that the aryl azides add to norbornene to give exclusively the stable triazole adducts.

Kinetic results for runs at three temperatures are given in Table IV. The clear facilitation of the reaction by electron-withdrawing substituents is graphically illustrated in the Hammett plots at 20, 25, and 35° (Figures 1, 2, and 3). Presented in Table V are the ρ -values for these plots.

A somewhat better correlation of the data was obtained with Taft's σ^0 -values²² than with the ordinary σ -values.²⁵ The difference, however, was not great; ordinary σ -values at 25°: $\rho = +0.85$, $r = 0.98$.

(23) W. L. Gore, "Statistical Methods for Chemical Experimentation," Interscience Publishers, Inc., New York, N. Y., 1952, Chapter 6.

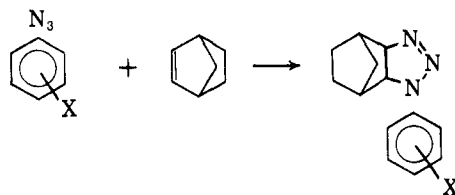
(24) P. A. S. Smith, J. H. Hall, and R. O. Kan, *J. Am. Chem. Soc.*, **84**, 485 (1962).

(25) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

Table III. Molar Extinction Coefficients for Substituted Aryl Azides and Triazolines in Ethyl Acetate Solvent

Temp., °C.	Substituent	Wave length, mμ		
		$\epsilon_{(\text{triazoline})}$	$\epsilon_{(\text{azide})}$	
20.40	H	320	6990	74.2
	<i>p</i> -CH ₃	315	8540	97.6
	<i>m</i> -CH ₃	310	9100	90.1
	<i>p</i> -CH ₃ O	325	6860	117
	<i>m</i> -CH ₃ O	320	7850	87.7
	<i>p</i> -Br	320	9750	113
	<i>m</i> -Br	315	8950	94.8
	<i>p</i> -NO ₂	390	6440	100
	<i>m</i> -NO ₂	390	1000	31.9
	25.10	H	320	6800
<i>p</i> -CH ₃		315	8380	97.6
<i>m</i> -CH ₃		310	9040	90.1
<i>p</i> -CH ₃ O		325	6860	117
<i>m</i> -CH ₃ O		320	7620	87.7
<i>p</i> -Br		320	9630	113
<i>m</i> -Br		315	8770	94.8
<i>p</i> -NO ₂		390	6020	100
<i>m</i> -NO ₂		390	945	31.9
35.87		H	320	6700
	<i>p</i> -CH ₃	315	8240	97.6
	<i>m</i> -CH ₃	310	8810	90.1
	<i>p</i> -CH ₃ O	325	6770	117
	<i>m</i> -CH ₃ O	320	7510	87.7
	<i>p</i> -Br	320	9330	113
	<i>m</i> -Br	315	8680	94.8
	<i>p</i> -NO ₂	390	5540	100
	<i>m</i> -NO ₂	390	891	31.9

Table IV. Rates of Addition in Ethyl Acetate for the Reaction



Temp., °C.	X	$k \times 10^3, \text{l. mole}^{-1} \text{min.}^{-1}$	k_x/k_0	σ^{0a}
20.40 ± 0.04	H	0.672 ± 0.002 ^b	1.00	0.00
	<i>p</i> -CH ₃	0.593 ± 0.009	0.882	-0.15
	<i>m</i> -CH ₃	0.589 ± 0.005	0.876	-0.07
	<i>p</i> -CH ₃ O	0.580 ± 0.004	0.863	-0.16
	<i>m</i> -CH ₃ O	0.715 ± 0.003	1.06	+0.06
	<i>p</i> -Br	1.29 ± 0.02	1.92	+0.26
	<i>m</i> -Br	1.48 ± 0.04	2.20	+0.38
	<i>p</i> -NO ₂	4.46 ± 0.09	6.64	+0.73
	<i>m</i> -NO ₂	2.54 ± 0.02	3.79	+0.70
	25.10 ± 0.04	H	1.03 ± 0.01	1.00
<i>p</i> -CH ₃		0.871 ± 0.018	0.846	-0.15
<i>m</i> -CH ₃		0.880 ± 0.010	0.854	-0.07
<i>p</i> -CH ₃ O		0.871 ± 0.002	0.846	-0.16
<i>m</i> -CH ₃ O		1.09 ± 0.01	1.06	+0.06
<i>p</i> -Br		1.92 ± 0.02	1.86	+0.26
<i>m</i> -Br		2.29 ± 0.02	2.22	+0.38
<i>p</i> -NO ₂		6.34 ± 0.16	6.16	+0.73
<i>m</i> -NO ₂		3.99 ± 0.09	3.87	+0.70
35.87 ± 0.04		H	2.26 ± 0.07	1.00
	<i>p</i> -CH ₃	2.04 ± 0.04	0.903	-0.15
	<i>m</i> -CH ₃	2.01 ± 0.02	0.889	-0.07
	<i>p</i> -CH ₃ O	1.92 ± 0.07	0.850	-0.16
	<i>m</i> -CH ₃ O	2.36 ± 0.01	1.04	+0.06
	<i>p</i> -Br	4.32 ± 0.12	1.91	+0.26
	<i>m</i> -Br	4.66 ± 0.16	2.06	+0.38
	<i>p</i> -NO ₂	12.4 ± 0.4	5.49	+0.73
	<i>m</i> -NO ₂	8.33 ± 0.06	3.69	+0.70

^a See ref. 22. ^b Average deviation.

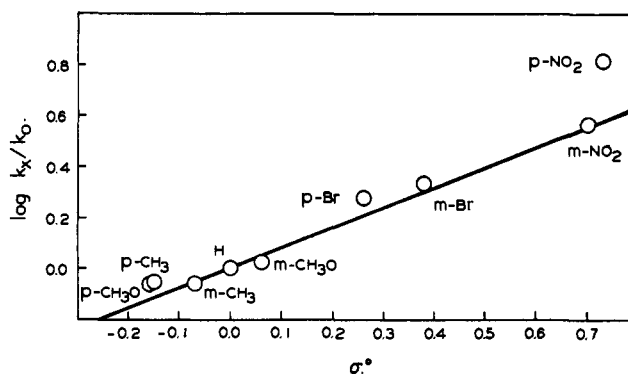


Figure 1. Correlation of $\log k_x/k_0$ and σ^0 for the addition of aryl azides to norbornene in ethyl acetate, 20.40°.

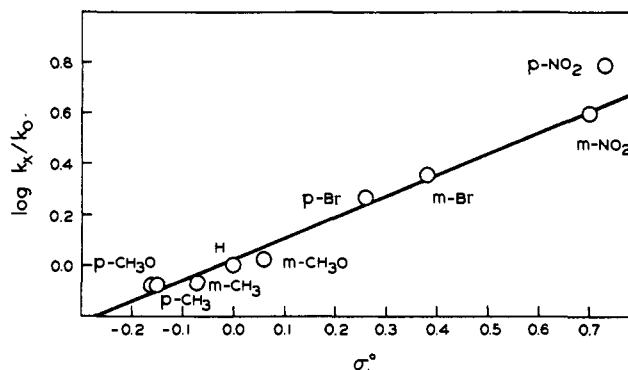


Figure 2. Correlation of $\log k_x/k_0$ and σ^0 for the addition of aryl azides to norbornene in ethyl acetate, 25.10°.

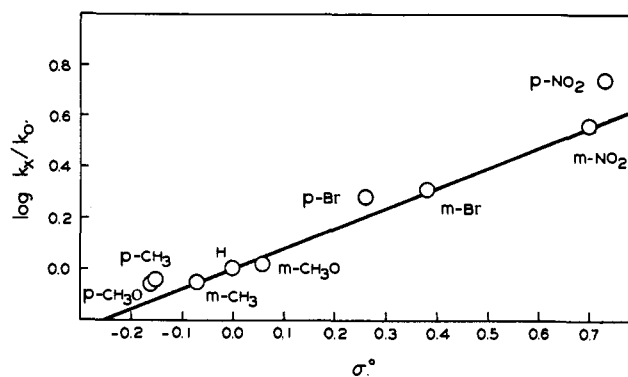


Figure 3. Correlation of $\log k_x/k_0$ and σ^0 for the addition of aryl azides to norbornene in ethyl acetate, 35.87°.

The σ^0 -value reflects polar effects transmitted (ultimately) to the reaction site by induction, and excludes polar effects resulting from direct resonance interaction of the substituent and the reaction center. Since

Table V. Hammett ρ -Values for the Addition of Aryl Azides to Norbornene in Ethyl Acetate Solvent

Temp., °C.	ρ^a	ρ^b
20.40	+0.79	0.99
25.10	+0.84	0.99
35.87	+0.77	0.99

^a Calculated according to the procedure recommended by Taft²⁰⁻²² using σ^0 -values for all substituents except *p*-NO₂. The *p*-NO₂ substituent was omitted from the ρ -calculation. ^b Correlation coefficient.

the magnitude of direct resonance interactions appears to be a function of the particular reaction under consideration, fixed σ -values for substituents capable of such interaction are not generally valid.²⁶ Therefore the *p*-NO₂ substituent (the only one capable of direct resonance interaction in the system under investigation) was excluded from the ρ -calculation. Indeed, the poor fit of the *p*-NO₂ substituent to the Hammett line suggests a significant resonance interaction for this group.

Activation parameters for the addition reaction are given in Table VI.

Table VI. Activation Parameters for the Addition of Substituted Aryl Azides to Norbornene in Ethyl Acetate Solvent

Substituent	ΔH^* , kcal./mole	ΔS^* , e.u. ^a
H	14.7 ± 0.9 ^b	-31.0 ± 3.1 ^b
<i>p</i> -CH ₃	15.0 ± 0.9	-30.4 ± 3.0
<i>m</i> -CH ₃	14.9 ± 0.9	-30.9 ± 3.1
<i>p</i> -CH ₃ O	14.5 ± 0.9	-31.9 ± 3.2
<i>m</i> -CH ₃ O	14.5 ± 0.9	-31.6 ± 3.2
<i>p</i> -Br	14.7 ± 0.9	-29.9 ± 3.0
<i>m</i> -Br	14.0 ± 0.9	-32.0 ± 3.2
<i>p</i> -NO ₂	12.5 ± 0.9	-34.9 ± 3.5
<i>m</i> -NO ₂	14.4 ± 0.9	-29.4 ± 2.9

^a Calculated for 25.10° from the Eyring equation. ^b Maximum error.

A ΔH^* vs. ΔS^* plot of the data in Table VI gave a scattering of points with a least-squares "slope" of 403°. However, the rather low correlation coefficient, $r = +0.85$, indicates that the system under study does not strictly obey the isokinetic relationship.²⁷ We therefore can attach no significance to the 403° value.

The effect of various solvents on the rate of phenyl azide addition to norbornene is given in Table VII.

Table VII. Rates of Addition of Phenyl Azide to Norbornene in Various Solvents at 25.10°

Solvent	Dielectric constant ^a	$k \times 10^3$, l. mole ⁻¹ min. ^{-1b}
Cyclohexane	2.0	1.59 ± 0.02 ^c
Ethyl acetate	6.0	1.03 ± 0.02
Acetonitrile	37.5	1.40 ± 0.02

^a A. A. Maryott and E. R. Smith, National Bureau of Standards Circular No. 514, U. S. Government Printing Office, Washington, D. C., 1951. ^b Determined by the initial rate method at 320 μ m; extinction coefficients for phenyl azide: 65.8 (cyclohexane), 71.5 (acetonitrile); extinction coefficients for adduct: 6140 (cyclohexane), 7270 (acetonitrile). ^c Average deviation.

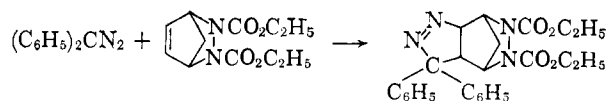
Discussion

The relative indifference to solvent polarity found in the present investigation (Table VII) parallels a similar insensitivity reported for the addition of diphenyldiazomethane to 2,3-dicarbethoxy-2,3-diazabicyclo[2.2.1]hept-5-ene.²⁸ This result is consistent with Huisgen's

(26) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959); R. O. C. Norman, G. K. Radda, D. A. Brimacombe, P. D. Ralph, and E. M. Smith, *J. Chem. Soc.*, 3247 (1961).

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

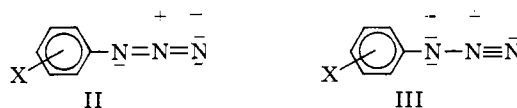
(28) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (1961).



view of 1,3-dipolar addition as a multicenter process in which both new bonds are simultaneously formed.^{14, 15, 28} Support for a one-step, concerted addition is also found in the activation entropies presented in Table VI. The relatively large negative values indicate a highly ordered transition state, as expected for a simultaneous multicenter process. It may be safely assumed here that the magnitude and sign of the ΔS^* values do not reflect large solvation changes, such as are encountered in the Menshutkin reaction.²⁹

Our results are not consistent with the two-step reaction path proposed by Awad and associates for the addition of aryl azides to N-arylmaleimides.³⁰ According to this scheme, nucleophilic attack by the azide moiety initially results in a zwitterionic intermediate; completion of addition is then accomplished in a second step. It should be pointed out, however, that this proposal is unsupported by kinetic data.

If, on the basis of the above-mentioned solvent and entropy data, one accepts a concerted multicenter addition process, then the sizable substituent effect ($\rho = +0.84$ at 25°) remains to be explained. Although the polar substituent effect may be viewed as affecting the energy content of either the azide reactant or the transition state (or both), interpretation of the results in terms of the former does not appear to be fruitful. Approximating the ground-state electronic distribution in the azide by the primary (all-octet) resonance contributors II and III, we find no persuasive reason for the facilitation of reaction by electron-withdrawing groups.



The same conclusion is reached when nonoctet structures are included in the analysis. On the other hand, a plausible explanation arises from consideration of the transition state.

The solvent and entropy of activation data point to a concerted mechanism; the substituent effect is most readily explicable in terms of the stabilization of negative charge in the transition state. An entirely analogous situation has been noted in the Diels-Alder reaction.^{31, 32} With regard to the Diels-Alder reaction, Woodward and Katz have suggested, in essence, that the formation of the two new bonds may proceed (through a single transition state) unevenly³³; a charge imbalance in the transition state must therefore result. This view, which preserves the integrity of a highly ordered transition state, is well suited to the present work. We believe that our results are in accord with a one-step addition process that involves a transition

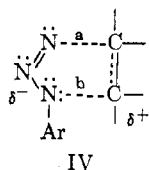
(29) N. J. T. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, 1353 (1936); H. G. Grimm, H. Ruf, and H. Wolff, *Z. physik. Chem. (Leipzig)*, **B13**, 301 (1931).

(30) W. I. Awad, S. M. A. R. Omran, and F. Nagieb, *Tetrahedron*, **19**, 1591 (1963).

(31) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 510 ff.

(32) G. Kresze, J. Firl, H. Zimmer, and V. Wollnik, *Tetrahedron*, **20**, 1605, (1964).

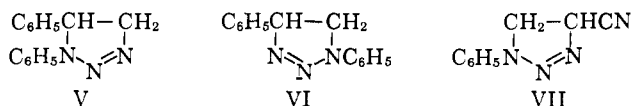
(33) R. B. Woodward and T. J. Katz, *ibid.*, **5**, 70 (1959).



state approximated by IV. In IV bond formation at a has progressed to a greater extent than at b; consequently, the development of partial charge is as indicated. Rate enhancement by electron-withdrawing substituents is then attributable to the stabilization of partial negative charge on the α -nitrogen in the transition state.

The unsatisfactory fit of the p -NO₂ substituent (using σ^0) in the Hammett plots (Figures 1-3) suggests the development of considerable negative charge. This substituent appears to stabilize the transition state in an "exceptional" manner, by a direct resonance interaction. To place the p -NO₂ substituent on the Hammett line (25°) would require a σ -value of +0.93, considerably larger than the σ^0 -value (+0.73) though less than the older $\sigma^-_{p\text{-NO}_2}$ (+1.27).²⁵

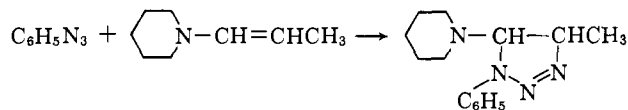
Our interpretation of the aryl azide-norbornene addition finds confirmation in orientational results obtained by others working with different systems. Thus Buckley has shown that phenyl azide adds stereospecifically to styrene to produce triazoline V, rather than VI.^{7a} In



terms of a transition state corresponding to IV, it is clear that the phenyl group (formerly of styrene) is favorably situated for the stabilization of partial positive charge only in the transition state leading to V.

Similarly, the structure of the phenyl azide-acrylonitrile adduct^{7d} VII is explicable when consideration is given to the inductive effect of the nitrile group. The partial positive charge developed in transition is better accommodated on the β - than the α -carbon.

Munk and Kim¹¹ and others^{12,13} have found that phenyl azide adds to enamines in a highly stereospecific manner. The specificity, in this case, presumably results from the conjugative stabilization imparted by the enamino nitrogen to the partial positive charge in the favored transition state.



In common with other 1,3-dipolar additions, it seems likely that the addition of aryl azides to olefins occurs via an essentially concerted process, involving a transition state in which charge is partially developed. Furthermore, from the available evidence it appears that (in transition) bond formation from the *terminal* azido nitrogen to the olefinic carbon is more complete than bond formation from the α -azido nitrogen to the other carbon. The consequent charge imbalance (as detected by substituent and orientational effects) suggests an initial electrophilic attack by the terminal nitrogen. However, the actual charge distribution in the transition state may well be quite sensitive to the structures of the particular azide-olefin pair undergoing reaction. In view of the relatively few systems studied, a thorough generalization regarding the azide-olefin reaction is not justified at this time.

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The Stereochemistry of Free-Radical Addition to Dienes. The Addition and Cooxidation of Thiols with Piperylene¹

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The stereochemical course of the addition and cooxidation reactions of thiols with cis- and trans-1,3-pentadiene (piperylene) was examined. Aromatic thiol gave 1,2-adducts with better than 90% retention of configuration while the formation of 1,2-adducts from aliphatic thiols showed a relatively low degree of retention of configuration. The reaction of thiols with cis- and trans-piperylene in the presence of oxygen (cooxidation) led to the formation of allylic alcohols. The 1,2-adduct alcohols were formed with complete retention of geometry. The 1,4-addition and cooxidation products were almost

entirely trans. The geometry of 1,2-reaction products was used to measure the degree of retention of configuration of the allylic radical intermediates. In those instances where the allylic radicals retained their configuration, the geometry of the 1,4-reaction product obtained was related to the conformation of the reacting diene.

Introduction

The abstraction of a hydrogen atom from the allylic position of olefins results in the formation of allylic free radicals. The allylic free radicals produced in this fashion, during the *t*-butyl hypochlorite chlorination of olefins, were capable to maintaining their stereochemi-

(1) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

(2) Esso Research Center, Linden, N. J.