J = 7.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.6, 30.0, 45.5, 59.7.

***N*,*N*-Dimethyl-*N*-(3-hydroxypropyl)amine (9)** was prepared from *N*,*N*-dimethyl-*N*-(3-chloropropyl)amine by alkaline hydrolysis. It was purified at 120 °C by gas chromatography, flow rate 25 mL/min He, detector 180 °C, injector 180 °C, and collector 190 °C: ^{1}H[22] NMR ($CDCl_3$) δ 1.69 (m, 2 H), 2.26 (s, 6 H), 2.54 (t, J = 6 Hz, 2 H), 3.81 (t, J = 5 Hz, 2 H), 5.46 (b s, 1 H).

Rate Constant Determinations. The kinetic apparatus consisted of (a) a Spectra-Physics DCR11 Nd:YAG pulsed laser with second and third harmonic (532 and 355 nm) capability which delivers 10-ns pulses at rates up to 10 pps, (b) a germanium (Judson 2 or 5 mm ϕ) diode detector/customized preamplifier, (c) various optics, the most important of which is a 10-nm narrow band pass nonfluoresceing filter centered at 1.27 μm placed just ahead of the detector, (d) a 100-MHz LeCroy transient digitizer/signal averager interfaced to a 80386 based PC/AT computer, and (e) an energy meter. Since the experimental decay is a convolution of the detector response (fwhm of approximately 10 μs for the 5 mm ϕ-detector; 5 μs for the 2 mm ϕ-detector) and the sample decay, it was necessary to implement a numerical deconvolutional analysis in order to accurately extract measured lifetimes 2 μs $\le \tau \le$ 100 μs from the recorded data. With this treatment lifetimes as low as 2 μs for certain nondeuterated solvent–sensitizer–amine combinations were available. The numerical deconvolution analysis of Demas[23] for exponential decays also corrects artifacts caused by scattered excitation light that may reach the detector was used. This analysis was implemented on our laboratory computer by using a general scientific/engineering analysis/data acquisition program called ASYST. Signal averaging 100 experiments, each with laser pump energies $\le$5 mJ gave 8192-point decay curves each of which produced pseudo-first-order rate constants with correlation coefficients (square root) better than 0.99.

Sample preparation was conducted by adding varying amounts of a stock solution of the amine to a stock solution of oxygen saturated sensitizer. This method insured the same sensitizer concentration in each experiment. At least five pseudo-first-order rate constants were collected for each amine. This experiment was repeated at least twice with fresh stock solutions for every amine–sensitizer–solvent combination.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation, Grants CHE-8722088 and RII-8610680. We also thank Professor Peter Ogilby (University of New Mexico) for his helpful advice on the construction of our germanium preamplifier/detector.

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Solvent and Aryl-Substituent Effects on the Rates of Thermal Decomposition of α-Azidostyrenes

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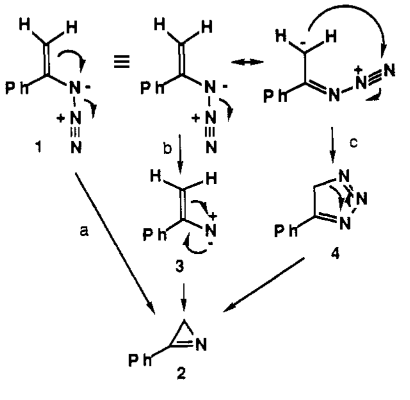
The effect on the rates of first-order thermolysis of α-azidostyrenes by aryl substitution have been measured in benzyl alcohol and 1-butanol in the temperature range 60–100 °C. Values for ΔH^{*} are in the range 24–28 kcal/mol, and for ΔS^{*}, +1 to −9 eu. The rate constants of the meta and para substituents are correlated with σ^{+} substituent constants where $\rho = -0.7$ (r = 0.98) in both solvents. Relative to α-azidostyrene, 2-methyl-α-azidostyrene and 2,4,6-trimethyl-α-azidostyrene experience retardation of thermolysis by factors of 0.97 and 0.58, respectively, in 1-butanol at 80 °C. The activation parameters, ρ value, σ^{+} rate correlation, and the steric retardation support a concerted mechanism where, in the transition state, positive charge is delocalized to the aryl ring, coplanarity of the developing azirine ring and the aryl ring being required. Thermolysis rates of α-azidostyrene at 80.2 °C are little affected by changes in solvent polarity, but are markedly accelerated in methyl acrylate, in which ΔH^{*} = 20 kcal/mol and ΔS^{*} = −17 eu, supporting a hypothesis by others that this reaction does not produce a nitrene intermediate, as was first suggested, but is likely a 1,3-dipolar cycloaddition mechanism of the azide function of α-azidostyrene with methyl acrylate to give a triazoline, which rapidly loses nitrogen.

Mechanistic studies have sought to determine whether thermal decomposition of α-azidostyrene (1) proceeds via concerted migration of a hydrocarbon group with dinitrogen loss (Scheme I, path a), involves the intermediacy of a nitrene species (path b), followed by ring closure to an azirine or other nitrene reactions, or involves the possibility (path c) that an intramolecular [3 + 2] cycloaddition yields an unstable isotriazole which extrudes dinitrogen to provide azirine as product, mechanistic pathways proposed by Smolinsky.[1] Arguments for one or the other paths have been reviewed.[2]

Azirine **2** is clearly established as the major thermolysis product of **1**. It has been isolated as the gas phase pyrolysis product of **1**,[1a] it is the major product of thermolysis in various hydrocarbons, acetonitrile, and dimethyl sulfoxide,[3] and it is formed in high yield, as are various other para-

Scheme I



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[1] (a) Smolinsky, G. *J. Am. Chem. Soc.* **1961**, *83*, 4483. (b) Smolinsky, G. *J. Org. Chem.* **1962**, *27*, 3557.

[2] (a) Hassner, A. In *Azides and Nitrenes, Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984, Chapter 2. (b) L'abbe, G. *Angew. Chem., Int. Ed. Eng.* **1975**, *14*, 775.

[3] Woerner, F. P.; Reimlinger, H. *Chem. Ber.* **1970**, *103*, 1908.

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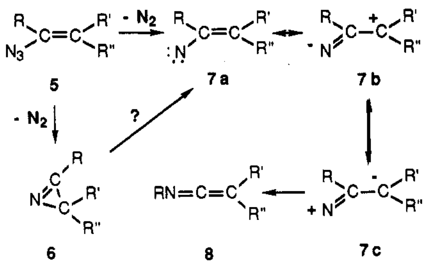
Scheme II



substituted styryl azirines by thermolysis of the azides in refluxing toluene.[4,5] Boyer et al.[6] reported that 2, 3,6-diphenylpyridazine, and 2,5-diphenylpyrrole were formed from thermal decomposition of neat 1 at room temperature. L'abbe has suggested[2b] that intermolecular 1,3-cycloaddition of 1 could lead to the formation of the 2,5-diphenylpyrrole. Smolinsky[1b] found 2,5-diphenylpyrazine to be the product of hydrolysis of 2, presumably via phenacylamine which self-condenses.

L'abbe and Mathys[7] noted that the E_a and $\Delta S^{\ddagger}$ values for thermolysis of β-styryl azides (26–30 kcal/mol and −3 to +5 eu) are comparable with those for azide reactions where neighboring-group participation has been observed, as opposed to the values (40 kcal/mol and +18 eu) reported for aryl azide to arylnitrene conversion. L'abbe concluded that either path a or path c is consistent with the kinetic studies.[2b] Recognizing that the kinetic studies[7] of β-styryl azides were likely of reactions not leading predominantly to azirines, Hassner, Wiegand, and Gottlieb[8] measured the simultaneous first-order thermolysis of 1 and appearance of 2 in bromobenzene-d_5 at temperatures of 65–100 °C and reported $\Delta H^{\ddagger} = 26.8 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -2 \pm 2$ eu. Considering also that thermolyses of vinyl azides is more facile when the stereochemistry around the double bond is *E*, as compared to *Z*,[9,10] they suggested that the thermolysis of 1 likely proceeds by path a. These authors formulated empirical rules based on the identity of the R group for predicting whether nitriles or azirines will be the major products of vinyl azide thermolyses; where the α-substituent (such as phenyl in 1) can support a positive charge, concerted decomposition to azirines is predicted.

Rappoport and Gazit report isolation of a ketene imine from the thermal decomposition of vinyl azides having strongly electron withdrawing substituents and propose the sequence shown in Scheme II for vinyl azide thermolysis when R′ and R″ are carbomethoxy groups.[11]

They consider that although thermal loss of nitrogen is most likely a concerted process leading to 6, a nitrene species 7 could, in the compounds they studied, form directly from the azide or result from azirine ring-opening. Where R′ and R″ are electron-withdrawing groups, the observed ketene imine product was considered to result from migration of group R to nitrogen as would be facilitated in nitrene canonical resonance form **7c**. Where groups R′ and R″ are not electron-withdrawing, group R would migrate to the positively charged carbon of canonical form **7b** to yield a nitrile.

Table I. Rate Constants *k* and Activation Parameters for the Thermolysis of Aryl-Substituted α-Azidostyrenes in Various Solvents

T, °C	solvent	$10^5\,k$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
α-Azidostyrene (1)				
59.9	benzyl alcohol	1.2[a]		
70.3	benzyl alcohol	4.0[a]		
80.2	benzyl alcohol	11.9 ± 0.9	25.3 ± 0.4	−5.3 ± 1.4
90.0	benzyl alcohol	30.8 ± 0.4		
100.0	benzyl alcohol	83.7 ± 5.5		
60.0	1-butanol	1.2[a]		
70.3	1-butanol	4.1 ± 0.3		
80.2	1-butanol	10.2 ± 0.1	23.9 ± 0.8	−9.3 ± 2.3
90.0	1-butanol	27.4 ± 4.2		
60.0	methyl acrylate	5.1 ± 0.6		
70.3	methyl acrylate	11.2 ± 1.0		
80.2	methyl acrylate	32.0 ± 7.2[b]	20.4 ± 2.0	−17.0 ± 8.6
80.2	DMF	7.9[a]		
80.2	DMF/water[c]	8.2[a]		
80.2	toluene	8.1 ± 0.2		
92.3	di-*n*-butylamine	33.2[a]		
4-Bromo-α-azidostyrene (9)				
80.2	benzyl alcohol	10.0 ± 0.6	27.5 ± 0.6	0.8 ± 1.8
90.0	benzyl alcohol	29.1 ± 2.8		
100.0	benzyl alcohol	79.0 ± 1.8		
80.2	1-butanol	8.2 ± 0.5		
2-Methyl-α-azidostyrene (10)				
70.3	1-butanol	3.1 ± 0.2		
80.2	1-butanol	9.94 ± 0.01	25.4 ± 0.8	−5.2 ± 2.3
90.0	1-butanol	24.6 ± 0.9		
4-Methyl-α-azidostyrene (11)				
70.3	benzyl alcohol	5.4 ± 0.1		
80.2	benzyl alcohol	14.4 ± 0.4	24.9 ± 0.8	−5.8 ± 2.3
90.0	benzyl alcohol	40.4 ± 1.1		
80.2	1-butanol	12.6 ± 0.3		
4-Methoxy-α-azidostyrene (12)				
70.3	benzyl alcohol	7.0 ± 0.1		
80.2	benzyl alcohol	19.1 ± 1.0	24.5 ± 0.4	−6.5 ± 1.2
90.0	benzyl alcohol	51.2 ± 1.4		
80.2	1-butanol	15.5 ± 0.2		
3-Nitro-α-azidostyrene (13)				
80.2	benzyl alcohol	7.2 ± 0.2	25.0 ± 0.7	−7.0 ± 2.0
90.0	benzyl alcohol	19.1 ± 1.5		
100.0	benzyl alcohol	48.5 ± 4.5		
80.2	1-butanol	5.8 ± 0.4		
2,4,6-Trimethyl-α-azidostyrene (14)				
70.3	1-butanol	1.56 ± 0.04		
80.2	1-butanol	5.3 ± 0.1	25.8 ± 1.1	−5.5 ± 3.1
90.0	1-butanol	12.7 ± 0.7		

[a] Result of a single determination. [b] The larger than normal standard error arises from gasometric measurements near the boiling point of the solvent. [c] 10 mole percent water.

Although several kinetic investigations of thermolysis of 1 have been made,[3,5,8] the only report of the effect of aryl substituents on thermolyses of vinyl azides is that chloro and methyl groups in the para position of β-azidostyrenes produce negligible effects.[7]

Discussion and Results

The rates of decomposition of seven aryl-substituted α-azidostyrenes in benzyl alcohol and/or 1-butanol at temperatures 60–100 °C and the resultant activation parameters are provided in Table I.

The reactions are cleanly first-order and were followed to over 97% completion by measurement of volume of nitrogen evolved as a function of time at constant pressure. Benzyl alcohol was selected for its potential to trap reactive

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(4) Hortmann, A. G.; Robertson, D. A.; Gillard, B. K. *J. Org. Chem.* **1972**, *37*, 322.

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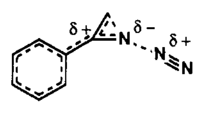
decomposition intermediates and its low vapor pressure, but later decompositions were carried out in the more volatile 1-butanol to facilitate solvent removal for product studies. For 1, the rate constants are similar to those found by others.[3,5,8]

The ρ value from Hammett plots of the rate data for the meta- and para-substituted azides at 80.2 °C in both benzyl alcohol and 1-butanol was −0.7, with σ^+ correlation (r = 0.98). Use of the p-methoxy substituent was important to distinguish clearly σ^+ from σ correlation.

2,4,6-Trimethyl-α-azidostyrene (**14**) thermolyzes markedly more slowly than does **1** in 1-butanol and gives 2-(2′,4′,6′-trimethylphenyl)azirine (**15**) in 75% yield. Azirine **15** is a solid and is relatively stable at room temperature.

For purposes of verifying azirines to be the products, thermolyses of **9**, **11**, **12**, and **13** were followed in bromobenzene at 90.0 °C, combining gasometric measurements with the ^{1}H NMR technique of Hassner et al.[8] Solutions of the azides were heated in NMR tubes, and the first-order rates of gas evolution were monitored until 50–75% of theoretical gas volume had been collected. The magnitude of new singlet signals near δ 1.6, characteristic of azirine protons, corresponded to the extent of reaction completion and to the decrease in intensity of the signals for the vinyl protons of the azides, and no other new signals were evident. The values of the rate constants in these concentrated bromobenzene solutions were 60–80% of those found in the dilute alcohol solutions and were well-correlated by σ^+ constants (ρ = −0.9, r = 0.99).

The activation parameters, ρ value, ϵ^+ rate correlation, steric retardation demonstrated by o-methyl groups as in **14** and **10**, and product studies suggest a mechanism where, in a transition state such as **16**, positive charge develops at a site where the aryl ring may delocalize the charge and where coplanarity of the developing azirine ring and the aryl ring are required in the transition state. This is as would be expected for concerted decomposition as in path a.



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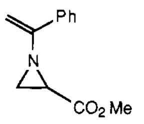
Except when methyl acrylate is solvent, the rates of thermolysis of **1** are not much affected by change in solvent polarity, suggestive that the transition state has minimal asymmetrical charge separation. The entropy of activation values are more negative than those found by Hassner et al. in bromobenzene-d_5. Hydrogen bonding by the alcohols may be a possible explanation. However, because of the uncertainty inherent in $\Delta S^{\ddagger}$ values, these differences may not be significant.

Nomura et al.[12] thermally decomposed **1** at 80 °C in the refluxing dipolarophilic solvent methyl acrylate and reported that the yield of products from addition to the double bond of the solvent, 2-carbomethoxy-1-(1-phenylvinyl)aziridine (**17**) (6% yield) and 2-phenyl-4-carbomethoxy-Δ^1-pyrroline (**18**) (68% yield), exceeded the amount of **2** formed (15%).



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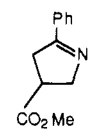

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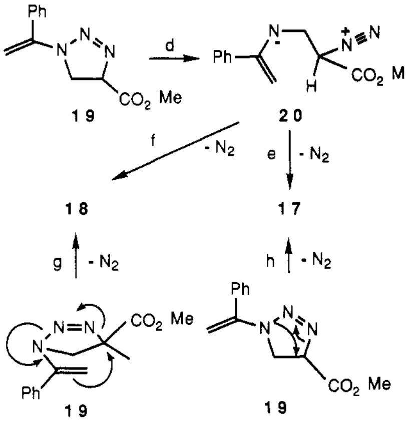
Scheme III



Although these authors presented no mechanistic conclusion regarding their findings, their premise was that the dipolarophile solvent is trapping nitrene **3**, an active 1,3-dipole.

As may be seen in Table I, the rate constants and the entropy of activation for **1** change considerably when methyl acrylate is used as solvent. Considering the large negative entropy of activation, this decomposition is unlikely to be following either path a or path b (nitrene intermediate) but rather is a 1,3-dipolar cycloaddition mechanism involving the azide function of **1** and the ene function of methyl acrylate, consistent with an earlier suggestion[2a] that **17** might arise by loss of nitrogen from triazoline **19**. It has been demonstrated[13] that vinyltriazolines pyrolyze to vinylaziridines. High-resolution ^{1}H NMR analysis of the collected solutions from kinetic determinations, after removal of the methyl acrylate in vacuo, showed the products to be 61% **17**, with **2** and **18** each comprising 5–10% of the mixture.

The possibility that vinyl azides might experience loss of nitrogen in a concerted fashion to give azirines, which may then ring-open to provide nitrenes[11] (e.g., conversion of **6** to **7a** in Scheme II), seems inappropriate for explanation of formation of **17** and **18**, in methyl acrylate, considering that the reaction kinetics indicate the thermolysis to be unlike that in the other solvents investigated.

Azirine **2** is sufficiently thermally stable as to be recovered unchanged after heating to 98 °C for 40 h in n-heptane.[14] However, rearrangement of 2-allyl-2-methyl-3-phenyl-2H-azirine[15] at temperatures of 190 °C and above and racemization of optically active 3-methyl-2-phenyl-2H-azirine[16] above 105 °C have been rationalized as involving nitrenes formed by thermolysis of the azirines. Imine **18** has been formed from photolysis of **2** in methyl acrylate via an intermediate nitrile yield.[17]

The possibility should be considered that the formation of **19** via 1,3-cycloaddition of **1** with methyl acrylate at the relatively low temperatures of 60–80 °C offers explanation for the formation of both **17** and **18** via the following modification of a mechanism which was proposed (a diradical being mentioned as an alternative to the ionic intermediate) for the thermal conversion of bicyclic triazolines to aziridines or imines.[18] Nitrogen atom attack on

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[17] Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 1945.

[18] Hassner, A.; Amarasekara, A. S.; Andisik, D. *J. Org. Chem.* **1988**, *53*, 27.

the carbon bearing the diazonium group, as in path e (Scheme III), gives **17** as proposed by Hassner;[2a] alternatively, S_N2 attack by the vinyl carbon atom (path f) would yield **18**. Concerted thermal reactions of **19**, as shown in paths g and h, are also possible routes to **18** and **17**.

The extent to which any one of these reactions takes place would be a function of temperature.

The minor amounts of **2** found by the earlier investigators[12] of thermolysis of **1** in methyl acrylate were likely due to the parallel reaction process of concerted unimolecular thermal decomposition. Concerted decomposition to azirines, which will be thermal equilibrium with vinyl nitrenes, has been suggested to be occurring in parallel with an intramolecular 1,3-cycloaddition reaction in the thermolysis of azidocinnamates bearing ortho-olefinic substituents, the partitioning between these two pathways being temperature-dependent, with 1,3-cycloaddition favored at lower temperatures.[19]

Experimental Section

Kinetics. Solutions of azides (0.056 M) were stirred in a gas-tight system with a Vibro-mixer[20] to provide surface agitation for promotion of free exchange of nitrogen between the liquid and gas phases. The azide was dissolved in 2 mL of solvent, and this solution was injected via syringe into 35 mL of solvent at the bath temperature. The gasometric kinetic measurements were carried out by a computer-controlled device which monitored the volume of nitrogen evolved at constant pressure.[21] The gas volumes collected were the theoretical volumes. When the concentration of azide in benzyl alcohol was increased 3-fold, the rate constant did not increase. The entropies of activation were calculated from the rate constants at 80.2 °C by the equation $\Delta S^{*} = 4.576 \log k_1$ $(s^{-1}) - 49.14 - 4.576 \log T + E_a/T$, provided by L'abbe and Mathys.[7]

Materials. The α-azidostyrenes were prepared by the method of Hassner, Fowler, and Levy.[22] Toluene (Mallinckrodt ScintillAR grade) and di-*n*-butylamine were distilled from CaH_2 under a nitrogen atmosphere, and the toluene was passed through basic alumina for removal of trace amounts of water prior to use. Benzyl alcohol was distilled from CaH_2 under a nitrogen atmosphere or used as obtained from Aldrich as anhydrous grade. Bromobenzene was passed through sodium hydroxide pellets and molecular sieves and then distilled under a nitrogen atmosphere. DMF (anhydrous), methyl acrylate, and 1-butanol (anhydrous) were obtained from Aldrich and were used without further purification.

4-Bromo-α-azidostyrene (9): mp 20–22 °C; IR (neat), 2185 (m), 2120 (s), 2090 (s) (N═N═N), 1604 (m), 1583 (m), 1482 (m), 1307 (m), 1289, 1210 (m), 1088 (m), 1011 (m), 906 ($C{=}CH_2$, m), 831 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.92, 5.38 (2 H, doublets, J = 3 Hz, $C{=}CH_2$), 7.38 (4 H, s, coalesced AA′XX′, Ar H); ^{13}C NMR ($CDCl_3$) δ 144.1, 133.2, 131.5, 127.0, 123.3, 98.1. Anal. Calcd for $C_8H_6N_3Br$: C, 42.88; H, 2.70; N, 18.76; Br, 35.66. Found: C, 42.91; H, 2.70; N, 18.62; Br, 35.75.

2-Methyl-α-azidostyrene (10): very pale yellow liquid, mp <–20 °C; IR (neat) 2200, 2145, 2105 (N═N═N, s), 1630, 1290, 1270, 1212 (m), 873 (br, m), 769 (m), 734 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.24, 7.18 (4 H, m, Ar H), 5.05, 4.70 (2 H, doublets, J = 1.0 Hz, $C{=}CH_2$), 2.4 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ 145.4 (α carbon), 136.0, 134.9, 130.4, 129.2, 129.1, 125.9, 102.6 (β carbon), 19.7. This compound was previously prepared by Smolinsky.[1b]

4-Methyl-α-azidostyrene (11): pale yellow liquid, mp <–20 °C; IR (neat) 2104, 2142 (N═N═N, s), 1294 (m), 910 ($C{=}CH_2$, m), 820 (m), 732 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (3 H, s, CH_3), 4.90, 5.36 (2 H, doublets, J = 2 Hz, $C{=}CH_2$), 7.15, 7.47 (4 H, doublets, J_{AX} = 9 Hz, AA′XX′, Ar H); ^{13}C NMR ($CDCl_3$) δ 145.0, 139.1, 131.5, 129.1, 125.4, 97.1, 21.2. Anal. Calcd for $C_9H_9N_3$: C, 67.90; H, 5.70; N, 26.40. Found: C, 68.01; H, 5.77; N, 26.25.

4-Methoxy-α-azidostyrene (12): white plates from petroleum ether, mp 39–40 °C; IR (KBr) 2120, 2095 (N═N═N, s), 1602, 1295, 1248, 1176 (m), 1026, 905 (m), 836, 828 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.79 (3 H, s, OCH_3), 4.83, 5.29 (2 H, doublets, J = 3 Hz, $C{=}CH_2$), 6.85, 7.45 (4 H, doublets, J_{AX} = 9 Hz, AA′XX′, Ar H); ^{13}C NMR ($CDCl_3$) δ 160.4, 144.7, 126.9, 113.8, 96.1, 55.3 (two aromatic carbon resonances are not resolved). Anal. Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.67; H, 5.35; N, 24.32.

3-Nitro-α-azidostyrene (13): mp 42–43 °C; recrystallized from petroleum ether; IR (KBr) 2164, 2146, 2114, 2090 (N═N═N, m), 1610 (m), 1526 (NO_2), 1485 (m), 1345 (NO_2), 1312, 1285 (m), 903 ($C{=}CH_2$, m), 883 (m), 840, 800 (m), 736 (m), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.05, 5.56 (2 H, doublets, J = 3 Hz, $C{=}CH_2$), 7.3–8.5 (4 H, complex splitting, Ar H); ^{13}C NMR ($CDCl_3$) δ 148.4, 143.1, 135.9, 131.2, 129.5, 123.7, 120.5, 99.8. Anal. Calcd for $C_8H_6N_4O_2$: C, 50.52; H, 3.18; N, 29.47. Found: C, 50.91; H, 3.22; N, 29.83.

2,4,6-Trimethyl-α-azidostyrene (14): very pale yellow liquid, mp <–20 °C; IR (neat) 2985, 2930, 2878 (CH, s), 2185, 2112, 2098 (N═N═N, s), 1630, 1610, 1445 (m), 1380 (m), 1278, 1220 (m), 1168 (m), 1079 (m), 1030 (m), 885 ($C{=}CH_2$, m), 849, 725 (m), 650 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.89 (2 H), 5.09, 4.50 (2 H, doublets, J = 0.6 Hz, $C{=}CH_2$), 2.28 (9 H); ^{13}C NMR ($CDCl_3$) δ 143.1, 138.4, 136.3, 131.6, 128.2, 103.2, 21.1, 19.7.

Conversion of the iodo azide adduct from 2,4,6-trimethylstyrene[23,24] to the vinyl azide was not complete in 21 h. Acetonitrile was added in an amount equal to the quantity of ether present, and the reaction was heated at 50–60 °C, with distillation of ether, until TLC analysis (silica gel GF) revealed that the reaction was complete (0.5 h). In the workup, the acetonitrile-soluble product was salted out of the water wash (yield = 63%).

2-(2′,4′,6′-Trimethylphenyl)-1-azirine (15): colorless solid, chromatography on neutral silica gel with benzene as eluant, followed by recrystallization from cyclopentane, mp 55–56 °C; IR (FTIR) 1719.5 (m), 1609.9, 1380.2, 996.2, 854.6 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (s, 2 H), 2.61 (s, 6 H), 2.33 (s 3 H), 1.71 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 163.1, 142.9, 141.3, 129.4, 119.1, 21.5, 19.9, 19.3 (CH_2); CI mass spectrum (methane as reagent gas), M + 1 peak at 160; EI (70 eV) mass spectrum, m/e (relative intensity) 159 (M^+), 158 ($M^+ - H$) (100), 144, 132, 117, 115, 91, 77. Anal. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.97; H, 7.93; N, 8.73.

Product Studies by Thermolysis in Bromobenzene. The azides (0.3 to 0.4 mmol) were dissolved in 0.6 g of bromobenzene in 5-mm NMR tubes. After determination of the ^1H NMR spectra (no TMS), these were connected by flexible tubing to the computer-controlled device that monitored the volume of nitrogen evolved when the tubes were suspended in a constant-temperature bath at 90 °C. When substantial gas evolution had occurred, the ^1H NMR spectrum was reexamined after addition of TMS. The only changes in the spectra in the range δ 0.0–6.5 were reductions in the intensity of the vinyl doublet signals and complementary appearances of singlet signals at δ 1.64, 1.66, 1.66, and 1.71 for **9**, **11**, **12**, and **13**, respectively.

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