(NCH$_3$/NCH$_2$ attack product ratio 3.6); after 4 days no $\mathbf{3}^{2+}$ or **19** and 77% **16**, 19% **18** (attack product ratio 4); and after 5 days 68% **16**, 12% **18** (attack product ratio 5.7, only 80% of the initial $\mathbf{3}^{2+}$ present accounted for). Analysis by adding a weighed amount of 1,4-dibromobenzene at this point gave the yields of **23**:**25** as 62:11% (5.7 ratio).

Acknowledgment. We thank the National Institutes of Health for partial financial support of this work under GM-29549. We thank R. W. Alder and K.-D. Asmus for preprints of their work. We thank Professor Asmus and his graduate students, M. Göbl and J. Mönig for the pulse radiolysis measurements, which were carried out with the assistance of NATO Travel Grant 104/80.

Registry No. $\mathbf{3}^{2+}$, 73843-82-0; $\mathbf{3}^{2+}$-d_6·2BF$_4^-$, 103094-89-9; 3^{2+} (monoalkylated), 103094-90-2; **5**, 6523-29-1; **5** (amide), 1632-26-4; 2-formyl-**5**, 23014-04-2; **5**-d_3, 103094-91-3; $\mathbf{6}^{2+}$, 82415-31-4; $\mathbf{6}^{2+}$·2BF$_4^-$, 82415-32-5; **7**(I)$^+$I$^-$, 103094-92-4; **7**(Br)$^+$Br$^-$, 103094-93-5; 8^+, 103094-84-4; $\mathbf{8}^+$I$^-$, 103094-96-8; $\mathbf{8H}^{2+}$, 103094-85-5; **9**(OH)$^+$Br$^-$, 103094-94-6; $\mathbf{10}^{2+}$, 103094-82-2; $\mathbf{10}^{2+}$·2BF$_4^-$, 103094-95-7; **11**, 103094-97-9; $\mathbf{14}^+$, 103094-83-3; $\mathbf{14}^+$I$^-$, 103094-98-0; **16**, 90827-82-0; 18, 103094-87-7; **19**, 103094-86-6; **21**, 73321-18-3; CO$_3^{2-}$, 3812-32-6; I$^-$, 20461-54-5; Cl$^-$, 16887-00-6; Et$_4$NCl, 56-34-8; n-Bu$_4$NI, 311-28-4; 1,4-diiodobutane, 628-21-7; 1,4-dibromobutane, 110-52-1; bis(deuteriomethyl)hexahydropyridazine, 26163-38-2; bis(ethyl carbamate), 4114-28-7; 1,2-diazabicyclo[2.2.2]octane, 329-94-2.

Kinetics of Thermolysis of Vinyl Azides. Empirical Rules for Formation of Azirines and Rearranged Nitriles[1]

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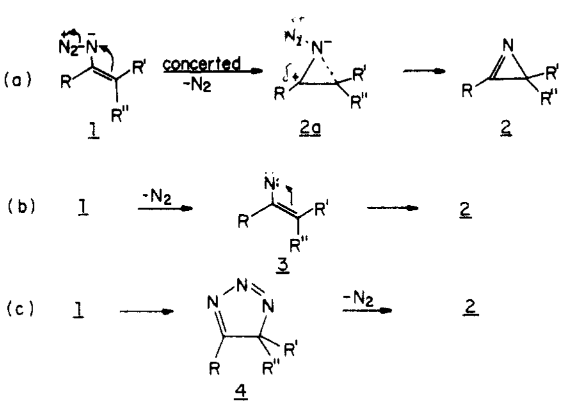
Received October 17, 1985

An evaluation of reported thermolyses of acyclic and cyclic vinyl azides R(N$_3$)C=CR′ leads to the empirical generalization that when R is aryl, alkyl, a heteroatom, or even alkoxycarbonyl, 1-azirines are usually formed upon thermolysis. When R is H or keto carbonyl (and depending on the β-substituents R′), nitriles or heterocycles are usually isolated. The kinetics of the thermolysis of α-azidostyrene (**10**) were followed by NMR, both by disappearance of **10** and appearance of azirine **11**, and are consistent with a concerted loss of nitrogen and ring closure. A reexamination of the kinetics of α-azidochalcone (**15**) thermolysis, which normally leads to rearranged nitrile **19**, revealed the intermediacy of azirine **16** which was isolated and thermolyzed. For the first time we were able to compare kinetic and thermodynamic data for vinyl azide to azirine conversion with those of azirine to nitrile rearrangement. The latter process appears to proceed via the dipolar form of a vinyl nitrene intermediate. A general scheme explaining the empirical findings is discussed.

Although thermolysis and photolysis of vinyl azides **1** to 1-azirines **2** are well established and synthetically useful reactions,[2] their mechanistic pathway has not yet been clearly established. Three major pathways have been proposed for these transformations: (a) loss of nitrogen occurring concertedly with ring formation; (b) the intermediacy of a vinyl nitrene (**3**) (presumably a singlet) which can undergo symmetry-allowed electrocyclic ring closure to **2**; (c) intramolecular [3 + 2] cycloaddition of the azido group to the double bond, followed by loss of N$_2$ from an intermediate triazole **4**.



Ab initio calculations[3a] for the process 1 → 4 → 2 predicted an energy of activation of 32.9 kcal/mol or 41.4 kcal/mol depending on the method used. More recent calculations[3b] favor rate-determining formation of a vinyl nitrene or a more or less concerted loss of nitrogen and indicate almost no activation energy for vinyl nitrene to azirine conversion. Attempts to clarify the mechanism of vinyl azide to azirine thermolysis have included a kinetic study by L'abbé and Mathys.[4] For the vinyl azides **1** (R = H or C=O and R′, R″ = H, Ar, ArC=O, Me), they found energies of activation (26–30 kcal/mol) and ΔS^* values (−3 to +5 eu) which are not compatible with the nitrene pathway (b), when compared to data ($E_a \sim 40$ kcal/mol, $\Delta S^* \sim +18$ eu) reported for aryl azide to arylnitrene conversion. Although path a could not be excluded, these authors favored pathway c since the kinetic data compared more favorably with those observed for pyrazoline formation from diazoalkenes.[4]

However, not all vinyl azides yield azirines upon thermolysis; in many cases[5] nitriles or heterocycles such as indoles are the reaction products (see Table I). We have critically examined a large number of reported thermolyses (usually at 35–150 °C)[6] of both cyclic and acyclic vinyl azides having a variety of substitution patterns. The reported products lead us to propose the following empirical generalizations: *Thermolyses of vinyl azides 1 to isolable*

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[1] Part 28. Small Rings. For part 27, see: Hassner, A.; Belinka, A., Jr.; Steinfeld, A. S. *Heterocycles* **1982**, *18*, 179.

[2] For recent reviews, see: (a) Hassner, A. In *Azides and Nitrenes. Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: Orlando, 1984; Chapter 2. (b) Nair, V. In *Small Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, 1983; Vol. 42, Part 1, pp 215–332. (c) Moore, H. W.; Goldish, D. M. In *The Chemistry of Functional Groups*, Suppl. D.; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Chapter 8, p 321.

[3] (a) Burke, L. A.; Leroy, G.; Nguyen, M. T.; Sana, M. *J. Am. Chem. Soc.* **1978**, *100*, 3668. (b) Yamabe, T.; Kaminoyama, M.; Minato, T.; Hori, K.; Isomura, K.; Taniguchi, H. Tetrahedron **1984**, *40*, 2099.

[4] L'abbé, G.; Mathys, G. *J. Org. Chem.* **1974**, *39*, 1778.

[5] Isomura, K.; Kobayashi, S.; Taniguchi, H. *Tetrahedron Lett.* **1968**, 3499. Isomura, K.; Okada, M.; Taniguchi, H. *Ibid.* **1969**, 4073.

[6] Pyrolyses at higher temperature or in the vapor-phase may proceed through different intermediates. Similarly thermolysis of 1-azirines at higher temperatures often lead to a mixture of many products.

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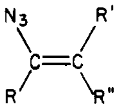
Table I. Major Products from Vinyl Azide Thermolysis



1

vinyl azide 1					vinyl azide 1				
R	R′	R″	product type	ref	R	R′	R″	product type	ref
Ph, Ar	H	H	azirine	12, 18a	Ph	Me	N_3	PhCN	32
Ph, PhC═C	Ph	H	azirine	12,31	PhC═O	Me	H	azirine	15
Ph	H	alkyl	azirine	12, 30	PhC═O	Ar	H	nitrile	15, 28
Ph	-O-		nitrile	22	F	F	CF_3	azirine	27
2-pyridyl	H	H	pyrrole, polymer	19	OMe	CF_3	CF_3	azirine	27
alkyl	H	H	azirine	12	NR_2	Me	H	azirine	29
alkyl	alkyl	H	azirine	12	H	H, Me	PhC═O	(azirine) isoxazole	9a
Me	CO_2Et	H	azirine	12	H	H	Ar	nitrile, (indole)	5
Me	Ph	C═CPh_2	pyrrole	17	H	H	*t*-Bu	polymer	11
CO_2Me	H	CO_2Me	azirine	9b	H	Me, H	C═CHR	pyrrole	17
CO_2Et	Ar, C═CHAr	H	azirine, indole, pyrrole	7, 8, 17d	H	Ph	C═CPh_2	nitrile	17
Me	CN	CN	trapped ketene imine	26					

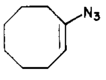
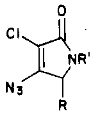
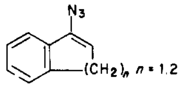
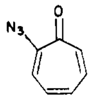
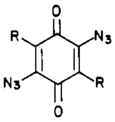
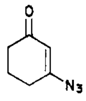
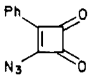
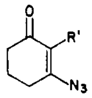
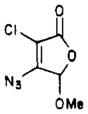
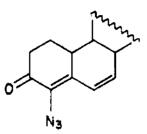
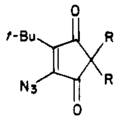
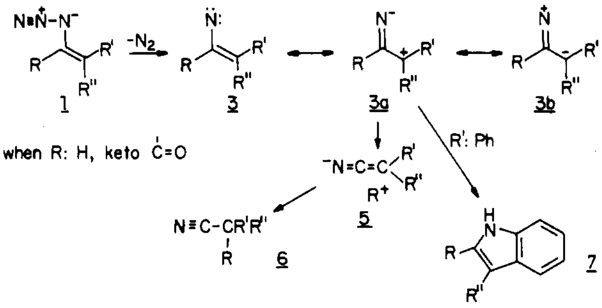
cyclic vinyl azide	product type	ref	cyclic vinyl azide	product type	ref
	azirine	12		nitrile	37
	polymer (trapped azirine)	11, 12		nitrile	38
	nitrile	33	 **32**	trapped ketene imine **34**	24
	nitrile	35	 **29**	trapped azirine **31**	23
	nitrile	34		nitrile	20
	nitrile	36			

Table II. Rate Constants *k* and Activation Parameters for the Thermolysis of α-Azidostyrene (10) in C_6D_5Br

T, °C	10^5k, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
63.8 ± 0.5	1.37 ± 0.07	27.31 ± 0.04	26.8 ± 0.7	-2 ± 2
80.4 ± 0.5	9.48 ± 0.2	27.33 ± 0.04		
100.0 ± 0.5	72.2 ± 1	27.37 ± 0.04		

*1-azirines **2** usually take place when the α-substituent (R in **1**) is aryl, alkyl, a heteroatom, and often alkoxycarbonyl. If the α-substituent (R) is a proton, keto carbonyl, or a substituent destabilizing an adjacent positive charge and in the case of cyclic vinyl azides, the azirine is rarely isolated. Instead rearrangement to nitriles **6** or formation of heterocycles such as indoles **7** are observed.* β-Substituents too have a pronounced effect upon product formation and if R′ or R″ is aryl or vinyl, indoles or other cyclic products are also or exclusively formed.[5,7,8] When R′ is C═O isoxazoles result.[9] In very rare cases ketene imines are formed as major products.

The α-substituents favoring rearrangement to nitriles **6** (R = H, C═O) appear to be capable of supporting a positive charge. A reasonable pathway for nitrile for-



mation is shown below (**1** → **3** → **5** → **6**) and is consistent with the zwittazido cleavage mechanism first proposed by Moore for cyclic vinyl azides (e.g., **8** → **8a** → **9**),[10] although

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(7) Hemetsberger, H.; Knittel, D. *Monatsh. Chem.* **1972**, *103*, 194.

(8) Grant, R. D.; Moody, C. J.; Tsoi, S. C. *J. Chem. Soc., Chem. Commun.* **1982**, 884.

(9) (a) Isomura, K.; Hirose, Y.; Shuyama, H.; Abe, S.; Ayabe, G.; Taniguchi, H. *Heterocycles* **1978**, *9*, 1207. (b) L'abbé, G.; Dekerk, J. P.; Van Stappen, P. *Bull. Soc. Chim. Belg.* **1981**, *90*, 1073.

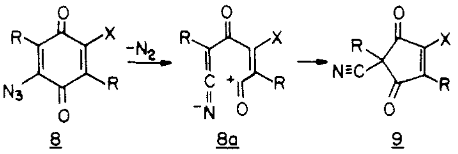
(10) Moore, H. W. *Acc. Chem. Res.* **1979**, *12*, 125.

(11) Hassner, A.; Anderson, D. J. *J. Org. Chem.* **1973**, *38*, 2565.

(12) (a) Hassner, A.; Fowler, F. W. *J. Am. Chem. Soc.* **1968**, *90*, 2869. (b) Fowler, F. W.; Hassner, A.; Levy, L. A. *Ibid.* **1967**, *89*, 2077.

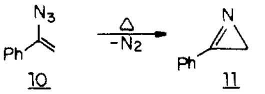
(13) Meek, J. S.; Fowler, J. S. *J. Org. Chem.* **1968**, *33*, 3418.

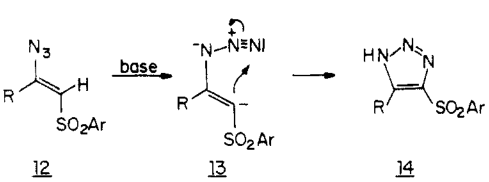
a radical pair intermediate or a 1,2-shift should also be considered.



A careful examination of all vinyl azides employed in the kinetic study cited above[4] reveals that they are of type **1** where R is H or keto C=O. They do not lead to azirines but yield mainly nitriles **6** and other products.[5,15] In a few rare cases (e.g., **1**, R = H, R′ = Me, R″ = PhC=O and R, R′ = H, R″ = Ph) azirines can either be trapped as an unstable intermediate or can be isolated (*photolysis* at low temperature). They are further shown to be convertible to nitriles and indoles upon heating.[5,9,11] Since, only the disappearance of the azide was measured in the kinetic study an important question arises: Do the kinetic results actually apply to the conversion of vinyl azides to nitriles or the conversion to azirines?

In order to shed light on this confusing situation, we decided to examine the kinetics of the thermolysis of a bona fide vinyl azide–azirine transformation. Furthermore, these data were compared to those obtained from a vinyl azide leading to a nitrile. The thermolysis of α-azidostyrene in bromobenzene-d_5 at 65–100 °C (NMR) was examined by following both the disappearance of vinyl azide **10** (vinylic Hs at δ 5.2 and 4.7) and the appearance of 2-phenyl-1-azirine (**11**) (CH_2 at δ 1.6). The kinetics were cleanly first order (see Table II) and the thermodynamic data ($\Delta H^{\ddagger}$ = 26.8 ± 0.7 kcal/mol, $\Delta S^{\ddagger}$ = −2 ± 2 eu) are similar to those found[4] for the thermolyses that actually yield nitriles. These results and the fact that the rate of vinyl azide to azirine conversion is influenced by the stereochemistry around the olefinic double bond (*E* faster than *Z*)[3b,12] are consistent with concerted pathway a. In our opinion path c is also less likely to be involved because the initially formed 4*H*-triazoles are expected to rearrange to 1*H*-triazoles (see **14**) and such have been isolated[13,14] only from vinyl azides (see **12** → **14**) where a negative charge was generated on the β-carbon, so as to enable nucleophilic attack on the azide function.





Next we reexamined the thermolysis of vinyl azide **15**, which had been shown[15] to rearrange to nitrile **19** at 140 °C and for which trapping of cleavage fragments (i.e., **5**) was possible in the presence of alcohols or amines.[16] When the reaction was followed at 80 °C by NMR at 300 MHz the appearance of an intermediate was revealed as starting azide disappeared. This intermediate rapidly disappeared, apparently being converted to rearranged nitrile **19** (see Figure 1). In fact we were able to isolate the intermediate by careful chromatography and identify it as 2-benzoyl-3-phenyl-1-azirine (**16**), which showed expected spectral characteristics (IR 1720 cm^{-1}, ^1H NMR singlet at δ 3.50, ^{13}C NMR δ 182.4 C=O, 165.3 C=N, 37.7 tertiary C) and to convert it to nitrile **19** by thermolysis at 80–100 °C.

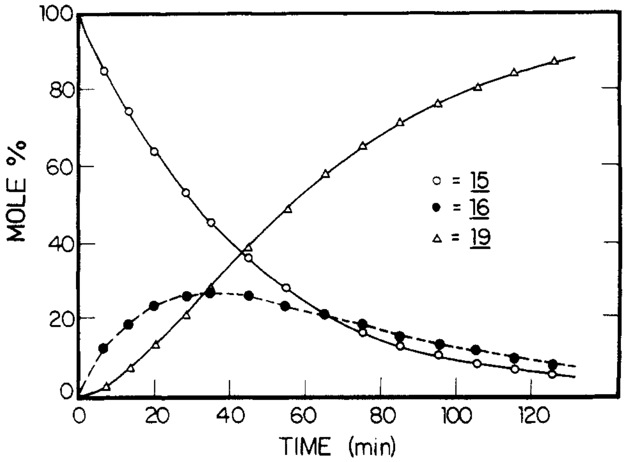
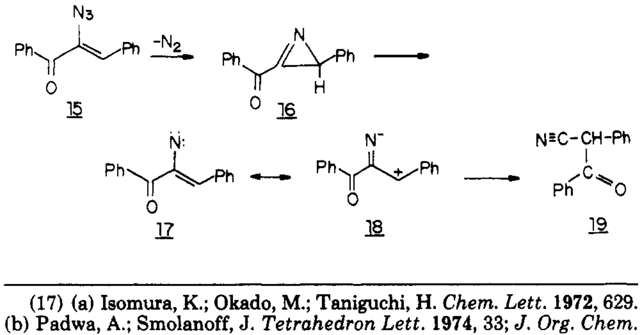


Figure 1. Thermolysis of α-azidochalcone (**15**) in bromobenzene-d_5 at 96.5 °C. Relative concentration of (○) **15**, (●) intermediate 2-benzoyl-3-phenyl-1-azirine (**16**), and (△) final product, nitrile **19**.

Table III. Rate Constants *k* and Activation Parameters for the Thermolysis of α-Azidochalcone (15) and 2-Benzoyl-3-phenyl-1-azirine (16) in C_6D_5Br

T, °C	10^5k, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
		α-Azidochalcone (15)		
68.1 ± 0.5	1.13 ± 0.06	27.79 ± 0.06	30 ± 1	+9 ± 3
96.5 ± 0.5	39.8 ± 0.6	27.55 ± 0.04		
		2-Benzoyl-3-phenyl-1-azirine (16)		
63.3 ± 0.5	1.83 ± 0.05	27.07 ± 0.04	26 ± 1	−3 ± 3
94.1 ± 0.5	53.7 ± 2	27.15 ± 0.06		

The kinetics of conversion of **15** to **16** as well as of **16** to **19** in bromobenzene-d_5 (see Table III) are quite similar to those of **10** and agree with L'abbé's kinetic data on **15** in toluene. A consistent explanation for nitrile formation involves a vinylnitrene intermediate **17** and is indicated by **16** → **17** → **19**. Though attempts to trap vinylnitrenes from thermolysis of vinyl azides have thus far not been successful, their intermediacy in the thermal fragmentation of 1-azirines has been postulated by several workers and confirmed by trapping and racemization experiments.[17]



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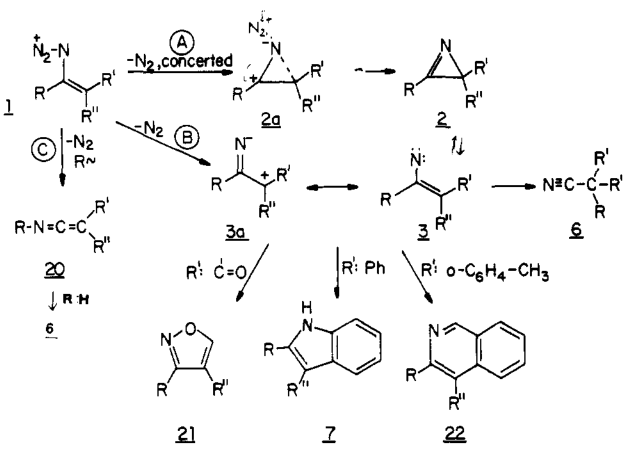
(14) Henriet, M.; Houtekie, M.; Techy, B.; Touillaux, R.; Ghosez, L. *Tetrahedron Lett.* **1980**, *21*, 223.

(15) Knittel, D.; Hemetsberger, H.; Leipert, R.; Weidmann, H. *Tetrahedron Lett.* **1970**, 1459. Among the eight α-azidochalcones studies, only one led on thermolysis to an azirine: the 2-(p-chlorobenzoyl)-3-(2,6-dichlorophenyl)-1-azirine, which was thermolyzed to a nitrile at 180 °C.

(16) Hassner, A.; Belinka, B. A., Jr.; Hendler, J. M. *J. Org. Chem.* **1981**, *46*, 631.

(17) (a) Isomura, K.; Okado, M.; Taniguchi, H. *Chem. Lett.* **1972**, 629. (b) Padwa, A.; Smolanoff, J. *Tetrahedron Lett.* **1974**, 33; *J. Org. Chem.* **1976**, *41*, 543. (c) Padwa, A.; Carlsen, P. H. J. *J. Org. Chem.* **1978**, *43*, 2029. (d) Isomura, K.; Taniguchi, H.; Tanaka, T.; Taguchi, H. *Chem. Lett.* **1977**, 401. (e) Isomura, K.; Ayabe, G. I.; Hatano, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1252.

Scheme I

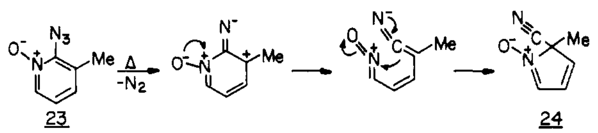


It appears that a major contributing resonance structure of the vinylnitrene **17** is **18**, which then leads to fragmentation when the α-substituent can support a positive charge well. The nitrene can fragment to radicals or more likely to an intimate ion pair **5** that corresponds to zwitterion **8a** in cyclic systems and which can recombine to **19**. Alternatively, **17** can undergo a benzoyl group migration leading to **19**.

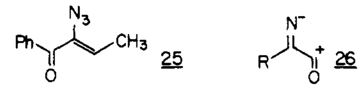
Since the thermodynamic data for vinyl azide to azirine conversion (i.e., **15** → **16**) are comparable in magnitude to those of the cleavage of azirine (**16** → **19**), it is reasonable to postulate the following general scheme for vinyl azide thermolysis.

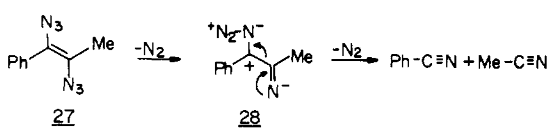
In this scheme, a vinyl azide has three options to loose N_2: A, B, and C. Path A illustrates the concerted formation of azirines when the α-substituent R can support a positive charge (R = aryl, alkyl, NR_2, OR, F, and often also CO_2R). Path B leads to vinylnitrene when the α-substituent R does not stabilize an adjacent positive charge (R′ = H, keto C=O) but the β-substituents R′ and R″ can support a positive charge at the β-carbon. Path C depicts migration of the α-substituent R to nitrogen to form ketene imine **20**. Although the latter have rarely been isolated, this pathway may account for formation of nitriles **6** when R = H. Even when azirines **2** are preliminarily formed, they can thermally cleave to vinylnitrenes **3** if the process is favored by the factors operating in path B. Indoles **7**, pyrroles, isoquinolines **22**, or isoxazoles **21** can be formed via vinylnitrene **3** when appropriate β-substituents (aryl, vinyl, carbonyl) are present.

Process A most likely has a slightly lower energy barrier than formation of a vinylnitrene, that is when the α-substituents are capable of stabilizing the transition state **2a** leading to azirine. This is, for instance, reflected in the greater thermal stability of several 2-methyl-3,3-disubstituted-azirines compared to the 2-unsubstituted homologues.[17,18] However, in cases where the α-substituent R destabilizes the azirine or the transition state **2a** leading to it (e.g., R = C=O or H and also R = 2-pyridyl[19]), vinylnitrene formation either from the vinyl azide or from the azirine becomes favorable and finally leads to a polymer, a nitrile, and/or a heterocycle. In the case of five- or six-membered ring vinyl azides, ring strain usually prevents formation of the bicyclic fused azirine and favors the now lower energy path via the vinylnitrene. The latter often polymerizes but, if a substituent capable of carrying a positive charge (e.g., C=O)[20] is present, cleavage can occur. Such examples are even found in aromatic azides (see **23** → **24**).[21]



Finally as expected, the β-substituents R′ and R″ can also exert an influence on the course of the reaction by stabilizing the charged character of the vinylnitrene. For instance, thermolysis of **25** leads to an isolable azirine,[15] while changing CH_3 to aryl (cf. **15**) stabilizes the transition state leading to cleavage either via **2** or directly through path B and nitrile **6** is formed. Consistent with the above is the fact that azidoketenes are unstable and yield nitriles, presumably via **26**.[22] The presence of a β-azido function (i.e., **27**) also helps stabilize the positive charge in the vinylnitrene **28**, thus favoring cleavage.[32]





Other examples of β-substituent effects come from azirine decomposition. Azirines with a 2-carbethoxy substituent (R = CO_2Et) are usually isolable and quite stable thermally, but the presence of a benzofuran-2-yl group at the 3-position (R′ in **2**) labilizes them sufficiently to open at 35 °C.[17d] Furthermore, while thermolysis of vinyl azides shows negligible rate sensitivity to the electronic character of the para substituent of the β-aryl group,[4] thermolysis of azirines exhibits a negative ρ value of −0.8,[25] consistent with the intermediacy of **3** ↔ **3a**.

Though cyclic vinyl azides usually undergo thermal ring cleavage or polymerization because of the strain in the fused azirine, there are a few examples reported[23] that apparently thermolyze via a fused azirine (see **29**) which is trapped in the presence of an alcohol (**29** → **31**). Such trapping of fused azirines has been shown to occur in vinyl azide photolysis as well.[12a] The β-carbonyl substituent in vinyl azide **29** may destabilize the polar form **3a**, thus favoring path A. In the absence of the β-alkyl substituent (compare **29** to **32**) ring expansion to **34** takes place.[24] This can be explained by a contribution from dipolar form **33**, which after protonation and alkyl migration leads to **34**. A similar situation (anion stabilization by two cyano groups as in **36**) may pertain to **35**, which gives an ethanol addition product **37** apparently derived from a ketene imine.[26]

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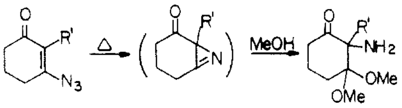
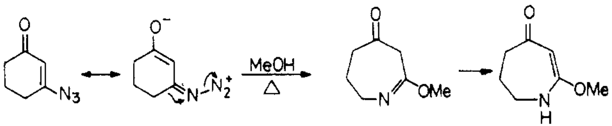
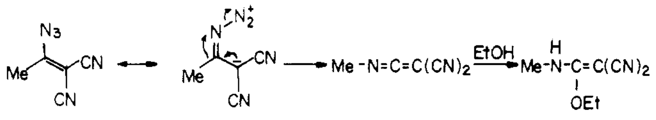
A further example appears to be the formation of isocyanate **41** upon thermolysis of azirine **38**;[27] this can be explained by the intermediacy of **39** and **40**.



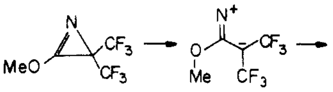
29 30 31



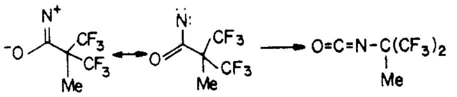
32 33 34



35 36 37



38 39



40 41

Experimental Section

The melting point of azide **15** is uncorrected. The infrared spectrum of azirine **16** was recorded on a Perkin-Elmer Model 177 grating infrared spectrometer. The mass spectrum was obtained with a Finnigan 4021 EI CI mass spectrometer. The NMR spectra were recorded at 300.1 (^{1}H) and 75.5 (^{13}C) MHz on a Bruker AM 300 spectrometer. Unless otherwise specified, spectral data refer to $CDCl_3$ solutions, with tetramethylsilane as internal reference. Solvents were obtained from Bio-Lab Ltd. Laboratories, Jerusalem, and Frutarom Laboratory Chemicals, Haifa, Israel, and were used as such. Merck silica gel 60 (230–400 mesh) and Merck aluminum oxide 60 active basic from E. Merck AG, Darmstadt, West Germany, were used as chromatographic materials.

Samples of the azides **10**[39] and **15**[28] were prepared according to the literature. Compound **10** was purified prior to use by filtration through a batch of basic alumina and twice repeated crystallization at -10 °C from a small amount of ether. Traces of the solvent were removed in vacuo in the cold, yielding light yellow crystals, mp 0–2 °C. Compound **15** was purified prior to use by recrystallization from ether–pentane: mp 63–64 °C (lit.[28] mp 63.5–64 °C).

2-Benzoyl-3-phenyl-1-azirine (16). α-Azidochalcone (**15**) (1.83 g, 7.34 mmol) was refluxed in 25 mL of dry CCl_4 for 1.5 h. After removing the solvent in vacuo, most of the starting material was recovered by crystallization from 5 mL of ether–pentane (1:2) at −10 °C. The crude azirine in the mother liquor was flash chromatographed on silica gel (120 g) using ether–pentane (1:5) as eluent. After 0.33 g of **15** in the first fraction, azirine **16** was eluted. Evaporation under reduced pressure gave 0.26 g of spectroscopically pure **16** as a yellow oil; 1.36 g of azide **15** were recovered by recrystallization. Yield of **16**: 63% of the unrecovered chalcone.

16: IR (neat) 3070, 3036, 1720, 1668, 1600, 1498, 1454, 1323, 1229, 1179, 1009 cm^{-1}; ^{1}H NMR[40] ($CDCl_3$) δ 8.30 (2 H, dd, o), 7.72 (1 H, tt, p), 7.57 (2 H, tt, m), 7.31 (3 H, m, m′, and p′), 7.19 (2 H, dd, o′), 3.51 (1 H, s, 3-H); ^{13}C NMR[40] ($CDCl_3$) δ 182.42 (s, C=O), 165.26 (s, 2-C), 138.78 (s, ipso), 135.43 (d, p), 134.53 (s, ipso′), 129.50 (d, o), 129.17 (d, m), 128.37 (d, m′) 127.78 (d, p′), 126.31 (d, o′), 37.74 (d, 3-C); MS (EI, 30 eV) *m/e* (relative intensity) 221 (99, M$^+$), 105 (100, PhCO$^+$); other peaks have less than 10% relative intensity.

Kinetics. The kinetic data were obtained from the integration of the nonaromatic proton signals of starting material and products as a function of time. Bromobenzene-d_5 (Aldrich) was used as a solvent and was additionally dried by passing through basic alumina prior to use. Solutions were prepared in oven-dried NMR tubes and initial substrate concentrations were 0.01–0.03 M; within this range there was no measurable effect of concentration on the kinetic results. Probe temperatures were measured with an Omega 870 digital thermometer with an alumel–chromel thermocouple before and after each experiment; readings were within 0.5 °C. Rate constants were deduced from semilog plots of the molar fractions obtained from the NMR integrals. $\Delta G^{\ddagger}$ values were then calculated by using the Eyring equation.

Acknowledgment. We are greatful to the Minerva Foundation for a fellowship to N.H.W., to Prof. H. Tauiguchi for stimulating discussions and to the Japan Ministry of Culture for a visiting professorship to A.H.

Registry No. 10, 16717-64-9; 15, 26087-01-4; 16, 102682-71-3; 19, 5415-07-6.

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(40) Multiplicities of the ^{1}H NMR data are derived from the shape of the signals regardless of fine splitting or smaller side signals. The terms ipso, o, m, and p are used for the benzoyl group whereas ipso′, o′, m′, and p′ belong to the 3-phenyl group. Assignments of the ^{13}C NMR signals are derived from chemical shifts and from the residual coupling constants in an off-resonance decoupled spectrum.