0.0258 mol) in benzene (20 ml) were mixed and stirred overnight and upon work-up gave 2.15 g (50%) of bis(2,4-dinitrophenyl) disulfide, mp *ca.* 310°, and 2.92 g (50%)[8] of 1,1-bis(2,4-dinitrophenylthio)-2-*N*-ethylcyclohexylaminoethene (**4**): mp 186–188° (orange crystals from CH_3CN); ir (KBr) 3045 (w), 2960 (m), 2925 (w), 1565 (s, broad, C=C), 1510 (s, NO_2), 1420 (w), 1325 (s, NO_2), 1295 (w), 1125 (w), 1040 (m), 910 (m), 830 (m), and 730 cm^{-1} (m); nmr (DMSO-d_6) δ 8.87 (d, 2, J = 2 Hz, two nitrobenzene C_3 H's), 8.63 (dd, 2, J = 2, 8.5 Hz, two nitrobenzene C_5 H's), 8.01 (d, 2, J = 8.5 Hz, two nitrobenzene C_6 H's), 7.62 (s, 1, –C**H**=C), 3.93–3.28 (broad m, 3, –C$\mathbf{H_2}$$CH_3$ and NCH), 2.1–1.07 (br m, 13, –CH_2C$\mathbf{H_3}$ and five cyclohexyl CH_2's); mass spectrum (70 eV) *m/e* (rel intensity) 368 (9.9), 3.58 (20.9), 289 (13.9), 246 (10.2), 200 (13.6), 199 (18.1), 196 (11.5), 183 (22.1), 180 (22.9), 138 (10.9), 137 (11.6), 134 (18.4), 127 (28.4), 126 (15.9), 112 (13.2), 107 (14.7), 98 (15.5), 95 (21.3), 90 (13.2), 85 (13.6), 84 (100), 83 (21.7), 82 (11.6), 79 (26.0), 75 (12.2), 74 (15.5), 71 (22.2), 70 (10.0), 69 (23.8), 67 (12.7), 64 (59.6), 63 (52.7), 62 (12.5), 58 (10.8), 56 (46.9), 55 (39.2), 54 (10.9), 51 (12.40), 48 (17.7), 45 (19.2), 44 (57.3), 43 (12.1), 42 (12.9), 41 (38.8), 39 (20.6), 32 (8.1), 30 (43.3), 29 (17.5), 28 (73.6), 27 (16.3), 18 (96.7), 17 (20.0).

***N*,*N*-Diisopropylethylamine.**—A mixture of 2,4-dinitrobenzenesulfenyl chloride (5.00 g, 0.0213 mol) in dry benzene (25 ml) and *N*,*N*-diisopropylethylamine (2.75 g, 0.0123 mol) in benzene (20 ml) was stirred for 24 hr at room temperature under N_2 and processed as above to give 2.00 g (47%) of bis(2,4-dinitrophenyl) disulfide, mp *ca.* 310°, and 2.81 g (50%)[8] of 1,1-bis(2,4-dinitrophenylthio)-2-diisopropylaminoethene (**5**): mp 226–228° (bright red crystals from CH_3CN); ir (KBr) 3045 (w), 2895 (w), 1590 (s), 1570 (s, C=C), 1510 (s, NO_2), 1450 (w), 1335 (s, NO_2), 1300 (m), 1180 (w), 1150 (w), 1130 (w), 1090 (w), 1042 (m), 910 (m), 830 (m), and 730 cm^{-1} (m); nmr (DMSO-d_6) δ 8.90 and 8.87 (two overlapping d, 2, J = 2 Hz for each d, two dinitrobenzene C_3 H's), 8.62 and 8.59 (two overlapping doublet of doublets, 2, J = 2, 8 Hz for each d d, two dinitrobenzene C_5 H's), 8.00 and 7.98 (two overlapping d, 2, J = 8 Hz for each d, two dinitrobenzene C_6 H's), 7.74 (s, 1, –C**H**=C), 4.33 [broad m, 2, two –C**H**$(CH_3)_2$], 1.22 [d, 12, J = 6 Hz, two –CH$(C\mathbf{H_3})_2$]; mass spectrum (70 eV) *m/e* (rel intensity) 523 (4.9), 358 (11.1), 340 (42.2), 298 (28.3), 200 (12.5), 199 (22.5), 196 (14.0), 183 (29.7), 181 (14.7), 180 (31.8), 169 (11.1), 137 (13.7), 134 (19.3), 131 (10.0), 119 (13.1), 107 (12.4), 100 (17.6), 95 (18.2), 86 (55.1), 79 (14.9), 72 (17.5), 70 (54.2), 69 (54.9), 64 (25.9), 63 (34.5), 58 (23.6), 48 (10.5), 45 (13.5), 44 (86.0), 43 (100), 42 (23.6), 41 (37.7), 39 (19.0), 30 (19.6), 28 (15.9), 27 (16.2), 19 (12.7).

Anal. Calcd for $C_{20}H_{21}N_5O_8S$: C, 45.88; H, 4.04; N, 13.38; S, 12.25. Found: C, 45.94; H, 4.03; N, 13.32; S, 12.61.

Other Tertiary Amines.—Similar experimental conditions were applied to the reaction of 2,4-dinitrobenzenesulfenyl chloride and tri-*n*-propylamine, *N*-methylpiperidine, and tri-*n*-butylamine. In the last example the reaction mixture was refluxed for 1 hr. Each reaction gave bis(2,4-dinitrophenyl) disulfide, mp *ca.* 310° (77, 88, and 77% yield, respectively), and unreacted starting amine (85, 0, and 60% yield, respectively). The enaminic product observed in the preceding reactions was absent in these three examples.

Registry No.—**3**, 42362-43-6; **4**, 42362-44-7; **5**, 42362-45-8; **6**, 2217-55-2; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; triethylamine, 121-44-8; *N*,*N*-diethylcyclohexylamine, 91-65-6; *N*,*N*-diisopropylethylamine, 7087-68-5.

Catalysis by Tertiary Amines in the Thermolysis of Vinyl Azides to 1-Azirines

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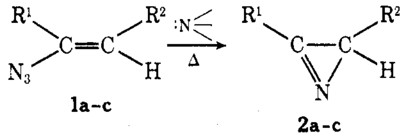
Recently, the chemistry of azirines has been widely studied and has aroused much interest. Azirines are generally prepared by pyrolysis[1] or photolysis[2] of corresponding vinyl azides. The more convenient procedure is to thermolyze the azides in aprotic solvents,[3–6] and the procedure is especially advantageous for the preparation on a large scale, although the yields are not always good. On the other hand, it has already been known that trivalent phosphines[7] and strong bases[8] catalyze the decomposition of azides and α-azido carbonyl compounds, respectively.

We have found a better method of converting vinyl azides **1a–c** to azirines **2a–c** by catalysis with tertiary amines. For instance, the azide **1a** was thermolyzed into the azirine **2a** quantitatively in refluxing toluene in the presence of 1,4-diazabicyclo[2.2.2]octane (Dabco). Without catalyst, the thermolysis was slow and gave a low yield. The results of the thermolyses are shown in Table I.



1a–c

2a–c

	R^1	R^2
a	C_6H_5	H
b	C_6H_5	CH_3
c	n-C_6H_{13}	H

TABLE I

THERMOLYSIS OF VINYL AZIDE IN THE PRESENCE OF TERTIARY AMINES

Run	Vinyl azide[a]	Solvent	Amine	Amine/ azide[b]	Temp, °C	Time, min	Yield of azirine,[c] %
1	**1a**	$C_6H_5CH_3$		0.0	110	40	65
2	**1a**	$C_6H_5CH_3$	$N(C_2H_5)_3$	1.4	110	30	85
3	**1a**	C_6H_5Cl	$N(C_2H_5)_3$	1.4	110	50	45
4	**1a**	$C_6H_5CH_3$	$PhN(C_2H_5)_2$	1.0	110	45	53
5	**1a**	$C_6H_5CH_3$	Dabco[d]	1.3	110	20	95
6	**1a**	$C_6H_5CH_3$	Dabco	0.013	110	50	93
7	**1a**	C_6H_6	Dabco	1.3	80	50	24[e]
8	**1b**	$C_6H_5CH_3$	Dabco	1.3	110	20	92
9	**1c**	$C_6H_5CH_3$	Dabco	1.3	110	75	44

[a] Concentrations of azide solutions were 10 wt % in all runs. [b] Mole ratio. [c] Determined by glpc and checked frequently during reactions until no large increase in the yield was found. [d] Diazabicyclo[2.2.2]octane. [e] Unchanged azide was recovered.

It is obvious that some tertiary amines not only accelerate the reaction rate but inhibit the formation of by-products, which are reported to be ketenimines and polymers in both pyrolytic and photolytic procedures.[1,2] Though α-azidostyrene (**1a**) is known to decompose slowly into the azirine **2a** even at room temperature,[9] the rate of the thermolysis greatly depends upon the temperature. As shown in Table I, changing a refluxing solvent from toluene to benzene caused the

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(1) G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

(2) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, **90**, 2869 (1968); *Tetrahedron Lett.*, 1545 (1967).

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

(4) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967).

(5) K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, 3499 (1968).

(6) F. P. Woerner and H. Reimlinger, *Chem. Ber.*, **103**, 1908 (1970).

(7) R. A. Abramovitch and E. P. Kyba in "The Chemistry of the Azido Group," S. Patai, Ed., Interscience, London, 1971, pp 294–296.

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

(9) J. H. Boyer, W. E. Krueger, and R. Modler, *Tetrahedron Lett.*, 5979 (1968).

remarkable retardation of the reaction. Chlorobenzene was also unsuitable for the solvent.

Among tertiary amines employed in the thermolysis, Dabco was the most effective and *N,N*-diethylaniline, which showed negative effect, was the least. With triethylamine, thermolysis gave the azirine **2a** in a high yield, but the reaction was slower than with Dabco. Hence, the order of the effectiveness is just in the order of basicity of the amines.

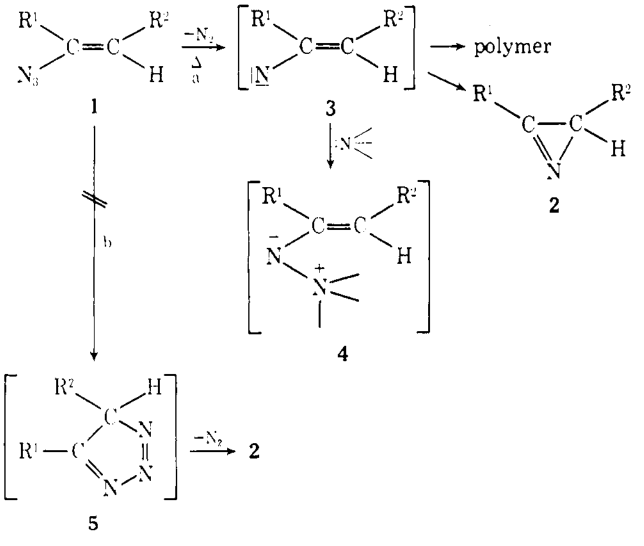
By measuring the rate of nitrogen evolution in the thermolyses, nitrogen release from the vinyl azide **1a** was found to obey good first-order kinetics. The rate constants are listed in Table II. The rates are equal within an experimental error when toluene was employed as a solvent, showing that these amines do not participate in the step of nitrogen release from the azide. The low rate in chlorobenzene is due to the increase in solvent polarity, since the highly polarized vinyl azide should be more stabilized than the intermediate or the product by a polar solvent. Consequently, it is reasonable to postulate a nitrene intermediate **3** which is formed with the release of nitrogen from the azide **1** in the initial step. The intermediate **3** will convert into an azirine **2** by intramolecular cyclization or into polymers. However, in the presence of a tertiary amine, the formation of a 1:1 adduct **4** is expected and this intermediate will give an azirine exclusively. Postulation of the adduct **4** is supported by the fact that a relatively stable adduct **6** is obtained in decomposition of benzenesulfonyl azide in refluxing pyridine.[10] Such a coordination is sterically hindered in the case of *N,N*-diethylaniline, which has poor coordinating ability because of its lower basicity. In this case, the presence of the amine instead promotes the polymerization reaction.

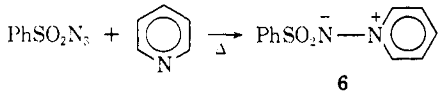
Table II

Rate Constant for N_2 Evolution in Thermolysis of α-Azidostyrene (**1a**) at 110°

Run[a]	Solvent	Amine catalyst	$k \times 10^3$, sec^{-1}
1	Toluene		2.03
2	Toluene	NEt_3	2.03
3	Chlorobenzene	NEt_3	1.04
4	Toluene	$PhNEt_2$	1.92
5	Toluene	Dabco	2.15

[a] Run numbers correspond to those in Table I.





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Our runs were not successful in capturing the nitrene **3**. Similar failures in detecting nitrenes are reported in some pyrolyses and photolyses of vinyl azides.[1,11,12] However, these failures to detect any of the nitrenes do not necessarily exclude the formation of a nitrene intermediate.

As an alternative mechanism, Smolinsky proposed a triazole intermediate **5** formed by an initial cyclization.[1] This cyclization does occur in a strong basic medium, but does not take place in neutral or protic solvents, as loss of nitrogen molecule occurs much faster.[6,13] If path b to a triazole **5** in neutral solvents is promoted by an amine as a base, the rate of nitrogen evolution of the thermolysis with amines should be greater than that without amines. However, the rates are equal and, therefore, path b may be excluded.

Experimental Section

Infrared spectra of the products were obtained on a JASCO IR-E spectrophotometer and showed good agreements with those of authentic samples. Gas-liquid phase chromatographic analyses were performed on a Ohkura MS-1100 instrument using the following column: 4 mm × 2 m, 3% silicon gum SE-52 on 80-100 mesh Chromosorb W.

Materials.—α-Azidostyrene (**1a**) was prepared by Smolinsky's procedure[1] and 1-azido-1-phenylpropene (**1b**) and 2-azido-1-octene (**1c**) were obtained by the method of Fowler.[4] Authentic azirines **2a-c** were prepared by photolysis of the corresponding vinyl azides:[2] **2a**, bp 76° (10 mm), ir 1745 cm^{-1} (C=N); **2b**, bp 78° (10 mm), ir 1740 cm^{-1} (C=N); **2c**, bp 87° (40 mm), ir 1765 cm^{-1} (C=N).

Thermolysis of Vinyl Azides.—The general procedure for the thermolysis was as follows. In a 50-ml three-necked flask fitted with a dropping funnel, a magnetic stirrer, a thermometer, and a condenser whose top was connected with a gas buret, a solution of a tertiary amine was heated to the reaction temperature under nitrogen atmosphere. Then a vinyl azide was added through the funnel all at once and the rate of nitrogen evolution was measured. On a parallel run performed under the same conditions, the yield of a produced azirine was estimated by glpc.

Registry No.—**1a**, 16717-64-9; **1b**, 28022-21-1; **1c**, 42393-62-4; **2a**, 7654-06-0; **2b**, 16205-14-4; **2c**, 42393-63-5.

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One-Step Synthesis of 1,1-Dimethyl- and 1-Spirocycloalkano-1,2,3,4-tetrahydro-β-carbolines

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The condensation of tryptamine and substituted tryptamines with aldehydes and with α-keto acids in aqueous solution to yield 1-alkyl- and 1-alkyl-1-carboxy-