50.5%) determined from the signal at δ 1.23 [-CH(CH$_3$)$_2$] and 4-isopropenylpyridine (**30**, 49.5%) determined from the signal at δ 2.13 [pyr-C(CH$_3$)=CH$_2$]. The nmr spectrum of the mixture had the following peaks: nmr (CDCl$_3$) δ 8.67–8.50 (m, 4, pyr C$_2$ H, C$_6$ H), 7.31 (m, 2, C$_3$ H, C$_5$ H, of 4-isopropenylpyridine), 7.16 (m, 2, C$_3$ H, C$_5$ H of 4-isopropylpyridine), 5.57 [s, 1, pyr-C(CH$_3$)=CH], 5.28–5.20 [m, 1, pyr-C(CH$_3$)=CH], 2.87 [septet, 1, pyr-CH(CH$_3$)$_2$], 2.13 [s, 3, pyr-C(CH$_3$)=CH$_2$], and 1.23 [d, 6, pyr-CH(CH$_3$)$_2$].

Registry No.—**11,** 69-30-0; **12,** 42362-46-9; **13,** 42362-47-0; **14,** 42362-48-1; **15,** 3678-72-6; **16,** 42362-50-5; **17,** 7669-54-7; **18,** 42362-51-6; **20,** 937-32-6; **21,** 42362-52-7; **23,** 931-59-9; **24,** 42362-53-8; **28,** 42362-54-9; **29,** 40473-14-1; **30,** 17755-30-5; **31,** 42362-57-2; 1-phenyl-1-(4-pyridyl)ethanol, 19490-94-9; phenyl disulfide, 882-33-7; Cl$_2$, 7782-50-5; 4-nitrophenyl disulfide, 100-32-3; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; trichloromethanesulfenyl chloride, 594-42-3; sulfur monochloride, 10025-67-9; diphenyl-4-pyridylmethyl disulfide, 42362-59-4.

Notes

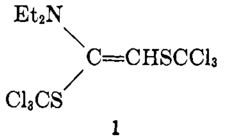
Reaction of Tertiary Aliphatic Amines with 2,4-Dinitrobenzenesulfenyl Chloride

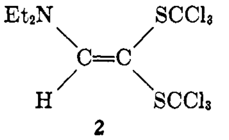
Vincent J. Traynelis* and James N. Rieck[1]

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

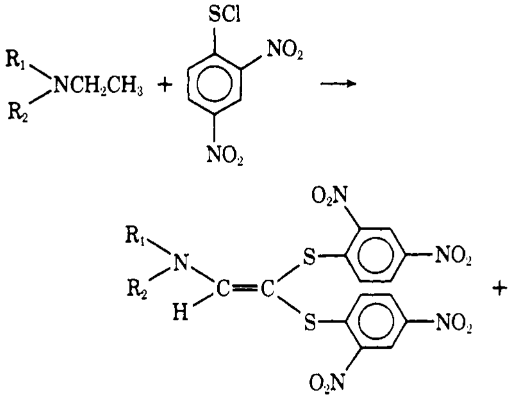
Received July 24, 1973

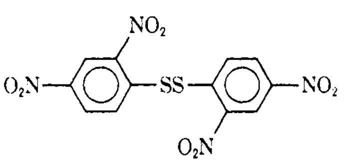
Sulfenyl chlorides react readily with primary and secondary amines to form sulfenamides;[2,3] however, tertiary amines appeared to be inert and useful as bases in the reactions of sulfenyl chlorides.[2] Some years ago Senning[4] observed a reaction between trichloromethanesulfenyl chloride and triethylamine which produced a bis(trichloromethylthio)-*N*,*N*-diethylaminoethene which was assigned structure **1**, although structure **2** could not be ruled out on the basis of spectral and chemical evidence. In a recent report Senning and Kelly[5] changed the assignment to structure 2, which was supported by an X-ray crystallographic study.[6] In addition they reported[5] that attempts to extend this reaction to several other amines, such as tri-*n*-propylamine, tri-*n*-butylamine, diethylmethylamine, and others, with trichloromethanesulfenyl chloride were unsuccessful and the reaction of triethylamine and *o*-nitrobenzenesulfenyl chloride or 1,2,2,2-tetrachloroethanesulfenyl chloride failed to produce any products.


1


2

In our study of the formation of *N*-arylthiopyridinium salts[7] we had occasion to examine the mixture of triethylamine and 2,4-dinitrobenzenesulfenyl chloride and observed that reaction occurred with the formation of 1,1-bis(2,4-dinitrophenylthio)-2-*N*,*N*-diethylaminoethene (**3**). This reaction has been extended with 2,4-dinitrobenzenesulfenyl chloride and *N*,*N*-diethylcyclohexylamine or *N*,*N*-diisopropylethylamine with the formation of **4** and **5**, respectively. However, similar reactions of 2,4-dinitrobenzenesulfenyl chloride with tri-*n*-propylamine, tri-*n*-butylamine, and *N*-methylpiperidine failed to produce the corresponding enamines. The yield for each of the enaminic products **3**, **4**, and **5** was approximately 50%[8] as was the yield of bis(2,4-dinitrophenyl) disulfide (**6**) in each reaction.


3, R$_1$ = R$_2$ = CH$_3$CH$_2$
4, R$_1$ = *c*-C$_6$H$_{11}$; R$_2$ = CH$_3$CH$_2$
5, R$_1$ = R$_2$ = (CH$_3$)$_2$CH


6

The accountability for the starting sulfenyl chloride was essentially quantitative in each reaction.

The assignment of structures **3**, **4**, and **5** was based on elemental analysis, on spectral data, and by analogy to compound **2** reported by Senning.[5] The infrared spectra showed the presence of the dinitrobenzene rings and the presence of the enaminic double bond (1585, 1565, 1570, and 1578 cm^{-1} [5] for **3**, **4**, **5**, and **2**, respectively) while the nmr had a characteristic olefinic peak (δ 7.43, 7.62, 7.74, and 7.55[5] for **3**, **4**, **5**, and **2**, respectively). In addition the nmr spectrum for **3** and **5** revealed the presence of two different dinitro-

---

[1] Abstracted from a portion of the Ph.D. Dissertation submitted by J. N. R. in April 1973 at West Virginia University.

[2] N. Kharasch, *J. Chem. Educ.*, **33**, 585 (1956).

[3] R. B. Langford and D. D. Lawson, *J. Chem. Educ.*, **34**, 510 (1957).

[4] A. Senning, *Angew. Chem., Int. Ed. Engl.*, **4**, 992 (1965).

[5] A. Senning and P. Kelly, *Acta Chem. Scand.*, **26**, 2877 (1972).

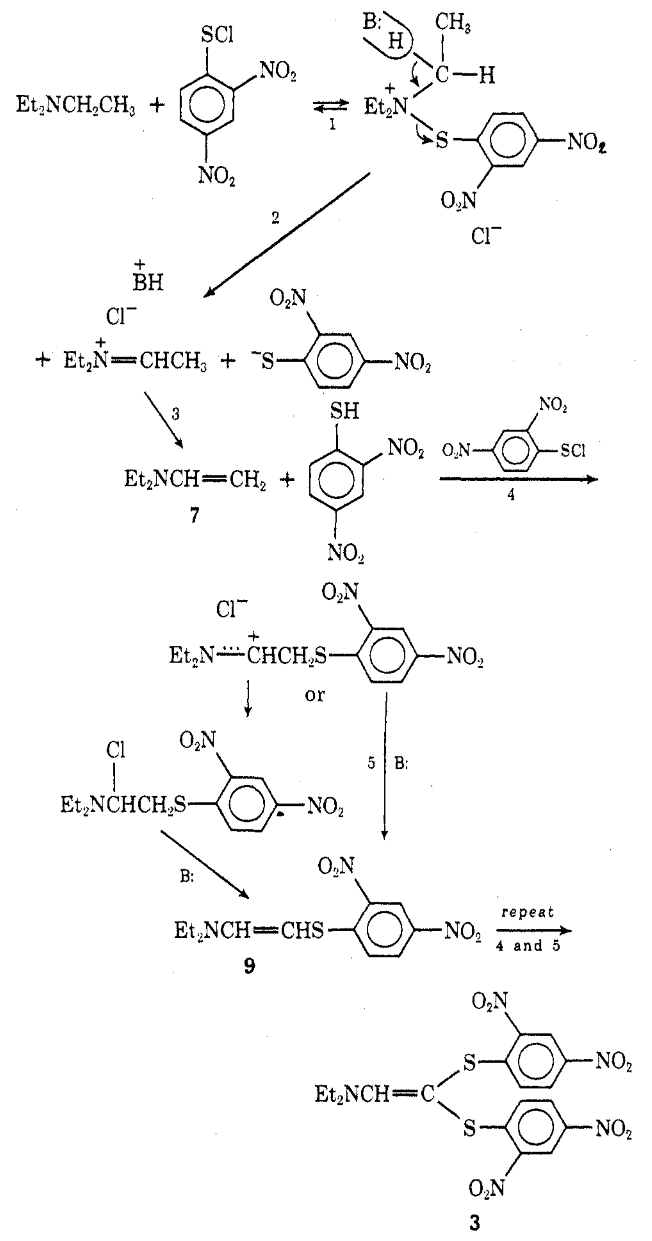
[6] See ref 5 for citation of paper, *Acta Chem. Scand.*, in press.

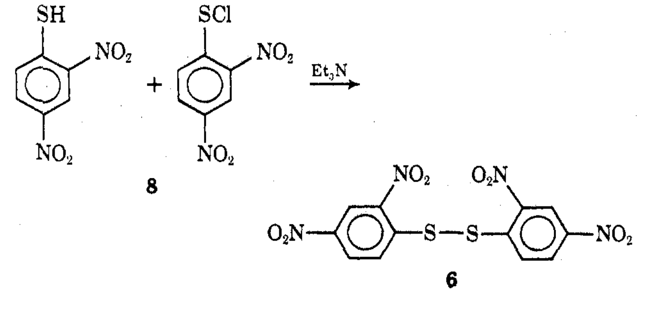
[7] V. J. Traynelis and J. N. Rieck, *J. Org. Chem.*, **38**, 4334 (1973).

[8] The yield of the enaminic products was based on 2,4-dinitrobenzenesulfenyl chloride.

benzene rings which overlapped but had identical coupling characteristics. Attempts to hydrolyze **3** under either acidic or basic conditions were unsuccessful, which parallel Senning's[5] observations.

The formation of these unique enamines may be rationalized by initial *N*-thioammonium salt formation and conversion to a *N*,*N*-diethylvinylamine (**7**), followed by an addition–elimination sequence of sulfenyl chloride to the enamine. The steps are detailed below. The reaction scheme proposed above resembles one offered by Senning[5] and parallels the reaction of triethylamine with trichloroacetyl chloride.[9-11] In the latter case only a single substitution occurs on the β





$$\mathrm{Et_2NCH_2CH_3 + Cl_3CCCl \longrightarrow Et_2NCH{=}CHCCCl_3}$$

carbon of the *N*,*N*-diethylvinylamine intermediate. Senning[5] has reported that the reaction of *N*,*N*-diethylvinylamine and trichloromethanesulfenyl chloride in the presence of trimethylamine leads to compound **2**. Further support for steps 4 and 5 can be found in the substitution of *o*-nitrobenzenesulfenyl chloride on the β carbon of enamines.[12-14] Failure to isolate the monosubstituted enamine **9** finds precedence in the reaction of heterocyclic methylene bases with *o*-nitrobenzenesulfenyl chloride, which led to the disubstituted enamine derivatives.[14]

The origin of the bis(2,4-dinitrophenyl) disulfide (**6**) can be explained by the reaction of 2,4-dinitrothiophenol (**8**), proposed as a by-product in the formation of *N*,*N*-diethylvinylamine (**7**), and 2,4-dinitrobenzenesulfenyl chloride. The yields of the enamine **3** and the disulfide **6** approach or are at their quantitative limits according to the proposed mechanism. The steps which require supportive evidence are steps 1 and 2, the formation of the *N*-thioammonium salt followed by elimination to an immonium ion. One also needs to consider why this reaction fails to produce the bisarylthioenamine when the tertiary amine lacks an ethyl group.

Experimental Section[15]

Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Tertiary Aliphatic Amines. Triethylamine.—A solution of 2,4-dinitrobenzenesulfenyl chloride (5.00 g, 0.0213 mol) in CH_2Cl_2 (40 ml) under N_2 was added to a stirred solution of triethylamine (3.68 g, 0.086 mol) in CH_2Cl_2 (30 ml) at 0° and the reaction mixture was stirred for 2 hr while it slowly warmed up to room temperature. The mixture was filtered and gave 2.1 g (50%) of bis(2,4-dinitrophenyl) disulfide, mp ~310° (lit.[16] mp 290–300°). The solvent was removed from the filtrate and left 2.5 g (47%)[8] of 1,1-bis(2,4-dinitrophenylthio)-2-*N*,*N*-diethylaminoethene (**3**). Recrystallization of the crude solid from CH_3CN gave an analytical sample as dark red crystals: mp 210–212°; ir (KBr) 3095 (w), 2980 (w), 2940 (w), 1585 (s, C=C), 1510 (s, NO_2), 1440 (w), 1330 (s, NO_2), 1300 (m), 1125 (w), 1074 (w), 1040 (m), 905 (m), 825 (m), and 728 cm^{-1} (m); nmr ($CDCl_3$) δ 9.13 and 9.08 (two overlapping d, 2, J = 2.5 Hz for each d, two dinitrobenzene C_3 H's), 8.55 and 8.51 (two overlapping doublet of doublets, 2, J = 2.5, 9 Hz for each d d, two dinitrobenzene C_5 H's), 7.93 and 7.90 (two overlapping d, 2, J = 9 Hz for each d, two dinitrobenzene C_6 H's), 7.43 (s, 1, -CH=C), 3.57 (q, 4, J = 7 Hz, 2 $-CH_2CH_3$), 1.27 (t, 6, J = 7 Hz, 2 $-CH_2CH_3$).

Anal. Calcd for $C_{18}H_{17}N_5O_8S_2$: C, 43.63; H, 3.46; N, 14.13; S, 12.92. Found: C, 44.09; H, 3.68; N, 14.11; S, 12.43.

***N*,*N*-Diethylcyclohexylamine.**—Using the above procedure 2,4-dinitrobenzenesulfenyl chloride (5.00 g, 0.0213 mol) in dry benzene (20 ml) and *N*,*N*-diethylcyclohexylamine (3.98 g,

---

[9] A. M. Platoshkin, Y. A. Cheburkov, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 112 (1969); *Chem. Abstr.*, **70**, 114541c (1969).

[10] R. R. Fraser and R. B. Swingle, *Tetrahedron*, **25**, 3469 (1969).

[11] R. Giger, R. Allain, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 120 (1970).

[12] M. E. Kuehne, *J. Org. Chem.*, **28**, 2124 (1963).

[13] G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **29**, 798 (1964).

[14] V. I. Dénes, M. Fărcăsan, and G. Ciurdaru, *Chem. Ber.*, **96**, 174 (1963).

[15] All melting points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Clark Microanalytical Laboratory, Urbana, Ill. Infrared spectra were determined on a Beckman IR-8 or a Beckman IR-20A spectrometer, nmr spectra were recorded on a Varian Associates Model HA-60-EL or A-60A spectrometer, and the mass spectra were obtained with a Nuclide Corp. 12-90G high-resolution mass spectrometer.

[16] N. Kharasch, W. King, and T. C. Bruice, *J. Amer. Chem. Soc.*, **77**, 931 (1955).

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, –CH=C), 3.93–3.28 (broad m, 3, –$\mathbf{CH_2}CH_3$ and NCH), 2.1–1.07 (br m, 13, –$CH_2\mathbf{CH_3}$ 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, –CH=C), 4.33 [broad m, 2, two –$CH(CH_3)_2$], 1.22 [d, 12, J = 6 Hz, two –$CH(CH_3)_2$]; 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

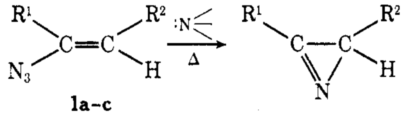
MITSUO KOMATSU,* SEIJI ICHIJIMA, YOSHIKI OHSHIRO, AND TOSHIO AGAWA

Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka, 565, Japan

Received July 20, 1973

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

---

(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).