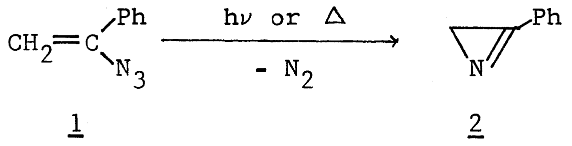
CHEMISTRY LETTERS, pp. 901-904, 1976. Published by the Chemical Society of Japan

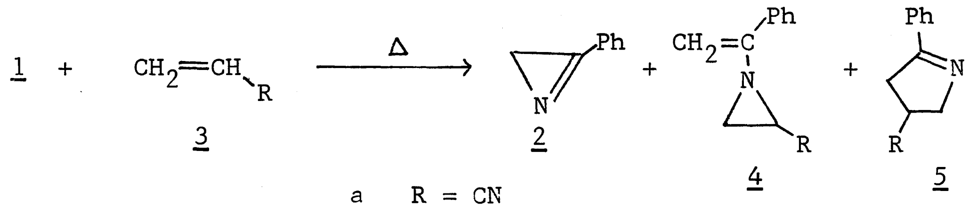
THERMAL DECOMPOSITION OF VINYL AZIDES IN ACRYLIC ACID DERIVATIVES: SYNTHESIS OF 1-VINYLAZIRIDINES

Yujiro NOMURA, Naoto HATANAKA, and Yoshito TAKEUCHI
Department of Chemistry, College of General Education,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

By the thermal decomposition of α- or β-azidostyrene and 2-azido-trans-2-butene in acrylonitrile or methyl acrylate were obtained 2-substituted 1-(1-phenylvinyl)aziridine, 1-trans-styrylaziridine, and 1-(1-methyl-cis-propenyl)aziridine, respectively, in good yields.

Thermal or photochemical decomposition of vinyl azides to 1-azirines has attracted attention;1~3) the thermolysis or photolysis of α-azidostyrene(1)4,5) gave 2-phenyl-1-azirine(2) nearly quantitatively. The decomposition of vinyl azides under the presence of a dipolarophile seems interesting because it was claimed1) that the decomposition proceeds via vinylnitrene, an active 1,3-dipole, though alternative pathways were also suggested.3) Thus, 1 was heated to reflux in excess acrylonitrile(3a) for 6.5 hr. After removal of acrylonitrile, three





a R = CN

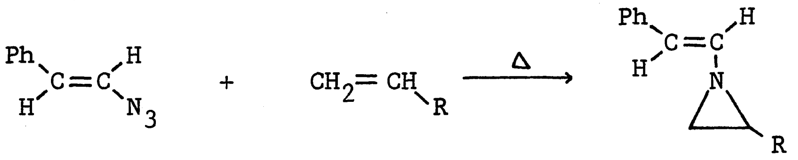
b R = CO_2Me

products, 2 (36 %), 2-cyano-1-(1-phenylvinyl)aziridine(4a, 45 %), 4-cyano-2-phenyl-1-pyrroline[6](5a, 7 %) were isolated from the residue; 2 and 4a were isolated by fractional distillation, and 5a (solid, mp 91.5-92.5°C) was independently separated from the reaction mixture by column chromatography on silica gel.

Similarly, 1 was heated to reflux in excess methyl acrylate(3b) to give 2 (15 %), 4b (68 %), and 5b[6] (6 %).

Separation of 1-vinylaziridines with column chromatography could not be adopted for the products were decomposed on silica gel or alumina. The yields of the products except 5a were estimated by vpc with naphthalene as an internal standard.

The reaction of β-azidostyrene(6)[7] with 3 afforded the corresponding 1-vinylaziridines(7) exclusively. Thus, 6 was heated to reflux in excess 3a or 3b for 2 hr. After removal of the solvent, 2-cyano- and 2-methoxycarbonyl-1-styrylaziridines(7a and 7b) were obtained by fractional distillation in 35 and 56 % yields respectively. The relatively low yield is responsible for the formation of polymeric substance.



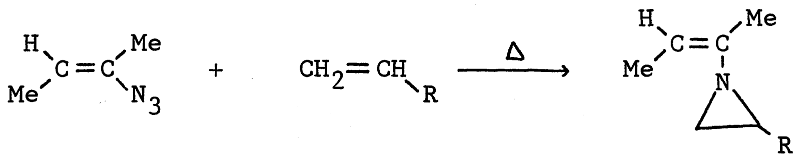
6 3 7

a R = CN

b R = CO_2Me

A large ^3J(14 Hz, see Table 1) for 7a and 7b clearly establishes the trans-configuration of styryl group.

Similarly, 2-azido-trans-2-butene(8)[5] was heated in refluxing 3a or 3b for 2.5 hr. After removal of the solvent, 1-(1-methyl-cis-propenyl)aziridines(9a and 9b) were obtained by fractional distillation in 73 and 83 % yields, respectively.



8 3 9

a R = CN

b R = CO_2Me

Though 1-vinylaziridines have the structure of enamine, they are not obtained by the conventional method of synthesis for enamines from carbonyl compounds and aziridines. Only a few of them have so far been prepared by the addition of aziridine to acetylenic compounds carrying strong electron-withdrawing substituent such as alkylsulfonyl, methoxycarbonyl, or cyano group to give a mixture of cis and trans products.[8,9] A noteworthy feature of the present method apart from its simplicity is the stereospecific preparation of vinylaziridines which seems to favor our method over the previous ones.

All of 1-vinylaziridines described here are new compounds, and the spectral data and elemental analyses are consistent with the proposed structure. Physical data for 1-vinylaziridines prepared from the vinyl azides are given in Table 1.

Table 1. Physical Data of 1-Vinylaziridines

	bp (°C)	MS (M^+)	ir $\nu_{C=C}$ (cm^{-1})	nmr (δ)** vinyl proton	nmr (δ)** aziridine ring proton
<u>4a</u>	112-113/0.5 mmHg	170	1640	4.42(d, J=1.6 Hz) 4.84(d, J=1.6 Hz)	2.2-2.5(m)
<u>4b</u>	110-112/0.5 mmHg	203	1620	4.52(d, J=1.6 Hz) 4.86(d, J=1.6 Hz)	2.0-2.6(m)
<u>7a</u>	53-54*	170	1640	6.14(d, J=14 Hz) 6.75(d, J=14 Hz)	2.3-2.6(m)
<u>7b</u>	112-114/0.1 mmHg	203	1630	6.01(d, J=14 Hz) 6.73(d, J=14 Hz)	2.0-2.6(m)
<u>9a</u>	44-45/0.3 mmHg 29.5-30.5*	122	1670	4.84(q, J=7 Hz)	2.2-2.7(m)
<u>9b</u>	45-47/0.2 mmHg	155	1670	4.73(q, J=7 Hz)	2.1-2.7(m)

* mp ** JEOL JMH-100, 100 MHz, $CDCl_3$, TMS as an internal standard

References

1) A. Hassner and F. W. Fowler, J. Am. Chem. Soc., 90, 2869 (1968).
2) M. Komatsu, S. Ichijima, Y. Ohshiro, and T. Agawa, J. Org. Chem., 38, 4341 (1973).
3) G. L'abbé and G. Mathys, J. Org. Chem., 39, 1778 (1974).
4) A. Hassner, F. W. Fowler, and L. A. Levy, J. Am. Chem. Soc., 89, 2077 (1967).
5) A. Hassner and F. W. Fowler, J. Org. Chem., 33, 2686 (1968).
6) A. Padwa, M. Dharan, J. Smolanoff, and W. I. Wetmore, Jr., J. Am. Chem. Soc., 95, 1945 (1973).
7) A. Hassner and F. Boerwinkle, J. Am. Chem. Soc., 90, 216 (1968).
8) W. E. Truce and C. G. Brady, J. Org. Chem., 31, 3542 (1966).
9) T. Sasaki, T. Yoshioka, and K. Shoji, J. Chem. Soc. (C), 1969, 1086.

(Received July 2, 1976)