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AZIRIDINAMINE CHEMISTRY, I. -- THERMAL DECOMPOSITION OF CIS AND TRANS-2,3-DIPHENYLAZIRIDINAMINE

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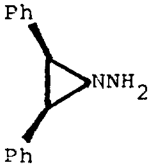
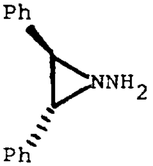
ABSTRACT: *Pyrolysis of the cis title compound gives over 99% trans-stilbene in various solvents at 33°-91°, while at higher temperatures 2,2-diphenylethanal hydrazone is produced: at 33°-175° the trans title compound gives 83-100% trans-stilbene.*

Reports concerning thermal decomposition of cis and trans-2,3-diphenylaziridinamine (1 and 2 respectively) appear to differ. Kirkley and Carpino have reported[1] that heating 1 at 120° without solvent gave 43% cis-stilbene, 27% trans-stilbene, and 30% of an unknown compound, while the decomposition of 2 in hot 95% ethanol gave 100% trans-stilbene.



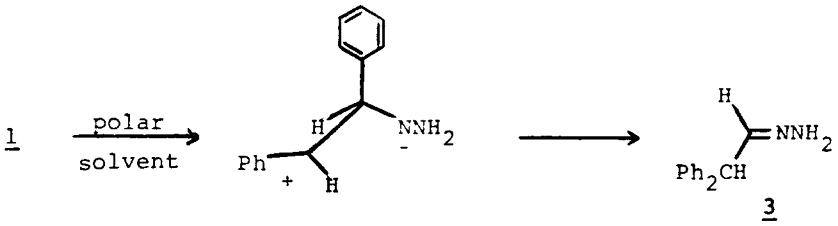
1



2

Eschenmoser et al. have reported[2] that pyrolysis of 1 in refluxing dichloromethane followed by silica gel chromatography gave 98.5% cis-stilbene; under similar conditions, 2 yielded 99.5% trans-stilbene. During a recent study of the reduction chemistry of compounds 1 and 2,[3] the decomposition behavior of these compounds again was studied, this time as a function of temperature and solvent. The results are listed in Tables 1 and 2.

Decomposition of 1[4] gives more than 99:1 trans:cis stilbenes at 33°-91° in all solvents used, although neat decomposition gives mixtures of trans:cis similar to those noted previously.[1a,5] At higher temperatures, a third product appears in the GC analysis and increases with temperature and solvent polarity, becoming essentially the sole product in acetonitrile at 175°. Spectral data[6] shows this third product to be 2,2-diphenylethanal hydrazone, 3. This product is apparently produced via a charge-separated intermediate, judging by the solvent effect on formation of 3. The putative intermediate then must undergo a 1,2-phenyl shift onto the (presumed) cationic center to give 3. Further experimentation is needed to show if the intermediate in this interesting rearrangement is also responsible for the stilbenes formed from 1 under other conditions.



Decomposition of **2** gives 83-100% *trans*-stilbene, with greater selectivity for *trans* reduction favored by higher reaction temperatures and lower solvent polarity. There is no reaction observed that is similar to that giving compound **3** from amine **1**, despite the slight solvent dependence that is observed.

The two aziridinamines thus decompose in quite different manners. While **1** exhibits nearly complete loss of stilbene stereochemistry, **2** exhibits mostly retention of stilbene stereochemistry. The results seem consistent with steric effects upon a multi-step fragmentation mechanism for these compounds. Decomposition of **1** presumably proceeds via broken-bond intermediate **4-c**,[7] which then undergoes rapid rotation of the benzylic center to relieve the eclipsed phenyl-phenyl steric strain. Loss of N_2H_2 (as either diimide, HN=NH, or as the isomer $N\text{-}NH_2$) would then have to be concerted with rotation, or else rapidly subsequent to it, since *trans*-stilbene is formed almost exclusively from **1**. Such behavior may be due to an energetic "recoil" effect, in which rapid rotation/decomposition of **4-c** permits relief of the steric strain in amine **1** (approximately 5.7 kcal/mole for **1** relative to amine **2**, if one uses the energy difference between *cis* and *trans* stilbene[8] as

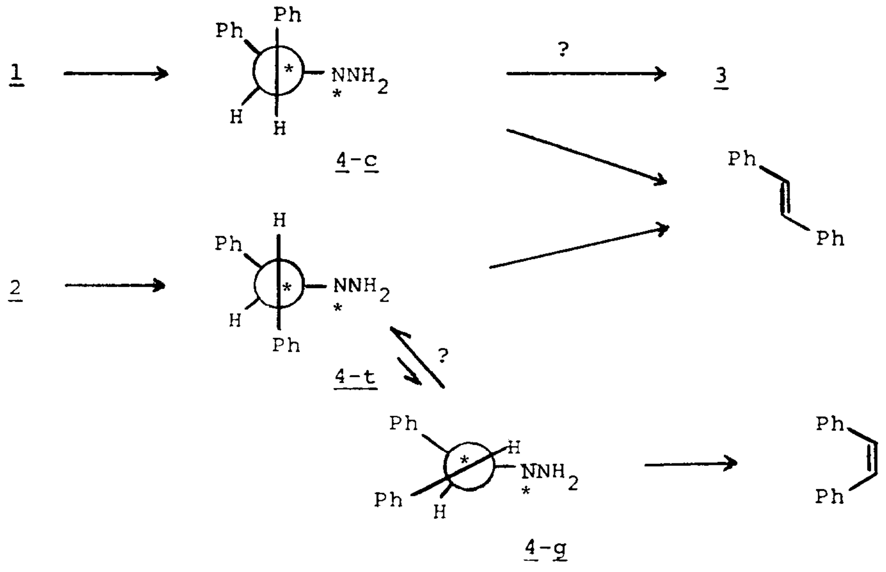


TABLE 1: Stilbenes from Thermal Decomposition of *Cis*-2,3-Diphenylaziridinamine, **1**.

°C/Time[a]	Solvent[b]	Percent Trans(Cis)-Stilbene[c]
33/4 days	PhH	99.5(0.5)
50/48h	CH	99.9(0.1)
50/48h	PhH	100.0(0.0)
50/48h	DME	100.0(0.0)
50/48h	MeCN	95.1(0.0)[d]
91/24h	PhH	99.4(0.6)
125/ 4h	PhH	85.4(1.1)[d]
175/ 3h	CH	99.5(0.5)
175/ 3h	PhH	17.5(0.1)[d]
175/ 3h	DME	42.2(0.0)[d]
175/ 3h	MeCN	0.0(0.0)[d]

[a] Reaction in sealed, base-washed Pyrex tubes, 0.02 *M* solutions of amine used.

[b] PhH = Benzene, CH = Cyclohexane, DME = Dimethoxyethane, MeCN = Acetonitrile.

[c] Analysis of products was done on a 6-foot 3% SE-30 column at 155° on a Varian Model 3700 Analytical Gas Chromatograph using a flame-ionization detector and electronic peak integrator.

[d] The balance of 100% for these reactions is 2,2-diphenylethanal hydrazone, **3**.

TABLE 2: Stilbenes from Thermal Decomposition of *Trans*-2,3-Diphenylaziridinamine, **2**.

°C/Time[a]	Solvent[b]	Percent Trans(Cis)-Stilbene[c]
33/4 days	PhH	88.7(11.3)
50/48h	CH	95.1(4.9)
50/48h	PhH	84.6(15.4)
50/48h	DME	86.9(13.1)
50/48h	MeCN	83.1(16.9)
91/24h	PhH	86.8(13.2)
125/ 4h	PhH	93.5(6.5)
125/ 4h	EtOH	100.0(0.0)
175/ 3h	CH	95.3(4.7)
175/ 3h	PhH	94.3(5.7)
175/ 3h	DME	96.6(3.4)
175/ 3h	MeCN	97.4(2.6)

[a] See note a in Table 1.

[b] PhH = Benzene, CH = Cyclohexane, DME = Dimethoxyethane, MeCN = Acetonitrile, EtOH = 95% ethanol.

[c] See note c in Table 1.

an estimate). On the other hand, single-bond cleavage of amine 2 should give intermediate 4-t initially. Since 2 does not have the eclipsed phenyl-phenyl strain of 1, 4-t is not as energetically "hot" a species as 4-c. Thus, 4-t might be expected to have a longer lifetime than 4-c, perhaps long enough to rotate to a conformer capable of giving the observed *cis*-stilbene before losing N_2H_2 (e.g., conformer 4-g).

Of course, other explanations might equally well fit the observed data. Experiments are therefore underway to establish more clearly the sequence of events and nature of transition states for these decompositions, as well as their possible relation to the rearrangement that gives hydrazone 3.

ACKNOWLEDGEMENTS: I thank the personnel of the Central Analytical Laboratory at the University of the West Indies at Mona for assistance in obtaining product analyses.

FOOTNOTES:

1a) L. A. Carpino, R. K. Kirkley, *J. Am. Chem. Soc.*, **92**, 1784(1970).

b) R. K. Kirkley, "Master's Thesis," University of Massachusetts, Amherst, MA, 1969.

2) R. Muller, D. Felix, J. Schreiber, A. Eschenmoser, *Helv. Chim. Acta*, **53**, 1479(1970).

3) See the subsequent article.

4) Compound 1 was synthesized by the method of footnote 2, compound 2 by the method of footnote 1a. Both were identified by comparison of spectral characteristics and melting points to the literature data.

5) Reproduction of the published conditions from footnote 2 for decomposition and workup of compound 1 gave 96-100% *trans*-stilbene in my hands, despite repeated efforts.

6) Spectral data for 3 -- ^{1}HNMR(,$CDCl_3$,60 MHz): 2.5(br s,NH_2), 4.76(d,J=2.5 Hz, Ph_2C-H), 7.2(m, 2 Ph), 9.83(d,J=2.5 Hz, N=C-H). -- MS(m/q,EI): 210(parent), 167(base, Ph_2CH+).

7) Asterisks indicate either a radical center or a charged (+,-) center.

8) R. T. Morrison, R. N. Boyd, "Organic Chemistry," 3rd edition, Allyn and Bacon, Boston, MA, USA, 1975, p. 402.

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