

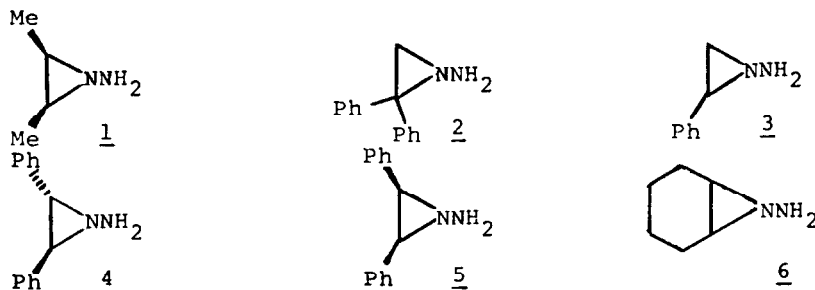
AZIRIDINAMINE CHEMISTRY, II. -- REDUCTION OF
ALKENES AND ALKYNES BY AZIRIDINAMINES

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ABSTRACT: *Copolyrolysis of several aziridinamines with alkenes and alkynes gives varying amounts of reduction--yields and stereochemistry of reduction vary substantially with the type of ring-substitution on the aziridinamines.*

Recently, cis-2,3-dimethylaziridinamine, 1, was found to reduce norbornene and 3-hexyne.¹ Since only one example of a similar reaction has been previously studied (reduction by 2,2-diphenylaziridinamine, 2²), this article is intended to present the results of reductions by compound 1, and in addition a preliminary study of the reduction chemistry of several other aziridinamines, 3-6.



Amines 1-4³, 5⁴, and 6³ were synthesized by literature methods: all were identified by comparison of their spectral data and physical properties to the literature data. Pyrolysis of 1-6 in the presence of 1-1.25 equivalents of norbornene followed by GC analysis of the crude reaction products shows varying yields of reduction to norbornane ranging from 0% for amine 5 to 74% for amine 4 (see Table 1). Reduction efficiency is improved by high reactant concentration and lower temperatures,⁵ but varies substantially with the type of ring-substitution on the aziridinamine. Amines 2 and 4 also reduce diethyl maleate to diethyl succinate (GC analysis, 10-foot 18% Carbowax 20M), while amine 5 gives no reaction at all under similar conditions; amines 3 and 6 only isomerize diethyl maleate to diethyl fumarate. Thus, the reduction efficiency of these amines is strongly dependent upon the amine substitution.

TABLE 1: Reduction of Norbornene to Norbornane by Aziridinamines 1-6.

Amine/Concentration(Solvent) ^a	Norbornene Concentration	% Reduction	°C/Time ^b
<u>1</u> /3.3 M (THF)	3.5 M	71 ± 2%	199°/2h
<u>2</u> /0.39 (DME)	0.48	30 ± 6	120°/1h
<u>3</u> /0.40 (DME)	0.50	22 ± 3	120°/1h
<u>4</u> /0.68 (DME)	0.76	47 ± 2	118°/2h
<u>4</u> /0.17 (DME)	0.19	28 ± 2	118°/2h
<u>4</u> /0.68 (DME)	0.76	74 ± 3	31°/14 days
<u>4</u> /0.17 (DME)	0.19	66 ± 3	31°/14 days
<u>5</u> /0.32 (DME)	0.40	none	118°/2h
<u>5</u> /0.3 (CH)	0.4	none	118°/2h
<u>6</u> /0.33 (DME)	0.40	3 ± 1	118°/2h
<u>6</u> /0.3 (CH)	0.4	4 ± 1	118°/2h

^aTHF = Tetrahydrofuran, DME = Dimethoxyethane, CH = Cyclohexane.

^bReaction in sealed, base-washed Pyrex tubes. Analysis on a 6-foot Poropak S column, using a Varian Model 3700 Analytical Gas Chromatograph and flame-ionization detector with electronic peak integrator (toluene internal standard).

TABLE 2: Reduction of 3-Hexyne to Hexenes by Cis-2,3-Dimethylaziridinamine, 1.

Temperature(°C) ^a	Cis/Trans-3-Hexene ^b
80	39/61
91	39/61
108	43/57
119	48/52
142	50/50
158	60/40
185	73/27

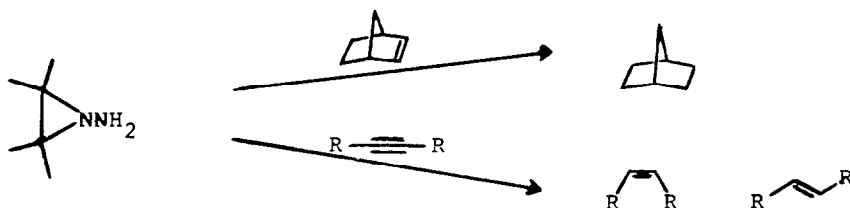
^aReaction in sealed Pyrex tubes containing solution 0.63 M in 1, 4.2 M in 3-hexyne, with THF solvent. Reactions were run to at least 90% amine decomposition; about 30% reduction occurs under these conditions.

^bAnalysis on a 10-foot dibutyl tetrachlorophthalate column at 28°.

TABLE 3: Reduction of Diphenylacetylene to Stilbenes by Aziridinamines 3 and 6.

Amine	Temperature(°C)/Time	Percent Cis Reduction ^a
<u>6</u> 	31°/5 days	100
		80 - 83
	65°/17h	100
		77 - 78
	89°/ 4h	100
		84 - 85
	115°/ 2h	100
		84 - 85
	158°/ 2h	100
		92 - 94

^aAnalysis by GC on a 10-foot 16% Carbowax 20M column, as in Tables 1 and 2.



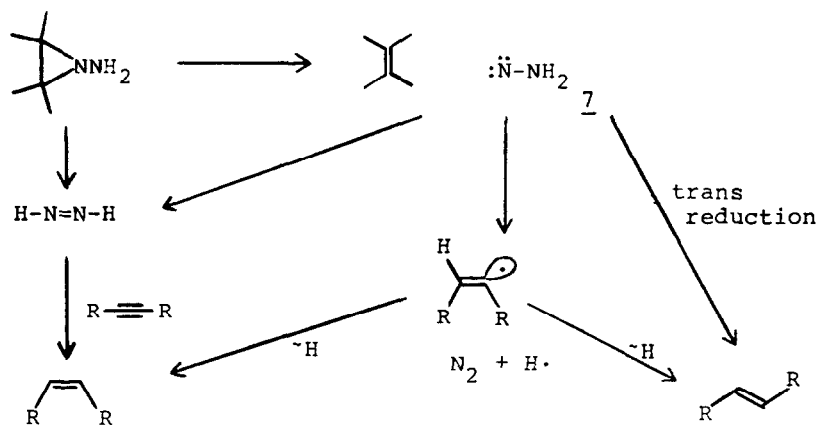
Copyrolysis of 3, 4, and 6 at 125° with five equivalents of diethyl acetylene dicarboxylate gives 5-20% reduction to mixtures of diethyl maleate and diethyl fumarate. However, only in the reduction by 4 does isomerization of the product maleic ester to the secondary product, fumaric ester, seem ruled out, so only here is it possible that diethyl fumarate is produced as a primary product by trans reduction. Amine 5 gives no reaction, while amine 2 reduces the acetylene to give only diethyl maleate, which is consistent with the selective cis reduction demonstrated earlier for 2.²

Copyrolysis of 1 with excess 3-hexyne at various temperatures gives mixtures of cis and trans-3-hexenes, as shown in Table 2.^{1,6} The proportion of cis isomer increases from 39% at 80° to 73% at 185° . A plausible explanation for this behavior is that diimide, the suspected reducing agent from amine 2,² is also produced from amine 1, and is more readily produced at high temperatures to give more cis reduction. At lower temperatures, another reduction process must be occurring. To see if this behavior occurs for other aziridinamines, amines 3 and 6 were pyrolyzed with excess diphenylacetylene, and the product stilbenes analyzed directly by gas chromatography (Table 3). Amine 6 gives only cis-stilbene at all temperatures, while amine 3 gives about 20% trans-stilbene at 30° - 89° , which proportion drops to about 7% at 158° .⁷

Thus, reduction of alkenes and alkynes varies substantially with the substitution upon the ring of the aziridinamine. Reduction by diimide, which is consistent with the results from amines 2 and 6, cannot be the sole pathway of reduction in the cases of amines 1, 3, and 4. Other reasonable mechanistic pathways include production of 1,1-diazene, 7, to give direct trans reduction, or, more likely, a radical chain initiated by 7 and involving the starting amine and/or solvent (see Scheme 1). It is possible that 7 may isomerize to diimide⁸ and/or that diimide is produced directly from decomposition of aziridinamines.

The observed variation in the reduction characteristics of these aziridinamines is novel, and further experiments therefore are underway in an attempt to clarify the nature of the reducing agents in these reductions, and to identify the origin of the substituent effect upon aziridinamine reduction efficiency and stereochemistry.

SCHEME 1



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FOOTNOTES:

- 1) P. M. Lahti, "Research Report," California Institute of Technology, Pasadena, CA 1979, p. 5 ff.
- 2) R. Annunziata, R. Fornasier, F. Montanari, *J. Org. Chem.*, **39**, 3195(1974).
- 3) D. Felix, R. Muller, V. Horn, S. Soos, J. Schreiber, A. Eschenmoser, *Helv. Chim. Acta*, **55**, 1272(1972).
- 4) L. A. Carpino, R. K. Kirkley, *J. Am. Chem. Soc.*, **92**, 1784(1970).
- 5) Compound 1 requires many days to decompose at less than 80^o, so its chemistry was not examined below this temperature.
- 6) I am most grateful to Professor Peter B. Dervan for permission to publish this data, which was obtained while I was a pre-doctoral fellow under his supervision. See also footnote 1.
- 7) Controls show that the isomeric hexenes and stilbenes do not interconvert under the reaction conditions.
- 8) C. A. Casewit, W. A. Goddard, III, *J. Am. Chem. Soc.*, **102**, 4057(1980).

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