Evidence for the Formation of Diimide in the Thermal Fragmentation of 1-Amino-2,2-diphenylaziridine

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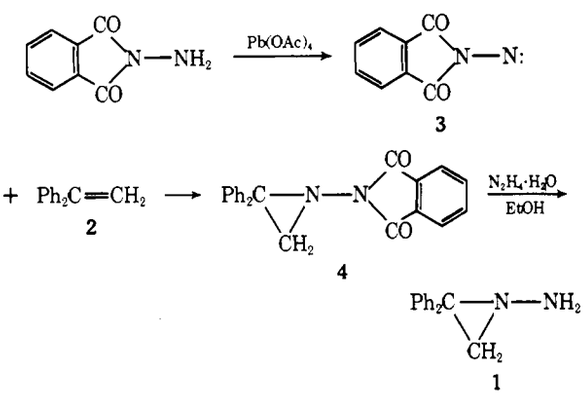
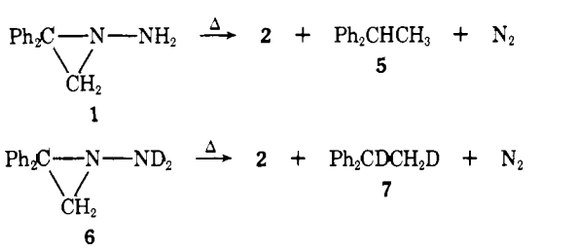
Thermal decomposition of 1-amino-2,2-diphenylaziridine gives a mixture of 1,1-diphenylethylene and 1,1-diphenylethane. When the decomposition is carried out in the presence of highly reactive, strained olefins, these are selectively hydrogenated. Starting from *N,N*-dideuterio-2,2-diphenyl-1-aminoaziridine, deuterium is added to ethylenic double bonds. Comparison with the stereochemical results obtained in reductions with different sources of diimide supports the conclusion that the latter is the reducing species.

In connection with the synthesis of compounds whose molecular asymmetry is due solely to a tricovalent nitrogen atom,[1,2] 1-amino-2,2-diphenylaziridine (**1**) has been prepared *via* addition of phthalimidonitrene (**3**) to 1,1-diphenylethylene (**2**) according to Rees,[3] and hydrazinolysis of the adduct **4**.

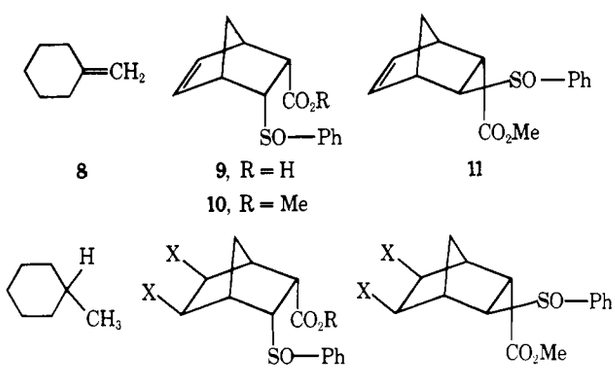


In the nmr spectra of aziridines **1** and **4** phenyls bound to the heterocyclic ring appear as a doublet and the methylene protons as an AB quartet, thus indicating the existence of a high barrier to pyramidal inversion at nitrogen, in agreement with the structural characteristics of the molecule.[4] The spectrum of **4** remains unaltered up to 150°.

Aziridine **1** is thermally unstable and at room temperature decomposes in a few hours, with evolution of gas and formation of a mixture of 1,1-diphenylethylene (**2**) and 1,1-diphenylethane (**5**).[5] The fragmentation can be easily followed by nmr spectroscopy. If aminoaziridine **1** is converted into the *N,N*-dideuterio derivative **6** by isotopic exchange with D_2O, fragmentation affords a mixture of 1,2-dideuterio-1,1-diphenylethane (**7**) and 1,1-diphenylethylene (**2**).

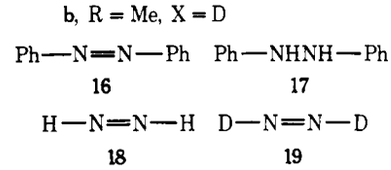


To ascertain if the formation of diphenylethane (**5**) and of the dideuterio derivative **7** occurs through an internal rearrangement or the formation of a species capable of hydrogenating (or deuterating) the double bond of diphenylethylene in an intermolecular process, decomposition of aziridine **1** was repeated in the presence of highly reactive, strained olefins. Starting from methylenecyclohexane (**8**) and from norbornenes **9–11**, methylcyclohexane (**12**) and norbornanes **13a–15a** were obtained, respectively. Azobenzene (**16**) afforded hydrazobenzene (**17**). When the reaction was carried out with dideuterioaziridine **6**, a molecule of deuterium was added to the C–C double bond. In the cases examined, the 5,6-dideuterionorbornanes **13b–15b** were identical with the products of addition (very likely from the cis-exo direction) of dideuteriodiimide (**19**), produced *via* azodicarboxylic acid,[7] to norbornenes **9–11**.



8 **9**, R = H; **10**, R = Me **11**

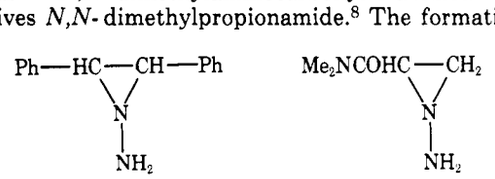
12 **13a**, R = H, X = H; **b**, R = H, X = D; **14a**, R = Me, X = H; **b**, R = Me, X = D **15a**, X = H; **b**, X = D



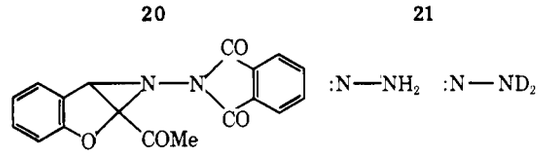
16 **17**

18 **19**

The facile fragmentation of *N*-aminoaziridines analogous to **1** is known.[8-10] The main products are the corresponding ethylene derivatives, which often are formed in a very stereospecific way.[8] In the thermal decomposition of *trans*-2,3-diphenyl-1-aminoaziridine (**20**), 1,2-diphenylethane has been isolated together with *trans*-stilbene, whereas *N,N*-dimethylaminocarbonyl-1-aminoaziridine (**21**) gives *N,N*-dimethylpropionamide.[8] The formation of



20 **21**



22 **23** **24**

Table I
Reduction of Camphene (25)

Reagent	Yield, %	Endo, % 27	Exo, % 28
1	39	92.5	7.5
N_2H_4, $NaIO_4$	33	88.2	11.8
$HO_2CN{=}NCO_2H$	18	91.5	8.5
N_2H_4, O_2		92[a]	8[a]
H_2, C/Pd	100	72.3	27.7
H_2, C/Pt		75[a]	25[a]

[a] Reference 15.

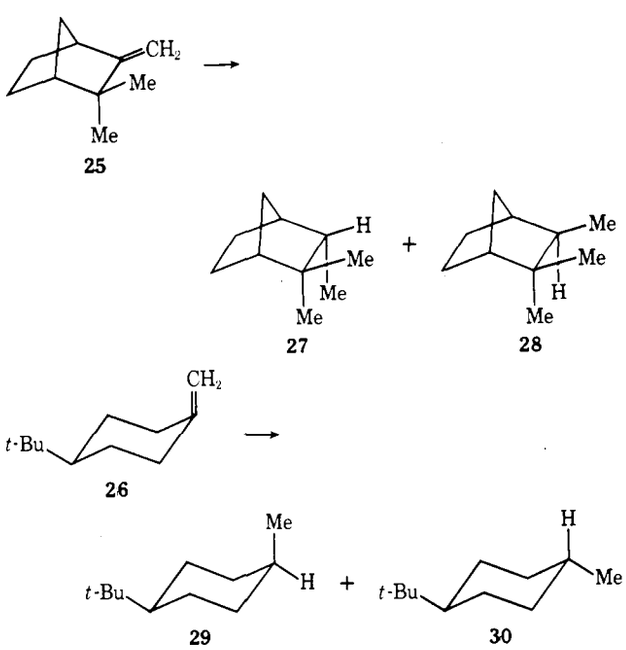
Table II
Reduction of 4-*tert*-Butylmethylenecyclohexane (26)

Reagent	Yield, %	Cis, % 29	Trans, % 30
1	77	48.1	51.9
N_2H_4, $NaIO_4$	50	51.0	49.0
$HO_2CN{=}NCO_2H$	44	49.6	50.4
N_2H_4, O_2		49[a]	51[a]
H_2, C/Pd	100	81.1	18.9
H_2, C/Pt		83[a]	17[a]

[a] Reference 15.

the latter has been interpreted[8] by the intervention of an intramolecular process. Phthalimidonitrene (**3**) is produced by heating bicyclic aziridine **22**,[10] and finally aminonitrene (**23**) has been considered[9] as a possible transient product of the thermal fragmentation of *cis*- and *trans*-2,3-diphenyl-1-aminoaziridine (**24**). On this basis it seemed likely that fragmentation of aminoaziridines **1** and **6** could yield aminonitrenes **23** and **24**, which as such or through conversion to the tautomeric diimides **18** and **19** are the reducing species. Cis hydrogenation by a nonsymmetric isomer **23** of diimide cannot be ruled out *a priori*, even if, for diimide obtained by conventional methods, spectroscopic results and chemical behavior seem to exclude the existence of nonsymmetric species.[11,12]

In order to obtain information on this point, we hydrogenated camphene (**25**) and 4-*tert*-butylmethylenecyclohexane (**26**) with aminoaziridine **1**, with diimide produced by oxidation of hydrazine with sodium metaperiodate[13] and by decarboxylation of azodicarboxylic acid,[7,14] and with hydrogen on Pd/C catalyst.



It was known[15] that in these substrates catalytic and diimide reductions occur with different diastereomeric selectivities.

As shown in Tables I and II, the results of the reactions with aziridine **1** are consistent with those obtained with known sources of diimide and differ from those obtained in catalytic conditions.

It seems therefore that diimides **18** and **19** are the reducing species produced by fragmentation of **1** and **6**. At this moment it is only an hypothesis that diimides in their turn come from an internal rearrangement of aminonitrenes **23** and **24**.

Experimental Section

Nuclear magnetic resonance and infrared spectra were determined with a Varian A-60 instrument and a Perkin-Elmer 237 spectrometer, respectively. Glc analyses were performed on a Fractovap GP chromatograph equipped with flame detectors. The columns were a 0.8 in. × 3.2 ft 3% SE-30, 10% Carbowax 20M on 60–80 mesh Chromosorb W, and a 0.1 in. × 163.8 ft glass capillary column on OV-101.

2,2-Diphenyl-1-phthalimidoaziridine (4). A solution of lead tetraacetate (4.9 g, 11 mmol) in anhydrous dichloromethane (15 ml) was added to a stirred suspension of *N*-aminophthalimide[3,16] (1.62 g, 10 mmol) in 1,1-diphenylethylene (9.0 g, 50 mmol) and anhydrous dichloromethane (25 ml) at room temperature under a dry nitrogen atmosphere during 10 min. After a further 30 min the mixture was filtered, the precipitate was washed with anhydrous dichloromethane, and the combined solutions were evaporated to dryness under vacuum at 15–20°. The oily, yellow residue was purified by dry column chromatography on basic alumina (about 30 g, eluent diethyl ether). Extraction with chloroform gave **4** (1.1 g, 32%) as a yellowish solid, mp 167–168°, from methanol: nmr ($CDCl_3$) τ 2.45 (4 H, s), 2.7 (10 H, m), 5.3, 7.14 (2 H, q, J = 3 Hz).

Anal. Calcd for $C_{22}H_{16}O_2N_2$: C, 77.64; H, 4.71; N, 8.22. Found: C, 77.40; H, 4.56; N, 8.14.

1-Amino-2,2-diphenylaziridine (1). A suspension of phthalimidoaziridine **4** (500 mg, 1.47 mmol) in hydrated hydrazine (147 mg, 2.94 mmol) and 95% ethanol (12 ml) was stirred at room temperature until complete solution (5 min). After 10 min the precipitated *N,N*-phthaloylhydrazine, mp >300°, was filtered and washed with ethanol, and the combined solutions were evaporated under vacuum at 15–20°. Ice water was added and the organic phase was extracted five times with cold dichloromethane. The combined solutions of dichloromethane were washed with 2 *N* aqueous potassium hydroxide, water, and saturated aqueous sodium chloride, dried over magnesium sulfate, and evaporated to dryness under vacuum. Work-up was carried out below 5°, and as fast as possible. The oily residue was 1-amino-2,2-diphenylaziridine (**1**), together with minor amounts (about 5–10%) of 1,1-diphenylethylene (**2**), as shown by aromatic and ethylenic absorptions in the nmr spectrum ($CDCl_3$) at τ 2.71 and 4.6, respectively: nmr ($CDCl_3$) τ 2.7 (10 H, d), 6.97 (2 H, broad s, disappears in D_2O), 7.65 (2 H, q, J = 0.7 Hz). The thermal instability of **1** prevented further purification and elemental analysis.

Fragmentation of 1-Amino-2,2-diphenylaziridine. 1,1-Diphenylethane (5). Aziridine **1** in $CDCl_3$ solution at 40° decomposed in 3 hr to give nitrogen and a mixture of 1,1-diphenylethylene (**2**) and 1,1-diphenylethane (**5**), in a ratio of 3:7 (by nmr).

The presence of **5** in the reaction mixture was confirmed by comparison with an authentic sample:[17] nmr ($CDCl_3$) τ 2.85 (10 H, s), 5.95 (1 H, q), 8.40 (3 H, d).

Fragmentation of *N,N*-Dideuterio-1-amino-2,2-diphenylaziridine. 1,2-Dideuterio-1,1-diphenylethane (7). A solution of aziridine **1** (80 mg) in $CDCl_3$ (2 ml) was shaken with D_2O (1 ml) at about 5°, the organic phase was separated, and the operation was repeated twice, until disappearance of the nmr absorption at τ 6.57. The $CDCl_3$ solution was dried over anhydrous magnesium sulfate. Nmr spectra indicated disappearance of aziridine **1**, and progressive appearance during about 4.30 hr of 1,2-dideuterio-1,1-diphenylethane (**7**) (broad singlet at τ 8.40, CH_2D, centered with respect to the CH_3 doublet of **5**), together with minor amounts of diphenylethylene (**2**) and isotopically normal diphenylethane (**5**).

A sample of 7 was prepared by slow addition at 0° of CH_3COOD (1.2 g, 20 mmol) in CH_3OD (0.5 ml) to a solution of 1,1-diphenylethylene (**2**, 360 mg, 2 mmol) and potassium azodicarboxylate (98 mg, 5 mmol) in CH_3OD (7 ml). After 1 hr pentane was added, and the solution was washed with water, concentrated sulfuric acid, and again with water. Evaporation of the solvent and distillation of the oily residue afforded 1,2-dideuterio-1,1-diphenylethane (**7**): bp 148° (22 mm); n_D 1.5759; nmr ($CDCl_3$) τ 2.81 (10 H, s), 8.40 (2 H, broad s).

Methylcyclohexane (12). A solution of aziridine 1 (84 mg, 0.4 mmol) and methylenecyclohexane (**8**, 19 mg, 0.2 mmol) in $CDCl_3$ (1 ml) was kept at 40° for 12 hr to give methylcyclohexane (**12**), diphenylethylene (**2**), and diphenylethane (**5**) in a ratio of 50:35:15 (glc analysis).

3-*endo*-*syn*-Phenylsulfinylbicyclo[2.2.1]heptane-2-*endo*-carboxylic Acid (13a). A solution of aziridine **1** (84 mg, 0.4 mmol) and norbornene derivative **9**[18] (52 mg, 0.2 mmol) in CD_3OD (1.5 mol) was left at room temperature for 2 hr until no more gas was evolved. The nmr spectrum (CD_3OD) indicated disappearance of vinylic absorption at τ 3.6. The solvent was evaporated, 5% aqueous sodium hydroxide was added, and the alkaline solution was washed with diethyl ether and acidified to give **13a** (50 mg, 96%), mp 180–182° (lit.[19] mp 184–185°). The nmr spectrum (NaOD, D_2O) of **13a** was identical with that of an authentic sample.[19]

The methyl ester **14a** was similarly obtained from **10** and **1** in $CHCl_3$ solution: mp 117–118° from light petroleum (lit.[18] mp 119–120°); nmr ($CDCl_3$) τ 2.40 (5 H, m), 6.50 (3 H, s), 6.70–8.75 (10 H, m); no vinylic absorption at τ 3.55.

5,6-Dideuterio-3-*endo*-*syn*-phenylsulfinylbicyclo[2.2.1]heptane-2-*endo*-carboxylic Acid (13b). A solution of aziridine 1 (84 mg, 0.4 mmol) in anhydrous DMSO (3 ml) and D_2O (0.5 ml) was added to a solution of acid **9**[20] (52 mg, 0.2 mmol) in anhydrous DMSO (4 ml) at room temperature. Immediate evolution of gas was observed. After 30 min aqueous sodium hydrogen carbonate was added, and the mixture was washed with diethyl ether and acidified with aqueous hydrochloric acid. The precipitated norbornane was filtered, washed with water, and dried: 45 mg (90%); mp 183–184° also in mixture with the hydrogenated analogous **13a**; nmr (DMSO-d_6) τ 2.68 (5 H, s), 5.63 (1 H, m), 5.83 (1 H, m), 6.32 (1 H, m), 6.52 (1 H, m), 7.40 (2 H, m), 8.51 (2 H, broad s). From the ethereal phase a mixture of diphenylethylene and diphenylethane was recovered.

Acid **13b** was also prepared as follows. CH_3COOD (1.2 g) was slowly dropped into a solution of acid **9** (200 mg, 1 mmol) and potassium azodicarboxylate (400 mg, 2.5 mmol) in DMSO (7 ml). After 4 hr, 160 mg (75%) of **13b**, mp 183–184°, was isolated. Nmr spectra of this sample and of that obtained from dideuterioaziridine were identical.

The **methyl ester 14b** was obtained by shaking a solution of 1 (84 mg, 0.5 mmol) in $CDCl_3$ (1 ml) with D_2O (1 ml), and adding to the organic phase a solution of **10**[21] (56 mg, 0.2 mmol) in $CDCl_3$ (0.5 ml). The mixture was left 2 hr at room temperature. Work-up afforded **14b**, which was purified by column chromatography (silica, light petroleum–diethyl ether): 35 mg (60%); mp 115–117°, not depressed in mixture with a nondeuterated sample of **14a**; nmr ($CDCl_3$) τ 2.40 (5 H, m), 6.50 (3 H, s), 7.0 (2 H, m), 7.30 (2 H, m), 8.45 (2 H, broad s), 8.75 (2 H, s).

Methyl 3-*exo*-*anti*-phenylsulfinylbicyclo[2.2.1]heptane-2-*endo*-carboxylate (15a) was obtained similarly to ester **14a** from ester **11**[21] and aziridine 1 in 83% yield: mp 115–116° from cyclohexane; nmr ($CDCl_3$) τ 2.48 (5 H, m), 6.56 (3 H, s), 6.82 (1 H, m), 7.25 (3 H, m), 8–9 (6 H, m).

Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.7; H, 6.5. Found: C, 64.42; H, 6.60.

Methyl 5,6-dideuterio-3-*exo*-*anti*-phenylsulfinylbicyclo-[2.2.1]heptane-2-*endo*-carboxylate (15b) was obtained similarly to ester **14b** from ester **11** and aziridine 1 in $CDCl_3$–D_2O in 80% yield, and purified by column chromatography (silica, light petroleum–diethyl ether): mp 108–109°, not depressed in mixture with the nondeuterated analogous **15a**; nmr ($CDCl_3$) τ 2.48 (5 H, m), 6.55 (3 H, s), 6.82 (1 H, m), 7.25 (3 H, m), 8–9 (4 H, m).

The same compound, with identical melting point and nmr spectrum, was obtained from ester **11** and potassium azodicarboxylate in DMSO–CH_3CO_2D, as described above for acid **13b**.

Hydrazobenzene (17). Azobenzene (19 mg, 0.1 mmol) and aziridine **1** (84 mg, 0.4 mmol) in CH_2Cl_2 solution (1 ml) were left for 3 hr at room temperature until no more gas was evolved. Column chromatography (silica, light petroleum) afforded 16 mg (84%) of hydrazobenzene, mp 124–125°.

Reductions of Camphene (25) and of 4-*tert*-Butylmethylenecyclohexane (26). A. With Aziridine 1. A solution of **1** (420 mg, 2 mmol) and **25** or **26**[22] (0.5 mmol) in CH_2Cl_2 (2 ml) was left at room temperature for 24 and 4 hr, respectively, until no more gas was evolved.

B. With Hydrazine and Sodium Metaperiodate.[14] To a solution of **25** or **26** (1 mmol) and hydrated hydrazine (40 mmol) in ethanol (5 ml) were added 2 drops of glacial acetic acid, 2 drops of saturated aqueous copper sulfate, and (dropwise, 1 hr) a solution of sodium metaperiodate (1.06 g, 5 mmol) in H_2O (10 ml) at room temperature. The reaction mixture was filtered, diluted with brine, and extracted with pentane.

C. With Potassium Azodicarboxylate.[7,15] Glacial acetic acid (1.2 g, 20 mmol) in methanol (1 ml) was added dropwise at room temperature to a solution of **25** or **26** (1 mmol) and potassium azodicarboxylate (776 mg, 4 mmol) in methanol (5 ml). After 1 hr the mixture was diluted with brine and extracted with pentane.

D. Catalytic Reduction. It was carried out in ethanol with 10% Pd/C catalyst and the products were extracted with pentane.

The solvent (methylene chloride or pentane) was evaporated under vacuum at about 10° and the reaction mixture was analyzed by glc on capillary columns at 80° (see Tables I and II).

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Registry No.—**1**, 52165-45-4; **2**, 530-48-3; **4**, 52165-46-5; **5**, 612-00-0; **6**, 52165-47-6; **7**, 52165-48-7; **8**, 1192-37-6; **9**, 52194-78-2; **10**, 52224-95-0; **11**, 52194-79-3; **12**, 108-87-2; **13a**, 52165-49-8; **13b**, 52194-80-6; **14a**, 52224-96-1; **14b**, 52165-35-2; **15a**, 52194-76-0; **15b**, 52194-77-1; **17**, 122-66-7; *N*-aminophthalimide, 1875-48-5; potassium azodicarboxylate, 4910-62-7; azobenzene, 103-33-3.

References and Notes

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