

- (6) (a) A. Mannschreck, H. A. Staab, and D. Wurmb-Gerlich, *Tetrahedron Lett.*, 2003 (1963); (b) H. A. Staab and D. Lauer, *Chem. Ber.*, **101**, 864 (1968).
- (7) (a) L. Pappalardo, J. Elguero, and C. Marzin, *C. R. Acad. Sci., Ser. C*, **277**, 1163 (1973); (b) J. Elguero, C. Marzin, and L. Pappalardo, *Bull. Soc. Chim. Fr.*, 1137 (1974); (c) J. Elguero, A. Fruchier, L. Knutsson, R. Lazaro, and J. Sandstrom, *Can. J. Chem.*, **52**, 2744 (1974); (d) J. Elguero, C. Marzin, and M. E. Peck, *Org. Magn. Reson.*, **7**, 445 (1975).
- (8) E. Noe and M. Raban, *J. Am. Chem. Soc.*, **97**, 5811 (1975).
- (9) In methanol a substantial amount of the *Z,Z* isomer (ca. 40%) of diacetamide is observed in equilibrium with the *E,Z* form (E. A. Noe and M. Raban, unpublished results).
- (10) Chemical shift data from ambient spectra are given in Table III.
- (11) G. S. Reddy, L. Mandell, and J. H. Goldstein, *J. Chem. Soc.*, 1414 (1963).
- (12) A. Mannschreck, W. Seitz, and H. A. Staab, *Ber. Bunsenges. Phys. Chem.*, **67**, 470 (1963).
- (13) The low temperature spectra of **1f** were taken in a series of solvents, dichloromethane, vinyl chloride, dichloromethane-dimethyl ether, and dichloromethane-bromotrifluoromethane, in order to minimize the possibility that the chemical shift equivalence derived from accidental coincidence of signals from the two diastereomers rather than rapid exchange.
- (14) M. Raban and R. Keintz, unpublished results.
- (15) The situation in simple *N,N*-dialkylamides is more complicated.<sup>3a,16,17</sup> In *N,N*-dimethylamides, RCON(CH<sub>3</sub>)<sub>2</sub>, the methyl group *cis* to the carbonyl oxygen atom is shifted *upfield* relative to the *trans* methyl group. The direction of this shift was rationalized by taking into account the placement of methyl protons out of the plane of the carbonyl group and into a region of shielding by the anisotropic amide group. Perhaps the greater planarity in imides and acylimidazoles leads to results which are more consistent with the well-established model of the magnetic anisotropy of the isolated carbonyl group (in ketones and aldehydes) in which protons near the nodal plane of the carbon-oxygen double bond are deshielded. It may be noted that *N*-acylanilides, which have a similar geometry, exhibit consistent downfield shifts for the ortho protons which are *cis* to the carbonyl group. The methyl group in *N,N*-diethylamides also exhibits a downfield shift for the methyl *cis* to the amide oxygen.
- (16) A. H. Lewin and M. Frucht, *Org. Magn. Reson.*, **7**, 206 (1975).
- (17) (a) H. Paulsen and K. Todt, *Angew. Chem., Int. Ed. Engl.*, **5**, 899 (1966); (b) H. Paulsen and K. Todt, *Z. Anal. Chem.*, **235**, 29 (1968).
- (18) L. L. Graham, *Org. Magn. Reson.*, **4**, 335 (1972).
- (19) M. T. Rogers and C. W. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).
- (20) L. W. Reeves, R. C. Shaddick, and K. N. Shaw, *Can. J. Chem.*, **49**, 3683 (1971).
- (21) L. R. Isbrandt and M. T. Rogers, *Chem. Commun.*, 1378 (1971).
- (22) S. Sternhell, *Q. Rev., Chem. Soc.*, **23**, 236 (1969).
- (23) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).
- (24) P. Laszlo in "Progress in Nuclear Magnetic Resonance Spectroscopy", Vol. 3, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Elmsford, N.Y., 1967, Chapter 6.
- (25) (a) R. J. Abraham and T. M. Sivers, *Tetrahedron*, **28**, 3015 (1972); (b) R. J. Abraham and E. Bretschneider in "Internal Rotation in Molecules", W. J. Orville-Thomas, Ed., Wiley, New York, N.Y., 1974, Chapter 13.
- (26) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).
- (27) J. M. Gross, and D. G. Rush, *Chem. Ind. (London)*, 1766 (1968).
- (28) H. A. Staab, *Angew. Chem.*, **74**, 407 (1962).
- (29) H. W. Thompson and R. J. L. Popplewell, *Z. Electrochem.*, **64**, 746 (1960).
- (30) (a) The free energies of activation at coalescence for *N,N*-dimethylamides, RCON(CH<sub>3</sub>)<sub>2</sub>, used in construction of Figure 5 are literature values or were calculated from literature activation parameters for nonpolar solvents (R,  $\Delta G_c^\ddagger$  in kcal/mol, solvent, reference): H, 20.6, C<sub>2</sub>Cl<sub>4</sub>, 30b; CH<sub>3</sub>, 17.3, CCl<sub>4</sub> (1.7 mol %), 30c; CH<sub>3</sub>CH<sub>2</sub>, 16.6, CCl<sub>4</sub> (11 mol %), 30d; CH(CH<sub>3</sub>)<sub>2</sub>, 16.2, *o*-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (33 mol %), 30e; CF<sub>3</sub>, 18.3, CCl<sub>4</sub> (11.25 mol %), 20; C(CH<sub>3</sub>)<sub>3</sub>, 11.9, CH<sub>2</sub>Cl<sub>2</sub> (10 mol %), 30f. (b) T. Drakenberg, K.-I. Dahlquist, and S. Forsen, *J. Phys. Chem.*, **76**, 2178 (1972). (c) R. C. Neuman, Jr., and V. Jonas, *J. Org. Chem.*, **39**, 929 (1974). (d) J. C. Woodbrey and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 13 (1962). (e) G. Isaksson and J. Sanstrom, *Acta Chem. Scand.*, **21**, 1605 (1967). (f) L. L. Graham and R. E. Diel, *J. Phys. Chem.*, **73**, 2696 (1969).
- (31) R. C. Neuman, Jr., and V. Jonas, *J. Am. Chem. Soc.*, **90**, 1790 (1968); *J. Org. Chem.*, **39**, 925 (1974).
- (32) (a) H. A. Staab and B. Polenski, *Justus Liebigs Ann. Chem.*, **655**, 95 (1962); (b) H. A. Staab, *Chem. Ber.*, **89**, 1927 (1956); (c) *ibid.*, **89**, 2088 (1956); (d) H. A. Staab and G. Walther, *ibid.*, **95**, 2070 (1962).
- (33) G. S. Reddy, *Chem. Ind. (London)*, 1426 (1965).
- (34) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
- (35) S. Martinez-Carrera, *Acta Crystallogr.*, **20**, 783 (1966).
- (36) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

## Reduction of 1,3-Diphenyl-2,2-dihaloaziridines with Tri-*n*-butyltin Hydride

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1,3-Diphenyl-2,2-dihaloaziridines (**1**–**5**) were prepared by the addition of dihalocarbene (CClF, CBrF, CClBr, CCl<sub>2</sub>, and CBr<sub>2</sub>) to *N*-benzylideneaniline in *n*-hexane. These aziridine compounds were reduced with tri-*n*-butyltin hydride in *n*-pentane at room temperature to give the corresponding 1,3-diphenyl-2-haloaziridines (**6**–**8**). The reduction of **1**, **2**, and **3** proceeded stereospecifically, i.e., with retention of configuration, indicating that the intermediate 2-fluoro- and 2-chloro-2-aziridinyl radicals are pyramidal, and configurationally stable enough to abstract hydrogen from tri-*n*-butyltin hydride much more rapidly than invert their configurations.

It is known that the configurational stability of cyclopropyl radicals is strongly dependent on the nature of the  $\alpha$  substituent, i.e., the substituent at the radical carbon.<sup>1</sup> The energy barriers for inversion of the cyclopropyl (A), the  $\alpha$ -chlorocyclopropyl (B), and the  $\alpha$ -fluorocyclopropyl (C) radicals have been calculated to be 0.8, 4.0, and 10.5 kcal/mol, respectively, by use of the CNDO/2 approximation.<sup>2</sup> These calculations indicate that the configurational stability of these radicals increases in the order A < B < C, which is in good agreement with that of the degree of stereospecificity observed in a number of reactions proceeding via these radicals, such as the reduction of cyclopropyl halides with organotin hydrides, the brominative decarboxylation of silver cyclopropanecarboxylates, and the thermal decomposition of cyclopropanepercarboxylic acid esters. Thus, cyclopropyl radical (A)<sup>3</sup> inverts its configuration so fast that it behaves as if it were planar, whereas the  $\alpha$ -fluorocyclopropyl radical (C) reacts

stereospecifically, i.e., with complete retention of configuration, in many reactions.<sup>1,4,5</sup> The inversion rate of the  $\alpha$ -chlorocyclopropyl radical<sup>1,6</sup> is between those of the radicals cited above.

Recently, we have shown that the configurational stability of the  $\alpha$ -fluorocyclopropyl radical is also affected by the  $\beta$  substituent.<sup>7</sup> Our findings are again in agreement with the prediction made theoretically by Dewar and Bingham.<sup>8</sup>

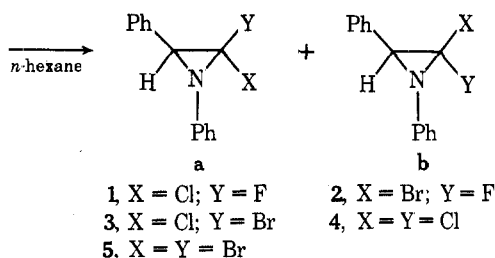
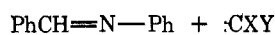
As compared with cyclopropyl radicals, however, there have been very few studies on the configurational stability of other three-membered-ring radicals containing a heteroatom in the ring, such as oxiranyl, 2-aziridinyl, and thiiranyl radicals. Altman and his collaborator have shown both theoretically<sup>2</sup> and experimentally<sup>9</sup> that the energy for inversion of the oxiranyl radical is larger than that of the corresponding cyclopropyl radical.

We have now extended our studies to the hitherto unexa-

mined 2-aziridinyl radical, with the expectation that the 2-aziridinyl radical might have a larger configurational stability than the cyclopropyl radical, as does the oxiranyl radical. In the present paper will be described the results of the studies on the reduction of 1,3-diphenyl-2,2-dihaloaziridines with tri-*n*-butyltin hydride.

### Results

**Preparation of 1,3-Diphenyl-2,2-dihaloaziridines.** The aziridine compounds employed in this study were prepared by the reaction of dihalocarbene with *N*-benzylideneaniline.<sup>10</sup>



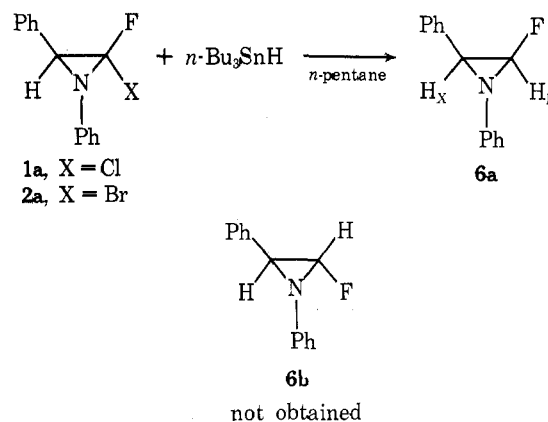
All of the aziridine compounds prepared gave satisfactory elemental analyses as well as ir, NMR, and mass spectra.

Since chlorofluoro-, bromofluoro-, and chlorobromocarbenes and *N*-benzylideneaniline are both unsymmetrical, two isomers of the aziridine should be expected. In fact, from chlorobromocarbene and the anil, usual treatment of the reaction mixture and recrystallization from *n*-pentane gave a mixture of two isomers (**3a** and **3b**) of 1,3-diphenyl-2-chloro-2-bromoaziridine in 61% yield. The NMR spectrum of the product showed the absorptions at  $\delta$  3.50 (singlet), 3.66 (singlet), and 6.90–7.50 (multiplet). Heating the mixture of the two isomers in refluxing *n*-hexane–benzene (1:1) for a week resulted in the decomposition of one isomer (**3a**), with the other isomer (**3b**) left unchanged. The NMR spectrum of the remaining unchanged isomer showed the absorptions at  $\delta$  3.66 (singlet, 1 H) and 6.90–7.50 (multiplet, 10 H). Column chromatography (silica gel, *n*-pentane eluent) of the two isomers gave pure **3a** which had the absorptions at  $\delta$  3.50 (singlet, 1 H) and 6.90–7.50 (multiplet, 10 H) in its NMR spectrum. The isomer ratio in the product was 2.3/1, with the isomer (**3b**) having the absorption at  $\delta$  3.66 predominating. Although neither these NMR data nor the ir and mass spectral data of the isomers were sufficient to determine their configurations (*E* or *Z*), the results of the reduction of each isomer allowed us to assign the *Z* configuration to **3a** and the *E* configuration to **3b**.<sup>11</sup>

In the NMR spectrum of the product obtained from chlorofluorocarbene and the anil, only one doublet ( $\delta$  3.48, doublet,  $J = 3.5$  Hz, 1 H) was observed in addition to a complex multiplet due to phenyl protons ( $\delta$  6.90–7.58, 10 H). Similarly, the NMR spectrum of the bromofluorocarbene adduct showed one alicyclic hydrogen ( $\delta$  3.50, doublet,  $J = 4.0$  Hz) and ten aromatic hydrogens ( $\delta$  6.92–7.60, multiplet). These doublets are due to the benzylidene proton coupled with the fluorine on the adjacent carbon. The magnitudes of the coupling constants suggest that these aziridines are the *E* isomers (**a**).<sup>12</sup> The absence of other absorptions which could possibly be attributed to the other isomer (**b**) indicates that these recrystallized products contain only one isomer (**a**) and that the reaction occurs with high stereoselectivity.<sup>14</sup> An analogous stereoselective addition was observed in the reaction of excess  $\text{LiCHCl}_2$  with *N*-benzylideneaniline in ether at temperatures below  $-70^\circ\text{C}$ .<sup>15</sup>

**Reduction of 1,3-Diphenyl-2,2-dihaloaziridines with Tri-*n*-butyltin Hydride.** 1,3-Diphenyl-2-chloro-2-fluoroaziridine (**1**) was reduced with a small excess of tri-*n*-butyltin

hydride in *n*-pentane at room temperature under nitrogen atmosphere for 5 days. The reduction product was isolated by use of column chromatography (alumina). The NMR spectrum of the product proved that only one isomer of 1,3-diphenyl-2-fluoroaziridine (**6a**) was formed. The NMR spec-



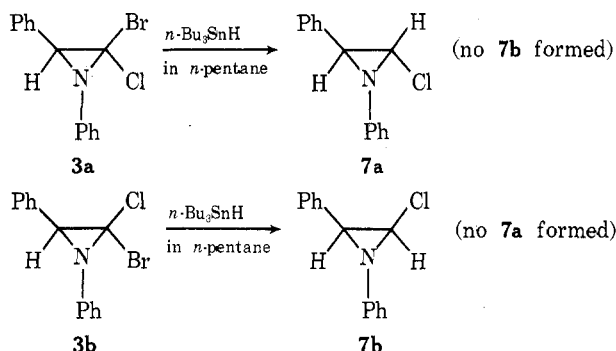
trum in carbon tetrachloride showed the absorptions at  $\delta$  5.03 (double doublet,  $J = 4.0$  and 79.0 Hz, 1 H), 3.16 (double doublet,  $J = 3.5$  and 4.0 Hz, 1 H), and 6.90–7.58 (multiplet, 10 H). The smaller coupling constant (4.0 Hz) at  $\delta$  5.03 is due to the interaction between  $\text{H}_M$  and  $\text{H}_X$ , and the larger one (79.0 Hz), to that between  $\text{H}_M$  and F. Similarly, the coupling constants of 4.0 and 3.5 Hz at  $\delta$  3.16 can be attributed to the interaction between  $\text{H}_X$  and  $\text{H}_M$ , and between  $\text{H}_X$  and F, respectively. These magnitudes of the coupling constants suggest that the reduction product formed was the isomer (**6a**) whose fluorine atom was trans to the hydrogen ( $\text{H}_X$ ) at the adjacent ring carbon.<sup>12,16</sup> This means that the reduction proceeded with retention of the original configuration.

A similar stereospecificity was observed in the reduction of 1,3-diphenyl-2-bromo-2-fluoroaziridine (**2a**). **2a** was converted into **6a**, with no sign of **6b** being formed.

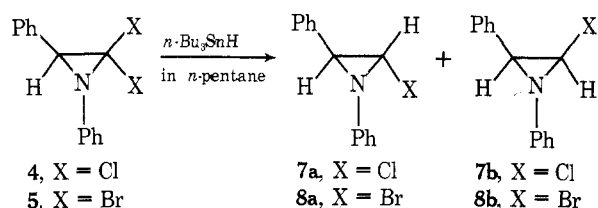
A mixture of isomers (**3a** and **3b**) of 1,3-diphenyl-2-chloro-2-bromoaziridine was similarly reduced in *n*-pentane. An attempt to isolate the reduction product (**7**) by column chromatography was unsuccessful because it was too unstable under the chromatographic conditions.<sup>17</sup> Inspection of the NMR spectrum of the reaction mixture in *n*-pentane revealed the peaks at  $\delta$  3.20 (doublet,  $J = 5.0$  Hz), 3.26 (doublet,  $J = 2.0$  Hz), 4.27 (doublet,  $J = 2.0$  Hz), 4.32 (doublet,  $J = 5.0$  Hz), and 7.15–7.80 (multiplet) in addition to the peaks due to *n*-pentane, phenyl group, and the *n*-butyl group of *n*-butyltin bromide. After removal of the *n*-pentane from the reaction mixture, benzene was added to the residue. The NMR spectrum of the benzene solution showed the peaks at  $\delta$  2.87 (doublet,  $J = 5.0$  Hz), 3.16 (doublet,  $J = 2.0$  Hz), 4.08 (doublet,  $J = 2.0$  Hz), and 4.11 (doublet,  $J = 5.0$  Hz) in addition to the peaks due to the *n*-butyl group of *n*-butyltin bromide and phenyl group. That these four doublets are due to aziridine ring hydrogens of the reduction product is supported by the comparison of the  $\delta$  values and the coupling constants with those of 1,3-diphenyl-2-chloroaziridine prepared by Deyrup et al.<sup>15,16</sup> and of other analogous aziridine compounds.<sup>18</sup> The larger coupling constant ( $J = 5.0$  Hz) is attributed to the *cis* isomer (**7b**), and the smaller one ( $J = 2.0$  Hz) to the *trans* isomer (**7a**).

Each isomer of **3** was reduced separately under the same conditions. The NMR spectra of the reaction mixture confirmed that only one isomer was formed from each of the isomers (**7a** from **3a**, **7b** from **3b**), which indicated that the reduction of **3** also proceeded stereospecifically.

1,3-Diphenyl-2,2-dichloroaziridine (**4**) and 1,3-diphenyl-2,2-dibromoaziridine (**5**) were similarly reduced in *n*-pentane.



The reduction products (**7** and **8**) could not be isolated because of their instability under the chromatographic conditions. The NMR spectra (in *n*-pentane and in benzene) of the reaction mixture obtained in the reduction of **4** had the peaks, except a small one due to the unreacted starting material (**4**), at the



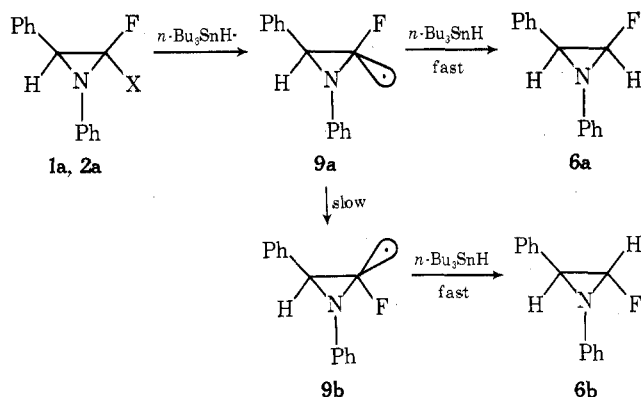
same positions as the reaction mixture obtained from an isomeric mixture of **3**. The isomer ratio of the reduction product (**7b/7a**) was calculated from peak areas in NMR to be 1.9/1.

Similarly, the NMR spectrum (in benzene) of the reaction mixture obtained in the reduction of **5** showed complex aromatic peaks and four doublets, two of which ( $J = 5.0$  Hz) centered at  $\delta$  2.88 and 4.26, and the other two ( $J = 2.0$  Hz) centered at  $\delta$  3.25 and 4.17, in addition to the peaks due to the *n*-butyl group of *n*-butyltin bromide. The isomer ratio (**8b/8a**) was 2.0/1.

### Discussion

The reduction of organic halides with organotin hydride have been rationalized as a free-radical chain reaction<sup>19</sup> and the intermediacy of a free radical has been postulated also in the reduction of some 7,7-dihalonorcaranes<sup>20</sup> and of some *gem*-dihalocyclopropanes<sup>21</sup> with organotin hydride. It is of little doubt that the reduction of **1**–**5** is a radical chain reaction which involves intermediate formation of the 2-halo-2-aziridinyl radical as one of the chain-propagating steps.

The experimental results obtained in the reduction of **1** and **2** demonstrate that the 2-fluoro-2-aziridinyl radical (**9a**) thus formed is pyramidal and abstracts hydrogen from tri-*n*-butyltin hydride much more rapidly than it inverts its configuration to **9b**; if it is planar, or if the inversion occurs before



hydrogen abstraction, a mixture of the two isomeric 1,3-diphenyl-2-fluoroaziridines (**6a** and **6b**) must be formed. The

application of the same argument to the reduction of **3a** and **3b** leads to the conclusion that the 2-chloro-2-aziridinyl radicals are also pyramidal and are configurationally very stable.

A similar stereospecificity was observed in the reduction of *gem*-halofluorocyclopropanes with tri-*n*-butyltin hydride,<sup>4,5</sup> while the other hitherto known  $\alpha$ -substituted cyclopropyl radicals, formed in the reduction of  $\alpha$ -substituted cyclopropyl halides with organotin hydride or in the Hunsdiecker reaction of  $\alpha$ -substituted cyclopropanecarboxylic acids, were found to lose their original configurations completely or partly during the reaction. Thus, 7-cyano-, 7-phenyl-, or 7-methoxycarbonyl-7-norbornyl radical equilibrates between its isomeric configurations before hydrogen abstraction.<sup>22</sup> The 7-chloro-7-norbornyl radical<sup>1,6</sup> can retain its original configuration to some extent, but not completely.

These results demonstrate that the 2-aziridinyl radical has a stronger tendency to retain its configuration than the cyclopropyl radical. One of the possible explanations is to attribute it to the increase of *s* character of the radical orbital of carbon in the aziridinyl radical, caused by the electronegative nitrogen atom.<sup>23</sup>

The **b** isomer of 1,3-diphenyl-2-chloroaziridine (**7**) was preferentially formed in the reduction of 1,3-diphenyl-2,2-dichloroaziridine (**4**). This may be explained by postulating that the sterically less hindered chlorine, i.e., the one trans to the phenyl group at the adjacent carbon, is abstracted by the tri-*n*-butyltin radical more easily than the *cis* chlorine<sup>24</sup> and that the resulting 2-chloro-2-aziridinyl radical retains its configuration when it abstracts hydrogen from tri-*n*-butyltin hydride. The preferential formation of the **b** isomer of 1,3-diphenyl-2,2-dibromoaziridine (**8**) in the reduction of 1,3-diphenyl-2,2-dibromoaziridine (**5**) might be explained in a similar way, but no definite conclusion can be drawn at present, because the configurational stability of the 2-bromo-2-aziridinyl radical has not been examined so far.

### Experimental Section

Infrared spectra were obtained with a Shimadzu IR-400 or a Japan Spectroscopic Co. IR-DS 402G infrared spectrometer. <sup>1</sup>H NMR spectra were obtained with a Varian Associates T-60A or a JEOLCO 4H-100 NMR spectrometer in carbon tetrachloride with tetramethylsilane as internal reference. Mass spectra were obtained with a Shimadzu LKB-9000 or a Hitachi RMS-4 mass spectrometer. Isomer distributions were calculated from peak area in NMR spectra. All melting points are uncorrected. All chemicals were reagent grade and used without further purification. Solvents were distilled through a 25-cm Vigreux column and, if necessary, were purified in the usual manner prior to use.

**Preparation of 1,3-Diphenyl-2,2-dihaloaziridines. 1,3-Diphenyl-2-chloro-2-fluoroaziridine (1).** To a stirred solution of 18.1 g (0.10 mol) of *N*-benzylideneaniline and 4.8 g (0.20 mol) of sodium hydride in 200 ml of *n*-hexane, cooled to 0 °C in an ice bath, was added 32.2 g (0.20 mol) of methyl dichlorofluoroacetate, under a nitrogen atmosphere, at such a rate that the temperature should not rise above 5 °C. After the addition was over, the mixture was warmed up to 20–30 °C and then for 3 h at room temperature. The reaction mixture was suction filtered, the residue was washed three times with *n*-hexane, and the solvent was removed in vacuo from the combined filtrates, leaving a dark brown viscous liquid. *n*-Pentane was added to this liquid and then the solution was filtered again. The filtrate (*n*-pentane solution) was stored for 20 h at –20 °C to give as precipitates 5.7 g (23% yield) of 1,3-diphenyl-2-chloro-2-fluoroaziridine (**1**). Recrystallization from *n*-pentane gave pale yellow crystals; mp 54–55 °C; ir (KBr) 3040 (w), 1600 (vs), 1495 (s), 1410 (s), 1275 (w), 1235 (m), 1130 (s), 1040 (w), 840 (w), 760 (s), 695 cm<sup>–1</sup> (s); NMR  $\delta$  3.48 (d,  $J_{\text{HF}} = 3.5$  Hz, 1 H), 6.90–7.58 (m, 10 H); mass spectrum  $m/e$  249 (P + 2), 247 (P), 229, 227, 212. Anal. Calcd for C<sub>14</sub>H<sub>11</sub>NCIF: C, 67.89; H, 4.48. Found: C, 67.98; H, 4.37.

**1,3-Diphenyl-2-bromo-2-fluoroaziridine (2a).** To a stirred solution of 18.1 g (0.10 mol) of *N*-benzylideneaniline and 22.4 g (0.20 mol) of potassium *tert*-butoxide in 200 ml of *n*-hexane, cooled to 0 to –10 °C in an ice-salt bath, was added 38.4 g (0.20 mol) of dibro-

mofluoromethane, under nitrogen atmosphere, over 2 h. After the addition was over, the mixture was stirred for 2 h at 0 to  $-10^{\circ}\text{C}$  and then for 3 h at room temperature. The reaction mixture was worked up as described above. Light-tan crystals of 1,3-diphenyl-2-bromo-2-fluoroaziridine (**2**) were obtained in 28% yield: mp  $57-59^{\circ}\text{C}$ ; ir (KBr) 3035 (w), 1600 (s), 1495 (vs), 1404 (s), 1275 (w), 1230 (w), 1120 (s), 1035 (w), 835 (w), 755 (vs),  $695\text{ cm}^{-1}$  (vs); NMR  $\delta$  3.50 (d,  $J_{\text{HF}} = 4.0\text{ Hz}$ , 1 H), 6.95–7.55 (m, 10 H); mass spectrum  $m/e$  293 (P + 2), 291 (P), 273, 271, 212. Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{NBrF}$ : C, 57.56; H, 3.80. Found: C, 57.59; H, 3.75.

**1,3-Diphenyl-2-bromo-2-chloroaziridine (3)** was prepared by the same method as described for the preparation of **2**. Dibromochloromethane was used as carbene precursor instead of dibromofluoromethane. The pale yellow crystals of **3** were obtained in 61% yield, mp  $89-91^{\circ}\text{C}$ . The NMR spectrum of the crystals (in  $\text{CCl}_4$ ) showed absorptions at  $\delta$  3.50 (s), 3.66 (s), and 6.90–7.50 (m), indicating the existence of a mixture of isomers of **3** (**a** and **b**). Column chromatography (alumina, *n*-pentane eluent) gave only one isomer (**3a**) (assignment was made from the results of reduction), and the other isomer (**3b**) could not be isolated because of its decomposition. Pure **3b** was obtained by heating a mixture of **3a** and **3b** in refluxing *n*-hexane–benzene (1:1) for a week, which resulted in the decomposition of **3a**, with **3b** left unchanged. The isomer ratio of **3a/3b** was 1/2.3.

**3a**: mp  $92-94^{\circ}\text{C}$ ; ir (KBr) 3045 (w), 1590 (vs), 1305 (s), 1265 (w), 1095 (w), 805 (s), 760 (s),  $690\text{ cm}^{-1}$  (s); NMR  $\delta$  3.50 (s, 1 H), 6.90–7.50 (m, 10 H). Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{NBrCl}$ : C, 54.49; H, 3.59. Found: C, 54.65; H, 3.50.

**3b**: mp  $94-96^{\circ}\text{C}$ ; ir (KBr) 3045 (w), 1588 (vs), 1306 (s), 1265 (w), 1100 (w), 805 (s), 760 (s),  $690\text{ cm}^{-1}$  (s); NMR  $\delta$  3.66 (s, 1 H), 6.90–7.50 (m, 10 H). Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{NBrCl}$ : C, 54.49; H, 3.59. Found: C, 54.73; H, 3.48.

Mass spectrum (a mixture of **3a** and **3b**):  $m/e$  311 (P + 4), 309 (P + 2), 307 (P), 274, 272, 230, 228.

**1,3-Diphenyl-2,2-dichloroaziridine (4)** was prepared in 55% yield according to the method of Cook and Fields;<sup>25</sup> mp  $97-99^{\circ}\text{C}$ ; ir (KBr) 3045 (w), 1590 (vs), 1390 (s), 1265 (w), 1100 (w), 820 (s), 765 (s),  $695\text{ cm}^{-1}$  (s); NMR  $\delta$  3.95 (s, 1 H), 6.90–7.50 (m, 10 H); mass spectrum  $m/e$  267 (P + 4), 265 (P + 2), 263 (P), 230, 228. Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{NCl}_2$ : C, 63.66; H, 4.20. Found: C, 63.41; H, 4.12.

**1,3-Diphenyl-2,2-dibromoaziridine (5)**. To a stirred slurry of *N*-benzylideneaniline (0.10 mol) and potassium *tert*-butoxide (0.20 mol) in *n*-hexane (200 ml), bromoform (0.20 mol) was slowly added at  $-20$  to  $-30^{\circ}\text{C}$ . The reaction mixture was stirred for 3 h at this temperature and then for 5 h at room temperature. The mixture was suction filtered, the residue was washed three times with *n*-hexane, and the solvent was removed in vacuo from the combined filtrates, leaving a crystalline product. Recrystallization from *n*-pentane gave **5** in 35% yield as light-tan crystals: mp  $88-90^{\circ}\text{C}$ ; ir (KBr) 3050 (w), 1605 (vs), 1400 (s), 1280 (w), 1090 (w), 790 (s), 765 (s),  $700\text{ cm}^{-1}$  (s); NMR  $\delta$  3.58 (s, 1 H), 6.95–7.55 (m, 10 H). Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{NBr}_2$ : C, 47.63; H, 3.14. Found: C, 47.31; H, 3.05.

**Reduction of 1,3-Diphenyl-2-chloro-2-fluoroaziridine (1a)**. In a 50-ml, two-necked flask fitted with an inlet and an outlet tubes for nitrogen and a magnetic stirrer was placed a mixture of 5 mmol of 1,3-diphenyl-2-chloro-2-fluoroaziridine and 6 mmol of tri-*n*-butyltin hydride in *n*-pentane. The mixture was stirred at room temperature until an aliquot from the reaction mixture showed no absorption due to Sn–H stretching (near  $1820\text{ cm}^{-1}$ ), which took 5 days. The reduction product was isolated in 55% yield by use of column chromatography (alumina, *n*-pentane eluent): mp  $66-68^{\circ}\text{C}$ ; ir (KBr) 3020 (w), 1585 (s), 1480 (s), 1405 (s), 1265 (m), 1110 (s), 1010 (m), 760 (s),  $695\text{ cm}^{-1}$  (s); NMR  $\delta$  3.16 (q,  $J_{\text{HH}} = 4.0$ ,  $J_{\text{HF}} = 3.5\text{ Hz}$ , 1 H), 5.03 (q,  $J_{\text{HH}} = 4.0$ ,  $J_{\text{HF}} = 79.0\text{ Hz}$ , 1 H), 6.71–7.52 (m, 10 H). The NMR spectrum showed that the reduction product formed was one isomer of **6**, and the magnitudes of the coupling constant suggested that the isomer formed had the configuration (**a**) whose fluorine atom was trans to the hydrogen at the adjacent ring carbon. Mass spectrum:  $m/e$  213 (P), 193, 93, 66. Anal. Calcd for  $\text{C}_{14}\text{H}_{12}\text{NF}$ : C, 78.85; H, 5.67. Found: C, 78.71; H, 5.58.

The same product (**6a**) was obtained in 60% yield in the reduction of 1,3-diphenyl-2-bromo-2-fluoroaziridine (**2a**) with tri-*n*-butyltin hydride at room temperature for 4 days. The NMR spectrum also confirmed the formation of only one isomer (**6a**).

**Reduction of 1,3-Diphenyl-2-chloro-2-bromoaziridine (3a,b)**. The reduction of a mixture of isomers of **3** (**3b/3a** = 2.3) was conducted at room temperature for 24 h. Attempts to isolate the product (**7**) by column chromatography (alumina or silica gel, *n*-pentane eluent) or by recrystallization from *n*-pentane were unsuccessful. However, the NMR spectrum of the reaction mixture revealed the

formation of a mixture of isomers of **7** (**7b/7a** = 2.5). Each isomer of **3** was reduced separately under the same conditions (room temperature, 24 h). The NMR spectrum of the reaction mixture of **3a** in *n*-pentane showed the absorptions at  $\delta$  3.25 (d,  $J = 2.0\text{ Hz}$ ) [3.16 (d,  $J = 2.0\text{ Hz}$ ) in benzene] and 4.27 (d,  $J = 2.0\text{ Hz}$ ) [4.08 (d,  $J = 2.0\text{ Hz}$ ) in benzene] in addition to the peaks due to *n*-pentane, phenyl group, and the *n*-butyl group of *n*-butyltin bromide. The NMR spectrum of the reaction mixture of **3b** in *n*-pentane showed the absorptions at  $\delta$  3.20 (d,  $J = 5.0\text{ Hz}$ ) [2.87 (d,  $J = 5.0\text{ Hz}$ ) in benzene] and 4.32 (d,  $J = 5.0\text{ Hz}$ ) [4.11 (d,  $J = 5.0\text{ Hz}$ ) in benzene] in addition to the peaks due to *n*-pentane, phenyl group, and *n*-butyl group of *n*-butyltin bromide.

**Reduction of 1,3-Diphenyl-2,2-dichloroaziridine (4)**. The reduction was conducted at room temperature for 4 days. The reduction product (**7**) could not be isolated by column chromatography. The NMR spectrum of the reaction mixture showed the formation of the two isomers of **7** (**7b/7a** = 1.9/1).

**Reduction of 1,3-Diphenyl-2,2-dibromoaziridine (5)**. The reduction was conducted at room temperature for 23 h. The starting material (**5**) was completely consumed. The reduction product (**8**) could not be isolated by column chromatography because of its decomposition. The NMR spectrum of the reaction mixture showed the formation of the two isomers of **8** (**8b/8a** = 2.0/1).

**Registry No.**—**1a**, 57500-62-6; **2a**, 57500-63-7; **3a**, 57500-61-5; **3b**, 57500-60-4; **4**, 3543-98-4; **5**, 39072-51-0; **6a**, 60253-62-5; **7a**, 3683-71-4; **7b**, 952-87-4; **8a**, 60253-63-6; **8b**, 60253-64-7; CCIF, 1691-88-9; CClBr, 13590-47-1; CBrF, 4539-11-1;  $\text{CBr}_2$ , 4371-77-1; *N*-benzylideneaniline, 538-51-2; tri-*n*-butyltin hydride, 688-73-3.

## References and Notes

- T. Ishihara, K. Hayashi, T. Ando, and H. Yamanaka, *J. Org. Chem.*, **40**, 3264 (1975).
- L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 2531 (1971).
- D. E. Applequist and A. A. Peterson, *J. Am. Chem. Soc.*, **82**, 2372 (1960).
- T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *J. Am. Chem. Soc.*, **89**, 5719 (1967).
- T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970).
- L. A. Singer and J. Chen, *Tetrahedron Lett.*, 939 (1971).
- T. Ishihara, E. Ohtani, and T. Ando, *J. Chem. Soc., Chem. Commun.*, 367 (1975).
- R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **95**, 7180, 7182 (1973).
- L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 981 (1972).
- 1,3-Diphenyl-2,2-dichloroaziridine has already been prepared by this method; e.g., M. K. Mellahn, L. L. Augenstein, and J. L. McManaman, *J. Org. Chem.*, **36**, 3627 (1971).
- The configurations of **3a** and **3b** were assigned on the basis of the configurations of the reduction products, **7a** and **7b**, complete retention of configuration during the reduction being assumed. The alternative assignment is very unlikely, because it is implausible that the reduction of **1** and **2** proceed with complete retention while that of **3** proceeds with complete inversion.
- There are no data, in the literature, on coupling constants ( $J_{\text{HF}}^{\text{vic}}$ ) between ring hydrogen and fluorine in the aziridine compounds containing ring fluorine. This assignment was tentatively made by comparison of the coupling constants with those of the *gem*-halofluorocyclopropanes;  $J_{\text{HF}}^{\text{cis}}$  is 15.5–17.7 Hz and  $J_{\text{HF}}^{\text{trans}}$  is 3.0–9.4 Hz.<sup>4,13</sup>
- K. L. Williamson, Y.-F. Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Am. Chem. Soc.*, **90**, 6717 (1968); H. Yamanaka, T. Yagi, K. Teramura, and T. Ando, *Chem. Commun.*, 380 (1971).
- The possibility that the **b** isomer was formed but was lost during the workup may be ruled out, since 1,3-diphenyl-2,2-dichloro- (**4**) and -dibromoaziridine (**5**) are relatively stable under similar conditions.
- J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 321 (1965).
- J. A. Deyrup and R. B. Greenwald, *J. Am. Chem. Soc.*, **87**, 4538 (1965).
- The instability of **7** was reported by Deyrup et al.<sup>15</sup> They isolated it incompletely from the reaction mixture by column chromatography using inactive alumina, but neither their method nor its modification gave satisfactory results in our hands.
- M. Ueyama and K. Tori, *Nippon Kagaku Zasshi*, **92**, 741 (1971); M. Ohtsuru and K. Tori, *J. Mol. Spectrosc.*, **27**, 296 (1968).
- H. G. Kuivila, *Acc. Chem. Res.*, **1**, 299 (1968), and references cited therein.
- D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).
- L. J. Altman and T. R. Erdman, *Tetrahedron Lett.*, 4891 (1970).
- T. Ando, K. Wakabayashi, H. Yamanaka, and W. Funasaka, *Bull. Chem. Soc. Jpn.*, **45**, 1576 (1972).
- L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1969).
- The reduction of a mixture of **3a** and **3b** with less than stoichiometric *n*- $\text{Bu}_3\text{SnH}$  for a shorter period showed that **3b** was more reactive than **3a**. This means that the bromine trans to the phenyl group on the adjacent carbon is more reactive than bromine cis to the phenyl group.
- A. G. Cook and E. K. Fields, *J. Org. Chem.*, **27**, 3686 (1962).