Nuclear Magnetic Resonance Spectra and Nitrogen Inversion in 1-Alkyl-2-aryl-3-carboaziridines

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The proton magnetic resonance spectra of several *cis*- and *trans*-1-alkyl-2-aryl-3-benzoylaziridines and *cis*- and *trans*-methyl-1-alkyl-2-aryl-3-aziridine carboxylates were studied over a temperature range of 70 to −40°. The spectra of the cis aziridines show slight temperature dependence while the corresponding trans isomers exhibit major changes in the same temperature range. The results are rationalized in terms of the nitrogen inversion process. Evidence is presented which indicates that the trans isomers exist in a preferred conformation with the *N*-alkyl group syn to the carbonyl. The chemical shifts of the ring protons are rationalized in terms of the anisotropies of the C–N bonds, C–C bonds, and the van der Waals dispersion effects.

Since the first study of the nitrogen inversion process of 1-alkylaziridines utilizing variable-temperature pmr by Bottini and Roberts,[3] the subject has been of intense interest to several investigators.[4] This fact, coupled with our continued interest in aziridine ketones[5] and more recently methyl aziridinecarboxylates,[6] has led us to a detailed pmr study of 1-alkyl-2-aryl-3-benzoylaziridines and 1-alkyl-2-aryl-3-aziridinecarboxylates. Previous reports of the pmr spectra of the cis and trans forms of 1-alkyl-2-aryl-3-aroylaziridines[7] and 1-alkyl-2,-3-dibenzoylaziridines[8] have dealt primarily with chemical shifts, solvent-induced chemical shift differences, and, where appropriate, the spin–spin coupling constants of the aziridine ring protons. When the ring protons are nonequivalent, the vicinal proton coupling constants J_{cis} and J_{trans} lie in the ranges 6.5–7.5 and 2.0–3.5 Hz, respectively. The same reports[7,8] indicated that no additional multiplicity was observed in the ring proton spectra of the aziridine ketones, presumably because the spectra were determined at temperatures where the inversion process was too rapid.

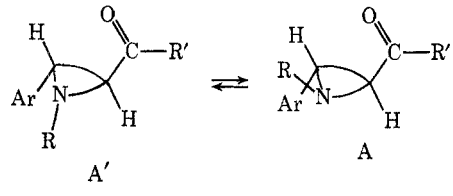
The pmr spectra of these aziridines would be expected to exhibit an AX or AB pattern for the ring protons, C_2 H and C_3 H, if the inversion process is fast relative to the nmr time scale.

By examination of the possible conformations of the trans aziridines (Scheme I), one can see that if the rate of inversion is slowed sufficiently it may be possible to observe A and A′. The ring protons in A would be expected to exhibit an AX or AB pattern and similarly the ring protons in conformer A′ should exhibit an AX or AB pattern. Hence there is a possibility of observing as many as eight lines for the ring protons if the rate of inversion is sufficiently slowed. One will also note that the *N*-alkyl groups of the two conformers may be in different magnetic environments and hence two separate signals for these groups are possible. The greatest effect would be expected for those protons bonded to the carbon atom α to the nitrogen of the *N*-alkyl group. In addition the relative populations of conformers A and A′ may be different.

If the same rationale is applied to the cis aziridines (Scheme II), similar conclusions result.

SCHEME I

POSSIBLE CONFORMATIONS OF *trans*-1-ALKYL-2-ARYL-3-CARBOAZIRIDINES

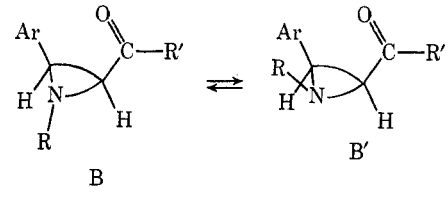


A′ ⇌ A

R = alkyl; R′ = Ph, OCH_3; Ar = Ph, p-$C_6H_5C_6H_4$

SCHEME II

POSSIBLE CONFORMATIONS OF *cis*-1-ALKYL-2-ARYL-3-CARBOAZIRIDINES



B ⇌ B′

R = alkyl; R′ = Ph, OCH_3; Ar = Ph, p-$C_6H_5C_6H_4$

We now wish to report the synthesis of several new cis–trans pairs of 1-alkyl-2-aryl-3-aroylaziridines and methyl 1-alkyl-2-aryl-3-aziridinecarboxylates and, also, to report the salient features of the pmr spectra of these and other aziridine ketones and esters. These new data, when examined in light of previous pmr studies of the nitrogen inversion process in aziridines, indicate that the *N*-alkyl substituent in several of the aziridines in question occupies a preferred conformation with respect to the ring carbon substituents.

Results and Discussion

Preparation of Materials.—The previously described methods of Cromwell[9] and Southwick[10] were successfully applied to the synthesis of the 1-alkyl-2-aryl-3-aroylaziridines employed in this study. The cis and trans forms of the methyl 1-alkyl-2-aryl-3-aziridine carboxylates were produced upon treatment of a ben-

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(2) To whom inquiries should be addressed.
(3) A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 5203 (1958).
(4) More recently, (a) J. D. Roberts, *et al.*, *ibid.*, **91**, 642 (1969); (b) K. Mislow, *et al.*, *ibid.*, **92**, 4050 (1970).
(5) For preceding paper in this series see D. K. Wall, J. L. Imbach, A. E. Pohland, R. C. Badger, and N. H. Cromwell, *J. Heterocycl. Chem.*, **5**, 77 (1968).
(6) (a) P. B. Woller and N. H. Cromwell, *ibid.*, **5**, 579 (1968); (b) *J. Org. Chem.*, **35**, 888 (1970).
(7) A. E. Pohland, R. C. Badger, and N. H. Cromwell, *Tetrahedron Lett.*, 4369 (1965).
(8) A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, *J. Amer. Chem. Soc.*, **87**, 1050 (1965).
(9) N. H. Cromwell, *et al.*, *ibid.*, **73**, 1044 (1951).
(10) P. L. Southwick and W. L. Walsh, *ibid.*, **77**, 405 (1955).

zene or methanol solution of methyl α-bromo-*p*-phenylcinnamate with a 15-fold excess of the primary amine of choice at room temperature for 24–28 hr.[6]

The infrared and ultraviolet spectra of the aziridine ketones and esters are in accord with spectral data of analogous aziridines.[6b,11]

Proton Magnetic Resonance Spectra at 37°.—The ring proton spectra of the cis and trans forms of methyl 1-alkyl-2-aryl-3-aziridinecarboxylates show the same general characteristics as reported for the analogous 1-alkyl-2-aryl-3-aroylaziridines.[7] Thus, the ring protons of the cis isomer appear at higher field than those of the corresponding trans forms. In the trans forms in which the carbonyl group is in the cisoid conformation,[11] both C_2 H and C_3 H are strongly deshielded by the anisotropy of the C_2 phenyl substituent and the carbonyl moiety. Replacement of the phenyl substituent by a methyl substituent in the ketone series results in C_2 H being shifted to higher fields. In 1-cyclohexyl-2-benzoylaziridine, that proton at C_3 which has a cis stereochemical relationship with respect to the aroyl group is strongly deshielded relative to the remaining proton at C_3 which is trans to this same group. Similarly, in 1-methyl-2-phenylaziridine the proton at C_3 which is cis to the C_2 phenyl substituent is deshielded relative to the proton at C_3 which is trans to the same group.[12] The net result of the diamagnetic anisotropic effects of the aryl and carbonyl groups is that the ring protons of the cis isomers are shielded (or less strongly deshielded) relative to the corresponding trans isomers and are thus shifted to higher field. Similar chemical shift differences between protons α to the carbonyl groups of the cis and trans forms of 1-alkyl-2,3-diaroylaziridines[8] and 1,2-dibenzoylcyclopropanes[13] have been observed. The C_2 aryl substituent exerts a slight shielding effect on the methoxy carbonyl protons of the cis aziridine esters and also aids in assigning the proper stereochemical configuration in this series.

The multiplicities of the ring protons in the aziridine ketones are as anticipated for vicinal protons in which the chemical shift difference between the two nuclei is less than or equal to the coupling constant. Thus one observes either a single peak, a triplet, or a quartet. In contrast, the differences in chemical shift for C_2 H and C_3 H in the aziridine esters are sufficiently large (24–30 Hz) in comparison to J so that doublets are observed for each of these protons. Observed coupling constants of 7.0–7.5 and 2.5–3.0 Hz for the cis and trans aziridine esters, respectively, are of the same magnitude as reported for the analogous 1-alkyl-2-aryl-3-aroylaziridines.[7]

In contrast to the cis series, the ring proton spectra of the trans aziridines are greatly affected by the *N*-alkyl substituent and the effects, in turn, are solvent and temperature dependent. While the cis ring protons are sharp at 37° in chloroform solution, the trans isomers are broadened. Thus the half-widths of C_2 H are 1.0, 3.2, and 6.0 Hz for the trans aziridine ketones when the *N*-alkyl substituents are isopropyl (or cyclohexyl) ethyl (or benzyl) and methyl, respectively. At the same time the resonance signals from the methine, methylene, and methyl groups attached to the nitrogen atom are broadened to the extent that they appear as poorly resolved multiplets. In general, the C_2 H line width is greater than the line width of C_3H. This may be due to coupling of the C_2 H to the adjacent (ortho) protons of the C_2 aryl substituent. At 37° in carbon tetrachloride and benzene the line width of C_2 H in *trans*-1-ethyl-2(*p*-biphenyl)-3-benzoylaziridine (**9b**) is 1.4 and 1.6 Hz, respectively, while the line width in chloroform is 3.2 Hz. In addition, the methylene protons of the ethyl group appear as a slightly broadened quartet in carbon tetrachloride and benzene in contrast to the unresolved multiplet observed in chloroform solution. The appearance of the methylene resonance signals is not appreciably altered upon replacement of the proton at C_2 by deuterium.

The methylene protons of the *N*-benzyl group in *cis*- and *trans*-1-benzyl-2-phenyl-3-benzoylaziridine (**6a,b**) and methyl *cis*- and *trans*-1-benzyl-2-(*p*-biphenyl)-3-aziridine carboxylate (**12a,b**) are diastereotopic in all conformations and hence anisochronous.

The methylene protons in **6a** and **12a** appear as two distinct doublets (J = 14.0–15.0 Hz), whereas the methylene protons in **6b** and **12b** appear as broadened singlets.

The *N*-isopropyl methyl groups in *cis*- and *trans*-1-isopropyl-2-(*p*-biphenyl)-3-benzoylaziridine (**4a,b**) and *cis*- and *trans*-1-isopropyl-2-(*p*-biphenyl)-3-aziridinecarboxylate (**10a,b**) are also diastereotopic in all conformations. The methyl groups in **4a** and **10a**, however, appear as a doublet in deuteriochloroform, a broadened doublet in benzene, and two distinct doublets in carbon tetrachloride. In contrast, the methyl groups of the trans isomers **4b** and **10b** appear as two doublets in all of these solvents. The methine proton of the *N*-isopropyl group of **4a** and **10a** appears as a multiplet of at least nine lines in deuteriochloroform in comparison to the unresolved multiplet observed for this proton in **4b** and **10b**.

Variable-Temperature Proton Magnetic Resonance Spectra.—The partial pmr spectrum of *trans*-1-methyl-2-(*p*-biphenyl)-3-benzoylaziridine (**2b**) (Table I) appears in Figure 1. At 66°, the *N*-methyl protons appear as a singlet with a line width at half-height of 1.5 Hz. The ring protons at C_2 and C_3 exhibit a line width of

TABLE I

PMR SPECTRA OF *trans*-1-METHYL-2-(*p*-BIPHENYL)-3-BENZOYLAZIRIDINE[a]

Temp, °C	V_{H_2}[a] (width)[b]	V_{H_3}[a] (width)[b]	V_{CH_3}[a] (width)[b]	V'_{CH_3}[a,c]
66	215 (0.8)	206 (1.8)	159 (1.5)	
40	216 (1.0)	207 (3.5)	160 (3.6)	
37	215 (1.1)	206 (3.5)	160 (4.2)	
34	216 (1.5)	207	161 (4.6)	154
20	219 (1.8)	206 (2.2)	163 (1.8)	143
−6	220 (1.4)	207 (1.8)	163 (1.5)	140
−23	220 (1.2)	207 (1.8)	163 (1.5)	141

[a] Pmr spectra were determined on a Varian A-60D spectrometer with deuteriochloroform solutions. Chemical shifts are concentration independent and are reproducible within ±1 Hz. Tetramethylsilane (TMS) was the internal standard (0.0 Hz). All chemical shifts are given in hertz downfield relative to TMS. [b] Widths are line widths at half-heights and are expressed in hertz. [c] V' is the chemical shift in hertz of the methyl group of the minor invertomer.

(11) N. H. Cromwell, R. E. Bambury, and J. L. Adelfang, *J. Amer. Chem. Soc.*, **82**, 4241 (1960).

(12) S. J. Brois, *Tetrahedron*, **26**, 227 (1970).

(13) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Amer. Chem. Soc.*, **85**, 1001 (1963).

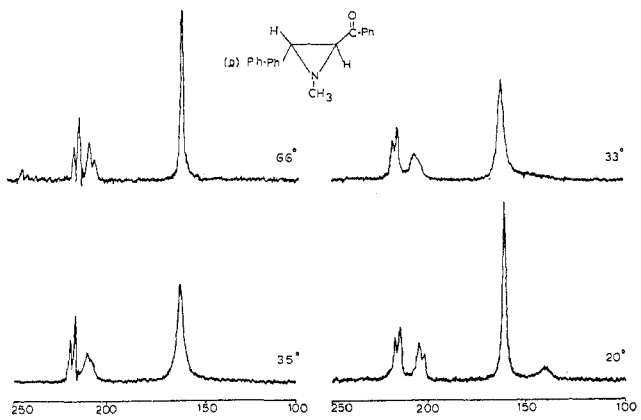


Figure 1.—Variable-temperature pmr spectra of *trans*-1-methyl-2-(*p*-biphenyl)-3-benzoylaziridine.

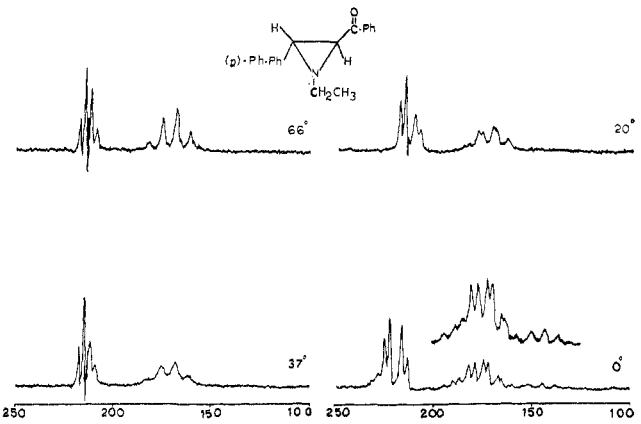


Figure 2.—Variable-temperature pmr spectra of *trans*-1-ethyl-2-(*p*-biphenyl)-3-benzoylaziridine.

1.8 and 0.8 Hz, respectively. Upon cooling to 37°, the line widths increase significantly to 4.2 Hz for the *N*-methyl resonance and 3.5 and 1.1 Hz for the ring protons at C_2 and C_3, respectively. When the temperature is lowered to 34°, the *N*-methyl signal is split into two separate broad peaks of unequal intensity. Further cooling results in a sharpening of these peaks and an increase in the chemical shift difference between them. The signals for the ring protons sharpen considerably. We feel that these observations can best be explained by the nitrogen inversion process. At 66° the rate of inversion is rapid and one observes an averaged signal for the two conformers (Scheme I). As the temperature is lowered the inversion rate is slowed. Hence at 37° the *N*-methyl signal has broadened by a factor of 2.8. Further cooling decreases the rate of inversion to the extent that the two separate *N*-methyl resonances appear, each resonance corresponding to one invertomer. Cooling to 20° and lower results in a further decrease in the inversion rate and hence a sharpening of the individual signals. At +2.0° the ratio of the two conformers is 83:17 by integration of the separate methyl resonances. Hence $\Delta F = -0.84$ kcal/mol (at 274°K). The ratio is constant, within experimental error, over the temperature range studied. As mentioned earlier, the ring protons in each conformer should appear as an AB or AX pattern. Unfortunately, the AB pattern corresponding to the ring protons in the minor invertomer are not resolved from the two doublets of the major conformer. There is a noticeable reproducible broadening downfield of the two sets of doublets of the major conformer which we believe is due to the ring protons of the minor conformer. Further support for this rationale was obtained by examination of the pmr spectrum of *trans*-1-ethyl-2-d_1-2-(*p*-biphenyl)-3-benzoylaziridine (**3'b**) at several temperatures. The proton at C_3 appeared as a singlet at 33° and higher temperature, but, when the spectrum was recorded at −31°, the signal was split into two peaks of unequal intensity. The smaller peak, which may be due to C_3 H of the minor conformer, appears downfield of the major resonance by approximately 2 Hz.

Figure 2 indicates that additional multiplicities are present, however. The methylene protons of the *N*-ethyl group are diastereotopic and hence will have different chemical shifts. This difference, however, may be small. The additional multiplicities observed may be due to slight changes in the relative chemical shifts of these protons with decreasing temperature.

Cooling may also slow the rate of rotation about the C–N bond resulting in nonequivalent methylene protons. An ABX_3 pattern would be observed for the ethyl group of each conformer in either case. We believe that the observed multiplicities of the methylene resonances and the spectra of **3'b** at lower temperatures are consistent with the presence of two detectable conformations (A and A') further complicated by nonequivalent methylene protons.

The pmr spectra of methyl *trans*-1-ethyl-2-(*p*-biphenyl)-3-aziridinecarboxylate (**9b**) over the temperature range studied resembles that of *N*-ethylaziridinyl ketone **4**. At 65° the methylene protons of the *N*-ethyl group appear as a sharp quartet. The ring protons appear as well-resolved doublets at 196 and 154 Hz for C_2 H and C_3 H, respectively. Cooling to 37° produces a broadening of both the ring protons and the methylene protons of the *N*-ethyl group. At 0° fine structure appears within the methylene protons resonance and additional multiplets appear 20 Hz upfield. Again we attribute the additional multiplicities to a decrease in the rate of inversion and to a nonequivalence of the methylene protons.

trans-1-Isopropyl-2-(*p*-biphenyl)-3-benzoylaziridine (**4b**) exhibits variable-temperature pmr spectra consistent with the other aziridinyl ketones and esters studied. At 66° the methine proton of the *N*-isopropyl group exhibits a sharp heptet. The ring protons appear as a sharp AB quartet. Cooling to 37° broadens the *N*-isopropyl methine resonance by a factor of 1.8. Further cooling to 0° produces a small broad resonance 47 Hz upfield from the methine resonance. While this broad resonance is reproducible at low temperatures (0 to −40°) and is not present at higher temperatures, it could not be resolved into individual lines. Nevertheless we believe that this upfield resonance is due to the methine proton of the *N*-isopropyl group of the minor conformer, while the heptet downfield which is sharp again at low temperatures is the analogous signal of the major conformer. The changes in ring proton spectra over the temperature range studied resemble the variations observed with the *trans*-*N*-methyl- and -*N*-ethylaziridinyl ketones.

The pmr spectrum of *trans*-1-benzyl-2-phenyl-3-benzoylaziridine (**6b**) at 70° yields a singlet at 244 Hz

for the benzyl protons. Upon cooling to 37° this sonance is considerably broadened. Further cooling to 20° produces a broad AB quartet (J_{AB} = 13.5 Hz). At 0° this quartet is considerably sharpened. The ring protons at 66° appear as an A_2 singlet at 217 Hz. Cooling, however, affects the chemical shift so that at 20° the ring protons appear as a AX pattern (two doublets). Examination of **6'b** (deuterium at C-2) results in a singlet for H-3 at 217 Hz. Upon cooling to 30° an additional singlet appears at 202 Hz which is of a minor intensity. Additionally a shoulder appears on the singlet at 217 Hz. The pmr spectrum of **6''b** (deuterium at C-2 and C-3) at 66° exhibits a singlet for the benzyl protons. Cooling to 20° results in an AB quartet for the benzyl protons and an additional singlet at 218 Hz which was masked by the ring protons in **6b** and **6'b**. We believe that the AB quartet for the benzyl protons is the result of magnetic nonequivalence resulting from restricted rotation about the *N*-benzyl C–N bond or slight changes in relative chemical shifts of the diastereotopic methylene protons with changing temperature. The singlet at 218 Hz in **6''b**, however, may be due to the benzylic protons of the minor conformer and results from a decrease in the rate of inversion. The singlet at 202 Hz in **6'b** is due to the proton at C_3 of the minor conformer.

The pmr spectrum of *cis*-1-benzyl-2-phenyl-3-benzoylaziridine (**6a**) gives an AB quartet (J = 13.8 Hz) for the benzylic protons at 66° and an AB triplet (J = 7.0 Hz) for the ring protons. Cooling to −20° changes the AB triplet of the ring protons to an AB quartet. We believe that this change is due only to a slight change in the relative chemical shifts of C_2 H and C_3 H and not to a slowed inversion process. Substitution of deuterium at C_2 resulted in a singlet for proton at C_3 at all temperatures.

Padwa[14] has reported the variable-temperature pmr spectra of *trans*-1-benzyl-2-phenyl-3-(*p*-tolyl)aziridine (**16b**). At high temperatures the ring protons appeared as an A_2 singlet. On cooling this singlet was split into two doublets of equal intensity. This spectral change was attributed to a slower rate of inversion at low temperature. The effects of temperature with regard to the *N*-benzyl group resonances were omitted. These results were compared with *trans*-1-benzyl-2,3-dibenzoylaziridine (**18b**). This may not be a valid comparison, however. The ring protons in **18b** are constitutionally equivalent if the inversion process is relatively fast. With a decrease in the rate of inversion, one would expect the ring protons to become nonequivalent, since one ring proton would be syn to the *N*-benzyl group and one anti. This would result in an AB quartet. The ring protons in **16b**, however, are constitutionally nonequivalent and it is simply fortuitous that they have the same chemical shift. It is not necessary that the relative chemical shifts of C_2 H and C_3 H remain constant with changing temperature (*e.g.*, see Table I). Hence the changes in the pmr spectra of **16b** with decreasing temperature may be due to small changes in the relative chemical shift of C_2 H and C_3 H and not to a decrease in the rate of nitrogen inversion. Our argument is strengthened since the pmr spectra of **6a** with decreasing temperature exhibits a similar spectral change, while the same compound with deuterium substituted at C_2 (**6'b**) showed no change with decreasing temperature. Additional peaks which are due to the nitrogen inversion process may be obscured and only be visible through deuterium labeling studies similar to those conducted for **6b**.

The pmr spectra of methyl *trans*-1-benzyl-2-(*p*-biphenyl)-3-aziridinecarboxylate (**12b**) is less complicated than the corresponding aziridinyl ketone, since the ring protons appear as an AX pattern (two doublets). The methylene protons of the *N*-benzyl group appear as a sharp singlet at 65°. Cooling to 37° produces a noticeable broadening of the methylene protons and broadening of the ring protons. The benzylic protons appear as an AB quartet (J = 12.5 Hz) at 10° while a singlet appears 20 Hz upfield. The AB quartet again is attributed to the diastereotopic methylene protons of the major conformer. The upfield singlet may be due to the diastereotopic methylene protons of the minor conformer.

Both methyl *trans*-1-*tert*-butyl-2-(*p*-biphenyl)-3-benzoylaziridinecarboxylate (**13b**) and *trans*-1-*tert*-butyl-2-phenyl-3-benzoylaziridine (**7b**) showed little change in their pmr spectra over the temperature range studied. This may be due to an inability to attain a sufficiently low temperature to slow the rate of inversion to the degree necessary for observation by pmr. This is not unexpected, since Roberts[3] has observed that the rate of inversion increased with the increase in the size of the *N*-alkyl group.

In general the pmr spectra of the *trans*-1-alkyl-2-aryl-3-benzoylaziridines and the methyl *trans*-1-alkyl-2-aroyl-3-aziridinecarboxylates at low temperatures exhibit a pattern consistent with the presence of two conformers. The protons of the *N*-alkyl group which are α to the nitrogen atom in the preferred conformation are 10–30 Hz downfield to the respective protons of the minor conformer. The carbonyl moiety, the C_2-aryl substituent, and the aziridine ring are all capable of exerting anisotropic effects on these protons. However, for either the carbonyl or the 2-aryl substituent to effectively shield these protons, the *N*-alkyl substituent must be syn to these groups. Replacement of the 2-phenyl substituent by methyl **15b** does not appreciably alter the magnitude of the shielding experienced by the cyclohexyl methine proton in *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridine (**5b**). However, reduction of this aziridine ketone to the corresponding aziridinecarbinol **20**[5] shifts the methine resonance upfield to an extent that it is now masked by the resonances of the other protons in the cyclohexane ring. The pmr spectra of *trans*-1-methyl-2,3-dibenzoylaziridine (**17b**) exhibits a resonance at 157 Hz which is attributed to the *N*-methyl resonance. One will note that the *N*-methyl group must be syn to a benzoyl group and hence will be influenced by the carbonyl moiety. The major conformer of *trans*-1-methyl-2-(*p*-biphenyl)-3-benzoylaziridine (**2b**) exhibits a resonance at 162 Hz which is attributed to the *N*-methyl group. Reduction of the above *N*-methylaziridine **2b** with lithium aluminum hydride produced a single aziridinecarbinol **19**. The pmr spectrum of this carbinol exhibited an *N*-methyl resonance at 128 Hz which was 34 Hz upfield from the *N*-methyl resonance of the corresponding aziridine ketone. These results seem to indicate that the preferred conformation of **2b** is the conformer with the

(14) A. Padwa and L. Hamilton, *J. Amer. Chem. Soc.*, **89**, 105 (1967).

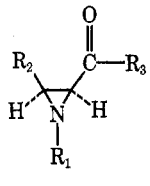
N-alkyl group and the benzoyl occupying a syn relationship (structure A, Scheme I). Further, the fact that in the other trans aziridine ketones and aziridine esters whose pmr spectra were temperature dependent, the protons α to the nitrogen of the *N*-alkyl substituent were at lower field in the major conformer. This seems to indicate that the preferred conformation may be that in which the *N*-alkyl substituent is syn to the carbonyl moiety. Sterically there appears to be little difference between the two conformers (A and A′). In conformer A′, however, the nitrogen lone pair is in close proximity to the nonbonded electrons of the carbonyl group. Such an electronic interaction may be sufficient to destabilize A′. In conformer A, on the other hand, the nitrogen lone pair and the nonbonded electrons of the carbonyl group are situated in a manner as to minimize these interactions.

The pmr spectra of the analogous *cis*-aziridinyl ketones and methyl *cis*-aziridinecarboxylates studied, however, exhibited only slight changes with decreasing temperature. This may be due to failure to lower the temperature sufficiently to slow the rate of inversion. A second explanation, however, seems more reasonable. Conformer B (see Scheme II) would be expected to be greatly favored over conformer B′ from steric considerations. If the equilibrium concentration of B′ is very low relative to B, conformer B′ would not be observed by pmr even if the temperature was lowered to sufficiently slow the rate of inversion.

Inspection of the chemical shifts of the ring protons of the *cis*-aziridinyl ketones and methyl *cis*-aziridinecarboxylates (Table II) indicates a downfield shift in

TABLE II

CHEMICAL SHIFTS OF RING PROTONS AND PROTONS α TO THE NITROGEN OF THE *N*-ALKYL GROUP IN THE CIS AZIRIDINES[a]



				—Chemical shift, Hz—		
Compd	R_1	R_2	R_3	H_α	H_2	H_3
2a	CH_3	Ar[b]	Ph[b]	152	183	193
3a	C_2H_5	Ar	Ph	156[d]	184	194[c]
4a	*i*-C_3H_7	Ar	Ph	111	188	197
5a	C_6H_{11}	Ph	Ph	60–120[e]	187	197[c]
6a	CH_2Ph	Ph	Ph	220, 235[d]	192	199
7a	*tert*-C_4H_9	Ph	Ph		205	205
9a	C_2H_5	Ar	OCH_3	150[d]	174	150[c]
10a	*i*-C_3H_7	Ar	OCH_3	100	174	154
11a	C_6H_{11}	Ar	OCH_3	60–120[f]	175	155[c]
12a	CH_2Ph	Ar	OCH_3	215, 236[d]	182	159
13a	*tert*-C_4H_9	Ar	OCH_3		190	162[c]

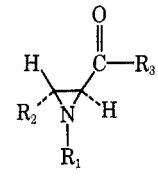
[a] Pmr spectra were determined on a Varian Associates Model A-60 or A-60D spectrometer at 37° in deuteriochloroform. Chemical shifts are given in hertz downfield from tetramethylsilane, an internal standard. For compound preparation, see for **2a**, **5a**, and **6a**, ref 9; **7a**, ref 20; **10a** and **11a**, ref 6a; other aziridines, this paper. [b] Ar = *p*-biphenyl; Ph = phenyl. [c] The assignment of the ring protons was established by preparation of these compounds with deuterium at C_2. [d] Nonequivalent methylene protons. [e] Methine proton masked by cyclohexyl methylene envelope. [f] See ref 3.

both C_2 H and C_3 H as the size of the *N*-alkyl group is varied (*i.e.*, Me < Et < *i*-Pr ~ C_6H_{11} ≪ *tert*-Bu). This downfield shift seems to be a function of steric crowding on the α carbon of the *N*-alkyl group. Hence the sterically bulky *tert*-butyl group is responsible for the largest downfield shift. This shift may be due to intramolecular van der Waals dispersion effects.[15] Such effects have also been noted recently by Brois[12] in *N*-alkylaziridines and *N*-alkylstyrenimines.

Careful examination of the chemical shifts of the trans isomers (Table III) indicates that the C_2 H is

TABLE III

CHEMICAL SHIFTS OF RING PROTONS AND PROTONS TO THE NITROGEN OF THE *N*-ALKYL GROUP IN THE TRANS AZIRIDINES[a]



				—Chemical shift, Hz—		
Compd	R_1	R_2	R_3	H	H_2	H_3
1b	H	Ar[b]	Ph[b]	163	191	213[c]
2b	CH_3	Ar	Ph	160	202	213
17b	CH_3	PhCO	Ph	157	238	238
3b	C_2H_5	Ar	Ph	173	211	217[c]
4b	*i*-C_3H_7	Ar	Ph	181	215	220
15b	C_6H_{11}	CH_3	Ar	127	161	199
5b	C_6H_{11}	Ph	Ph	127	214	218[c]
6b	CH_2Ph	Ph	Ph	242	217	217[c]
7b	*tert*-C_4H_9	Ph	Ph		231	204[c]
9b	C_2H_5	Ar	OCH_3	186	195	165[c]
10b	*i*-C_3H_7	Ar	OCH_3	181	195	164
11b	C_6H_{11}	Ar	OCH_3	128	196	164
12b	CH_2Ph	Ar	OCH_3	240	198	163
13b	*tert*-C_4H_9	Ar	OCH_3		218	165

[a] Pmr spectra were determined on a Varian Associates Model A-60 or A-60D spectrometer in deuteriochloroform at 37°. Chemical shifts are given in hertz downfield from tetramethylsilane (TMS). Chemical shifts are reproducible to ±1 Hz. For compound preparation, see for **5b** and **6b**, ref 9; **7b**, A. Padwa and W. Eisenhardt, *J. Amer. Chem. Soc.*, **90**, 2442 (1968); **15b**, N. H. Cromwell and R. J. Mohrbacher, *ibid.*, **75**, 6252 (1953); **17b**, ref 8; **10b** and **11b**, ref 6a; other aziridines, this paper. [b] Ar = *p*-biphenyl, Ph = phenyl. [c] The assignment of the ring protons was established by preparation of these compounds with deuterium at C_2.

shifted downfield as the size of the nitrogen substituent is increased from methyl to *tert*-butyl. This downfield shift again can be attributed to an intramolecular van der Waals dispersion effect[14] if one assumes that the trans isomers exist in a preferred conformation in which the substituent on nitrogen is syn to the carbonyl group and C_2 H. This is in agreement with the low-temperature pmr studies discussed earlier. Concomitant with the large deshielding effect of the bulky *tert*-butyl group is an apparent shielding effect on C_3 H which is anti to the *tert*-butyl group. This effect is much larger in the aziridinyl ketones than in the methylaziridinyl esters. A similar effect was noted by Brois[15] and was attributed to a distortion of the electron cloud away from the substituents syn to the *tert*-butyl group and toward the substituents on the opposite side of the ring. In contrast to the observations of Brois,[15] however, is the downfield shift of the ring protons when the substituent on the

(15) For a discussion of these effects see L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 71.

nitrogen is changed from hydrogen to methyl. Brois observed an opposite effect and attributed it to the anisotropy of the C–N bond of the alkyl group. Our systems seem to indicate a deshielding effect similar to a dispersion effect in going from hydrogen to methyl, although the magnitude of this effect is much larger than would be expected.

Experimental Section

Melting points were determined by the capillary method and are uncorrected. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill. The infrared spectra were determined on Perkin-Elmer Model 237 or 621 instruments. The 60-MHz nmr spectra were determined on Varian A-60 or A-60D spectrometers and the chemical shifts are reported in parts per million (δ) relative to internal tetramethylsilane (δ 0.0).

A. Synthesis of Aziridine Ketones. Preparation of β-(*p*-Biphenyl)-β-methoxyaminopropiophenone (21).—By a modification of a previously published procedure,[16] 0.47 g (10 mmol) of methoxyamine[17] was added to a suspension of 2.50 g (8.7 mmol) of *trans*-4-phenylchalcone[18] in 20 ml of methanol. The suspension was warmed slightly below reflux for 5.5 hr. The reaction mixture was cooled and 2.56 g (88%) of **21** was collected. Recrystallization from ethanol gave white plates: mp 81–82°; ir (KBr) $\nu_{C=O}$ 1675 cm^{-1}; pmr ($CDCl_3$) δ 3.36 (d, J = 5.5 Hz, 2 H, C_α H), 3.45 (s, 3 H, $-OCH_3$), 4.72 (t, J = 5.5 Hz, 1 H, C_β H), 6.02 (br s, 1 H, NH), and 7.18–8.19 (m, 14 H, aromatic).

Anal. Calcd for $C_{22}H_{21}O_2N$: C, 79.73; H, 6.29; N, 4.23. Found: C, 79.64; H, 6.32; N, 4.34.

***trans*-2-(*p*-Biphenyl)-3-benzoylaziridine (1b).**—By a modification of a previously published procedure,[16] 0.36 g (6.67 mmol) of sodium methoxide in methanol was added dropwise to a warm solution of 1.12 g (3.38 mmol) of **21** in 70 ml of methanol. After stirring for 2 hr, the resultant red solution was cooled, yielding 0.92 g (90.7%) of an orange solid. The solid was dissolved in ether and washed free of base. The ether solution was dried ($MgSO_4$) and concentrated, and the residue recrystallized from ethanol giving **1b** as white needles: mp 117–118°; ir (KBr) $\nu_{C=O}$ 1662 cm^{-1}; pmr ($CDCl_3$) δ 2.72 (br s, 1 H, NH), 3.19 (br d, J = 2.3 Hz, 1 H, C_2 H), 3.55 (d, J = 2.3 Hz, 1 H, C_3 H), and 7.23–8.14 (m, 14 H, aromatic).

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.73; N, 4.68. Found: C, 84.05; H, 5.70; N, 4.78.

***trans*-1-Methyl-2-(*p*-biphenyl)-3-benzoylaziridine (2b).**—Methylamine (0.76 g, 25 mmol) was dissolved in 50 ml of ether cooled to 0°. To this solution were added 1.27 g (5.0 mmol) of iodine and 1.44 g (5.0 mmol) of *trans*-4-phenylchalcone.[18] After stirring for 6 hr at room temperature, the reaction mixture was diluted with benzene. The precipitated amine salt was removed by filtration and the filtrate was washed with water. The dried ($MgSO_4$) filtrate was concentrated and the pale yellow residue was recrystallized from ether to afford 1.25 g (80%) of *trans*-1-methyl-2-(*p*-biphenyl)-3-benzoylaziridine (**2b**): mp 100–101°; pmr ($CDCl_3$) δ 2.66 (br s, 3 H, methyl), 3.36 (br, s, 1 H, C_2 H), 3.55 (d, J = 2.6 Hz, 1 H, C_3 H), 7.2–7.7 and 7.9–8.1 (two m, 14 H, aromatic); ir (CCl_4) $\nu_{C=O}$ 1675 cm^{-1}.

Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.39; H, 6.29; N, 4.44.

1-Ethyl-2-(*p*-biphenyl)-3-benzoylaziridine, *cis* and *trans* (3a,b).—A solution of 1.27 g (5.0 mmol) of iodine and 1.2 g (25.0 mmol) of ethylamine in 25 ml of benzene was stirred at 10° while 1.42 g (5.0 mmol) of 4-phenylchalcone[18] was added. Stirring was continued until the initial yellow-red color was discharged (2–4 hr). Work-up according to the procedure described above gave a pale yellow solid which was recrystallized from methanol. *trans*-1-Ethyl-2-(*p*-biphenyl)-3-benzoylaziridine (**3b**), mp 96–97°, was obtained in 60% yield: pmr ($CDCl_3$) δ 1.10 (t, J = 7.0 Hz, 3 H, methyl), 2.86 (br q, J = 7 Hz, 2 H, methylene), 3.51 (br d, J = 2.7 Hz, 1 H, C_2 H), 3.61 (d, J = 2.7 Hz, 1 H, C_3 H), 7.1–7.6 and 7.8–8.0 (two m, 14 H, aromatic); ir (CCl_4) $\nu_{C=O}$ 1673 cm^{-1}.

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.47; N, 4.28; mol wt, 327.41. Found: C, 84.12; H, 6.49; N, 4.20; mol wt, 327 (mass spectrum).

The residue remaining after evaporation of the methanol filtrate was extracted several times with hot petroleum ether (bp 30–60°) and the insoluble material was recrystallized from ether–petroleum ether (1:1, v/v) to afford a pure sample of the corresponding cis aziridine: mp 109–111°; pmr ($CDCl_3$) δ 1.27 (t, J = 7.4 Hz, 3 H, methyl), 2.13–2.96 (m, 2 H, methylene), 3.06 (d, J = 7.3 Hz, 1 H, C_2H), 3.23 (d, J = 7.4 Hz, 1 H, C_3 H), 7.0–7.5 and 7.8–8.0 (two m, 14 H, aromatic); ir (CCl_4) $\nu_{C=O}$ 1670 and 1691 cm^{-1}.

Anal. Found: C, 84.32; H, 6.59; N, 4.31; mol wt, 327 (mass spectrum).

The cis/trans ratio was *ca.* 1:4 as determined from the pmr spectrum of the crude material.

1-Isopropyl-2-(*p*-biphenyl)-3-benzoylaziridine, *cis* and *trans* (4a,b) were produced by reaction of 4-phenylchalcone[18] (1.42 g, 5.0 mmol) with a mixture of 1.27 g (5.0 mmol) of iodine and isopropylamine (1.37 g, 25.0 mmol) in 25 ml of benzene. After work-up of the reaction mixture according to the above procedure, the crude material was extracted twice with hot petroleum ether. The residue was recrystallized from the same solvent to afford 0.35 g (26%) of pure *cis*-1-isopropyl-2-(*p*-biphenyl)-3-benzoylaziridine (**4a**): mp 108–110°; pmr ($CDCl_3$) δ 1.26 (d, J = 6.1 Hz, 6 H, isopropyl methyls), 1.85 (m, 1 H, isopropyl methine), 3.13 (d, J = 7.4 Hz, 1 H, C_2 H), 3.28 (d, J = 7.3 Hz, 1 H, C_3 H), 7.0–7.5 and 7.8–8.0 (two m, 14 H, aromatic); ir (CCl_4) $\nu_{C=O}$ 1670 and 1695 cm^{-1}.

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10; mol wt, 341.43. Found: C, 84.14; H, 6.87; N, 3.90; mol wt, 341 (mass spectrum).

The combined petroleum ether extracts were evaporated. The residue was diluted with pentane and cooled to produce a pale yellow solid. Recrystallization of this material from a minimal amount of methanol afforded 1.0 g (74%) of the corresponding trans aziridine (**4b**): mp 83–85°; pmr ($CDCl_3$) δ 0.94 and 1.21 (two d, J = 6.3 Hz, 3 H, each, isopropyl methyls), 3.59 (br d, J = 2.8 Hz, 1 H, C_2 H), 3.66 (d, J = 2.8 Hz, 1 H, C_3 H), 7.2–7.7 and 8.0–8.2 (two m, 14 H, aromatic); ir (CCl_4) $\nu_{C=O}$ 1673 cm^{-1}.

Anal. Found: C, 84.28; H, 6.78; N, 4.12; mol wt, 341 (mass spectrum).

The two aziridines were obtained in an overall yield of 80%.

B. Synthesis of Deuterium Labeled 1-H and 1-Alkyl-2-aryl-3-aroylaziridines. ***trans*-2-d_1-2-(*p*-Biphenyl)-3-benzoylaziridine (1′b).**—Base-catalyzed condensation of *p*-phenylbenzaldehyde-d_1 with acetophenone afforded 1-(*p*-biphenyl)-3-d_1-3-phenyl-2-propen-1-one (β-d_1-4-phenylchalcone), mp 109–110° (lit.[18] 110°). Reaction of labeled 4-phenylchalcone with methoxyamine followed by ring closure with sodium methoxide as described for **1b** gave **1′b**. Mixture melting point determination with **1b** showed no depression. The ring proton spectra consisted of a singlet at δ 3.55.

1-Ethyl-2-d_1-2-(*p*-biphenyl)-3-benzoylaziridine, *cis* and *trans* (3′a,b).—Bromination and subsequent dehydrohalogenation of β-d_1-4-phenylchalcone with *N*-methylpiperidine afforded 1-phenyl-2-bromo-3-d_1-3-(*p*-biphenyl)-2-propen-1-one (α-bromo-β-d_1-4-phenylchalcone), mp 29–31° (lit.[18] 30–31°). Reaction of the labeled α-bromo-4-phenylchalcone with ethylamine as previously described produced **3′a** and **3′b**. The ring proton spectra of **3′a** and **3′b** consisted of singlets at δ 3.23 and 3.61, respectively.

1-Cyclohexyl-2-d_1-2-phenyl-3-benzoylaziridine was produced as a mixture of the cis and trans (**5′a,b**) forms by treatment of the deuterium labeled α-bromochalcone with 2 equiv of cyclohexylamine in benzene. The isomeric aziridines were separated by fractional crystallization. Mixture melting point experiments with unlabeled samples showed no depression. The pmr spectrum ($CDCl_3$) confirmed the introduction of deuterium at C_2. Thus singlets were observed at δ 3.28 and 3.63 for the cis and trans forms, respectively.

1-*tert*-Butyl-2-d_1-2-phenyl-3-benzoylaziridine, *cis* and *trans* (7′a,b).—Base-catalyzed condensation of benzaldehyde-d_1 with acetophenone afforded 1,3-diphenyl-3-d_1-2-propen-1-one (β-d_1-chalcone), mp 56–57° (lit.[19] 58°). Reaction of β-d_1-chalcone with 1 equiv of iodine and 5 equiv of *tert*-butylamine in methanol for

(16) The procedure was developed by A. H. Blatt, *J. Amer. Chem. Soc.*, **61**, 3494 (1939); however, the structure of the product was incorrectly assigned as an α-amino-α,β-unsaturated ketone. Later N. H. Cromwell, *et al.*, *ibid.*, **73**, 1044 (1951), correctly assigned the structure as the isomeric aziridine.

(17) M. Davies and N. A. Spears, *J. Chem. Soc.*, 3987 (1959).

(18) N. H. Cromwell, *et al.*, *J. Amer. Chem. Soc.*, **65**, 301 (1943).

(19) E. P. Kohler and H. M. Chadwell in "Organic Syntheses," Collect. Vol. IV, 2nd ed, A. H. Blatt, Ed., Wiley, New York, N. Y., 1941, p 78.

24 hr at room temperature with work-up in the usual manner produced a pale yellow oil. Column chromatography on silica gel and elution with 5% ether–petroleum ether produced the labeled trans isomer **7'b**. The ring proton spectra consisted of a singlet at δ 3.40. A mixture melting point with unlabeled compound showed no depression.

Elution with 15% ether–petroleum ether produced the cis isomer **7'a**. The ring proton spectra consisted of a singlet at δ 3.41. Mixture melting point with unlabeled compound showed no depression.

1-Benzyl-2-d_1-2-phenyl-3-benzoylaziridine, *cis* and *trans* (6'a,b).—Treatment of α-bromo-β-d_1-chalcone with 2 equiv of benzylamine in methanol yielded the isomeric aziridines. Column chromatography on silica gel eluting with 5% ether–petroleum ether produced **6'b**. Continued elution with 15% ether–petroleum ether produced **6'a**. Mixture melting points with unlabeled compounds showed no depressions. Pmr ring proton spectra of **6'a** and **6'b** showed singlets at δ 3.32 and 3.62, respectively.

1-Benzyl-2,3-d_2-2-phenyl-3-benzoylaziridine, *cis* and *trans* (6''a,b).—Treatment of α-bromo-β-d_1-chalcone with 3 equiv of benzylamine-d_2 in benzene with work-up and separation as above produced **6''a** and **6''b**.

C. Synthesis of Methyl *cis*- and *trans*-1-Alkyl-2-(*p*-biphenyl)-3-aziridinecarboxylates. Methyl 1-Ethyl 2-(*p*-biphenyl)-3-aziridinecarboxylate, *cis* and *trans* (9a,b).—A stirred suspension of 2.0 g (5.0 mmol) of methyl *trans*-α-bromo-*p*-phenylcinnamate[6b] (**22**) in 50 ml of methanol was cooled to 0° and treated with 3.4 g (75.0 mmol) of ethylamine. The reaction mixture was allowed to warm to room temperature. After stirring for 24 hr all solids had dissolved. The solvent and excess amine were removed under reduced pressure without heating. The residue was diluted with ether and the precipitated amine salt was collected. The filtrate was washed with water and dried (anhydrous $MgSO_4$), and the solvent was removed under reduced pressure. The residual oil was chromatographed on silica gel (80 g) and eluted successively with petroleum ether (500 ml) and ether–petroleum ether mixtures (1:49, 500 ml; 1:9, 500 ml; 15:85, 1 l.). The latter fractions afforded 0.15 g (16%) of methyl *trans*-1-ethyl-2-(*p*-biphenyl)-3-aziridinecarboxylate (**9b**): mp 89–91°; pmr ($CDCl_3$) δ 1.13 (t, J = 7.3 Hz, 3 H, methyl), 2.75 (d, J = 2.4 Hz, 1 H, C_3 H), 3.25 (br s) and 3.4–2.8 (m, 3 H, C_2 H and methylene, respectively), 3.80 (s, 3 H, methoxy), and 7.3–7.7 (m, 9 H, aromatic); ir (CCl_4) $\nu_{C=O}$ 1733 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.79; H, 6.88; N, 4.90.

Further elution with 20% ether–petroleum ether gave 0.80 g (84%) of a colorless oil which eventually crystallized upon standing in the freezer, mp <5°. This material was assigned the structure methyl *cis*-1-ethyl-2-(*p*-biphenyl)-3-aziridinecarboxylate (**9a**) on the following data: pmr ($CDCl_3$) δ 1.24 (t, J = 7.0 Hz, 3 H, methyl), 2.50 and-2.90 [two d, superimposed on a multiplet of 12 lines, 2.1–2.9 (4 H, C_3 H, C_2 H, and methylene, respectively)], 3.48 (s, 3 H, methoxy), and 7.3–7.8 (m, 9 H, aromatic); ir (neat) $\nu_{C=O}$ 1725 and 1750 cm^{-1}.

Anal. Found: C, 76.96; H, 6.59; N, 5.02.

Methyl 1-Benzyl-2-(*p*-biphenyl)-3-aziridinecarboxylate, *cis* and *trans* (12a,b).—A solution of 0.48 g (0.15 mmol) of **22**, 2.40 g (2.25 mmol) of benzylamine, and 12 ml of methanol was stirred at room temperature for 48 hr. The pale yellow oil obtained after work-up as in **9a,b** was chromatographed on silica gel. Elution with 2% ether–petroleum ether yielded 121 mg (23%) of **12b** as a colorless oil which was crystallized from petroleum ether (bp 60–70°): mp 64–65°; pmr ($CDCl_3$) δ 2.72 (d, J = 2.5 Hz, 1 H, C_3 H), 3.31 (br s, 1 H, C_2 H), 3.57 (s, 3 H, methoxy), 4.00 (br s, 2 H, benzylic), and 6.95–7.45 (m, 9 H, aromatic); ir (KBr) $\nu_{C=O}$ 1724 cm^{-1}.

Anal. Calcd for $C_{28}H_{21}NO_2$: C, 81.69; H, 5.74; N, 3.82. Found: C, 81.80; H, 5.69; N, 3.92.

Continued elution with 20% ether–petroleum ether yielded 371 mg (72%) of **12a**: mp 149–150°; pmr ($CDCl_3$) δ 2.65 (d, J = 6.5 Hz, 1 H, C_3 H), 3.03 (d, J = 6.5 Hz, 1 H, C_2 H), 3.49 (s, 3 H, methoxy), 3.80 (d of d, J = 14.0 Hz, 2 H, benzylic), and 7.15–7.75 (m, 9 H, aromatic); ir (KBr) $\nu_{C=O}$ 1741 cm^{-1}.

Anal. Found: C, 81.92; H, 5.72; N, 3.86.

Methyl 1-*tert*-Butyl-2-(*p*-biphenyl)-3-aziridinecarboxylate, *cis* and *trans* (13a,b).—A solution of **22** (1.59 g, 5.0 mmol) was dissolved in 7.3 g (0.10 mol) of *tert*-butylamine and 25 ml of acetonitrile and stirred for 5 days. A pale oil obtained after work-up as in **9a,b** was dissolved in methanol and 0.70 g (44%) of **22** was filtered off. After removal of the methanol from the filtrate, the resultant oil was chromatographed on silica gel. Elution with petroleum ether (bp 60–70°) followed by elution with 2% ether–petroleum ether afforded 150 mg (10%) of **13b** as a colorless oil which was crystallized from *n*-pentane: mp 79–81°; pmr ($CDCl_3$) δ 1.15 (s, 9 H, three methyls), 2.75 and 3.63 (two d, J = 2.5 Hz, 1 H each, C_3 H and C_2 H, respectively), 3.83 (s, 3 H, methoxy), and 7.1–7.6 (m, 9 H, aromatic); ir (KBr) $\nu_{C=O}$ 1727 cm^{-1}.

Anal. Calcd for $C_{29}H_{33}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.82; H, 7.47; N, 4.54.

Continued elution with 2% ether–petroleum ether afforded 325 mg (21%) of **13a** as a colorless oil which was crystallized from pentane: mp 88–90°; pmr ($CDCl_3$) δ 1.10 (s, 9 H, three methyls), 2.70 and 3.17 (two d, J = 6.5 Hz, 1 H each, C_3 H and C_2 H, respectively), 3.45 (s, 3 H, methoxy), and 7.2–7.7 (m, 9 H, aromatic); ir (CCl_4) $\nu_{C=O}$ 1755 and 1725 cm^{-1}.

Anal. Found: C, 77.62; H, 7.55; N, 4.57.

D. Synthesis of Deuterium Labeled Methyl 1-Alkyl-2-(*p*-biphenyl)-3-aziridinecarboxylates. Methyl 1-Ethyl-2-d_1-2-(*p*-biphenyl)-3-aziridinecarboxylate, *cis* and *trans* (9'a,b).—These compounds were prepared by the reaction of methyl *trans*-α-bromo-β-d_1-*p*-phenylcinnamate[6b] and a 15-fold excess of ethylamine in methanol. The products were isolated as described for **9a,b**. The ring proton spectra of these deuterium labeled aziridines appeared as singlets at 150 and 165 Hz for **9'a** and **9'b**, respectively, and confirmed the ring proton assignments.

Methyl 1-*tert*-Butyl-2-d_1-2-(*p*-biphenyl)-3-aziridinecarboxylate, *cis* and *trans* (13'a,b).—These products were prepared by the reaction of methyl *trans*-α-bromo-β-d_1-*p*-phenylcinnamate with a 15-fold excess of *tert*-butylamine. Products were isolated as in **13a** and **13b**. The ring proton spectra of **13'a** and **13'b** consisted of singlets at 162 and 165 Hz, respectively, and confirmed the ring proton assignments.

Reduction of 1b with Lithium Aluminum Hydride.—A solution of 376 mg (1.16 mmol) of the *N*-methylaziridine **1b** in 5 ml of dry benzene was added dropwise to a stirred suspension of 100 mg (2.63 mmol) of $LiAlH_4$ in 20 ml of dry ether. After the addition, the solution was refluxed for 4 hr. The excess $LiAlH_4$ was neutralized with water and 15% sodium hydroxide solution. The resultant precipitate was filtered and the filtrate was concentrated. Recrystallization of the resultant pale yellow crystals from petroleum ether afforded 45% of *trans*-1-methyl-2-(*p*-biphenyl)-3-(α-hydroxybenzyl)aziridine: mp 142–143°; pmr ($CDCl_3$) δ 2.18 (br s, 3 H, NCH_3), 2.35 (m, 1 H, C_3 H), 3.40 (br s, 2 H, C_2 H and OH), 4.93 (d, J = 4.0 Hz, 1 H, –CHOHPh), and 7.1–7.6 (m, 14 H, aromatic).

Anal. Calcd for $C_{22}H_{21}NO$: C, 83.80; H, 6.67; N, 4.44. Found: C, 83.98; H, 6.64; N, 4.50.

Registry No.—**1b**, 32044-30-7; **2a**, 32044-31-8; **2b**, 32044-32-9; **3a**, 32044-33-0; **3b**, 32044-34-1; **4a**, 32044-35-2; **4b**, 32044-36-3; **5a**, 2211-65-6; **5b**, 2211-61-2; **6a**, 6372-57-2; **6b**, 6476-12-6; **7a**, 20847-26-1; **7b**, 20847-27-2; **9a**, 32044-41-0; **9b**, 32044-42-1; **10a**, 23214-21-3; **10b**, 23214-22-4; **11a**, 32044-45-4; **11b**, 23214-20-2; **12a**, 32044-47-6; **12b**, 32044-48-7; **13a**, 32087-72-2; **13b**, 32044-49-8; **15b**, 32044-50-1; **17b**, 793-02-2; **21**, 32044-52-3; *trans*-1-methyl-2-(*p*-biphenyl)-3-(α-hydroxybenzyl)aziridine, 32044-53-4.

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