

Epimerization and Deuterium Exchange Studies in
Selected *cis,trans*-1-alkyl-2-aryl(alkyl)-3-arylaziridines

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A series of base catalyzed reactions performed on selected *cis,trans*-1-alkyl-2-aryl(alkyl)-3-arylaziridines at room temperature reveal the *cis* isomer to be of greater thermodynamic stability. Furthermore, base catalyzed deuterium exchange studies suggest this to be the case. Solvent effects on the isomeric *cis/trans* ratios are also presented and discussed.

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Several years ago we began an investigation of the epimerization of certain *cis* and *trans*-1-alkyl-2-aryl(alkyl)-3-arylaziridines. It was found (2) that *trans* and *cis*-1-cyclohexyl-2-methyl-3-(*p*-phenylbenzoyl)aziridine upon refluxing for 48 hours in methanol with an excess of sodium methoxide base present returned predominantly *cis* product (see Table I). Unfortunately, however, yields were low, as was also the case for Turner and Lutz (3), who later found that a *cis-trans* mixture of 1-benzyl-2,3-dibenzoylaziridine heated for 36 hours in absolute methanol would give a 3:1 *cis/trans* mixture. More recently Padwa and coworkers (4,5) have increased this yield to 80% in the system *cis* and *trans*-1-*t*-butyl-2-benzoyl-3-methylaziridine by eliminating the base and relying on heating at 77° in a sealed tube for a 16 hour period in deuteriomethanol. The result found here was again a mixture in which the *cis* isomer predominated.

The problem, however, with these earlier studies, insofar as predicting which isomer is the thermodynamically more stable, lies in the fact that isomeric carboaziridines undergo facile thermally induced C-C bond scission of the aziridine ring in the 65-80° temperature range with the mode of rearrangement being solvent

dependent (6). In fact the earlier studies of Turner and Lutz (7) show the *cis-trans* equilibrium constant, *K*, to vary from 5.25 in DMSO to 0.32 in *t*-butyl alcohol for the base catalyzed epimerizations of 1-cyclohexyl(benzyl)-2,3-dibenzoylaziridines. Thus, since basic equilibrations are known to lead to the thermodynamically most stable isomers (8,9), it appeared to us that studies which would avoid both C-C bond scissions and medium effects should be undertaken.

Results and Discussion

The systems which were synthesized for these studies are presented in Table II, and the experimental results of the % epimerization and % deuterium exchange studies are presented in Table III.

Since it has already been established (9) that the *trans* isomers of 1-alkyl-2-aryl-3-carboaziridines exist in a preferred conformation with the *N*-alkyl group *syn* to the carbonyl, while for the *cis* it is *anti*, one might predict on an *ab initio* basis greater stability for the *cis* isomer owing to fewer non-bonded interactions. Leaving theory aside for the moment, however, one finds upon examination of Table III that *net* epimerization of **1a** to **1b** is

TABLE I
Qualitative Epimerization Studies in Methanol (2)

Aroylaziridine	Temperature	Time (Days)	α -Proton Exchange	% Yield	Ratio of <i>cis/trans</i>
<i>trans</i> -1-cyclohexyl-2-methyl-3-(<i>p</i> -phenylbenzoyl) aziridine	reflux	2	complete	50	100:1
<i>cis</i> -1-cyclohexyl-2-methyl-3-(<i>p</i> -phenylbenzoyl) aziridine	reflux	2	complete	52	100:1

TABLE II

Selected *cis,trans*-1-Alkyl-2-aryl(alkyl)-3-arylaziridines

Compound	R ₁	R ₂	R ₃
1a or 1b	C ₆ H ₁₁	Ph	Ph
2a or 2b	CH ₃	Ph	Ph-Ph- <i>p</i>
3a or 3b	C ₆ H ₁₁	CH ₃	Ph-Ph- <i>p</i>
4 (<i>anti</i> only)	C ₆ H ₁₁	H	Ph-Ph- <i>p</i>
5 (<i>trans</i> only)	H	Ph	Ph-Ph- <i>p</i>
6a or 6b	C ₆ H ₁₁	Ph	Ph-Ph- <i>p</i>

11.0% after 24 hours and steadily increases to a value of 43.9% after 168 hours. Similarly, there is a *net* epimerization of **2a** to **2b** ranging from 54.8 to 59.3% in the 48-125 hour time period, and the **3a** *net* epimerization to **3b** goes from 27.4 to 53.5% in the 48-192 hour time period. However, unlike these trisubstituted aziridines, those possessing only two substituents at the carbon atoms, **5** show an inability to epimerize to their *Z* (*zusammen*) analogs. Furthermore, since base concentration was kept to only a small fraction of the amount of carboaziridine present, it must be assumed that the product of the epimerization is dependent on the nature of the given 1-alkyl-2-aryl(alkyl)-3-carboaziridine and not on base concentration (11). Hence, the data in Table III serves as a good indication of the relative stability of the *cis* and *trans* isomers.

Presented in Table III are also data obtained from α -ring proton exchange studies and some interesting facts are observed. To begin with the rate of deuterium exchange is much faster for the *cis* isomers containing aryl and aroyl groups across the ring carbon atoms than for

the *trans* analogs. This suggests that good conjugation exists between these groups in the *trans* isomer thereby inhibiting deuterium exchange. This is borne out by the fact that **1b** exchanges much faster than **1a** while **3b** exchanges moderately faster than **3a** and is further substantiated by nmr shifts of the α - and β -hydrogens (13). Since the α - and β -hydrogens are more deshielded in the *trans* isomer it can be further postulated that double bond character due to hyperconjugation is greater in the *trans* isomer (14). Hence hydrogen abstraction becomes more difficult for the *trans* isomer (15). Worth noting also is the fact that compound **5** does not undergo α -ring proton exchange because the hydrogen on nitrogen is more acidic (and more easily removed) thereby preventing formation of the carbanion at the α -position.

In principle then, *cis* isomer stability appears greater than that of the *trans* analog when these systems tend toward equilibrium. Hence the *cis* aziridiny ketone skeleton is of greater thermodynamic stability than that of the more highly conjugated *trans* compound. This seems reasonable from a careful examination of molecular models which suggest fewer lone pair - lone pair interactions in the *cis* carbanion and is consistent with Gillespie-Nyholm VSEPR theory (16). Furthermore, 1,2- and 1,3-non-bonded interactions can be minimized in the *cis* isomer owing to the ability of the R₁ (except in **5**) substituent to be *anti* to R₂ (except in **4**) and R₃, e.g., see Scheme 1.

The *trans* carbanion **7** is very unstable since the unshared pair of electrons on nitrogen and the carbanion would be on the same side of the plane that contains the aziridine ring, thereby causing a 1,2 - lone pair - lone pair repulsion between the two pairs of electrons. The *cis* carbanion **9** is more stable since the unshared pair of electrons on the nitrogen and the carbanion are much further apart. Hence, it would quickly take up either hydrogen or deuterium and retain its configuration.

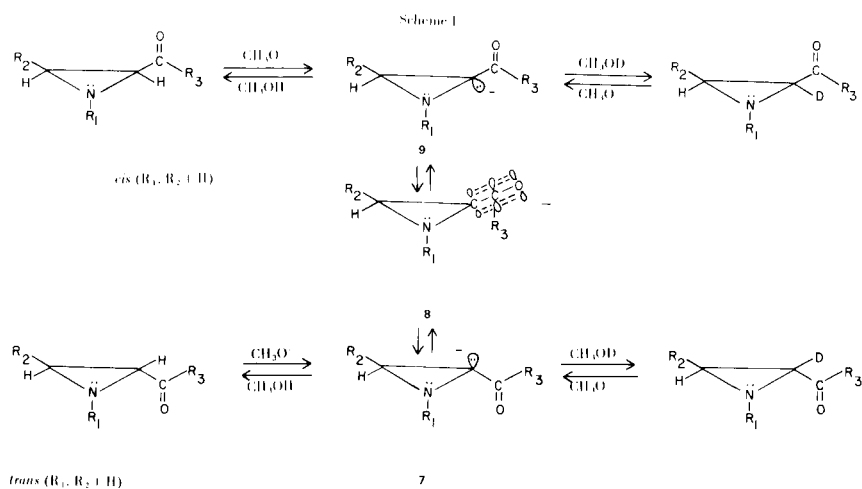


TABLE III
Epimerization and Base Catalyzed α -Ring Proton Exchange of
Aryl(alkyl)arylaziridines With a Catalytic Amount of Sodium Methoxide in Methanol (10)

Compound	Concentration	Hours	Base Concentration	% Epimerization (a)	% α -Ring Proton Exchange
1a	0.164M	24	0.0492M	19.3	47.1
	"	48	"	27.6	94.3
	"	72	"	40.3	complete
	"	96	"	47.3	complete
	"	120	"	53.0	complete
	"	168	"	59.6	complete
1b	0.164M	1	0.0492M	none	18.2
	"	6	"	trace	complete
	"	24	"	8.3	complete
	"	48	"	14.7	complete
	"	96	"	14.7	complete
	"	168	"	15.7	complete
2a	0.12M	1.5	0.036M	29.8	44.8
	"	2	"	32.6	56.1 (c)
	"	3	"	35.1 (b)	83.8
	"	4	"	44.9 (b)	complete
	"	9	"	53.8	complete
	"	24	"	64.6	complete
	"	48	"	65.1	complete
	"	125	"	73.1	complete
	"	168	"	77.1	complete
2b	0.12M	48	0.036M	5.8	[complete] (d)
	"	125	"	18.3	[complete]
3a	0.12M	24	0.036M	15.1	57.8
	"	36	"	23.0 (c)	65.3
	"	48	"	31.0	--
	"	72	"	38.1	--
	"	96	"	--	complete
	"	192	"	65.4	complete
3b	0.12M	8	0.036M	none	54.7
	"	24	"	trace	90.5
	"	36	"	trace	complete
	"	48	"	3.6	complete
	"	96	"	--	complete
	"	192	"	12.1	complete
4	0.12M	24	0.036M	none	--
	"	48	"	none	--
5	0.12M	24	0.036M	none	none

(a) Epimerization studies were done independent of deuterium exchange studies for all of these systems and were done with deuterium exchange studies for **1a**, **1b**, **2a**, and **2b**. (b) Average value. (c) Extrapolated value. (d) Although not studied here, complete deuterium exchange is known to occur in 1.5 days with *cis*-1-benzyl-2-phenyl-3-*p*-tolylaziridine (2).

On the other hand, the *trans* carbanion would stereomutate via an intermediate like **8** into **9** much faster than the *cis* carbanion owing to the instability of **7**. Furthermore, since prior work contends (9) that R₁ is *syn* to the carbonyl moiety and *anti* to R₂ in the *trans*-1-alkyl-2-aryl-3-carboaziridines, non-bonded interactions between the alkyl and aryl groups will further destabilize the aziridinyl ketone's ring system and allow facile formation

of **9**.

Undertaken next was a study of solvent effects upon the isomeric *cis/trans* ratio. Although Turner (3,7) reported on epimerizations of selected *trans* aziridinyl mono- and diketone(s), results were inconclusive for monoketoaziridines thereby necessitating further studies. It was found that when **2a**, **6a** or **6b** were epimerized in excess potassium *t*-butoxide the *cis/trans* ratio approached

TABLE IV

Epimerization of **2a**, **6a** and **6b** (0.116M) with Potassium *t*-Butoxide (0.348M) in Benzene and Ether

Compound	Time (Days)	% Yield	% Epimerization
2a	1	85	49.5
	2	86.4	53.2
	7	80.6	47.5
6a	1	93.3	48.4
	2	87	50.0
	7	95.3	52.0
6b	7	96.7	49.1

50% after 7 days (see Table IV). More interesting, however, is the fact that the ratio of *cis/trans* isomers are both solvent and base concentration dependent (see Table V and (10)). The marked decrease in *cis/trans* ratio for the aziridinyl ketone in benzene-ether follows the decrease in the dielectric constants of their solvents (methanol, *t*-butyl alcohol:tetrahydrofuran, benzene:ether) and is presumed to be a concomitant decrease in their solvating abilities. The more polar *cis* aziridinyl ketone is the more stable isomer in the most polar solvent (3,7). On the other hand, the increase in *cis/trans* ratio when large quantities of base are used is essentially due to a medium effect (*i.e.*, changing the dielectric constant and/or the polarity of the medium).

One final observation in our studies was that **5** would *not* undergo epimerization due to its inability to form a carbanion at the α -position and this is a positive factor in showing that carbanion formation is an essential step in the epimerization of aziridinyl ketones at room temperature. However, further studies are warranted because small amounts of decomposition products are observed even under room temperature conditions (17) (*i.e.*, even though C-C bond cleavage is highly improbable at 20-30°) (6).

EXPERIMENTAL

Infrared spectra were measured on either a Perkin-Elmer Model 137 or 237 double beam recording spectrophotometer and nmr were determined on a Varian A-60 high resolution spectrometer. Melting points were obtained with an electrically heated melt-temp apparatus and are uncorrected. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

trans and *cis*-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (**1a**) and (**1b**).

Following a modified procedure similar to that of Cromwell and Hoeksema (18) 44.6 g. (0.45 mole) of cyclohexylamine was added dropwise to a suspension of 55.1 g. (0.15 mole) of α,β -dibromochalcone in 150 ml. of dry benzene over a 10 minute period. The mixture was cooled to 15° and stirred for one hour. Next the mixture was stirred in the dark at 25° for one day and afterwards 51.2 g. (94.6% yield) of cyclohexylamine hydrobromide was removed by filtration. After reducing the total volume to 100 ml., 100 ml. of petroleum ether (b.p. 60-69°) was added and the mixture was stored in the freezer for 3 hours. Filtration and recrystallization from a 50:50 benzene/petroleum ether (b.p. 60-69°) mixture gave 16.9 g. (37.0% yield) of **1b**, m.p. 106-107° (lit. m.p. 107-109°); ir (carbon tetrachloride): ν C=O 1665 and 1685 cm^{-1} ; nmr (carbon tetrachloride, TMS) δ = 6.95-7.87 (m, 10H), 3.23 (d, J = 6.8 Hz, 1H), 3.08 (d, J = 6.8 Hz, 1H), 0.84-2.04 (m, 11H).

The benzene-petroleum ether filtrate from the *cis* isomer **1b** was evaporated to dryness in a vacuum at 25°, the residue mixed with 200 ml. of petroleum ether (b.p. 60-69°) and stored in the freezer for two days. Recrystallization from methanol gave 25.7 g. (55.1% yield) of white square crystals which were identified as **1a**: m.p. 99-101° (lit. m.p. 99-101°) (18); ir (carbon tetrachloride): ν C=O 1665 cm^{-1} ; nmr (carbon tetrachloride, TMS) δ = 7.04-8.06 (m, 10H), 3.55 (d, J = 2.8 Hz, 1H), 3.50 (d, J = 2.8 Hz, 1H), 2.25-2.93 (m, 1H), 0.90-2.03 (m, 10H).

trans-1-Methyl-2-phenyl-3-(*p*-phenylbenzoyl)aziridine (**2a**).

Following the procedure reported by Graff (12,19) 14.8 g. of **2a** was prepared in 31.8% yield, m.p. 118-120° (lit. m.p. 120-121°); ir (carbon tetrachloride): ν C=O 1670 cm^{-1} ; nmr (carbon tetrachloride, TMS) δ = 8.09 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.26-7.67 (m, 10H), 3.56 (d, J = 2.8 Hz, 1H), 3.40 (d, J = 2.8 Hz, 1H), 2.67 (s, 3H).

TABLE V

Base-Induced *cis-trans* Epimerization in 1-Methyl-2-phenyl-3-(*p*-phenylbenzoyl)aziridine

Aziridinyl Ketone Concentration	Base Concentration	Solvent	Temperature	Time (Days)	% Yield	% <i>cis</i>
0.0395M	0.0197M	<i>t</i> -butyl alcohol: THF (50:50)	25°	2	-- (a)	50
"	0.0395M	"	"	"	-- (a)	90
0.0116M	0.00578M	"	"	"	99	14
"	0.0116M	"	"	"	98	31
"	0.0347M	"	"	"	93.4	50
"	0.0116M	benzene:ether (50:50)	"	"	95.7	14.9
"	0.0347M	"	"	"	85	53.2

(a) % Yield estimated to be 85% or greater (11).

cis-1-Methyl-2-phenyl-3-(*p*-phenylbenzoyl)aziridine (**2b**).

A mixture of 0.520 g. (0.0016 mole) of the *trans* aziridinyl ketone and 0.239 g. (0.00432 mole) of sodium methoxide in 30 ml. of methanol and 5 ml. of tetrahydrofuran was stirred at 25° for 56 hours. The solvents were vacuum-stripped and dried, yielding 0.474 g. (91% yield) of yellowish solid. Recrystallization from methanol gave needle-like crystals **2b**: m.p. 138-139° (lit. m.p. 138-139°) (19); ir (carbon tetrachloride): ν C=O 1680 cm^{-1} ; nmr (carbon tetrachloride, TMS) δ = 7.95 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.05-7.57 (m, 10H), 3.21 (d, J = 6.8 Hz, 1H), 3.05 (d, J = 6.8 Hz, 1H), 2.67 (s, 3H).

trans and *cis*-1-Cyclohexyl-2-methyl-3-(*p*-phenylbenzoyl)aziridine (**3a**) and (**3b**).

Following the procedure of Cromwell and Mohrbacher (20) 10.9 g. of **3a** was prepared in 13.0% yield, m.p. 141-142° (lit. m.p. 141-142°); ir (carbon tetrachloride): ν C=O 1665 cm^{-1} ; nmr (carbon tetrachloride, TMS) δ = 8.12 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.29-7.63 (m, 5H), 3.32 (d, J = 2.7 Hz, 1H), 2.69 (d, J = 2.7 Hz, 1H), 2.15-2.83 (m, 1H), 0.83-2.02 (m, 10H), 1.34 (d, 3H).

From this same experiment (20) 18.0 g. of **3b** was obtained in 21.4% yield, m.p. 125-127° (lit. m.p. 127-128°); ir (carbon tetrachloride): ν C=O 1658 and 1685 cm^{-1} ; nmr (carbon tetrachloride, TMS) δ = 8.10 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.30-7.64 (m, 5H), 2.94 (d, J = 7.0 Hz, 1H), 2.11 (d, J = 7.0 Hz, 1H), 0.83-2.12 (m, 11H), 1.17 (d, J = 5.8 Hz, 3H).

Successive fractional recrystallizations from benzene and petroleum ether (b.p. 60-69°) yielded an additional 5.9 g. (total yield 20%) of **3a** and 39.1 g. (total yield 67.9%) of **3b**.

1-Cyclohexyl-2-*p*-phenylbenzoyl-aziridine (**4**).

Following the procedure of Cromwell and coworkers (21) 10.1 g. of **4** was prepared in 57.8% yield, m.p. 106-107° (lit. m.p. 106-107°); nmr (carbon tetrachloride, TMS) δ = 8.13 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.25-7.67 (m, 5H), 2.93 (dd, J = 6.8, 3.2 Hz, 1H), 2.29 (dd, J = 2.0, 3.2 Hz, 1H), 1.77 (dd, J = 2.0, 6.8 Hz, 1H), 0.93-2.08 (M, 11H).

 β -Phenyl- β -methoxyamino(*p*-phenyl)propiophenone (**5a**).

Following the published procedure similar to that of Blatt (21,22) 4.7 g. (0.100 mole) of methoxyamine was added to a suspension of 25 g. (0.0877 mole) of *p*-phenylchalcone in 100 ml. of methanol and 75 ml. of chloroform, and the suspension was warmed to just below its boiling point for 5.5 hours. It was then cooled, stored, in the refrigerator overnight, and filtered yielding 19.5 g. (67.1% yield) of light yellow solid (m.p. 100-103°). Three recrystallizations from 95% ethanol yielded white crystals identified as **5a**, m.p. 103.5-104.5°; ir (carbon tetrachloride): ν C=O 1680 cm^{-1} ; nmr (carbon tetrachloride, TMS) δ = 7.75 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.97-7.45 (m, 5H), 5.82 (s, 1H), 4.60 (dd, J = 6.9 Hz, 1H), 3.33 (m, 5H).

Anal. Calcd. for $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}$: C, 79.73; H, 6.39; N, 4.23. Found: C, 80.57; H, 6.45; N, 3.96.

The solvent of the filtrate of the reaction mixture was then removed by a vacuum rotatory evaporator at room temperature yielding 6.1 g. (21% yield) of light yellow solid (m.p. 83.5-89°). Two recrystallizations from 95% ethanol yielded light yellow crystals identified mainly as **5a** (m.p. 97.5-99°).

trans-2-Phenyl-3-(*p*-phenyl)benzoylaziridine (**5**).

Following the published procedure similar to that of Blatt (21,22) 11.2 g. (0.0338 mole) of **5a** was dissolved in 70 ml. of

methanol by warming the solution to just above its boiling point. A 3.66 g. (0.0677 mole) sample of sodium methoxide was added and washed down with 20 ml. of methanol. The red solution was stirred for two hours, during which time part of the product precipitated from the solution. The reaction mixture was stored in the refrigerator for 48 hours. Filtration of the reaction mixture yielded 9.2 g. (90.7% yield) of a reddish colored solid. The crude product was dissolved in chloroform until free of base, then the organic layer was dried over anhydrous sodium sulfate, and the solvent vacuum-stripped. One recrystallization from methanol after charcoal treatment and one from 95% ethanol yielded a light reddish solid identified as **5**: m.p. 138-140°; ir (carbon tetrachloride): ν C=O 1668 cm^{-1} ; nmr (carbon tetrachloride, TMS) δ = 7.88 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.16-7.55 (m, 10H), 3.45 (d, J = 2.2 Hz, 1H), 3.11 (d, J = 2.2 Hz, 1H), 2.70 (s, 1H).

Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{NO}$: C, 84.25; H, 5.73; N, 4.68. Found: C, 84.53; H, 5.84; N, 4.52.

Alternative Preparation of **5**.

Following the procedure reported by Graff (12,19) 15 g. (0.0338 mole) of 4'-phenylchalcone dibromide was prepared and then suspended in 75 ml. of anhydrous ether and 75 ml. of chloroform. Approximately 150 ml. of anhydrous ammonia was then condensed through a cold trap into a reaction flask with stirring in a dry-ice acetone bath for six hours; then the reaction flask was removed from the cold trap and stirred continuously for 12 more hours. Next, the solution was vacuum stripped and eluted on a silica gel column using first a 30% petroleum ether (b.p. 60-69°): benzene mixture and later a 30% ether: benzene mixture as the mobile phases. Two recrystallizations from methanol afforded 5.2 g. (51% yield) of **5**, m.p. 137-139°; nmr (carbon tetrachloride, TMS); ir (carbon tetrachloride), and elemental analysis identical to the product **5** described above.

Preparation of *trans* and *cis*-1-Cyclohexyl-2-phenyl-3-(*p*-phenylbenzoyl)aziridine (**6a**) and (**6b**).

Following the procedure reported by Graff and Cromwell (12), **6a** was isolated in 47% yield, m.p. 117-118° (lit. m.p. 117-118°), nmr (carbon tetrachloride, TMS) δ = 3.56 (t, 2H); **6b** was isolated in 44% yield, m.p. 144-146° (lit. m.p. 144-146°), nmr (carbon tetrachloride, TMS): δ = 3.17 (dd, 2H) (23).

Base Catalyzed Epimerization of the Aziridinyl Ketones.

A solution of the aziridinyl ketone and a very small, *i.e.* "catalytic", amount of sodium methoxide were dissolved in either a 1:2 tetrahydrofuran/methanol mixture **1a** and **1b**, or a 1:1 tetrahydrofuran/methanol mixture, **2a**, **2b**, **3a**, **3b**, **4** and **5**. The solution was stirred in a constant temperature water bath at $30 \pm 0.5^\circ$. The crude products were isolated in two different ways; however, both gave identical results. *Method 1*: The solvents were vacuum stripped at 25° until dryness, then the solid was dissolved in chloroform and the base was removed by filtration. Again the solvent was vacuum stripped, dried, and the crude product was analyzed by nmr. *Method 2*: The reaction solution was quenched with water and ether, dried and analyzed by nmr.

Base Catalyzed Deuterium Exchange of the α -Ring Proton.

A mixture of the aziridinyl ketone and sodium methoxide were dissolved in dry tetrahydrofuran and deuteriomethanol, and the solution was stirred in a constant temperature water bath at 30°. The solvents were vacuum stripped at 25° to dryness, and then the solid residue was dissolved in dry tetrahydrofuran and

the base filtered off. Again the solvent was evaporated with a rotatory vacuum evaporator and the crude product was analyzed by nmr.

Reaction of **2a**, **6a**, and **6b** with Excess Potassium *t*-Butoxide in Dry Benzene and Ether.

A solution of 4.79×10^{-4} mole of aziridinyl ketone and 1.44×10^{-3} mole of potassium *t*-butoxide were dissolved in 1:1 mixture of benzene and ether. The solution was stirred in a constant temperature water bath at 25°. The reaction mixture was washed with water until free of base, then dried with anhydrous sodium sulfate. The solvent was vacuum stripped and the crude product was analyzed by nmr.

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