Deprotonation of Ternary Iminium Salts[1]

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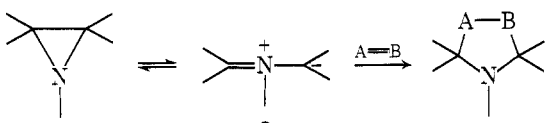
A series of aldiminium and ketiminium salts were prepared by alkylation of imines with methyl fluorosulfonate. Deprotonation of these salts was envisioned as an alternative route to azomethine ylides and thus as a new aziridine synthesis. Proton abstraction from these salts was attempted with a wide variety of bases. Of these, sodium bis(trimethylsilyl)amide proved to give the most favorable ratio of deprotonation to dealkylation in the conversion of *N*-(benzhydrylidene)methyl-*tert*-butylaminium fluorosulfonate to 1-*tert*-butyl-2,2-diphenylaziridine. Related aldiminium salts yielded products (1,2-diaminostilbenes and aminomethylaziridines) which were apparently derived from initial loss of the aldiminium vinyl proton. The mechanisms and implications of these reactions are discussed as well as the chemistry of some of the products.

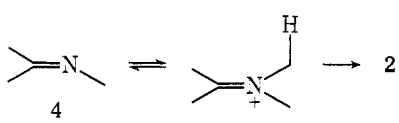
The thermal and photochemical ring openings of aziridines (**1**) have been studied extensively and the product azomethine ylides (**2**) have been employed in heterocyclic syntheses by taking advantage of the 1,3-dipolarophilic character of **2**.[2,3] Although reversion of **2** to **1** has been noted previously, this reversion has never been taken advantage of as a synthetic route to aziridines. Our interest in



1 **2**

the synthesis of functionally substituted and/or sterically crowded aziridines has prompted us to investigate the potential utility of azomethine ylide ring closures.

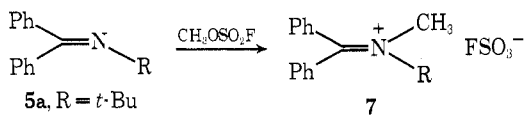
Our proposed approach to these ylides involved the deprotonation of iminium salts (**3**). These salts should in turn be available from the alkylation of the corresponding imines (**4**). The major anticipated problem with this approach



4 **3**

was the possible ease with which dealkylation of **3** could compete with the desired deprotonation. In this paper we would like to report the initial exploratory experiments by which we probed the potential utility of this synthetic approach.

Synthesis of Aldiminium and Ketiminium Salts. A series of ketimines (**5**) and aldimines (**6**) were prepared by standard procedures and alkylated with methyl fluorosulfonate and (in one case) methyl triflate. These alkylating agents were selected because of their reactivity and because the product anions would be relatively nonnucleophilic and thereby not contribute to competing dealkylation. The resultant salts were relatively stable and in one case (**7a**) could be purified sufficiently for analysis. The other salts, particularly the aldiminium salts (**8**), were less stable and hygroscopic.



5a, R = *t*-Bu
b, R = CH_3
c, R = Ph

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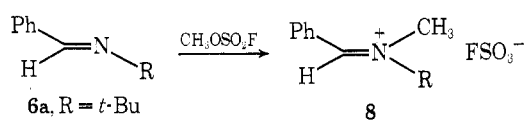
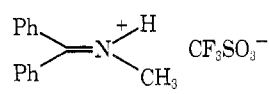


6a, R = *t*-Bu
b, R = CH_3

8

Although insoluble in most organic solvents, the salts were soluble in acetone, dimethyl sulfoxide, and liquid sulfur dioxide. The latter solvent was particularly useful for obtaining the NMR spectra which confirmed the assigned structures. The triflate analog of **7a** decomposed at its melting point (128°) with the liberation of a gas, presumably isobutene. A crystalline residue was assigned structure **9** on the basis of its NMR spectrum, which showed a de-



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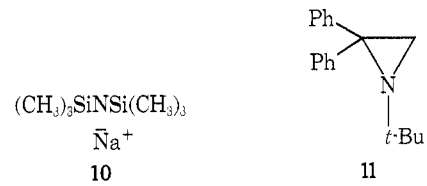
shielded methyl singlet (δ 3.47) and the conspicuous absence of a *tert*-butyl peak.

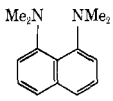
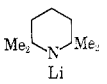
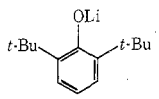
Deprotonation of the Ketiminium Salts. Our initial studies were directed toward deprotonation of iminium salt **7a**. A wide variety of previously and currently fashionable bases were tried and the results of these attempts are summarized in Table I. All deprotonations were carried out in an atmosphere of dry nitrogen at the indicated temperature. The reactions, following appropriate work-up, were analyzed by NMR spectroscopy. Most of the bases produced the desired aziridine. In most cases, however, the dealkylation product **5a** was present in relatively large amounts. Only in the case of sodium bis(trimethylsilyl)amide (**10**) was the high (nearly quantitative) conversion to the desired aziridine (**11**) achieved.



10 **11**

Aziridine **11** was identified by its NMR spectrum and elemental analysis. The former showed the characteristic aziridine methylene two-proton singlet at δ 2.16 in addition to the ten aryl protons and nine *tert*-butyl hydrogens. This aziridine is relatively unstable toward a variety of reagents and conditions. For example, passage of **11** through a column of Florisil afforded a mixture of 1-*tert*-butylamino-2,2-diphenylethylene and diphenylacetaldehyde (Scheme I). The latter presumably is a hydrolysis product of the enamine and can be reconverted to the enamine with *tert*-butylamine. This apparent acid-catalyzed ring opening of

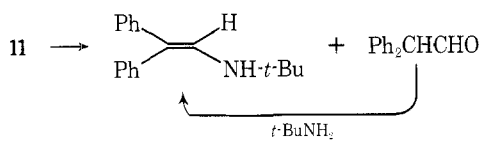
Table I
Aziridine:Imine (11:5a) Distribution Obtained from the Reaction of [$Ph_2C{=}N(Me)t\text{-}Bu$](OSO_2F) (7a) with Various Base-Solvent Combinations

Base	Ref	Solvent(s)	T_0[a]	11:5a[b]
n-BuLi		Ether–hexane	25	0[c]
	4	Ether	−78	*f*
	5	Ether–hexane	25	~0.7
		Ether–hexane	−78	1[d]
$NaCH_2S(O)Me$	6	DMSO[e]	25	2
KO-*t*-Bu	7	HMPA[e]	0	0.4
		Ether	−78	13
$KOCEt_3$	8	Xylene	25	13
$NaN(SiMe_3)_2$	9	SO_2	−78	0
(10)		DMSO[e]	25	11
		Ether	25	16
		Benzene	25	18
		Hexane	25	22

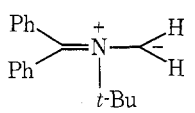
[a] Initial reaction temperature, °C. [b] Mole percent by NMR spectral assay. [c] Little, if any, 11 detected. [d] Recovered 70% of the iminium salt. [e] Homogeneous mixture. [f] No reaction.

11 has ample precedent and is apparently facilitated by the ability of the two phenyl groups to stabilize positive charge.[10]

Scheme I



Although all successful reactions were accompanied by a transient deep red color, attempts to trap intermediate **12** were unsuccessful. Norbornene, for example, failed to divert **12** from its ring closure to **11**. Other dipolarophiles



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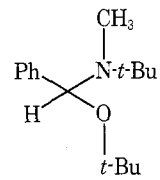
were either unreactive or consumed by the strongly basic conditions. Failure to trap the intermediate 1,3-dipole does not, of course, rule out its intermediacy.[11] The possible low steady-state concentration of **12** and the steric interference to cycloaddition posed by the two terminal phenyl groups could be expected to make trapping of the intermediates noncompetitive with ring closure.

Attempted deprotonation of the other iminium salts (**7b** and **7c**) were less successful. Reaction between these salts and **10** did occur (as evidenced by the formation of FSO_3Na and formation of organic solvent soluble material). The NMR spectral analyses of the reaction mixtures in some cases showed peaks in the area expected for the products. In addition, however, sizable amounts of dealkylated imines and other products were also noted, even when the optimal conditions developed for **7a** were employed. Because of the poor yields, the apparent lability of these aziridines, and the similar physical properties of imine and aziridine, the aziridines were not separated from the reaction mixture. The reasons for the depressed aziridine yields from the iminium salts **7b** and **7c** are not clear. Presumably, the bulk of the *tert*-butyl group (either by direct effect on the reactive site or indirect effect via imposing conformations on the phenyl groups) is especially favorable toward deprotonation as opposed to dealkylations.

Deprotonation Studies of the Aldiminium Salts. Products from the attempted deprotonation of the aldiminium salts **8a** and **8b** were dependent on the nature of the base. Potassium *tert*-butoxide in ether resulted in addition to the iminium bond of **8a** to yield *tert*-butyl ether **13** in



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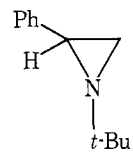
addition to dealkylation product and benzaldehyde. Comparison of the NMR spectrum of the crude reaction mixture with the spectrum of authentic[13] aziridine **14** revealed that **14** was not a component of the reaction mixture.



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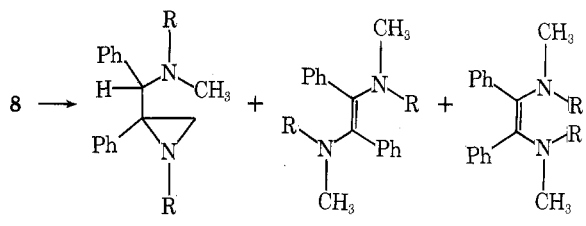
Treatment of the aldiminium salts **8a** and **8b** with **10** in benzene produced the unexpected results indicated in

Table II
Deprotonation of Aldiminium Salts



15 16 17

a, R = *t*-Bu	88[a,b]	11[a]	0[a]
b, R = CH_3	50[a]	25[a]	25[a]

[a] Product percentage. [b] Two diastereoisomers in ca. 5:1 ratio.

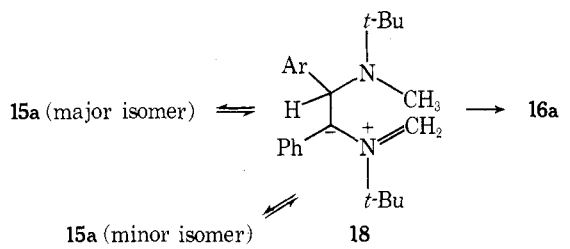
Table II. Neither salt yielded any isolable or spectrally detectable amounts of the desired aziridine **14**. Careful chromatography of the reaction mixture from **8a** yielded three isomers (as indicated by mass spectral and elementary analyses). Two of these were obviously closely related in structure and are assigned to the two diastereoisomers of **15a**. Each of the two diastereoisomers showed two *tert*-butyl groups, one methyl group, and ten aromatic protons in their NMR spectra. Both isomers showed a pair of doublets with chemical shifts and coupling constants in agreement with the assigned aziridine methylene group. In addition, both isomers showed a single unsplit methine proton. Neither isomer showed NH or imine peaks in their infrared spectra.[14]

The corresponding aziridines (**15b**) from **8b** could be detected spectrally but were too unstable to withstand chromotographic separation. Two other components were isolated and shown to be identical with the mixture of *E*- and *Z* diaminostilbenes **16b** and **17b** which had previously been prepared in a condensation reaction by Scheeren and van Helvoort.[15]

We assigned structure **17b** to the isomer with the more shielded methyl groups based on the assumption that two cis phenyl groups could not be coplanar with the double bond and in the resultant nonplanar conformation would effectively shield the methyl groups. The more deshielded methyl groups would thus correspond to the structure **16b** where the methyl groups could lie in the plane of the π system. In agreement with these assignments, **8a** produces only one (presumably less sterically crowded) isomer, **16a.** The chemical shift of the methyl group in this isomer corresponds closely to those assigned to **16b.**

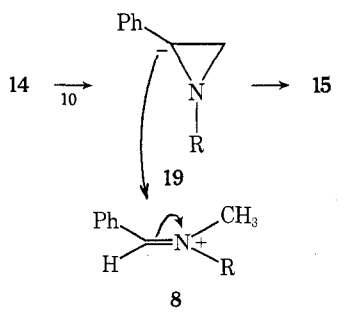
Further support for these assigned structures was found in the thermal chemistry of the two isomers of **15a.** Upon heating at 250°, both pure isomers produced mixtures which consisted of **16a** along with lesser amounts of the two diastereoisomers of **15a.** This process can be envisioned as an electrocyclic ring opening of aziridine **15a** to give 1,3-dipolar intermediate **18.** This intermediate can easily return to a mixture of the two isomers of **15a** or undergo 1,4-suprafacial hydrogen shift to **16a** (Scheme II).

Scheme II



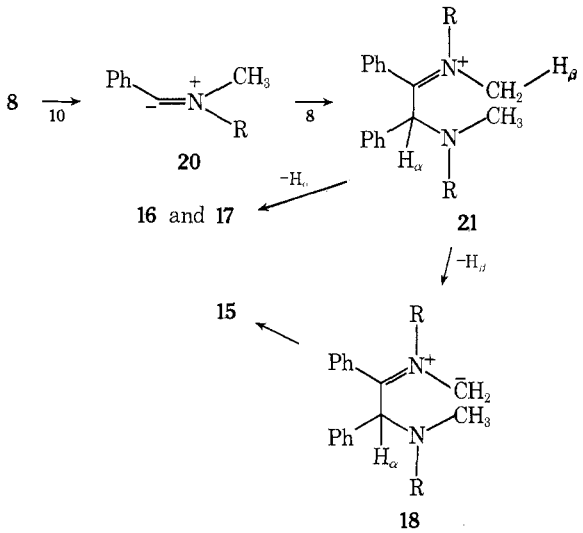
Several routes may be envisioned to explain the formation of **15–17.** It is, of course, possible that the desired aziridine **14** was produced in the reaction, deprotonated, and the resultant anion **19** attacked **8a** thereby yielding **15** (Scheme III). In order to test this hypothesis the reaction

Scheme III



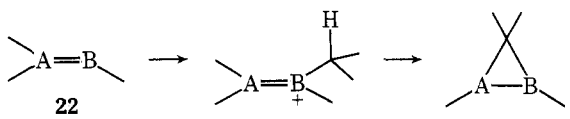
of **8a** with **10** was carried out in the presence of added authentic **14.** Upon completion of the reaction products **15–17** were again detected along with unchanged **14.** We conclude from this result (and the previously described product distributions) that aziridine **14** was neither produced nor consumed during this reaction. A second alternative is that depicted in Scheme IV. According to this alternative, the strong base removes a vinyl proton from **8** to produce intermediate **20.** The acidity of this vinyl hydrogen adjacent to a positively charged nitrogen is not surprising.[16] Attack of **20** on another molecule of **8a** would yield intermediate **21.** This intermediate has two acidic protons, H_α and H_β. Loss of H_β would yield 1,3-dipole **18,** which could, as previously mentioned, undergo ring closure to yield **15.** Loss of H_α would yield **16** and **17** directly. Although H_α is presumably the more acidic proton, it is also a sterically hindered proton. In agreement with the role of steric factors in the deprotonation of **21,** it is interesting to note that **21b** loses approximately equal amounts of H_α and H_β whereas **21a** prefers H_β to H_α by a factor of approximately 8:1. Alternatively, **16** and **17** could arise via 1,4-suprafacial shift indirectly via **18.**[17]

Scheme IV



Conclusions

The techniques for alkylation of imines and subsequent deprotonation described herein do not yet appear to constitute a general route to aziridines. Further work is needed (and in progress) to delineate the source of the limitations and hopefully to expand the reaction's scope. Application of this approach to related heterounsaturated systems (general formula **22**) also appears possible and a promising



route to a variety of heterocycles. Finally, the synthetic applications and chemistry of **20** and related ylides warrant additional investigation.

Registry No.—**5a,** 27126-13-2; **5b,** 13280-16-5; **5c,** 574-45-8; **6a,** 6852-58-0; **6b,** 622-29-7; **7a,** 55103-11-2; **7b,** 55103-12-3; **7c,** 55103-14-5; **8a,** 55103-16-7; **8b,** 55103-17-8; **9,** 55103-18-9; **10,** 1070-89-9; **11,** 55103-19-0; **13,** 55103-20-3; **14,** 18366-49-9; **15a** isomer 1, 55103-22-5; **15a** isomer 2, 55103-23-6; **15b,** 55103-21-4; **16a,** 55103-24-7; **16b,** 55103-25-8; **17b,** 55103-26-9; methyl fluorosulfonate, 421-20-5; *N*-(benzhydrylidene)methyl-*tert*-butylaminium triflate, 55103-27-0; 1-*tert*-butylamino-2,2-diphenylethylene, 55103-28-1; diphenylacetaldehyde, 947-91-1; *tert*-butylamine, 75-64-9; *N*-methyl-*N*-*tert*-butylbenzamide, 49690-12-2; *tert*-butylamine hydrochloride, 10017-37-5; benzoyl chloride, 98-88-4; hexamethyldisilazane, 999-97-3.

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EXPERIMENTAL SECTION

Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Model 137 spectrometer. Nuclear magnetic resonance (nmr) spectra were recorded on a 60 MHz Varian Associates A-60A high-resolution spectrometer at a sweep width of 500 Hz. Chemical shifts (δ) are reported in parts per million downfield from internal tetramethylsilane standard. Low-resolution mass spectra were measured on either an Hitachi Perkin-Elmer RMU-6E spectrometer or an AEI-MS-30 double-beam instrument. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia.

Except as noted, the syntheses, isolations and reactions of moisture-sensitive compounds were effected in a Labconco (Kansas City, Missouri) fiberglass drybox purged with dry nitrogen and equipped with an aspirator for suction filtration.

Ketimines 5a[19], 5b[19] and 5c[20] were prepared by the method of Moretti and Torre.[19] Aldimines 6a[21] and 6b[22] were formed from the corresponding amine and benzaldehyde. Molecular seives (4A) were used to remove water during the reaction.

General Procedure for the Preparation of the Ketiminium Salts. A 500-ml round-bottomed flask was equipped with a magnetic stirrer, placed in a drybox, and charged with the appropriate ketimine (5, 0.05-0.08 mol) and dry solvent. The flask was immersed in a Dry Ice-acetone bath and treated with approximately two equivalents of the appropriate alkylating agent. The cold bath was removed, and the system was stirred overnight at ambient temperature. The ketiminium salts thus prepared were collected by suction filtration in the drybox, washed with ether, dried, and weighed.

N-(Benzhydrylidene)methyl-tert-butylaminium Fluorosulfonate (7a). The general alkylation procedure was carried out with a mixture of N-(benzhydrylidene)tert-butylamine (5a, 11.87 g, 50.0 mmol), methyl fluorosulfonate (10.6 g, 7.5 ml, 93 mmole), and anhydrous ether (75 ml). The crude N-(benzhydrylidene)methyl-tert-butylaminium fluorosulfonate (7a, 16.95 g, 97%) melted with decomposition at 125°. Three recrystallizations from absolute ethanol produced the analytical sample of 7a: mp 128-128.5° dec; ir (Nujol) ν1590, 1290, 1180, 1080 cm^{-1}; nmr (SO_2) δ1.58 (singlet, 9H, tert-butyl), 3.78 (singlet, 3H, NCH_3), 7.2-7.8 (multiplet, 10H, aromatic); mass spectrum (15eV) m/e 41, 56 (base), 118, 194, 195; (70eV) m/e 77, 118 (base), 194, 195 (P^+ 351 unobsd).

Anal. Calcd for $C_{18}H_{22}FNO_3S$: C, 61.51; H, 6.31; N, 3.99. Found: C, 61.40; H, 6.39; N, 4.02.

N-(Benzhydrylidene)methyl-tert-butylaminium Triflate. This compound was prepared by a modification of the general alkylation procedure. Into a 25-ml round-bottomed flask equipped with a magnetic stirrer was placed N-(benzhydrylidene)tert-butylamine (5a, 2.85 g, 12 mmol) and dry chloroform (10 ml). The solution was stirred in an atmosphere of nitrogen, cooled to 0°, and treated with methyl triflate (1.97 g, 2.00 ml, 12 mmol). The opaque mixture was stirred at room temperature for 4.5 hours, and then concentrated in vacuo. Trituration of the residue with anhydrous ether produced a solid, which was collected by filtration, washed with ether, and dried. The crude N-(benzhydrylidene)-methyl-tert-butylaminium triflate was isolated in quantitative yield. It melted with decomposition at 113°. Two recrystallizations from ethanol-ether afforded the analytical sample: mp 114-115.5° dec; nmr (DMSO-d_6) δ1.48 (singlet, 9H, tert-butyl), 3.68 (singlet, 3H, NCH_3), 7.58 (ca. singlet, ca. 10H, aromatic).

Anal. Calcd for $C_{19}H_{22}F_3NO_3S$: C, 56.84; H, 5.52; N, 3.49. Found: C, 56.75; H, 5.60; N, 3.48.

N-(Benzhydrylidene)dimethylaminium Fluorosulfonate (7b). The general alkylation procedure was carried out with a mixture of N-(benzhydrylidene)methylamine (5b, 15.6 g, 80 mmol), methyl fluorosulfonate (17.0 g, 12.0 ml, 150 mmol), and ether (200 ml). Additional ether (150 ml) was added after the mixture had warmed to ambient temperature, to facilitate stirring. The usual work-up afforded N-(benzhydrylidene)dimethylaminium fluorosulfonate (7b, 24.6 g, 100%) as a white powder, which melted at 131-142°. Nmr (SO_2) δ3.86 (singlet, 6H, CH_3), 7.6-7.9 (multiplet, 10H, aromatic).

N-(Benzhydrylidene)methylanilinium Fluorosulfonate (7c). The general alkylation procedure was applied to the synthesis of salt 7c, starting with N-(benzhydrylidene)aniline (5c, 12.87 g, 50.0 mmol), methyl fluorosulfonate (10.6 g, 7.5 ml, 93 mmol), and ether (125 ml). Ketimine 5c was found to be relatively insoluble in ether at -78°, but the alkylation proceeded in the usual fashion. The crude N-(benzhydrylidene)methylanilinium fluorosulfonate (7c, 17.79 g, 96%) was obtained as a pale yellow powder: mp 215.5-220°; nmr (SO_2) δ4.22 (singlet, 3H, CH_3), 7.33 (ca. singlet, 5H, aromatic), 7.51 (ca. singlet, 5H, aromatic), 7.73 (singlet, 5H, aromatic).

Pyrolysis of N-(Benzhydrylidene)methyl-tert-butylaminium Triflate. N-(Benzhydrylidene)methylliminium Triflate (9). N-(Benzhydrylidene)-methyl-tert-butylaminium triflate (2.01 g, 5.0 mmol) was placed in a 2x20-cm Pyrex pyrolysis tube equipped for quantitating gas evolution. The tube was evacuated, filled with dry nitrogen, and heated with an oil bath at about 130°, until the volume of collected gas (98 ml, ca. 90% of the theoretical amount of isobutene) remained constant. Upon cooling, the melt solidified. The pyrolysis tube was cracked open and the crude N-(benzhydrylidene)methyliminium triflate (9) was recovered in quantitative yield: mp 108-110°; nmr (DMSO-d_6) δ3.47 (singlet, ca. 3H, CH_3), 7.70 (ca. singlet, ca. 10H, aromatic).

General Procedure for the Preparation of the Aldiminium Salts (8). All operations were performed in a drybox. Into an oven-dried flask equipped with a magnetic stirrer was placed a solution of the appropriate aldimine (6) in anhydrous ether. The flask was immersed in a Dry Ice-acetone bath, and to it was added (with stirring) methyl fluorosulfonate (1.8 equivalents). The cold bath was removed, and the mixture was allowed to stir overnight at ambient temperature. The aldiminium salt was then collected by filtration, washed with ether, dried, weighed, and stored in the drybox.

N-(Benzylidene)methyl-tert-butylaminium Fluorosulfonate (8a). The general alkylation procedure was followed with N-(benzylidene)-tert-butylamine (6a, 32.3 g, 0.200 mol), methyl fluorosulfonate (42.4 g, 30 ml, 0.37 mol), and ether (200 ml), in a 500-ml round-bottomed flask. The thick, white precipitate that resulted was allowed to warm to ambient temperature, and diluted with ether (100 ml) to facilitate stirring. The usual work-up afforded crude N-(benzylidene)methyl-tert-butylaminium fluorosulfonate (8a, 54.7 g, 99%) as a white powder which melted at ca. 154-173°. Nmr (SO_2): δ1.73 (singlet, 9H, tert-butyl), 3.83 (doublet, J=ca. 1.0 Hz, 3H, NCH_3), 7.6-8.1 (multiplet, 5H, aromatic), 9.03 (broad pseudosinglet, 1H, N=CH).

N-(Benzylidene)dimethylaminium Fluorosulfonate (8b). Aldiminium salt 8b was prepared in an inert atmosphere, but not in a drybox as per the general procedure. An oven-dried 500-ml three-necked round-bottomed flask was equipped with a gas inlet, drying tube, and magnetic stirrer. The flask was charged with N-(benzylidene)-methylamine (6b, 11.9 g, 0.100 mol) and anhydrous ether (100 ml), cooled with an ice bath, and purged with dry nitrogen. At 0°, methyl fluorosulfonate (21 g, 15 ml, 0.18 mol) was added, and the immediate, white precipitate was treated with additional ether (100 ml) to facilitate stirring. The thick mixture was stirred at 0° for one hour and then transferred to a drybox, where it was filtered, washed with ether, and dried. The crude N-(benzylidene)dimethylaminium fluorosulfonate (8b) was isolated as a white powder (22.3 g, 96%) which melted at 80-88.5° (sealed capillary). Nmr (SO_2) showed δ3.88 (doublet, J=ca. 1.3 Hz, 3H, CH_3), 3.98 (doublet, J=ca. 1.0 Hz, 3H, CH_3), 7.6-8.1 (multiplet, 5H, aromatic), 8.9-9.0 (multiplet, 1H, N=CH).

Sodium Bis(trimethylsilyl)amide (10). Sodium bis(trimethylsilyl)-amide (10) was prepared by slight modification of the method of Krüger and Niedzerprüm.[9] A 500-ml round-bottomed flask was placed in a drybox and charged with sodium amide (MC/B, Practical Grade, 19.51 g, 0.500 mol), hexamethyldisilazane (PCR, Inc., 80.7 g, 104 ml, 0.500 mol), molecular sieves (4A, ca. 10 g), and dry benzene (250 ml). The flask was stoppered and removed from the drybox. The black mixture was refluxed for four days, returned to the drybox, and filtered (hot) through Celite. The clear, colorless filtrate was evaporated to dryness in vacuo, first with a trapped water aspirator and then with a vacuum pump (ca. 0.03 mm). Precautions were taken to exclude moisture from the pure white powder. The sodium bis(trimethylsilyl)amide (10) was both weighed (81.02 g, 88%) and stored in the drybox.

Preparation and Titration of a Solution of Sodium Bis(trimethylsilyl)amide (10) in Benzene. A mixture of sodium bis(trimethylsilyl)-amide (10, 22.01 g, 0.120 mol) and molecular sieves (4A, ca. 5 g) was stirred in dry benzene (300 ml) in a drybox until all of the base had dissolved. The molecular sieves and any insoluble impurities were separated from the solution by filtration through Celite in the drybox. The filtrate was diluted with more benzene (100 ml) and the solution was stored in the drybox in an amber bottle.

The solution of 10 in benzene was assayed by carefully measuring three aliquots into 10-ml volumetric flasks, removing the flasks from the drybox, and quantitatively transferring their contents to three 100-ml round-bottomed flasks. Benzene was used to facilitate the transfer. The diluted aliquots were decomposed with distilled water (ca. 10 ml), and the resulting mixture was concentrated to dryness at reduced pressure. The residual sodium hydroxide was treated with distilled water (ca. 10 ml) and methyl red indicator (0.1% w/v in ethanol, 2 drops). In a typical assay, neutralization of the three samples required 25.9, 26.2, and 26.1 ml of standard 0.1000 M hydrochloric acid, indicating that the concentration of sodium bis(trimethylsilyl)amide in the benzene solution was 0.26 molar.

Treatment of 7a with Sodium Bis(trimethylsilyl)amide (10) in Hexane at 25° C. Purification of 1-tert-Butyl-2,2-diphenylaziridine (11). A mixture of N-(benzhydrylidene)methyl-tert-butylaminium fluorosulfonate (7a, 0.53 g, 1.5 mmol) and sodium bis(trimethylsilyl)amide (10, 0.29 g, 1.6 mmol) was stirred magnetically in a 25-ml round-bottomed flask, in a drybox. Hexane (10 ml) was added, and the mixture was stirred at ambient temperature for one hour. It was then removed from the drybox and filtered. The filtrate was concentrated in vacuo, and the residue was weighed (0.32 g) and then assayed by careful integration of its nmr spectrum. The relative distribution of 1-tert-butyl-2,2-diphenylaziridine (11), N-(benzhydrylidene)tert-butylamine (5a), and benzophenone was 21.5±1.0:1.0:1.3.[23]

The crude product from the reaction of 7a with NaN($SiMe_3$)$_2$ in hexane was dissolved in carbon tetrachloride (10 ml) and applied to a 2.5x16-cm column of Fisher Adsorption Alumina (80-200 mesh), which was packed in 20-40° petroleum ether. The column was eluted with 150 ml of carbon tetrachloride, at which point a 25-ml fraction was collected. Concentration of the fraction in vacuo produced a clear, colorless oil which crystallized on standing. The solid (mp 50-52°) was dissolved in ether, and the ethereal solution was treated with anhydrous magnesium sulfate and activated charcoal, filtered, and evaporated in vacuo. The dried (40°/0.20 mm) analytical sample of 1-tert-butyl-2,2-diphenylaziridine (11) melted at 50-52.5° and analyzed as follows: nmr (CCl_4) δ0.88 (singlet, 9H, tert-butyl), 2.16 (singlet, 2H, methylene), 7.0-7.5 (multiplet, 10H, aromatic); mass spectrum (70eV) m/e 194, 195 (base), 236, 251 (P^+).

Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 86.01; H, 8.44; N, 5.53.

Authentic 1-tert-Butylamino-2,2-diphenylethylene. Into a 250-ml round-bottomed flask equipped with a reflux condenser and heating mantle was placed diphenylacetaldehyde (19.6 g, 17.8 ml, 0.100 mol), tert-butylamine (14.6 g, 20 ml, 0.20 mol), molecular sieves (4A, ca. 10 g), and benzene (100 ml). The mixture was refluxed for two hours, and the resulting dark amber solution was cooled, treated with activated charcoal and anhydrous magnesium sulfate, and filtered through Celite. Concentration of the yellow filtrate in vacuo produced an oil, which was submitted to bulb-to-bulb distillation with a rotary evaporator (0.10 mm) and a Bunsen burner. The viscous, yellow distillate of 1-tert-butylamino-2,2-diphenylethylene (20.0 g, 80%) solidified on standing. It was recrystallized four times from absolute methanol to furnish the analytical sample of 31 as white crystals: mp 77-83°; nmr (CCl_4) δ1.18 (singlet, 9H, tert-butyl), 3.66 (broad doublet, J=13 Hz, 1H, NH, exchanges with D_2O), 6.54 (broad doublet, J=13 Hz, 1H, vinyl, collapses to a singlet with D_2O), 7.00 (ca. singlet, 5H, aromatic), 7.22 (ca. singlet, 5H, aromatic).

Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 85.88; H, 8.45; N, 5.61.

Treatment of 1-tert-Butyl-2,2-diphenylaziridine (11) with Florisil. 1-tert-Butylamino-2,2-diphenylethylene. A solution of crude 1-tert-butyl-2,2-diphenylaziridine (11, 0.50 g) in a mixed solvent of 20-40° petroleum ether and benzene (1:1, 10 ml) was applied to a 1.5x25-cm column of Florisil (Fisher, 100-200 mesh), packed in the same mixed solvent. The column was also eluted with the mixed solvent. The first 10-ml fraction that was eluted after the forerun was shown by nmr spectral comparison with authentic material to contain only 1-tert-butylamino-2,2-diphenylethylene (0.04 g). The concentrated, second 10-ml fraction consisted of a mixture (0.10 g) of enamine and diphenylacetaldehyde.

Attempting Trapping of the Ylide 12 with Norbornene. A 10-ml round-bottomed flask was placed in a drybox and charged with a mixture of N-(benzhydrylidene)methyl-tert-butylaminium fluorosulfonate (7a, 0.35 g, 1.0 mmol) and norbornene (0.94 g, 10 mmol). The mixture was stirred magnetically, and to it was added a solution of 0.26 M sodium bis(trimethylsilyl)amide (10) in benzene (5.5 ml, 1.4 mmol). The resulting slurry was stirred for one hour, and then filtered. Nmr spectral assay of the filtrate showed it to contain only the usual reaction product, 1-tert-butyl-2,2-diphenylaziridine (11), and unreacted norbornene.

Treatment of N-(Benzhydrylidene)dimethylaminium Fluorosulfonate (7b) with the Silylamide Base (10). A 300-ml round-bottomed flask was placed in a drybox and charged with N-(benzhydrylidene)dimethylaminium fluorosulfonate (7b, 9.28 g, 30 mmol). A solution of sodium bis(trimethylsilyl)amide (5.87 g, 32 mmol) in benzene (200 ml) was filtered onto the stirring salt. An immediate purple color developed, but it changed to brown during the 60-minute reaction time. Upon removal of the mixture from the drybox and exposure to the air, the mixture turned yellow. Filtration produced a clear, yellow solution, which darkened upon evaporation in vacuo at 35°. The residue was an amorphous, tan foam (6.26 g) whose nmr spectrum showed only broad, unidentified resonances.

Treatment of N-(Benzhydrylidene)methylanilinium Fluorosulfonate (7c) with the Silylamide Base (10). A 500-ml round-bottomed flask equipped with a magnetic stirrer was placed in a drybox and charged with N-(benzhydrylidene)methylanilinium fluorosulfonate (7c, 11.14 g, 30.0 mmol) and sodium bis(trimethylsilyl)-amide (5.87 g, 32.0 mmol). To the stirring solids was added dry benzene (250 ml). An immediate, persistent, deep red color developed. The mixture was stirred for one hour, removed from the drybox, and filtered. The filtrate was evaporated in vacuo (35°), and the dark red residue was treated with pentane at -78°. Evaporation of the pentane-soluble decantate produced a clear, dark amber syrup (6.45 g), whose nmr spectrum (CCl_4) showed a species with a prominent singlet at δ2.77. In addition, smaller amounts of N-(benzhydrylidene)aniline (5c), benzophenone, and N-methylaniline were indicated. Only the latter was recovered (in toto, ca. 5% by weight of the crude mixture) by extraction of the mixture with 1% aqueous perchloric acid, followed by basification (5% aqueous sodium bicarbonate) and extraction into carbon tetrachloride. The species which resonated at δ2.77 was not recovered by silica gel chromatography (Silica Gel G, E. Merck AG, 20-40° petroleum ether eluent). It could not be purified by distillation (0.15 mm) or by alumina column chromatography (e.g., 10% and 20% deactivated, benzene and 20-40° petroleum ether eluents).

Authentic N-Methyl-N-tert-butylbenzamide. A 25-ml round-bottomed flask equipped with a magnetic stirrer was charged with methyl-tert-butylamine hydrochloride[24] (1.24 g, 0.010 mol). The solid was stirred and cooled with an ice bath, and to it was added benzoyl chloride (Eastman, 1.57 g, 1.3 ml, 0.011 mol) and 10% aqueous sodium hydroxide (8 ml, 0.020 mol). After stirring for five minutes, the mixture was extracted with carbon tetrachloride. The organic extract was washed with water and saturated sodium chloride, dried with anhydrous magnesium sulfate, and concentrated in vacuo. The off-white residue (3.35 g) was freed of unreacted benzoyl chloride by washing with cold pentane. The crude N-methyl-N-tert-butylbenzamide (0.98 g, 51%) melted at 60-65°. Two recrystallizations from hot pentane afforded the analytical sample: mp 80-82°; ir (KBr) ν1625 cm^{-1}; nmr (CCl_4) δ1.42 (singlet, 9H, tert-butyl), 2.75 (singlet, 3H, NCH_3), 7.1-7.4 (multiplet, 5H, aromatic); mass spectrum (70eV) m/e 77, 105 (base), 106, 176, 191 (P^+).

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.48; H, 9.00; N, 7.23.

Authentic 1-tert-Butyl-2-phenylaziridine (14). 1-tert-Butyl-2-phenylaziridine (14) was prepared according to the procedure of Moyer.[13] The compound exhibited the following nmr spectrum in carbon tetrachloride: δ0.96 (singlet, 9H, tert-butyl), 1.44 (d of doublets, 1H, H_{cis}), 1.73 (d of doublets, 1H, H_{trans}), 2.46 (d of doublets, 1H, benzyl), 7.0-7.3 (multiplet, 5H, aromatic).

Treatment of N-(Benzylidene)methyl-tert-butylaminium Fluorosulfonate (8a) with Potassium tert-Butoxide. Isolation and Purification of Aminoether 13. N-(Benzylidene)methyl-tert-butylaminium fluorosulfonate (8a, 13.77 g, 50 mmol) was placed in a 500-ml round-bottomed flask in a drybox. The flask was immersed in a Dry Ice-acetone bath, and to salt 8a was added, with magnetic stirring, potassium tert-butoxide (5.83 g, 52 mmol) and anhydrous ether (300 ml). The cold bath was removed, and the pale yellow slurry was stirred for one hour. The mixture was then filtered through Celite, and the filtrate was removed from the drybox and evaporated in vacuo. The residue thus obtained was a clear, viscous, yellow oil (5.73 g) whose nmr spectrum indicated (vide infra) a product distribution of aminoether (8b):aldimine (6a):PhCHO:dimers (15a and 16a)::80:12:5:3 mol-%.

The crude mixture was distilled at reduced pressure (0.05 mm) and the fraction which boiled at 123-125° (0.98 g) was redistilled. The second distillation afforded the analytical sample of aminoether 8a: bp 73°/0.01 mm; nmr (CCl_4) δ1.15 (singlet, 9H, tert-butyl), 1.23 (singlet, 9H, tert-butyl), 2.21 (singlet, 3H, NCH_3), 5.65 (singlet, 1H, benzyl), 7.0-7.6 (multiplet, 5H, aromatic); mass spectrum (70eV) m/e 59 (base), 72, 77, 105, 106 (P^+ 249 unobsd).

Anal. Calcd for $C_{16}H_{27}NO$: C, 77.05; H, 10.91; N, 5.62. Found: C, 77.02; H, 10.95; N, 5.64.

Decomposition of Aminoether 13 with Deuterium Oxide. Deuterium oxide (MSD of Canada, Ltd., min 99.7 atom-% D, one drop) was added

to aminoether 13 in carbon tetrachloride. There was no spectral evidence for reaction within 15 minutes of the addition. However, it was shown by integrating the singlets at δ5.58 (13, benzyl) and 9.85 (PhCHO) that about half of the aminoether had decomposed after four hours. Complete decomposition of 13 was accomplished overnight. The reaction products, which were produced in equimolar quantities, were benzaldehyde, tert-butyl deuteroxide (t-BuOD), and the deuterated amine DN(Me)t-Bu. These products were identified by spiking the mixture with authentic samples, and noting their equivalence in the nmr spectrum.

Decomposition of Aminoether 13 with Aqueous Base. A mixture of aminoether 13 (1.00 g, 4.0 mmol) and 10% aqueous sodium hydroxide (24 ml, 4 mmol) was stirred magnetically in a 1.5x15-cm test tube. Benzoyl chloride (0.62 g, 0.51 ml, 4.4 mmol) was added, and the turbid, white mixture was stirred for five minutes. The system was extracted with carbon tetrachloride, and the organic extract was washed with saturated sodium chloride, dried with molecular sieves (4A), and evaporated in vacuo. The crude N-methyl-N-tert-butylbenzamide (0.32 g, 42%) was recrystallized from hot pentane, and the purified amide was found to melt at 79-81°. Its mixture melting point with an authentic sample was not depressed.

Treatment of N-(Benzylidene)methyl-tert-butylaminium Fluorosulfonate (8a) with Sodium Bis(trimethylsilyl)amide (10). Isolation and Purification of Diaminostilbene 16a and the Major and Minor Aminomethylaziridine Isomers (15a). A 2000-ml round-bottomed flask was placed in a drybox and charged with sodium bis(trimethylsilyl)amide (10, 22.01 g, 120 mmol) and dry benzene (460 ml). The system was stirred magnetically until solution was effected, at which time N-(benzylidene)methyl-tert-butylaminium fluorosulfonate (8a, 16.52 g, 60.0 mmol) was added. An immediate, intense yellow color was produced, but it lightened appreciably within five minutes after the addition of 8a. The slurry was stirred for one hour, removed from the drybox, and filtered. The filtrate was evaporated at reduced pressure, and the residue was treated with hexane, activated charcoal, and anhydrous magnesium sulfate. The mixture was filtered, and the filtrate was concentrated in vacuo. The nmr spectrum (benzene-d_6) of the resulting dark oil (13.77 g) indicated (vide infra) the presence of the diaminostilbene 16a and the major and minor isomers of the aminomethylaziridine 15, in the approximate ratio of 1.0:6.7:1.3. Also present were smaller amounts of N-(benzylidene)-tert-butylamine (6a) and several unidentified silylated species (1-6 Hz downfield from TMS).

A filtered solution of the crude product mixture (12.88 g) in benzene (100 ml) was chromatographed on a 2.5x65-cm column of silica gel (Baker, 60-200 mesh) packed in 30-60° petroleum ether. The column was eluted initially with benzene. The first six 10-ml fractions were combined and concentrated in vacuo to produce the crude diaminostilbene (16a) as a yellow powder. Recrystallization of the material from 95% ethanol, followed by sublimation (95-100°/0.025 mm), afforded the analytical sample of α,α'-bis(methyl-tert-butylamino)stilbene, 16a: mp 109.5-114.5°; nmr (CCl_4) δ0.91 (singlet, 18H, tert-butyl), 2.35 (singlet, 6H, NCH_3), 7.0-7.5 (multiplet, 10H, aromatic); mass spectrum (70eV) m/e 41 (base), 69, 149 (P^+ 351 unobsd).

Anal. Calcd for $C_{24}H_{34}N_2$: C, 82.23; H, 9.78; N, 7.99. Found: C, 81.96; H, 9.86; N, 8.01.

An additional 40-ml fraction was eluted from the column, and was shown by tlc analysis (benzene eluent) to contain a mixture of the diaminostilbene 16a (R_f 0.7) and the major aminomethylaziridine isomer (R_f 0.0-0.4). The next 100-ml fraction was evaporated in vacuo to afford the crude, major isomer of 15a (4.01 g) as a pale yellow powder. The material was purified by recrystallization from 95% ethanol, and sublimed (95°/0.025 mm). The off-white sample of major-15a melted at 117-119°, and analyzed as follows: nmr (CCl_4) δ0.71 (singlet, 9H, tert-butyl), 0.89 (singlet, 9H, tert-butyl), 1.74 and 1.98 (doublets, J=1.4 Hz, 2H, methylene), 2.33 (singlet, 3H, NCH_3), 4.48 (singlet, 1H, benzyl), 7.0-7.5 (multiplet, 10H, aromatic); mass spectrum (70eV) m/e 41, 42, 120, 176 (base), 351 (weak P^+).

Anal. Calcd for $C_{24}H_{34}N_2$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.13; H, 9.79; N, 8.06.

A final 350 ml of benzene was eluted, and the column was flushed with methanol. The first 10-ml fraction of methanol was discarded. The next 250-ml fraction was evaporated in vacuo, and the residue was dissolved in carbon tetrachloride. The solution was washed with saturated sodium chloride, dried with anhydrous magnesium sulfate, and concentrated in vacuo. The crude minor aminomethylaziridine isomer was obtained as a viscous, amber oil (0.91 g), which was crystallized at low temperature. The analytical sample of minor-15a, after recrystallization from 95% ethanol and sublimation (ca. 76°/0.025 mm), melted at 77.5-79°; nmr (CCl_4) δ0.77 (singlet, 9H, tert-butyl), 0.83 (singlet, 9H, tert-butyl), 1.13 and 1.68 (doublets, J=1.4 Hz, 2H, methylene), 2.78 (singlet, 3H, NCH_3), 4.13 (singlet, 1H, benzyl), 7.0-7.5 (multiplet, 10H, aromatic); mass spectrum (70eV) m/e 57, 72, 119, 206 (base), 351 (weak P^+).

Anal. Calcd for $C_{24}H_{34}N_2$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.10; H, 9.82; N, 8.00.

Pyrolyses of the Major and Minor Isomers of Aminomethylaziridine 15a. A 1.7x90-mm melting point capillary tube was filled to a depth of about 15 mm with the major isomer of aminomethylaziridine 15a. The capillary tube was sealed, and then heated in a Thomas-Hoover Unimelt capillary melting point apparatus (ca. 10 deg/min). The sample was observed to melt at 114.5-117°; the melt gradually became yellow (ca. 200°), and turned orange upon continued heating. When the oil bath had reached 250°, the capillary was withdrawn, cleaned with carbon tetrachloride, and cracked open. The section of the capillary which contained the orange melt was inserted into an nmr sample tube, and carbon tetrachloride (ca. 0.5 ml) and the tetramethylsilane standard were added. The nmr sample tube was capped and shaken to leach the melt from the broken capillary. The nmr spectrum of the resulting solution indicated that the predominant pyrolysis product of major-15a was the diaminostilbene 16a, in addition to lesser amounts of the starting material and the minor isomer (8.6:1). These spectral assignments were supported by tlc assay.

The pyrolysis was repeated with the minor isomer of aminomethylaziridine 15a. This compound melted at 77-80°, but showed the same color changes as did major-15a. The nmr spectrum of the melt also indicated that diaminostilbene 16 was the predominant pyrolysis product. Compound 16 was accompanied by smaller amounts of the starting isomer (minor-15a) and the major isomer (1:1.5).

Attempted Trapping with Norbornene. A 25-ml round-bottomed flask was placed in a drybox and charged with N-(benzylidene)methyl-tert-butylaminium fluorosulfonate (7a, 0.41 g, 1.5 mmol), norbornene (1.41 g, 15 mmol) and dry benzene (5 ml). The mixture was stirred magnetically, and to it was added a 0.26 M solution of sodium bis(trimethylsilyl)amide (10) in benzene (11.5 ml, 3.0 mmol). The system was stirred at ambient temperature for one hour, removed from the drybox, and filtered through Celite. The filtrate was concentrated in vacuo (thereby removing any unreacted norbornene), and the resulting amber semisolid (0.45 g) was shown by nmr spectral assay to contain only the usual reaction products (vide supra).

Stability of 1-tert-Butyl-2-phenylaziridine (14) to the Deprotonation Conditions. 1-tert-Butyl-2-phenylaziridine (14, ca. 75 mg) was dissolved in benzene-d_6 (ca. 1 ml) in an nmr sample tube. Sodium bis(trimethylsilyl)amide (10, ca. 100 mg) was then added. The mixture was shaken mechanically for one hour, and then treated with deuterium oxide (3 drops). The sample tube was shaken again and centrifuged. The nmr spectrum of the organic layer indicated that no deuterium exchange had taken place.

In a related experiment, a mixture of 1-tert-butyl-2-phenylaziridine (14, 0.26 g, 1.5 mmol) and a 0.26 M solution of sodium bis(trimethylsilyl)amide (10) in benzene (5.8 ml, 1.5 mmol) was stirred magnetically in a 10-ml round-bottomed flask, in a drybox. After one hour, N-(benzylidene)methyl-tert-butylaminium fluorosulfonate (8a, 0.41 g, 1.5 mmol) was added. The slurry was stirred for an additional 60 minutes, removed from the drybox, and filtered. The filtrate was concentrated in vacuo to produce a clear, dark amber liquid (0.57 g), whose nmr spectrum indicated only the usual mixture of products (vide supra) and the intact 1-tert-butyl-2-phenylaziridine (14).

Stability of the Major Isomer of Aminomethylaziridine 15a to Sodium Bis(trimethylsilyl)amide (10). A 25-ml round-bottomed flask was placed in a drybox and charged with the major isomer of 15a (0.21 g, 0.60 mmol), sodium bis(trimethylsilyl)amide (10, 0.44 g, 2.4 mmol), and dry benzene (10 ml). The solution was stirred magnetically for one hour, removed from the drybox, and washed with water. The benzene layer was treated with activated charcoal and anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The resulting pale yellow powder was shown by nmr spectroscopy to be the recovered aminomethylaziridine, major-15a (0.19 g, 91%).

Authentic α,α'-Bis(dimethylamino)stilbene Isomers (16b and 17b). The mixture of E- and Z-isomers of compound (16b and 17b) was prepared from α-(dimethylamino)phenylacetonitrile[25] by a published procedure.[15] The crude product mixture was shown by nmr spectroscopy to contain approximately equal amounts of the two isomers. Although the isomers were not separated, the mixture was purified by double distillation (109-110°/0.025 mm) and two column chromatographies (Fisher Alumina, Basic, Brockman Activity I, benzene eluent). nmr (CCl_4), entgegen (16b) δ2.28 (singlet, 12H, CH_3), 7.18 (ca. singlet, 10H, aromatic); zusammen (17b) δ2.67 (singlet, 12H, CH_3), 6.88 (ca. singlet, 10H, aromatic).

Treatment of N-(Benzylidene)dimethylaminium Fluorosulfonate (8b) with the Silylamide Base (10). A 200-ml round-bottomed flask was placed in a drybox and charged with N-(benzylidene)dimethylaminium fluorosulfonate (8b, 3.50 g, 0.015 mol) and sodium bis(trimethylsilyl)amide (10, 5.50 g, 0.030 mol). To the stirring mixture was added dry benzene (115 ml). A brilliant orange color developed immediately, but it faded to yellow within one minute after the rapid addition of benzene. The mixture was stirred at ambient temperature for one hour, removed from the drybox, and filtered through Celite. Concentration of the filtrate in vacuo produced a dark semisolid (4.43 g) whose nmr spectrum (CCl_4) indicated the presence of the aminomethylaziridine 15b [δ2.02 and 2.13 (doublets, methylene), 2.20 (amino-CH_3's); 4.45 (singlet, benzyl)], and about an equal amount of the diaminostilbene isomers 16b and 17b (ca. 1:1). In addition, there were many other unidentified resonances present in the spectrum.

In a typical separation attempt, the crude product mixture was dissolved in benzene (15 ml) and applied to a 2x20-cm column of basic alumina (Fisher, Brockman Activity I, 80-200 mesh) packed in 30-60° petroleum ether. The first (orange) 20-ml fraction of eluate was shown by nmr spectroscopy to contain the mixture of the α,α'-bis(dimethylamino)stilbene isomers (16b and 17b, 0.35 g). The supposed aminomethylaziridines 15b were not eluted from the column, even after flushing with methanol.

References and Notes

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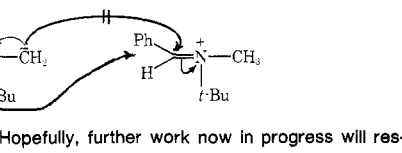
(17) A third possible route to the observed products has been considered.[18] This route involves attack of the 1,3-dipolar species formed from **8** on a second molecule of **8**. Subsequent deprotonation and/or hydride shifts could yield **15–17**. Although we can not rigorously exclude this possibility, the necessary exclusive mode of attack seems sterically and electronically improbable. Hopefully, further work now in progress will resolvthis point.



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