Involvement of Azomethine Ylides in the Thermal Rearrangement of Aziridinyl Ketones to Pyrroles

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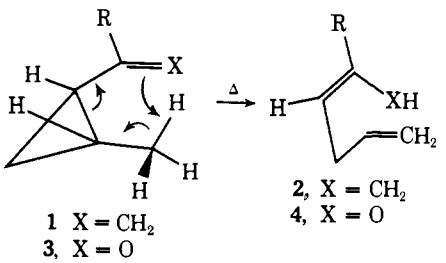
Abstract: Thermolysis of a number of *N*-alkyl-2-aroyl-3-methylaziridines has been found to afford *N*-alkyl-3-arylpyrroles in high yield. Kinetic studies show that *trans*-*N*-*tert*-butyl-2-benzoyl-3-methylaziridine rearranges 40 times more rapidly than the corresponding cis isomer at 70°. A mechanism involving conrotatory opening of the aziridine ring to an azomethine ylide is proposed to account for the observed rearrangement patterns. The higher energy requirement for rearrangement of the cis isomer was attributed to the stereochemical consequences of orbital symmetry control. Support for the proposed mechanism was obtained by trapping the 1,3 dipoles with dimethyl acetylenedicarboxylate. The thermal rearrangement of 2-*tert*-butyl-3-methyl-5-phenyl-4-isoxazoline was shown to involve an aroylaziridine as a transient intermediate. The excited state behavior of a set of stereoisomeric aziridinyl ketones was also studied.

The thermal "ene reaction" of three-membered rings, which takes place with a sigmatropic 1,5-hydrogen shift and concomitant ring cleavage, is a well-documented reaction (eq 1).[1-27] A cis relationship between the π system and the alkyl group on the vicinal ring carbon has been proposed as being necessary for these rearrangements to proceed.[4-9] The lack of reaction of the corresponding trans isomer under similar reaction conditions and the low energy and large negative entropy of activation for the cis isomer constitute compelling support for the concertedness of the reaction.[5-9] Much higher temperatures are required to effect the rearrangement of *trans*-1-alkyl-2-vinylcyclopropanes.[24] The reason for this is evident from an examination of molecular models. The trans isomer would require severe distortions to achieve a geometry where hydrogen transfer might become possible. The transition state for the homodienyl 1,5-hydrogen shift has been rationalized in terms of a nonplanar conformation (i.e., **1**) in which the migrating hydrogen and the methylene group of the cyclopropane ring are anti, with the plane of the ring parallel to that of the π bond.[3] Models indicate that this conformation is the most



1 X = CH_2
3, X = O

2, X = CH_2
4, X = O

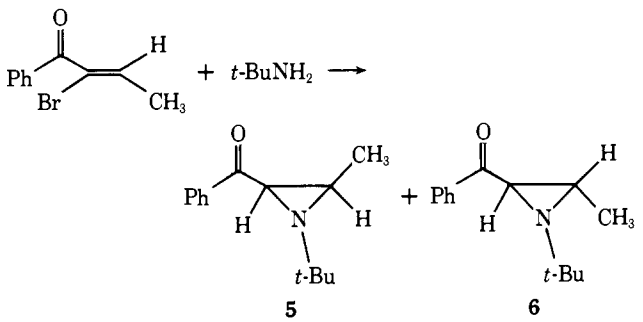
(1)

favorable for overlap of the developing p orbitals derived from the cyclopropane ring bond with the olefinic group and also the developing p orbital derived from the C–H bond. The selection rules for these homodienyl [1,5]-hydrogen shifts are similar to those for 1,5-dienyl shifts and predict that suprafacial migration of the hydrogen atom is a thermally allowed process.

We recently found an unusual variation in an apparent homodienyl "ene" reaction while examining the thermal rearrangement of *N*-alkyl-2-aroyl-3-methylaziridines to *N*-alkyl-3-arylpyrroles.[28] Our observations indicated that this system differed dramatically from heretofore observed three-membered ring "ene" reactions, in that the trans isomer reacted at a faster rate than the corresponding cis form. The present publication describes our preliminary findings in detail and delineates the significant role played by azomethine yields in the overall thermal chemistry of this ring system.

Results and Discussion

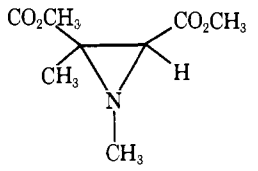
cis- and *trans*-*N*-*tert*-butyl-2-benzoyl-3-methylaziridines (**5** and **6**) were conveniently prepared from α-bromoethylideneacetophenone and *tert*-butylamine according to established procedures.[29] Stereochemical assignments were made on the basis of uv and NMR spectroscopy. Evidence has been obtained demonstrating that in a given pair of β-substituted aziridinyl ketone stereoisomers, the isomer possessing the trans structure exhibits an absorption maximum in the π–π^* transition at longer wavelengths than does the cis isomer.[30] This difference was attributed to the nature of the electrical interaction between the three ring and the carbonyl group.[29] As expected, the uv spectrum of *cis*-aziridine **5** exhibited a maximum at 245 nm (ϵ 13,200) while the maximum for the corresponding trans isomer (**6**) was shifted to slightly longer wavelength (247 nm, ϵ 13,500) and had a slightly greater intensity. Structural assignments were further strengthened by NMR measurements. The ring protons of the cis isomer are known to absorb at higher field than those of the trans form.[31] The chemical shift of the aziridine ring protons of **5** appeared at δ 2.22–2.48 (m) and 3.12 (d, J = 7.0 Hz), while the corresponding trans isomer **6** exhibited signals at δ 2.64–2.88 (m) and 3.16 (d, J = 3.0 Hz). Finally, isomerization of **6** to the thermodynamically more stable cis form (**5**) could be readily effected with methanolic sodium methoxide[32] providing additional support for the structural assignments. A number of related *N*-alkyl-2-aroyl-3-methylaziridines (**11–16**) were also prepared by similar procedures and their stereochemistry was assigned by similar spectroscopic arguments (see Experimental Section).



5 **6**

With the stereochemistry of the isomeric *cis*- and *trans*-*N*-alkyl-2-aroyl-3-methylaziridines firmly established, a detailed study of their thermal behavior was undertaken. Thermolysis of 140 mg of *cis*-aziridine **5** in methanol at 120° for 3 hr afforded 110 mg (80%) of *N*-*tert*-butyl-3-

Table I. Rates of Thermal Rearrangement of *N*-Alkyl-2-benzoyl-3-methylaziridines and Related Systems



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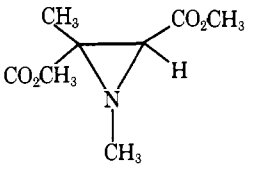


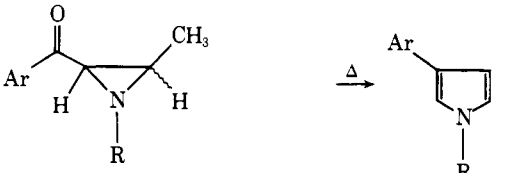
II

Compd[a]	*T*, °C	*k*, sec^{-1}	Rel rate (70°)	$\Delta H^{\dagger}$, kcal/mol	$\Delta S^{\dagger}$, eu
5	100	1.18×10^{-4}			
	110	3.23×10^{-4}	1	27.7	−2.3
	120	1.05×10^{-3}			
6	70	1.52×10^{-4}			
	80	4.54×10^{-4}	40	25.4	−1.7
	90	2.16×10^{-3}			
15	100	3.2×10^{-4}			
	105	4.8×10^{-4}	6.1	21.5	−17.2
	110	7.0×10^{-4}			
16	100	2.1×10^{-4}			
	105	3.2×10^{-4}	4.7	19.7	−22.9
	110	4.3×10^{-4}			
I	70	2.0×10^{-5}	5.2		
II	70	1.46×10^{-5}	3.8		

[a] See ref 19 for rates of last two aziridines.

phenylpyrrole (**7**). This compound was identified by comparison with an authentic sample.[33] Similar reactions were observed with *trans*-aziridine **6** as well as with aziridines **11–16**.

The rate data for the thermolysis of aziridines **5** and **6** together with those of related compounds are summarized in Table I. The disappearance of *cis*-aziridine **5** and the appearance of pyrrole **7** in methanol was followed simulta-

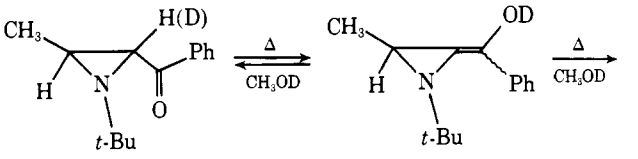


5 (cis), **6** (trans), R = *t*-Bu; Ar = Ph
11 (cis), **12** (trans), R = *t*-Bu; Ar = BiPh
13 (cis), **14** (trans), R = C_6H_{11}; Ar = BiPh
15 (cis), **16** (trans), R = CH_3; Ar = Ph

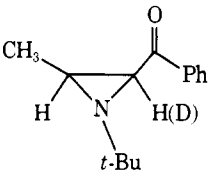
7, R = *t*-Bu, Ar = Ph

neously by NMR spectroscopy. The reaction followed first-order kinetics, and rate constants were determined at three different temperatures constant to ±0.5°, 100° ($k = 1.18 \times 10^{-4}$ sec^{-1}), 110° ($k = 3.23 \times 10^{-4}$ sec^{-1}), and 120° ($k = 1.05 \times 10^{-3}$ sec^{-1}). An Arrhenius plot gives $E_a = 28.6 \pm 0.5$ kcal/mol and log $A = 12.8$ from which values of $\Delta H^{\dagger} = 27.7$ kcal and $\Delta S^{\dagger} = -2.3$ eu can be calculated. The reaction kinetics encountered with *trans*-aziridine **6** were more complicated since the thermolysis of **6** in methanol at 80° produced *cis*-aziridine **5** as well as pyrrole **7**. It should be pointed out, however, that with the lower temperature and short reaction times used for the thermolysis of *trans*-aziridine **6**, the cis isomer (**5**) did not appreciably rearrange to pyrrole **7**. The concentration of all three compounds was followed simultaneously by NMR spectroscopy. By using steady state approximations and by numerical integration of the resultant differential equations with the program KINET,[34] an analytical function was obtained for the concentration of the trans isomer. The results indicate that *trans*-aziridine **6** also proceeds on to pyrrole by a first-order rate process (i.e., $k = 1.52 \times 10^{-4}$ sec^{-1} (70°), $k = 4.54 \times 10^{-4}$ sec^{-1} (80°), and $k = 2.16 \times 10^{-3}$ sec^{-1} (90°), $E_a = 26.4 \pm 0.5$ kcal/mol, and log $A = 13.0$). These data correspond to $\Delta H^{\dagger} = 25.4 \pm 0.5$ kcal/mol and $\Delta S^{\dagger} = -1.7$ eu. Extrapolation of the data for the cis isomer to 70° indicates that the *trans*-aziridine **6** rearranges 40 times more rapidly than the corresponding cis isomer.

In order to help elucidate the mechanism for the *trans*-**6** → *cis*-**5** aziridine epimerization, we studied the thermal rearrangement of both aziridines in deuteriomethanol at 77° for 15 hr. Recovered starting material (80%) from the *cis*-aziridine **5** run was found to have incorporated one deuterium atom into the 2 position of the aziridine ring. The fact that addition of an excess of dimethyl fumarate to a solution of **5** did not significantly affect either the rate of disappearance of starting ketone or the amount of pyrrole formed strongly argues against the involvement of azomethine ylides in the *trans*- → *cis*-aziridine isomerization. This conclusion was reached by knowing that azomethine ylides can be readily trapped in the presence of dipolarophiles.[35] Consequently, one would have anticipated a marked diminution in the yield of the pyrrole if an azomethine ylide were involved in the trans → cis isomerization. Similar results were obtained with *trans*-aziridine **6**, except that in



6 **8**



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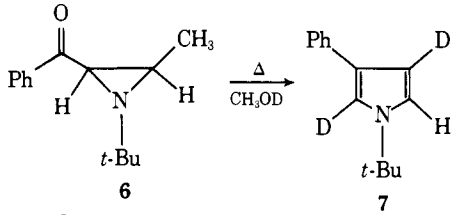
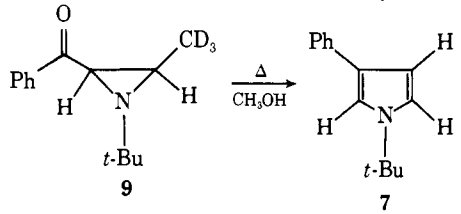
this case the recovered aziridine was mostly the epimerized cis *2-d*$_1$ isomer. The most direct interpretation of the above data involves enol **8** as the reactive intermediate responsible for the epimerization. This suggestion is quite reasonable since enolization has been implicated in the cis-trans interconverson of other aroylaziridines[32,36] as well as with the related dypnone oxide system.[37]

It is especially interesting to note that the pyrrole isolated from the thermolysis of the *cis*-aziridine in CH_3OD contained deuterium atoms *in both the 2 and 4 positions of the pyrrole ring*. A control experiment indicated that pyrrole **7** only incorporates deuterium into the 2 position of the ring



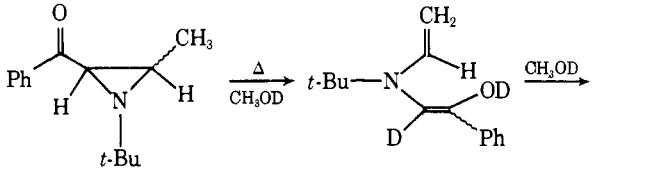
6 **7**



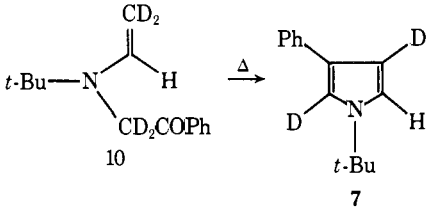
9 **7**

under the reaction conditions used. A further experiment utilizing *cis-N-tert*-butyl-2-benzoyl-3-methylaziridine-*3-methyl-d*$_3$ (**9**) and methanol confirmed this intermolecular

hydrogen exchange. No detectable deuterium was found in the final product (**7**) when deuterated *cis*-aziridine **9** was heated at 120° in methanol for 2.5 hr. Similar results were obtained with the corresponding *trans*-aziridines. These observations may be explained in terms of a rapid intermolecular exchange of the vinyl hydrogens of the initially formed enamine (**10**) with the solvent prior to cyclization to the



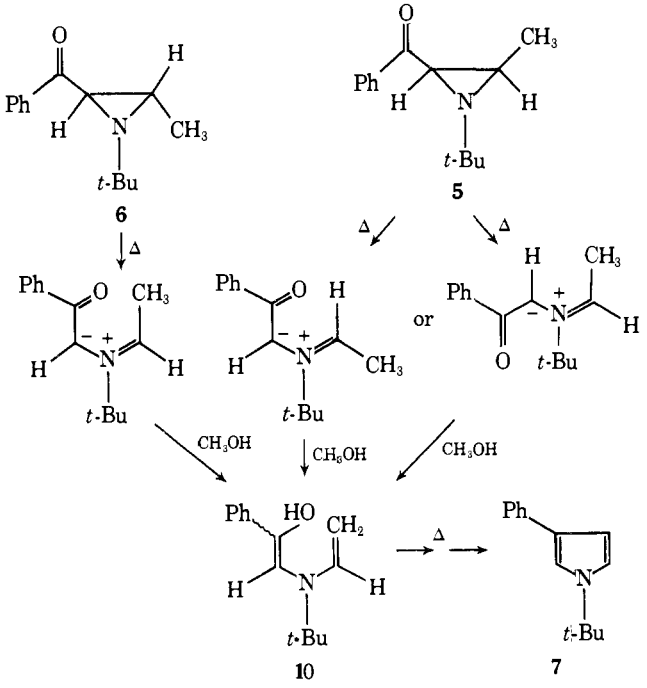
5 (or **6**)



10 **7**

pyrrole. It should also be pointed out that recovered *cis*-aziridine **5** did not incorporate deuterium into the methyl group when **5** was heated in deuteriomethanol. A similar set of results was obtained when deuterated *cis*-aziridine **9** was heated in methanol. The recovered ketone did not exchange hydrogen for deuterium. The lack of deuterium incorporation on the methyl group of aziridine **5** argues against the "enolene" mechanism[7-9] for rearrangement of these aziridines. Also noteworthy is the absence of a primary deuterium isotope effect on the rate of rearrangement of *cis*-aziridine **9**. These observations coupled with the fact that *trans*-aziridine **6** rearranges at a faster rate than the cis isomer (**5**) mitigate against a homodienyl 1,5 shift as the mechanism responsible for the formation of enol **10**.

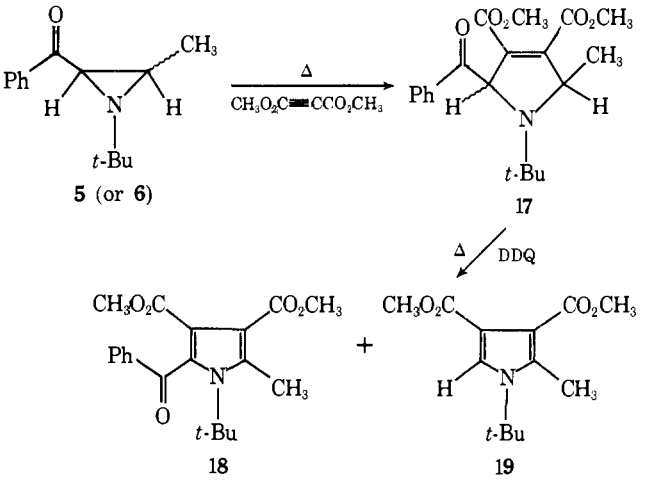
The simplest mechanism consistent with the observed rearrangement patterns of the substituted aziridines examined is the one outlined below. It is based on the knowledge



6 **5** **10** **7**

that aziridines readily undergo thermal cleavage to azomethine ylides by conrotation of the substituent groups.[35] The higher energy requirement for rearrangement of the cis isomer (**5**) (see Table I) can be attributed to the stereochemical consequences of orbital-symmetry control. Conrotatory rotation in either direction for the cis isomer causes one of the rotating groups to encounter a large steric interaction with the adjacent *tert*-butyl group. With the trans isomer, however, conrotation will result in a smaller steric interaction since neither the methyl nor benzoyl group needs to rotate toward the large *tert*-butyl group. Since no adduct was formed when the thermolyses were carried out in methanol in the presence of a potent dipolarophile, it would appear that the initially formed azomethine ylides have very short lifetimes in methanol and undergo rapid exchange with the protic solvent.

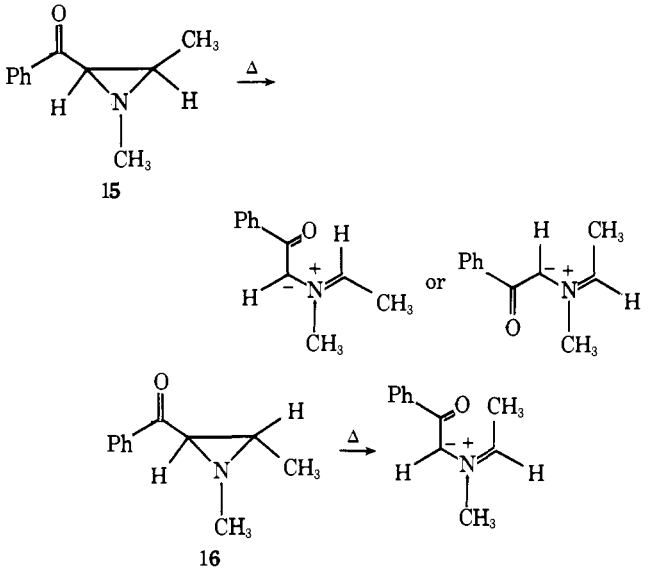
Further support for the above mechanism was obtained by carrying out the thermolysis of the aziridine (**5** or **6**) in a nonprotic solvent. Under these conditions, the azomethine ylides could be trapped by 1,3-dipolar cycloaddition with an added dipolarophile prior to the formation of pyrrole **7**.[38] Thus, heating *cis*-**5** or *trans*-**6** aziridine with dimethyl



5 (or **6**) **17** **18** **19**

acetylenedicarboxylate in chloroform at 120° gave an excellent yield of the crystalline *N*-*tert*-butyl-2-benzoyl-3,4-dicarbomethoxy-5-methyl-2,5-dihydropyrrole (**17**), mp 129–139°. The structure of the cycloadduct (**17**) was confirmed by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to *N*-*tert*-butyl-2-benzoyl-3,4-dicarbomethoxy-5-methylpyrrole (**18**) and *N*-*tert*-butyl-2-methyl-3,4-dicarbomethoxypyrrole (**19**). Most importantly, no detectable quantities of pyrrole **7** were observed in this trapping experiment. A control reaction demonstrated that the aziridines were smoothly converted into pyrrole **7** in chloroform at 120° in the absence of the dipolarophile. The trapping experiments clearly indicate that the aziridines open to a 1,3 dipole prior to the transfer of a hydrogen atom.

Both the kinetic and product studies in the series of aziridines investigated indicate that these thermal rearrangements proceed by conrotatory ring opening of the aziridine to form an azomethine ylide intermediate. The difference in rates between the *cis*-**5** and *trans*-**6** isomers is consistent with this interpretation. The steric congestion which results from the methyl (or benzoyl) *tert*-butyl interaction in the 1,3 dipole generated from the *cis*-aziridine accounts for the slower rate of reaction of this isomer. It is interesting to note that when a methyl group replaces the *tert*-butyl substituent on the nitrogen atom of the aziridine ring, the cis and trans isomers rearrange at essentially the same rate (see Table I). In this case, the steric interactions in the 1,3 dipoles are more equally balanced as a result of the smaller size of the group located on the nitrogen atom. What is particularly interesting, however, is the fact that the activation parameters in the *N*-methylaziridine system are substan-



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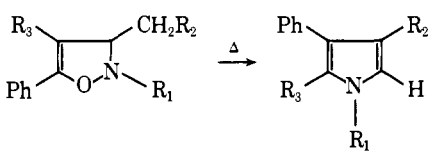
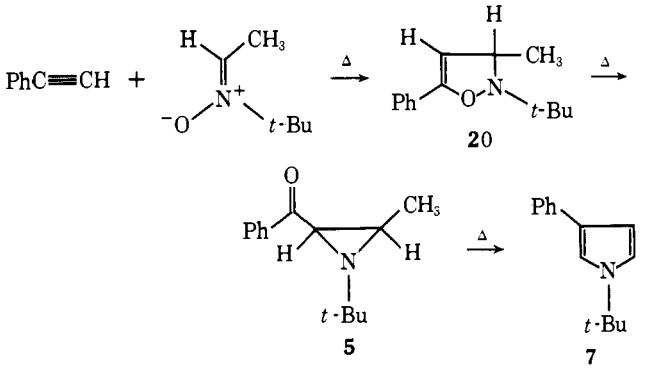
tially different from those encountered in the *N-tert*-butyl system (see Table I). The *N*-methylaziridines show a substantial decrease in both the entropy and energy of activation when compared to the *tert*-butyl system. These effects oppose each other and the net result is a similar rate of reaction of the two systems. Similar relationships have been observed in a wide number of organic reactions and attempts have been made to account for it in rather general terms.[39,40] The difference in the value of the activation parameters in the aziridine systems may well represent an example of the general mechanism by which an energy lowering at the transition state can be purchased at the cost of degrees of freedom, a situation which will always establish an energy–entropy parallelism. One possible source for the entropy lowering may be the difference in the degree of solvation of the transition states leading to the azomethine ylides in the two systems. Reactions of neutral molecules which yield ions are known to result in negative entropies of activation as a consequence of charge solvation.[41] The increase in solvent orientation in such a process would be expected to be substantially larger in the absence of any steric effects which minimize solvation of the developing charges. The presence of the bulky *tert*-butyl group on the nitrogen atom will prevent solvent molecules from effectively solvating the developing charges in the transition state. Consequently, the transition state in the *N*-methyl system will be more highly solvated than that in the related *tert*-butyl system. This will result in a diminution of the entropy of activation. In turn, this is balanced by a lowering of the enthalpy of activation as a result of a less congested transition state.

It is interesting at this point to note that the thermal conversion of 4-isoxazolines into pyrroles[42,43] has been postulated to involve an aroylaziridine as a transient intermedi-



ate.[44] The first step of this reaction was suggested to proceed by homolysis of the relatively weak O–N linkage to give a diradical intermediate which recloses to generate the aziridine ring.[44] The subsequent conversion of the transient aziridine to the pyrrole could then proceed by a mechanism similar to the one outlined above. In an attempt to ascertain the plausibility of this scheme, we have investigated the thermal behavior of 2-*tert*-butyl-3-methyl-5-phenyl-4-isoxazoline (**20**). This compound was conveniently prepared by reacting *N-tert*-butyl-α-methylnitrone with phenylacetylene.



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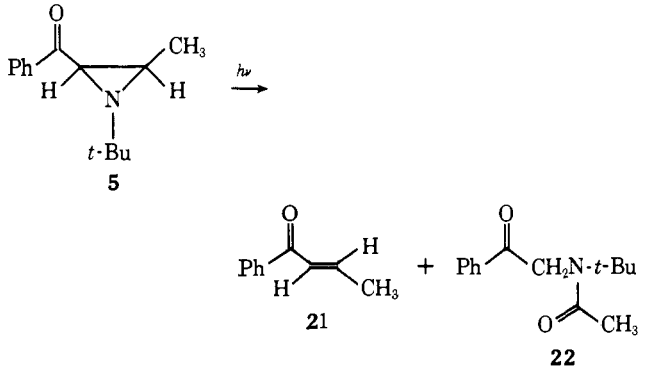
Thermolysis of **20** at 120° in methanol for 1 hr gave *N-tert*-butyl-3-phenylpyrrole (**7**) in good yield. Most importantly, NMR studies of the reaction clearly showed the presence of (ca. 10%) *cis-N-tert*-butyl-2-benzoyl-3-methylaziridine (**5**) during the early stages of the thermolysis. Consideration of the product distribution as a function of time in a number of experiments showed that as isoxazoline **20** disappeared, *cis*-aziridine **5** first appeared and was then converted into pyrrole **7**. This observation provides strong support for the mechanism previously suggested for the thermal rearrangements of 4-isoxazolines.[44]

As part of our inquiries dealing with the chemistry of methylbenzoylaziridines, we decided to investigate the chemical response of these systems to ultraviolet irradiation. In previous studies we had found that the nature and position of substituents about the aziridine ring produced markedly different photochemical results.[45,46] For example, in order to account for the products obtained from the irradiation of *trans-N*-benzyl-2-phenyl-3-benzoylaziridine, we proposed that the reaction proceeds by intramolecular hydrogen transfer from carbon to the p_y orbital of oxygen of the n–π^* state.[45] The course of the overall photoreaction was noted to be drastically altered for the corresponding cis isomer. We previously suggested that the excited state of the *cis*-aziridine undergoes hydrogen abstraction followed by homolytic cleavage to give a radical which can lead to the observed products by a succession of hydrogen abstraction and photoelimination reactions.[45]

Because such strikingly different photobehavior was observed with a set of stereoisomeric aziridinyl ketones, an investigation of the photochemistry of *cis*- and *trans-N-tert*-butyl-2-benzoyl-3-methylaziridines (**5** and **6**) seemed desirable. Our expectation was that the cis isomer would undergo a 1,5-hydrogen transfer to produce *N-tert*-butyl-3-phenylpyrrole (**7**) on electronic excitation but that the trans isomer (**6**) would not. Irradiation of *cis*-aziridine **5** was



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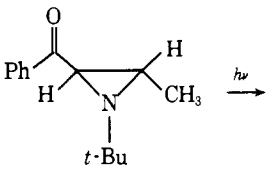
22

found to give 1-phenyl-2-buten-1-one (**21**, 27%) and *N*-acetyl-*N*-phenacyl-*tert*-butylamine (**22**, 16%) as the two major components of a rather complex reaction mixture. No detectable quantities of pyrrole **7** were observed in the crude photolysate. Photolysis of the corresponding trans isomer **6** afforded **21** (37%) and 3-*tert*-butylamino-1-phenyl-2-buten-1-one (**23**, 16%) as the major photoproducts. Again,



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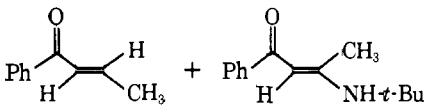

21 **23**

no pyrrole **7** was found in the reaction mixture. The absence of pyrrole **7** indicates that these aziridines do not undergo disrotatory photochemical ring opening to give azomethine ylides. The formation of **23** from the irradiation of *trans*-aziridine **6** finds analogy in earlier work on related aziridines[46] and may very well proceed by transfer of an electron from nitrogen to the excited n-π^* state followed by a 1,5-proton shift.[46] The mechanism by which these aziridines are converted to 1-phenyl-2-buten-1-one (**21**) is not known and further work must be done before this path can be established.[47] It would appear that the photochemistry of these aziridines is more complicated than the previously studied cases. Further work on the excited state behavior of these systems is in progress and will be reported at a later date.

Experimental Section

All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with a Varian Associates high-resolution spectrometer and at 100 MHz using a Jeol-MH-100 spectrometer.

Preparation of *cis*- and *trans*-1-*tert*-Butyl-2-benzoyl-3-methylaziridine (5 and 6). A solution containing 4.0 g of α-bromoethylideneacetophenone and 8.0 ml of *tert*-butylamine in 10 ml of benzene was stirred at room temperature for 3 days. At the end of this time, 3 ml of anhydrous ether was added and the precipitated *tert*-butylamine hydrobromide salt was removed by filtration. The solvent was removed under reduced pressure and the oily residue was dissolved in pentane. Cooling the solution to −78° afforded 220 mg of *trans*-1-*tert*-butyl-2-benzoyl-3-methylaziridine (**6**). Recrystallization of **6** from pentane gave colorless crystals: mp 48–49°; ir (KBr) 3.40, 5.96, 6.23, 6.92, 7.10, 7.35, 7.90, 8.20, 10.00, 11.12, 13.30, 14.50 μ; NMR ($CDCl_3$) δ 1.20 (s, 9 H), 1.42 (d, 3 H, J = 6.0 Hz), 2.64–2.88 (m, 1 H), 3.16 (d, 1 H, J = 3.0 Hz), 7.2–8.14 (m, 5 H); uv (methanol) λ_{max} 247 nm (ϵ 13,500); *m/e* 217 (M^+), 199, 160, 146, 143 (base), 115, 105, and 77.

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.40; H, 8.92; N, 6.38.

The corresponding cis isomer **5** was obtained by removing the solvent from the above mother liquors and dissolving the oily residue in 100 ml of methanol which contained 240 mg of sodium methoxide. The above solution was stirred at room temperature for 7 hr. After this time the solvent was removed under reduced pressure and the residue was dissolved in ether and washed with water. The ethereal layer was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Thick layer chromatography of the residue (1:1 pentane-ether) gave 1.8 g (46%) of a crystalline solid **5**: mp 40–41°; ir (neat) 3.40, 5.91, 6.25, 7.10, 7.25, 7.35, 8.20, 8.60, 9.50, 9.90, 10.70, 11.10, 11.73, 12.01, 13.70, and 14.42 μ; NMR ($CDCl_3$) δ 1.04 (s, 9 H), 1.12 (d, 3 H, 6.0 Hz), 2.22–2.48 (m, 1 H), 3.12 (d, 1 H, J = 7.0 Hz), and 7.36–8.10 (m, 5 H); uv (methanol) 245 nm (ϵ 1700); *m/e* 217 (M^+), 199, 160, 146, 143 (base), 115, 105, and 77.

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.06; H, 8.80; N, 6.20.

Thermolysis of *cis*- and *trans*-1-*tert*-Butyl-2-benzoyl-3-methylaziridine. A solution containing 140 mg of *cis*- or *trans*-aziridine (**5** or 6) in 25 ml of methanol was heated in a sealed tube at 120° for 3 hr. After removal of the solvent, the crude oil was chromatographed on a thick layer plate using a 1:1 pentane–ether mixture as the eluent. The major component amounted to 110 mg (80%) of a clear oil, whose structure is assigned as *N*-*tert*-butyl-3-phenylpyrrole (**7**): ir (neat) 3.30, 6.24, 6.70, 7.30, 7.43, 8.12, 8.70, 9.12, 10.20, 10.80, 13.30, and 14.40 μ; NMR ($CDCl_3$) δ (s, 9 H), triplets at 6.31 (1 H, J = 2.0 Hz), 6.62 (1 H, J = 2.0 Hz), and 6.90 (1 H, J = 2.0 Hz), and a multiplet centered at 7.20 (5 H); uv (methanol) 256 nm (ϵ 9700); *m/e* 199 (M^+), 144, 143 (base), 116, 115, 57, and 41. This material was identical in all respects to an authentic sample of *N*-*tert*-butyl-3-phenylpyrrole (**7**).[33]

Preparation and Thermolysis of *cis*- and *trans*-*N*-*tert*-Butyl-2-benzoyl-3-methylaziridine-*3-methyl-d*$_3$. A mixture containing 1.5 ml of 1-phenyl-2-buten-1-one, 1.5 ml of deuterium oxide, a catalytic quantity of sodium deuteroxide, and 9 ml of dioxane was heated at 140° for 24 hr. The mixture was then cooled, dried over magnesium sulfate, and subjected to the above procedue for another exchange. After the third exchange, the solvent was removed under reduced pressure and the residue was distilled at 65–75° (0.05 mm). The NMR spectrum of the distillate indicated that the methyl protons had been exchanged by deuterium to ca. 98%. The above deuterated ketone was brominated with bromine in carbon tetrachloride and subsequently dehydrobrominated with triethylamine in benzene to give deuterated α-bromoethylideneacetophenone. This enone was converted to the deuterated aziridines by the method described above. NMR and mass spectral analysis of the aziridines indicated that both isomers contained at least 75% deuterium in the methyl group (i.e., CD_3, 75%; CHD_2, 16%; CH_2D, 5%.

A solution containing 75 mg of the *cis*- and/or *trans*-aziridine in 2 ml of methanol was heated in a sealed tube at 125° for 3 hr. Removal of the solvent under reduced pressure gave an oily residue which mainly contained *N*-*tert*-butyl-3-phenylpyrrole. Mass spectral and NMR analysis of the purified pyrrole showed that it contained less than 1% of deuterium.

1,3-Dipolar Cycloaddition of *N*-*tert*-Butyl-2-benzoyl-3-methylaziridine with Dimethyl Acetylenedicarboxylate. A 500-mg sample of *cis*-*N*-*tert*-butyl-2-benzoyl-3-methylaziridine (**5**) was dissolved in 2 ml of chloroform containing 3.25 g of dimethyl acetylenedicarboxylate and the resulting solution was heated at 120° in a sealed tube for 1 hr. The solvent and excess dimethyl acetylenedicarboxylate were removed under reduced pressure and the residue was chromatographed on a silica gel column (80 g) using chloroform–ethyl acetate (9:1) as the eluent. The major band isolated from the column contained 302 mg of a white solid, mp 129–130°. The structure of this material was identified as *N*-*tert*-butyl-2-benzoyl-3,4-dicarbomethoxy-5-methyl-2,5-dihydropyrrole (**17**) on the basis of the following physical and chemical data: ir (KBr) 5.77, 5.90, 6.34, 7.60, 7.95, 8.15, 8.78, 10.55, 11.44, 13.20, and 14.50 μ; uv (methanol) 247 (ϵ 17,000) and 309 nm (ϵ 16,800); NMR δ 1.07 (3 H, d, J = 6 Hz), 1.39 (9 H, s), 3.50 (3 H, s), 3.60 (3 H, s), 4.98 (1 H, q, J = 6 Hz), 7.40 (1 H, s), 7.2–7.8 (5 H, m).

Anal. Calcd for $C_{20}H_{25}NO_5$: C, 66.83; H, 7.01; N, 3.90. Found: C, 66.67; H, 6.84; N, 3.84.

The structure of dihydropyrrole **17** was further confirmed by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to the corresponding pyrrole. A mixture of 60 mg of **17** and 40 mg of DDQ in 5 ml of benzene was allowed to reflux for 5 hr. The solvent was removed under reduced pressure and the dark residue was passed through a small neutral alumina column using benzene–chloroform (1:1) as the eluent to give a 2:1 mixture of two components. This mixture was subjected to preparative thick layer chromatography. The plate was developed with a 93% benzene–7% ethyl acetate solution. The upper band contained 20 mg of a white solid, mp 161–162°, whose structure was assigned as *N*-*tert*-butyl-

2-benzoyl-3,4-dicarbomethoxy-5-methylpyrrole (**18**) on the basis of the following data: ir (KBr) 3.40, 5.82, 5.89, 6.03, 6.70, 6.90, 7.59, 7.90, 8.10, 8.54, 9.20, 11.00, 11.60, 12.13, 12.35, 12.70, 12.85, 13.57, and 13.90 μ; uv (methanol) 211 (ϵ 26,600) and 251 nm (ϵ 19,700); NMR ($CDCl_3$) δ 1.62 (9 H, s), 2.67 (3 H, s), 3.30 (3 H, s), 3.77 (3 H, s), 7.2-8.0 (5 H, m).

Anal. Calcd for $C_{20}H_{23}NO_5$: C, 67.21; H, 6.49; N, 3.92. Found: C, 67.20; H, 6.48; N, 3.91.

The second component isolated from the thick layer plate (40 mg) was identified as *N-tert*-butyl-2-methyl-3,4-dicarbomethoxypyrrole (**19**), mp 97-98°, on the basis of the following evidence: ir (KBr) 3.39, 5.87, 6.55, 6.92, 7.80, 8.30, 8.55, 9.10, 9.42, and 12.98 μ; uv (methanol) 212 (ϵ 17,300) and 260 nm (ϵ 8100); NMR ($CDCl_3$) δ 1.60 (9 H, s), 2.54 (3 H, s), 3.76 (3 H, s), 3.82 (3 H, s), and 7.30 (H, s); *m/e* 253 (M^+), 222, 221, 166, 165 (base), 134, 107, and 57.

Anal. Calcd for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.64; H, 7.36; N, 5.55.

Irradiation of *cis*-*N*-*tert*-Butyl-2-benzoyl-3-methylaziridine. A solution of 150 mg of *cis*-aziridine **5** in 150 ml of methanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia Type L, 450 W) with a Pyrex filter for 45 min. Concentration of the solution left an oily residue which was subjected to thick layer chromatography using a benzene-chloroform-ether (3:3:2) mixture as the eluent. The first band (R_f 0.70) contained 28 mg (27%) of 1-phenyl-2-buten-1-one. The structure of this material was verified by comparison with an authentic sample. The second band from the thick layer plate (R_f 0.50) was unreacted starting material (37 mg). The slowest moving component (R_f 0.25) was a crystalline solid (26 mg, 16%), mp 88-89°, whose structure was assigned as *N*-acetyl-*N*-phenacyl-*tert*-butylamine (**22**) on the basis of the following data: ir (KBr) 3.35, 5.89, 6.07, 7.12, 8.14, 8.32, 10.10, 13.22, 14.00, and 14.50 μ; *m/e* 233 (M^+); NMR ($CDCl_3$) δ 1.43 (9 H, s), 1.98 (3 H, s), 4.79 (2 H, s), and 7.4-8.1 (5 H, m).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.86; H, 8.18; N, 6.00.

Structure **22** was further confirmed by an unequivocal synthesis. A solution containing 1.3 g of *tert*-butylamine in 5 ml of ether was added to an ice-cooled solution of α-bromoacetophenone (1.3 g) in 5 ml of ether. The resulting mixture was stirred at room temperature for 3 hr. After this time the mixture was acidified with dilute hydrochloric acid and was subsequently extracted with water. The acidic layer was separated from the organic solvent and was then made alkaline by treatment with aqueous sodium hydroxide. This aqueous layer was then extracted with ether and the ethereal solution was dried over magnesium sulfate. Evaporation of the solvent left a semisolid which was taken up in 20 ml of pentane. A 1.5-g sample of acetic anhydride was added to the above solution and the mixture was allowed to stir at room temperature for 3 hr. The solution was then washed with a 10% hydrochloric acid solution followed by a 10% sodium hydroxide solution and was then dried over magnesium sulfate. Removal of the solvent left an oily residue which was chromatographed on a silica gel column (30 g) using a benzene-chloroform-ether (3:3:2) mixture as the eluent. The second fraction contained 250 mg of *N*-acetyl-*N*-phenacyl-*tert*-butylamine (**22**), mp 88-89°. The infrared and NMR spectra of this material were identical in all respects with those of a sample of **22** obtained from the irradiation of cis aziridine **5**.

Irradiation of *trans*-*N*-*tert*-Butyl-2-benzoyl-3-methylaziridine. A solution of 100 mg of *trans*-aziridine **6** in 150 ml of methanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia Type L, 450 W) with a Pyrex filter for 5 hr. Removal of the solvent left a dark brown residue which was subjected to thick layer chromatography using a benzene-chloroform-ether (3:3:2) mixture as the eluent. The upper band (R_f 0.7) contained 25 mg (37%) of 1-phenyl-2-buten-1-one (**21**). The second major band contained 56 mg (16%) of a clear oil which was distilled at 115-117° (0.05 mm). The structure of this compound was assigned as 3-*tert*-butylamino-1-phenyl-2-buten-1-one (**23**) on the basis of its characteristic ir and NMR spectra: ir (neat) 3.34, 6.20, 7.50, 8.08, 8.35, 9.12, 9.34, 9.70, 11.50, and 13.60 μ; NMR ($CDCl_3$) δ 1.36 (9 H, s), 2.20 (3 H, s), 5.57 (1 H, s), and 7.2-8.0 (5 H, m).

Thermolysis of *cis*- and *trans*-1-Cyclohexyl-2-methyl-3-(*p*-phenylbenzoyl)aziridine. *cis*- and *trans*-1-cyclohexyl-2-methyl-3-(*p*-phenylbenzoyl)aziridine (**13** and **14**) were prepared according to the procedure of Cromwell and Mohrbacher.[48] Fractional crystallization of the crude mixture from pentane afforded the individual isomers (i.e., *cis*-**13**, mp 127-128°, and *trans*-**14**, mp 141-142°). A solution containing 100 mg of the cis or trans isomer (**13** or **14**) in 25 ml of methanol was heated at 165° for 30 min. The solvent was removed under reduced pressure and the residue was subjected to thick layer chromatography using a 10% ethyl acetate-benzene mixture as the eluent. The fastest moving band amounted to 67 mg (66%) of *N*-cyclohexyl-3-biphenylpyrrole: mp 99-100°; ir (KBr) 6.20, 6.40, 6.70, 7.02, 8.23, 8.90, 9.20, 10.73, 11.80, 12.75, 13.12, and 14.40 μ; uv (methanol) 300 nm (ϵ 32,000); NMR ($CDCl_3$) δ 1.1-2.2 (m, 10 H), 3.6-3.92 (1 H, m) 6.52 (1 H, t, J = 20 Hz), 6.76 (1 H, t, J = 2.0 Hz), 7.08 (1 H, t, J = 2.0 Hz), 7.34-7.50 (2 H, d), 7.64 (m, 7 H); *m/e* 301 (M^+ and base), 219, 246, 191, 189, 165, and 55.

Anal. Calcd for $C_{22}H_{23}N$: C, 87.66; H, 7.69; N, 4.65. Found: C, 87.64; H, 7.73; N, 4.63.

Thermolysis of *cis*- and *trans*-*N*-*tert*-Butyl-2-methyl-3-(*p*-phenylbenzoyl)aziridine. The mixture of aziridines was prepared by a modification of the procedure of Cromwell and Mohrbacher.[48] To a suspension containing 1 g of α,β-dibromo-*p*-phenylbutyrophenone in 10 ml of dry benzene was added 15 ml of *tert*-butylamine. The suspension was allowed to stir at room temperature for 3 days. Anhydrous ether was then added to the reaction mixture so as to precipitate *tert*-butylamine hydrobromide. After removal of the hydrobromide salt by filtration, the residue was triturated with petroleum ether and the resulting solution was evaporated under reduced pressure to give 572 mg of a mixture of aziridines. Recrystallization of the mixture from hexane gave 266 mg of *cis*-1-*tert*-butyl-2-methyl-3-(*p*-phenylbenzoyl)aziridine (**11**) as a crystalline solid: mp 102-104°; ir (KBr) 5.93, 6.23, 7.33, 8.10, 9.43, 9.73, 9.92, 10.03, 11.05, 11.55, 12.60, 13.23, 13.33, 13.83, 14.33, and 14.43 μ; uv (methanol) 287 nm (ϵ 28,000); NMR ($CDCl_3$) δ 1.0-1.06 (s, 12 H), 2.15 (1 H, m), 2.90 (1 H, d, J = 6.0 Hz), 7.20-8.10 (m, 9 H); *m/e* 275, 260, 252, 220, 219, 191, 181, 153, 152, 86 (base), and 57.

Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.84; H, 7.84; N, 4.76.

All attempts to obtain a pure sample of the corresponding trans isomer (**12**) failed. This can be attributed to the ready isomerization of the trans isomer to the thermodynamically more stable *cis*-aziridine (**11**) on chromatography.

A solution containing 110 mg of *cis*-aziridine **11** in 25 ml of methanol was heated at 165° for 30 min. The solvent was removed under reduced pressure and the residue was recrystallized from ethanol to give 73 mg (71%) of *N*-*tert*-butyl-3-biphenylpyrrole: mp 95-97°; ir (KBr) 6.20, 6.40, 6.70, 7.30, 7.40, 8.03, 8.18, 8.65, 8.98, 9.13, 10.83, 11.98, 12.06, 12.83, 13.13, and 14.47 μ; uv (methanol) 298 nm (ϵ 29,800); NMR ($CDCl_3$) δ 1.38 (s, 9 H), three triplets at 6.44 (1 H, J = 2.5 Hz), 6.75 (1 H, J = 2.5 Hz), and 7.08 (1 H, J = 2.5 Hz), and a multiplet centered at 7.45 (9 H); *m/e* 275 (M^+), 260, 220, 219 (base), 217, 190, and 165. The structure of the pyrrole was further verified by comparison with an authentic sample.[33]

Since the pure *trans*-aziridine (**12**) was not available, a mixture enriched in this isomer (65% trans-35% cis) was heated in methanol at 165° for 30 min. The only product isolated (70%) was *N*-*tert*-butyl-3-biphenylpyrrole.

Preparation of *cis*- and *trans*-2-Benzoyl-1,3-dimethylaziridine (15 and 16). A solution containing 4.0 g of α-bromoethylideneacetophenone and 4.65 g of methylamine in 50 ml of benzene was stirred at 0° for 1 hr. The reaction mixture was then washed with a saturated sodium chloride solution and dried over magnesium sulfate. Removal of the solvent gave a clear oil which was recrystallized from pentane to give 1.93 g (62%) of *cis*-2-benzoyl-1,3-dimethylaziridine (**15**) as colorless crystals: mp 42-43°; ir (KBr) 3.35, 5.95, 6.25, 6.90, 7.18, 8.19, 8.50, 9.06, 11.20, 13.40, 14.40 μ; NMR ($CDCl_3$) δ 1.13 (3 H, d, J = 6.0 Hz), 1.8-2.3 (1 H, m), 2.51 (3 H, s), 2.90 (1 H, d, J = 8 Hz), 7.3-8.1 (5 H, m); uv (methanol) λ_{max} 247 nm (ϵ 15,000).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.25; H, 7.48; N, 7.98.

The corresponding trans isomer (**16**) was prepared by treating a solution containing 7.3 g of crotonophenone and 6.2 g of methylamine in 230 ml of a benzene-ether mixture (1:1) at −10° with 150 ml of benzene which contained 12.7 g of iodine. The resulting

solution was stirred at −10° for 5 hr. At the end of this time the reaction mixture was washed with water, dilute sodium thiosulfate, and finally with a saturated sodium chloride solution. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give an orange-red oil. Distillation of the oil at 75° (0.05 mm) gave 7.25 g of a clear yellow oil which proved to be a 1:6 mixture of *cis*- and *trans*-2-benzoyl-1,3-dimethylaziridine. Part of the mixture (3.0 g) was separated by scanning liquid-liquid partition chromatography.[45] The major peak contained 2 g of a clear oil which was distilled at 75° (0.05 mm) to give 1.73 g of pure *trans*-2-benzoyl-1,3-dimethylaziridine (**16**) as a clear oil: ir (neat) 3.36, 5.96, 6.24, 6.90, 8.19, 9.30, 9.85, 11.00, 11.88, 13.12, and 14.45 μ; uv (methanol) λ_{max} 248 nm (ϵ 13,800); NMR ($CDCl_3$) at 25°, δ 1.28 (1.5 H, d, J = 6 Hz), 1.41 (1.5 H, d, J = 6 Hz), 2.1–2.5 (1 H, m), 2.48 (1.5 H, s), 2.55 (1.5 H, s), 2.65 (0.5 H, d, J = 3.0 Hz), 3.20 (0.5 H, d, J = 3.0 Hz), 7.1–8.0 (5 H, m). The complexity of the NMR spectrum is due to the slow inversion rate of the *N*-methyl group on the NMR time scale. When the NMR tube containing the trans isomer (**16**) was heated to 85°, a new spectrum was obtained which showed peaks at δ 1.32 (3 H, d, J = 6 Hz), 2.51 (3 H, s), 2.4–3.3 (2 H, m), and 7.1–8.0 (5 H, m).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.51; H, 7.46; N, 7.70.

The cis and trans isomers could be interconverted by treating a solution containing 50 mg of the appropriate aziridine with 10 mg of sodium methoxide in 6 ml of methanol at 25° for 24 hr. The mixture was concentrated under reduced pressure and the residue was taken up in chloroform. The chloroform solution was washed with water and dried over magnesium sulfate. Removal of the solvent gave a clear oil which was shown to be a 4:1 mixture of *cis*- and *trans*-2-benzoyl-1,3-dimethylaziridine (**15** and **16**) by NMR analysis. The same ratio of isomers was obtained starting with either isomer.

Thermolysis of *cis*- and *trans*-2-Benzoyl-1,3-dimethylaziridine. A solution containing 100 mg of *cis*- or *trans*-aziridine (**15** or **16**) in 10 ml of methanol was heated in a sealed tube at 130° for 1 hr. After removal of the solvent the crude oil was chromatographed on a thick layer plate using a benzene–chloroform–ether mixture (15:15:10) as the eluent. The major component amounted to 56 mg (62%) of a low-melting solid, mp 44–45° (lit.[49] 43–44°), whose structure is assigned as *N*-methyl-3-phenylpyrrole on the basis of the following data: ir (KBr) 6.23, 7.34, 8.27, 9.20, 10.81, 12.65, 13.32, 14.47 μ; NMR ($CDCl_3$) δ 3.62 (3 H, s), 6.43 (1 H, t, J = 2 Hz), 6.62 (1 H, t, J = 2 Hz), 6.87 (1 H, t, J = 2 Hz), 7.0–7.6 (5 H, m); uv (methanol) 205, 233, and 279 nm (ϵ 25,400, sh, 13,200); *m/e* 157 (M^+, base), 142, 129, 128, 116, 115, and 89.

Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.95; H, 7.01; N, 8.85.

Preparation of 2-*tert*-Butyl-3-methyl-5-phenyl-4-isoxazoline (20). A 1.3-g sample of acetaldehyde in 5 ml of carbon tetrachloride was added to an ice-cooled solution of *tert*-butylhydroxylamine (1.78 g)[50] in 10 ml of carbon tetrachloride. The mixture was stirred at room temperature for 1 hr and was then dried over magnesium sulfate. Evaporation of the solvent left 2.3 g (100%) of *N*-*tert*-butyl-α-methylnitrone as a colorless oil: NMR ($CDCl_3$) δ 1.49 (9 H, s), 1.99 (3 H, d, J = 6 Hz), 6.95 (1 H, q, J = 6 Hz); ir (neat) 6.33 μ. A solution containing 2.3 g of the above nitrone and 2.4 g of phenylacetylene in 10 ml of benzene was heated at 70° for 42 hr. The solvent was removed under reduced pressure and the dark brown residue was chromatographed through a silica gel column (120 g) using a benzene–chloroform–ether (2:2:1) mixture as the eluent. The major component was a clear oil which was purified by distillation at 75–77° (0.05 mm) to give 1.05 g (24%) of 2-*tert*-butyl-3-methyl-5-phenyl-4-isoxazoline (**20**): ir (neat) 3.34, 6.00, 6.69, 6.90, 7.32, 8.20, 9.39, 9.72, 11.10, 12.95, 13.20, 13.70, and 14.53 μ; uv (methanol) 229 (ϵ 13,900), 245 (sh), 282 (ϵ 5750); NMR ($CDCl_3$) δ 1.16 (9 H, s), 1.29 (3 H, d, J = 7 Hz), 4.32 (1 H, dq, J = 7 and 3 Hz), 5.12 (1 H, d, J = 3 Hz), 7.1–7.6 (5 H, m); *m/e* 217 (M^+), 199, 143 (base), 116, 115, 105, and 102.

Thermal Rearrangement of 2-*tert*-Butyl-3-methyl-5-phenyl-4-isoxazoline. A solution containing 217 mg of 2-*tert*-butyl-3-methyl-5-phenyl-4-isoxazoline (**20**) in 5 ml of methanol was heated in a sealed tube at 120° for 1 hr. The NMR spectrum of the oil remaining after removal of the solvent clearly showed the presence of *cis*-*N*-*tert*-butyl-2-benzoyl-3-methylaziridine (**5**) (ca. 10%) as well as *N*-*tert*-butyl-3-phenylpyrrole (**7**) (45%). Pyrrole **7** was isolated in high purity by thick layer chromatography and was identical in all respects with an authentic sample.[33]

Kinetic Procedure. The following methods were used in determining the kinetics of the rearrangement of the substituted aziridinyl ketone to the N-alkyl substituted 3-phenylpyrrole. Solutions containing the aziridine (0.25–1.0 *M*) in distilled methanol were sealed in ampoules made from 8-mm Pyrex tubing, which were then placed in a large thermostated oil bath. At definite time intervals tubes were removed and immediately cooled in a Dry Ice–acetone bath. Another kinetic procedure that was also used involved heating a 0.25 *M* solution of the appropriate aziridine in a sealed NMR tube in the probe of a Jeol JNM-MH-100 nuclear magnetic resonance spectrometer. The desired temperature was maintained by a Jeol temperature controller which was accurate to ±0.5°. Similar kinetic values were obtained by both methods (i.e., within experimental error). The disappearance of the aziridine and the appearance of the pyrrole were followed simultaneously by NMR spectroscopy. The curves obtained were in good agreement with first-order kinetics through 5 half-lives. The observed rate constants are listed in Table I and were determined through the use of curve fitting program KINET and were found to be independent of the initial concentration over the range studied. At least three determinations were made at each temperature.

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Rearrangement during Thermal Decomposition of 3-Homoadamantyl Acetate[1]

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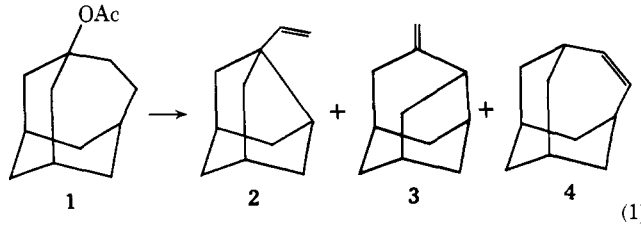
Abstract: Pyrolysis of 3-homoadamantyl acetate provided 3-vinylnoradamantane, 4-methyleneprotoadamantane, and 4-homoadamantene in the approximate ratio, 30:65:5. Reaction was performed at 470–600° with varying flow rates. Ozonolysis and hydrogenation were carried out with the major products. Addition of formic acid and acid-catalyzed polymerization involving 4-methyleneprotoadamantane apparently proceeded with rearrangement to the adamantyl nucleus. Thermolysis of 4,4-dideuterio-3-homoadamantyl acetate provided a primary deuterium isotope effect of 2.3, in addition to other mechanistic insight. Ester decomposition is believed to proceed via a six-membered cyclic transition state.

In connection with our interest[4,5] in the limits of Bredt's rule in caged tricyclic systems, we have investigated the decomposition of 3-homoadamantyl acetate (**1**). There has been considerable, recent activity aimed at the generation of bridgehead olefins.[6-9] Various techniques have been used to produce highly strained alkenes, including Hofmann elimination,[6] bisdehalogenation of vicinal dihalides,[7] rearrangement of bridgehead carbenes,[8] and perester thermolysis.[9c] However, we have found no reports[10] on the decomposition of bridgehead esters to give "anti-Bredt's rule" olefins.

Gas-phase pyrolysis of esters is generally used to introduce a double bond without isomerization. Rearrangement is not usually observed except in the absence of a β hydrogen or the presence of a cerain type of cyclic structure.[11] With the homoadamantyl system, it was anticipated that decomposition of **1** might take place with intermediate formation of bridgehead olefin or with concerted rearrangement.

Results and Discussion

Pyrolysis of 3-homoadamantyl acetate[12] (**1**) afforded 3-vinylnoradamantane (**2**), 4-methyleneprotoadamantane (**3**), and 4-homoadamantene (**4**) in combined yields of 30–60% (eq 1). The relatively low yield reflects, in part, losses from trapping and work-up with the small scale runs. It is pertinent that doubling the yield (30 → 60%) did not significantly alter the product composition. No more than very small amounts of a few other, unidentified products were present according to GLC. The olefins amounted to approximately 85% of the collected product, with the remainder consisting of material nonvolatile under GLC conditions. The ratio **3**:**2** varied in the range of 2–3:1 depending on flow rate at temperatures of 500–600°, while **4** comprised only a few percent of the product, decreasing with increasing temperature. The conditions entailed passage of the vapor (ca. 2 g) during 2 to 4 hr through a Vycor tube containing Vycor chips at 470–600° with nitrogen as the carrier gas. The flow rate of the nitrogen was approximately 3–9 l./min.



(1)

The structures of the olefins were determined by NMR, ir, mass spectral, and elemental analysis. In addition, comparison was made with authentic materials in the case of **3** and **4**. As an alternate route, the Wittig reaction was used to synthesize olefin **3** from ketone **5**. Treatment of the carbonyl compound with ylide, $Ph_3P^+CH_2^-$, afforded the desired alkene in only 10% yield.

Further verification was provided by chemical behavior. Olefins **2** and **3** were transformed by ozonolysis to the known ketone, 4-protoadamantanone[13] (**5**), and 3-noradam-