an acidic solution and the formation of methyl ethers is a result of an acid-catalyzed ring opening of the bicyclobutane.[26] This acid in the case of $[Rh(CO)_2Cl]_2$ can be formulated as arising from an anionic carbene complex[2] and the first spectroscopic evidence of the detection of this carbene complex in the bicyclobutane reaction solution has been presented.[27] For $PdCl_2(PhCN)_2$, the formation of methyl ethers is also the result of an acid-catalyzed ring opening, this acid resulting from the reaction of palladium π-allyl complexes with methanol.

(26) The acid-forming reaction of bicyclobutanes and other metals in alcohols has also been described. See (a) L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *J. Amer. Chem. Soc.*, **94**, 9222 (1972); (b) E. Muller, *Tetrahedron Lett.*, 1201, 1203 (1973).

(27) The possibility that a rhodium complex containing a methanol ligand which increases in acidity upon coordination with the bicyclobutane cannot be ruled out as a competing process. See ref 4 and 10.

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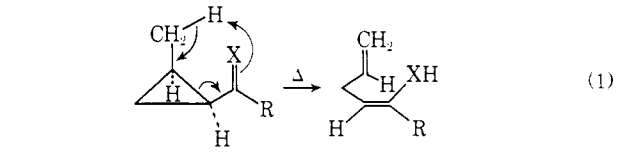
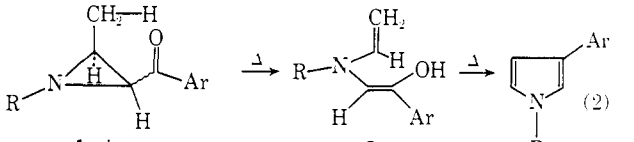
Mechanism and Stereochemical Control in the Thermal Rearrangement of Aziridinyl Ketones to Pyrroles

Sir:

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).[1-14] 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.[3-7] The lack of reaction of the corresponding trans isomer under more vigorous conditions and the low energy and large negative entropy of activation for the cis isomer constitute compelling support for the concertedness of the reaction.[3-7] We now wish to report that the thermal rearrangement of a related series of aziridinyl ketones (**1** and **2**) to *N*-alkyl-3-arylpyrroles[15] (**4**) (eq 2) differs dramatically from heretofore observed three-membered ring ene reactions, in that the trans isomer reacts at a faster rate than the corresponding cis form.



(1)



(2)

1, cis
2, trans
3
4

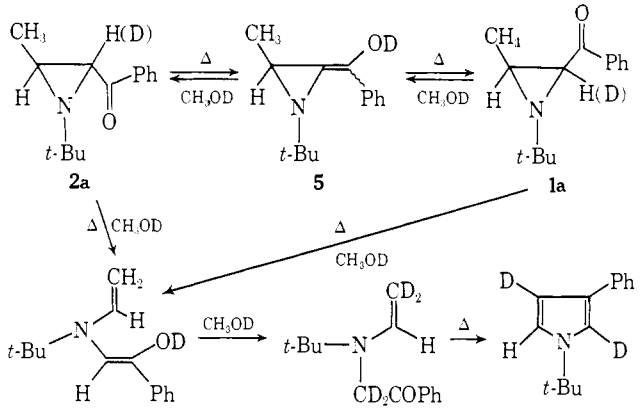
a, R = *t*-Bu; Ar = Ph
b, R = *t*-Bu; Ar = Biph
c, R = C_6H_{11}; Ar = Biph

Thermolysis of 140 mg of *cis*-aziridine **1a** in methanol at 120° for 3 hr afforded 110 mg (80%) of *N-tert*-butyl-3-phenylpyrrole (**4a**). This compound was identified by comparison with an authentic sample.[16] Similar reactions were observed with *trans*-aziridine **2a** as well as with aziridines **1b**,**2b** and **1c**,**2c**. The disappearance of *cis*-**1a** and the appearance of pyrrole **4a** in ethylene glycol was followed simultaneously by nmr spectroscopy. The reaction followed first-order kinetics, and rate constants were determined at three different temperatures constant to ±0.5°, 100 (k = 1.18×10^{-4} sec^{-1}), 110 (k = 3.23×10^{-4} sec^{-1}), and 120° (k = 1.05×10^{-3} sec^{-1}). An Arrhenius plot gives E_a = 28.6 ± 0.5 kcal/mol and log A = 12.8, from which values of $\Delta H^{\ddagger}$ = 27.7 kcal/mol and $\Delta S^{\ddagger}$ = −2.3 eu can be calculated. The reaction kinetics encountered with *trans*-aziridine **2a** were more complicated since the thermolysis of **2a** in methanol at 80° produced *cis*-aziridine **1a** as well as pyrrole **4a**. 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,[17] an analytical function was obtained for the concentration of the trans isomer.[18] The results indicate that *trans*-**2a** also proceeds on to pyrrole by a first-order rate process (*i.e.*, k_{2a} = 1.52×10^{-4} sec^{-1} (70°), k_{2a} = 4.54×10^{-4} sec^{-1} (80°), and k_{2a} = 2.16×10^{-3} sec^{-1} (90°), E_a = 26.4 ± 0.5 kcal/mol, and log A = 13.0). Extrapolation of the data for the cis isomer to 80° indicates that the *trans*-aziridine rearranges 39 times more rapidly than the corresponding cis isomer.

In order to help elucidate the mechanism for the *trans*- → *cis*-aziridine isomerization, we have studied the thermal rearrangement of both aziridines in deuteriomethanol at 77° for 15 hr. Recovered starting material (80%) from the *cis*-aziridine run was found to have incorporated one deuterium atom into the 3 position of the aziridine ring. The fact that addition of an excess of dimethyl fumarate to a solution of **1a** 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

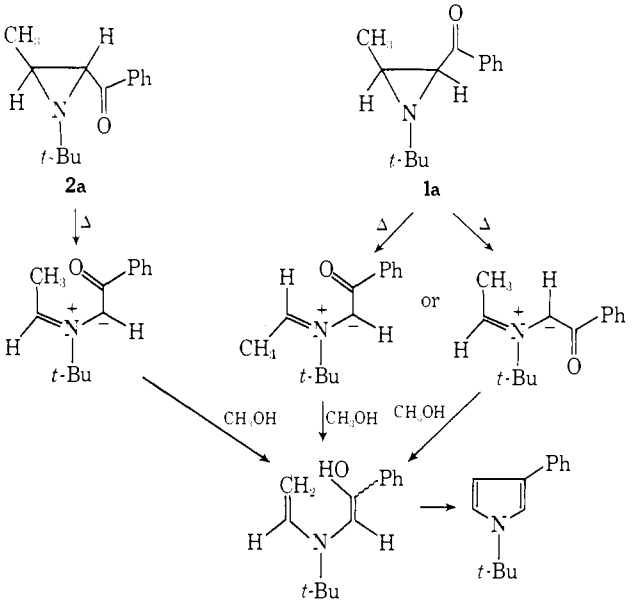
(1) K. von Auwers and O. Ungemach, *Justus Liebigs Ann. Chem.*, **511**, 152 (1934).
(2) D. S. Class, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963).
(3) D. E. McGreer, N. W. K. Chiu, and R. S. McDaniel, *ibid.*, 415 (1964); *Can. J. Chem.*, **46**, 2217 (1968).
(4) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1968).
(5) R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, **87**, 2281 (1965).
(6) R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *ibid.*, **89**, 1404 (1967).
(7) J. M. Watson, J. L. Irvine, and R. M. Roberts, *ibid.*, **95**, 3348 (1973).
(8) G. Ohloff, *Tetrahedron Lett.*, 3795 (1965).
(9) P. Scribe, M. R. Monot, and J. Wiemann, *ibid.*, 5157 (1967).
(10) W. Ando, *ibid.*, 929 (1969).
(11) M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968); **94**, 7469 (1972).
(12) E. J. Corey, H. Yamamoto, D. K. Herron, and K. Achiva, *ibid.*, **92**, 6635 (1970).
(13) D. V. Kashelikar and P. E. Fanta, *ibid.*, **82**, 4930 (1960).
(14) H. L. Wehrmeister, *J. Org. Chem.*, **30**, 664 (1965).
(15) The thermal conversion of several 4-isoxazolines into pyrroles has been postulated to involve aroylaziridines as transient intermediates; see A. K. Harada and H. Kano, *Tetrahedron Lett.*, 4875 (1969).
(16) A. Padwa, F. Albrecht, P. Singh, and E. Vega, *J. Amer. Chem. Soc.*, **93**, 2928 (1971).
(17) Appreciation is expressed to J. L. Dye of Michigan State University for a copy of the program KINET; see J. L. Dye and V. Nicely, *J. Chem. Educ.*, **48**, 433 (1971).
(18) With the lower temperature and short reaction times used for the thermolysis of *trans*-**2a**, the cis isomer did not appreciably rearrange to pyrrole **4a**.

ylides in the trans → cis isomerization.[19] Similar results were obtained with *trans*-aziridine **2a**, except that in this case the recovered aziridine was mostly the epimerized cis *3-d*$_1$ isomer. The most direct interpretation of the above data involves enol **5** as the reactive intermediate responsible for the epimerization.



It is 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.[21] A further experiment utilizing *cis-N-tert*-butyl-2-methyl-3-benzoylaziridine-*2-methyl-d*$_3$[22] (**6**) and methanol confirmed this intermolecular hydrogen exchange. No detectable deuterium was found in the final product **4a** when deuterated *cis*-aziridine **6** was heated at 120° in methanol for 2.5 hr. These observations may be explained in terms of a rapid intermolecular exchange of the vinyl hydrogens of enamine **3** with the solvent prior to cyclization. It should also be pointed out that recovered *cis*-aziridine **1a** did not incorporate deuterium into the methyl group when **1a** was heated in deuteriomethanol.[23] The lack of deuterium incorporation on the methyl group also argues against the "enolene" mechanism[5-7] for rearrangement of these aziridines. Also noteworthy is the absence of a primary deuterium isotope effect on the rate of rearrangement of *cis*-aziridine **6**.

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 that aziridines readily undergo thermal cleavage to azomethine ylides by conrotation of the substituent groups.[20] The higher energy requirement for rearrangement of the cis isomer 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 the presence of a potent dipolarophile, it would appear that the initially formed azomethine ylides have very short lifetimes and undergo rapid exchange with the protic solvent.



The difference in the thermal behavior observed with these aziridines and those studied previously[20,24] can be attributed to the availability of a proton β to the nitrogen atom which can be lost to form an enamine. Further work on the thermal and photochemical behavior of these systems is in progress and will be reported at a later date.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-37550). The National Science Foundation also provided financial assistance in the purchase of the nmr spectrometer used in this research.

(19) Since azomethine ylides can be readily trapped in the presence of dipolarophiles,[20] one would anticipate a marked diminution in the yield of pyrrole if an azomethine ylide were involved in the trans → cis isomerization.

(20) R. Huisgen and H. Mader, *J. Amer. Chem. Soc.*, **93**, 1777 (1971).

(21) A control experiment indicated that pyrrole **4a** only incorporates deuterium into the 2 position of the ring under these conditions.

(22) Crotonophenone-d_3 was obtained by exchanging the methyl protons with sodium hydroxide, D_2O, and dioxane at 80°. The deuterated ketone was subsequently converted to aziridine **6**.

(23) Similar results were obtained upon heating *cis*-aziridine **6** in methanol. The recovered ketone did not exchange hydrogen for deuterium.

(24) A. Padwa and W. Eisenhardt, *J. Org. Chem.*, **35**, 2472 (1970).

(25) Alfred P. Sloan Foundation Fellow, 1968–1972; NATO Senior Postdoctoral Fellow, 1973.

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Restricted Rotation Involving the Tetrahedral Carbon. V. Direct Observation of the Hindered Rotation of a Methyl Group by High Resolution Nuclear Magnetic Resonance Spectroscopy[1]

Sir:

We wish to report an observation of splitting of a methyl signal in high resolution proton nmr spectroscopy. Since the barrier to rotation of the methyl group is rather low,[2] the rotation of methyl groups has gen-

(1) H. Nakanishi, O. Yamamoto, M. Nakamura, and M. Ōki, *Tetrahedron Lett.*, 727 (1973).

(2) The barrier to rotation of the methyl group in 2,2-dimethylpropane, which is one of a typical example of high barrier, is reported to be 4.3 kcal/mol from far-infrared studies (J. R. During, *et al.*, *J. Chem. Phys.*, **52**, 2046 (1970)), whereas Allinger, *et al.*, calculated the barrier to be 4.64 kcal/mol (*J. Amer. Chem. Soc.*, **90**, 1199 (1968)).