β-Lactam of Dimethylketene and Benzophenone Anil. To a solution of 0.90 g of triethylamine (0.089 mole) and 2.0 g of benzophenone anil[23] (0.078 mole) in 45 ml of benzene was added, at reflux temperature, and under an argon atmosphere, 0.85 g of isobutyryl chloride (0.080 mole) in 20 ml of benzene. The mixture was stirred and refluxed for an additional 4.0 hr and cooled to room temperature, and the precipitated triethylammonium chloride was filtered off. The filtrate was concentrated *in vacuo* to an oil which was crystallized from ether–petroleum ether to give 1.2 g of a solid, mp 91–104°. Several recrystallizations from ether–petroleum ether raised the melting point to 122–124°. The infrared spectrum of this material was different, in the same solvent, from that of the α-adduct of benzophenone and dimethyl-N-(phenyl)ketenimine: characteristic infraredb and at 1745 cm^{-1} (dichloromethane); mass spectrometric molecular weight: 327.164316; theoretical for $C_{23}H_{21}NO$: 327.162306.

Relative Rates, Quantum Yields, and Quenching Experiments. All quantitative measurements were made on a rotating assembly with a central light source. Samples in 13-mm Pyrex ampoules were placed in holders on the assembly 5.5 cm from a 450-w Hanovia lamp, No, 679A-36, maintained in a water-jacketed, Pyrex immersion well. Corning 2 × 2 in. filters of the types indicated in the text were mounted in four filter holders flush against the well. The rest of the well was taped to eliminate stray light. All studies were made at room temperature. Samples in 13-mm, Pyrex test tubes were degassed to 5×10^{-3} mm in two freeze–thaw cycles and then sealed. In experiments where naphthalene filters were used, the samples were prepared in 7-mm Pyrex test tubes which, after degassing and sealing, were positioned with a cork in 13-mm Pyrex test tubes partly filled with a 1.0 *M* naphthalene in cyclohexane solution. The "tube within a tube" arrangement was then placed in the rotating assembly. Benzophenone–benzhydrol actinometry[14a] was used for quantum yield determinations. In the quantum yield experiments for ketenimines **5**, **6**, and **9** (Figure 4) actinometry was accomplished with solutions of 0.10 *M* benzophenone and 0.10 *M* benzhydrol in benzene. An actinometer quantum yield of 0.66 was used.[14a] In the quantum yield determinations for the benzophenone–ketenimine **5** reaction in the presence of 0.10 *M* naphthalene, actinometer tubes containing 0.10 *M* benzophenone and 1.0 *M* benzhydrol in benzene were used with a quantum yield of 0.97[14a] (Figure 6).

Mass Spectrometric Analyses.[24] All mass spectra were taken on an AEI MS-9 spectrometer at an ionizing voltage of 70 ev and a probe temperature of *ca.* 150°.

Ultraviolet Spectral Analysis of Benzophenone–Ketenimine 5 Solution. The ultraviolet spectrum of a solution of 0.05 *M* benzophenone and 0.50 *M* dimethyl-N-(cyclohexyl)ketenimine in benzene was recorded on a Cary 14 spectrometer using 1-mm cells and was identical with the additive spectrum of the individual solutions from 340 to 400 mμ.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for a grant (197-G) in support of this work and the National Science Foundation for funds used in the purchase of the AEI MS-9 spectrometer. Professor Paul D. Bartlett is thanked for his generosity and understanding while L. A. S. was a postdoctoral candidate in his laboratory from 1962 to 1964 when some of this work was initiated.

(23) G. Reddelien, *Ber.*, **48**, 1469 (1915).

(24) We wish to thank Mr. Bill Klymus for technical assistance in running the mass spectra.

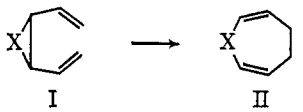
The Valence Isomerization of 1,2-Divinylaziridines. Synthetic and Kinetic Studies[1,2]

Eugene L. Stogryn and Stanley J. Brois

Contribution from the Esso Research and Engineering Company, Linden, New Jersey 07036. *Received September 29, 1966*

Abstract: The 1,2-divinylaziridine IV has been prepared by the low-temperature addition of hexafluoro-2-butyne to 2-vinylaziridine. Rate measurements of 1,2-divinylaziridine IV valence isomerization to the azepine V gives the kinetic expression $k_1 = 10^{12} \exp(-16{,}500/RT)$. It was established that the rate of the valence isomerization process is far less than that for inversion about the ring nitrogen. The low-temperature addition of hexafluoro-2-butyne to *trans*-2,3-divinylaziridine has yielded 1,2,3-trivinylaziridine VIII. The latter aziridine was shown to isomerize to the corresponding azepine IX at the same rate as the divinylaziridine IV.

Recent valence isomerization studies of *cis*-divinyl, three-membered rings have indicated that the thermal requirements for the transformation I → II is dependent upon the nature of the ring.



I II

X=C, N, O, S

The temperature necessary to induce ring expansion of I increases in the order: carbon,[3,4] nitrogen,[1] oxygen,[5] sulfur.[1] The fact that the above sequence also corresponds to increasing ring stability[6] suggests that the relief of ring strain plays an important role in the valence isomerization process. Consonant with this idea is the finding that *cis*-2,3-divinylaziridine requires a significantly lower isomerization temperature relative to the 60° reported[5] for *cis*-divinyloxirane and the 100° observed for *cis*-divinylthiirane.

The difficulty in assigning the isomerization temperature to the nitrogen analog lies in the limitations of the

(1) Paper II in this series: E. L. Stogryn and S. J. Brois, *J. Org. Chem.*, **30**, 88 (1965).

(2) Presented in part before the Division of Organic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(3) E. Vogel, K. H. Oh, and K. Gajek, *Ann.*, **644**, 172 (1961).

(4) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(5) E. L. Stogryn, M. H. Gianni, and A. J. Passanate, *J. Org. Chem.*, **29**, 1275 (1964).

(6) (a) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Am. Chem. Soc.*, **86**, 4628 (1964); (b) R. A. Nelson and R. S. Jessup, *J. Res. Natl. Bur. Std.*, **48**, 206 (1952).

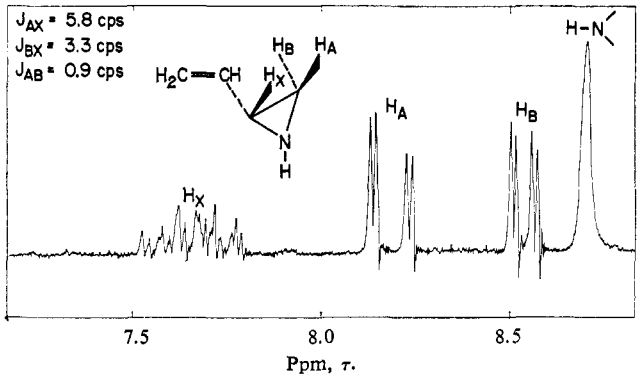


Figure 1. The nmr spectrum of the ring protons of 2-vinylaziridine as a 50% CCl_4 solution.

known synthetic methods for preparing divinylaziridines. With the synthetic methods currently available, valence isomerization appears to be synchronous with aziridine ring formation. For example, the addition of carbethoxynitrene to benzene is reported[7,8] to yield N-carbethoxyazepine exclusively. Ring closure of *threo*-3-ethylamino-4-hydroxy-1,5-hexadiene sulfate ester with base gave only N-ethyl-4,5-dihydroazepine.[1] In both instances the divinylaziridines were not detected. The intermediacy of the three-membered ring could only be inferred from mechanistic considerations.

The purpose of the present study was to prepare and isolate a divinylaziridine and determine the thermodynamic parameters for the thermal reorganization process.

Results and Discussion

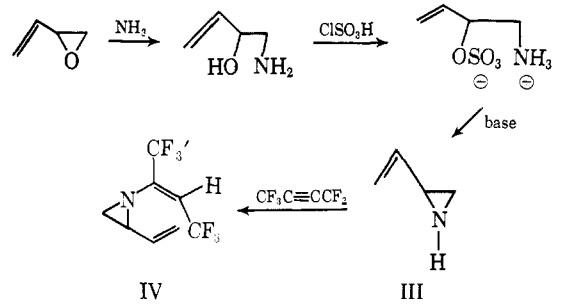
The successive placement of vinyl groups on the aziridine ring has led to isolable 1,2-divinylaziridines capable of undergoing a Cope rearrangement. These aziridines possess sufficient stability so that the thermodynamic parameters defining their isomerization to the valence isomeric azepines could be assessed.

The first vinyl group was readily introduced into the ring *via* modification of the Wenker aziridine synthesis. Attachment of a second vinyl group, however, required a very mild vinylation method. The low-temperature N-vinylation[9,10] of aziridines by activated acetylenes appeared to uniquely fulfill this requirement. Accordingly, the synthetic approach we devised to prepare the 1,2-divinylaziridine system for our study is depicted in Scheme I.

The ammonolysis of butadiene monoxide gave 1-amino-3-buten-2-ol.[11] Treatment of the amino alcohol with chlorosulfonic acid afforded the corresponding sulfate ester in quantitative yield. Ring closure was effected by the addition of an aqueous solution of the sulfate ester to a hot aqueous sodium hydroxide solution and isolating the 2-vinylaziridine by distillation. The 2-vinylaziridine was obtained as a colorless liquid, bp 97–99°, in 49% yield.

(7) K. Hafner and C. Konig, *Angew. Chem. Intern. Ed. Engl.*, 2, 96 (1963).
(8) W. Lwowski, T. J. Marieich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, 85, 1200 (1963).
(9) J. E. Dolfini, *J. Org. Chem.*, 30, 1298 (1965).
(10) E. Winterfeldt and H. Preuss, *Chem. Ber.*, 99, 450 (1966).
(11) M. G. Ettlinger, *J. Am. Chem. Soc.*, 72, 4792 (1950).

Scheme I



IV III

The nmr spectrum of 2-vinylaziridine showed a complex vinyl multiplet at τ 4.5–5.13. The well-defined ring proton spectrum is illustrated in Figure 1.

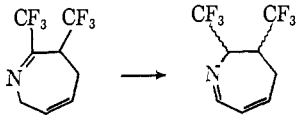
The J_{vic} and J_{gem} values for the ring protons in 2-vinylaziridine are in excellent agreement with those reported for 2-phenylaziridine (styrenimine).[12] It is noteworthy that the magnetically anisotropic 2-vinyl and 2-phenyl groups in aziridines exert a shielding effect on ring protons *cis* to these groups.

When hexafluoro-2-butyne was added to a Freon 11 solution of 2-vinylaziridine at −76°, a quantitative yield of a single product was obtained after the homogeneous reaction mixture was allowed to stir at 25° overnight. The infrared spectrum of the adduct did not exhibit terminal vinyl, enamine, or aziridine ring absorption bands. The conspicuous absence of the N–H stretching frequency in the infrared indicated that N-vinylation of the aziridine had occurred. The proton and fluorine nmr spectra revealed that the material isolated was not the 1,2-divinylaziridine (IV), but rather the valence isomeric azepine V. The ^1H spectrum of the neat azepine disclosed a condensed triplet (H_5 and H_6), a broad singlet (H_7), a nonet (H_3) with J_{CF_3-H} = 9.6 cps, and a condensed pentuplet (H_4), which were centered at τ 4.38, 5.32, 6.26 and 7.42, respectively. The relative intensities of the resonance signals were in accord with theory.

The ^{19}F spectrum of V[13] (neat) was measured at 56.4 Mc/sec and chemical shifts were measured in ppm from CCl_3F, internal reference. The spectrum of V showed two signals at +63.8 and +73.1 ppm. The doublet (J_{CF_3-H} = 9.6 cps) at low-field strength is assigned to the fluorines of the CF_3 group. Interestingly, the high-field signal arises from CF_3' attached to the trigonal carbon of the azepine V. Further resolution shows long-range coupling ($J_{CF_3-CF_3}$ = 5 cps) between the fluorines of the trifluoromethyl groups.

It appears that the expected divinylaziridine formed, but under the experimental conditions IV isomerized to the azepine.

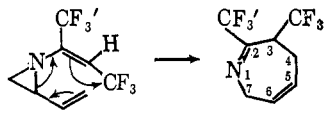
(12) S. J. Brois, *J. Org. Chem.*, 27, 3532 (1962).
(13) The ^{19}F nmr spectrum of V after 24 hr at 25° showed that approximately 30% of the unconjugated azepine was converted to its conjugated isomer Va *via* prototropy. The CF_3 resonance signals exhibited by Va



V Va

appeared as identical multiplets (five lines resolved) of equal intensity (J_{CF_3-H} = 9.5 cps) at +67.0 and +71.6 ppm relative to CCl_3F internal reference.

While the magnitude of $J_{CF_3-CF_3}$ (~5 cps) suggests that the trifluoromethyl groups are in close spatial proximity, the assignment of the stereochemistry of these groups must await further study.



IV V

Clearly then, the 1,2-divinylaziridine IV possesses the requisite electronic and geometrical features necessary for valence isomerization.

Aziridine Formation. When the adduction temperature was maintained at −76° and the product work-up effected at low temperature, the aziridine IV was isolable in better than 90% yield.

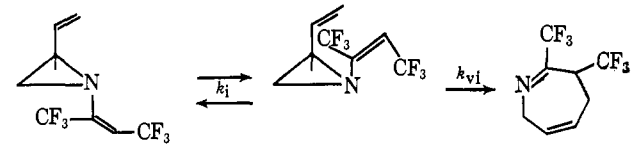
The infrared spectrum of IV showed absorbances ascribable to terminal vinyl, enamine, and aziridine functional groups. The proton spectrum of IV disclosed a vinyl resonance between τ 4.18 and 4.95 and two multiplets centered at τ 7.15 and 7.65 assignable to the aziridine ring protons. The ^{19}F spectrum consisted of two equally intense signals. A broad higher field peak centered at +67.0 ppm relative to internal CCl_3F is assigned to the CF_3' group, the broadening being most likely due to the combined effects of weak CF_3–CF_3 and *cis*-CF_3–H interactions. The downfield peak centered at +54.6 ppm comprises a doublet (J_{CF_3-H} = 9.2 cps) of quartets ($J_{CF_3-CF_3}$ = 1.5 cps) and is assigned to the CF_3 group. The magnitude of the CF_3–CF_3 coupling constant provides a valuable clue to the stereochemistry of the CF_3 groups. It has been found[14] that *trans*-CF_3–CF_3 coupling is much weaker than *cis*-CF_3–CF_3 coupling, the former having values of 1.1–2.5 cps, the latter being of the order of 11.5–13 cps. Accordingly, we propose that the CF_3 groups in structure IV are *trans* to each other.[15]

Thermodynamic Parameters. A kinetic analysis of the valence isomerization of the unusually stable divinylaziridine IV, employing gas–liquid partition chromatography, proved quite feasible and, as expected, the transformation IV → V exhibited good first-order kinetics at the three temperatures investigated. The observed rates were k 297.7°K = 1.28×10^{-4} sec^{-1}, k_1 306.2°C = $2.42 \times {}_1 10^{-4}$, and k_1 317.7°K = 6.14×10^{-4} sec^{-1}, giving rise to the rate expression $k_1 = 10^{12} \exp(-16{,}500/RT)$ from which $\Delta S^{\ddagger}_{298} = -21.0$ eu.

The magnitude of the frequency factor and $\Delta S^{\ddagger}$ are explicable in terms of a sizable entropy loss accompanying the formation of the transition complex *via* the *cis* invertomer of IV and clearly lends support to a "no-mechanism" reaction path. Undoubtedly, orientation effects and steric effects arising from the CF_3 groups contribute to the large negative $\Delta S^{\ddagger}$. The role of trifluoroalkyl and carboalkoxy substituents in the thermal reorganization of the 1,2-divinylaziridine system is currently being studied.

Effect of Inversion on Isomerization. In the facile thermal reorganization of rigid ring systems such as divinylcycloalkanes,[16–20] divinyloxiranes,[5] and 2,3-divinylaziridines,[1] the vinyl groups must be in the *cis* configuration to assume the six-center transition state postulated for the "no-mechanism" reaction. Obviously in the *trans*-divinyl three-membered rings such a transition state is unattainable for geometrical reasons, and accordingly the rate-determining step of rearrangement involves a preliminary *trans* → *cis* isomerization.

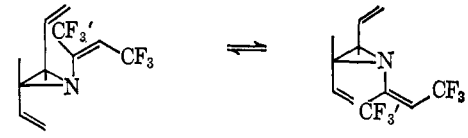
In the 1,2-divinylaziridine system where inversion at the nitrogen atom gives rise to *cis* and *trans* conformers of IV, only the *cis* invertomer possesses the requisite geometry for facile rearrangement *via* a rate-determining "no-mechanism" process. In light of the above analysis, the thermal reorganization of IV under the present experimental conditions involves the *cis* invertomers exclusively.



trans invertomer *cis* invertomer

It is well known that the nitrogen inversion rates for N-alkylaziridines are sufficiently slow at room temperature to permit the detection of discrete *cis* and *trans* invertomers.[21–23] However, the attachment of unsaturated groups to nitrogen appears to greatly enhance the inversion process. Recent evidence for high rates of nitrogen inversion of N-vinylaziridines reported by Kostyanovskii, *et al.*,[24] suggests that rapid inversion should also occur in IV.

Nonetheless, the possibility that the rate of inversion exerts a measurable effect on the rate of valence isomerization (k_{vi}) of IV could not be completely discounted. Accordingly, consideration was given to the synthesis of an aziridine system in which the effect of inversion on the thermal reorganization process was obviated. This idea was realized by the formation of VIII *via* the N-vinylation of 2,3-divinylaziridine with hexafluorobutyne-2. By virtue of the *trans* geometry of the 2,3-divinyl groups, the inverting N-vinyl is always *cis* to one of the C-vinyl groups.



VIII

Thus a kinetic study of the rearrangement of VIII would provide an isomerization rate unaffected by an inversion process. If the energy barrier to inversion is negligible, the presence of the third vinyl group should

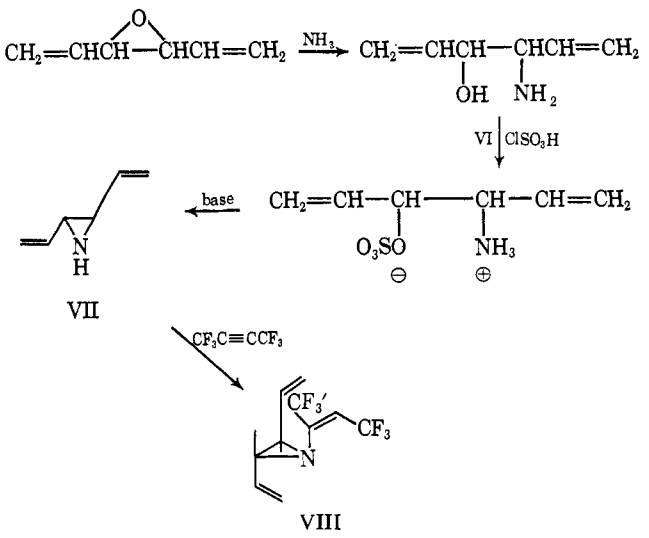
(14) G. V. D. Tiers, *J. Chem. Phys.*, **35**, 2263 (1961); G. V. D. Tiers, *J. Phys. Chem.*, **66**, 1192 (1962); P. M. Treichel, E. Pitcher, and G. Andreades, *J. Am. Chem. Soc.*, **84**, 864 (1962); F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962); T. B. Wilford and F. G. A. Stone, *ibid.*, **4**, 93 (1965).

(15) Dolfini[9] and Winterfeldt[10] have described the predominance of *cis* addition to acetylenes activated by carboalkoxy groups. The extent of *cis* or *trans* addition appears to be a function of solvent. In marked contrast to these reports, we find exclusive *trans* addition to the acetylenic group activated by trifluoromethyl. A more detailed account of the addition of aziridines to activated acetylene will be presented at a later date.

(16) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).
(17) E. Vogel, *ibid.*, **1**, 53 (1962).
(18) W. von E. Doering and W. R. Roth, *ibid.*, **2**, 115 (1963).
(19) G. S. Hammond and C. D. DeBoer, *J. Am. Chem. Soc.*, **86**, 899 (1964).
(20) D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).
(21) A. T. Bottini and J. D. Roberts, *ibid.*, **80**, 5203 (1958).
(22) A Lowenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, **82**, 3599 (1960).
(23) A. T. Bottini, R. L. Van Etten, and A. J. Davidson, *ibid.*, **87**, 755 (1965).
(24) R. G. Kostyanovskii, O. A. Yuzhakova, and V. F. Bystrov, *Zh. Vses. Khim Obshchestva im. D. I. Mendeleeva*, **10** (2), 229 (1965).

have little effect on the rate of valence isomerization of IV. The validity of this premise was tested by the synthesis and subsequent rearrangement of VIII. The preparative route to VIII is outlined in Scheme II.

Scheme II



Unlike the ammonolysis of butadiene monoxide, formation of 3-hydroxy-4-amino-1,5-hexadiene from 2,3-divinyloxirane and ammonia was slow and afforded only moderate yields of VI.

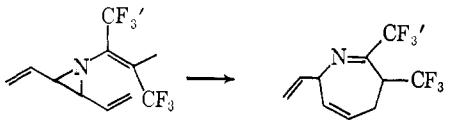
Nmr analysis showed VI to be a *ca.* 2:1 mixture of *erythro*:*threo* diastereomers. The observed ratio is consistent with a *trans* ring opening since the oxirane also comprised a *ca.* 2:1 mixture of *trans*:*cis* isomers.

Reaction of VI with chlorosulfonic acid gave a quantitative yield of the sulfate ester. Ring closure of the latter with caustic afforded only *trans*-2,3-divinylaziridine VII. The absence of the *cis*-aziridine isomer is explicable on the basis of its susceptibility to valence isomerization to the corresponding azepine as previously reported.[1] The infrared spectrum of VII showed the presence of terminal vinyl (6.11, 10.12, and 10.95 μ) and N–H (3.05 μ) groups. The characteristic vinyl resonance signal (multiplet at τ 4.0–5.10) and ring proton signal (quartet centered at τ 7.73) having the expected intensities are in full accord with the proposed structure.

Treatment of a Freon 11 solution of VII with hexafluoro-2-butyne at −76° gave after 2 hr a quantitative yield of VIII. Absorption bands ascribable to terminal vinyl, enamine, and aziridine were noted in the infrared spectrum of the trivinylaziridine. The proton spectrum of VIII in CCl_4 exhibited resonances owing to vinyl protons at τ 4.25–4.92 and a broadened doublet center at τ 6.92 ascribable to the aziridine ring protons.

By analogy with the ^{19}F spectrum of IV, the trivinylaziridine in $CFCl_3$ exhibited two sets of lines. The line at +55.3 ppm relative to internal CCl_3F is attributable to the CF_3 group. Further resolution showed two condensed quartets arising from coupling of the CF_3 group with hydrogen ($J_{CF_3-H} \cong 9.2$ cps) and with the CF_3' group ($J_{CF_3-CF_3} \cong 1.5$ cps). The high-field signal at +66.3 ppm which appeared as a broadened singlet is attributable to the CF_3' group. The magnitude of $J_{CF_3-CF_3}$ indicates, as in IV, that the trifluoromethyl groups are *trans* to each other.

The valence isomerization of VIII was effected by allowing the trivinylaziridine to stand at room temperature for several hours.[25]



VIII IX

The ^{19}F spectrum of IX was similar to V and exhibited a multiplet (six lines resolved) (CF_3) and quartet (CF_3') centered at +65.6 and +71.3 ppm relative to internal CCl_3F, respectively, with $J_{CF_3-H} \cong 10.0$ cps and $J_{CF_3-CF_3} \cong 5.5$ cps.

The rate of rearrangement of the trivinylaziridine at room temperature was conveniently determined by measuring the disappearance of the trifluoromethyl signals in the ^{19}F nmr spectrum at half-hour intervals at 23°. Freon 11 was employed as an internal reference. The reaction showed good first-order kinetics with $k_1(296°K) = 1.5 \times 10^{-4}$ sec^{-1}. A comparison of the kinetic data for IV and VIII reveals that these aziridines rearrange at essentially the same rate at room temperature. Accordingly, the energy barrier to inversion is negligible and does not appear to exert a significant influence on the valence isomerization of 1,2-divinylaziridines.

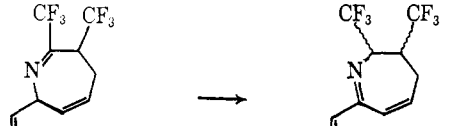
It is apparent that the 1,2-divinylaziridine system, like its *cis*-2,3 isomer,[1] can assume the requisite six-center transition-state geometry for valence isomerization. It is reasonable to argue that the rather substantial differences in the rates of valence isomerization for these positional isomers are explicable in terms of relative bond strengths, differences in transition-state geometries, and substituent effects. In light of our recent findings,[26] however, we believe that substituents exert a very prominent effect on the rate of thermal reorganization of 1,2-divinylaziridines.

Experimental Section

1-Amino-3-buten-2-ol Sulfate Ester. Chlorosulfonic acid, 43 ml, was slowly added to a rapidly stirred solution of 1-amino-3-buten-2-ol[11] (46.1 g, 0.528 mole) in 300 ml of anhydrous ether at 0°. The reaction mixture became gummy and difficult to stir after about half of the chlorosulfonic acid had been added. However, continued agitation for 3–4 hr (after completion of chlorosulfonic acid addition) resulted in the formation of a white solid. Filtration and washing with ether and then 2-propanol yielded 86.3 g (97.5%) of the sulfate ester, mp 162–165° dec.

Anal. Calcd for $C_4H_9NO_4S$: C, 28.74; N, 8.38. Found: C, 28.76; N, 8.96.

(25) By analogy with V, the ^{19}F nmr spectrum of IX after 6 hr at 23° revealed that approximately 40% of IX was converted to its cross-conjugated isomer *via* prototropy. As one might expect, isomerization



IX IXa

of IX to IXa is faster than the corresponding transformation of V to Va. By analogy with Va, the CF_3 resonance signals assigned to IXa appeared as identical multiplets (five lines resolved) of equal intensity at +66.0 and +72.3 ppm with $J_{CF_3-H} = 9.5$ cps. On the basis of the 5 cps F–F coupling constant between the CF_3 groups in the cross-conjugated isomer, we propose that the stereochemistry of IXa and Va is identical. Unequivocal stereochemical assignments however must await further study.

(26) Manuscript in preparation.

2-Vinylaziridine (III). The sulfate ester (86.3 g, 0.515 mole) in 100 ml of water was added rapidly to 300 g of a hot 33% sodium hydroxide solution. The reaction was heated sufficiently, during and after completion of addition, to affect distillation. The aqueous distillate was cooled, saturated with potassium hydroxide, extracted with ether, and dried over potassium hydroxide. Distillation through a spinning-band column gave 20.4 g (49% yield) of 2-vinylaziridine, bp 97–99°. Major infrared absorbances appeared at 3.05 (s), 6.10 (s), 10.10 (s), 11.03 (vs), 12.05 (s), and 12.5 (s) μ.

Anal. Calcd for C_4H_7N: C, 69.57; H, 10.14. Found: C, 69.54; H, 10.53.

1-[1,2-Bis(trifluoromethyl)]vinyl-2-vinylaziridine (IV). Hexafluoro-2-butyne (4.06 g, 0.025 mole), was condensed into a glass pressure reactor containing 1.38 g (0.02 mole) of 2-vinylaziridine in 2 ml of Freon 11, at −196°. The reactor was then placed in a −76° bath and kept there, with occasional shaking, for 2 hr. By rapidly stripping off solvent and excess reactant at below room temperature, a >90% yield of 1-[1,2-bis(trifluoromethyl)]vinyl-2-vinylaziridine was realized. Distillation of the aziridine IV by procedures other than a rapid trap–trap distillation on a vacuum line invariably resulted in isomerization of IV. Major infrared absorbances appeared at 6.02 (vs), 6.95 (m), 7.69 (vs), 7.90 (vs), 8.35 (s), 8.60 (s), 10.15 (w), 10.80 (w), and 11.62 (w) μ.

Anal. Calcd for $C_9H_7F_6N$: C, 41.56; N, 6.06. Found: C, 41.61; N, 5.94.

2,3-Bistrifluoromethyl-3,4-dihydro-7H-azepine (V). By allowing the 1,2-divinylaziridine IV to stand overnight at room temperature or for several hours at higher temperatures, there was obtained a pale yellow oil. Rapid vacuum distillation through a short-path still gave 2,3-bistrifluoromethyl-3,4-dihydro-7H-azepine as a water-white liquid, bp 75° (43 mm). Major infrared absorbances appeared at 5.95 (m), 7.0 (m), 7.29 (m), 7.39 (s), 7.65 (s), 7.85 (vs), 8.23–8.95 (vs), 9.30 (s), 10.20 (s), 10.36 (s), 11.00 (w), and 11.65 (w) μ.

Anal. Calcd for $C_9H_7F_6N$: C, 41.56; F, 49.35; N, 6.06. Found: C, 41.70; F, 49.80; N, 6.18.

3-Amino-4-hydroxy-1,5-hexadiene (VI). A mixture 91.3 g (0.95 mole) of 2,3-divinyloxirane, 500 ml of tetrahydrofuran, and 1.3 l. of concentrated ammonium hydroxide was rapidly stirred for 1 week at room temperature and then at reflux temperatures for 4 hr. Removal of the volatile materials on a vacuum stripper left a viscous residue from which 37.2 g (34.8%) of 3-amino-4-hydroxy-1,5-hexadiene, bp 90–92° (11 mm), was isolated. On standing, the amino alcohol partially solidified. Isolation of the solid and recrystallization from benzene gave a white solid, mp 59–61°. No attempt was made to determine the stereochemistry of this solid amino alcohol.

Anal. Calcd for $C_6H_{11}NO$: C, 63.72; N, 12.39. Found: C, 63.20; N, 12.63.

***trans*-2,3-Divinylaziridine (VII).** The reaction of 13.3 g (0.117 mole) of 3-amino-4-hydroxy-1,5-hexadiene in 500 ml of anhydrous ether with 15.0 g (0.129 mole) of chlorosulfonic acid yielded 22.1 g (97%) of the corresponding sulfate ester, mp 178–180° dec.

Anal. Calcd for $C_6H_{11}NO_4S$: C, 37.31; N, 7.25. Found: C, 37.41; N, 7.42.

In the manner previously described, the sulfate ester gave a 28.6% yield of *trans*-2,3-divinylaziridine, bp 55–56° (30 mm). The infrared spectrum of VII showed major absorbances at 3.05 (m), 6.11 (s), 10.12 (s), 10.95 (vs), 11.90 (vs), and 12.30 (m) μ.

Anal. Calcd for C_6H_9NO: C, 75.79; H, 9.47. Found: C, 76.02; H, 9.48.

1-[1,2-Bis(trifluoromethyl)]vinyl-2,3-divinylaziridine (VIII). The preparation of this trivinylaziridine was analogous to that described for the synthesis of IV. Thus, 0.33 g (3.5 mmoles) of 2,3-divinylaziridine in 1 ml of Freon 11 when treated with 1.0 g (6 mmoles) of hexafluorobutyne-2 at −76° for 2 hr yielded VIII quantitatively. The major infrared absorbances appeared at 6.0 (m), 7.88 (vs), 8.31 (s), 8.70 (vs), 10.11 (m), 10.75 (m), and 11.53 (w) μ.

Anal. Calcd for $C_{10}H_9F_6N$: C, 46.69; N, 5.45. Found: C, 46.09; N, 5.14.

2,3-Bis(trifluoromethyl)-7-vinyl-3,4-dihydro-7H-azepine (IX). Heating the trivinylaziridine VIII at 50° for 1–2 hr gave a pale yellow liquid. A trap–trap distillation of the latter on a vacuum line gave IX as a water-white liquid. The infrared spectrum of IX disclosed major absorbances at 6.15 (w), 6.31 (m), 7.10 (w), 7.30 (m), 7.60 (m), 7.85 (vs), 8.2–8.95 (vs), 10.05 (m), 10.60 (m), 10.95 (m), 12.55 (m), and 14.10 (m) μ.

Kinetic Measurements. The progress of the thermal valence isomerization of the 1,2-divinylaziridine was followed by gas chromatographic analysis. Good resolution of the divinylaziridine IV and the generated valence isomeric azepine V was realized with a column of silicone oil on Firebrick maintained at room temperature. Under the conditions of operation, the aziridine had three times the retention time of benzene, and the azepine had twelve times the retention time of benzene. The kinetics were all performed with the internal standard benzene so that the gas chromatographic measured areas could be related to the internal standard.

The Polar Fluorination of Propenylbenzene[1,2]

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Abstract: It has been demonstrated that elemental fluorine will add to *cis*- and *trans*-propenylbenzene in a predominately *cis* manner. Fluorination in methanol will produce the diastereoisomeric 1-methoxy-2-fluoropropylbenzenes in addition to the vicinal difluorides; *trans* dehydrofluorination of vicinal difluorides will predominate only in very favorable situations.

The previous investigations[1,3,4] of the direct fluorination of the carbon–carbon double bond have shown that the adducts are of predominately *cis* configuration. Fluorination of 1,1-diphenylethylene produced both direct adduct as well as 1,1-diphenyl-2-fluoroethylene.[1] It was postulated that molecular adducts as well as "open" carbonium ions were involved.

It appeared of interest to study an aliphatic olefin to assess the effect, if any, of sovent polarity and temperature on the stereospecificity of the addition. In this paper we present the results of fluorine addition to *cis*- and *trans*-propenylbenzene.

Results

The identification of the products followed a scheme essentially as outlined in Scheme I. In nonpolar

(1) For part III of the low-temperature fluorination series see R. F. Merritt, *J. Org. Chem.*, **31**, 3871 (1966).

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(3) R. F. Merritt and T. E. Stevens, *J. Am. Chem. Soc.*, **88**, 1822 (1966).

(4) R. F. Merritt, *J. Org. Chem.*, **31**, 1859 (1966).