1-chloro-2-methylpropene, 0.04 mole of *t*-butyl acetate, 0.12 mole of isobutylene dichloride, 0.08 mole of 1,3-dichloro-2-methylpropene, 0.21 mole of 2-chloro-1,1-dimethylethyl acetate, 0.01 mole of 2-chloro-2-methylpropyl acetate, 0.02 mole of 2-methyl-1,1,2-trichloropropane, 0.07 mole of 2-methyl-1,2,3-trichloropropane, and 0.05 mole of 1,1-bis(chloromethyl)ethyl acetate. The only pure material isolated on fractionation of this mixture was a cut of 8.5 g. of **1,1-bis(chloromethyl)ethyl acetate** distilling at 59–60° (5 mm.), $n^{25}D$ 1.4502. The n.m.r. spectrum for this compound consisted of a simple three-line spectrum since all hydrogens are on isolated carbons. The acetate methyl group fell at 2.0 p.p.m., the two equivalent chromethyl groups fell at 3.9 p.p.m., and the remaining methyl group gave a line falling at 1.6 p.p.m.

2-Chlorocyclohexyl Acetate.—A run was carried out as described for method B employing cyclohexene (all added at the start) as the olefin and using sodium acetate in the place of potassium acetate. The salt was filtered from the reaction mixture and acetic acid was removed to a pot temperature of 80° at water pump pressure. The residue was treated with 50 ml. of water to dissolve the remaining salt. The organic phase was separated, dried over sodium sulfate, and fractionated, yielding 37 g. (24%) of *trans*-1,2-dichlorocyclohexane at 56–57° (6 mm.), $n^{25}D$ 1.4878 [lit.[22] b.p. 88–89° (30 mm.), $n^{20}D$ 1.4904]; 103 g. (58%) of 2-chlorocyclohexyl acetate at 85–86° (6 mm.), $n^{25}D$ 1.4658 [lit.[23] b.p. 100–100.3° (12 mm.), $n^{20}D$ 1.4644]; and 15 g. (7%) of impure 2-chlorocyclohexyl chloroacetate at 116–118° (5 mm.), $n^{25}D$ 1.4849.[24]

2-Chloro-1-phenylethyl Acetate.—A run was carried out as described above for cyclohexene, except that styrene was used as the olefin. Fractionation gave 18 g. (13%) of β-chlorostyrene at 80–82° (10 mm.), $n^{25}D$ 1.5741 [lit.[25] b.p. 89–92° (15 mm.), $n^{18}D$ 1.5781]; 67 g. (38%) of styrene dichloride at 90–92° (4 mm.), $n^{25}D$ 1.5492 [lit.[26] b.p. 90° (4 mm.), $n^{15}D$ 1.5544]; and 85 g. (43%) of 2-chloro-1-phenylethyl acetate at 111–112° (3 mm.), $n^{25}D$ 1.5164.

2-Chlorocyclohexyl Chloroacetate.—A mixture of 2 moles of cyclohexene and 1 mole of chloroacetic acid was maintained at 40–45° (warming initially to dissolve the acid, and then mild cooling) while 1 mole of chlorine was added during 3 hr. After the addition was complete, a solution of 70 g. of sodium carbonate in 150 ml. of water was cautiously added. The organic phase was separated, dried, and the excess cyclohexene was removed at water pump pressure. The residue was fractionated, yielding 84 g. (55%) of *trans*-1,2-dichlorocyclohexane at 65–67° (10 mm.), $n^{25}D$ 1.4872; an intermediate cut of 10 g., $n^{25}D$ 1.4930; and then 53 g. (25%) of 2-chlorocyclohexyl chloroacetate at 132–133° (10 mm.), $n^{25}D$ 1.4860.

2-Chlorocyclohexyl Dichloracetate.—A run was carried out as described in the preceding paragraph except that dichloroacetic acid was used in place of the chloroacetic acid. Fractionation gave 83 g. (54%) of *trans*-1,2-dichlorocyclohexane at 66–67° (10 mm.), $n^{25}D$ 1.4881; an intermediate cut of 19 g., $n^{25}D$ 1.4890; and 61 g. (25%) of 2-chlorocyclohexyl dichloroacetate at 139–140° (11 mm.), $n^{25}D$ 1.4919.

N-(β-Chloroisopropyl)acetamide.[27]—To a mixture of 200 ml. of chloroform and 82 g. (2 moles) of acetonitrile were added concurrently 1 mole of chlorine and 1 mole of propylene during 2 hr. with mild cooling to maintain the temperature at 40–45°. After the additions were complete, the mixture was maintained below 20° while a solution of 53 g. of sodium carbonate in 300 ml. of water was added (initially very exothermic!); then the organic phase was separated and dried, and the solvent and propylene dichloride were removed at water pump pressure. The residue was fractionated, yielding 37 g. (27%) of the amide at 108–110° (2 mm.), $n^{25}D$ 1.4778. This material was a very viscous colorless liquid which froze with fracturing when cooled in Dry Ice and melted at −11°.

Anal. Calcd. for $C_5H_{10}ClNO$: C, 44.29; H, 7.43; Cl, 26.15; N, 10.33. Found: C, 44.00; H, 7.10; Cl, 25.80; N, 9.90.

The n.m.r. spectrum for the above compound was consistent for the structure named and consisted of a broad band centered at 7.8 p.p.m., representing one hydrogen, and assigned to the amide hydrogen; a doublet centered at 1.3 p.p.m. (J = 7 c.p.s.), assigned to the methyl group of the N-alkyl grouping; a doublet centered at 3.6 p.p.m. (J = 7 c.p.s.), assigned to the two hydrogens of the chloromethyl group; a complex multiplet centered at 4.2 p.p.m. (J = 7 c.p.s.), representing one hydrogen and assigned to the methine group; and a singlet at 2.05 p.p.m., assigned to the three hydrogens of the acetyl grouping.

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(25) F. Bergmann, A. Kalmus, and E. Breuer, *J. Am. Chem. Soc.*, **80**, 4543 (1958).
(26) M. F. Handley, U. S. Patent 2,776,982 (1957); *Chem. Abstr.*, **51**, 8143 (1957).
(27) This experiment was repeated using 1 mole of acrylonitrile (and no acetonitrile or propylene) to see if this material could serve as both the olefin and nitrile in preparing a chlorinated amide. No such product was detected in the reaction mixture, the major product being 2,2,3-trichloropropionitrile. It was obtained in 82% yield based on the unrecovered acrylonitrile, b.p. 60–61° (25 mm.), $n^{22}D$ 1.4655. The n.m.r. spectrum of this material consisted of a single line falling at 4.2 p.p.m., assigned to the two equivalent hydrogens on the 3-carbon. *Anal.* Calcd. for $C_3H_2Cl_3N$: Cl, 67.14. Found: Cl, 67.00.

Valence Tautomerism of Vinyl-Substituted Three-Membered Heterocycles. II. Conversion of N-Ethyl-2,3-divinylaziridine to N-Ethyl-4,5-dihydroazepine

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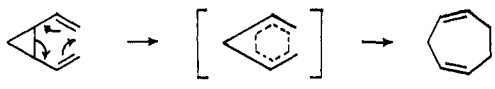
Cyclization of 3-ethylamino-4-hydroxy-1,5-hexadiene, obtained from the aminolysis of 1,2-divinylethylene oxide, gave rise to a mixture of *trans*-N-ethyl-2,3-divinylaziridine and its valence isomer, N-ethyl-4,5-dihydroazepine. The origin of the azepine VI was established by the isolation and ring closure of the *erythro* IIa and *threo* IIb, amino alcohols. The *erythro* isomer cyclized to yield only *trans*-aziridine V. Even at room temperature the *cis*-aziridine isomerized to azepine VI as rapidly as it was generated from the *threo*-amino alcohol IIb.

Small strained carbocycles, with *cis*-oriented olefinic groups are subject to thermally induced ring expansions[1-3] by a Cope[4]-type rearrangement mechanism. Replacement of one of the vinyls by unsaturated hetero atoms, *e.g.*, isocyanate, does not destroy the lability of the small ring toward enlargement. Accordingly, lactams are formed by the thermolysis of *cis*-2-vinylcyclopropyl isocyanate.[1,5] Recent reports have extended the scope of valence isomerization of strained rings systems to include small heterocycles. These



(1) E. Vogel, *Angew. Chem., Intern. Ed. Eng.*, **2**, 1 (1963).
(2) E. Vogel, *ibid.*, **1**, 53 (1962).
(3) W. E. Doering and W. R. Roth, *ibid.*, **2**, 115 (1963).
(4) For recent reviews of the Cope rearrangement, see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1962, p. 505; S. J. Rhoads, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers Inc., New York, N. Y., 1963, p. 684.
(5) W. E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

are systems in which the ring undergoing expansion contains the hetero atom. Thermolysis of 1,2-divinylethylene oxide[6,7] results in the formation of its valence isomer, 4,5-dihydrooxepine. The addition of carbethoxy nitrene to benzene was reported to give rise to N-carbethoxyazepine.[8,9] Presumably, formation of the azepine involved the intermediacy of N-carbethoxy-7-azanorcaradiene.

Valence isomerization also occurs with the *trans* isomers, but at considerably higher temperatures than the corresponding *cis* isomers. This relationship between the stereochemical disposition of the vinyl groups and the thermal requirement for isomerization is independent of the size or type of ring. However, in analogous systems, the temperature of ring enlargement appears to be dependent upon the type of atoms in the small ring. For example, whereas *cis*-1,2-divinylcyclopropane undergoes ring enlargement at $-40°$ *cis*-1,2-divinylethylene oxide does not isomerize below *ca.* 60°. The alleged 7-azanorcaradiene is reported to be nonisolable at room temperature. It appears to isomerize to N-carbethoxyazepine as rap ly as it is formed. The influence of the nitrogen atom on the nature of the valence isomerization reaction of aziridines is difficult to ascertain in this bicyclic system because of the restriction of rotation of the vinyl groups. The expected increase in entropy probably manifests itself as a decrease in the temperature required for isomerization. It is plausible that any stabilizing effect that nitrogen exerts may be nullified in the strained bicyclic 7-azanorcaradiene structure.

The purpose of this investigation was to prepare a divinyl aziridine in which there was no restriction on the rotation of the vinyl groups and thereby determine if the thermal behavior of the *cis* and *trans* isomers follows the pattern of the analogous carbocyclic and oxygen heterocyclic cases.

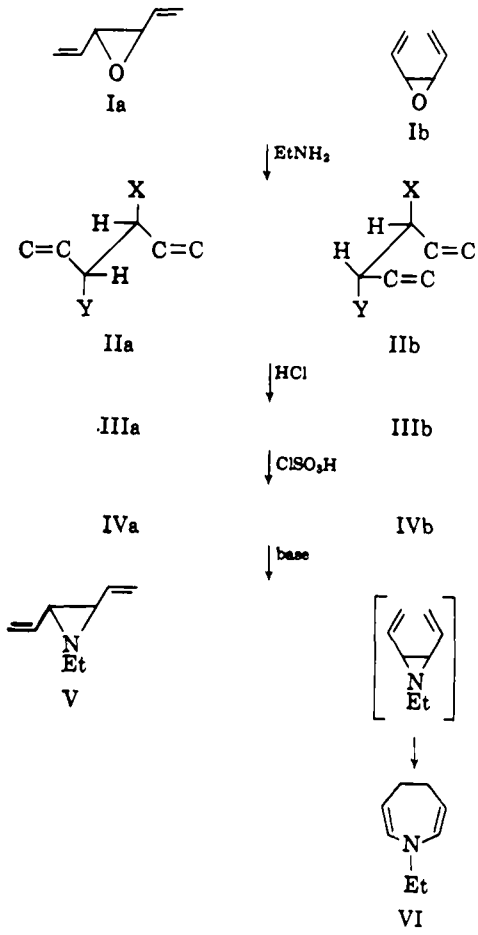
Results and Discussion

We have prepared 3-ethylamino-4-hydroxy-1,5-hexadiene and shown that subsequent transformations gave rise to a mixture of N-ethyl-2,3-divinylaziridine and its valence isomer, N-ethyl-4,5-dihydroazepine. The sequence of reactions leading to aziridine V and azepine VI are shown in Scheme I.

1,2-Divinylethylene oxide (*cis* and *trans*)[6] when heated for 3 days with ethylamine gave a mixture of IIa and IIb in 82% yield. The ethylamino alcohol distilled under vacuum as a colorless oil which solidified on standing. The infrared spectra showed multiple absorption in the 2.8–3.1-μ region due to inter- and intramolecular hydrogen bonding of the hydroxyl and amine groups. Olefin absorptions at 6.1, 10.1, and 10.85 μ due solely to terminal vinyl were observed. The proton spectrum of II confirmed the presence of an N-ethyl and two vinyl groups. Equally intense multiplets centered at *ca.* τ 5.9 and 7.1 were ascribable to the O- and N-methinyl protons, respectively.

A modification of Elderfield's[10] method for sulfate

SCHEME I



IIa and b, X = EtNH; Y = OH
IIIa and b, X = $EtNH_2^+Cl^-$; Y = OH
IVa and b, X = $EtNH_2^+$; Y = OSO_3^-

ester formation converted II into the inner sulfate salts IV in virtually quantitative yield. Cyclization of IV was accomplished by steam distillation of a caustic solution of the sulfate ester. A 32% yield of a mixture of V and VI in a ratio of 70:30 was obtained by this procedure.

Structural analysis of V and VI was performed on samples isolated by preparative gas chromatography. The aziridine V exhibited strong absorption in the infrared characteristic of terminal vinyl (6.1, 10.2, and 11.0 μ). Terminal vinyl functionality (multiplet between τ 4.15–5.0) was substantiated by n.m.r. The N-ethyl group appeared as quartet and triplet signals at τ 7.55 and 9.02 (benzene). Integration of the area at τ 7.55 indicated that the N-methine and methylene signals overlap.

An intense doublet at 6.0 and 6.1 μ in the infrared spectrum of the azepine VI can be assigned to an olefinic group in conjugation with an electronegative atom or group.[11,12] The presence of olefin in the *cis* configuration was indicated by infrared absorption at 13.6 μ. Proton resonances characteristic of N-ethyl, vinyl (multiplets centered at τ 4.33 and 5.38), and allylic protons (multiplet at τ 7.61) were observed for the azepine in benzene.

The establishment of the origin of the azepine VI is imperative to the evaluation of the differences in the

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susceptibility of the *cis*- and *trans*-divinylaziridine isomers toward thermally induced isomerizations. Aminolysis of epoxides[13,14] occurs by a *trans* ring-opening mechanism. Formation of aziridines by the Wenker[15] process has been shown[13] to proceed by a *trans* displacement of sulfate group. Therefore, the transformation of epoxide to aziridine is one of over-all retention of configuration. Since the 1,2-divinylethylene oxide used in the Scheme I was a *cis–trans* mixture, *cis*- and *trans*-aziridine should be the products of ring closure of IV unless one or both of the aziridines undergoes valence isomerization to VI. Evidence for the azepine VI having its origin in the *cis*-aziridine and not the *trans* was obtained by isolation of the *erythro* and *threo* diastereomers of II[16] and performing the ring closure by the sequence of reactions shown.

The *erythro*-ethylamino alcohol IIa was isolated as a white solid. The proton spectrum indicated IIa to be free of the *threo* isomer. Retention of configurational integrity during the transformation of IIa to IVa was confirmed by n.m.r. analysis.

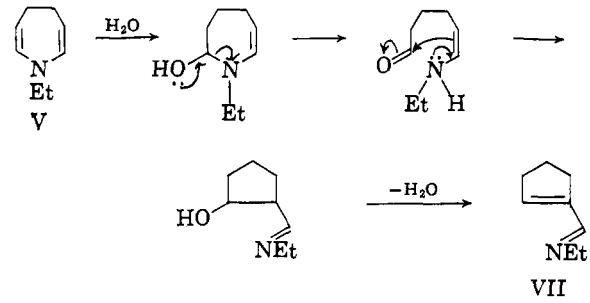
The *threo* isomer IIb was obtained from the filtrate of the *erythro* isomer as a viscous oil. Based on n.m.r. the configurational purity was 90%. The conversion of IIb to IVb also occurred without alteration of configurational composition.

Ring closure of the sulfate esters IV was accomplished with aqueous caustic at both room temperature and at steam distillation temperature. *erythro* IVa gave *trans*-aziridine V free of azepine VI, in 34% yield. Room temperature cyclization gave similar results. A 54% yield of a mixture of azepine VI and *trans*-aziridine V in a ratio of 89:11 was obtained from a closure of the *threo* isomer IVb. Since IVb had a configurational purity of 90%, the *trans*-aziridine was probably formed from the IVa contamination of IVb.

Discoloration and thickening occurred when the *trans*-aziridine was heated in a sealed tube for 1 hr. on a steam bath. Only 12% of the charge was volatile. This volatile material was the *trans*-aziridine V. No azepine VI could be detected. Since the azepine VI does not arise from *trans*-aziridine V under the condition of ring closure studied it must originate through the intermediacy of the *cis*-aziridine.

Thus, in the nitrogen heterocycles a relationship exists between geometry of the vinyl groups and the susceptibility toward ring expansion which is similar to that reported for carbocycles and oxygen heterocycles. The *cis* isomer always isomerizes at much lower temperatures than the *trans* isomer. On the other hand, the thermal requirements for valence isomerization of the bicyclic systems, norcaradiene and azanorcaradiene and the analogous open-chain systems appear quite similar. Even at low temperatures the small ring expands as rapidly as it is formed. There is therefore no dramatic effect on the the isomerization process owing to replacement of a carbon atom in the small ring by nitrogen.

SCHEME II



VII

The unusually high thermal stability reported[6] for *cis*-1,2-divinylethylene oxide appears to be peculiar to heterocycles having a group VI hetero atom. This idea is also supported by the fact that the *cis* isomer of 1,2-divinylethylene episulfide[17] has recently been prepared and isolated at above room temperature.

It is interesting to note that heating the azepine VI in the presence of moisture results in a ring contraction. A plausible reaction sequence for the ring contraction is shown in Scheme II. A preliminary ring opening *via* the N-hemiacetal followed by successive aldolization and dehydration yields VII. The *trans*-aziridine V does not yield VII even in the presence of moisture.

Experimental

3-Ethylamino-4-hydroxy-1,5-hexadiene (II).—A solution of 1,2-divinylethylene oxide (*cis* and *trans*), 29.1 g. (0.303 mole), in 260 ml. of ethylamine (70% aqueous solution) was heated at 55° for 3 days. The excess ethylamine was then removed by distillation. Extraction of the residue with ether, drying over $MgSO_4$, and distillation under reduced pressure gave 35.2 g. (82.3% yield) of 3-ethylamino-4-hydroxy-1,5-hexadiene, b.p. 82–85° (11 mm.). The distillate crystallized on standing.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.09; N, 9.93. Found: C, 68.36; N, 10.22.

***trans*-N-Ethyl-2,3-divinylaziridine (V)–N-Ethyl-4,5-dihydroazepine (VI).**—The amino alcohol II (20 g., 0.142 mole) in 50 ml. of anhydrous ether was treated with hydrogen chloride, at 0°, until precipitation of the hydrochloride salt III ceased. Chlorosulfonic acid, 18.6 g. (0.16 mole), was slowly added to the ether suspension of the hydrochloride salt while the temperature was kept at 0°. The reaction mixture became gummy and difficult to stir when approximately half of the chlorosulfonic acid had been added. However, the tacky material solidified after standing overnight at room temperature. Filtration and washing with ether afforded 31 g. (98.5% yield) of the sulfate ester IV.

Anal. Calcd. for $C_8H_{15}NO_4S$: C, 43.44; N, 6.33. Found: C, 43.68; N, 6.94.

Sulfate ester IV (10 g., 45.3 mmoles) dissolved in 40 ml. of water was dripped into 36 g. of a hot 50% sodium hydroxide solution. Gas chromatographic analyses of the steam-distilled product, 1.8 g. (32.3% yield), showed a 70:30 mixture of *trans*-N-ethyl-2,3-divinylaziridine (V) and N-ethyl-4,5-dihydroazepine (VI), respectively.

The composition of the mixture was determined on a Perkin-Elmer gas chromatographic, 2-ft. column (Dow Corning silicone oil No. 200 on firebrick) at 75°. The relative retention time of V to *n*-heptane was 3.54, and 10.5 for VI. Small amounts of V and VI were separable by rapid vacuum distillation. Prolonged periods of heating caused discoloration and polymerization of the crude mixture.

trans-N-Ethyl-2,3-divinylaziridine gave b.p. 56–58° (42 mm.); infrared maxima (neat) 3.20 (w), 3.35 (vs), 3.48 (s), 6.10 (vs), 6.90 (m), 7.10 (w), 7.30 (m), 7.45 (m), 10.20 (vs), 11.0 (vs), 11.9 (w), 13.04 (m), and 13.20 (m) μ. N-Ethyl-4,5-dihydroazepine gave b.p. 69–70° (20 mm.); infrared

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(16) Distinction between the *erythro*- and *threo*-amino alcohols was made on the basis of the splitting pattern observed for the N-methinyl proton resonance signal appearing at *ca.* τ 7.0. While the *threo* isomer IIb exhibited a doublet, J = 7.7 c.p.s. (methinyl–vinyl proton coupling), the *erythro* isomer IIa showed a quartet, J = 7.7 (methinyl–vinyl proton coupling) and 3.9 c.p.s. (vicinal proton coupling). Under higher resolution the N-methine doublet in the *threo* isomer showed further splitting indicating that the vicinal coupling constant is 0.5 c.p.s.

(17) Unpublished work of E. L. Stogryn and M. H. Gianni.

maxima (neat) 3.20 (w), 3.38 (vs), 6.0 (vs), 6.10 (vs), 7.06 (vs), 8.30 (m), 8.60 (vs), 9.16 (m), 11.11 (m), and 13.62 (s) μ.

Anal. Calcd. for $C_8H_{13}N$ (V and VI): C, 78.05; N, 11.38. Found (V): C, 77.27; N, 10.72. Found (VI): C, 78.42; N, 11.17.

erythro-**3-Ethylamino-4-hydroxy-1,5-hexadiene (IIa).**—The *erythro*-amino alcohol IIa was obtained by dissolving II in 1.5 times its volume of pentane. This solution was cooled in a −50° bath until crystallization occurred. Without agitation, the temperature was brought to 0°. Filtration and recrystallization from pentane yielded the *erythro*-amino alcohol IIa as a white solid, m.p. 45–45.5°.

The proton spectrum of IIa, in CCl_4, showed N-ethyl multiplets centered at τ 8.93 and 7.43, a complex vinyl multiplet between 3.90 and 5.13, and O- and N-methinyl multiplets centered at 5.91 and 7.0, respectively. The position of the hydroxy and amino proton signals coincided with the N-methinyl resonance. The signal intensities were in accord with theory.

threo-**3-Ethylamino-4-hydroxy-1,5-hexadiene (IIb).**—The filtrates from IIa isolation were combined, repeatedly cooled, and filtered until crystallization failed to occur upon cooling. In this manner the *threo* isomer IIb, with a configurational purity of 90% (by n.m.r.[16]), was obtained as a colorless oil.

The n.m.r. spectrum of the *threo*-amino alcohol gave N-ethyl signals centered at τ 8.93 and 7.45, a vinyl multiplet between 3.86 and 5.11, and O- and N-methinyl signals at 5.91 and 7.10, respectively. The relative signal intensities agreed with expectations. Hydroxyl and –NH signals appeared as a broad singlet at τ 6.22.

erythro-**3-Ethylamino-4-hydroxy-1,5-hexadiene Hydrochloride (IIIa).**—Dry hydrogen chloride was bubbled into an ethereal solution of IIa until precipitation ceased. Filtration and recrystallization from isopropyl alcohol gave IIIa, m.p. 119–120°.

threo-**3-Ethylamino-4-hydroxy-1,5-hexadiene Hydrochloride (IIIb).**—In a similar manner IIb yielded, after recrystallization from toluene, IIIb, m.p. 99–101°.

erythro-**3-Ethylamino-4-hydroxy-1,5-hexadiene Sulfate Ester (IVa).**—By the procedure previously described IIIa was converted to IVa quantitatively. Washing the crude reaction mixture with isopropyl alcohol gave IVa as a white solid, m.p. 176–178° dec.

threo-**3-Ethylamino-4-hydroxy-1,5-hexadiene Sulfate Ester (IVb).**—In a like manner IVb was obtained from IIIb. IVb recrystallized from isopropyl alcohol as a white solid, m.p. 205–207° dec.

Ring Closure of IVa.—The sulfate ester IVa (5 g., 26.6 mmoles) dissolved in 20 ml. of water was added dropwise to 18 g. (226 mmoles) of a hot 50% NaOH solution. Steam distillation during the addition resulted in the isolation of 0.95 g. (34.1% yield) of a pale yellow oil. Gas chromatographic analysis of this oil showed the presence of *trans*-N-ethyl-2,3-divinylaziridine, free of the azepine VI.

If the temperature of ring closure was ambient and the time of reaction was 24 hr., ring closure gave a 50.2% yield of V.

Ring Closure of IVb.—Cyclization of IVb was carried out in the manner described for the ring closure of IVa. At either steam-distillation temperatures or at ambient temperatures for 18 hr. a 54% yield of a pale yellow oil was obtained. The composition of this oil was 89% N-ethyl-4,5-dihydroazepine and 11% *trans*-N-ethyl-2,3-divinylaziridine according to gas chromatographic and n.m.r. analysis.

Cyclopentene-1-carboxaldehyde-N-ethylimine (VII).—N-ethyl-4,5-dihydroazepine was heated at 100° for 1 hr. in the presence of a trace of moisture. Gas chromatographic analysis showed the presence of a new product VII.

The proton spectrum of VII disclosed a slightly broad singlet at τ 2.0 (—N=CH—), a vinyl multiplet at 3.97, a N-methylene quadruplet centered at 6.60, an allylic multiplet centered at 7.55, a ring methylene pentuplet centered at 8.05, and methyl resonance at 8.83.

Reaction of VII with 2,4-dinitrophenylhydrazine reagent yields the corresponding hydrazone, m.p. 205–207°. No depression occurred when the hydrazone of VII was mixed with the 2,4-dinitrophenylhydrazone of cyclopentene-1-carboxaldehyde.[18]

(18) H. J. Shine and R. H. Snyder, *J. Am. Chem. Soc.*, **80**, 3064 (1958).

Phosphonic Acids and Esters. VIII. Facile Hydrolytic Cleavage of Carbon–Phosphorus Bonds in Pyrrylphosphonates and Phosphine Oxides[1,2]

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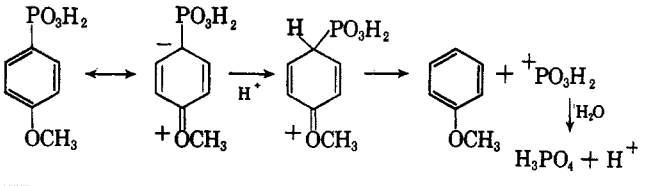
In contrast to the generally observed stability of the carbon–phosphorus bond of dialkyl arylphosphonates toward basic reagents, diethyl 2-pyrrylphosphonate undergoes a facile cleavage with the formation of pyrrole and 2-ethylpyrrole when treated with aqueous sodium hydroxide. Similar treatment of tri(2-pyrryl)phosphine oxide results in cleavage with the formation of pyrrole. The failure of the 1-methyl analogs to undergo cleavage under comparable conditions indicates that these degradations proceed by abstraction of the 1-proton of the pyrryl derivative, conversion of the resulting anion by protonation or alkylation to a pyrrolenine derivative, and collapse of the pyrrolenine to the observed products. The phosphonopyrroles polymerized in the presence of aqueous acid; evidence for the occurrence of electrophilic dephosphonations under these conditions was obtained.

In the great majority of arylphosphonic acids and their derivatives, the carbon–phosphorus bond is quite stable under hydrolytic conditions, resisting the action of both concentrated base and acid for extended periods of time.[4] However, in phosphonate structures which possess electron-donor groups (amino, dimethylamino, hydroxy, and methoxy) in *ortho* or *para* positions, this bond is cleaved readily by a variety of electrophilic reagents.[4] Lesfauries[5] has shown that *p*-anisylphosphonic acid is cleaved to anisole and phosphoric acid by the action of both hydrobromic and sulfuric acids and has postulated the following cleavage mechanism. In



(1) Part VII: M. Gordon, V. A. Notaro, and C. E. Griffin, *J. Am. Chem. Soc.*, **86**, 1898 (1964). A preliminary account of these results was given before the Symposium on Mechanisms of Reactions of Organophosphorus Compounds, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961.

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(3) (a) Taken in part from the M.S. Thesis of R. P. P., University of Pittsburgh, 1961; (b) National Science Foundation Undergraduate Research Participant, 1961–1962.

(4) For a summary of pertinent references, see L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957).

(5) P. Lesfauries, Dissertation, University of Paris, 1950, cited in ref. 4; M. P. Viout and P. Rumpf, *Compt. rend.*, **239**, 1291 (1954).