addition of ethyl acetate to afford 0.8 g (50%) of benz[a]indolizinium bromide (II, $R_1 = R_2 = R_3 = H$; $X = Br$) as the hemihydrate. The product had mp 207.5–209.5° after one recrystallization from absolute ethanol: nmr (CF_3COOH), δ 6.06 (s, 2, CH_2) and >7.5 (m, 8, aromatic).

When 10% hydrobromic acid was used as the solvent in the irradiation, the use of decolorizing charcoal was unnecessary and 1.18 g (75%) of the indolizinium salt (II, $R_1 = R_2 = R_3 = H$; $X = Br$) was isolated after an irradiation period of 8 hr.

Preparation of Bases. *E.g.*, **Pyrido[2,1-*a*]isoindole (III, $R_1 = R_2 = R_3 = H$).**—Pyrido[2,1-*a*]isoindolium bromide (1.0 g) dissolved in water (5 ml) was treated with saturated aqueous sodium carbonate solution until no further precipitation occurred. The precipitate was collected and dried under vacuum at room temperature to afford 0.73 g (100%) of a yellow solid. This could be recrystallized, with difficulty, from ethanol as yellow-green needles, mp 225° (charring above 205°). The product could also be purified by sublimation at 110° under reduced pressure.

The base (III, $R_1 = R_2 = R_3 = H$) dissolved when treated with 10% hydrobromic acid to give a solution which had the same ultraviolet spectrum as pyrido[2,1-*a*]isoindolium bromide (II, $R_1 = R_2 = R_3 = H$; $X = Br$). This solution was evaporated to dryness, the residue was dissolved in a minimum quantity of ethanol, and ethyl acetate was added to precipitate the salt (II, $R_1 = R_2 = R_3 = H$; $X = Br$).

Irradiation of N-benzyl-2-fluoropyridinium Bromide (IV, $R_1 = R_2 = R_3 = H$; $X = F$).—The quaternary salt (1.5 g) in water (430 ml) was irradiated, as previously described, for 6 hr. During this period, the dimer of N-benzyl-2-pyridone was precipitated. The precipitate was collected (0.3 g, 20%) and recrystallized from dimethyl formamide–ethanol to afford colorless plates, mp 215–216°, ν_{max}^{Nujol} 1670 cm^{-1} (amide C=O).

Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 76.80; H, 5.99; N, 7.56. Found: C, 77.16; H, 6.05; N, 7.68.

Dimerization of N-Benzyl-2-pyridone.[10]—N-Benzyl-2-pyridone (2.0 g, obtained by addition of saturated aqueous sodium carbonate solution to an aqueous solution of N-benzyl-2-bromopyridinium bromide) in 95% ethanol (430 ml) was irradiated for 2 days. The dimer which precipitated (0.6 g, 30%) was collected and recrystallized from dimethylformamide–ethanol to yield colorless plates, mp 215–218°. This product had identical physical and spectral characteristics with those of the product from irradiation of the 2-fluoropyridinium salt (IV, $R_1 = R_2 = R_3 = H$; $X = F$). The nmr spectrum of the dimer in trifluoroacetic acid showed four olefinic protons as two sets of multiplets centered at 403 and 376 cps. These had exactly the same splitting pattern as those of the dimer of N-methyl-2-pyridone.[10]

2-Bromo-N-(1′-naphthylmethyl)pyridinium Bromide.—2-Bromopyridine (7.9 g) and 1-bromomethylnaphthalene (11.1 g) in sulfolane (15 ml) were heated at 45° for 18 hr. The precipitated solid was suspended in ether, collected, and then recrystallized from ethanol–ethyl acetate to afford 12.1 g (65%) of colorless plates, mp 158.5°, $\lambda_{max}^{95\%\ EtOH}$ 278 mμ (log ϵ 4.11).

Anal. Calcd for $C_{16}H_{13}Br_2N$: C, 50.68; H, 3.46; N, 3.69. Found: C, 50.87; H, 3.46; N, 3.78.

Irradiation of 2-Bromo-N-(1′-naphthylmethyl)pyridinium Bromide.—The quaternary salt (2.0 g) in water (430 ml) was irradiated for 7 hr, during which the solution's ultraviolet spectrum showed a shift from a single maximum at 278 mμ to maxima at 272 and 375 mμ. Aqueous perchloric acid (25%) was then added to precipitate a crude perchlorate (1.05 g). After two recrystallizations from acetonitrile–ethanol, a product (VI or VII) was obtained (0.4 g, 18%), as yellow-green rhombs, mp 178–180.5°, $\lambda_{max}^{95\%\ EtOH}$ 272 and 375 mμ (log ϵ 3.92 and 3.92).

Anal. Calcd for $C_{16}H_{12}ClNO_4 \cdot 0.5H_2O$: C, 53.15; H, 3.60; N, 3.34. Found: C, 52.95; H, 3.71; N, 3.22.

The nmr spectrum of this compound in trifluoroacetic acid, showed a collection of protons between δ 8.77 and 7.45, weight of 10 (aromatic protons), and a singlet at 6.06, weight of 2 (methylene protons).

Registry No.—IIa, 13160-91-3; IIb, 13160-95-7; IIc, 13584-39-9; IId, 13584-40-2; IIe, 13584-41-3; IIf, 13584-42-4; IIIa, 245-30-7; IIIb, 13584-44-6; IIIc, 13584-45-7; IIId, 13584-46-8; IIIe, 13584-47-9; IVa, 13612-72-1; IVb, 13160-94-6; IVc, 13612-74-3; IVd, 13612-75-4; IVe, 13639-79-7; IVf, 13639-80-0; IVg, 13612-76-5; IVh, 13639-81-1; VI, 13612-77-6; VII, 13584-48-0; 2-bromo-N-(1′-naphthylmethyl)pyridinium bromide, 13584-49-1; dimer of N-benzyl-2-pyridone, 13573-31-4.

Pyrolysis Products of Cycloalkano[*a*]pyrroles

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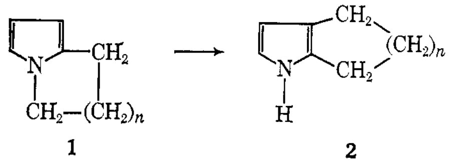
A reinvestigation of the pyrolysis of cycloheptano- and cyclohexano[*a*]pyrrole has shown that the major rearrangement products at 600° are the corresponding cycloalkano[*b*]pyrroles rather than those previously reported. Cyclopentano[*a*]pyrrole at 600° yields only 9% of the cyclopentano[*b*]pyrrole. At 650° cyclopentano[*a*]pyrrole produces primarily the isomeric 2- and 3-methylpyrroles, pyridine, 2-ethylpyridine, and 2-vinylpyridine.

Since the pyrolysis of N-substituted pyrroles, where the substituent is alkyl,[1] benzyl,[2,3] and phenyl,[4] invariably leads to the production of a mixture of 2 and 3 isomers and since the presence of a 3-substituted pyrrole had not been reported in the pyrolysis products of cycloalkano[*a*]pyrroles,[5] we decided to reinvestigate the pyrolysis of these compounds. In addition, two of the structures proposed for some of the products, *i.e.*, 9-azabicyclo[4.2.1]nona-1,3,5-triene and 10-azabicyclo[5.2.1]deca-1,3,5-triene, were highly strained and therefore open to question. In view of the facile formation of 3 isomers, the most probable rearrangement products should be the cycloalkano[*b*]pyrroles (**2**).



a, $n = 1$
b, $n = 2$
c, $n = 3$

The cycloalkano[*a*]pyrroles were pyrolyzed at several temperatures and the product compositions were determined. The results, given in Table I, confirm the

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[1] (a) I. A. Jacobson, Jr., H. H. Heady, and G. V. Dinneen, *J. Phys. Chem.*, **62**, 1563 (1958); (b) I. A. Jacobson, Jr., and H. B. Jensen, *ibid.*, **66**, 1245 (1962); (c) I. A. Jacobson, Jr., and H. B. Jensen, *ibid.*, **68**, 3068 (1964).

[2] L. A. Pine, *Dissertation Abstr.*, **24**, 522 (1963).

[3] J. M. Patterson and L. T. Burka, *J. Am. Chem. Soc.*, **88**, 3671 (1966).

[4] J. M. Patterson, unpublished results.

[5] J. M. Patterson, J. Brasch, and P. Drenchko, *J. Org. Chem.*, **27**, 1652 (1962).

TABLE I

PYROLYSIS PRODUCTS OF THE CYCLOALKANO[*a*]PYRROLES (1)

Cycloalkano[*a*]-pyrrole	Pyrolysis temp, °C	Recovered starting material, %	Cycloalkano[*b*]-pyrrole (2), %	Indole, %	Other components (minor) (%)
1a	600	90	9	...	Mixture[a] (1)
	625	85	11	...	Mixture[a] (4)
	650	40	13	2	Mixture[b]
1b	550	60	40	...	...
	575	35	57	...	1 unidentified (minor)
	590	18	75	Trace	4[a]
	600	15	62	3	6 unidentified
	625	10	35	14	10 unidentified
	650	9	11	13	14 unidentified
1c	600	25	51	...	10 unidentified (2–3 each)
	650	24	23	...	12 unidentified (4–5 each)

[a] Glpc retention times of two corresponded to pyridine and isomeric methylpyrroles. [b] Components were 2- and 3-methylpyrrole (21%), α-picoline (1%), pyridine (11%), 2-ethylpyridine (4%), and 2-vinylpyridine (4%).

expectation that the cycloalkano[*b*]pyrroles are the major rearrangement products.

The structures of the cycloalkano[*b*]pyrroles are based upon elemental analysis, spectroscopic evidence, and the production of known azabicycloalkanes on catalytic hydrogenation. The nuclear magnetic resonance (nmr) spectra show two pyrrole-ring hydrogens (chemical shifts fall in ranges of 5.65–5.72 and 6.20–6.34 ppm for the 4 and 5 protons, respectively) and an N–H hydrogen (*ca.* 7.1 ppm). The chemical shifts correspond well to those reported[6] for 2,3-dimethylpyrrole (4 proton, 5.72; 5 proton, 6.19; N proton, 7.1 ppm). For comparison, the cycloalkano[*a*]pyrroles showed three pyrrole-ring hydrogens (3 proton, 5.54–5.68; 4 proton, 5.68–5.92; 5 proton, 6.25–6.27 ppm) which fall in the range of those reported[6] for 1,2-dimethylpyrrole (3 proton, 5.67; 4 proton, 5.77; 5 proton 6.30 ppm). Infrared absorption by the cycloalkano[*b*]pyrroles at 3450 cm^{-1} verifies the presence of an N–H bond. The structures of other components in the pyrolysates are based upon comparisons of gas–liquid partition chromatography (glpc) retention times, infrared and nmr spectra, and physical properties of the components with those obtained from authentic samples.

While pyrolyses of cyclohexano[*a*]pyrrole (5,6,7,8-tetrahydroindolizine) at 550–600° produced only cyclohexano[*b*]pyrrole (4,5,6,7-tetrahydroindole) and recovered starting material, it had been reported[5] that these products were azabicyclo[4.2.1]nona-1,3,5-triene and 2-(butenyl)pyrrole. Identification of the 2-(butenyl)pyrrole was based upon the physical properties of the reduction product, 2-(butyl)pyrrolidine, and its picrate. It has been found, in the present experiments, that the reduction products of cyclohexano[*b*]pyrrole and indole possessed properties (boiling points and picrate melting points) which were identical with those previously reported[5] for the 2-(butyl)pyrrolidine. The nmr spectrum of the pyrrole, however, confirms the cyclohexano[*b*]pyrrole structure. In addition, the reduction products of cyclohexano[*b*]pyrrole and indole exhibited identical infrared and nmr spectra.

The azabicyclononatriene structure was based upon its conversion (through hydrogenation and methylation) to a substance believed to be homotropane.[5] We have not been able to reproduce material with the properties previously reported for the homotropane when either cyclohexano[*a*]pyrrole or cyclohexane[*b*]pyrrole were subjected to the same experimental conditions. Furthermore, it has been found that the reduction product of starting material, cyclohexano[*a*]pyrrole, produced a picrate with a melting point (228–229°) similar to that reported[5] (mp 228°) for the reduction product of azabicyclononatriene. Also, the recovered cycloalkano[*a*]pyrroles from the present experiments contained an impurity which showed absorption at *ca.* 3350 cm^{-1} and which could not be removed by fractional distillation. It could be removed by preparative glpc if the collection port was cleaned between fractions. In view of the above observations, it is concluded that the azabicyclononatriene structure is in error and that the substance was impure starting material.

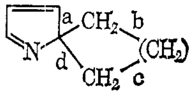
Cycloheptano[*a*]pyrrole (6,7,8,9-tetrahydro-5H-pyrrolo[1,2-*a*]azepine), previously reported[5] to give 2-(pentenyl)pyrrole and azabicyclo[5.2.1]deca-1,3,5-triene on pyrolysis, produced only cycloheptano[*b*]pyrrole (1,4,5,6,7,8-hexahydrocyclohepta[*b*]pyrrole) and recovered starting material as the major products in the present experiments. Since the recovered starting material contained an impurity absorbing at *ca.* 3350 cm^{-1}, and since the picrate of starting material reduction product (mp 217–218°) corresponded rather closely to that reported[5] for the azabicyclodecatriene reduction product (mp 216°), it is concluded that the substance previously assigned the azabicyclodecatriene structure was probably impure starting material.

The properties of the 2-(pentenyl)pyrrole previously reported[5] do not correspond to those obtained for cycloheptano[*b*]pyrrole (mp 48° and 104°, respectively). However, there is no doubt that in the present experiments cycloheptano[*b*]pyrrole is the major pyrolysis product. The experiments herein described were carried out under the conditions previously reported and a search was made for the 1-(pentenyl)pyrrole. This compound was not found and the authors have no explanation for its absence.

The composition of the cyclopentano[*a*]pyrrole (2,3-dihydro-1H-pyrrolizine) pyrolysate was investigated in greater detail than previously described. It is to be noted that reaction occurs only with difficulty when compared with that of the other cycloalkano[*a*]pyrroles, that greater quantities of decomposition products are obtained including methane and ethene, and that the pyridines produced by ring enlargement

(6) R. L. Hinman and S. Theodoropulos, *J. Org. Chem.*, **28**, 3052 (1963).

are the 2-substituted compounds. These observations are in accord with the postulate that the pyrrolenine[7] **3**



3

is an intermediate in the isomerization of the cycloalkano[*a*]pyrroles. The cycloalkano[*b*]pyrroles arise from the precursors produced on cleavage of bonds a or d in the intermediate when *n* is 1, 2, or 3. The low yield of cyclopentano[*b*]pyrrole (1,4,5,6-tetrahydrocyclopenta[*b*]pyrrole) relative to the yields of the other cycloalkano[*b*]pyrroles lends support to the proposed pyrrolenine **3** since the strained ring system in the pyrrolenine ($n = 1$) should make it the least easily attainable intermediate in the cycloalkano[*a*]pyrrole series.

Further evidence for the proposed intermediate ($n = 1$) comes from the composition of the ring-enlargement and decomposition products obtained during the pyrolysis of cyclopentano[*a*]pyrrole. While the ring-enlargement products usually observed during the isomerization of N-substituted pyrroles are the 3-substituted pyridines,[2,8] only 2-substituted pyridines were produced in the cyclopentano[*a*]pyrrole pyrolyses. Cleavage of each of the bonds in the highly strained four-membered ring leads to precursors of the observed products. Cleavage at bonds a or d gives the precursors of cyclopentano[*b*]pyrrole; cleavage at bonds bd or ac gives the precursors of the isomeric C-methylpyrroles, pyridine and ethene; cleavage at bonds bc gives the precursors of α-picoline and methane; and cleavage at bond b or bond c gives the precursor of 2-vinylpyridine and 2-ethylpyridine.

Experimental Section

Melting points were taken on a Fisher-Johns melting point block and are uncorrected. Boiling points are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 21 or on a Beckman IR-8 spectrophotometer; ultraviolet spectra were measured on a Perkin-Elmer Model 202 spectrophotometer; and nmr spectra were obtained on a Varian Associates HA-60-IL spectrometer in carbon tetrachloride solutions (*ca.* 10%) using tetramethylsilane (TMS) as an internal standard ($\delta = 0$). Gas chromatographic analyses and separations were made on an Aerograph Model A-700 gas chromatograph using either a 20 or 30% SE-30 column. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Cycloalkano[*a*]pyrroles.—The cycloalkano[*a*]pyrroles were synthesized from the corresponding furylalkylamine by cyclodehydration over alumina as previously described.[5]

Cyclopentano[*a*]pyrrole.—From furylpropylamine there was obtained a 50% yield of compound: bp 62–63° (11 mm); n^{25}D 1.5270; nmr spectrum (δ), 2.48 (multiplet, 4 H), 3.73 (triplet, 2 H), 5.92 (triplet, 1 H), 5.54 (multiplet, 1 H), 6.25 ppm (quartet, 1 H) [lit.[9] bp 70° (20 mm); n^{25}D 1.5267].

Cyclohexano[*a*]pyrrole.—The compound was obtained from furylbutylamine (60% yield): bp 85° (12 mm); n^{21}D 1.5320; nmr spectrum, 1.80 (multiplet, 4 H), 2.70 (triplet, 2 H), 3.80 (triplet, 2 H), 5.60 (multiplet, 1 H), 5.83 (triplet, 1 H), 6.25 ppm (triplet, 1 H) [lit.[5] bp 88–96° (14 mm); n^{25}D 1.5294].

Cycloheptano[*a*]pyrrole.—A 20% yield of the pyrrole was obtained from furylpentylamine: bp 89–90° (10 mm); mp 36° (light yellow solid); nmr spectrum, 1.70 (multiplet, 6 H), 2.68 (doublet, 2 H) 3.86 (doublet, 2 H), 5.68 (multiplet, 2 H), 6.27 ppm (triplet, 1 H) [lit.[5] bp 89–93° (10 mm); mp 36].

Pyrolysis of the Cycloalkano[*a*]pyrroles.—The pyrolyses were carried out in the apparatus previously described.[10]

Cycloheptano[*a*]pyrrole.—Five grams of the pyrrole, kept molten by a heat lamp, was injected into the pyrolysis tube at a rate of 4.5 g/hr and swept through the tube with nitrogen (120 ml/min). There was obtained 4.5 g of pyrolysate (90% recovery) from which 1.2 g of cycloheptano[*b*]pyrrole separated on cooling. Analysis and separation of the volatile pyrolysate by gas chromatography using a 20 ft × ³/₈ in. 30% SE-30 column at 150° showed two major components: starting material (*ca.* 25% and cycloheptano[*b*]pyrrole (*ca.* 50% yield including material which crystallized on cooling)). The identity of the starting material in pyrolysate was established by identical melting points, glpc retention times, and infrared and nmr spectra. The cycloheptano[*b*]pyrrole after recrystallization from carbon tetrachloride gave the following properties: mp 104°; $\nu_{\mathrm{CCl_4}}$ 3400–3450 cm^{-1} (pyrrole N–H); $\lambda_{\max}^{\mathrm{MeOH}}$ 221 mμ (ε 6350); nmr spectrum, 1.73 (multiplet, 6 H), 2.55 (multiplet, 4 H), 5.72 (triplet, 1 H), 6.19 (triplet, 1 H), 7.1 ppm (broad, 1 H).

Anal. Calcd for $C_9H_{13}N$: C, 79.97; H, 9.65; N, 10.38. Found: C, 79.89; H, 9.40; N, 10.40.

Cycloheptano-2,3-pyrrolidine.—Cycloheptano[*b*]pyrrole (0.5 g) was reduced in glacial acetic acid using a 5% rhodium–alumina catalyst (0.05 g) and an initial hydrogen pressure of 50 psi. After the catalyst was removed by filtration, the filtrate was poured into water, made strongly alkaline, and extracted with ether. The amine was obtained from the ether extract (after drying with sodium carbonate and distillation of the ether) by preparative glpc using a 5 ft × ¹/₄ in. 20% SE-30 column at 130°. The amine was a colorless liquid with an aminelike odor, n^{20}D 1.4918, ν_{neat} 3280 cm^{-1} (medium) (lit.[11] n^{20}D 1.4919). The amine formed a picrate which after recrystallization from ethanol–ether melted at 120° (lit.[11] mp 120–121°).

Anal. Calcd for $C_{15}H_{20}N_4O_7$: C, 48.91; H, 5.46; N, 15.18. Found: C, 48.57; H, 5.81; N, 15.15.

Cyclohexano[*a*]pyrrole.—At a rate of 4.5 g/hr, 9.5 g of cyclohexano[*a*]pyrrole was introduced into the pyrolysis tube, heated to 590°, and swept through the hot zone by nitrogen (120 ml/min). The major components were isolated by fractional distillation at 12 mm followed by preparative glpc. The isolated cyclohexano[*a*]pyrrole exhibited refractive index, nmr spectrum, and infrared spectrum which were identical with those obtained from starting material. Cyclohexano[*b*]pyrrole was a yellow liquid, bp 98° (10 mm), n^{20}D 1.5420, which solidified on standing. Recrystallization from Skellysolve A gave colorless crystals: mp 55°; $\nu_{\mathrm{CCl_4}}$ 3450 cm^{-1}; $\lambda_{\max}^{\mathrm{MeOH}}$ 219 mμ (broad) (ε 7500); nmr spectrum 1.69 (multiplet, 4 H), 2.40 (multiplet, 4 H) 5.65 (triplet, 1 H), 6.20 (triplet, 1 H), and 7.1 ppm (broad, 1 H).

Anal. Calcd for $C_8H_{11}N$: C, 79.30; H, 9.12; N, 11.58. Found: C, 79.42; H, 9.15; N, 11.59.

Octahydroindole from Cyclohexano[*b*]pyrrole.—Cyclohexano-[*b*]pyrrole (1 g) was reduced in glacial acetic acid using a platinum oxide catalyst (0.025 g) and an initial hydrogen pressure of 59 psi. The reaction mixture was worked up as described in the reduction of cycloheptano[*b*]pyrrole to give a yellow oil which on distillation produced a colorless liquid, bp 78° (18 mm), n^{22}D 1.4886, ν_{neat} 3275 cm^{-1} [lit.[12] bp 65° (12 mm), n^{20}D 1.4892]. The amine formed a picrate, mp 137° (lit.[12] mp 137–138°). An authentic sample of octahydroindole was prepared by the hydrogenation of indole using the conditions above. This compound and the reduction product of cyclohexano[*b*]pyrrole exhibited identical glpc retention times and infrared spectra.

In another experiment at 650°, indole was isolated by fractional distillation and preparative glpc. The substance thus isolated exhibited properties (*i.e.*, melting point, glpc retention time, nmr spectrum, and infrared spectrum) which were identical with those obtained from authentic indole.

The yield of major components was studied as a function of pyrolysis temperture. The results are reported in Table I.

Cyclopentano[*a*]pyrrole.—Product composition of the cyclopentano[*a*]pyrrole pyrolysate was studied as a function of temperature. Pyrolyses were carried out as described for the other cycloalkano[*a*]pyrroles. (See Table I.)

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[7] A pyrrolenine-type intermediate was also proposed by Pine[2] in the isomerization of N-benzylpyrrole.

[8] A. Pictet, *Ber.*, **38**, 1946 (1905).

[9] E. E. Schweizer and K. K. Light, *J. Org. Chem.*, **31**, 875 (1966).

[10] J. M. Patterson and P. Drenchko, *ibid.*, **27**, 1650 (1962).

[11] V. Prelog and U. Geyer, *Helv. Chim. Acta*, **28**, 576 (1945).

[12] R. Wilstatter and D. Jaquet, *Ber.*, **51**, 767 (1918).

Cyclopentano[*b*]pyrrole could be isolated most readily from pyrolysate produced at 600° and at an addition rate of 7.5 ml/hr. From 20 g of cyclopentano[*a*]pyrrole, there was obtained 2 g of a greenish yellow liquid: bp 67° (5 mm); 99.8% pure based on glpc; ν_{CCl_4} 3450 cm^{-1}; λ_{max}^{MeOH} 211 and 229 mμ (sh); nmr spectrum, 2.47 (multiplet, 6 H), 5.70 (triplet, 1 H) 6.34 (triplet, 1 H), and *ca.* 7.2 ppm (broad, 1 H).

Anal. Calcd for C_7H_9N: C, 78.46; H, 8.46; N, 13.08. Found: C, 78.65; H, 8.20; N, 13.27.

***cis*-Cyclopentano-2,3-pyrrolidine from Cyclopentano[*b*]pyrrole.**—Hydrogenation and work-up was the same as that described for reduction of the pyrroles above. The colorless liquid product was converted into the picrate and the picrate was recrystallized from ethanol: mp 110° (lit.[13] mp 111°).

Pyrolysis of Cyclopentano[*a*]pyrrole at 650°.—From 22.5 g of cyclopentano[*a*]pyrrole introduced at a rate of 4.5 ml/hr (nitrogen flow, 120 ml/min) there was obtained 19.8 g (87% recovery) of crude pyrolysate which was dissolved in ether and extracted with cold 5% hydrochloric acid. The ether solution was dried over magnesium sulfate and the ether was removed by distillation leaving 15.5 g of neutral components. The hydrochloric acid solution was made strongly alkaline and extracted with ether, and the ether extract was dried over sodium carbonate. Removal of the drying agent and ether left 3.5 g of basic components.

The major components of the neutral fraction were separated by fractional distillation and preparative glpc using a 10 ft × $^3/_8$ in. 30% SE-30 column at 190°.

2- and 3-Methylpyrrole.—The glpc retention time was identical with that of 2-methylpyrrole. The infrared spectrum was essentially identical with that of 2-methylpyrrole except for a strong absorption at 1065 cm^{-1} which is characteristic of 3-methylpyrrole.[1a] The nmr spectrum was consistent for a mixture of 2- and 3-methylpyrrole and showed methyl hydrogen peaks at 2.05 and 2.15 ppm which correspond to 3- and 2-methylpyrrole, respectively.[6]

Cyclopentano[*a*]pyrrole.—Properties including glpc retention time and infrared and nmr spectra were identical with those obtained from an authentic sample.

Cyclopentano[*b*]pyrrole.—Properties were identical with those obtained in the pyrolysis at 600°.

Indole.—Obtained as a yellow liquid which solidified and was recrystallized from Skellysolve A: mp 48–49°. The infrared and nmr spectra were identical with those obtained from an authentic sample.

Analysis of the basic fraction by glpc using a 6 ft × $^3/_8$ in. 20% SF-96 column at 90° showed the following four components (separated by preparative glpc): pyridine (50%), glpc retention time and infrared and nmr spectra were identical with those obtained from an authentic sample; α-picoline (8%), glpc retention time, infrared spectrum, and picrate melting point were identical with those obtained from an authentic sample; 2-ethylpyridine (21%), glpc retention time and infrared and nmr spectra were identical with those obtained from an authentic sample, picrate mp 103–105° (lit.[14] mp 107°); 2-vinylpyridine (21%), infrared spectrum identical with that obtained from an authentic sample, picrate mp 156–157° (lit.[15] mp 157–158.3°).

Anal. Calcd for $C_{13}H_{10}N_4O_7$: C, 46.72; H, 2.99; N, 16.75. Found: C, 46.56; H, 2.99; N, 16.57.

Gases formed during the 650° pyrolysis were passed into a 10-cm gas cell (after drying over Drierite and Ascarite) and the infrared spectrum was measured. The spectrum showed multiple absorbance at 1200–1400 with the main peak at 1306 cm^{-1} (lit.[16a] methane main peak at 1306 cm^{-1}) and at 800–1100 with the main peak at 950 cm^{-1} (lit.[16b] ethene main peak 949 cm^{-1}). Spectra of authentic methane and ethene accounted for all of the bands observed in the pyrolysis gas spectrum.

Cycloheptano-1,2-pyrrolidine.—Cycloheptano[*a*]pyrrole was reduced by the method described for cycloheptano[*b*]pyrrole and worked up similarly. The product was purified by preparative glpc using a 5 × $^1/_4$ in. 20% SE-30 column at 125°. The amine, a colorless liquid, $n^{20}D$ 1.4819, was converted into the picrate, mp 217–218° (lit.[17] $n^{20}D$ 1.4822, picrate mp 214–215°).

Cyclohexano-1,2-pyrrolidine.—The reduction procedure above gave a colorless liquid, bp 152°, $n^{22}D$ 1.4685, on reduction of cyclohexano[*a*]pyrrole. The picrate of the amine melted at 228–229° [lit.[17] $n^{20}D$ 1.4711, picrate mp 233–234°, bp 66–67° (18 mm)].

Registry No.—**1a**, 13618-87-6; **1b**, 13618-88-7; **1c**, 13618-89-8; **2a**, 13618-90-1; **2b**, 13618-91-2; **2c**, 13618-92-3; cyclohexano-1,2-pyrrolidine, 13618-93-4; cycloheptano-1,2-pyrrolidine, 5715-05-9; cycloheptano-2,3-pyrrolidine, 7140-62-7.

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Cyclization of 1-Alkylamino-3-halo-2-alkanols to 1-Alkyl-3-azetidinols

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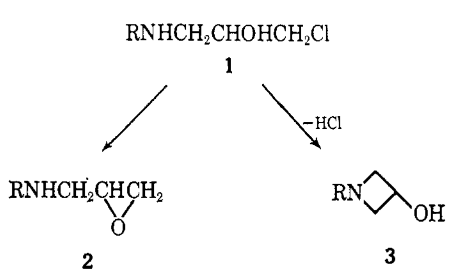
A two-step synthesis of 1-alkyl-3-azetidinols from primary alkylamines and epihalohydrins is described. 1-Alkylamino-3-chloro-2-alkanols carrying tertiary, secondary, and hindering primary N-alkyl groups cyclized spontaneously in up to 78% yields, optimally at about 50°. *n*-Alkyl or aryl groups did not provide sufficient hindrance or nucleophilicity. 1-*t*-Alkylamino-3-chloro-2-propyl acetates cyclized sluggishly and in lower yields than the propanols. The results were attributed to steric interaction of the N-alkyl and acetoxyl groups in the transition state.



Recently we described the conversion of unstable 1-alkylamino-3-chloro-2-propanols (**1**) to surprisingly stable N-alkyl-2,3-epoxypropylamines (**2**).[1] Storage of **1** resulted in diminished yields of **2** upon dehydrohalogenation. Subsequently, higher boiling oils were isolated; they have now been shown to contain new 1-alkyl-3-azetidinols (**3**).[2] This synthesis—the simplest and most direct method available for any azetidine—has been studied to determine the effects of structure and reaction conditions. The results suggest that any primary alkylamine which is at least moderately hindered may be converted to the azetidinol in useful

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