The pyrolysis products (9.6 g. from 11.2 g. of 2-methylpyrrole) from three experiments using 2-methylpyrrole (two carried out at 650°, one at 745°) were combined and separated as described previously. Prior to separation, gas chromatographic analysis showed 53% 2-methylpyrrole, 14.5% pyridine, and 13% pyrrole. The acid-insoluble fraction produced on distillation 0.3 g. (3%) pyrrole, b.p. 127–130°, $n^{25}\text{D}$ 1.5030; and 3.61 g. (33%) of 2-methylpyrrole, b.p. 140–144°, $n^{25}\text{D}$ 1.4998. The infrared spectra of the fractions were identical to those obtained from authentic samples of pyrrole and 2-methylpyrrole, respectively. The 2-methylpyrrole was also converted to the dioxime by the procedure of Janssen,[9] m.p. 67–68°, reported m.p. 69°.

The acid-soluble fraction was converted to the picrate which after several recrystallizations from 95% ethanol weighed 4.01 g. [equivalent to 1.04 g. (9%) pyridine], m.p. 145–163°. The picrate from an authentic sample of pyridine melted over the same range.

Pyrolysis of *N*-Methylpyrrole at 745°.—The sample was added to the reaction tube at such a rate that the average contact time was 1.9 sec. The relative concentrations (wt. %) of the major components in the volatile liquid product (gas chromatographic analysis) were *N*-methylpyrrole, 1.1%; 2-methylpyrrole, 7.2%; pyridine, 54%; and pyrrole, 31%.

The pyrolysis products from several experiments were combined (12 g. obtained from 14.8 g. of *N*-methylpyrrole) and separated chemically. Distillation of the acid-insoluble fraction produced pyrrole (1.8 g., 15%), b.p. 128–132° $n^{25}\text{D}$ 1.5010. The infrared spectrum of the pyrrole was identical to that obtained from an authentic sample. The acid soluble fraction was converted into the picrate, which after several recrystallizations weighed 12.0 g. (equivalent to 3.04 g., 21% pyridine), m.p. 145–163°. Authentic pyridine picrate melts over the same range. The picrate was converted into the methylpyridinium *p*-toluenesulfonate, m.p. 138–140°, (reported,[10] m.p. 139°).

Pyrolysis of 2-Methylpyrrole at 745°.—The contact time of the pyrolyzed sample was 1.8 sec. The relative concentrations of the major components in the volatile liquid pyrolysate were 2-methylpyrrole, 9.06%; pyridine, 49%; and pyrrole, 34%.

In another experiment, the crude pyrolysis product was distilled and the distillate analyzed by gas chromatography. The yields of products (based on moles of starting material) were pyridine, 26%, and pyrrole, 12%.

Acknowledgment.—This investigation was sponsored by the Office of Ordnance Research U. S. Army.

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[9] R. G. Janssen, E. R. Schiers, R. Van Meter, and J. S. Ball, *J. Am. Chem. Soc.*, **73**, 4040 (1951).

[10] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., Wiley & Sons, Inc., New York, 1948, p. 242.

Synthesis and Pyrolysis of Some Cycloalkano[*a*]pyrroles[1]

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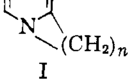
Cyclopentano[*a*]pyrrole, cyclohexano[*a*]pyrrole, and cycloheptano[*a*]pyrrole were synthesized by two reaction paths, pyrolyzed, and the major volatile pyrolysis products identified. Cyclopentano[*a*]pyrrole produced primarily 2-methylpyrrole and pyridine while cyclohexano[*a*]pyrrole was converted into (2-pyrryl)butene and the 2,5-bridged pyrrole compound, 9-azabicyclo[4.2.1]nona-1,3,5-triene. Cycloheptano[*a*]pyrrole, on pyrolysis was converted to the analogous compounds, 1-(2-pyrryl)-1-pentene and, most likely, 10-azabicyclo[5.2.1]deca-1,3,5-triene. The 2,5-bridged pyrrole compounds require that the nitrogen atom be bent out of the plane of the pyrrole ring. Spectral evidence is presented which supports this out-of-plane bending.

The pyrolysis of *N*-substituted pyrroles over the temperature range 475–745° produces the 2-substituted pyrrole and pyridine.[2,3] The research reported here involves an examination of the behavior of some cycloalkanopyrroles (I) under pyrogenic conditions which result in rearrangement.

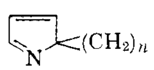


$n = 3, 4, 5$

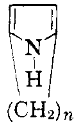
I

Possible rearrangement products (not involving decomposition) are:

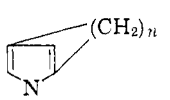
II



III



IV



V

The objectives of the research are threefold: the determination of the effect of ring size on the nature of the rearrangement products; the evaluation of the pyrolysis reaction as a synthetic route to II, III, and IV; and the elucidation of the reaction mechanism.

Discussion and Results

Two routes were utilized in the synthesis of the cycloalkano[*a*]pyrroles. The first, an extension of the experiments of Sorm and Arnold,[4] involved the

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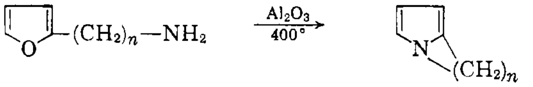
[1] Abstracted from the Ph.D. dissertations of Peter Drenchko, University of Kentucky, 1958, and of Jay Brasch, University of Kentucky, 1961.

[2] I. A. Jacobson, Jr., H. H. Heady, and G. U. Dinneen, *J. Phys. Chem.*, **62**, 1563 (1958) and references contained therein.

[3] J. M. Patterson and P. Drenchko, *J. Org. Chem.*, **27**, 1650 (1962).

[4] F. Sorm and E. Arnold, *Collection Czechoslov. Chem. Communs.*, **12**, 467 (1947).

cyclodehydration of the appropriate furylalkylamine over alumina at 400°.

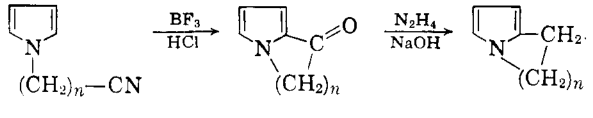


The size of the ring system fused to the pyrrole molecule influences the yield of product as expected. Thus the five-, six-, and seven-membered fused-ring compounds are formed in 43, 62, and 14% yields, respectively. The low yields observed in the formation of cycloheptano[a]pyrrole from furylpentylamine are not entirely due to the difficulty in closing the seven-membered ring.

Two other major products (14% yield each), in addition to the cycloheptano[a]pyrrole, were isolated and traces of pyrrole, *N*-methylpyrrole, and 2-methylpyrrole were identified by their gas chromatographic retention times. One of the products appears to be an *N*-substituted pyrrole (infrared spectrum) while the other is a blue oil which becomes greenish yellow when hot or on standing in a vacuum after several months. The blue compound contains a pyrrole ring (infrared spectrum) with a free N—H (3375 cm.$^{-1}$ S.) and perhaps a double bond (1620 cm.$^{-1}$), which on the basis of the ultraviolet spectrum is not conjugated with the pyrrole ring system. A molecular weight determination indicated that the substance was isomeric to cycloheptano[a]pyrrole. The passage of cycloheptano[a]pyrrole over alumina at 400° produced the blue compound in about 30% yield.

Cycloheptano[a]pyrrole could be purified chromatographically using diatomaceous earth as the absorbent; alumina caused decomposition.

The second route involved a modification of the internal Houben-Hoesch reaction used by Clemo and Ramage[5] followed by a Wolff-Kishner reduction of the ketone. The appropriate *N*-cyanoalkylpyrrole was treated with hydrogen chloride in the presence of a boron trifluoride-etherate catalyst.



The yields of cyclic ketone are also dependent on the size of the fused-ring system. Thus the five-, six-, and seven-membered ring systems are formed in 33, 59, and 31% yields, respectively.

The infrared and ultraviolet spectral properties of the cyclic ketones and the effect of ring size on these properties have been reported previously.[6]

The furylalkylamines, used in the cyclodehydration reaction, were synthesized from furfural or furylacrolein.

Furylacrylonitrile,[7] obtained from the condensation of furfural with cyanoacetic acid, was reduced to the furylpropylamine using a Raney nickel catalyst.

An extension of this procedure to furylacrolein afforded the furylpentadienenitrile, which was hydrogenated over Raney nickel to furylpentylamine. The decarboxylation proceeded with difficulty, yielding 60% of product after a five-day heating period Time could be saved by isolating the 2-cyano-5-(2-furyl)pentadienoic acid and by thermally decarboxylating the acid in polyethylene glycol.

Furylbutylamine was obtained by the hydrogenation of 4-(2-furyl)butyronitrile which, in turn, was synthesized from 3-(2-furyl)propanol by way of the *p*-toluenesulfonate and potassium cyanide.

The *N*-cyanoalkylpyrroles, precursors of the ketocycloalkano[a]pyrroles, were synthesized by alkylation of the pyrrole nitrogen.

N-(2-Cyanoethyl)pyrrole was obtained by the direct cyanoethylation[8] of pyrrole.

Attempts to produce *N*-(3-cyanopropyl)pyrrole from potassium pyrrole and γ-bromobutyronitrile failed. The compound could be prepared, however, in 20% over-all yield by the procedure of Clemo and Ramage[5] in which the *N*-(3-chloropropyl)pyrrole, obtained from the reaction of potassium pyrrole with 3-chloropropyl *p*-toluenesulfonate, was converted to *N*-(3-cyanopropyl)-pyrrole with potassium cyanide.

Application of the same alkylation procedure to potassium pyrrole and 4-chlorobutyl *p*-toluenesulfonate gave the *N*-(4-chlorobutyl)pyrrole in 17% yield. The use of a dimethylformamide solvent increased the yield to 32% after a reaction period of 48 hours. The use of longer reaction periods resulted in the formation of dipyrrylbutane. The *N*-(chlorobutyl)pyrrole was converted to *N*-(cyanobutyl)pyrrole in 95% yield on treatment with potassium cyanide in a dimethyl sulfoxide solvent.

A third approach, involving an internal Friedel-Crafts alkylation [*N*-(3-chloropropyl)pyrrole and magnesium iodide-magnesium oxide], did not produce the desired cycloalkano[a]pyrrole.

The cycloalkano[a]pyrroles were pyrolyzed at various temperatures, and the pyrolysis temperature which gave the maximum yield of the least complicated product mixture was selected for further study. The products which were identified were purified until they were homogeneous as shown by gas chromatographic analysis.

The pyrolysis of cyclopentano[a]pyrrole (I, *n* = 3) at 650° produced 2-methylpyrrole (14%) and pyridine (16%) as the major volatile liquid products. The products were identified by physical

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(5) G. R. Clemo and G. R. Ramage, *J. Chem. Soc.*, 49 (1931).

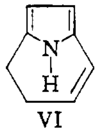
(6) J. M. Patterson, J. Brasch, and P. Drenchko, *J. Org. Chem.*, **26**, 4712 (1961).

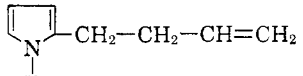
(7) J. M. Patterson, *Org. Syntheses*, **40**, 46 (1960).

(8) J. Corse, J. T. Bryant, and H. A. Shoule, *J. Am. Chem. Soc.*, **68**, 1911 (1946).

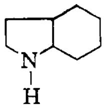
properties, gas chromatographic retention times, and by conversion to derivatives.

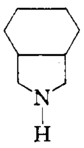
Cyclohexano[*a*]pyrrole (I, $n = 4$) was pyrolyzed at 553° and separated into a neutral and basic fraction. The basic fraction contained 13 components in trace amounts, which were not identified while the neutral fraction contained two new compounds, each formed in 13% yield, and traces of pyrrole, 2-methylpyrrole, and starting material. One of the compounds, a liquid, is assigned structure VI, 9-azabicyclo[4.2.1]nona-1,3,5-triene and the other, a solid, is assigned structure VII, 2-pyrrylbutene on the basis of the following facts.

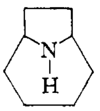

VI


VII

The N—H band (3350 cm.$^{-1}$) of VI is only of medium intensity while other substituted pyrroles, as well as compound VII (3330 cm.$^{-1}$, N—H), show bands of strong intensities. The weaker N—H band intensity is typical of cyclic secondary amines, and it is postulated that the reduced intensity observed in VI is the result of an out-of-plane bending of the nitrogen, giving it considerable secondary amine character. The double bond in VI appears to be conjugated since the ultraviolet spectrum shows a maximum at 271 mμ (ε 606). This is similar to that reported[9] for 2-propenylpyrrole, 270 mμ (ε 1130). The smaller ε value may be due to the less complete overlap of the double bond molecular orbital with that of the pyrrole ring caused by the strained bicyclic system. Compound VI was converted into a new pyrrole on reduction in the presence of palladium–charcoal, which preferentially catalyzes the reduction of the double bond.[9] Further reduction with a platinum oxide catalyst or reduction of VI with 5% rhodium-alumina catalyst produced the pyrrolidine $C_8H_{15}N$ which contained the characteristic secondary amine N—H band at 3380 cm.$^{-1}$. The pyrolidine, which was characterized as the picrate, is not octahydroindole[10] (VII) or perhydroisoindole[11] (IX) since the properties differ. The most likely structure is X. This was confirmed by the conversion of the pyrrolidine to homotropane[12] by methylation. Homotropane was identified by its boiling point, melting point of its picrate, and elemental analysis of the picrate.


VIII


IX

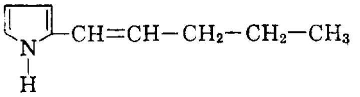

X

Compound VII was identified by its conversion to 2-butylpyrrolidine. Elemental analysis of VII indicated the presence of a double bond which, on the basis of the ultraviolet spectrum, appears to be unconjugated. The precise position of the double bond has not been located.

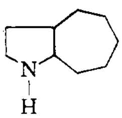
Cycloheptano[*a*]pyrrole (I, $n = 5$) when heated to 600° rearranged into two major neutral products, a liquid (XI, 11%), a solid (XII, 10%), and into several minor products, two of which were identified as pyridine and 2-methylpyrrole. The two major products were separated into two homogeneous fractions (analysis by gas chromatography) by fractional distillation.

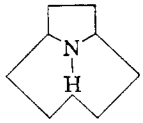
The infrared spectrum of each compound indicates that each contains the pyrrole ring system with an unsubstituted nitrogen. That liquid compound XI contains an N—H band of medium intensity, compared to XII or other pyrrole compounds, indicates a strained ring system involving out-of-plane bending of the nitrogen in compound XI, similar to that described earlier for the azabicyclononane molecule. The ultraviolet spectrum of each supports the supposition that double bonds are present and conjugated with the pyrrole ring.

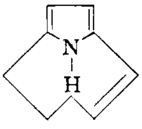
Since compound XII ($C_9H_{11}N$, according to elemental analysis) on hydrogenation produced 2-amylpyrrolidine, which was identical to an authentic sample synthesized from 2-pentanoylpyrrole, it is assigned structure XII, 1-(2-pyrryl)pentene.


XII

Compound XI was reduced to a new pyrrole using a palladium–charcoal catalyst (evidence for a double bond in the side chain) and thence to a pyrrolidine using a platinum oxide catalyst. The pyrrolidine, which absorbed in the infrared at 3330 cm.$^{-1}$ (N—H) was characterized as the picrate, m.p. 215–216°. Since the pyrrolidine is neither of the previously reported[13] cycloheptano-2,3-pyrrolidines (XIII), the structure XIV best fits the observed facts and the most probable structure of the liquid pyrolysis product is XI, 10-azabicyclo[5.2.1]deca-1,3,5-triene. The pyrrolidine, 1-azabicyclo[5.2.0]decane, is reported[14] to


XIII


XIV


XI

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[9] W. Herz and C. F. Courtney, *J. Am. Chem. Soc.*, **76**, 576 (1954).

[10] R. Willstatter, *Ber.*, **51**, 778 (1918).

[11] L. M. Rice and C. H. Grogan, *J. Org. Chem.*, **20**, 1687 (1955).

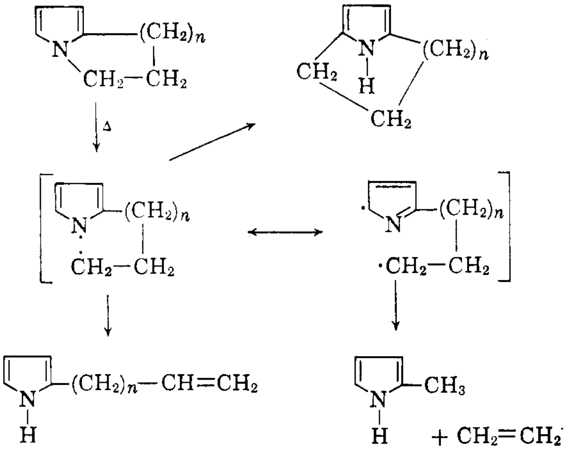
[12] A. C. Cope, H. R. Nace, and L. L. Bates, Jr., *J. Am. Chem. Soc.*, **72**, 1123 (1950).

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

[14] N. J. Leonard and W. E. Goode, *J. Am. Chem. Soc.*, **72**, 5404 (1950).

form a picrate, m.p. 214–215°. This structure differs from XIV in that it does not contain an N—H bond.

With the information available, a mechanism of the reaction would only be speculative. However, it may be postulated that the reaction involves a homolytic carbon-nitrogen bond cleavage to form a resonance stabilized diradical, which then forms a carbon-carbon bond by coupling at the 5-position, or an alkenylpyrrole by the elimination of a hydrogen atom, or 2-methylpyrrole by the elimination of ethylene in the case of cyclopentano-[*a*]pyrrole.



Experimental

Microanalyses were performed by Weiler and Strauss, Oxford, England. Melting points were taken on a Fisher-Johns melting point apparatus and are corrected. Boiling points are uncorrected. Infrared and ultraviolet absorption spectra were measured, respectively, with a Perkin-Elmer Model 21 recording spectrophotometer and with a Beckman Model DK-2 spectrophotometer. Gas chromatograms were obtained using a Carbowax 1500 column at 127°.

Synthesis of the Cycloalkano[*a*]pyrroles. 3-(2-Furyl)-propylamine.—To a solution of 93.2 g. (0.8 mole) of furylacrylonitrile[7] and 400 ml. of methanol, saturated with ammonia at 0–3°, 40 g. of Raney nickel[15] was added and the mixture hydrogenated at an initial pressure of 2000 lb. and 25°. When the theoretical quantity of hydrogen had reacted (20 hr.), the catalyst was removed by filtration through a Supercell filter cake and the clear yellow filtrate distilled under reduced pressure. The product weighed 64.4 g. (65%), b.p. 68–70° (6 mm.), $n^{25}\text{D}$ 1.4824. The boiling point previously reported[16] was 90.5° (15 mm.).

3-(2-Furyl)propyl *p*-Toluenesulfonate.—The ester was synthesized by adding 82.0 g. (0.44 mole) of *p*-toluenesulfonyl chloride to 50.4 g. (0.44 mole) of 3-(2-furyl)propanol, prepared by the hydrogenation[17] of furylacrolein, dissolved in 200 ml. of anhydrous pyridine cooled to 0°. After standing for four days at −15°, the reaction mixture was worked up in the usual way. The crude product which weighed 96.5 g. could not be distilled without violent decomposition and was therefore used directly in the next experiment.

4-(2-Furyl)butyronitrile.—To a solution of 60 g. of potassium cyanide in 200 ml. of water heated to 70°, the crude 3-(2-furyl)propyl *p*-toluenesulfonate (96.5 g.) was added over a period of 20 min. After work-up (extraction of the aqueous solution with benzene and drying), the residue was distilled at 1 mm. The material boiling at 77–83° contained, on the basis of nitrogen analysis, gas chromatographic analysis and infrared analysis, about 14% of 3-(2-furyl)propanol. The crude product was used directly in the following experiment.

4-(2-Furyl)butylamine.—From a mixture of 93.5 g. (0.7 mole) of 4-(2-furyl)butyronitrile, 300 ml. of methanol saturated with ammonia, and 20 g. of Raney nickel[15] hydrogenated at 25° and an initial hydrogen pressure of 1700 p.s.i., there was obtained 83.0 g. of crude product which boiled at 94–99° (12 mm.). This material was combined with the product from a similar experiment and purified by dissolving the amine (140 g.) in dilute hydrochloric acid followed by ether extraction of the acidic solution. After treatment with base and isolation, the residue was distilled under reduced pressure in a nitrogen atmosphere. The product weighed 107.3 g., b.p. 101–114° (11 mm.), $n^{25}\text{D}$ 1.4790.

Anal. Calcd. for $C_8H_{13}NO$: N, 10.08. Found: N, 9.96.

5-(2-Furyl)pentadienenitrile.—The procedure is essentially that used for the synthesis of furylacrylonitrile.[7] A mixture 664 g. (5.44 moles) of furylacrolein, 430 g. (4.94 moles) of 98% cyanoacetic acid, 19 g. of ammonium acetate, 870 ml. of toluene, and 696 ml. of pyridine was refluxed for 120 hr. during which time 120 ml. of water was collected. The reaction mixture was dissolved in chloroform, and the solution extracted with 10% hydrochloric acid, then with 10% sodium hydroxide solution, and finally with water. After drying the chloroform extract and removing the chloroform, the residue was distilled under reduced pressure. The fraction boiling at 150° (10 mm.) weighed 426 g. (60%), $n^{24}\text{D}$ 1.6830. The nitrile has strong absorption bands in the infrared at 734, 881, 980, 1015, 1150, 1470, 1600, 1620, and 2200 cm.$^{-1}$.

Anal. Calcd. for C_9H_7NO: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.02; H, 4.69; N, 9.77.

2-Cyano-5-(2-furyl)pentadienoic Acid.—The procedure was the same as that used in the previous experiment except that a shorter heating period was employed. A mixture of 26.8 g. (0.22 mole) of furylacrolein, 17.4 g. (0.20 mole) of 98% cyanoacetic acid, 0.6 g. of ammonium acetate, 50 ml. of toluene, and 22 ml. of pyridine was refluxed for 16 hr. The yellow-brown solid, which was obtained upon evaporation of the mixed solvent under reduced pressure, was triturated with dilute acid and dried (43 g.). The solid was dissolved in 1 *M* sodium bicarbonate solution, precipitated with 2.5 *M* hydrochloric acid, and recrystallized three times from a methanol–water solvent. The product (29.5 g., 78%) was obtained as orange crystals, m.p. 232–233° (dec.). An ultraviolet spectrum (ethanol) shows maxima at 242 mμ (ϵ 5400) and 325 mμ (ϵ 11,800).

Anal. Calcd. for $C_{10}H_7NO_2$: C, 63.49; H, 3.73; N, 7.41. Found: C, 63.26; H, 3.66; N, 7.19.

The acid was decarboxylated with the classical catalyst (copper oxide–quinoline) to the 5-(2-furyl)pentadienenitrile.

5-(2-Furyl)pentylamine.—The general procedure is the same as that described for the formation of furylpropylamine. From 140 g. (0.97 mole) of 5-(2-furyl)pentadienenitrile, dissolved in 220 g. of methanol saturated with ammonia and 40 g. of Raney nickel, there was obtained 107 g. (72%) of furylpentylamine, b.p. 78° (2 mm.). The products from several experiments were combined and purified by the procedure used for furylbutylamine. From 150 g. of crude amine, 110 g. of material boiling at 80–85° (3 mm.) was obtained. A portion of the sample was redistilled for analysis, b.p. 87.5° (3.5 mm.), $n^{24}\text{D}$ 1.4850.

Anal.[18] Calcd. for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.68; H, 10.10; N, 8.98.

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[15] A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).

[16] F. Sorm and J. Brandejs, *Collection Czecholslov. Chem. Communs.*, **12**, 444 (1947).

[17] K. Hofmann, C. Chen, A. Bridgewater, and A. E. Axelrod, *J. Am. Chem. Soc.*, **69**, 191 (1947).

Cyclodehydration of the Furylalkylamines.—The apparatus consisted of a vertically arranged Vycor reactor tube (2.5 × 30 cm.) in a continuous flow system. The reactor, maintained at a temperature of 390–400°, contained 40 ml. of a Puralox catalyst, $^1/_8$-in. activated alumina pellets. A Vycor preheater tube containing 30 ml. Berl saddles was used to volatilize the sample which was introduced into the preheater from a dropping funnel and flushed through the system by a stream of dry nitrogen or argon. The condensed product was added to an ether–water mixture which was then saturated with Dry Ice followed by separation from the carbonic acid solution. After a second treatment, the combined aqueous portions were extracted with ether, the ether layers combined and dried over sodium sulfate or magnesium sulfate. After removal of the drying agent by filtration and evaporation of the ether, the product was obtained by vacuum distillation.

Cyclopentano[*a*]pyrrole from 3-(2-Furyl)propylamine.—From 80 g. (0.64 mole) of 3-(2-furyl)propylamine, added at an HLSV (hourly liquid space velocity) of 0.15 and a nitrogen flow rate of 250 ml./min., there was obtained 29.6 g. (42.5%) of cyclopentano[*a*]pyrrole, b.p. 70–72° (12 mm.), n^{25}_{D} 1.5264. Sorm and Arnold[4] report a boiling point 62–64° (11 mm.). The ultraviolet spectrum (95% ethanol) has a maximum at 263 mμ (ε 287).

Cyclohexano[*a*]pyrrole from 4-(2-Furyl)butylamine.—From 80 g. (0.575 mole) of 4-(2-furyl)butylamine added at an HLSV of 0.2 and a nitrogen flow rate of 440 ml./min., there was obtained 46 g. (62.3%) of cyclohexano[*a*]pyrrole, b.p. 88–96° (14 mm.), n^{25}_{D} 1.5294, $\lambda_{\max}$ (95% ethanol) 263.5 mμ (ε 287).

Anal. Calcd. for $C_8H_{11}N$: C, 79.21; H, 9.15; N, 11.56. Found: C, 78.84; H, 8.96; N, 11.80.

Cycloheptano[*a*]pyrrole from 5-(2-Furyl)pentylamine.—From 40 g. (0.26 mole) of 5-(2-furyl)pentylamine, added at an HLSV of 1.0 and an argon flow rate of 440 ml./min., there was obtained 4.8 g. (13.6%) of cycloheptano[*a*]pyrrole, b.p. 89–93° (10 mm.), n^{25}_{D} 1.5246, d^{25}_{4} 0.978 which crystallized to light tan crystals, m.p. 32°. The cycloheptano[*a*]pyrrole was further purified chromatographically using petroleum ether (b.p. 60–70°) and a column packed with diatomaceous earth. From 11.8 g. of cycloheptano[*a*]pyrrole, 10.1 g. of light yellowish crystals, m.p. 36° were obtained. The purity of the crystals as determined by gas chromatography was 99%. The molecular weight was determined cryoscopically in naphthalene. The ultraviolet absorption spectrum (in ethanol) showed a maximum at 263 mμ (ε 2300).

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36; mol. wt., 135. Found: C, 79.52; H, 9.72; N, 10.25; mol. wt., 132.

In addition to the cycloheptano[*a*]pyrrole, there was obtained 4.9 g. of a yellow oil, b.p. 81° (10 mm.), n^{25}_{D} 1.4976, d^{25}_{4} 0.926, $\lambda_{\max}$ (ethanol) 239 mμ (ε 4200), 271.5 mμ (ε 2700); 4.0 g. of a blue oil, b.p. 120–121° (10 mm.), n^{25}_{D} 1.5057, d^{25}_{4} 0.993, $\lambda_{\max}$ (ethanol) 229 mμ (ε 7300), 269 mμ (ε 3100), mol. wt. (cryoscopically in naphthalene) 132; and 3.0 g. of a yellow-green oil, b.p. 134–144° (1 mm.), n^{25}_{D} 1.5550, d^{25}_{4} 1.155, $\lambda_{\max}$ (ethanol) 250 mμ (ε 4000). Each fraction gave a positive Ehrlich test.

The blue material changes color (greenish yellow) when hot or on several months standing. The blue color is unchanged when oxygen is bubbled through the liquid. The substance is insoluble in water and 5% hydrochloric acid; shaking the oil with 5% hydrochloric acid changes the color to yellow. An infrared spectrum contains typical pyrrole bands, N—H band (3375 cm.$^{-1}$) and possibly a double bond band (1620 cm.$^{-1}$).

3-Chloropropyl *p*-Toluenesulfonate.—The procedure described by Rossander and Marvel[19] was employed. The reaction of 56.9 g. (0.60 mole) of propylene chlorohydrin with 126 g. (0.65 mole) of *p*-toluenesulfonyl chloride produced 94.1 g. (63%) of the ester, b.p. 189–192° (5 mm.), n^{20}_{D} 1.5234. Literature values[20] are b.p. 188–192° (5 mm.) and n^{20}_{D} 1.5230.

4-Chlorobutyl *p*-Toluenesulfonate.—Using the method of Rossander and Marvel[19] 146 g. (1.35 moles) of tetramethylene chlorohydrin and 277 g. (1.45 moles) of *p*-toluenesulfonyl chloride, produced 169.5 g. (87%) of 4-chlorobutyl *p*-toluenesulfonate, b.p. 160° (0.5 mm.), n^{26}_{D} 1.5200, d^{25}_{4} 1.260.

Anal. Calcd. for $C_{11}H_{15}SO_3Cl$: C, 50.28; H, 5.75; S, 12.21; Cl, 13.11. Found: C, 50.38; H, 5.75; S, 12.44; Cl, 13.34.

***N*-(3-Chloropropyl)pyrrole.**—The procedure used was that of Clemo and Ramage.[5] From 27.4 g. (0.26 mole) of potassium pyrrole and 60.8 g. (0.24 mole) of 3-chloropropyl *p*-toluenesulfonate in 300 ml. of anhydrous benzene, 13.98 g. (40.5%) of *N*-(3-chloropropyl)pyrrole, b.p. 90–93° (13 mm.), n^{25}_{D} 1.5056 was obtained. The literature[5] boiling point is 87° (15 mm.).

***N*-(4-Chlorobutyl)pyrrole.**—To 30 g. (0.28 mole) of potassium pyrrole dissolved in 80 g. of dimethylformamide, 30 g. (0.14 mole) of 4-chlorobutyl *p*-toluenesulfonate was added. After the heat of reaction subsided, the reaction mixture was allowed to stand for 48 hr. and then the solid which formed was removed by filtration. The filtrate was added to 300 ml. of water and the mixture extracted with three 75-ml. portions of ether. The ether extract was washed with water until neutral to litmus, dried over sodium sulfate, filtered, and then distilled. The *N*-(chlorobutyl)-pyrrole was obtained in 32% yield (7.0 g.), b.p. 95° (12 mm.), n^{25}_{D} 1.5050.

Anal. Calcd. for $C_8H_{12}NCl$: C, 60.95; H, 7.68; N, 8.89; Cl, 22.49; Found: C, 61.01; H, 8.16; N, 8.51; Cl, 22.32.

In a similar experiment in which the reaction mixture was allowed to stand for one week, only a 5% yield of *N*-(4-chlorobutyl)pyrrole was obtained. The major product isolated was 1,4-di(1-pyrryl)butane (27%), b.p. 130° (3 mm.), n^{25}_{D} 1.5362. The compound gave a negative test for halogen and a positive Ehrlich test.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.61; H, 8.79; N, 14.40.

***N*-(2-Cyanoethyl)pyrrole.**—The compound was prepared by a modification of the method of Corse, Bryant, and Shoule.[8] To a solution of 201 g. (3.0 moles) of pyrrole, 20 ml. of Triton B and 500 ml. of dioxane, 160 g. (3.02 moles) of acrylonitrile was added over a period of 45 min. The reaction mixture was stirred for 48 hr. at room temperature and then distilled under reduced pressure to give 277 g. (77%) of product, b.p. 132–133° (10 mm.), n^{26}_{D} 1.5088; lit.[5] b.p. 135–150° (8–10 mm.).

***N*-(3-Cyanopropyl)pyrrole.**—A solution prepared by dissolving 15 g. (0.1 mole) of sodium iodide and 14.36 g. (0.1 mole) of *N*-(3-chloropropyl)pyrrole in 100 ml. of acetone was heated at 50° for 4 hr. and then allowed to stand at room temperature for 2 days. After filtering the reaction mixture to remove sodium chloride and evaporating the acetone solvent, the crude product (21.3 g.) was added to a solution of 8.5 g. (0.13 mole) of potassium cyanide in 250 ml. of 95% ethanol and the mixture heated at gentle reflux for 48 hr. The reaction mixture, after cooling, was filtered, the solvent evaporated and the oily residue distilled under reduced pressure to give 6.46 g. (48%) of *N*-(3-cyanopropyl)pyrrole boiling at 145–150° (20 mm.), n^{25}_{D} 1.5024. The boiling point reported in the lit.[5] is 152° (23 mm.).

***N*-(4-Cyanobutyl)pyrrole.**—The method of Smiley and Arnold[21] was adapted. A slurry of 11.0 g. (0.225 mole) of sodium cyanide in 55 ml. of dimethyl sulfoxide was heated to 90°, the heat removed, and 27.0 g. (0.173 mole) of *N*-(4-chlorobutyl)pyrrole added slowly so that the temperature

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[18] Analysis by Schwarzkopf Microanalytical Laboratory.

[19] S. S. Rossander and C. S. Marvel, *J. Am. Chem. Soc.*, **50**, 1491 (1928).

[20] H. Gilman and N. J. Beaber, *ibid.*, **45**, 839 (1923).

[21] R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960).

remained below 110°. The milky mixture was stirred 10 min. at about 50°, poured into 200 ml. of water, and the mixture extracted with three 50-ml. portions of ether. The extract was washed with a saturated sodium chloride solution, dried over calcium chloride, filtered, and the ether distilled. Distillation of the residue produced 35.3 g. of colorless oil, b.p.124° (3 mm.). An analytical sample was obtained by redistillation, b.p. 119–120° (3 mm.), $n^{25}\text{D}$ 1.4972.

Anal. Calcd. for $C_9H_{12}N_2$: C, 72.93; H, 8.16; N, 18.91. Found: C, 73.07; H, 8.15; N, 19.20.

Cyclization of the *N*-(Cyanoalkyl)pyrroles.—The procedure used was a modification of that described by Clemo and Ramage.[5] Dry hydrogen chloride was bubbled into a solution of the *N*-(cyanoalkyl)pyrrole in anhydrous ether containing a boron trifluoride etherate catalyst. After the solution became saturated with the hydrogen chloride it was allowed to stand for 24–36 hr. The ether and the boron trifluoride were removed by distillation under reduced pressure and the residue was triturated with anhydrous ether three times, the ether being removed by distillation under reduced pressure. The residue was hydrolyzed by adding dilute ammonium hydroxide and chloroform and then refluxing for 18 hr. The chloroform layer was separated, the aqueous layer extracted with chloroform, and the combined chloroform extracts were dried over calcium chloride. The residue obtained after removing the drying agent by filtration and evaporating the chloroform was extracted with eight 50-ml. portions of petroleum ether (b.p. 60–70°). Upon cooling at −15°, the product crystallized from the solvent. The spectra of the cyclic ketone products are reported elsewhere.[6]

4-Ketocyclopentano[*a*]pyrrole.—From 24 g. (0.2 mole) of *N*-(2-cyanoethyl)pyrrole, 800 ml. of anhydrous ether and 100 ml. of boron trifluoride etherate there was obtained 7.92 g. (33%) of the pyrrole compound, b.p. 152–158° (23 mm.), m.p. 53–55°, (lit.[5] value, m.p. 54°).

5-Ketocyclohexano[*a*]pyrrole.—From 4.3 g. (0.032 mole) of *N*-(3-cyanopropyl)pyrrole, 200 ml. of anhydrous ether, and 5 ml. of boron trifluoride etherate, there was obtained 2.62 g. (58.7%) of the pyrrole compound, m.p. 32–33° (reported[5] m.p. 34°).

6-Ketocycloheptano[*a*]pyrrole.—From 19.0 g. (0.128 mole) of *N*-(4-cyanobutyl)pyrrole, 650 ml. of anhydrous ether, and 20 ml. of boron trifluoride etherate, there was obtained 6.0 g. (31%) of the pyrrole compound, m.p. 31–32°. After a further recrystallization from petroleum ether (b.p. 60–70°) the melting point was 32.5–34.5°.

Anal. Calcd. for $C_9H_{11}NO$: N, 9.39. Found: N, 9.45.

Cycloheptano[*a*]pyrrole from 6-Ketocycloheptano[*a*]pyrrole.—A mixture of 5.0 g. (0.033 mole) of the ketone, 8.15 g. of potassium hydroxide, 6.0 ml. of 85% hydrazine hydrate, and 60 ml. of diethylene glycol was refluxed for $5^1/_2$ hr. The mixture was then distilled until the temperature of the mixture reached 195°. The distillate was extracted with three 25-ml. portions of ether and the extracts were combined, washed with water, and dried over sodium sulfate. Upon removal of the drying agent and evaporation of the ether, there was obtained 3.2 g. of white crystals, m.p. 34°. The residue from the distillation was diluted with 60 ml. of water made acidic by the addition of 36 ml. of 6 *N* hydrochloric acid and extracted with three 25-ml. portions of ether. After washing and drying the ether extracts, the drying agent was removed by filtration and the ether evaporated. An additional 1.1 g. of white crystals, m.p. 32° was obtained. The total yield of product was 4.3 g. (95%). A petroleum ether (b.p. 60–70°) solution of the pyrrole was purified chromatographically on a diatomaceous earth column. The recovery of the cycloheptano[*a*]pyrrole, m.p. 37° was nearly quantitative. The infrared spectrum of the product was identical to the one obtained from cycloheptano[*a*]pyrrole synthesized by the cyclodehydration of furylpentylamine.

Cyclohexano[*a*]pyrrole.—The procedure was similar to that used in the reduction of the ketocycloheptano[*a*]pyrrole. From 4.83 g. (0.035 mole) of 5-ketocyclohexano[*a*]pyrrole, 6 g. of sodium hydroxide, 70 ml. of diethylene glycol, and 10 ml. of 85% hydrazine hydrate refluxed for 18 hr., there was obtained 2.27 g. (56.8%) of cyclohexano[*a*]pyrrole, b.p. 87–88° (13 mm.), $n^{25}\text{D}$ 1.5280. The infrared spectrum was identical to the one obtained from cyclohexano[*a*]pyrrole obtained by the cyclodehydration of furylbutylamine.

Cyclopentano[*a*]pyrrole.—The procedure is similar to that described for the previous experiment. From a mixture of 6.9 g. (0.058 mole) of 4-ketocyclopentano[*a*]pyrrole, 8.0 g. of sodium hydroxide, 150 ml. of diethylene glycol, and 12 ml. of 85% hydrazine hydrate refluxed for 6 hr., there was obtained 4.2 g. (66.6%) of cylopentano[*a*]pyrrole, b.p. 63° (10 mm.), $n^{25}\text{D}$ 1.5264.

Pyrolysis of the Cycloalkano[*a*]pyrroles. Apparatus.—The pyrolyses were carried out in the apparatus described previously.[3]

Procedure and Analysis.—The pyrolyzate was weighed, dissolved in ether, and the ether solution extracted with 5% hydrochloric acid or 0.6 *N* sulfuric acid, washed with a saturated sodium chloride solution until neutral, and dried. The acid extract was made basic, extracted with ether and the ether extracts were dried. The neutral and basic fractions, respectively, were obtained by removing the drying agent by filtration and by distilling the two ether extracts. The composition of each fraction (neutral and basic) was investigated by gas chromatography, and the major components were separated by distillation and identified by chemical and physical means.

Pyrolysis of Cyclopentano[*a*]pyrrole.—To the reactor tube heated to 651° and with a nitrogen flow rate of 140 ml./min., 26.53 g. (0.248 mole) of cyclopentano[*a*]pyrrole (99.3% pure as determined by gas chromatography) was added at an HLSV of 0.37. The crude pyrolyzate (21.4 g.), containing 2.3 g. of carbon, was separated into a neutral and basic fraction.

Distillation of the neutral fraction gave 2.82 g. (14%) of 2-methylpyrrole, b.p. 140–146°, $n^{25}\text{D}$ 1.4999 [lit.,[22] b.p. 144–145° (717 mm.), $n^{16}\text{D}$ 1.5035] and 4.16 g. (15.6%) of cyclopentano[*a*]pyrrole, b.p. 71–76° (12 mm.), $n^{25}\text{D}$ 1.5245. An infrared spectrum was identical to that obtained from an authentic sample. The 2-methylpyrrole was further identified by conversion to the dioxime, m.p. 68.5° (lit.,[23] m.p. 69°).

The basic fraction was dissolved in 95% ethanol and treated with an alcoholic solution of picric acid. The tan solid which separated was removed from the accompanying tarry material by extraction with hot 95% ethanol. On cooling, the ethanol deposited 12.0 g. (equivalent to 3.1 g. of pyridine, 15.8%) of crude picrate, m.p. 115–135°. After several recrystallizations from 95% ethanol, 10.21 g. of the picrate, m.p. 153–168°, was obtained. The picrate of an authentic sample of pyridine also melted at 153–168°. Some of the picrate was hydrolyzed and converted into the *p*-toluenesulfonate derivative, m.p. 138.5–140° after rerecrystallization from a 95% ethanol–ethyl acetate mixture (lit.,[24] m.p. 139°).

Pyrolysis of Cyclohexano[*a*]pyrrole.—To the reactor tube heated to 553° and with an argon flow rate of 140 ml./min., 34.49 g. (0.285 mole) of cyclohexano[*a*]pyrrole (100% pure as determined by gas chromatography) was added at an HLSV of 0.21. The crude pyrolyzate weighed 33.2 g. and was separated into a neutral and basic fraction.

The basic fraction (4.5 g.) contained thirteen components as shown by gas chromatographic analysis. An attempted

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(22) A. Pictet, *Ber.*, **37**, 2793 (1904).

(23) R. G. Janssen, R. R. Schierz, R. Van Meter, and J. S. Ball, *J. Am. Chem. Soc.*, **73**, 4040 (1951).

(24) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., J. Wiley and Sons, Inc., New York, 1948, p. 242.

reduced pressure distillation causes the product to turn into a brown tar.

Analysis of the neutral fraction (28.0 g.) by gas chromatography showed the presence of two major components and three minor components. The retention times of two of the minor components corresponded to pyrrole and 2-methylpyrrole.

Three fractional distillations of the neutral fraction produced *ca.* 0.5 g. of cyclohexano[*a*]pyrrole; 4.5 g. (13%) of 9-azabicyclo[4.2.1]nona-1,3,5-triene, b.p. 91–94° (33 mm.), $n^{25}\text{D}$ 1.5320, $\lambda_{\max}$ (ethanol) 226 mμ (ϵ 2160), 252 mμ (ϵ 880), shoulder 271 mμ (ϵ 606), shoulder 285 mμ (ϵ 424) infrared band at 3350 cm.$^{-1}$ (NH); and 4.55 g. (13%) of 2-pyrrylbutene, b.p. 106° (15 mm.), m.p. 55–56°, $n^{25}\text{D}$ 1.5398, pyrrole end absorption rising to 218 mμ, infrared band 3330 cm.$^{-1}$ (N—H).

Anal. Calcd. for $C_8H_{11}N$ (pyrrylbutene): C, 79.29; H, 9.15; N, 11.56. Found: C, 78.90; H, 8.83; N, 11.98.

The fractions gave a positive Ehrlich test and were homogeneous according to gas chromatographic analysis.

2-Butylpyrrolidine.—A mixture of 2.0 g. (0.0165 mole) of (2-pyrryl)butene, 0.2 g. of 5% rhodium on alumina, and 10 ml. of acetic acid was shaken under a hydrogen pressure of 45 p.s.i. using a heat lamp to effect solution. When hydrogen uptake ceased, the mixture was added to 300 ml. of water layered over with 100 ml. of ether and filtered. The filtrate was acidified with 5 ml. of concentrated hydrochloric acid, extracted with three 100-ml. portions of ether, made basic with sodium hydroxide solution, and extracted with five 50-ml. portions of ether. The ether extract was dried and the ether evaporated leaving 1.0 g. (48%) of brown oil with an amine-like odor, b.p. 153° (760 mm.), lit.,[25] b.p. 154–156°. A red picrate was formed, m.p. 137° with decomposition, lit.[26] m.p. 137°.

9-Azabicyclo[4.2.1]nonane.—9-Azabicyclo[4.2.1]nona-1,3,5-triene (2.0 g., 0.0168 mole) was hydrogenated in 10 ml. of acetic acid (initial hydrogen pressure 45 p.s.i.) using a 5% rhodium–alumina catalyst. After 4 hr., the mixture was diluted with 300 ml. of water and filtered; the filtrate was acidified with 5 ml. of concentrated hydrochloric acid and extracted with three 100-ml. portions of ether. The aqueous solution was made basic with 20% sodium hydroxide and extracted with five 50-ml. portions of ether. Evaporation of the ether from the dried ether extract yielded 2.0 g. (95%) of brown oil with a piperidine-like odor, b.p. 148° (760 mm.). The product was characterized as the picrate, m.p. 228° with darkening at 227°.

Anal. Calcd. for $C_{14}H_{18}N_4O_7$: C, 47.45; H, 5.12; N, 15.81. Found: C, 47.65; H, 5.06; N, 15.71.

9-Azabicyclo[4.2.1]nona-1,3-diene.—A mixture of 2.1 g. (0.0176 mole) of 9-azabicyclo[4.2.1]nona-1,3,5-triene, 0.5 g. of 5% palladium–charcoal, and 30 ml. of ethanol was shaken under hydrogen (initial pressure 45 p.s.i.). When hydrogen uptake ceased, the mixture was filtered and distilled giving 1.3 g. (61%) of brown oil, b.p. 190° (760 mm.). An ultraviolet spectrum in ethanol showed pyrrole end absorption rising to 219 mμ (ϵ 2700).

9-Azabicyclo[4.2.1]nonane from the Diene.—9-Azabicyclo[4.2.1]nona-1,3-diene (1.0 g., 0.0087 mole) was hydrogenated in acetic acid (5.0 ml.) using a platinum oxide catalyst (0.1 g.). When the hydrogen uptake ceased, the mixture was diluted with 200 ml. of water, filtered, made basic with 20% sodium hydroxide, and steam distilled. The distillate was saturated with potassium carbonate, extracted with three 80-ml. portions of ether, and the ether extract dried over potassium carbonate. Removal of the drying agent and the ether left 0.6 g. (55%) of yellow oil, b.p. 149° (760 mm.) with a piperidine-like odor. The picrate of the oil melted at 228° (darkening at 227°), and when mixed with the picrate obtained from the rhodium-alumina reduction of the triene, melted at 227°. The infrared spectra of the two bases were identical.

***N*-Methyl-9-azabicyclo[4.2.1]nonane (Homotropane).**—A modification[27] of the Eschweiler-Clarke reaction[28] was used to methylate 1.5 g. (0.012 mole) of 9-azabicyclo[4.2.1]-nonane using 2.7 ml. of 25% formaldehyde solution and 1.0 g. of formic acid. Distillation of the crude product (0.8 g.) from a sodium hydroxide pellet yielded *ca.* 0.1 g. (7.5%) of colorless oil, b.p. 74° (25 mm.) (lit.[12] b.p. 80–82° (30 mm.). The residue was solid. The oil formed a yellow picrate, m.p. 271° with darkening at 269° (lit.[12] m.p. for homotropane picrate, 272–273°).

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 48.91; H, 5.47. Found: C, 48.99; H, 5.25.

Pyrolysis of Cycloheptano[*a*]pyrrole.—To the reactor tube heated to 600° and with an argon flow rate of 140 ml./min., 8.8 g. (0.065 mole) of cycloheptano[*a*]pyrrole was added at an HLSV of 0.45. The crude pyrolyzate (8.7 g.) was separated into a neutral fraction (6.15 g.) and a basic fraction (2.5 g.).

The basic fraction contained seven components according to the gas chromatogram. A micro distillation produced 0.1 g. of pyridine as the only identifiable product. The picrate of the product, m.p. 162°, did not depress the melting point of an authentic sample of pyridine picrate when mixed with it. Small quantities (total of 0.2 g.) of other liquids were obtained in the distillation and were not identified.

Fractional distillation of the neutral fraction yielded 0.6 g. of pale yellow oil, b.p. 71–78° (63 mm.) (gas chromatogram contained six peaks, one corresponding to 2-methylpyrrole); 0.93 g. (10.7%) of a pale yellow oil (which is probably 10-azabicyclo[5.2.1]deca-1,3,5-triene), b.p. 86–87° (63 mm.), $n^{24}\text{D}$ 1.5299, $\lambda_{\max}$ (ethanol) 220 mμ (ϵ 9330), 287 mμ (ϵ 405), 294 mμ (ϵ 270), infrared band at 3320 cm.$^{-1}$ (N—H); 0.35 g. of a mixture containing mostly 1-(2-pyrryl) pentene and a little of the azabicyclodecatriene; and 0.55 g. (9.7%) of 1-(2-pyrryl)pentene, a yellow oil, b.p. 94–97° (8 mm.), $n^{24}\text{D}$ 1.5630, crystallizing to white needles, m.p. 48°, $\lambda_{\max}$ (ethanol) pyrrole end absorption at 218 mμ, 271 mμ (ϵ 676), 288 mμ (ϵ 540), infrared band at 3330 cm.$^{-1}$ (N—H).

Anal. Calcd. for $C_9H_{13}N$ (pyrrylpentene): C, 79.95; H, 9.69; N, 10.36. Found: C, 80.08; H, 9.49; N, 10.21.

2-Pentanoylpyrrole.—The procedure described by Herz[29] was adapted. From 39.5 g. (0.59 mole) of pyrrole and 100 g. (0.606 mole) of valeryl bromide, there was obtained 13.0 g. (14.6%) of colorless oil, b.p. 115° (4 mm.). The compound was characterized by conversion to 2-pentylpyrrole.

2-Pentylpyrrole.—The 2-pentanoylpyrrole (13.0 g., 0.086 mole) was reduced using the Huang-Minlon modification of the Wolf-Kishner reduction. The crude brown oil product (10.5 g.) on distillation gave 7.9 g. (67%) of colorless oil with an unpleasant peppery odor, b.p. 80–83° (5 mm.), $n^{25}\text{D}$ 1.4850. An infrared spectrum (liquid film) showed intense bands at 713, 784, 1025, 1470, 2860, 2940, and 3400 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{15}N$: C, 78.77; H, 11.02; N, 10.21. Found: C, 78.51; H, 11.03; N, 10.32.

2-Pentylpyrrolidine.—2-Pentylpyrrole (2.0 g., 0.0146 mole) was reduced in acetic acid (10 ml.) using a 5% rhodium–alumina catalyst and an initial hydrogen pressure of 45 p.s.i. The product, obtained by the work-up described for the reduction of 1-pyrrylbutene, was a brown oil with an amine-like odor, 1.60 g., b.p. 153° (760 mm.). An infrared spectrum (liquid film) showed intense bands at 1460, 2850, 2920 cm.$^{-1}$ and a medium band at 3300 cm.$^{-1}$. The phenylthiourea derivative melted at 111°.

2-Pentylpyrrolidine from 1-(2-Pyrryl)-1-pentene.—The

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[25] K. Hess, *Ber.*, **52**, 1638 (1919).

[26] H. Normant, *Compt. rend.*, **232**, 1358 (1951).

[27] G. P. Menshikov and Y. Shadanovich, *Ber.*, **69B**, 1799 (1936).

[28] H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *J. Am. Chem. Soc.*, **55**, 4571 (1933).

[29] W. Herz, *J. Org. Chem.*, **22**, 1260 (1957).

procedure and work-up were the same as that described for the reduction of 2-pentylpyrrole. From 0.25 g. (0.00185 mole) of 1-(2-pyrryl)pentene in 9.0 ml. of acetic acid and 0.1 g. of 5% rhodium–alumina, there was obtained 0.2 g. (78%) of brown oil with an amine-like odor, b.p. 153° (760 mm.). An infrared spectrum of the crude oil was identical to the one obtained in the previous experiment except for more intense peaks at 1400 and 1545 cm.$^{-1}$. The phenylthiourea derivative melted at 110°. The melting point of a mixture of the phenylthiourea with the phenylthiourea from the previous experiment was 111° with softening at 109°.

10-Azabicyclo[5.2.1]deca-1,3-diene (?).—The 10-azabicyclo[5.2.1]deca-1,3,5-triene (0.25 g., 0.0019 mole), obtained from the pyrolysis of cycloheptano[*a*]pyrrole, was dissolved in ethanol (8 ml.) and hydrogenated using a 5% palladium-on-charcoal catalyst. After the usual work-up, there was obtained 0.25 g. of brown liquid, b.p. 217° (760 mm.), λ_{max} (ethanol) typical pyrrole end absorption at 218 mμ. The product was insoluble in 5% hydrochloric acid solution and gave a negative Ehrlich test.

10-Azabicyclo[5.2.1]decane (?).—From 0.2 g. (0.0015 mole) of 10-azabicyclo[5.2.1]deca-1,3-diene in 5 ml. of acetic acid and 0.1 g. of platinum oxide there was obtained 0.2 g. of yellow oil with an amine-like, camphor-like odor, b.p. 150° (760 mm.). The picrate of the product melted at 216° with darkening at 215°.

Anal. Calcd. for $C_{15}H_{20}N_4O_7$ (picrate): C, 48.91; H, 5.47. Found: C, 49.24; H, 5.20.

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Polynuclear Heterocycles. I. 1*H*-Benzo[*b*]pyrido[1,2,3-*mn*]phenoxazin-1-one and Related Substances[1a]

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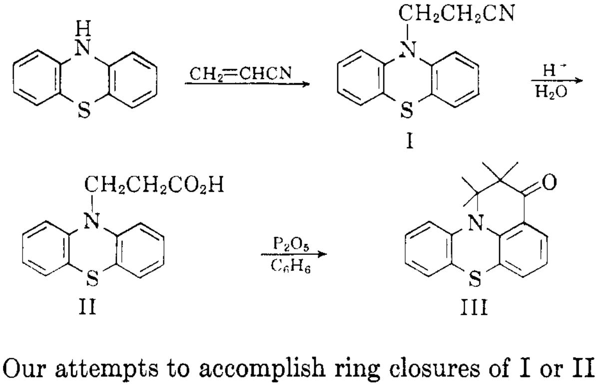
The conditions are described for the conversion of certain cyanoethylated heterocyclic compounds into their corresponding cyclic ketone derivatives. The properties of these ketone derivatives have been investigated. A brief discussion of the spectroscopic data is given.

As an extension of studies of ring closure in heterocyclic systems,[1] the preparation and properties of the interesting compound, 1,2-dihydro-3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (III), were investigated. The preparation of III has been reported as indicated by the following equations.[2]



Our attempts to accomplish ring closures of I or II by means of other agents—such as hydrobromic acid in acetic acid, polyphosphoric acid, boron trifluoride, or hydrochloric acid in acetic acid—gave, at best, very poor yields of III. The cyclization of I was not possible owing to rapid reverse cyanoethylation under these conditions.

Compound III may be readily dehydrogenated with palladium–charcoal to 3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (IV).

The condensation product of III with benzaldehyde is believed to be 2-benzyl-3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (V) and not the benzylidene compound suggested by Mackie and Cutler.[3] The structure shown is assigned to V because its ultraviolet spectrum is almost identical with that of IV, indicating that the exocyclic double bond of the intermediate benzylidene compound has migrated into the ring. The tendency toward aromaticity is apparently the driving force in this reaction. It has also been found that III is smoothly reduced to 2,3-dihydro-1*H*-pyrido[3,2,1-*kl*]phenothiazin-3-ol (VI) with sodium borohydride in wet dioxane. The latter material has been made previously by reduction of III with lithium aluminum hydride in ether.[4]

It was of interest to extend this investigation to the benzologs (VII, VIII, and IX) of phenothiazine, phenoxazine, and dihydrophenazine.

The angular compounds VIIIa, VIIIb, and IXb were prepared as described previously.[5–7] The linear derivatives VIIa, VIIb, and VIIc were prepared by the treatment of a 2,3-naphthalenediol with *o*-aminothiophenol, *o*-aminophenol, and *o*-

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(1)(a) Contribution No. 2222 from the Kodak Research Laboratories; (b) G. A. Reynolds, J. A. VanAllan, and J. F. Tinker, *J. Org. Chem.*, **24**, 1205 (1959).

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