Anal Calcd. for $C_{10}H_{13}N \cdot HCl$: C, 65.37; H, 7.68; N, 7.63. Found: C, 65.52; H, 7.69; N, 7.85.

The acetyl derivative melted at 118–118.5°.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.00; H, 7.88; N, 7.07.

***cis*-3-Phenylcyclobutylamine (VIII).**—A sample of the (oily) *cis*-3-phenylcyclobutanecarboxylic acid (0.18 g., 1 mmole) was degraded as described above. The acetyl derivative of the resulting amine melted at 124.5–126.5°, and this melting point remained undepressed by admixture of a sample of the *N*-(3-phenylcyclobutyl)acetamide prepared by Burger and Bennett[1] from the amine obtained by reduction of 3-phenylcyclobutanone oxime with lithium aluminum hydride. The infrared spectra of the two *N*-acetyl derivatives were also identical, but different from that of the *trans*-*N*-acetyl derivative (m.p. 118–118.5°, above).

***trans*-3-Phenylcyclobutylamine from *cis*-3-Phenylcyclobutanol.**—*cis*-3-Phenylcyclobutanol (XII) was prepared[8] by reduction of pure 3-phenylcyclobutanone with lithium aluminum hydride in 88% yield. It boiled at 121–122°/3 mm., $n^{30}D$ 1.5395. A solution of XII (1.85 g., 12.5 mmoles) in 6 ml. of dry pyridine was treated with 2.48 g. (13 mmoles) of *p*-toluenesulfonyl chloride at 10° and allowed to stand at 20° for 12 hr. The mixture was poured into excess 2 *N* hydrochloric acid and the oil which separated was extracted into ether. After work-up, the oily *cis*-3-phenylcyclobutyl toluenesulfonate (XIII) weighed 3.35 g. (88%), and was used in the next step.

A solution of XIII (3.33 g.) and sodium azide (1.37 g.) in 5 ml. of ethanol and 2 ml. of water was refluxed for 12 hr., cooled, diluted with water, and extracted with ether. The residue from the washed and dried ether solution weighed 1.28 g. (67%). The azide (XI) boiled at 85.5°/0.85 mm.–91.5°/1.4 mm. A solution of the azide (0.6 g.) in 5 ml. of ether was added to a solution of 0.4 g. of lithium aluminum hydride in 10 ml. of ether at 15–20°. The mixture was stirred at 25–30° for 2 hr., then decomposed with water and 30 ml. of 2 *N* hydrochloric acid and worked up. The oily amine (0.25 g., 49%) yielded an acetyl derivative, m.p. 118–118.5°. The melting point was not depressed by admixture with a sample of the acetyl derivative obtained by degradation of *trans*-3-phenylcyclobutanecarboxylic acid (VII), and the infrared spectra of the two amides were identical. A mixture melting point with *cis*-*N*-(3-phenylcyclobutyl)acetamide (m.p. 125.5–126.5°) was 89–99°.

4-Cyano-2,2-diphenylbutyraldehyde (XV).—Freshly distilled acrylonitrile (11.7 g., 0.22 mole) was added to a rapidly stirred mixture of 39.2 g. (0.2 mole) of diphenylacetaldehyde and 0.5 ml. of 10 *N* potassium hydroxide solution. After spontaneous heating subsided, the mixture was kept at 95–100° for 1 hr., cooled, 3 ml. of 2 *N* hydrochloric acid was added, and the organic material taken up in ether–benzene (1:1). Removal of the solvent from the washed and dried solution left 49.1 g. of solid which was recrystallized from methanol, m.p. 81–82°.

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 82.16; H, 5.99; N, 5.56.

4-Cyano-2,2-diphenylbutyl *p*-Toluenesulfonate (XVII).—A solution of 1.76 g. (0.045 mole) of sodium borohydride in 10 ml. of water was added to a solution of 14.9 g. (0.06 mole) of 4-cyano-2,2-diphenylbutyraldehyde in 100 ml. of methanol at a temperature below 25°, and the mixture was allowed to stand at 15–20° for 14 hr. Then 150 ml. of 2 *N* hydrochloric acid was added at 20°, the mixture was diluted with water, and thoroughly extracted with ether. The thick oily residue from the washed and dried ether extracts weighed 14.3 g. This crude 4-cyano-2,2-diphenylbutanol (XVI) was dissolved in 100 ml. of dry pyridine and treated, with stirring at *ca.* 5°, with 12.4 g. (0.065 mole) of *p*-toluenesulfonyl chloride. After being stirred at 20° for 15 hr., the mixture was decomposed with 200 ml. of 10 *N* hydrochloric acid and ice, and the separated solid was washed, filtered, and recrystallized from ethanol, m.p. 111.5–113°. The yield was 13.0 g.

Anal. Calcd. for $C_{24}H_{23}NO_3S$: C, 71.09; H, 5.72. Found: C, 70.81; H, 5.54.

Acknowledgment.—We are grateful to Smith Kline & French Laboratories for support of this study, to Dr. Gerald Dudek of Harvard University for measuring the NMR spectra of VI and VII, and to Dr. Dudek and Dr. Walter E. Thompson of SKF Laboratories for interpreting the spectra. Professors E. R. Buchman and J. D. Roberts of the California Institute of Technology have given us permission to use unpublished data.

Pyrolysis of *N*-Methylpyrrole and 2-Methylpyrrole[1]

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N-Methylpyrrole and 2-methylpyrrole were pyrolyzed at various temperatures and the composition of the volatile liquid pyrolysis products was determined. The relative quantities of the major reaction products, 2-methylpyrrole, pyridine and pyrrole, were found to vary with the pyrolysis temperature.

The thermal rearrangement of *N*-methylpyrrole to 2-methylpyrrole and pyridine had been reported in the literature,[2] but little information on the effect of temperature on the product composition was disclosed.

In order to gain further information on the behavior of *N*-substituted pyrroles at high temperatures and to determine conditions which effected their rearrangement, *N*-methylpyrrole was pyrolyzed at 550, 560, 650, and 745° and 2-methylpyrrole was pyrolyzed at 650 and 745°. In 1958, Jacobson, Heady, and Dinneen[3] reported the results of a similar study with *N*-methylpyrrole

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[1] Abstracted from the Ph.D. dissertation of Peter Drenchko, University of Kentucky, 1958.

[2] A. Pictet and A. Steinmann, *Ber.*, **37**, 2792 (1904); W. Reppe, *Ann.*, **596**, 80 (1955).

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

over the temperature range 475 to 700° and in detail over the range 475–575°. Since our experiments were concerned with the higher temperature range, we wish to report our results at this time.

Results and Discussion

The yields of the major components in the volatile liquid pyrolysis products were determined by gas chromatographic analysis when *N*-methylpyrrole was pyrolyzed at 552, 560, and 650° and 2-methylpyrrole was pyrolyzed at 650°. The results of the pyrolyses are summarized in Table I.

TABLE I

PYROLYSIS OF *N*-METHYLPYRROLE AND 2-METHYLPYRROLE

Temp.	Av. Contact Time, Sec.	Major Components in the Volatile Products (Wt. %) *N*-Methylpyrrole	2-Methylpyrrole[a]	Pyridine	Pyrrole
552	4.8	78	14	...	...
560	1.8	71	12	...	...
650	1.8	3.0	85	1.6	2.9
	4.4	1.0	59	2.0	5.0
	2.0[b]	...	86	2.3	...
	4.6[b]	...	84	4.0	2.5

[a] May contain an undetermined quantity of 3-methylpyrrole, ref. 3. [b] 2-Methylpyrrole.

The contact time was arbitrarily calculated by dividing the volume in the reactor which contained the crushed Berl saddles by the flow rate of gases through the reactor. The products were identified by comparing their retention times with those of authentic samples. In the experiments at 745°, the products were isolated and identified by physical properties, infrared spectra, and derivatives.

Over the temperature range of 550–650°, high-boiling materials were not observed and only a little decomposition was apparent in the reaction tube. On a weight basis, the volatile liquid product obtained corresponded to 90–95% of the starting material. Jacobson, Heady, and Dinneen[3] reported about 1% gas formation at 625°, consisting mainly of hydrogen and methane. Since decomposition did not appear to be extensive, it is assumed that the gas chromatographic analysis approximated product yield over this temperature range.

N-Methylpyrrole at 650° was converted primarily into 2-methylpyrrole (85%). Lesser amounts (2–5%) of pyrrole and pyridine were obtained. Under similar conditions, 2-methylpyrrole was recovered in 85% yield and comparable quantities (to the *N*-methylpyrrole experiment) of pyridine and pyrrole were formed. Jacobson, Heady, and Dinneen[3] reported the formation of methylpyrroles and traces of pyrrole, dimethylpyrroles, indoles, benzene and pyridines in the 600–700° range.

At 745°, considerable carbonization was observed (up to 40% in some experiments). At this temperature then, the analyses indicate only the relative concentrations of the major components of the volatile liquid product. Both *N*-methylpyrrole and 2-methylpyrrole produced pyrrole and pyridine in comparable yields. Thus, *N*-methylpyrrole gave 54% pyridine and 31% pyrrole while 2-methylpyrrole gave 59% pyridine and 34% pyrrole. In each experiment small quantities (2–7%) of 2-methylpyrrole were found in the liquid product.

Experimental

***N*-Methylpyrrole.**—*N*-Methylpyrrole was prepared from potassium pyrrole and methyl iodide using an ether solvent,[4] from the same reactants using a dimethylformamide solvent, and from sodium pyrrole and methyl iodide using a liquid ammonia solvent.[5] Purification was accomplished by refluxing the *N*-methylpyrrole with potassium metal followed by distillation. The *N*-methylpyrrole, b.p. 110.5–111°, n^{25}D 1.4845, was 99.8% pure as determined by gas chromatographic analysis.

2-Methylpyrrole.—2-Methylpyrrole was prepared from 2-pyrrolealdehyde semicarbazone by the procedure of Cantor, Lancaster, and VanderWerf.[6] The product, b.p. 147.3–148°, n^{16}D 1.5031 was 95% pure as determined by gas chromatographic analysis. The impurity was pyrrole.

Apparatus.—The pyrolyses were carried out in a vertically arranged Vycor reactor tube (104 × 2.5 cm.), which was heated by a 68.5-cm. long Ampcoloy A-3 block furnace of the type described by Thomas and Egloff.[7] The reactor tube was fitted with a Vycor thermocouple well used for measurement of the reaction temperature. Twenty milliliters of crushed Berl saddles (4–6 mesh) was used as a heat exchanger in the reactor. The temperature was regulated to ±1° over the volume which contained the Berl saddles as determined by calibration under reaction conditions. The sample was introduced at a constant rate from a syringe mounted on a syringe drive,[8] then volatilized by a heated Pyrex tube and swept through the reactor by a stream of nitrogen or argon gas. The liquid products were collected in a series of traps cooled in a Dry Ice–acetone mixture and weighed. The major components in the crude product were identified (retention times) and their relative quantities determined by gas chromatographic analysis using a 1-m. Carbowax 1500 column at 127°.

Chemical Separations of the Pyrolysis Products.—Chemical separations were effected by dissolving the liquid pyrolysis product in ether, filtering the ether solution, and extracting with dilute sulfuric acid. The ether solution was washed with sodium bicarbonate solution, water and then dried over sodium sulfate. The products in the ether fraction (acid-insoluble) were separated by fractional distillation. The sulfuric acid extracts were made alkaline, extracted with ether and the extracts dried. The components of the acid-soluble fraction were separated by fractional distillation.

Pyrolysis of *N*-Methylpyrrole and 2-Methypyrrole over the Temperature Range 550–650°.—The samples were introduced into the sample vaporizer at an HLSV (hourly liquid space velocity) of 0.37 while the flow rate of the nitrogen carrier gas was varied. The results are summarized in Table I.

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(4) K. Hess and F. Wissing, *Ber.*, **47**, 1416 (1914).

(5) N. D. Scott, U. S. Patent 2,488,336, November 15, 1949.

(6) P. G. Cantor, B. Lancaster, and C. A. VanderWerf, *J. Org. Chem.*, **21**, 418 (1956).

(7) C. L. Thomas and G. Egloff, "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publishing Corp., New York, 1941, p. 167.

(8) V. I. Kamarewsky and E. A. Knaggs, *Ind. & Eng. Chem.*, **43**, 1414 (1951).

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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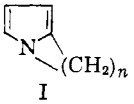
Cyclopentano[*a*]pyrrole, cyclohexano[*a*]pyrrole, and cycloheptano[*a*]pyrrole were synthesized by two reaction paths, pyrolyzed, and the major volatile pyrolysis products identified. Cyclopentano[*a*]pyrrole produced primarily 2-methylpyrrole and pyridine while cyclohexano[*a*]pyrrole was converted 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.

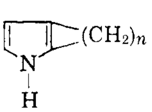
The pyrolysis of *N*-substituted pyrroles over the temperature range 475–745° produces the 2-substituted pyrrole and pyridine.[2,3] The research reported here involves an examination of the behavior of some cycloalkanopyrroles (I) under pyrogenic conditions which result in rearrangement.



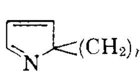
I

$n = 3, 4, 5$

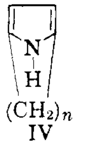
Possible rearrangement products (not involving decomposition) are:



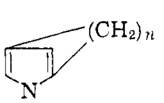
II



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).