portions of water. After drying over $MgSO_4$, the ether was removed under reduced pressure at temperatures not exceeding 0°. The white solid residue was then crystallized by dissolving it in pentane at 0°, cooling in liquid N_2, and quickly filtering out the crystalline peroxide. Traces of solvent were removed by pumping at 10^{-6} mm and 0° for 1 hr. The solid was then weighed (in the cold room) and dissolved in CCl_4 (or other solvent) at 0°. The iodometric assay of the peroxide prepared in this way is 93–96%.

Pivaloyl Peroxide. This compound was prepared by the method of Kochi and Mocadlo.[26] The solid peroxide was dissolved in CCl_4 without weighing and used immediately. *Caution:* A sample of the solid peroxide detonated during an attempt to weigh it at 3°.

Iodometric Titrations. To an aliquot of the peroxide solution is added 25 ml of acetone (saturated with O_2) and then a saturated *clear colorless* solution of NaI in 3 ml of carbonated acetone. The mixture is stored for 30 min in the dark, then diluted with 150 ml of carbonated water, and titrated with thiosulfate to a starch–iodine end point, with stirring.

(26) J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965).

Trimethylacetic *tert*-Butylcarbonic Anhydride. This carboxy-inversion product was synthesized by the general method of Michejda and Tarbell,[27] and characterized by its infrared bands at 1804 and 1760 cm^{-1}.

Adamantane-1-formyl Peroxide. In an attempted preparation of this peroxide by the method used for pivaloyl peroxide, the solid produced was found to be devoid of oxidizing power.[28]

Acknowledgment. The authors wish to thank Professor J. Saltiel and his collaborators for many helpful discussions. Financial support of this research by the Chemistry Programs, National Science Foundation Grants No. GP 8015 and GP 15991, is gratefully acknowledged.

(27) C. J. Michejda and S. Tarbell, *ibid.*, **29**, 1168 (1964).

(28) The products of an attempted preparation are reported to be the alcohol, acid, and ester, indicating a rapid ionic decomposition: L. F. Fieser, M. Z. Nazer, S. Archer, D. A. Berberian, and R. G. Slighter, *J. Med. Chem.*, **10**, 517 (1967).

Thermal Isomerization of Substituted Allylpyrroles

John M. Patterson,* Jan W. de Haan,[1] Michael R. Boyd, and J. Douglas Ferry

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506. *Received June 25, 1970*

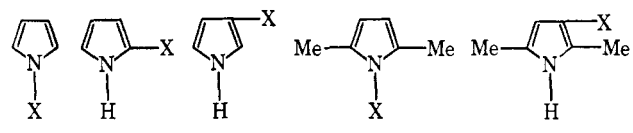
Abstract: *N*-(Substituted allyl)pyrroles, where the substituted allyl group is α-methylallyl, *trans*-crotyl, and *cis*-crotyl, on thermolysis isomerize to the corresponding 2-substituted pyrroles without rearrangement of the migrating allyl group and to the 3-substituted pyrroles with inversion of the allyl group. Since the reactions were found to be first order and intramolecular, these results are regarded as evidence for competing [1,5] and [3,3] sigmatropic shifts, respectively. Activation parameters for these reactions are consistent with this viewpoint. The interconversion of 2- and 3-(substituted allyl)pyrroles probably involves competing [1,5] and [3,3] sigmatropic shifts as well. The thermolysis of *N*-(substituted allyl)-2,5-dimethylpyrroles produces a mixture of inverted and noninverted 3-(substituted allyl)-2,5-dimethylpyrroles.

Alkyl and benzyl substituents in the pyrrole molecule upon heating migrate irreversibly from the N to the 2 position and reversibly from the 2 to 3 position.[2-4] Similar migrations in which the 2 and 5 positions of the pyrrole ring are blocked probably proceed through 2,2-dialkyl-2*H*-pyrrole (α-pyrrolenine) intermediates.[4] The values of the activation parameters[2,3] and the fact that the migrations occur with a large degree of retention of configuration[5] indicate that these reactions might involve thermal [1,5] sigmatropic shifts of allyl groups similar to those observed in alkyl-substituted cyclopentadienes.[6]

Inversion of the allyl group is characteristic of the Claisen or Cope rearrangement[7] and such rearrangements of the amino-Claisen type have been reported[8] recently in the isoxazolinone and pyrazolinone series. Most quantitative information about Claisen shifts (kinetic parameters and product production) has been obtained from solution studies,[9] and only limited information is available from rearrangements carried out in the gas phase. This report is concerned with the thermal behavior of (substituted allyl)pyrroles in the gas phase.

Results

Compounds I–IV, where X refers to a substituted allyl group such as α-methylallyl (a), *trans*-crotyl (b), and *cis*-crotyl (c), were pyrolyzed in a gas-phase flow



reactor. Compounds I–III were thermolyzed at temperatures ranging from 466 to 550°, and IVa and IVb were thermolyzed at temperatures ranging from 387.5 to 450.6° and from 436.5 to 483.0°, respectively.

(1) On leave of absence from the Laboratory of Instrumental Analysis, University of Technology, Eindhoven, The Netherlands.

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

(3) L. A. Pine, *Diss. Abstr.*, **24**, 522 (1963).

(4) J. M. Patterson and S. Soedigdo, *J. Org. Chem.*, **33**, 2057 (1968).

(5) (a) J. M. Patterson and L. T. Burka, *J. Amer. Chem. Soc.*, **88**, 3671 (1966); (b) J. M. Patterson, L. T. Burka, and M. R. Boyd, *J. Org. Chem.*, **33**, 4033 (1968).

(6) (a) J. W. de Haan and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **87**, 298 (1968); (b) W. C. Herndon and J. M. Manion, *J. Org. Chem.*, **33**, 4504 (1968).

(7) A. Jefferson and F. Scheinmann, *Quart. Rev. Chem. Soc.*, **22**, 391 (1968).

(8) Y. Makisumi and T. Sasatani, *Tetrahedron Lett.*, 543 (1969); Y. Makisumi, *ibid.*, 6413 (1969).

(9) S. J. Rhoads in "Molecular Rearrangements," Vol. 1, P. de Mayo Ed., Interscience, New York, N. Y., 1964, p 655.

The N-substituted pyrroles and dimethylpyrroles were synthesized by adaptations of methods previously described.[5b] The 2- and 3-substituted pyrroles were obtained either from preparative pyrolysis mixtures, or from the reaction of pyrrylmagnesium bromide or 2,5-dimethylpyrrylmagnesium bromide with 3-chloro-1-butene.

The details of the syntheses, preparative pyrrolysis experiments, structural assignments, and kinetic experiments are described in the Experimental Section.

From experiments carried out at constant temperature and at variable residence times, the primary reactions listed in Table I were identified. The method by which these primary reactions were distinguished from all other reactions is outlined in the Experimental Section. Activation parameters of the primary reactions along with the reaction rates at 500° are included in Table I. Activation parameters for the thermal rearrangement of *N*-methylpyrrole using the present experimental procedures were $\Delta H^{\pm}$ = 58.5 kcal/mol and $\Delta S^{\pm}$ = 4.0 eu, as compared with $\Delta H^{\pm}$ = 56.8 kcal/mol and $\Delta S^{\pm}$ = −1.3 eu, reported by Jacobson.[2]

Table I. Kinetic Parameters for the Thermal Rearrangements of Substituted Allylpyrroles and Substituted Allyl dimethylpyrroles

Reaction	Type	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu	$k_{500°}$, 10^{-2} sec^{-1}
Ia → IIa	1,5	43.0 ± 2.1	−13.5	1.30
Ib → IIb	1,5	46.7 ± 1.8	−8.3	1.56
Ic → IIc	1,5	48.1 ± 1.8	−7.4	0.99
Ia → IIIb	3,3	37.3 ± 0.7	−20.1	1.88
Ia → IIIc	3,3	40.6 ± 0.9	−18.6	0.47
Ib → IIIa	3,3	38.9 ± 2.0	−19.8	0.77
Ic → IIIa	3,3	42.7 ± 2.0	−17.3	0.23
IIa → IIIa	1,5	41.2 ± 2.0	−15.5	1.50
IIb → IIIb	1,5	41.8 ± 1.0	−14.5	1.68
IIc → IIIc	1,5	46.6 ± 1.0	−8.3	1.67
IIIa → IIa	1,5	44.3 ± 2.0	−10.3	2.73
IIIb → IIb	1,5	44.2 ± 0.9	−10.1	3.22
IIIc → IIc	1,5	47.1 ± 0.9	−6.4	3.14
IIa → IIIb	3,3	36.0 ± 2.0	−22.9	1.07
IIa → IIIc	3,3	40.0 ± 2.0	−21.9	0.13
IIb → IIIa	3,3	37.0 ± 1.8	−22.7	0.62
IIIa → IIb	3,3	38.3 ± 1.8	−18.6	2.08
IIIa → IIc	3,3	39.9 ± 2.0	−19.4	0.49
IIb → IIa	3,3	38.8 ± 1.7	−21.9	0.29
IIa → IIb	3,3	31.7 ± 1.0	−24.1	9.80
IIa → IIc	3,3	32.8 ± 1.0	−26.1	1.71
IIb → IIa	3,3	33.0 ± 1.5	−25.5	2.03
IIc → IIa	3,3	33.8 ± 1.5	−26.0	0.94
IVa → Va	1,5	48.0 ± 1.0	−4.0	0.39[a]
IVb → Vb	1,5	49.8 ± 0.5	+0.7	1.17[a]
IVa → Vb	3,3	41.8 ± 0.2	−7.6	5.06[a]
IVa → Vc	3,3	45.1 ± 0.5	−6.6	0.81[a]
IVb → Va	3,3	44.4 ± 0.6	−7.0	1.09[a]

[a] Rate constant at 440°.

The more relevant experimental results are the following.

(a) Preliminary thermolysis experiments with *N*-allylpyrrole established that both 2- and 3-substituted pyrroles are primary products, in contrast with results reported for *N*-alkyl-[2] and *N*-benzylpyrroles.[3] The overall rearrangement rate of the 2,5-dimethyl derivative is considerably higher than that of the parent compound.

(b) *N*-α-Methylallyl and *N*-*trans*-crotylpyrroles produced the same product mixture at 570 and 600°, respectively.

(c) Direct formation of 3-X pyrrole or 2-X^{-1} pyrrole from N-X pyrrole[10] was not detected within the limits of accuracy of the measurements (see Experimental Section). Similarly, no direct interconversion of 3-X and 3-X^{-1} pyrroles was observed.

(d) Under the conditions of the kinetic measurements only small amounts (usually less than 2%) of decomposition products (pyrrole, C_4–C_8 olefins, and smaller fragments) were observed; recombination products of higher molecular weight than the reactants were not observed.

(e) Both *trans*- and *cis*-crotyl products are formed from α-methylallyl reactants; the trans configuration is clearly favored in all cases.

(f) The Claisen reaction rates are generally largest for α-methylallyl reactants and smallest for *cis*-crotyl reactants.

(g) Both inverted and noninverted 3-(substituted allyl)-2,5-dimethylpyrroles were obtained on pyrolysis of the N isomer.

Discussion

The observed thermal isomerizations could arise by either of two reaction pathways: an intramolecular multicenter rearrangement or a radical process involving dissociation–recombination or a chain. The data described in the Results section (e) in addition to the highly specific product formation and negative entropies of activation make the latter possibilities unlikely. The reactions are best regarded as competing intramolecular sigmatropic shifts of the order [1,5] and [3,3]. The calculated activation parameters are consistent with this viewpoint.

The shifts from N to the 2 or 5 positions and thence to the 3 or 4 positions of the pyrrole ring involve [1,5] shifts. 2*H*-Pyrrole (α-pyrrolenine) intermediates are presumably formed which subsequently rearrange to 2- and 3-substituted pyrroles by rapid hydrogen shifts.[11] In cyclopentadiene systems, $\Delta H^{\pm}$ for an H migration is *ca.* 23 kcal/mol[12] compared to 40–44 kcal/mol for a methyl shift.[6] In the kinetic experiments no measurable amounts of 3-X pyrrole (III) were formed directly from N-X pyrrole (I). This is probably the result of largely differing rate constants for the H and X shifts in the intermediates.

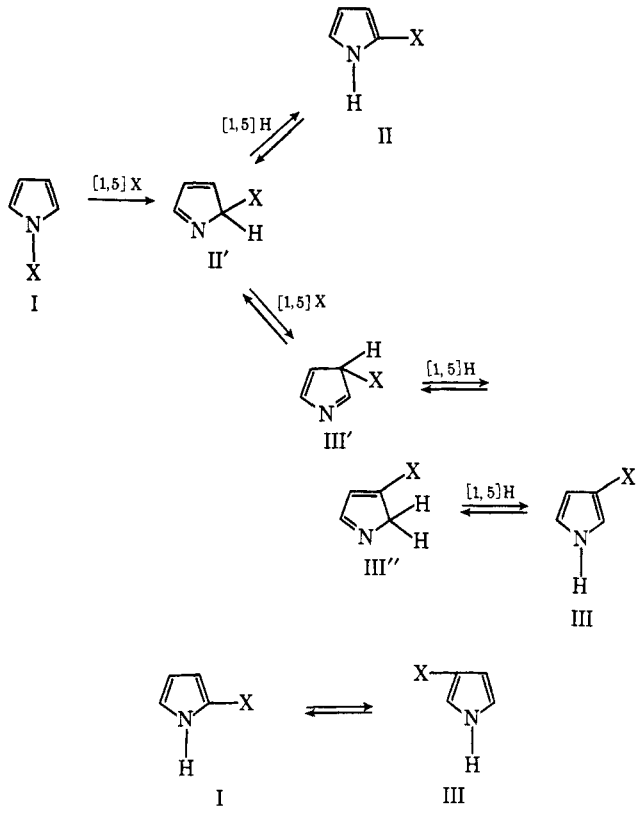
The conversion of 2- and 3-X (X^{-1}) pyrroles to the N-X (X^{-1}) pyrroles either did not occur or was slow relative to the forward reactions.

An alternative pathway for the interconversion of 2-X and 3-X pyrrole, which involves complete cleavage of the C–X bond in an early stage of the reaction, would be expected to have energies of activation close to the bond dissociation energy. The thermal dissociation of the (substituted allyl)pyrroles to pyrroles and low-boiling fragments at 500–650° gave typical parameters of $\Delta H^{\pm}$ = 70–73 kcal/mol and $\Delta S^{\pm}$ = 0–8 eu. Since

(10) In equations and discussion, X refers to the unrearranged substituted allyl group and X^{-1} refers to the rearranged substituted allyl group produced during the course of migration.

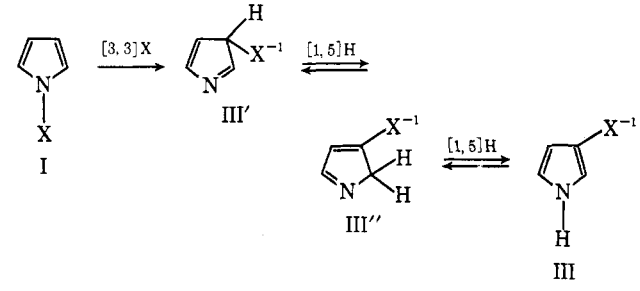
(11) Hydrogen and deuterium shifts were observed in deuterated pyrrole on pyrolysis under conditions used for the isomerizations of the (substituted allyl) pyrroles. These migrations were partially intermolecular.

(12) S. McLean and R. Hayes, *Tetrahedron Lett.*, 2385 (1964).

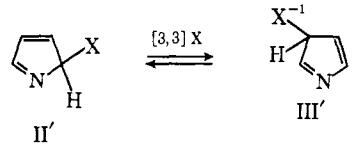


the values of E_a for the kinetic experiments were between 41 and 46 kcal/mol, the radical-cleavage pathway is excluded.

The formation of 3-X^{-1} pyrrole (III) from N-X pyrrole (I) involves a [3,3] shift in which the 3*H*-pyrrole intermediate formed initially undergoes two consecutive H shifts to yield the product.



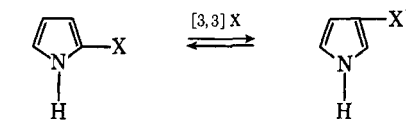
A possible additional path for the formation of III from I involves an initial [1,5] X migration to form II′ which, in turn, rearranges by a [3,3] X migration to III′. Since the 1,5 H shift in II′ back to the pyrrole is probably more rapid than alternate pathways, contributions to the formation of III by this route are unlikely. In addition, one would expect a $\Delta H^{\ddagger}$ for the formation of III from I through II′ to be very similar to that obtained for the observed [1,5] X shift since the primary



steps are the same (typical $\Delta H^{\ddagger}$ values for a [1,5] X shift range from 46 to 48 kcal/mol, Table I). Since the $\Delta H^{\ddagger}$ values for the N-X to 3-X^{-1} shift differ by about 6–7 kcal/mol, this pathway can be eliminated.

The formation of II from I through the intermediacy of III′ likewise is unlikely because of the relatively more rapid 1,5 H shift back to the pyrrole.

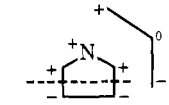
An alternative to the proposed [3,3] mechanism for the interconversion of 2-X pyrrole and 3-X^{-1} pyrrole cannot be rejected on the basis of the experimental



results reported herein. However, this pathway does not appear to be likely in view of the fact that the topologically analogous shifts (N-X pyrrole to 2-X^{-1} pyrrole and 3-X pyrrole to 3-X^{-1} pyrrole) have not been observed.

The interconversion of 2-X pyrrole and 2-X^{-1} pyrrole also probably involves a [3,3] shift, the only alternative being a [1,3] shift in the allyl group. This possibility is rejected because of the very unfavorable sterochemistry for such a rearrangement.

Selection rules, developed for the prediction of thermal and photochemical sigmatropic migrations in alicyclic systems,[13] have been successfully applied to shifts of hydrogen atoms and alkyl groups in common ring compounds.[6,12,14] In view of the fact that alkyl substituents on the pyrrole ring enhance the isomerization rate and of the report of Pine that the transition state for benzyl migrations possesses substantial radical character, the transition state for the pyrrole isomerizations can be best approximated as a loose complex of radicals. Calculations by the SCF–INDO method[15] using coordinates for the pyrrole molecule[16] show that the highest occupied molecular orbital in the pyrrole radical has a node between atoms 2,5 and 3,4. Suprafacial rearrangements involving migrations from nitrogen to the 2 and 5 positions [1,5] without inversion of the allyl group, and migrations from nitrogen to the 3



ψ_3 of pyrrole, ψ_2 of allyl radical

and 4 positions [3,3] with inversion of the allyl group, are symmetry allowed.

The form of the transition states for the [3,3] shifts should reflect the experimental data summarized in the Results section (f, g).

Two model transition states can be envisioned for the migration. In one, the migrating allyl group lies parallel to the edge of the ring and in the second the migrating group lies across the ring. A consideration of the conformations of the migrating atoms relative to the pyrrole ring shows that the edge migration produces boat-like arrangements and the across migration produces chair-like arrangements. The chair-like tran-

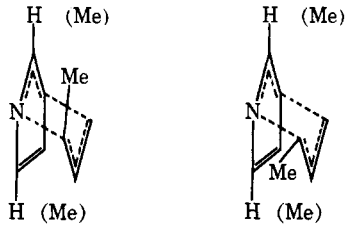
(13) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

(14) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964); A. P. ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 741 (1963); **84**, 241, 245 (1965); L. B. Jones and V. K. Jones, *J. Amer. Chem. Soc.*, **89**, 1880 (1967); **90**, 1540 (1968).

(15) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(16) L. E. Sutton, "Tables of Interatomic Distances," The Chemical Society, London, 1958.

sition state is usually favored over the boat-like conformation in [3,3] sigmatropic reactions.[17] Representative transition states are illustrated in VI and VII. The chair-like transition state (VI), in which the methyl substituent is axial, is the higher energy state which on collapse leads to the *cis*-crotylpyrrole product. The lower energy conformation (equatorial methyl) (VII) on collapse leads to the *trans*-crotylpyrrole.



VI VII

Calculations of $\Delta\Delta G^{\ddagger}$ from the experimental data in Table I show that the free energy of the trans configuration is lower than the cis by *ca.* 1.0–3.3 kcal/mol. These differences are comparable to those reported for similar transition states[18] involved in the Claisen and Cope rearrangements.

Similar transition states explain the observed reactivity of *trans*-crotyl and *cis*-crotyl groups in the rearrangements to α-methylallyl products.

Experimental Section

Boiling points are uncorrected. Gas chromatographic analyses and separations were made on a Hewlett-Packard Model 5750 gas chromatograph using the columns and temperatures specified. Infrared spectra were measured on a Beckman IR-8 spectrophotometer; ultraviolet spectra were measured on a Perkin-Elmer Model 202 spectrophotometer; nmr spectra (δ values) were measured on a Varian HA-60-IL spectrometer or a Varian T-60 spectrometer in carbon tetrachloride solutions (*ca.* 10%) using tetramethylsilane (TMS) or hexamethyldisiloxane (HMDS) as internal standards; and mass spectra were taken on a Hitachi RMU-70 mass spectrometer.

Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Spang Microanalytical Laboratories, Ann Arbor, Mich.

N-**Allylpyrrole** was synthesized by adaptation of the procedure reported previously.[5b] To a solution of 57 g (1.0 mol) of allylamine in 200 ml of glacial acetic acid was added 132 g (1.0 mol) of 2,5-dimethoxytetrahydrofuran and the mixture refluxed for 3 hr. The reaction mixture was cooled and poured into 800 ml of water, neutralized with a 25% sodium hydroxide solution, and extracted with three portions of ether. The ether extract was washed with water and dried over sodium bicarbonate. The residue, obtained after removal of the drying agent and the ether (rotary evaporator), was distilled at atmospheric pressure and yielded 48.0 g (45%) of colorless liquid: bp 146–147°; n^{25}D 1.4936; d^{25} 0.9113 g/ml; λ_{max}^{MeOH} 215 nm (ε 6183); nmr 4.24 (multiplet, 2 H), 4.89 (multiplet, 2 H), 5.75 (multiplet, 1 H), 5.92 (triplet, 3 H), and 6.36 ppm (triplet, 3 H).

Anal. Calcd for C_7H_9N: C, 78.50; H, 8.41; N, 13.08. Found: C, 78.40; H, 8.49; N, 12.69.

The pyrrole showed a single peak on glpc analysis (6 ft × 0.125 in. 10% UC-W98 column at 160°).

N-**Allyl-2,5-dimethylpyrrole** was synthesized by an adaptation of the procedure reported previously.[5b]. A solution of 28.5 g (0.5 mol) of allylamine and 57 g (0.5 mol) of 2,5-hexanedione was refluxed for 4 hr during which time the water formed in the reaction was removed by azeotropic distillation. After removal of the benzene, the residue was distilled at reduced pressure through a 10-cm Vigreux column to yield 60.5 g (89%) of a colorless liquid: bp 74° (15 mm); n^{25}D 1.4996; d^{25} 0.9141 g/ml; λ_{max}^{MeOH} 216 nm (ε 7281); nmr 2.05 (singlet, 6 H), 4.23 (multiplet, 2 H), 4.67 (multiplet, 1 H), 4.87 (multiplet, 1 H), 5.54 (singlet, 2 H), and 5.75 ppm (multiplet, 1 H).

Anal. Calcd for $C_9H_{13}N$: C, 80.01; H, 9.62; N, 10.37. Found: C, 79.93; H, 9.83; N, 10.06.

N-α-**Methylallylpyrrole.** The pyrrole was synthesized by the procedure described for *N*-allylpyrrole using α-methylallylamine (bp 60°, n^{25}D 1.4090) prepared by the method of Roberts and Mazur.[19] From 15 g (0.21 mol) of the amine and 28 g (0.21 mol) of 2,5-dimethoxytetrahydrofuran in 42 ml of acetic acid, there was obtained 8.6 g (34%) of product: bp 156°; n^{25}D 1.4884; λ_{max}^{MeOH} 207 nm (ε 8440); ν_{CCl_4} 2980, 1268, 1085, 925, 710 cm^{-1}; nmr 1.51 (doublet, 3 H), 4.50 (complex quartet, 1 H), 5.00 (complex multiplet, 2 H), 5.85 (multiplet, 1 H), 5.92 (triplet, 2 H), and 6.50 ppm (triplet, 2 H). Analysis by glpc showed a single peak (6 ft × 0.125 in. 10% UC-W98 at 130°); parent peak (mass spectrum) *m/e* 121.

Anal. Calcd for $C_8H_{11}N$: C, 79.33; H, 9.09; N, 11.57. Found: C, 79.05; H, 8.95; N, 11.46.

N-**Crotylpyrrole.** The procedure was the same as that used for *N*-allylpyrrole. From 35.5 g (0.5 mol) of crotylamine (bp 82°, n^{25}D 1.4321; prepared by method used for α-methylallylamine) and 66 g (0.5 mol) of 2,5-dimethoxytetrahydrofuran in 100 ml of acetic acid, there was obtained 22.1 g (36.6%) of a mixture consisting of *ca.* 80% trans and 20% cis isomer, bp 172°. Hydrogenation of a small portion over 10% palladium on charcoal produced *N*-*n*-butylpyrrole.[20]

N-*trans*-**Crotylpyrrole.** The pyrrole was obtained by preparative glpc using a 10 ft × 0.375 in. 20% UC-W98 column at 160°: n^{25}D 1.4975; λ_{max}^{MeOH} 210 nm (ε 7850); ν_{CCl_4} 2912, 1280, 970, 720 cm^{-1}; nmr (HMDS) 1.60 (multiplet, 3 H), 4.21 (multiplet, 2 H), 5.41 (multiplet, 2 H), 5.85 (triplet, 2 H), and 6.33 ppm (triplet, 2 H); parent peak (mass spectrum) *m/e* 121.

Anal. Calcd for $C_8H_{11}N$: C, 79.33; H, 9.09; N, 11.57. Found: C, 79.38; H, 9.08; N, 11.59.

N-*cis*-**Crotylpyrrole** was obtained from glpc separation of the trans isomer: n^{25}D 1.5050; λ_{max}^{MeOH} 206 nm (ε 6400); ν_{CCl_4} 2912, 1280, 720, 662 cm^{-1}; nmr (HMDS) 1.64 (complex doublet, 3 H), 4.37 (complex doublet, 2 H), 5.50 (septet, 2 H), 5.85 (triplet, 2 H), and 6.34 ppm (triplet, 2 H); parent peak (mass spectrum) *m/e* 121. The purity of the sample was 99% (glpc analysis).

N-α-**Methylallyl-2,5-dimethylpyrrole.** The pyrrole was synthesized by the procedure used for the preparation of *N*-allyl-2,5-dimethylpyrrole. From 9.6 g (0.12 mol) of α-methylallylamine and 15.4 g (0.14 mol) of 2,5-hexanedione there was obtained 14.9 g (71%) of pyrrole: bp 192–195°; n^{25}D 1.4950: λ_{max}^{MeOH} 211 nm (ε 6580); ν_{CCl_4} 2980, 2938, 1715, 1394, 1280, 940 cm^{-1}; nmr 1.51 (doublet, 3 H), 2.11 (singlet, 6 H), 4.70 (complex multiplet, 1 H), 5.06 (complex multiplet, 2 H), 5.51 (singlet, 2 H), and 5.97 ppm (complex multiplet, 1 H). The product was 99.9% pure (glpc analysis on 6 ft × 0.125 in. 10% UC-W98 column at 155°). Catalytic hydrogenation over 10% palladium on charcoal produced *N*-*sec*-butyl-2,5-dimethylpyrrole.[5b]

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.64; H, 10.10; N, 9.28

The parent peak (mass spectrum) was noted at *m/e* 149.

N-**Crotyl-2,5-dimethylpyrrole.** The procedure used for the synthesis of *N*-allyl-2,5-dimethylpyrrole gave an 88% yield of the isomeric pyrroles (*ca.* 80% trans and 20% cis), bp 115° (40 mm). Catalytic hydrogenation of a small portion of the mixture produced *N*-butyl-2,5-dimethylpyrrole.[21]

N-*trans*-**Crotyl-2,5-dimethylpyrrole.** The pyrrole was obtained by preparative glpc using a 10 ft × 0.375 in. 30% Carbowax 20M column at 200°: n^{25}D 1.5007; λ_{max}^{MeOH} 205 nm (ε 8350); ν_{CCl_4} 2913, 1670, 1405, 965 cm^{-1}; nmr 1.60 (multiplet, 3 H), 2.07 (singlet, 6 H), 4.20 (multiplet, 2 H), 5.25 (multiplet, 2 H), and 5.50 ppm (singlet, 2 H); parent peak (mass spectrum) *m/e* 149. The sample was 100% pure (glpc analysis on 6 ft × 0.125 in. 10% UC-W98 column at 180°).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.55; H, 10.11; N, 9.36.

N-*cis*-**Crotyl-2,5-dimethylpyrrole.** The pyrrole was obtained in the glpc separation of the trans isomer: n^{25}D 1.5070; λ_{max}^{MeOH} 205 nm (ε 8850); ν_{CCl_4} 2913, 1655, 1402, 670 cm^{-1}; nmr 1.68 (complex doublet, 3 H), 2.10 (singlet, 6 H), 4.31 (complex doublet, 2 H), 5.34 (multiplet, 2 H), and 5.50 ppm (singlet, 2 H); parent peak (mass

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spectrum) *m/e* 149. The sample purity was 99% (glpc analysis on a 6 ft × 0.125 in. 10% UC-W98 column at 180°).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.54; H, 10.18; N, 9.32.

Pyrolyses of the Pyrroles. Large scale pyrolyses were carried out by using the procedure and apparatus previously described[3] for the purpose of product identification.

Pyrolysis of *N*-Allylpyrrole. From 20 g of the pyrrole added to the reactor at 620° (3.9 g/hr) there was obtained 17.0 g (85% recovery) of pyrolysate consisting of (glpc analysis on a 6 ft × 0.125 in. 10% UC-W98 column at 160°) pyrrole (8%), *N*-allylpyrrole (11%), 2-allylpyrrole (53%), and 3-allylpyrrole (26%). The components of the pyrolysate were separated by preparative glpc using a 10 ft × 0.375 in. 30% Carbowax 20M column at 195 and 210°. Pyrrole and *N*-allylpyrrole gave ir and nmr spectra which were identical with those obtained from authentic samples. The 2-allylpyrrole was 99.9% pure: bp 170°; $n^{25}D$ 1.5153; d^{25} 0.9456 g/ml; λ_{max}^{MeOH} 216 nm (ε 7525); ν_{CCl_4} 3398, 3478 cm^{-1} (N–H); nmr 3.20 (doublet, 2 H), 5.00 (multiplet, 2 H), 5.84 (multiplet, 3 H), 6.40 (multiplet, 1 H), and 7.41 ppm (singlet, 1 H).

Anal. Calcd for C_7H_9N: C, 78.50; H, 8.41; N, 13.08. Found: C, 78.51; H, 8.65; N, 13.00.

The 3-allylpyrrole was 99.9% pure: bp 181°; $n^{25}D$ 1.5140; d^{25} 0.9461 g/ml; λ_{max}^{MeOH} 214 nm (ε 5940); ν_{CCl_4} 3405, 3495 cm^{-1} (N–H); nmr 3.17 (doublet, 2 H), 5.00 (multiplet, 2 H), 5.84 (multiplet 2 H), 6.38 (multiplet, 2 H), and 7.46 ppm (singlet, 1 H).

Anal. Calcd for C_7H_9N: C, 78.50; H, 8.41; N, 13.08. Found: C, 78.61; H, 8.54; N, 12.91.

A portion of the gases produced during pyrolysis was examined in a 10-cm gas cell and was found to consist mainly of propene.

Pyrolysis of *N*-Allyl-2,5-dimethylpyrrole. From 28.2 g pyrolyzed at 525° there was obtained 27.2 g (96.5% recovery) of pyrolysate which consisted of 2,5-dimethylpyrrole (7%), *N*-allyl-2,5-dimethylpyrrole (16%), 2-allyl-3,5-dimethylpyrrole (10%), and 3-allyl-2,5-dimethylpyrrole (65%). The mixture was separated by glpc using a 10 ft × 0.375 in. 30% Carbowax 20M column at 204 and 220°. 2,5-Dimethylpyrrole and *N*-allyl-2,5-dimethylpyrrole gave ir and nmr spectra which were identical with those obtained from authentic samples. No evidence for the presence of 2,4-dimethylpyrrole was found.

2-Allyl-3,5-dimethylpyrrole was 100% pure (glpc analysis): bp 88° (13 mm); $n^{20}D$ 1.5120; d^{25} 0.9222 g/ml; λ_{max}^{MeOH} 212 nm (ε 7190); ν_{CCl_4} 3465 cm^{-1} (N–H); nmr 1.87 (singlet, 3 H), 2.06 (singlet, 3 H), 3.12 (doublet, 2 H), 4.95 (multiplet, 2 H), 5.43 (multiplet, 1 H), 5.77 (multiplet, 1 H), and 7.09 ppm (singlet, 1 H).

Anal. Calcd for $C_9H_{13}N$: C, 80.01; H, 9.62; N, 10.37. Found: C, 79.79; H, 9.90; N, 10.22.

3-Allyl-2,5-dimethylpyrrole was 99.8% pure: bp 80° (5 mm); $n^{25}D$ 1.5143; d^{25} 0.9208 g/ml; λ_{max}^{MeOH} 214 nm (ε 7150); ν_{CCl_4} 3470 cm^{-1} (N–H); nmr 1.97 (singlet, 3 H), 2.03 (singlet, 3 H), 2.98 (doublet, 2 H), 4.84 (multiplet, 2 H), 5.47 (multiplet, 1 H), 5.74 (multiplet, 1 H), and 7.00 ppm (singlet, 1 H).

Anal. Calcd for $C_9H_{13}N$: C, 80.01; H, 9.62; N, 10.37. Found: C, 80.00; H, 9.78; N, 10.11.

Pyrolysis of *N*-Crotylpyrrole. The pyrolysate obtained from reaction of a mixture consisting of *ca.* 80% *trans*-crotyl and 20% *cis*-crotylpyrroles at 600° contained (glpc analysis) the following: 2-α-methylallylpyrrole (11%), 2-*trans*-crotylpyrrole (26%), 2-*cis*-crotylpyrrole (12%), 3-α-methylallylpyrrole (9%), 3-*trans*-crotylpyrrole (14%), and 3-*cis*-crotylpyrrole (6%). Pyrrole (7%), *N*-*trans*-crotylpyrrole (4%), and *N*-*cis*-crotylpyrrole (2%) were identified on the basis of glpc retention times. The mixture was separated into the following components using a 10 ft × 0.375 in. 30% Carbowax 20M column at 160°.

2-α-Methylallylpyrrole was 100% pure (glpc analysis): $n^{25}D$ 1.5058; λ_{max}^{MeOH} 218 nm (ε 6590); ν_{CCl_4} 3500 cm^{-1} (N–H); nmr 1.33 (doublet, 3 H), 3.40 (multiplet, 1 H), 4.90 (multiplet, 1 H), 5.13 (multiplet, 1 H), 5.90 (multiplet, 3 H), 6.50 (multiplet, 1 H), and 7.66 ppm (broad, 1 H); molecular ion *m/e* 121.086 ± 0.003 (theory 121.089).

Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.27; H, 9.16; N, 11.62.

2-Crotylpyrrole was obtained initially as a mixture of 49% 2-*trans*-crotylpyrrole and 51% 2-*cis*-crotylpyrrole: molecular ion at *m/e* 121.093 (theory 121.089).

Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.22; H, 9.24; N, 11.53.

The mixture was separated further by preparative glpc.

2-*trans*-Crotylpyrrole was 99% pure (glpc analysis): $n^{25}D$ 1.5110; λ_{max}^{MeOH} 218 nm (ε 8520); ν_{CCl_4} 3500 (N–H), 965 cm^{-1}; nmr 1.71 (multiplet, 3 H), 3.26 (multiplet, 2 H), 5.55 (multiplet, 2 H), 5.80 (multiplet, 1 H), 5.98 (multiplet, 1 H), 6.48 (multiplet, 1 H), and 7.63 ppm (broad, 1 H); molecular ion *m/e* 121.087 (theory 121.089).

Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.03; H, 9.06; N, 11.47.

2-*cis*-Crotylpyrrole was 98.7% pure (glpc analysis): ν_{CCl_4} 3500 (N–H), 665 cm^{-1}; nmr 1.63 (doublet, 3 H), 3.26 (doublet, 2 H), 5.48 (multiplet, 2 H), 5.71 (multiplet, 1 H), 5.88 (multiplet, 1 H), 6.41 (multiplet, 1 H), and 7.53 ppm (broad, 1 H).

3-α-Methylallylpyrrole was 100% pure (glpc analysis): $n^{25}D$ 1.5052; λ_{max}^{MeOH} 210 nm (ε 8070); ν_{CCl_4} 3500 cm^{-1} (N–H); nmr 1.30 (doublet, 3 H), 3.33 (multiplet, 1 H), 4.81 (multiplet, 2 H), 5.05 (multiplet, 1 H), 5.96 (multiplet, 2 H), 6.45 (multiplet, 2 H), and 7.53 ppm (broad, 1 H); molecular ion *m/e* 121.083 ± 0.005 (theory 121.089).

Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.35; H, 9.26; N, 11.50.

3-Crotylpyrrole was obtained initially as a mixture of 83% 3-*trans*-crotylpyrrole and 17% 3-*cis*-crotylpyrrole: molecular ion at *m/e* 121.088 (theory 121.089).

Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.35; H, 9.25; N, 11.53.

The mixture was separated further by preparative glpc.

3-*trans*-Crotylpyrrole was 97.8% pure (glpc analysis): $n^{25}D$ 1.5135; λ_{max}^{MeOH} 206 nm (ε 7920); ν_{CCl_4} 3500 (N–H), 960 cm^{-1}; nmr 1.61 (multiplet, 3 H), 3.07 (multiplet, 2 H), 5.46 (multiplet, 2 H), 5.90 (multiplet, 1 H), 6.33 (multiplet, 1 H), 6.50 (multiplet, 1 H), and 7.60 ppm (broad, 1 H); molecular ion *m/e* 121.090 (theory 121.089).

Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.29; H, 9.18; N, 11.56.

3-*cis*-Crotylpyrrole was 99% pure (glpc analysis): ν_{CCl_4} 3500 (N–H), 660 cm^{-1}; nmr 1.60 (doublet, 3 H), 3.10 (doublet, 2 H), 5.40 (multiplet, 2 H), 5.86 (multiplet, 1 H), 6.31 (multiplet, 1 H), 6.45 (multiplet, 1 H), and 7.70 ppm (broad 1 H).

Pyrolysis of *N*-α-Methylallylpyrrole. The 570° pyrolysate was analyzed using a 6 ft × 0.125 in. Carbowax 20M column at 130°: 2-α-methylallylpyrrole (10%), 2-*trans*-crotylpyrrole (26%), 2-*cis*-crotylpyrrole (10%), 3-α-methylallylpyrrole (5%), 3-*trans*-crotylpyrrole (16%), and 3-*cis*-crotylpyrrole (6%). On the basis of glpc retention times *N*-α-methylallylpyrrole (5%) and pyrrole (4%) were also present in the pyrolysate. Separation of the pyrolysate was accomplished using a 10 ft × 0.375 in. 30% Carbowax 20M column at 160°. The glpc retention times and the ir and nmr spectra of the individual components were identical with those obtained from the components produced in the pyrolysis of *N*-crotylpyrrole.

Reaction of Pyrrylmagnesium Bromide with 3-Chloro-1-butene. To a stirred solution of pyrrylmagnesium bromide (prepared from 28.4 g of pyrrole, 9.6 g of magnesium, and 44 g of ethyl bromide) in 500 ml of ether was added 45 g of 3-chloro-1-butene in 100 ml of ether. After stirring for 24 hr at room temperature, 150 ml of an ice–water mixture was added and the mixture made acidic with 5% HCl. The ether layer was separated and dried over magnesium sulfate. The residue obtained after removal of drying agent and ether was flash distilled at 110° (1 mm) and analyzed by glpc on a 6 ft × 0.125 in. Carbowax 20M column at 130°. The following components were isolated by preparative glpc using a 10 ft × 0.375 in. 30% Carbowax 20M column at 160° and exhibited glpc retention times and ir and nmr spectra which were identical with those obtained in the pyrolysis of *N*-α-methylallylpyrrole and *N*-crotylpyrrole: 2-α-methylallylpyrrole (25%), 2-*trans*-crotylpyrrole (15%), 2-*cis*-crotylpyrrole (2%), 3-α-methylallylpyrrole (11%), 3-*trans*-crotylpyrrole (7%), and 3-*cis*-crotylpyrrole (1%). Unreacted pyrrole (26%) was identified by its glpc retention time.

Pyrolysis of *N*-Crotyl-2,5-dimethylpyrrole. A mixture of *ca.* 80% of *N*-*trans*-crotyl- and 20% *N*-*cis*-crotyl-2,5-dimethylpyrroles was pyrolyzed at 530° and the pyrolysate analyzed by glpc using a 6 ft × 0.125 in. Carbowax 20M column at 120°. The products were 2-*trans*-crotyl-3,5-dimethylpyrrole (7%), 3-α-methylallyl-2,5-dimethylpyrrole (11%), 3-*trans*-crotyl-2,5-dimethylpyrrole (27%), and 3-*cis*-crotyl-2,5-dimethylpyrrole (6%). Also present in the pyrolysate based upon glpc retention times were 2,5-dimethylpyrrole (2%), *N*-*trans*-crotyl-2,5-dimethylpyrrole (28%), and *N*-*cis*-crotyl-2,5-dimethylpyrrole (8%). The pyrroles produced in the pyrolysis were isolated by preparative glpc using a 10 ft × 0.375 in. 30% Carbowax 20M column at 200° and gave the following properties.

2-*trans*-Crotyl-3,5-dimethylpyrrole was 100% pure (glpc analysis): $n^{25}D$ 1.5073; λ_{max}^{MeOH} 207 nm (ε 6210); ν_{CCl_4} 3490 (N–H), 975

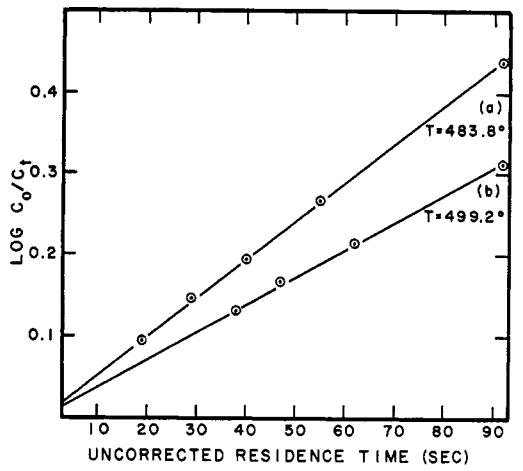

Figure 1. First-order plots for the pyrolysis of *N*-α-methylallylpyrrole at 483.8° (a) and *N*-*trans*-crotylpyrrole at 499.2° (b).

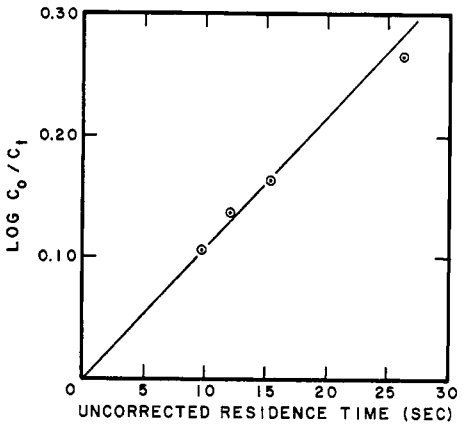

Figure 2. First-order plot for the pyrolysis of 2-α-methylallylpyrrole at 486.6°.

cm^{-1}; nmr 1.67 (multiplet, 3 H), 1.90 (singlet, 3 H), 2.10 (singlet, 3 H), 3.11 (multiplet, 2 H), 5.47 (multiplet, 3 H), and 7.10 ppm (broad, 1 H); molecular ion *m/e* 149.120 ± 0.001 (theory 149.120).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.84; H, 10.13; N, 9.93. Found: C, 80.72; H, 9.88; N, 9.59.

3-α-Methylallyl-2,5-dimethylpyrrole was 98% pure (glpc analysis): $n^{25}D$ 1.5072; λ_{max}^{MeOH} 210 nm (ε 7340); ν_{CCl_4} 3495 (N–H), 1640, 920 cm^{-1}; nmr 1.22 (doublet, 3 H), 2.08 (singlet, 3 H), 2.13 (singlet, 3 H), 3.23 (multiplet, 1 H), 4.72 (multiplet, 1 H), 4.97 (multiplet, 1 H), 5.52 (multiplet, 1 H), 5.88 (multiplet, 1 H), and 7.15 ppm (broad, 1 H).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.45; H, 10.17; N, 9.39.

3-*trans*-Crotyl-2,5-dimethylpyrrole was 100% pure (glpc analysis): $n^{25}D$ 1.5135; λ_{max}^{MeOH} 207 nm (ε 8860); ν_{CCl_4} 3500 (N–H), 970 cm^{-1}; nmr 1.60 (multiplet, 3 H), 2.01 (singlet, 3 H), 2.08 (singlet, 3 H), 2.92 (multiplet, 2 H), 5.32 (multiplet, 1 H), 5.43 (multiplet, 2 H), and 7.03 ppm (broad, 1 H); molecular ion *m/e* 149.120 (theory 149.120).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.50; H, 10.21; N, 9.48.

3-*cis*-Crotyl-2,5-dimethylpyrrole was 97% pure (glpc analysis): $n^{25}D$ 1.5185; λ_{max}^{MeOH} 207 nm (ε 7230); ν_{CCl_4} 3500 (N–H), 715 cm^{-1}; nmr 1.70 (multiplet, 3 H), 2.10 (singlet, 3 H), 2.15 (singlet, 3 H), 3.02 (multiplet, 2 H), 5.35 (multiplet, 1 H), 5.48 (multiplet, 2 H), and 7.10 ppm (broad, 1 H); molecular ion *m/e* 149.137 ± 0.015 (theory 149.120).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.54; H, 10.20; N, 9.38.

Pyrolysis of *N*-α-Methylallyl-2,5-dimethylpyrrole. Pyrolysis of the pyrrole at 530° produced the following products (glpc analysis using a 6 ft × 0.125 in. Carbowax 20M column at 120°): 2-*trans*-crotyl-3,5-dimethylpyrrole (13%), 3-α-methylallyl-2,5-dimethylpyrrole (7%), 3-*trans*-crotyl-2,5-dimethylpyrrole (30%), and 3-*cis*-crotyl-2,5-dimethylpyrrole (14%). These products were isolated by preparative glpc using a 10 ft × 0.375 in. 30% Carbowax 20M column at 180° and gave glpc retention times and ir and nmr spectra which were identical with those obtained from the products produced in the pyrolysis of *N*-crotyl-2,5-dimethylpyrrole.

Also present in the pyrolysate were *N*-α-methylallyl-2,5-dimethylpyrrole (4%, glpc retention time and nmr) and 2,5-dimethylpyrrole (21%, glpc retention time, ir, and nmr).

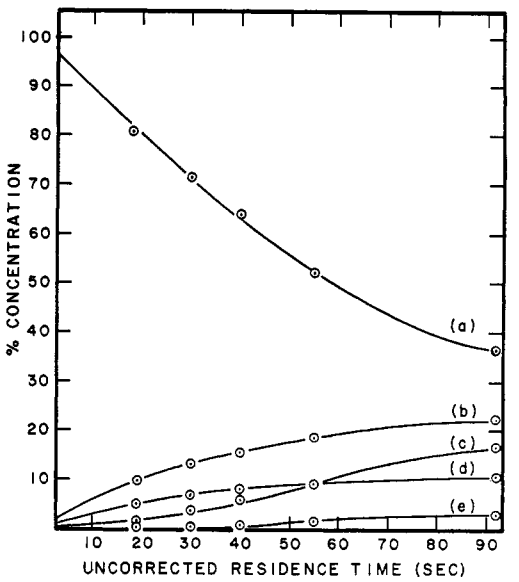

Figure 3. Composition of pyrolysate formed from *N*-α-methylallylpyrrole at 483.8° *vs.* time: (a) *N*-α-methylallylpyrrole, (b) 3-*trans*-crotylpyrrole, (c) 2-*trans*-crotylpyrrole, (d) 2-α-methylallylpyrrole, and (e) 3-α-methylallylpyrrole.

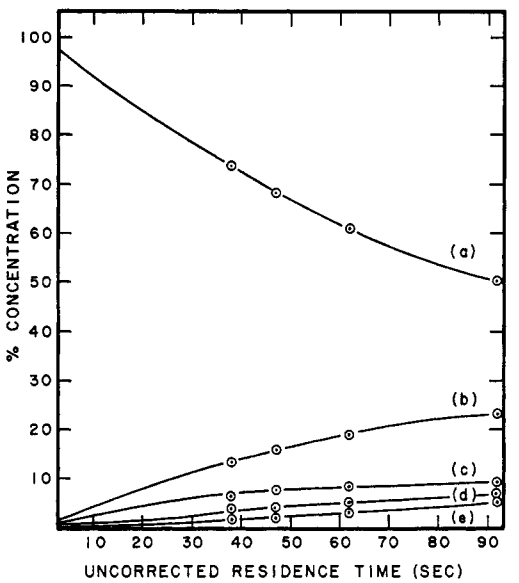

Figure 4. Composition of pyrolysate formed from *N*-*trans*-crotylpyrrole at 499.2° *vs.* time: (a) *N*-*trans*-crotylpyrrole, (b) 2-*trans*-crotylpyrrole, (c) 3-α-methylallylpyrrole, (d) 2-α-methylallylpyrrole, and (e) 3-*trans*-crotylpyrrole.

Reaction of 2,5-Dimethylpyrrylmagnesium Bromide with 3-Chloro-1-butene. The procedure was that used for the reaction of pyrrylmagnesium bromide with 3-chloro-1-butene. The neutral fraction consisting primarily of 2,5-dimethylpyrrole, 3-α-methylallyl-2,5-dimethylpyrrole, and 3-*trans*-crotyl-2,5-dimethylpyrrole was separated by preparative glpc using a 10 ft × 0.375 in. 30% Carbowax 20M column at 200°. The retention times and ir and nmr spectra of the substituted dimethylpyrroles were identical with those obtained from the pyrolysis products of *N*-crotyl-2,5-dimethylpyrrole and *N*-α-methylallyl-2,5-dimethylpyrrole.

Table II. Primary and Secondary Rearrangement Products of *N*-α-Methylallylpyrrole at 475.8 and 511.5°

Reaction	Time, sec	$k \times 10^{-2}$, sec^{-1}	Total convn, %	Concentration of products, % IIa	IIb	IIc	IIIa	IIIb	IIIc
I → (IIa, IIIb, IIIc) → (IIb, IIc, IIIa)[a,b]	6.5	2.89	17.1	4.6	1.4	0.3	0.1	8.6	2.1
IIa → IIb	3.4	4.13	14.0	0.8	−0.8				
IIa → IIc	3.4	0.79	3.8	0.2		−0.2			
IIa → IIIa	3.4	0.52	1.7	0.1			−0.1		
IIIb → IIb	3.4	1.06	6.8		−0.6			0.6	
IIIc → IIc	3.4	0.97	3.2			−0.1			0.1
I → (IIa, IIIb, IIIc)[c]	6.5	2.89		5.7	0.0	0.0	0.0	9.2	2.2
I → (IIa, IIIb, IIIc) → (IIb, IIc, IIIa)[a,d]	6.2	10.55	48.4	10.0	9.3	2.5	1.0	20.3	5.3
IIa → IIb	3.3	11.37	30.2	5.3	−5.3				
IIa → IIc	3.3	2.10	6.5	1.1		−1.1			
IIa → IIIa	3.3	1.95	5.6	1.0			−1.0		
IIIb → IIb	3.3	4.32	14.5		−3.6			3.6	
IIIc → IIc	3.3	4.34	14.6			−1.0			1.0
I → (IIa, IIIb, IIIc)[c]	6.2	10.55		17.4	0.4	0.4	0	23.9	6.3

[a] Experimental concentrations of primary and secondary products. [b] Temperature 475.8°. [c] Concentrations corrected for secondary reactions. [d] Temperature 511.5°.

Table III. Thermal Rearrangement of *N*-α-Methylallylpyrrole

Temp, C°	Res time, sec	Concn of products, % IIa	IIIb	IIIc	Total convn, %	Rate constants, 10^{-2} sec^{-1} [a] k_{tot}	k_{IIa}	k_{IIIb}	k_{IIIc}
475.8	6.49	5.7	9.2	2.2	17.1	2.89	0.95	1.55	0.37
478.3	6.47	6.3	10.3	2.4	19.0	3.26	1.08	1.77	0.41
481.2	6.44	7.2	11.2	2.8	21.2	3.70	1.26	1.95	0.49
484.5	6.41	8.1	12.2	3.1	23.4	4.16	1.44	2.17	0.55
486.2	6.40	8.5	13.0	3.3	24.8	4.45	1.53	2.33	0.59
489.2	6.37	9.0	13.5	3.5	26.1	4.73	1.64	2.45	0.64
491.2	6.36	9.9	14.6	3.8	28.3	5.23	1.83	2.70	0.70
494.5	6.33	10.9	16.0	4.2	31.1	5.88	2.06	3.02	0.80
500.8	6.28	13.2	18.7	5.0	36.9	7.33	2.62	3.72	0.99
502.3	6.27	13.7	19.4	5.1	38.2	7.68	2.75	3.90	1.03
505.8	6.24	15.0	20.8	5.3	41.2	8.50	3.10	4.30	1.10
511.5	6.19	17.4	23.9	6.3	48.4	10.55	3.86	5.30	1.40

[a] Rate constants should be divided by 2 to correct for degeneracy of the N to 2 and N to 3 migrations.

Reaction of 2,4-Dimethylpyrrylmagnesium Bromide with 3-Chloro-1-butene. The procedure was that used for the reaction of pyrrylmagnesium bromide with 3-chloro-1-butene. The main neutral products, 2-*trans*-crotyl-3,5-dimethylpyrrole and 2-α-methylallyl-3,5-dimethylpyrrole, were separated by preparative glpc using a 10 ft × 0.375 in. 30% Carbowax 20M column at 200°. The glpc retention time and ir and nmr spectra of the 2-*trans*-crotyl-3,5-dimethylpyrrole were identical with those obtained from one of the pyrolysis products produced from *N*-α-methylallyl-2,5-dimethylpyrrole and from *N*-crotyl-2,5-dimethylpyrrole.

The 2-α-methylallyl-3,5-dimethylpyrrole which was not found in the pyrolysates gave the following properties: 99.3% pure (glpc analysis); $n^{25}D$ 1.5038; λ_{max}^{MeOH} 210 nm (ε 7520); ν_{CCl_4} 3490 (N–H), 1640, 920 cm^{-1}; nmr 1.28 (doublet, 3 H), 1.93 (singlet, 3 H), 2.15 (singlet, 3 H), 3.50 (multiplet, 1 H), 4.88 (multiplet, 1 H), 5.12 (multiplet, 1 H), 5.48 (doublet, 1 H), 5.97 (multiplet, 1 H), and 7.10 ppm (broad, 1 H); molecular ion *m/e* 149.119 (theory 149.120).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.59; H, 10.01; N, 9.46.

Kinetic Studies. Reaction rates for the gas-phase isomerizations were obtained by using the previously described[22] system of a capillary flow reactor coupled directly to a gas chromatograph. The capillary reactor consisted of an 8 ft × 0.04 in i.d. gold tube wrapped around a silver-plated copper heat sink. Reactor temperatures were measured with an iron–constantan thermocouple connected to a Leeds and Northrup millivolt potentiometer. Analyses of the isomerization products were carried out on a 6 ft × 0.125 in. Carbowax 20M column at 150°. Most of the experiments were carried out with the reactor and the glpc system in parallel.

(22) C. A. M. G. Cramers and A. I. M. Keulemans, *J. Gas Chromatogr.*, **5**, 58 (1967); C. A. M. G. Cramers, Thesis, Eindhoven, 1967.

The order of the isomerization reactions for the compounds investigated was determined by measuring the concentrations of reactants and products at four or five residence times and by plotting log C_0/C_t *vs.* time. The straight lines obtained confirmed the first-order character of the isomerizations. Typical first-order plots are given in Figures 1 and 2. Rate constants were calculated from $kt = \ln C_0/C_t$ in which t is the residence time in the reactor and C_0 and C_t are the concentrations of the reactant at time zero and after t seconds, respectively. The residence times were obtained from flow rate measurements and were corrected for thermal expansion of the carrier gas, reactants, and products. Concentration values were obtained from the chromatograms by the electronic integration of peaks.

In the treatment of parallel reactions the total rate constant, obtained from the disappearance of the reactant, was divided as follows

$$C \xleftarrow{k_2} A \xrightarrow{k_1} B$$

$$k_1 + k_2 = k = 1/t \ln A_0/A_t$$

$$k_1 = B_t/(B_t + C_t)(1/t) \ln A_0/A_t, \text{ etc.}$$

Tentative identifications of secondary reactions were obtained from plots of concentrations of reactants and products *vs.* time (see Figures 3 and 4). Those products, whose relative increases in concentration on going to longer residence times were clearly higher than those for other products, were regarded as secondary products. The tentative identifications were substantiated by comparing the results of thermal rearrangements of all products under comparable conditions. Representative results for the rearrangement of *N*-α-methylallylpyrrole (I), at 475.8 and 511.5° (see Table II), illustrate how the secondary reaction assignments were verified.

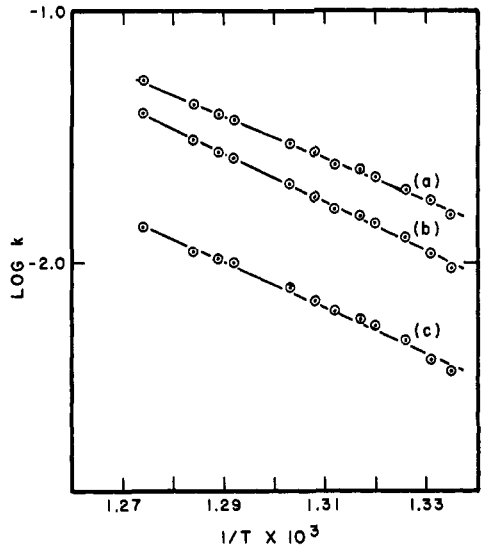

Figure 5. Arrhenius plots for the conversion of *N*-α-methylallylpyrrole into 3-*trans*-crotylpyrrole (a), 2-α-methylallylpyrrole (b), and 3-*cis*-crotylpyrrole (c).

Rate constants for product isomerizations were calculated from the experiments run under the same conditions as those used for the N isomers. The conversions of products in Table II (fifth column) were calculated from the rate constants using $kt = \ln C_0/C_t$ assuming that the effective residence time of a primary product in the reactor was *ca.* 55% of that of the reactant. The corrections applied to the primary reactions (last six columns in Table II) were calculated from the conversion (column five) and the original concentration of the primary product. From the corrected concentrations found, it is evident that, within the limits of accuracy of the concentration measurements estimated at *ca.* ±3% relative, the quantities of IIb, IIc, and IIIa observed can be accounted for as secondary rearrangement products from IIa, IIIb, and IIIc.

The effect of temperature on the rate constants of the primary reactions was obtained by measuring the concentrations as a function of temperature. Usually 20 to 30 measurements were taken at 2–4° intervals over a range of 40–50° and for two residence times in the reactor. Corrections for secondary reactions were applied in a way analogous to the procedure outlined in Table II. In most experiments, equilibrium reactions were studied where the total conversion did not exceed *ca.* 20%. Values of the rate constant calculated for each corrected measurement were plotted *vs.* the reciprocal temperature and least-squares fits were calculated. Typical results for the isomerization of *N*-α-methylallylpyrrole at 12 representative temperatures are given in Table III and in Figure 5.

Activation parameters, obtained from the Arrhenius equation in the usual way, are reported in Table I. Application of the correction factors introduces uncertainties in the values of the concentrations and the magnitude of these uncertainties, which are estimated to be 3–5%, depends largely on the relative reaction rates in the particular system.

N-α-Methylallyl and *N*-*trans*-crotyl-2,5-dimethylpyrroles were found to follow first-order kinetics. Rate constants as a function of temperature were determined by measuring the concentrations of products and reactant over the range of 387.5–450.6° (12 temperatures) for the *N*-α-methylallyl compound and over the range of 436.5–483.0° (16 temperatures) for the *N*-*trans*-crotyl compound. Activation parameters were obtained for the formation of the 3-(substituted allyl)-2,5-dimethylpyrroles in the way described previously for the pyrroles. The data along with rate constants at 440° are reported in Table I.

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