Photoisomerization of (Substituted allyl)dialkylpyrroles

John M. Patterson,* J. Douglas Ferry, and Michael R. Boyd

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506. *Received November 29, 1972*

Abstract: *N*-(Substituted allyl)-2,5-dimethylpyrroles undergo photoisomerization to the corresponding 2-(substituted allyl)-2,5-dimethyl-2*H*-pyrroles (major product) and 3-(substituted allyl)-2,5-dimethylpyrroles (minor product) with inversion and noninversion of the migrating allyl group. Competitive photocleavage is also observed. The irradiation of (substituted allyl)methylethylpyrroles results in group migrations which show a slight preference for the methyl terminus. Evidence for an intramolecular migration in the isomerization is presented.

On photolysis N-substituted pyrroles have been reported to follow two different reaction paths: substituent cleavage and substituent migration. The presence of C substituents on the pyrrole ring appears to determine the extent to which each of these paths is followed. Thus, the irradiation of *N-tert*-butyl- or *N*-benzyl-2,4-diphenylpyrrole produces 2,4-diphenylpyrrole[1] (95 and 80% conversions, respectively), while irradiation of *N*-benzylpyrrole or *N*-benzyl-2,5-dimethylpyrrole produces products in which the benzyl substituent has migrated to the 2 and 3 positions of the pyrrole ring.[2] Since photointerconversion of the 2- and 3-benzylpyrroles was not observed (although an irreversible photoisomerization of 2- to 3-cyanopyrrole has been reported[3]), the formation of 3 isomer probably arises from a direct N to 3 migration. The introduction of methyl substituents in the 2 and 5 positions of the pyrrole ring does not inhibit the migration, instead the overall conversion is improved and the benzyl group migrates to give the 2*H*-pyrrole as the major product. Some N to 3 migration is observed along with *ca.* 8% photocleavage.

The study reported herein was undertaken to examine the migrating propensity of the allyl group in dimethylpyrrole systems and to determine whether a photo-Claisen reaction competed with the expected N to 2 and N to 3 shifts as was recently reported for the thermally induced[4] isomerizations of these compounds.

As was observed with the *N*-benzyldimethylpyrroles, the photolysis of *N*-allyl-2,5-dimethylpyrrole produces the corresponding 2 and 3 isomers in 34 and 5% yields, respectively. Similarly, the irradiation of the *N*-(substituted allyl)-2,5-dialkylpyrroles (**1**, **5**), where X is α-methylallyl (a), *trans*-crotyl (b), and *cis*-crotyl (c), resulted in group migration to the 2 and 3 positions of the pyrrole ring with and without inversion of the substituted allyl group. The major products of reaction were the 2*H*-pyrroles (**2**, **6**, **7**); minor amounts of 3-substituted pyrroles (**3**, **8**, **9**) and cleavage products (*ca.* 10%) were obtained. The results are summarized in Tables I–III.[5]

Table I. Products from the Irradiation of *N*-(Substituted allyl)-2,5-dimethylpyrrole at 254 nm[a]

N-Substituted pyrrole photolyzed[b]	Substituted 2*H*-pyrrole			3-Substituted pyrrole		
	2a	**2b**	**2c**	**3a**	**3b**	**3c**
1a (26.2)[c]	17.0	10.4	11.2	2.0	2.0	1.2
1b (30.3)[c]	15.2	19.7	0	2.3	3.8	0
1c (39.4)[c]	14.4	0	17.4	3.0	0	3.0

[a] Relative product yields from glpc analysis. [b] Cleaved 2,5-dimethylpyrrole, **4**, obtained in *ca.* 10% yield. [c] Recovered starting material. Isomerization of the substituted allyl group in recovered starting material was not observed.

Table II. Effect of Oxygen and Air on the Photoisomerization of *N*-α-Methylallyl-2,5-dimethylpyrrole[a] (**1a**)

	Substituted 2*H*-pyrrole			3-Substituted pyrrole			Dimethylpyrrole,
Gas[b]	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**	**4**
Nitrogen	11.2	6.6	7.8	3.4	2.1	2.6	7.7
Air	11.0	6.6	7.4	2.4	1.8	1.6	7.8
Oxygen	12.0	7.2	8.1	2.7	1.8	1.7	9.5

[a] Yields determined by glpc using hexadecane as an internal standard. Average deviations of the glpc analyses were ±2% for **2**, **4**, and **1a** (recovered) and ±15% for **3**. [b] Recovered **1a** from the nitrogen, air, and oxygen experiments was 38.2, 40.0, and 31.3%, respectively.

Table III. Effect of Crowding at the Migration Terminus. Photolysis of *N*-(Substituted allyl)-2-methyl-5-ethylpyrroles (**5**)[a]

Pyrrole photolyzed[b,c]	Substituted 2*H*-pyrrole[d]					
	6a	**6b**	**6c**	**7a**	**7b**	**7c**
5a	9.0	4.5	(11.5)[e]	7.1	(11.5)[e]	5.5
5b	8.6	12.1	*e*, *f*	6.5	(10.3)[e]	0
5c	9.3	0	(12.2)[e]	7.2	*e*, *f*	10.1

[a] Relative product yields from glpc analysis. [b] Cleaved methylethylpyrrole was obtained in *ca.* 9–12% yield. [c] Recovered *N*-(substituted allyl)methylethylpyrrole, obtained in 19–28% yield, showed no isomerization of substituted allyl group. [d] Isomeric 3-(substituted allyl)methylethylpyrroles were obtained in *ca.* 2% yield each. However, **5b** produced no *cis*-crotylpyrrole product and **5c** produced no *trans*-crotylpyrrole product. [e] Isomers not resolved by glpc. [f] Product yield probably zero, since in Table I *trans*-crotyl reactant did not produce *cis*-crotyl product. See also entry under **5c**; *cis*-crotyl reactant did not produce *trans*-crotyl product, **6b**.

The structures and properties of the *N*-allyl- and *N*-(substituted allyl)-2,5-dimethylpyrroles have been reported previously.[4] The *N*-(substituted allyl)-2-methyl-5-ethylpyrroles were synthesized analogously from 2,5-heptanedione and the appropriate amine.

Photolysis products were isolated by preparative

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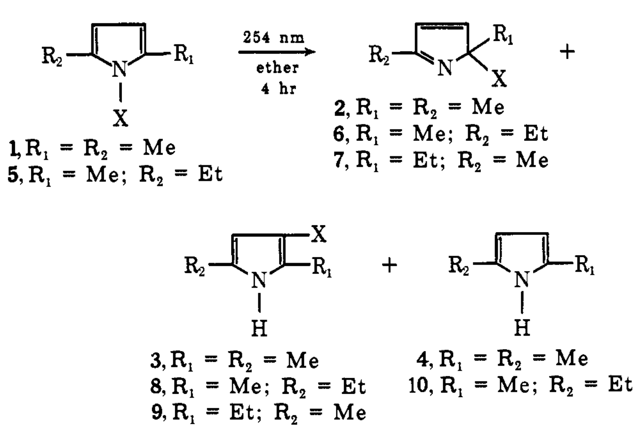
[1] A. Padwa, R. Gruber, D. Pashayan, M. Bursey, and L. Dusold, *Tetrahedron Lett.*, 3659 (1968).

[2] J. M. Patterson and L. T. Burka, *Tetrahedron Lett.*, 2215 (1969).

[3] H. Hiraoka, *Chem. Commun.*, 1306 (1970).

[4] J. M. Patterson, J. W. deHaan, M. R. Boyd, and J. D. Ferry, *J. Amer. Chem. Soc.*, 94, 2487 (1972).

[5] Comparisons of the glpc analyses with and without the use of internal standards show the same product ratios. Products yields determined without the use of internal standards were within 10% of the values reported in those experiments where internal standards were used.



1, $R_1 = R_2 = Me$
5, $R_1 = Me$; $R_2 = Et$

2, $R_1 = R_2 = Me$
6, $R_1 = Me$; $R_2 = Et$
7, $R_1 = Et$; $R_2 = Me$

3, $R_1 = R_2 = Me$
8, $R_1 = Me$; $R_2 = Et$
9, $R_1 = Et$; $R_2 = Me$

4, $R_1 = R_2 = Me$
10, $R_1 = Me$; $R_2 = Et$

X = α-methylallyl, **a**; *trans*-crotyl, **b**; *cis*-crotyl, **c**

glpc from large scale runs after separation into neutral and basic fractions. The unreacted starting materials, cleaved pyrroles, 3-allyldimethylpyrrole, and 3-(substituted allyl)dimethylpyrroles[4] were identified by comparisons of glpc retention times, infrared spectra, and nmr spectra with those obtained from authentic samples. Structural determinations of the 2-(substituted allyl)-2,5-dialkyl-2*H*-pyrroles were based upon elemental analyses, infrared and nmr spectra, and the fact that these same compounds were produced by reaction of 3-chloro-1-butene with the appropriate 2,5-dialkylpyrrylmagnesium bromide.[6] The methylethyl-2*H*-pyrroles with the methyl singlet at *ca.* 1.16 ppm were assigned structure **6** and those with the methyl singlet at *ca.* 2.18 ppm were assigned structure **7**.

The isomeric 3-*trans*- and 3-*cis*-crotylmethylethylpyrroles were synthesized by the thermolysis of a mixture of the six isomeric 2-(substituted allyl)methylethyl-2*H*-pyrroles at 100°. The isomeric 3-(α-methylallyl)methylethylpyrroles were not produced in the pyrolysis. Structures of the crotyl products were established by elemental analyses and spectral properties. The position of the crotyl substituent in the ring relative to the methyl and ethyl substituents was determined by decoupling experiments. Pyrroles with structure **9** exhibited long-range coupling of the ring proton with methyl protons but not with the methylene protons in ethyl. Those pyrroles with structure **8** showed ring proton–methylene proton coupling but no ring proton–methyl coupling.

The 3-(substituted allyl)methylethylpyrroles produced in the photolysis reactions were identified on the basis of comparisons of glpc retention times with those obtained from the pyrroles isolated in the thermolysis experiments and by analogy with the products produced in the (substituted allyl)dimethylpyrrole photolyses.

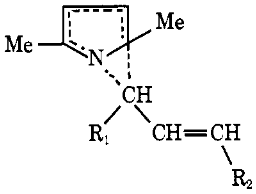
The influence of substituents on the product distribution was investigated by carrying out the photolyses of the *N*-(substituted allyl)dialkylpyrroles under identical conditions. In these irradiations both the 2*H*-pyrroles **2**, **6**, and **7** and the pyrroles **3**, **8**, and **9** containing inverted and noninverted allyl substituents were formed, with the 2*H*-pyrroles being the major products of reaction.

That the migrations are intramolecular is supported by the observations that recovered starting materials **1** and **5** do not contain isomerized allyl substituent, that neither products **2**, **6**, **7**, or **3b** undergo interconversion or are isomerized further on isolation followed by extended irradiation, and that the photolyses of the *N*-*trans*-crotyl compounds **1b** and **5b** produced only *trans*-crotyl (**2b**, **6b**, **7b**, **3b**, **8b**, **9b**) and α-methylallyl (**2a**, **6a**, **7a**, **3a**, **8a**, **9a**) products.[7] Additional evidence for a nondissociated radical or concerted process was obtained from experiments run in air and oxygen atmospheres. Photolyses in nitrogen and air showed no significant differences in yields and in product ratios, and although the yields of products obtained in the oxygen photolyses were slightly larger, the product ratios were essentially the same as those found in the nitrogen experiments (see Table II).

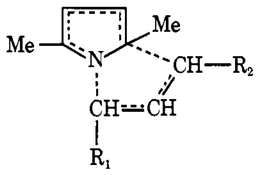
In thermal reactions, 2*H*-pyrroles appear to be intermediates in the isomerization of *N*-(substituted allyl)-dimethylpyrroles to the corresponding 3-(substituted allyl)pyrroles.[4] The direct N to 3 shift of the migrating group as was observed in the formation of 3 isomer during the photolysis of *N*-benzyl-2,5-dimethylpyrrole[2] is also involved in the formation of 3 isomers in the photolysis of *N*-(substituted allyl)-2,5-dialkylpyrroles since the further irradiation of the isolated 2*H*-pyrrole product does not give rise to the 3-(substituted allyl)-pyrroles.

Experiments in which the extent of product formation was measured as a function of time showed that cleaved-pyrrole yield increases paralleled isomerized-pyrrole yield increases. Furthermore, the irradiation of isolated isomerization products **2**, **6**, **7**, and **3b** did not produce cleavage products (dimethylpyrrole or methylethylpyrrole). These observations indicate that the cleavage reaction is competitive with the isomerization reaction and that the cleavage products observed arise solely from excited N isomer.

If one assumes that the transition state geometries of the photoisomerizations are essentially those in a vibrationally excited ground state, product composition can be explained in terms of the effects of steric interactions on relative transition state stability. Transition states for 1,2 shifts involving noninversion of the allyl group have the forms **11** and **12** while those for 1,2 shifts with inversion of the allyl group have the forms **13** and **14**. In the transition states **11** and **12** there is probably little electron delocalization in the migrating group (since *trans*-crotyl migration produced no *cis*-crotyl product) and therefore essentially no



11, $R_1 = Me$; $R_2 = H$
12, $R_1 = H$; $R_2 = Me$



13, $R_1 = Me$; $R_2 = H$
14, $R_1 = H$; $R_2 = Me$

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[6] The reaction of alkyl halides with dialkylpyrrylmagnesium halides is known to produce 2,2,5-trialkyl-2*H*-pyrroles: (a) J. M. Patterson and S. Soedigdo, *J. Org. Chem.*, 33, 2057 (1968); (b) H. Booth, A W. Johnson, and F. Johnson, *J. Chem. Soc.*, 98 (1962).

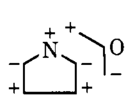
[7] Similarly, the irradiation of *N*-*cis*-crotyl compounds gave rise only to *cis*-crotyl and α-methylallyl products. No *trans*-crotyl products were detected.

stabilization through alkyl substitution. Transition states **13** and **14** should be both stabilized by alkyl substitution in the migrating group relative to transition states **11** and **12**. Destabilizing factors arising from steric interactions at the migration terminus appear in transition states **11** and **14**. A consideration of product distributions suggests that the steric effects are slightly more important than other factors in determining product composition. Further evidence for the existence of steric crowding at the migration terminus was obtained from experiments involving the irradiation of *N*-(substituted allyl)-2-methyl-5-ethylpyrrole. Isomerizations involving both inversion and noninversion of the substituted allyl group were observed with migrations to the methyl terminus being slightly favored (see Table III).

A comparison of the results of the photoisomerization reactions with those of the previously reported thermal isomerizations[4] indicates that steric factors apparently influence the extent of inversion and noninversion of the substituted allyl group during migration, *i.e.*, crotyl products are favored in both the thermally induced and the photoinduced isomerizations regardless of the initial configuration of the migrating group. In addition, the migratory aptitudes, based on overall rearrangement, in the two reactions are the same: α-methylallyl > *trans*-crotyl > *cis*-crotyl. The α-methylallyl group migrates with a slight preference for inversion in both thermal and photo reactions. In the former, the migration from the N to the 3 position is favored over the N to 2 position migration while in the latter the N to 2 position migration is favored. Migrations from the N to the 2 position without inversion are favored by *trans*- and *cis*-crotyl groups in both thermal and photo processes.

In thermal reactions, the α-methylallyl group rearranged to the *trans*- and *cis*-crotyl configuration with trans always in excess. However, in the photo reactions, the α-methylallyl group on rearrangement gives *ca.* equal distributions of the *trans*- and *cis*-crotyl configurations.

The transition-state model developed for the derivation of selection rules for the thermal isomerization of allylic pyrroles[4] can be modified for photoinduced isomerizations by using the lowest unoccupied molecular orbital of pyrryl radical (ψ_4) in the pyrryl–allyl radical complex. Selection rules predicted by this model indicate that N to 2 migrations with allyl inversion and N to 3 migrations without allyl inversion should be favored over other concerted paths. The results show that the predicted routes are not favored.



ψ_4 of pyrrole, ψ_2 of allyl radical

Experimental Section

Boiling points are uncorrected. Gas chromatographic analyses were made on a Hewlett-Packard Model 5750 gas chromatograph (equipped with a flame ionization detector and electronic integrator) using 6 ft × 0.125 in. Carbowax 20M and UCW-98 Hewlett-Packard high-efficiency packed columns at 80° programmed at 6°/min to 150°. Preparative scale separations of the photolyzates were carried out using a 10 ft × 0.375 in. 20% UCW-98 column at 140–200° for the neutral fraction and a 15 ft × 0.375 in. 10% Carbowax 20M column at 90° for the basic fraction. Infrared spectra were measured on a Beckman IR-8 spectrophotometer; ultraviolet spectra were measured on a Perkin-Elmer Model 202 spectrophotometer; nmr spectra 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; mass spectra were taken on a Hitachi RMU-7 mass spectrometer.

Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. 48106.

Synthesis of *N*-Allyl- and *N*-(Substituted allyl)dimethylpyrroles. The synthesis and properties of *N*-allyl-, *N*-α-methylallyl-, *N*-*trans*-crotyl-, and *N*-*cis*-crotyl-2,5-dimethylpyrroles have been previously described.[4]

***N*-α-Methylallyl-2-methyl-5-ethylpyrrole.** The pyrrole was synthesized by the procedure used for the preparation of *N*-α-methylallyl-2,5-dimethylpyrrole. From 19 g (0.26 mol) of α-methylallylamine and 34 g (0.26 mol) of heptanedione, obtained by acid cleavage of 2-methyl-5-ethylfuran,[8] there was obtained 33.4 g (86%) of pyrrole, 99.2% pure (glpc analysis): bp 98° (17 mm); $n^{25}\text{D}$ 1.4881; uv max (MeOH) 210 nm (ϵ 5160); ir (CCl_4) 2980, 2940, 1660, 940 cm^{-1}; nmr (CCl_4) δ 1.16 (t, 3), 1.57 (d, 3), 2.20 (s, 3), 2.57 (q, 2), 4.47 (m, 1), 5.07 (m, 1), 5.62 (s, 2), and 6.00 (complex m, 1).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.91; H, 10.49; N, 8.52.

***N*-Crotyl-2-methyl-5-ethylpyrrole.** The pyrrole was synthesized by the procedure used for *N*-α-methylallyl-2-methyl-5-ethylpyrrole. From 18.6 g (0.15 mol) of heptanedione[8] and 10.4 g (0.15 mol) of crotylamine and 5 ml of acetic acid in 150 ml of benzene, there was obtained 17.8 g (75%) of a mixture consisting of *ca.* 80% trans and 20% cis isomers, bp 95–97° (9 mm).

***N*-*trans*-Crotyl-2-methyl-5-ethylpyrrole.** The pyrrole was obtained by preparative glpc using a 12 ft × 0.375 in. 30% UCW-98 column at 140°: $n^{25}\text{D}$ 1.4980; uv max (MeOH) 225 nm (ϵ 6482); ir (CCl_4) 2980, 2940, 1520, 1420, 965 cm^{-1}; nmr (CCl_4) δ 1.22 (t, 3), 1.67 (m, 3) 2.17 (s, 3), 2.50 (q, 2), 4.30 (m, 2), 5.37 (m, 2), and 5.63 (s, 2); molecular ion at *m/e* 163.137 (theory 163.136). The sample was 100% pure (glpc analysis on a 6 ft × 0.125 in. Carbowax 20M column).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.52; N, 8.58. Found: C, 81.01; H, 10.51; N, 8.70.

***N*-*cis*-Crotyl-2-methyl-5-ethylpyrrole.** The pyrrole was separated from *N*-*trans*-crotyl-2-methyl-5-ethylpyrrole and was 98% pure (glpc analysis): $n^{25}\text{D}$ 1.5024; uv max (MeOH) 223 nm (ϵ 6113); ir (CCl_4) 2980, 2950, 1440, 640, cm^{-1}; nmr (CCl_4) δ 1.20 (t, 3), 1.72 (complex d, 3), 2.17 (s, 3), 2.51 (q, 2), 4.43 (complex d, 2), 5.50 (m, 2), and 5.67 (s, 2); molecular ion at *m/e* 163.131 (theory 163.136).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.52; N, 8.58. Found: C, 81.00; H, 10.62; N, 8.56.

2-Methyl-5-ethylpyrrole. The pyrrole was synthesized by the procedure of Young and Allen.[9] From 40 g (0.3 mol) of 2,5-heptanedione[8] and 100 g (0.87 mol) of ammonium carbonate there was obtained 31 g (95%) of pyrrole: bp 78–80° (7.5 mm), lit.[10] bp 74–75 (11 mm); glpc purity, 99.2%; $n^{25}\text{D}$ 1.5015; uv max (MeOH) 216 nm (ϵ 6370); ir (CCl_4) 3480 cm^{-1} (N–H); nmr (CCl_4) δ 1.17 (t, 3), 2.13 (s, 3), 2.50 (q, 2), 5.60 (d, 2), and 7.33 (brd s, 1).

Anal. Calcd for $C_7H_{11}N$: C, 77.01; H, 10.16; N, 12.83. Found: C, 77.09; H, 10.08; N, 12.75.

Preparative Photolyses. The pyrroles were irradiated in ether solution (1:3) in a 2.8 × 27 cm water-jacketed quartz tube using a Rayonet Reactor at 254 nm. The quartz vessel was rinsed with an acetone solution of triethylamine and dried prior to use. The photolyzates were separated into neutral and base fractions by extraction with 0.05 *N* HCl. The components of these fractions were isolated by preparative glpc.

Photolysis of *N*-α-Methylallyl-2,5-dimethylpyrrole. From the irradiation of 10.48 g of the pyrrole in 32 ml of ether for 86 hr there was obtained 10.05g of photolyzate. The components of the mixture were (glpc): 2-α-methylallyl-2,5-dimethyl-2*H*-pyrrole (18%), 2-*trans*-crotyl-2,5-dimethyl-2*H*-pyrrole (10%), 2-*cis*-crotyl-2,5-dimethyl-2*H*-pyrrole (12%), *N*-α-methylallyl-2,5-dimethylpyrrole (21%), 2,5-dimethylpyrrole (7%), 3-α-methylallyl-2,5-dimethyl-

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[8] H. Hunsdiecker, *Ber.*, **75B**, 447 (1942).

[9] D. M. Young and C. F. H. Allen, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 219.

[10] H. Fischer, E. Sturm, and H. Friedrich, *Justus Liebigs Ann. Chem.*, **461**, 260 (1928).

pyrrole (4%), 3-*trans*-crotyl-2,5-dimethylpyrrole (2%), and 3-*cis*-crotyl-2,5-dimethylpyrrole (3%).

Extraction of the photolyzate produced 5.85 g of bases and 3.07 g of neutrals. The per cent yields (based on 10.48 g of starting material) of fraction components were determined by glpc analysis using hexadecane as an internal standard. From the base fraction there was obtained 2-α-methylallyl-2,5-dimethyl-2*H*-pyrrole (4.1%), 2-*trans*-crotyl-2,5-dimethyl-2*H*-pyrrole (14.1%), and 2-*cis*-crotyl-2,5-dimethyl-2*H*-pyrrole (12.7%). The base components on isolation by preparative glpc exhibited the following properties.

2-α-Methylallyl-2,5-dimethyl-2*H*-pyrrole was 100% pure (glpc analysis): n^{25}D 1.4665; uv max (MeOH) 211 nm (ϵ 3730); ir (CCl_4) 1614, 918 cm^{-1}; nmr (CCl_4) δ (pair of diastereomers) 0.77 and 0.93 (pair of doublets, 3), 1.13 (s, 3), 2.17 (s, 3), 2.46 (q, 1), 4.83 (m, 1), 5.07 (m, 1), 5.63 (m, 1), 6.10 and 6.13 (pair of doublets, 1), 7.08 and 7.13 (pair of doublets, 1); molecular ion at *m/e* 149.123 (theory 149.120).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.37; H, 10.07, N, 9.42.

2-*trans*-Crotyl-2,5-dimethyl-2*H*-pyrrole was 99.5% pure (glpc analysis): n^{25}D 1.4630; uv max (MeOH) 219 nm (ϵ 3330); ir (CCl_4) 1614, 970 cm^{-1}; nmr (CCl_4) δ 1.15 (s, 3), 1.62 (d, 2), 2.15 (complex s, 5), 5.32 (m, 2), 6.10 (d, 1), and 7.17 (d, 1); molecular ion at *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, 80.35; H, 10.10; H, 9.42.

2-*cis*-Crotyl-2,5-dimethyl-2*H*-pyrrole was 98% pure (glpc analysis): n^{25}D 1.4695; uv max (MeOH) 219 nm (ϵ 3370); ir (CCl_4) 1614, 665 cm^{-1}; nmr (CCl_4) δ 1.18 (s, 3), 1.57 (d, 3), 2.17 (s, 3), 2.30 (m, 2), 5.30 (m, 2), 6.10 (d, 1), and 7.10 (d, 1); molecular ion at *m/e* 149.122 (theory 149.120).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.51; H, 10.24; N, 9.41.

The retention times, the infrared spectra, and the nmr spectra of the dimethyl-2*H*-pyrroles were identical with those obtained from the reaction of 2,5-dimethylpyrrylmagnesium bromide with 3-chloro-1-butene.

From the neutral fraction there was obtained *N*-α-methylallyl-2,5-dimethylpyrrole (14.1%), 2,5-dimethylpyrrole (3.9%), 3-α-methylallyl-2,5-dimethylpyrrole (2.0%), 3-*trans*-crotyl-2,5-dimethylpyrrole (1.0%), and 3-*cis*-crotyl-2,5-dimethylpyrrole (0.8%). The neutral components on separation by preparative glpc gave glpc retention times, infrared spectra, and nmr spectra which were identical with the properties previously reported for these compounds.[4]

Photolysis of *N-trans-* and *N-cis*-Crotyl-2,5-dimethylpyrroles. The photolyzate obtained from the irradiation of 10.5 g of a mixture of 82% *N-trans*-crotyl- and 18% *N-cis*-crotyl-2,5-dimethylpyrroles in 32 ml of ether for 21 hr consisted of (glpc analysis) 2,5-dimethylpyrrole (5%), 2-α-methylallyl-2,5-dimethyl-2*H*-pyrrole (7%), 2-*trans*-crotyl-2,5-dimethyl-2*H*-pyrrole (8%), 2-*cis*-crotyl-2,5-dimethyl-2*H*-pyrrole (3%), *N-trans*-crotyl-2,5-dimethylpyrrole (55%), and *N-cis*-crotyl-2,5-dimethylpyrrole (13%). The 3-α-methylallyl-, 3-*trans*-crotyl-, and 3-*cis*-crotyl-2,5-dimethylpyrroles were also present in combined yield of 1%. The components of the base and neutral fractions (obtained by acid extraction) were separated by preparative glpc. The glpc retention times, the infrared spectra, and nmr spectra obtained from each of the components listed above were identical with those obtained from the photolysis products of *N*-α-methylallyl-2,5-dimethylpyrrole.

Photolysis of *N*-Allyl-2,5-dimethylpyrrole. The photolyzate obtained from the irradiation of 8.2 g of the pyrrole in 25 ml of ether for 89 hr contained (glpc analysis): 2-allyl-2,5-dimethyl-2*H*-pyrrole (28%), *N*-allyl-2,5-dimethylpyrrole (43%), 2,5-dimethylpyrrole (8%), and 3-allyl-2,5-dimethylpyrrole (8%).

2-Allyl-2,5-dimethyl-2*H*-pyrrole was isolated (extraction and preparative glpc) from the base fraction and was 100% pure (glpc): bp 50° (11 mm); n^{25}D 1.4640; uv max (MeOH) 207 nm (ϵ 3690); ir (CCl_4) 1614 cm^{-1}; nmr (CCl_4) δ 1.20 (s, 3), 2.22 (s, 3), 2.33 (d, 2), 4.97 (complex m, 2), 5.72 (complex m, 1), 6.28 (d, 1, J = 5 Hz), 7.20 (d, 1, J = 5 Hz).

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.78; H, 9.62; N, 10.43.

N-Allyl-2,5-dimethylpyrrole, 2,5-dimethylpyrrole, and 3-allyl-2,5-dimethylpyrrole were isolated by preparative glpc from the neutral fraction. The glpc retention times, nmr spectra, and infrared spectra were identical with those obtained from authentic samples.

Photolysis of *N*-α-Methylallyl-2-methyl-5-ethylpyrrole. The photolyzate obtained from the irradiation of 5.89 g of the pyrrole in 18 ml of ether for 7.5 hr was analyzed by glpc: 2-methyl-5-ethylpyrrole (6%), 2-α-methylallyl-2-methyl-5-ethyl-2*H*-pyrrole and 2-α-methylallyl-5-methyl-2-ethyl-2*H*-pyrrole (5%), 2-*trans*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole (4%), 2-*cis*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole and 2-*trans*-crotyl-5-methyl-2-ethyl-2*H*-pyrrole (7%), 2-*cis*-crotyl-5-methyl-2-ethyl-2*H*-pyrrole (4%), and *N*-α-methylallyl-2-methyl-5-ethylpyrrole (64%). The six corresponding isomeric 3-(substituted allyl)methylethylpyrroles were obtained in combined yield of 4%.

The base fraction (obtained by acid extraction) consisted of 2-α-methylallyl-2-methyl-5-ethyl-2*H*-pyrrole and 2-α-methylallyl-5-methyl-2-ethyl-2*H*-pyrrole (21%), 2-*trans*-crotyl-5-methyl-2-ethyl-2*H*-pyrrole (22%), 2-*cis*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole (14%), and 2-*cis*-crotyl-5-methyl-2-ethyl-2*H*-pyrrole (17%). The base components were isolated by preparative glpc and exhibited the following properties.

2-α-Methylallyl-2-methyl-5-ethyl-2*H*-pyrrole was 100% pure (glpc): n^{25}D 1.4645; uv max (MeOH) 211 nm (ϵ 4088); ir (CCl_4) 1612, 915 cm^{-1}; nmr (CCl_4)δ (pair of diastereomers) 0.73 and 0.93 (pair of doublets, 3), 1.13 and 1.17 (pair of singlets, 3), 1.20 (t, 3), 2.45 (m, 3), 4.83 (m, 1), 5.05 (m, 1), 5.65 (m, 1), 6.17 and 6.18 (pair of doublets, 1), 7.10 and 7.15 (pair of doublets, 1); molecular ion at *m/e* 163.131 (theory 163.136).

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.72; H, 10.55; N, 8.46.

2-α-Methylallyl-5-methyl-2-ethyl-2*H*-pyrrole was 100% pure (glpc): n^{25}D 1.4643; uv max (MeOH) 217 nm (ϵ 4748); ir (CCl_4) 1612, 915 cm^{-1}; nmr (CCl_4) δ (pair of diastereomers) 0.60 (t, 3), 0.73 and 0.87 (pair of doublets, 3), 1.67 (m, 2), 2.18 (s, 3), 2.60 (m, 1), 4.83 (m, 1), 5.05 (m, 1), 5.57 (m, 1), 6.20 (m, 1), 7.00 and 7.05 (pair of doublets, 1); molecular ion *m/e* 163.131 (theory 163.136).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.64; H, 10.30; N, 8.78.

2-*trans*-Crotyl-2-methyl-5-ethyl-2*H*-pyrrole was 100% pure (glpc): n^{25}D 1.4666; uv max (MeOH) 220 nm (ϵ 3540); ir (CCl_4) 1612, 1450, 968 cm^{-1}; nmr (CCl_4) δ 1.16 (s, 3), 1.20 (t, 3), 1.62 (complex d, 3), 2.22 (complex m, 2), 2.48 (q, 2), 5.32 (complex m, 2), 6.15 (d, 1), and 7.13 (d, 1); molecular ion at *m/e* 163.136 (theory 163.136).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.75; H, 10.47; N, 8.66.

2-*trans*-Crotyl-5-methyl-2-ethyl-2*H*-pyrrole and 2-*cis*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole were isolated as a mixture consisting (based on integration of the nmr spectrum) of 80% trans and 20% cis: n^{25}D 1.4705; uv max (MeOH) 220 nm (ϵ 2390); ir (CCl_4) 1612, 1438, 968 cm^{-1}; nmr (CCl_4) δ 0.62 (t, 3), 1.58 (q, 2), 1.62 (complex d, 3), 2.17 (complex s, 5), 5.30 (complex m, 2), 6.13 (d, 1), and 7.07 (d, 1); molecular ion at *m/e* 163.135 (theory 163.136).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.66; H, 10.43; N, 8.47.

2-*cis*-Crotyl-5-methyl-2-ethyl-2*H*-pyrrole was 100% pure (glpc): n^{25}D 1.4699; uv max (MeOH) 221 nm (ϵ 3310); ir (CCl_4) 1614, 660 cm^{-1}; nmr (CCl_4) δ 0.66 (t, 3), 1.58 (complex d, 6), 2.18 (s, 3), 2.30 (m, 2), 5.28 (m, 2), 6.17 (d, 1), and 7.08 (d, 1); molecular ion *m/e* at 163.127 (theory 163.136).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.70; H, 10.56; N. 8.49.

N-α-Methylallyl-2-methyl-5-ethylpyrrole and 2-methyl-5-ethylpyrrole were isolated from the neutral fraction by preparative glpc. The glpc retention times, infrared spectra, and nmr spectra obtained were identical with those obtained from authentic samples. Four of the six isomeric 3-(substituted allyl)methylethylpyrroles were identified by comparisons of their glpc retention times with samples obtained from the 2*H*-pyrroles on thermolysis.

Photolysis of *N*-Crotyl-2-methyl-5-ethylpyrrole. The photolyzate obtained from the irradiation of 8 g of a mixture of 82% *N-trans*-crotyl and 18% *N-cis*-crotyl-2-methyl-5-ethylpyrrole in 24 ml of ether for 51.5 hr was analyzed by glpc: 2-α-methylallyl-2-methyl-5-ethyl-2*H*-pyrrole (9%), 2-α-methylallyl-5-methyl-2-ethyl-2*H*-pyrrole (7%), 2-*trans*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole (11%), a mixture of 2-*trans*-crotyl-5-methyl-2-ethyl-2*H*-pyrrole and 2-*cis*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole (11%), 2-*cis*-crotyl-5-methyl-2-ethyl-2*H*-pyrrole (2%), *N-trans* crotyl-2-methyl-5-ethylpyrrole (23%), 2-methyl-5-ethylpyrrole (10%), and *N-cis*-crotyl-2-methyl-5-ethylpyrrole (7%). The following components had glpc retention times corresponding to (substituted allyl)pyrroles: 3-*trans*-crotyl-5-methyl-2-ethylpyrrole (2%), 3-*cis*-crotyl-5-methyl-2-ethylpyrrole and 3-*trans*-crotyl-2-methyl-5-ethylpyrrole mixture (2%), and 3-*cis*-crotyl-2-methyl-5-ethylpyrrole (1%). Two additional components in combined yield of 2% were observed. Based on results from the photolysis of the substituted dimethylpyrroles, these substances are probably 3-α-methylallyl-5-methyl-2-ethylpyrrole and 3-α-methylallyl-2-methyl-5-ethylpyrrole. The components of the base and neutral fractions (obtained by acid extraction) were separated by preparative glpc. The glpc retention times, infrared spectra, and nmr spectra obtained from each of the components [excepting the 3-(substituted allyl)methylethylpyrroles] listed above were identical with those obtained from the photolysis products of *N*-α-methylallyl-2-methyl-5-ethylpyrrole. The 3-(substituted allyl)methylethylpyrroles had retention times identical with those obtained from the pyrrole fraction produced on photolysis of *N*-α-methylallyl-2-methyl-5-ethylpyrrole.

Synthesis of 2-(Substituted allyl)-2,5-dimethyl-2*H*-pyrroles by the Grignard Reaction. The procedure used was that previously described[6a] for the synthesis of 2-benzyl-2,5-dimethyl-2*H*-pyrrole except that warm potassium hydroxide solution was used in the basification step. The reaction of 2,5-dimethylpyrrylmagnesium bromide (prepared from 4.8 g (0.2 mol) of magnesium, 21.8 g (0.2 mol) of ethyl bromide in 500 ml of ether) and 19.2 g (0.2 mol) of 3-chloro-1-butene gave a basic fraction (6.2 g) which on distillation yielded 4.2 g of product, bp 60–62° (10 mm). The product mixture consisted of 2-α-methylallyl-2,5-dimethyl-2*H*-pyrrole (18%), 2-*trans*-crotyl-2,5-dimethyl-2*H*-pyrrole (72%), and 2-*cis*-crotyl-2,5-dimethyl-2*H*-pyrrole (10%). The percentages of products may not reflect the true composition arising from the Grignard reaction since it has been found that 2-α-methylallyl-2,5-dimethyl-2*H*-pyrrole isomerizes to the corresponding 2- and/or 3-crotyl compounds on mild heating (*ca.* 120°). In addition, the 2-α-methylallyl-2,5-dimethyl-2*H*-pyrrole may undergo acid-catalyzed isomerization to the 2-crotyl compound during the acid extraction. The components were separated by preparative glpc. The glpc retention times, infrared spectra, and nmr spectra obtained were identical with those obtained from the 2*H*-pyrroles isolated in the photolysis reaction.

Syntheses of 2-(Substituted allyl)-2-methyl-5-ethyl-2*H*-pyrroles by the Grignard Reaction. The procedure was that employed in the synthesis of the (substituted allyl)dimethyl-2*H*-pyrroles. Distillation of the base fraction yielded 3.5 g of product, bp 66–67° (3.5 mm). Analysis (glpc) showed the following components: 2-α-methylallyl-2-methyl-5-ethyl-2*H*-pyrrole (8%), 2-α-methylallyl-5-methyl-2-ethyl-2*H*-pyrrole (2%), 2-*trans*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole (39%), 2-*cis*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole (10%), 2-*trans*-crotyl-5-methyl-2-ethyl-2*H*-pyrrole (31%), and 2-*cis*-crotyl-5-methyl-2-ethyl-2*H*-pyrrole (10%). The components were separated by preparative glpc and were found to exhibit glpc retention times, infrared spectra, and nmr spectra identical with those obtained from the products of the photolysis of *N*-α-methylallyl-2-methyl-5-ethylpyrrole.

Preparation of the 3-(Substituted allyl)methylethylpyrroles. The isomeric 3-(crotyl)methylethylpyrroles were produced by heating a mixture of 5 g of the six isomeric 2-(substituted allyl)methylethyl-2*H*-pyrroles in an oil bath at 100° for 7 hr. The components were isolated by preparative glpc, and the structural assignments for the components are based upon nmr decoupling experiments (degassed 10% solutions in CCl_4) and the following properties.

3-*trans*-Crotyl-5-methyl-2-ethylpyrrole was 100% pure (glpc): $n^{25}D$ 1.5085; uv max (MeOH) 212 nm (ε 6920); ir (CCl_4) 3500, 980 cm^{-1}; nmr (CCl_4) δ 1.13, (t, 3), 1.63 (complex m, 3), 2.16 (s, 3), 2.47 (q, 2), 2.98 (complex m, 2), 5.43 (complex m, 3), and 7.21 (brd, 1); molecular ion at *m*/*e* 163.136 (theory 163.136).

The pyrrole-ring proton at the 4 position was coupled to the protons on the 5-methyl substituent and not coupled to the methylene protons on the 2-ethyl substituent.

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.52; N, 8.58. Found: C, 80.82; H, 10.69; N, 8.51.

3-*cis*-Crotyl-5-methyl-2-ethylpyrrole and 3-*trans*-crotyl-2-methyl-5-ethylpyrrole were collected as a mixture containing 33% of the cis isomer and 67% of the trans isomer. Analysis (glpc) showed only one peak: $n^{25}D$ 1.5095; uv max (MeOH) 212 nm (ε 7120); ir (CCl_4) 3500, 980 (trans), 680 (cis) cm^{-1}; nmr (CCl_4) δ 1.13 (t, 3 cis), 1.15 (t, 3 trans), 1.63 (complex m, 2), 2.05 (s, 3 trans), 2.13 (s, 3 cis), 2.47 (q, 2), 2.98 (complex m, 2), 5.42 (complex m, 3), and 7.16 (brd, 1); molecular ion at *m*/*e* 163.132 (theory 163.136).

In the minor component, the pyrrole-ring proton at the 4 position was coupled with the protons on the 5-methyl substituent and not coupled with the methylene protons on the 2-ethyl substituent. In the major component, the pyrrole-ring proton at the 4 position was coupled with the methylene protons on the 5-ethyl substituent and not coupled with the protons on the 2-methyl substituent.

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.52; N, 8.58. Found: C, 80.96; H, 10.52; N, 8.53.

3-*cis*-Crotyl-2-methyl-5-ethylpyrrole was 100% pure (glpc): $n^{25}D$ 1.5142; uv max (MeOH) 212 nm (ε 6430); ir (CCl_4) 3500, 680 cm^{-1}; nmr (CCl_4) δ 1.17 (t, 3), 1.67 (complex d, 3), 2.08 (s, 3), 2.48 (q, 2), 3.03 (complex d, 2), 5.45 (complex d, 3), and 7.30 (brd, 1); molecular ion at *m*/*e* 163.131 (theory 163.136).

The pyrrole-ring proton at the 4 position was coupled with the methylene protons on the 5-ethyl substituent and not coupled with the protons on the 2-methyl substituent.

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.52; N, 8.58. Found: C, 80.68; H, 10.64; N, 8.70.

Comparative photolyses were carried out to evaluate the effect of various parameters on the photoisomerization. The samples (*ca.* 150 mg) were irradiated simultaneously at 254 nm (Rayonet Reactor) in ether (pyrrole:ether ratio, 1:3) using matched quartz tubes (6 mm o.d. × 30 cm) which had been previously rinsed with an acetone solution of triethylamine and dried. The sample tubes were placed in a water-jacketed quartz chamber for temperature control during the irradiation. The results of the photolyses of the *N*-(substituted allyl)dimethylpyrroles and the *N*-(substituted allyl)-methylethylpyrroles are reported in Tables I and III, respectively.

Irradiation of *N*-α-Methylallyl-2,5-dimethylpyrrole in Nitrogen, Air, and Oxygen. A mixture of 800 mg of *N*-α-methylallyl-2,5-dimethylpyrrole, 80 mg of hexadecane, and 3 ml of ether was divided among four photolysis tubes. The four tubes, after degassing by the freeze–thaw method and sealing under nitrogen, air, or oxygen, were irradiated simultaneously for 4 hr using a merry-go-round sample holder. The results are reported in Table II.

Irradiation of the Substituted 2*H*-Pyrroles. Ether solutions (pyrrole:ether ratio, 1:3) of each (*ca.* 100 mg) of the following compounds (2-α-methylallyl-, 2-*trans*-crotyl-, and 2-*cis*-crotyl-2,5-dimethylpyrrole; 2-α-methylallyl- and 2-*trans*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole) were irradiated 10–20 hr using the conditions previously described for the irradiation of the *N*-(substituted allyl)-dimethylpyrroles. Analysis (glpc) showed only the presence of starting material.

Irradiation of 3-*trans*-Crotyl-2,5-dimethylpyrrole. An ether solution (pyrrole:ether ratio, 1:3) was irradiated as described previously for the N isomer for 9 hr. Analysis (glpc) showed only the presence of starting material.