

- (39) 1,3-Diphenylisbenzothiophen has shown the similar photochemical behavior. The fluorescence of 1,3-diphenylisbenzothiophen was readily quenched by **2** ($K_{qT_s} = 3.3 \pm 0.3 M^{-1}$ in ethanol), and the adduct formation was observed. The detailed results will be reported at a later date.
- (40) (a) K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, **92**, 4143

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- (41) S. Ito, K. Sakan, and Y. Fujise, *Tetrahedron Lett.*, 2873 (1970).
- (42) The [6 + 4] adduct is the major product in the reaction of tropone with isobenzofuran: H. Takeshita, Y. Wada, A. Mori, and T. Hatsui, *Chem. Lett.*, 335 (1973).

Thermal Rearrangements of (Substituted allyl)dialkyl-2*H*-pyrroles

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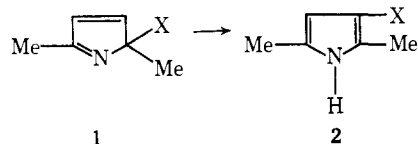
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Abstract: The thermal behavior of simple substituted 2*H*-pyrroles, which are contained in tetrahydrocorrin systems and are intermediates in trialkylpyrrole isomerizations, was examined to elucidate possible competitive [1,5] and [3,3] sigmatropic rearrangement paths. The major path followed in the rearrangement of (substituted allyl)dialkyl-2*H*-pyrroles depends upon the substitution pattern of the migrating allyl group. Crotyl substituents migrate by a [1,5] shift (without inversion) from the 2- to the 3-position of the ring. On the other hand, the α -methylallyl group migrates by competitive [3,3] shifts (with inversion): migration from the 2- to the 5-position and migration from the 2- to the 4-position. Of the two migrations, the former is the more rapid. The transition state in the more rapid migration presumably possesses the more stable 2*H*-pyrrole configuration as compared with the latter path which contains the less stable 3*H*-pyrrole configuration.

N-(Substituted allyl)pyrroles undergo thermal isomerization involving competitive [1,5] and [3,3] sigmatropic shifts of the allyl group.¹ When the 2- and 5-positions of the pyrrole ring are substituted with alkyl groups, allylic migration to the 3-position of the pyrrole ring occurs with both inversion and noninversion of the allyl substituent. The *N*- to 3-migration without inversion suggests that this competitive rearrangement path proceeds by consecutive [1,5] shifts involving 2*H*-pyrrole intermediates. Evidence for the participation of such 2*H*-pyrrole intermediates in the thermal isomerization of other trisubstituted pyrroles has been reported,² and it has been found that these 2*H*-pyrrole species (2-benzyl-2,5-dimethyl-2*H*-pyrrole) undergo a facile isomerization to the corresponding 3-isomer (3-benzyl-2,5-dimethylpyrrole).³ An investigation of possible competitive [1,5] and [3,3] sigmatropic shifts of allyl groups in the nickel tetrahydrocorrin system (contains a 2*H*-pyrrole species) by Grigg and coworkers⁴ showed that the 3-methyl-2-butenyl group migrated without inversion. However, because of low conversions (*ca.* 2%) it was not possible to exclude other competing paths. In order to elucidate the migration modes of substituted allyl groups in 2*H*-pyrrole systems, we have investigated the pyrolytic behavior of (substituted allyl)dialkyl-2*H*-pyrroles.

Results and Discussion

Initial pyrolyses with 2- α -methylallyl- (**1a**) and 2-crotyl-2,5-dimethyl-2*H*-pyrrole (**1b**) at 180° showed that the major (*ca.* 90%) thermolysis product in either experiment was 3-crotyl-2,5-dimethylpyrrole (**2b**). While these results



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

suggested that, as one possibility, the 2-methylallyl group migrated from the 2- to 3-position with inversion, such 2- to

3-migrations with inversion were considered to be unlikely in the pyrolysis of 2- α -methylallylpyrrole.¹ In addition, nmr studies of the isomerization of 2-crotyl-2,5-dimethyl-2*H*-pyrrole (**1b**) at 100° indicated that the compound rearranged predominately to the 3-crotyl compound (without inversion), while, on the other hand, the pyrolysis of 2- α -methylallyl-2,5-dimethyl-2*H*-pyrrole (**1a**) produced initially a 2-crotyl-2,5-dimethyl-2*H*-pyrrole (**1b**) which on further heating was converted to the 3-crotyl-2,5-dimethylpyrrole (**2b**). The formation of the 3-crotyl isomer in the latter experiment conceivably could have arisen from one or from combinations of the following paths: an across-the-ring migration of the α -methylallyl substituent from the 2- to 5-position with inversion followed by a shift of the crotyl group to the 4-position without inversion (eq 1); an inversion of the α -methylallyl substituent at the 2-position followed by a 2 to 3 shift of the crotyl group (eq 2); or an

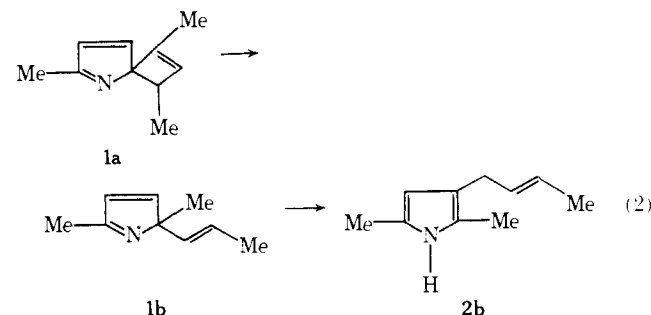
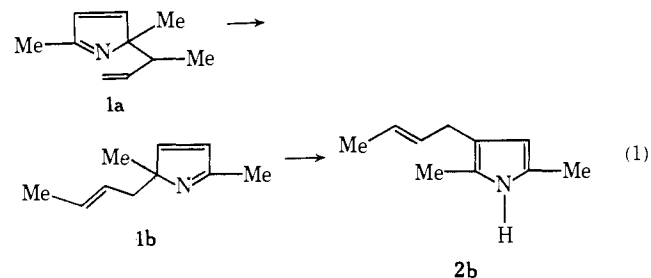
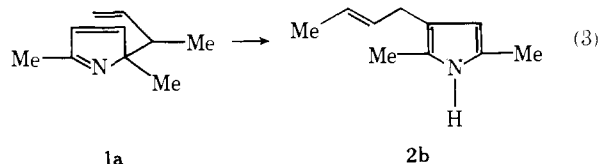


Table I. Glpc Analysis^a of 2*H*-Pyrrole Pyrolyses Followed by Nmr

2 <i>H</i> -Pyrrole	T, °C	—3-Crotylmethylethylpyrroles, ^b %—			
		2-Methyl-5-ethyl		5-Methyl-2-ethyl	
		Trans (5b)	Cis (5c)	Trans (6b)	Cis (6c)
3a	70			91 ^c	3
4a	70	91 ^{d,e}	3	1	
3b	100	73 ^{d,f}	2	4	
4c	100		3	11	60 ^{g,h}

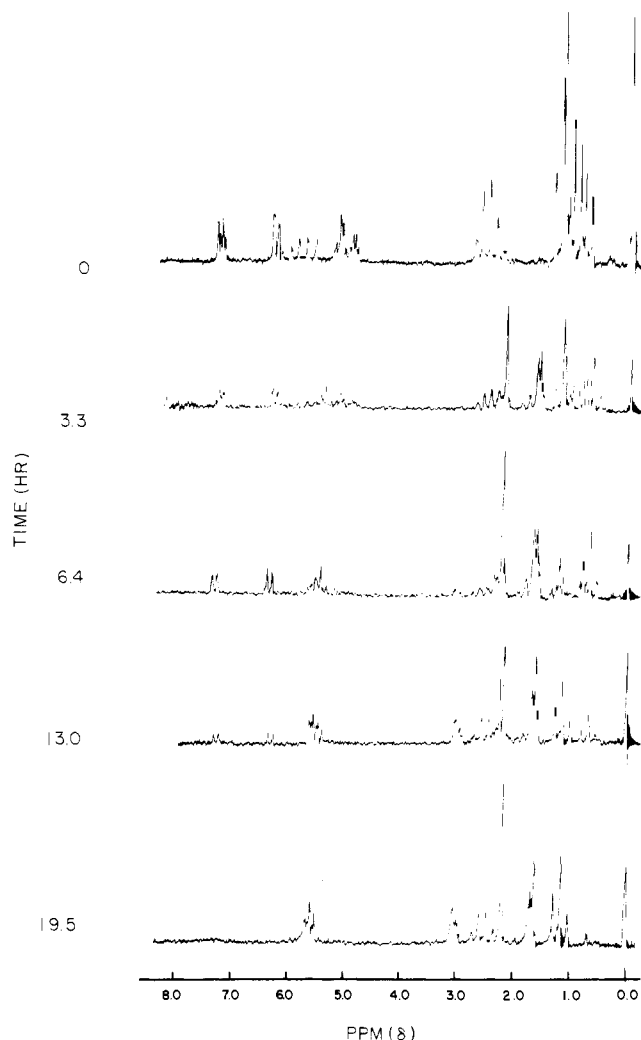
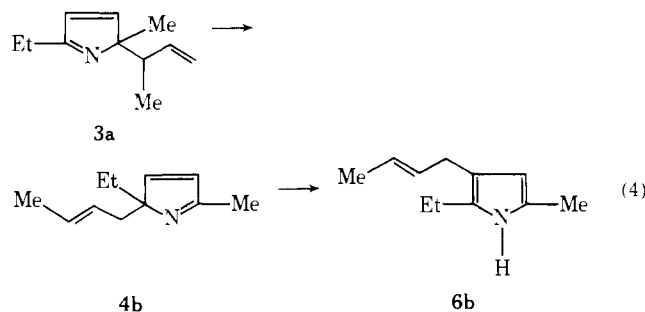
^a Values reported are area %. ^b Identifications of minor components are based on glpc retention times. ^c Three additional unidentified products of 1, 1, and 4% were present. ^d 5b is not separable from 6c by glpc; however, the infrared spectrum showed no cis absorption. ^e Two additional unidentified products of 1 and 2% were present. ^f Unisomerized 2*H*-pyrrole (13%), four unidentified products of 1% each, and one unidentified product (2%) were present. ^g 6c is not separable from 5b by glpc; however, the infrared spectrum showed no trans absorption. ^h Unisomerized 2*H*-pyrrole (4%) and five unidentified products of 1, 2, 1, 11, and 12% were present.

across-the-ring migration of the α -methylallyl group from the 2- to 4-position with inversion (eq 3).

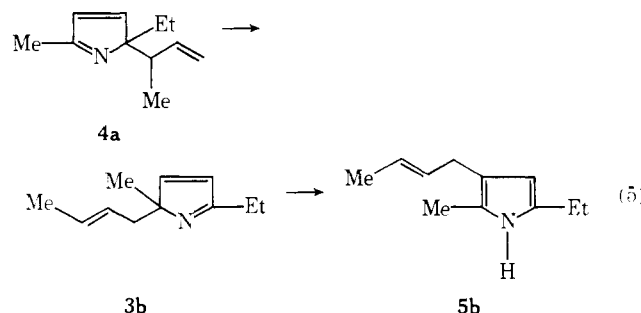


The major isomerization paths followed were identified by carrying out the pyrolyses of 2- α -methylallyl-2-methyl-5-ethyl-2*H*-pyrrole (3a), 2- α -methylallyl-5-methyl-2-ethyl-2*H*-pyrrole (4a), 2-*trans*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole (3b), and 2-*cis*-crotyl-5-methyl-2-ethyl-2*H*-pyrrole (4c), following the isomerizations by nmr and analyzing the final product mixture by glpc (see Table I).

The nmr spectrum of 3a, which consists of absorptions of a pair of diastereomers,⁵ underwent substantial change after heating at 70° for 2 hr (see Figure 1). In addition to a reduction in intensities of original absorptions, a new triplet, multiplet, and singlet appeared at 0.68, 1.63, and 2.18 ppm, respectively. The two pairs of doublets in the ranges of 6.11–6.21 and 7.03–7.20 ppm became multiplets. These new absorptions correspond to those exhibited by 2-crotyl-5-methyl-2-ethyl-2*H*-pyrrole (4b). After 4.5 hr, the nmr spectrum consisted predominately of the spectrum of 4b. Minor absorbances at 1.13 (t), 1.63 (m), 2.15 (s), 3.00 (m), and 5.45 (m) ppm are attributed to the presence of a small amount of 3-*trans*-crotyl-5-methyl-2-ethylpyrrole (6b) and after a heating period of 19.5 hr the spectrum became identical with that of 6b. Decoupling experiments⁵ verified the structural assignment. The infrared spectrum of 6b was identical with that obtained from an authentic sample and showed trans absorption (970 cm⁻¹) but no cis. The changes are summarized in eq 4.

**Figure 1.** Pyrolysis of 3a.

Similar results were observed in the pyrolysis of 4a at 70°. Isomerization initially to 2-*trans*-crotyl-2-methyl-5-ethyl-2*H*-pyrrole (3b) was observed followed by conversion to 3-*trans*-crotyl-2-methyl-5-ethylpyrrole (5b) on extended heating. The infrared spectrum of the pyrolyzate was identical with an authentic sample of 5b and showed no cis absorption. The intermediate 3b was synthesized⁵ and pyro-



lyzed at 100°. Isomerization occurred producing mainly 5b (Table I) with no evidence (nmr) of a new 2*H*-pyrrole or of α -methylallyl absorptions.

These data exclude the conversion of 1a to 1b by path 2 (eq 2) and show that the competitive [1,5] and [3,3] sigmatropic migrations of substituted allyl groups in 2*H*-pyrroles are highly sensitive to structural features of the migrating groups. The crotyl substituent rearranges predominantly⁶ by a [1,5] sigmatropic shift (without inversion), while the

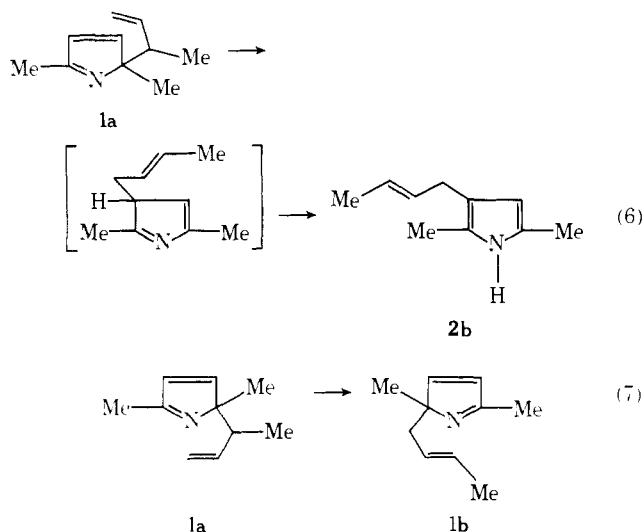
Table II. Thermal Rearrangement of 1a and 1b at 201.0°

Residence time, sec	2H-Pyrrole pyrolyzed	Products, %					
		1a	1b	1c	2a	2b	2c
33.2	1a	61.5	21.5	6.2	1.5	8.9	0.5
28.2	1b	1.6	92.1		0.5	5.8	

α -methylallyl group migrates by competitive [3,3] shifts (eq 1 and 3). A comparison of the rates of production of 4b and 6b from 3a in the nmr pyrolyses (see Figure 1) indicates that the formation of 4b has progressed to a considerable extent before detectable quantities of 6b appear. This suggests that [3,3] shifts involving positions 2 and 5 are somewhat more rapid than [3,3] shifts involving positions 2 and 4. Additional support for the 2 to 5 [3,3] shift being the faster process was obtained from relative rate data derived from the pyrolysis of 1a and 1b at 201° (Tables II and III).

In the pyrolysis of 1a, product 2b arises from the parallel pathways outlined in eq 1 and 3. The formation of 2b by path 1 (eq 1) is the result of the consecutive conversions of 1a to 1b and 1b to 2b. Approximate rate constants for each of these conversions were estimated from the data obtained from the pyrolysis of 1a and 1b (see Table II), and the concentration of 2b formed by the consecutive reactions in path 1 was calculated in the usual way.⁷ The concentration of 2b arising from path 3 (eq 3) was determined by the difference of the experimental concentration of 2b (Table II) and the concentration calculated for path 1. Relative rate data for the competing processes in the pyrolyses were derived from these concentrations and are summarized in Table III.

The greater reactivity of 1a in the 2 to 5 shift (eq 6) as compared with the 2 to 4 shift (eq 7) can be rationalized, if



it is assumed that bond formation has progressed to a considerable extent in the transition state (transition state

Table III. Relative Rates for the Isomerization of 1a and 1b at 201.0°

Reaction	Type	Rel rate
1a → 2a	1,5	1
1a → 2b	3,3	5
1a → 1b	3,3	14
1b → 2b	1,5	4
1b → 2a	3,3	0.3

structure resembles product structure). Since 2H-pyrroles had been found to be more stable than 3H-pyrroles in thermolysis reactions,⁸ the transition state involving 2- to 5-migrations is the more stable one.

The chair-like transition state previously described for the isomerization of allylpyrroles¹ appears to be valid in the 2H-pyrrole system also. In the pyrolysis of 1a, *trans*-crotyl product is produced at a faster rate than is *cis*-crotyl product.

Experimental Section

The synthesis, separation, and characterization of starting materials used and pyrolysis products encountered in these experiments have been described previously.⁵

Nmr spectra were measured on degassed CCl₄ solutions (*ca.* 10%) using HMDS as the lock signal and TMS as internal standard. The samples were heated to 70 or 100° either in the spectrometer or externally, and runs were made using both Varian HA-60-1L and T-60 spectrometers. Glpc analyses were carried out on a Hewlett-Packard 5750 gas chromatograph using a 6 ft × 0.125 in. Carbowax 20M HP high-efficiency packed column at 140°.

Pyrolyses were carried out in the apparatus previously described¹ with the reactor and gas chromatograph in series. Product analyses were run on the Carbowax 20M column at 115° for low boiling products and at 160° for the higher boiling products. The rate of disappearance of 2- α -methylallyl-2,5-dimethyl-2H-pyrrole was followed at 182°, and a plot of $\ln C_0/C$ vs. residence time yielded a straight line.

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References and Notes

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