1,3-Diphenylisobenzothiophen has shown the similar photochemical behavior. The fluorescence of 1,3-diphenylisobenzothiophen was readily quenched by 2 (K_q = 3.3 ± 0.3 M⁻¹) in ethanol, and the adduct formation was observed. The detailed results will be reported at a later date.


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

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{N} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{N} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

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

Table I. Glpc Analysisa of 2H-Pyrrole Pyrolysies Followed by Nmr

<table>
<thead>
<tr>
<th>2H-Pyrrole</th>
<th>T, °C</th>
<th>Trans (5b)</th>
<th>Cis (5c)</th>
<th>Trans (6b)</th>
<th>Cis (6c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>70</td>
<td>91e</td>
<td>3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>70</td>
<td></td>
<td></td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>3b</td>
<td>100</td>
<td>73f</td>
<td></td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>4c</td>
<td>100</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Values reported are area %. Identifications of minor components are based on glpc retention times.

E-1.51 and [3,3]-sigma-tropic migrations of substituted allyl groups in 2H-pyrroles are highly sensitive to structural features of the migrating groups. The crotyl substituent rearranges predominately by a [1,5] sigmatropic shift (without inversion), while the
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 structure resembles product structure). Since 2H-pyrroles had been found to be more stable than 3H-pyrroles in thermolysis reactions, the transition state involving 2- to 5-migrations is the more stable one.

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

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°C either in the spectrometer or externally, and runs were made using both Varian HA-60-H and T-60 spectrometers. Glpc analyses were carried out on a Hewlett-Packard 5750 gas chromatograph using a 6 ft x 0.125 in. Carbowax 20M HP high-efficiency packed column at 140°C.

Pyrolyses were carried out in the apparatus previously described with the reactor and gas chromatograph in series. Product analyses were run on the Carbowax 20M column at 115°C for low boiling products and at 160°C for the higher boiling products. The rate of disappearance of 2-α-methylallyl-2,5-dimethyl-2H-pyrrole was followed at 182°C, and a plot of ln C₀/C vs. residence time yielded a straight line.

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References and Notes

6. In the migration of the trans-crotyl group in 3b, inversion could not have occurred to an extent greater than 2% since this was the largest yield of an unidentified component (a possible α-methylallylpyrrole).