Hauser and Taylor have shown\(^1\) that \(\alpha\)-(dimethylamino)-phenylacetonitrile (I), dissolved in liquid ammonia, can be benzylated in the presence of sodium or potassium amides (1).

\[
\begin{align*}
\text{I: } & \quad \text{CN} \quad \text{C}_6\text{H}_5\text{-N}(\text{CH}_3)_2 \quad \text{NH}_2^-/\text{NH}_1 \quad \text{CN} \quad \text{R} \\
\text{II: } & \quad \text{CN} \quad \text{C}_6\text{H}_5\text{-N}(\text{CH}_3)_2 \\
\text{III: } & \quad \text{CN} \quad \text{C}_6\text{H}_5\text{-CH-CH-CH}_2
\end{align*}
\]

Under the influence of the amide used, the products (II) can eliminate hydrocyanic acid, giving rise to \(\alpha\)-dimethylamino-stilbenes (III). The latter reaction (2) proceeds very easily even in the absence of bases, e.g. during crystallisation or distillation of II. This facile elimination is ascribed to the presence of the lone pair on the amino substituent.
It appeared that in higher boiling solvents (reaction temperature above 120°) the parent compound (I) could be converted into α,α'-bis(dimethylamino)stilbene (V) in the presence of a strong base (NaH).

\[
\begin{align*}
&\text{CN} \\
&C_6H_5-\text{CHN(CH}_3)_2 & \text{NaH} & 120^\circ \rightarrow & C_6H_5 - \text{CH} \quad \text{CH} - C_6H_5 & \text{(3)} \\
&C_6H_5-\text{N(CH}_3)_2 & & & \\
\end{align*}
\]

Under these circumstances the second step (4) is so fast that the intermediate (IV) cannot be isolated.

Reactions like (3) appear to be restricted to nitriles with strongly donating α-substituents, which facilitate substitution of the cyanide ion and prevent addition of the reagent to the nitrile. Investigations with other nitriles containing electron-donating groups will determine the scope of the reaction.

Experimental. With assistance of Mrs. F. Janssen.

Because α-(dimethylamino)phenylacetonitrile (I) is the only α-sec.aminophenylacetonitrile described in the literature, several other members of this series (Table I) have been prepared according to Hauser's method.

For the preparation of 1,2-di-sec. amino-1,2-diphenylethenes a suspension of 0.15 mole (3.7 g) of sodium hydride in 75 ml of diglyme was heated to 150°. Under stirring 0.12 mole of an α-sec.aminophenylacetonitrile was added dropwise so that the mixture boiled gently.
Table I

α-sec. Aminophenylacetonitriles, C₆H₅CH(CN)NRR'

<table>
<thead>
<tr>
<th>NRR'</th>
<th>b.p./mm</th>
<th>mp.</th>
<th>nD¹⁰</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>diethylamino</td>
<td>90-93°/0.5</td>
<td>1.5045</td>
<td>95%</td>
<td></td>
</tr>
<tr>
<td>pyrrolidino</td>
<td>100-102°/0.5</td>
<td>1.5328</td>
<td>88%</td>
<td></td>
</tr>
<tr>
<td>piperidino</td>
<td>110°/0.6</td>
<td>65-66°</td>
<td>85%</td>
<td></td>
</tr>
</tbody>
</table>

After addition stirring was continued for 3 hours at 150°.

The solvent was removed under diminished pressure, ether was added and some ethanol to destroy unreacted hydride. The ethereal solution was washed several times with water, dried and distilled. The lower boiling fractions contained small amounts of benzamide (C₆H₅CONRR'), probably due to oxidation, and monoaminostilbene, C₆H₅CH=C(NRR')C₆H₅. When the reaction was carried out under nitrogen benzamide formation was not observed but the yield did not rise substantially.

α,α'-Di-sec. aminostilbenes, C₆H₅C(NRR')=C(NRR')C₆H₅

<table>
<thead>
<tr>
<th>NRR'</th>
<th>b.p./mm</th>
<th>yield</th>
<th>cis/trans ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethylamino</td>
<td>121-123°/0.5 (solid to 52°)</td>
<td>55%</td>
<td>1</td>
</tr>
<tr>
<td>diethylamino</td>
<td>123-125°/0.5</td>
<td>45%</td>
<td>1</td>
</tr>
<tr>
<td>pyrrolidino</td>
<td>170-173°/0.7 (solid to 83°)</td>
<td>55%</td>
<td>0.25</td>
</tr>
<tr>
<td>piperidino</td>
<td>172-174°/0.4 (solid to 92°)</td>
<td>55%</td>
<td>2</td>
</tr>
</tbody>
</table>

The α,α'-di-sec. aminostilbenes isolated as cis/trans mixtures (Table II) were identified by NMR (Varian-HA-100) and MS (Varian-Mat SM1-B). Unfortunately, the separation of the mixtures was unsuccessful both with GLC and on distillation.
References


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