Reaction of 3-acetyl-4-hydroxy-2-methoxy-4-phenylcrotonic acid lactones (2a,b) with hydrazine dihydrochloride (3) gave a mixture of azines (5a,b and 6a,b), and these structures were definitely determined by crystallographic analyses of 5b and 6b.

Recently we reported that the reaction of benzaldehydes with ethyl 2,4-dioxopentanoate gave 3-acetyl-2,4-dihydroxy-4-phenylcrotonic acid lactones (e.g., 1a,b), and these lactones take the open form structures, 3-benzylidene-2,4-dioxopentanoic acids (1'a,b), in water because these are soluble in NaHCO₃ solution under the evolution of carbon dioxide. The present paper describes the reactions of 1a,b and their methyl ethers (2a,b) with hydrazine dihydrochloride (3).

When a solution of 1a in 70% CH₃CN was refluxed with an equimolar of 3, the compound 4a, yellow needles of mp 190-191°C, was obtained in 85% yield as a single product. Anal. Calcd. for
C_{24}H_{20}N_{20}O_{6}: C, 66.66; H, 4.66; N, 6.48. Found: C, 66.46; H, 4.67; N, 6.48. Azine(4a) was not soluble in NaHCO₃ solution but soluble in dil. NaOH solution, and gave wine-red color when treated with a solution of FeCl₃. Similarly, reaction of 1b with 3 gave the compound 4b, yellow needles of mp 158-160°, in good yield. On the other hand, 2a was treated with an equimolar of 3 in MeOH at room temperature to give a mixture of 5a, yellow needles of mp 187-189°C[C_{26}H_{24}N_{20}O_{6}(460 M^+)] and 6a, red needles of mp 183-185°C[C_{26}H_{24}N_{20}O_{6}(460 M^+)] in a ratio of 57:43 in 83% yield.

\[
\begin{align*}
\text{1a, b} & \quad \text{1' a, b} \\
\text{CH₂N₂} & \quad \text{COOH} \\
\text{Ar} & \quad \text{CH₃} \\
\text{COOCH₃} & \quad \text{OH} \\
\text{NH} & \quad \text{Ar} \\
\text{Ar} & \quad \text{CH₃} \\
\text{H} & \quad \text{Ar} \\
\text{CH₂N₂} & \quad \text{CH₃} \\
\text{Ar} & \quad \text{CH₃} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{2a, b} & \quad \text{3} \\
\text{CH}_3\text{OH} & \quad \text{CH}_3\text{OH} \\
\text{Ar} & \quad \text{Ar} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{4a, b} & \quad \text{NN₂NH₂·2HCl(3)} \\
\text{70% CH₃CN} & \quad \text{70% CH₃CN} \\
\text{5a, b} & \quad \text{5a, b} \\
\text{6a, b} & \quad \text{6a, b} \\
\end{align*}
\]

\[
\begin{align*}
\text{a} & : \text{Ar=phenyl} \\
\text{b} & : \text{Ar=o-chlorophenyl}
\end{align*}
\]
Similarly, treatment of 2b with 3 gave a mixture of 5b, yellow needles, and 6b, red needles, in a ratio of 50:50 in 90% yield. Methylation of 4a,b by action of diazomethane afforded 6a,b. From these results, 4a,b, 5a,b and 6a,b were supposed to be azine derivatives. Theoretically, three stereostructures are possible for azine as shown in Fig. 1.

The syn and anti designation in this paper refers to the relationship of the bond of C-R and N-N.

Spectral data and Rf-value of azines(4a,b-6a,b) were listed on Table I and it should be noted that on the pmr spectra the signals of each two methyl protons on C=N bond, methoxy protons and methine protons appeared as singlet, and C-methyl resonances of 5a,b were observed upfield shift of 0.38-0.40 ppm than that of 6a,b. Since these data, however, did not provide the definitive evidence of the structure of azines, we decided to determine the crystal structures of 5b and 6b. The crystal data are followings: a=18.899(3) Å, b=17.250(3) Å, c=15.490(3) Å and space group, Pbca, for 5b and a=20.132(4) Å, b=6.162(1) Å, c=19.954(3) Å and space
Table I. Physical Properties of Azines

<table>
<thead>
<tr>
<th></th>
<th>4a</th>
<th>4b</th>
<th>5a</th>
<th>5b</th>
<th>6a</th>
<th>6b</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Color</strong></td>
<td>Yellow</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Red</td>
<td>Red</td>
</tr>
<tr>
<td><strong>Formula (Mass m/e)</strong></td>
<td>C\textsubscript{24}H\textsubscript{20}N\textsubscript{2}O\textsubscript{6}</td>
<td>C\textsubscript{24}H\textsubscript{18}N\textsubscript{2}O\textsubscript{6}Cl</td>
<td>C\textsubscript{26}H\textsubscript{24}N\textsubscript{2}O\textsubscript{6}</td>
<td>C\textsubscript{26}H\textsubscript{22}N\textsubscript{2}O\textsubscript{6}Cl</td>
<td>C\textsubscript{26}H\textsubscript{24}N\textsubscript{2}O\textsubscript{6}</td>
<td>C\textsubscript{26}H\textsubscript{22}N\textsubscript{2}O\textsubscript{6}Cl</td>
</tr>
<tr>
<td><strong>Mp (°C)</strong></td>
<td>190-191</td>
<td>158-160</td>
<td>187-189</td>
<td>187-188</td>
<td>183-185</td>
<td>190-192</td>
</tr>
<tr>
<td>(Recryst. Solvent)</td>
<td>(DMF-H\textsubscript{2}O)</td>
<td>(DMF-H\textsubscript{2}O)</td>
<td>(MeOH)</td>
<td>(AcOEt)</td>
<td>(AcOEt)</td>
<td>(AcOEt)</td>
</tr>
<tr>
<td><strong>IR ν \textsubscript{KBr} cm\textsuperscript{-1}</strong></td>
<td>1780</td>
<td>1785</td>
<td>1760</td>
<td>1765</td>
<td>1755</td>
<td>1765</td>
</tr>
<tr>
<td></td>
<td>1760</td>
<td>1640</td>
<td>1660</td>
<td>1630</td>
<td>1650</td>
<td>1260</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>1255</td>
<td>1255</td>
<td>1260</td>
<td>1260</td>
<td>1260</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1170</td>
<td>1165</td>
<td>1170</td>
<td>1170</td>
<td>1170</td>
</tr>
<tr>
<td><strong>UV λ \textsubscript{EtOH} nm (log ε)</strong></td>
<td>253(4.16)</td>
<td>250(4.10)</td>
<td>304(4.43)</td>
<td>308(4.40)</td>
<td>305(4.40)</td>
<td>310(4.31)</td>
</tr>
<tr>
<td></td>
<td>317(3.80)</td>
<td>318(3.94)</td>
<td>327(4.29)</td>
<td>330(4.35)</td>
<td>325(4.37)</td>
<td>330(4.32)</td>
</tr>
<tr>
<td></td>
<td>455(4.01)</td>
<td>463(4.15)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>PMR δ(DMSO-d\textsubscript{6})</strong></td>
<td>1.94(s)</td>
<td>1.91(s)</td>
<td>1.32(s)</td>
<td>1.35(s)</td>
<td>1.70(s)</td>
<td>1.75(s)</td>
</tr>
<tr>
<td>2 × -CH\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 × -OCH\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 × -CH\textsubscript{2}</td>
<td>6.25(s)</td>
<td>6.54(s)</td>
<td>6.21(s)</td>
<td>6.54(s)</td>
<td>6.24(s)</td>
<td>6.56(s)</td>
</tr>
<tr>
<td><strong>Rf-value</strong></td>
<td>0</td>
<td>0</td>
<td>0.48</td>
<td>0.67</td>
<td>0.61</td>
<td>0.70</td>
</tr>
<tr>
<td>(Al\textsubscript{2}O\textsubscript{3}/Benzene)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
group, Pbcn, for 6b. From these data and density (1.414 g. cm\(^{-3}\)),
the molecular weight of 6b was equal to half of that determined
by mass spectrometry, suggesting that the molecule of 6b, itself,
has a center of symmetry on the middle of =N-N= bond. On the other
hand, the crystal of 5b occupied one molecule per asymmetric unit,
judging from the crystal data and density (1.388 g. cm\(^{-3}\)). Firstly,
we determined the crystal structure of 6b. As might have been ex-
pected from these data, 6b has a center of symmetry in a molecule,
as shown in Fig. 2, corresponding to anti-anti form of Fig. 1.

From this result and the data of pmr spectrum, the structure
of 5b should have the syn-anti
form of Fig. 1, although crystal
determination is undergoing
at present. The details of
these crystal structure will
be published elsewhere.

When a solution of 2a,b
in MeOH was refluxed with 3
for 3 hr, the ratio of the
products 5a : 6a and 5b : 6b
changed to 72 : 28 and 55 : 45, Fig. 2
respectively. Furthermore, Molecular Structure of Azine(6b)
refluxing in MeOH for 72 hr,
methyl 4-(a-methoxybenzyl)-5-methylpyrazole-3-carboxylates (7a,b)
[7a : oil, IR \(\nu_{\text{CHCl}_3}\) cm\(^{-1}\) : 3480 (NH), 1720 (CO). Pmr (CDCl\(_3\)) \(\delta\) :
2.20 (3H, s, CH\(_3\)), 3.40 (3H, s, OCH\(_3\)), 3.85 (3H, s, COOCH\(_3\)), 6.15(}
1H, s, CH), 9.90(1H, bs, NH). Mass spectrum : m/e 260(M+). 7b : C_{14}H_{15}N_{2}O_{3}(294 M^+) : mp 155-156°. IR v_{max}^\text{KBr} cm^{-1} : 3280(NH), 1720 (CO). PMR(CDCl_{3}) \delta : 2.10(3H, s, CH_{3}), 3.50(3H, s, OCH_{3}), 3.90(3H, s, COOCH_{3}), 6.35(1H, s, CH), 10.50(1H, bs, NH) were obtained in 75-80% yield. Analogously, refluxing a MeOH solution of 1a,b with 3 for 24 hr gave pyrazoles(7a,b) in 70-75% yield.

Acknowledgement

We thank Drs. S. Matsunaga and A. Numata for the measurements of Mass and PMR spectra, and Mrs. Y. Tsujibo for the microanalyses.

REFERENCES


Received, 17th April, 1978