was evaluated by the method of integration, as described in the earlier paper\(^1\). It was found that \(k_2\) increased with increasing water-content (or dielectric constant) of the medium. This shows that the activated complex formed in the reaction is more polar than the reactants\(^5-7\).

Figure 1 shows a plot of \(\log k_2\) against \((D-1)/(2D+1)\). The plot, being linear\(^9\), is consistent with the assumption that the reaction is between two dipolar molecules.

**FIG. 1.** Chlorination of paranitrophenol in acetic acid-water mixed solvents at 26° C. Plot of \(\log k_2\) against \((D-1)/(2D+1)\).

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**ALKYL ARYL ESTERS OF PHOSPHOROUS ACID**

It is known that allyl phenols have bacteriostatic and fungistic activity\(^1\). In view of this it was of interest to prepare a number of phosphorus containing derivatives of allyl phenols which could be expected to have insecticidal activity.

In the present work we have investigated the reaction of 4-allyl-2-methoxy phenyl phosphorodichloride with alcohols in presence of a base. Thus when 4-allyl-2-methoxy phenyl phosphorodichloride\(^6\) (I) was reacted with methanol in presence of dimethyl-amine in ether, we obtained 4-allyl-2-methoxyphenyl dimethyl phosphate (II).

\[
\begin{align*}
\text{CH}_2\equiv\text{CH}-\text{CH}_2 & \quad \text{O} \quad \text{P} \quad \text{Cl} \\
\text{OCH}_3 & \\
\text{CH}_2\equiv\text{CH}-\text{CH}_2 & \quad \text{O} \quad \text{P} \\
\text{OCH}_3 & \quad \text{OCH}_3 \\
\end{align*}
\]

The reaction was conducted in stream of inert gas and in cold. The ester (II) thus obtained was a high boiling liquid. Its IR spectrum shows \(\text{P} - \text{O} - \text{CH}_3\) band at 1031 cm\(^{-1}\) and \(\text{C} = \text{C}\) stretching vibration at 1626 cm\(^{-1}\). The tervalent state of phosphorus in these compounds was proved by the absence of \(\text{P} = \text{O}\) absorption and also by the qualitative reaction with cuprous chloride, which went with an exothermic effect. Further identification of its structure was achieved by its PMR spectrum which shows absorption at \(3.15-3.40\) due to three methoxy protons of the phenolic moiety. The six methoxy protons attached to phosphorus absorbs slightly downfield at \(3.4-3.9\). The two methylene protons of the allyl group attached to the aromatic nucleus gives multiplet at \(4.9\) while the terminal methylene protons of the allyl group absorbs still downfield at \(5.15\). The methine protons appear at \(5.35\). Aromatic protons \((3H)\) absorb in the range \(6.50-6.85\).

**EXPERIMENTAL**

4-Allyl-2-methoxy phenyl phosphorodichloride.—27.5 g of phosphorus trichloride was added with stirring under nitrogen atmosphere to 32.8 g of 4-allyl-2-methoxy phenol. The addition was exothermic and a simultaneous change in colour from yellow to red was observed. The reaction mixture was then heated at 155° until no more HCl came off. As a result of vacuum distillation we isolated 4-allyl-2-methoxy phenyl phosphorodichloride.
TABLE I

4-Allyl-2-methoxy phenyl dialkyl phosphites

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>R</th>
<th>% Yield</th>
<th>B.P./Press in mm (Bath temp.)</th>
<th>% Req'd</th>
<th>% Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methyl</td>
<td>30-2</td>
<td>10.5/15 (130°C)</td>
<td>56.25</td>
<td>6.48</td>
</tr>
<tr>
<td>2</td>
<td>n-Propyl</td>
<td>39-0</td>
<td>155/19 (156°C)</td>
<td>61.53</td>
<td>7.51</td>
</tr>
<tr>
<td>3</td>
<td>t-Propyl</td>
<td>30-6</td>
<td>109/11 (134°C)</td>
<td>61.53</td>
<td>7.20</td>
</tr>
<tr>
<td>4</td>
<td>n-Butyl</td>
<td>25-1</td>
<td>120/9 (140°C)</td>
<td>63.52</td>
<td>8.36</td>
</tr>
<tr>
<td>5</td>
<td>n-Amyl</td>
<td>32-0</td>
<td>132/12 (155°C)</td>
<td>65.49</td>
<td>9.01</td>
</tr>
<tr>
<td>6</td>
<td>n-Hexyl</td>
<td>20-7</td>
<td>115/9 (135°C)</td>
<td>66.66</td>
<td>9.12</td>
</tr>
</tbody>
</table>

(25.4 g), B.P. 147-149°C (12 mm; Bath temp. 180°C), Found %P, 11-84; C₉H₃Cl₂ OP Calcd. %P; 11-69.

4-Allyl-2-methoxy phenyl dialkyl phosphites.—To a mixture of 0-08 M of an alcohol, 0-08 M of dimethyl amine in 75 ml of ether was added 0-04 M of 4-allyl-2-methoxy phenyl phosphoro- dichloride. The temperature of the reaction mixture was kept at -5 to -15°C. The mixture was refluxed for 2 hrs after the addition, cooled and precipitated hydrochloride was filtered off. After removal of the solvent, residue was fractionated under reduced pressure. Physical and analytical data of esters thus obtained are given in Table I.

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The same isquinolone (IVa) is also formed when 3-methylsouccoumarin (IIIa) and also 4-carboxy-3-methylsouccoumarin (IIIb) are reacted with aq. ethanolamine (IIIa and IIIb are obtained in quantitative yield from II by rearrangement with H₂SO₄).