合成されたジアルキルアゾフェンフェンリン酸および関連化合物：Ⅱ 原子ホスファート化合物の研究

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of clay, and we can recognize the quantitative relation between the lowering of acidity and decomposition. From this result, hydrogen ions H+ are supposed to have large effect upon the decomposition.

8. From the result as abovementioned, we shall be able to consider the stabilization mechanism by addition of stabilizers which author recommended, such as polyoxyethylene alkyl ether, polyoxyethylene dialkyl phenyl ether, polyoxyethylene phenyl ether, and polyoxyethylene alkyl phenyl ether. I presume that non-covalent electron pairs in the molecule of the compound used as a stabilizer might preferably seize hydrogen ions to prevent them from reacting with malathion and methyl parathion.

9. Moisture in both kieselguhr and bentonite is much and the latter contains much alkali metals and alkaline earth metals. Talc is less acidic than clay and pH value is > 7 under various influence of Mg++, Fe+++ free bond, alkali impurities etc. Therefore, it is very difficult to judge the decomposition rate by acidity only.

10. Author could not find out the regularity between acidity of mineral carrier and decomposition rate, but we can suppose for H+ to be an important factor of decomposition of organophosphorus dust insecticide.

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16. Dialkyl Azophenyl Phosphate 及び関連化合物の合成 有機磷化合物の研究 第2報 永江

Dialkyl 質換-phenyl phosphate 及び thiophosphate の殺虫効果に及ぼす影響があるが phenyl 質にかえた場合の殺虫効果に及ぼす影響を知る為に、新に 12 種の dialkyl 4'-質換 azophenyl phosphate 及び thiophosphate (一般式 (RO)2P(X)OCaH 4-N=N-2C4H 4-Y; R=CH3, C2H5; X=O, S; Y=H, Cl, NO2) を合成した。此等の化合物はすべて著色結晶でその中で 4 種は対応 azophenol との附加化合物を与えた。

Metcalf et al.1) studied on the insecticidal effectiveness of many dialkyl substituted phenyl phosphates and thiophosphates, and they found that there were general correlations between their chemical structures and biological properties as follows. (1) Compounds with phosphoryl groups were more active than those with thiophosphoryl groups. (2) Methyl and ethyl esters were more active than their higher homologs. (3) Presence of nitro groups on an aromatic ring was required for high effectiveness, and the maximum effectiveness was associated with nitro group in the para position. (4) Introduction of methylene or imine between benzene nucleus and phosphorus atom destroyed effectiveness.

Lately, Fukuto et al.2) found that there were rather precise correlations between hydrolysis constants, frequencies of phosphorus-oxygen-carbon stretching vibrations, inhibition of fly-brain cholinesterase, biological activities of dialkyl substituted phenyl phosphates and Hammett’s constants (σ values) of meta or para substituents of their benzene nuclei. From these data, compounds containing such substituents with favorable σ values as p-nitro or p-cyano were highly active.

If the hydrolysis of these compounds and phosphorylation of cholinesterase by them are due to E effect of para-substituents (e.g. Equations 1 and 2), dialkyl 4'-substituted azophenyl phosphates and thiophosphates containing substituents...
with favorable E effect, will be also active to insects as shown in Equation 3.

\[
(\text{RO})_2\text{P} = \text{O} \rightarrow \text{N}=\text{O} \quad (\text{Equation 1})
\]

To ascertain this, we have synthesized twelve new compounds of dialkyl azophenyl phosphates and related compounds. These compounds were obtained in high yields as colored crystals by the interaction of dialkyl chlorophosphates or thiophosphates and appropriate azophenols in the presence of anhydrous sodium carbonate in acetone, and the experimental results are shown in Table 1. Some of them formed addition compounds with the starting azophenols as shown by the elemental analysis and partition paper chromatography described in the experimental part.

Biological properties of these chemicals are reported in elsewhere\(^5\). In brief, (1) compounds with 4'-nitro groups were the most active, and 4'-chloro or no 4'-substituted compounds, especially the latter, were less active, (2) phosphoryl and thiophosphoryl groups did not show any apparent differences, (3) there was no obvious correlation between methyl and ethyl esters.

**Experimental**

Dialkyl chlorophosphates. Dimethyl and diethyl chlorophosphate were prepared by the chlorination of dialkyl phosphites with sulfuryl chloride as described by Fitzer et al\(^5\). Dimethyl chlorophosphate: bp 73° at 14 mm. Diethyl chlorophosphate: bp 83° at 12 mm.

Dialkyl chlorothiophosphates. Dimethyl and diethyl chlorophosphate were prepared from phosphorus pentasulfide and appropriate alcohols as described by Fletcher et al\(^5\). Dimethyl chlorothiophosphate: bp 66° at 16 mm. Diethyl chlorothiophosphate: bp 85° at 10 mm.

Azophenols. Azophenols were prepared by the coupling of phenol with appropriate diazonium salts. They were used without any purifications. Azophenol: mp 149-150°. 4'-Chloroazophenol: mp 157°. 4'-Nitroazophenol: mp 213°.

General Procedure for dialkyl azophenyl phosphates and thiophosphates and their 4'-substituted derivatives.

A mixture of equimolar quantities (usually 0.1 mole) of appropriate dialkyl chlorophosphate or thiophosphate, azophenol or 4'-substituted azophenol, and anhydrous sodium carbonate in acetone (100-200 cc per 0.1 mole) was stirred and heated at reflux for three to five hours. After cooling to the room temperature, the reaction mixture was filtered to remove sodium chloride and sodium bicarbonate. The filtrate was concentrated in vacuo to remove acetone. The residue was dissolved in ether, washed with dilute sodium carbonate and water, dried over anhydrous sodium sulfate, and then ether was distilled off. Crude product was obtained as crystals in quantitative yield, and purified by crystallization from n-hexane or methanol. Experimental data are given in Table 1.

Partition paper chromatography.

Compounds I-IV were paper-chromatographed using Toyo Filter Paper No. 51, silicone oil (Silicone KF-54, from Shinetsu Chemical Co., Ltd.) as stationary phase and the upper layer of the mixture of chloroform, alcohol and water (10:10:6) as mobile solvent by ascending method. In each case, two spots were obtained, and their colors were deepened by spraying 5% alcoholic potassium hydroxide. One spot corresponding to phosphate or thiophosphate was detected by spraying Hanes-Ischerwood reagent followed by ultra-violet radiation\(^6\). Experimental data are given in Table 2.

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* All melting points are uncorrected.
Table 1. Synthesis of dialkyl azophenyl phosphate and related compounds

$\text{(RO)}_2 \text{PO-} \overset{\text{N=N-}}{\text{N=N-}} \text{Y}$

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>X</th>
<th>Y</th>
<th>Mp (°C)</th>
<th>Yield (%)</th>
<th>Formula</th>
<th>Crystal Form</th>
<th>N% Calcd.</th>
<th>Found</th>
<th>P% Calcd.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CH₃</td>
<td>O</td>
<td>H</td>
<td>88-90</td>
<td>40</td>
<td>C₁₄H₁₈N₂O₄P</td>
<td>Yellow prisms</td>
<td>10.37</td>
<td>10.25</td>
<td>7.65</td>
<td>7.36</td>
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<tr>
<td>II</td>
<td>C₂H₅</td>
<td>O</td>
<td>Cl</td>
<td>48-50</td>
<td>48</td>
<td>C₁₄H₁₈N₂O₂P</td>
<td></td>
<td>9.69</td>
<td>10.01</td>
<td>7.16</td>
<td>7.14</td>
</tr>
<tr>
<td>III</td>
<td>CH₃</td>
<td>Cl</td>
<td>127-129</td>
<td>45</td>
<td></td>
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<td>9.22</td>
<td>9.78</td>
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<tr>
<td>IV</td>
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<td>O</td>
<td>Cl</td>
<td>132-134</td>
<td>53</td>
<td>C₁₄H₁₈ClN₂O₄P</td>
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<td>8.66</td>
<td>9.00</td>
<td>6.39</td>
<td>6.01</td>
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<tr>
<td>V</td>
<td>CH₃</td>
<td>NO₂</td>
<td>99-101</td>
<td>62</td>
<td></td>
<td>C₁₄H₁₄N₂O₂P</td>
<td>Red needles</td>
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<td>11.41</td>
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<td>Cl</td>
<td>73-76</td>
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<tr>
<td>VII</td>
<td>CH₃</td>
<td>S</td>
<td>H</td>
<td>45-47</td>
<td>96</td>
<td>C₁₄H₁₄N₂O₂PS</td>
<td>Yellow prisms</td>
<td>8.69</td>
<td>8.68</td>
<td>9.62</td>
<td>10.01</td>
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<tr>
<td>VIII</td>
<td>C₂H₅</td>
<td>Cl</td>
<td>50-52</td>
<td>98</td>
<td></td>
<td>C₁₄H₁₄N₂O₂PS</td>
<td></td>
<td>8.66</td>
<td>8.05</td>
<td>8.85</td>
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<tr>
<td>IX</td>
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<td>Cl</td>
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<td>87</td>
<td></td>
<td>C₁₄H₁₄ClN₂O₄PS</td>
<td></td>
<td>7.85</td>
<td>7.81</td>
<td>8.69</td>
<td>8.46</td>
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<tr>
<td>X</td>
<td>C₂H₅</td>
<td>Cl</td>
<td>50-52</td>
<td>99</td>
<td></td>
<td>C₁₄H₁₄ClN₂O₄PS</td>
<td></td>
<td>7.28</td>
<td>7.43</td>
<td>8.06</td>
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<tr>
<td>XI</td>
<td>CH₃</td>
<td>NO₂</td>
<td>99-101</td>
<td>62</td>
<td></td>
<td>C₁₄H₁₄N₂O₂PS</td>
<td>Red prisms</td>
<td>11.53</td>
<td>11.54</td>
<td>8.44</td>
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<tr>
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<td>C₂H₅</td>
<td>Cl</td>
<td>73-75</td>
<td>94</td>
<td></td>
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<td></td>
<td>10.63</td>
<td>10.33</td>
<td>7.84</td>
<td>7.49</td>
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a) Nos. I ~ II were recrystallized from n-hexane, and III ~ VII from methanol.

Table 2. Partition paper chromatography of dialkyl azophenyl phosphate and related compounds.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>a) Rf</th>
<th>b) Rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.05</td>
<td>0.46</td>
</tr>
<tr>
<td>II</td>
<td>0.02</td>
<td>0.46</td>
</tr>
<tr>
<td>Azophenol</td>
<td>0.45</td>
<td>—</td>
</tr>
<tr>
<td>III</td>
<td>0.05</td>
<td>0.21</td>
</tr>
<tr>
<td>IV</td>
<td>0.02</td>
<td>0.22</td>
</tr>
<tr>
<td>4-Chloroazophenol</td>
<td>0.23</td>
<td>—</td>
</tr>
</tbody>
</table>

a) Sprayed with 5% alcoholic potassium hydroxide.
b) Sprayed with Hanes-Ischerwood reagent, followed by UV radiation.

Summary

Dialkyl 4'-substituted azophenyl phosphates and thiophosphates with general formula (RO)₂ P(X)-OC₆H₄-N=N-C₆H₄-Y were synthesized by the reaction of 4'-substituted azophenols with dialkyl chlorophosphates or thiophosphates in the presence of anhydrous sodium carbonate in acetone. Twelve new compounds were obtained as colored crystals. When X=O and Y=H or Cl, addition compounds with 1/2 mole of the starting azophenols were obtained.

Acknowledgement

We wish to express our thanks to Ph. Dr. Kizo Hiratsuka, Head of this Institute, for his kind encouragement and guidance during this work. Our thanks are also due to Mr. Ken’ichi Kojima and his assistants for bioassay and helpful discussions concerning this work.

Literature Cited