COMMUNICATION 13. DIESTERS OF 2-(2-ALKOXYETHOXY)VINYLPHOSPHONO-MONO-, DI-, AND -TRI-THIOIC ACIDS

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This paper describes the preparation and some of the properties of diesters of 2-(2-alkoxyethoxy)vinylphosphono-mono-, -di-, and -tri-thioic acids. The information in the literature on such esters is very limited. We have found a simple and readily accessible method for the synthesis of 2-alkoxy- and 2-phenoxy-vinylphosphonothioic dichlorides and 2-(2-alkoxyethoxy)vinylphosphonothioic dichlorides by the action of hydrogen sulfide on the product of the addition of phosphorus pentachloride to a vinyl ether [1].

The phosphonothioic dichlorides being readily accessible, we decided to prepare derivatives of these (esters and thio esters) by the reactions:

\[
\begin{align*}
\text{ROCH}_2\text{CH}_2\text{O}-\text{CH} &= \text{CHPOCl}_2 + 2\text{NaSR} = \text{ROCH}_2\text{CH}_2\text{O}-\text{CH} &= \text{CHPS(OH)}_2 + 2\text{NaCl}, \\
\text{ROCH}_2\text{CH}_2\text{O}-\text{CH} &= \text{CHPSCl}_2 + 2\text{NaOR} = \text{ROCH}_2\text{CH}_2\text{O}-\text{CH} &= \text{CHPS(OH)}_2 + 2\text{NaCl}, \\
\text{ROCH}_2\text{CH}_2\text{O}-\text{CH} &= \text{CHPSCl}_2 + 2\text{NaSR} = \text{ROCH}_2\text{CH}_2\text{O}-\text{CH} &= \text{CHPS(SR)}_2 + 2\text{NaCl}.
\end{align*}
\]

In this way we prepared S,S-diethyl 2-(2-methoxyethoxy)- and 2-(2-butoxyethoxy)-vinylphosphonothioates, O,O-dimethyl and O,O-diethyl 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)- and 2-(2-butoxyethoxy)-vinylphosphonothioates, and diethyl 2-(2-methoxyethoxy)- and 2-(2-ethoxyethoxy)-vinylphosphonithioates. The constants of these compounds are given in the table.

Diesters of 2-(2-alkoxyethoxy)vinylphosphono-mono-, -di-, and -tri-thioic acids are liquids of somewhat unpleasant odor, soluble in all organic solvents, and distillable only under reduced pressure.

EXPERIMENTAL

O,O-Dimethyl 2-(2-Methoxyethoxy)vinylphosphonothioate \(\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH} = \text{CHPS(OCH}_3)_2\) Sodium methoxide was prepared in a three-necked flask fitted with stirrer and reflux condenser from 40 ml of absolute methanol and 2.3 g of sodium, and it was stirred and cooled with ice water while 10.55 g of 2-(2-methoxyethoxy)vinylphosphonothioic dichloride was gradually added. The reaction mixture was then diluted with 100 ml of absolute ether and set aside overnight. On the next day the mixture was heated for two hours in a water bath at 35°; the ether layer was then removed, and the precipitate present was washed several times with ether. Vacuum fractionation gave a product amounting to 6.8 g (56%), having b.p. 119° (2 mm); \(\text{nD}^2 1.4775; \text{d}_4^0 1.1624\).

O,O-Diethyl 2-(2-Methoxyethoxy)vinylphosphonothioate \(\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH} = \text{CHPS(OCH}_3)_2\) 2-(2-Methoxyethoxy)vinylphosphonothioic dichloride (11.85 g) was added with cooling and slow stirring to sodium methoxide prepared from 2.3 g of sodium and 50 ml of absolute ethanol. When reaction was complete, the mixture was diluted with 120 ml of absolute ether and set aside overnight. On the next day the mixture was warmed in a water bath and the ether layer was poured off, the precipitate being washed several times with ether. Drying over sodium sulfate followed by vacuum fractionation yielded 10 g (73.5%) of a substance having b.p. 120° (1 mm); \(\text{nD}^2 1.4769; \text{d}_4^0 1.0904\).

O,O-Dimethyl 2-(5-Ethoxyethoxy)vinylphosphonothioate \(\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH} = \text{CHPS(OCH}_3)_2\) 2-(2-Ethoxyethoxy)vinylphosphonothioic dichloride (12.45 g) was added gradually with cooling and stirring to sodium methoxide prepared...
TABLE

<table>
<thead>
<tr>
<th>Formula</th>
<th>B.P.°C (P in mm)</th>
<th>nD</th>
<th>d4</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃-O-CH₂-CH₂-O-CH₃ CHPO(SC₂H₅)₂</td>
<td>150/1</td>
<td>1.5511</td>
<td>1.1435</td>
<td>80</td>
</tr>
<tr>
<td>n-C₄H₉-O-CH₂-CH₂-O-CH₃ = CHPO(SC₂H₅)₂</td>
<td>186/2</td>
<td>1.5305</td>
<td>1.1180</td>
<td>87</td>
</tr>
<tr>
<td>CH₃-O-CH₂-CH₂-O-CH₂ = CHPS(OCH₃)₂</td>
<td>119/6</td>
<td>1.4775</td>
<td>1.1624</td>
<td>58</td>
</tr>
<tr>
<td>CH₃-O-CH₂-CH₂-O-CH₂ = CHPS(OCH₃)₂</td>
<td>120/1</td>
<td>1.4760</td>
<td>1.0904</td>
<td>73</td>
</tr>
<tr>
<td>C₂H₅-O-CH₂-CH₂-O-CH₃ = CHPS(OCH₃)₂</td>
<td>127/2</td>
<td>1.4712</td>
<td>1.1321</td>
<td>78</td>
</tr>
<tr>
<td>C₂H₅-O-CH₂-CH₂-O-CH₂ = CHPS(OCH₃)₂</td>
<td>133/2</td>
<td>1.4695</td>
<td>1.0781</td>
<td>82</td>
</tr>
<tr>
<td>n-C₄H₉-O-CH₂-CH₂-O-CH₃ = CHPS(OCH₃)₂</td>
<td>141/1</td>
<td>1.4690</td>
<td>1.0922</td>
<td>73</td>
</tr>
<tr>
<td>n-C₄H₉-O-CH₂-CH₂-O-CH₂ = CHPS(OCH₃)₂</td>
<td>145/1</td>
<td>1.4680</td>
<td>1.0256</td>
<td>80</td>
</tr>
<tr>
<td>CH₂-O-CH₂-CH₂-O-CH₂ = CHPS(SC₂H₅)₂</td>
<td>157/2</td>
<td>1.5890</td>
<td>1.1579</td>
<td>75</td>
</tr>
<tr>
<td>C₂H₅-O-CH₂-CH₂-O-CH₂ = CHPS(SC₂H₅)₂</td>
<td>176/2</td>
<td>1.5745</td>
<td>1.1417</td>
<td>83</td>
</tr>
</tbody>
</table>

from 2.3 g of sodium and 50 ml of absolute methanol. When the addition was complete, the mixture was diluted with 100 ml of ether. On the next day treatment as described above yielded 9.7 g (78%) of a substance having b.p. 127° (2 mm); nD 1.4712; d4 1.1321.

Found %: P 12.95; 12.84
Calculated %: P 12.84

O,O-Diethyl 2-(2-Ethoxyethoxy)vinylphosphonothioate CH₂OCH₂CH₂OCH₂ = CHPS(OCH₃)₂. 2-(2-Ethoxyethoxy)vinylphosphonothioic dichloride (12.45 g) was added gradually with cooling and stirring to sodium ethoxide prepared from 2.3 g of sodium and 50 ml of absolute ethanol. When the addition was complete, the reaction mixture was diluted with 100 ml of ether and set aside overnight. On the next day the ether layer was poured off and the precipitate was washed several times with ether. Fractional distillation under reduced pressure yielded 11.4 g (82%) of a substance having b.p. 133° (2 mm); nD 1.4695; d4 1.0781.

Found %: P 10.15; 10.14
Calculated %: P 10.10

O,O-Dimethyl 2-(2-Butoxyethoxy)vinylphosphonothioate n-C₄H₉OCH₂CH₂OCH₂ = CHPS(OCH₃)₂. 2-(2-Butoxyethoxy)vinylphosphonothioic dichloride (8 g) was added gradually with stirring and cooling to sodium methoxide prepared from 50 ml of absolute methanol and 1.3 g of sodium. When reaction was complete, the mixture was diluted with 110 ml of absolute ether. On the next day the mixture was "warmed in a water" bath for two hours, the ether layer was poured off, and the precipitate was washed repeatedly with ether. The ether solution of the reaction mixture was dried over sodium sulfate. Fractionation then gave 6.5 g (83%) of a substance with b.p. 141° (1 mm); nD 1.4690; d4 1.0692.

Found %: P 10.77; 10.95
Calculated %: P 11.19

O,O-Diethyl 2-(2-Butoxyethoxy)vinylphosphonic dichloride (18.9 g) was added gradually with stirring to sodium ethoxide prepared from 60 ml of absolute ethanol and 2.3 g of sodium. When the addition was complete, the mixture was diluted with 120 ml of absolute ether. On the next day the above-described operations yielded 17 g (80%) of a substance having b.p. 145° (1 mm) nD 1.4680; d4 1.0296.

Found %: P 10.52; 10.32
Calculated %: P 10.47