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Derivatives of Some 2-Chloroethylphosphonic Acid Esters, with Plant Growth Regulating Activity

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Derivatives of Some 2-Chloroethylphosphonic Acid Esters, with Plant Growth Regulating Activity

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A method for the synthesis of esters of 2-(dimethylsulfonium)ethylphosphonic acid and the results of some trials showing the plant growth regulating activity of these compounds are presented. For the synthesis of the mentioned compounds, dimethyl sulphide is reacted with 2-chloroethylphosphonic acid esters; these esters are obtained through the complex^[1] of AlCl₃, PCl₃ and 1.2-dichloroethan (1). Using the optimum reaction conditions, very good yields were obtained (96-99%). This complex is reacted with different alcohols to give 2-chloroethylphosphonic acid esters (2) (R=Me, Et, Pr, i-Pr, Bu, i-Bu, Pe). Using the optimum reaction conditions, in the case of methanol the maximum obtained yield was 50%. In the case of the other alcohols, the obtained yields were between 76 and 83%. An exception is i-propanol, whose ester was obtained with low yields and the reaction parameters modification have little influence on the yield. The reaction of the esters with dimethyl sulphide gives, in good yields (between 69 and 79%), esters of 2-(dimethylsulfonium)ethylphosphonic acid (3), substances with plant growth regulating activity.

$$\begin{aligned} \{\text{CICH}_2\text{CH}_2\text{PCl}_3\}^+ [\text{AICl}_4]^- + 3\text{ROH} \rightarrow \text{CICH}_2\text{CH}_2\text{P(O)}(\text{OR})_2 + \text{AICl}_3 + \text{RCl}_3 \\ (1) & (2) & + 3\text{HCl} \end{aligned}$$

$$\label{eq:CICH2CH2PONOR} \begin{split} \mathsf{CICH}_2\mathsf{CH}_2\mathsf{P}(\mathsf{O})(\mathsf{OR})_2 + (\mathsf{CH}_3)_2\mathsf{S} \to (\mathsf{CH}_3)_2\mathsf{S}^+\mathsf{CH}_2\mathsf{CH}_2\mathsf{P}(\mathsf{O})(\mathsf{OR})_2 \cdot \mathsf{CI}^-\\ (3) \end{split}$$

The plant growth regulating activity of the obtained compounds was tested. In ripening tomatoes, increasing of the quantity of ripe fruits up to 25% over untreated control was obtained. In cucumber plants, increasing of the proportion of female flowers (fruit bearing) up to 36% over untreated control was obtained. In blackcurrants, the tested compounds have accelerated and concentrated fruit ripening and improved fruit quality.

References

[1] L. Maier, Phosphorus & Sulphur, 11, 149 (1981).