Synthesis of Sulfur-35 and Phosphorus-32 Labeled 0-2-(Ethylthio)ethyl 0,0-Diethyl Phosphorothioate

ERNEST M. HODNETT, THOMAS E. MOORE and JOHN E. LOTHERS, JR., Oklahoma State University, Stillwater

Soon after G. Schrader (1951) of Farbenfabriken Bayer, Germany, synthesized 0-2-(ethylthio)ethyl O,O-diethyl phosphorothioate in 1948, this compound was shown to be an effective systemic insecticide. This ester can be transported throughout the plant without damage to it, but can kill or severely harm insects or warm-blooded animals which feed upon the plant. Studies of the absorption, translocation and retention of the insecticide in the plant are most conveniently done by the use of tracer techniques. Consequently the compound has been synthesized with sulfur-35 and with phosphorus-32 in the molecule.

The reactions used in both syntheses are:

$$PCl_3 + S \xrightarrow{AlCl_3} SPCl_3$$

$$SPCl_3 + 2\ NaOC_2H_5 \longrightarrow SPCl(OC_2H_5)_2 + 2\ NaCl$$

$$SPCl(OC_2H_5)_2 + HOC_2H_4SC_2H_5 \xrightarrow[K_2CO_3]{Cu} SP(OC_2H_5)_2(OC_2H_4SC_2H_5) + HCl$$

The two procedures differ only slightly so only one is outlined. The radioactive element was introduced as either elementary sulfur-35 or phosphorus-32 trichloride in the first step of the reaction. Yields of the radioactive products based on the activities of the starting materials were good.

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EXPERIMENTAL

Preparation of 0-2-(Ethylthio)ethyl 0,0-Diethyl Phosphorothioate-S^{35}. Ten

millicuries of elemental sulfur-35 in benzene solution (from Oak Ridge National Laboratory) was placed in a 25-ml. flask and the benzene was removed by vacuum distillation. To the flask was added 1.2 g. (37.5 mmoles) of sulfur, 0.2 g. (1.5 mmoles) of aluminum chloride, and 5 g. (36 mmoles) of phosphorus trichloride. The mixture was heated slowly to 80° and held at that temperature for one-half hour until the reaction was complete. More heat was applied and $S^{35}PCl_3$ distilled at 123-125° through a short fractionating column.

To this compound was added dropwise with stirring a solution prepared by adding 1.4 g (61 mmoles) of sodium to 24 g. (521 mmoles) of absolute ethyl alcohol. After the mixture had stood at room temperature for 5 minutes, it was added to 75 ml. of water. The oil which separated was dried with anhydrous calcium chloride, and then distilled at 84-87° and 15 mm. pressure.

A mixture of 2.86 g. (27 mmoles) of 2-(ethylthio)ethyl alcohol, 5.4 g. (39 mmoles) of powdered potassium carbonate, 1.6 ml. of benzene, and 0.1 g. of powdered copper was heated to 55° in a flask. The 0,0-diethyl phosphorothioyl-S^{35} chloride just prepared was added slowly with stirring. After the mixture was stirred at 60° for three hours, 10 ml. of water was added and the mixture was stirred for 30 minutes without heating. The reaction mixture was extracted with benzene several times. The benzene extracts were combined and subjected to reduced pressure and slowly rising temperatures until 90° and a pressure of 2 mm. was reached. The 0-2-(ethylthio)ethyl 0,0-diethyl phosphorothioate-S^{35} was filtered through charcoal. The yield of ester was 9.69 g. or 47.5% based on the sulfur used.

LITERATURE CITED

Schrader, G. 1951. Die Entwicklung neuer Insektizide auf Grundlage organischer Fluor- und Phosphor-Verbindungen, Monograph 62, Verlag Chemi, Weinheim.