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Synthesis of Carbon-14 and Sulfur-35 Labeled O-Ethyl-S-Phenyl-Ethyl-Phosphonodithioate

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O-Ethyl-S-phenyl-ethyl-phosphonodithioate *, a candidate broad spectrum insecticide ⁽¹⁾, was labeled in the ethoxy moiety with carbon-14 and in the thiophenyl moiety with sulfur-35 to facilitate residue and metabolism studies.

O-1- ^{14}C -ETHYL-S-PHENYL-ETHYL-PHOSPHONODITHIOATE

S-Phenyl-ethyl-phosphonochloridithioate, 0.34 ml (430 mg or 1.82 mmole) was added dropwise with stirring to a suspension of 122.4 mg (1.8 mmole) of sodium ethylate, having a specific activity of 5.75 mC per mmole, in anhydrous ether at -70°C . The reaction mixture was stirred and allowed to warm to room temperature over a period of one hour. The resultant mixture was washed to pH-7 with four 1.5 ml portions of distilled water. The product was dried over magnesium sulfate and filtered into a 25 ml pear-shaped flask. The volume was adjusted to 10 ml. A one λ sample of this solution was spotted on a 50 cm \times 100 cm Brinkmann thin layer chromatography plate, pre-coated with a 250 micron layer of silica gel F₂₅₄. Authentic O-ethyl-S-phenyl-ethyl-phosphonodithioate was spotted on the same plate and the co-chromatogram developed with hexane/chloroform 60/40 for a distance of 5 cm. Visualization with N,2,6-trichloro-*p*-benzoquinoneimine (TCQ) showed two minor impurities. The plate was exposed to Kodak no-screen medical X-ray film for thirty minutes. Development of the radioautograph disclosed only one spot. Ether was evaporated from the solution yielding 368 mg of product, 83 % of theory.

* Dyfonate ® : registered trademark of Stauffer Chemical Company.

One λ of the product was dissolved in 100 λ of carbon disulfide. A 1.5 λ portion of this solution was injected into a Varian Aerograph 204-1B gas chromatography instrument which was fitted with a 6 foot \times 1/4 inch pyrex column, packed with 3 % OV-1 on 60/80 mesh gas chrom Q, a hydrogen flame ionization detector (mass purity) and a Cary ion chamber and vibrating reed electrometer (radiochemical purity). The injection port was at 240° C. The column was programmed from 100 to 250° C at 10° C/minute. The hydrogen flame ionization detector and splitter were at 275° C. The ion chamber had a volume of 275 ml and was heated to 290° C. Argon was used as a carrier gas and as an ion chamber purge gas. The resulting chromatogram disclosed a radiochemical purity of 98 + %. A radioautograph of a two-dimensional thin layer chromatogram which was developed vertically with hexane/chloroform 60/40 and horizontally with ethylacetate/chloroform 50/50, showed only one spot, thus indicating a radiochemical purity of 98 + %.

O-ETHYL-³⁵S-PHENYL-ETHYL-PHOSPHONODITHIOATE

Sodium dispersion, 0.48 ml (53 mg or 2.3 mmole), containing 110 mg of sodium per ml of dispersion in xylene was suspended in 2.5 ml of anhydrous tetrahydrofuran under an argon atmosphere in a 10 ml two-neck flask fitted with a condenser refrigerated to -30° C, a magnetic stirrer and a gas inlet tube. Five ml of a tetrahydrofuran solution containing 105 mg (.95 mmole) of thiophenol-³⁵S with a specific activity of 33 mC per mmole was added dropwise with mixing to the sodium dispersion at -7° C. The mixture was stirred for ten minutes, and 0.11 ml (115 mg or 1.045 mmole) of diluent thiophenol added dropwise to the reaction. The resultant mixture was warmed to 40° C over a period of thirty minutes and maintained at that temperature for one hour. O-Ethyl-ethyl-phosphonochloridothioate, 0.3 ml (345 mg or 2 mmole) was added dropwise to the sodium thiophenate mixture at -7° C. The reaction mixture was allowed to reach ambient temperature over a period of thirty minutes. The solvent was stripped under a slow stream of argon, the residue taken up in six ml of ether and washed to pH-7 with four one-ml portions of distilled water. The ether solution was dried over magnesium sulfate and filtered into a 25 ml pear-shaped flask. The volume was adjusted to 10 ml and a 1 λ sample of this solution spotted to a 50 cm \times 100 cm Brinkmann thin layer chromatography plate, precoated with a 250 micron layer of silica gel F₂₅₄. Authentic O-ethyl-S-phenyl-ethyl-phosphonodithioate was spotted on the same plate and the co-chromatogram developed with hexane/chloroform 60/40 for a distance of five cm. Visualization with N,2,6-trichloro-*p*-benzoquinoneimine showed one minor impurity. The plate was exposed to Kodak no-screen medical X-ray film for thirty minutes. Two dark spots resulted. The impurity was readily identified as diphenyl disulfide. A subsequent preparative thin layer chromatogram of this product followed by counting of the bands in a liquid scintillation counter disclosed that 98.5 %

of the radioactivity was contained in the product band. The product was stripped of ether to yield 471 mg, 96 % of theory. The product contained 97.5 % of its theoretical radioactivity based upon the initial activity, the activity upon completion of the preparation, the elapsed time between the two countings and radioactive half-life for sulfur-35.

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Microsynthèse de Polyphényle Deutééré, à haute teneur isotopique

Reçu le 22 juillet 1968

La microsynthèse à hauts rendements chimique et isotopique du polyphényle deutéré, comme étape préalable, indispensable à la tritiation à haute activité spécifique de ce composé, est décrite ci-après,

1. — SCHÉMA DE LA SYNTHÈSE DU POLYPHÉNYLE.

Quel que soit l'isotope de l'hydrogène, la synthèse du polyphényle se ramène au schéma suivant.

PREMIÈRE ÉTAPE.

