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Synthesis of carbon-14 labeled S-(O, O-diisopropylphosphorodithioate) of N-(2-mercaptoethyl)benzenesulfonamide

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Labeled ^{14}C -benzene S-(O,O-diisopropylphosphorodithioate) of N-(2-mercaptoethyl) benzenesulfonamide of a specific activity of 0.1 mC/m mole was prepared for residue and metabolism studies. The overall yield was 60% of a 95% radiochemically pure product.

S-(O,O-diisopropylphosphorodithioate) of N-(2-mercaptoethyl) benzenesulfonamide* [I] was first prepared and shown to be a selective pre-emergent herbicide by Fancher and Dewald ⁽¹⁾.

To facilitate residue and metabolism studies, [I] was prepared with a carbon-14 label in the benzene ring. The reaction scheme is shown in figure 1.

Uniformly ^{14}C labeled benzene was chlorosulfonated with chlorosulfonic acid in carbon tetrachloride. The resulting benzenesulfonyl chloride was treated

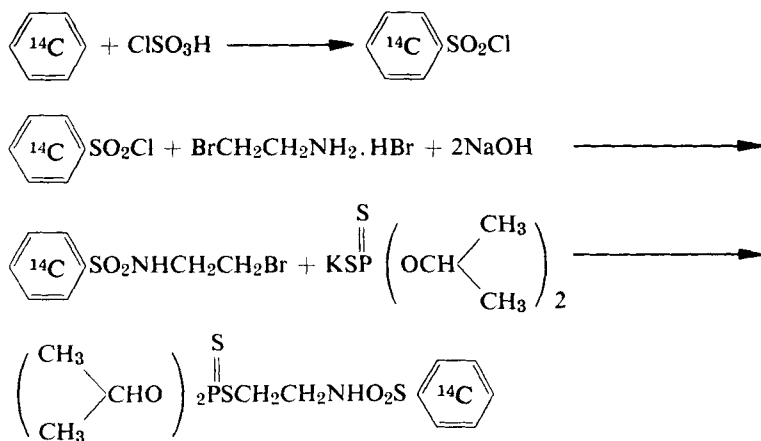


FIG. 1 — The reaction scheme

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with β -bromoethylamine hydrobromide to yield N- β -bromoethylbenzene sulfonamide, which when reacted with an excess of potassium *O,O*-diisopropyldithiophosphoric acid, gave a 60% yield of [I]. The identity of the product was established by infrared and thin layer chromatographic comparison with an authentic sample.

The chlorosulfonation of labeled benzene was accomplished on a five millimole scale by the method of Clark, *et. al.* ⁽²⁾ with some modification to facilitate the micro scale synthesis.

Radiolabeled benzene (14.0 mg, 0.5 mC, 0.18 mmoles) was distilled on a vacuum manifold into a vacuum jacketed, microdropping funnel and was added to an excess (25 mmoles) of chlorosulfonic acid. An additional 376 mg (4.82 mmoles) of non-radioactive benzene was then added. After reaction was complete, the product was taken up in chloroform. The excess chlorosulfonic acid was decomposed with ice, and the solution was dried by passing over a 2.5 cm ID column containing 1.5 g of florine, 60-100 mesh. The product was characterized by infrared comparison with an authentic sample. Yield: 550 mg, 94.7%. 2-Bromoethylamine hydrobromide (1130 mg, 5.5 mmoles) in 5 ml of water and 6 ml of ether were added to the ¹⁴C-benzene-sulfonylchloride. Sodium hydroxide (440 mg, 11.0 mmoles) in 1.5 ml of ice water was added over a period of 30 min while stirring at 0°C. After the addition was complete, 6 ml of ether was added, and the aqueous phase was removed. The ether phase was washed with 3 ml of dilute hydrochloric acid, 3 ml of water, and evaporated. Potassium-*O,O*-diisopropyl phosphorodithioate (1700 mg, 6.5 mmoles) and 12 ml of acetone were added. The mixture was heated under reflux for 4 hours, cooled to room temperature, and then taken up in 25 ml of benzene. The benzene phase was washed with two 10 ml portions of water and dried by passing it through a 2.5 cm ID column containing 1.5 gms of florisil, 60-100 mesh. The benzene was evaporated yielding 1190 mg of product, 60.2% of theory based on benzene. The identity of the product was established by comparative infrared spectra with an authentic sample.

The 1190 mg of product were dissolved in 119 ml of ether, and 1 ml of the ethereal solution was dissolved in 10 ml of toluene. Ten λ of the toluene solution were spotted on a thin layer chromatography plate coated with a 250 micron layer of silica gel G, (Brinkman Co., Westbury, New York). The plate was developed in a 15% solution of ethyl acetate in benzene for 20 min. The plate was dried, and the resulting chromatograph was covered with Eastman Kodak SP351 x-ray film for 4 days. The film was developed and exhibited two spots (R_f 4.2, 5.8). The two spots were eluted and counted with a Packard Tri-Carb liquid scintillation counter. The spot whose R_f value (4.2) corresponded to that of the product contained 95% of the radioactivity.

A.D. GUTMAN AND M.E. BROKKE

Stauffer Chemical Company, Richmond Research Center
Richmond, California

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