

A CONVENIENT PREPARATION OF PENTACHLORONITROBENZENE-U-¹⁴C

Summary

Starting with benzene-U-¹⁴C pentachloronitrobenzene-U-¹⁴C has been prepared by nitration followed by chlorination with antimony pentachloride in the presence of aluminum chloride.

Key Words: nitrobenzene-U-¹⁴C, perchlorination, antimony pentachloride

Introduction

The preparation of carbon-14 labeled pentachloronitrobenzene-U-¹⁴C, a broad spectrum fungicide, has been reported (1,2). In both cases the compound was prepared by exhaustive chlorination of nitrobenzene with gaseous chlorine in chlorosulfonic acid.

This note describes a less involved modus of chlorination of nitrobenzene.

Benzene-U-¹⁴C was nitrated according to Spitzer and Steward (3) in trifluoroacetic acid with the aid of sodium nitrate. This method is especially well suited for small scale preparations due to its simplicity and ease of execution.

The use of transition metal chlorides such as antimony pentachloride in the chlorination (4) or perchlorination (5) of aromatic compounds has been documented. Even though nitrobenzene is known to retard such reactions by coordinating with the metal halide (6), it has been successfully monochlorinated to predominantly m-chloronitrobenzene (7) with the aid of antimony pentachloride.

Addition of aluminum chloride and elevation of the reaction temperature was found to give polychlorination to yield pentachloronitrobenzene. As a byproduct some hexachlorobenzene also formed. It could be easily separated from the desired pentachloronitrobenzene-U- ^{14}C by preparative TLC.

Experimental

Liquid scintillation counting was done with a Packard Model 3003 liquid scintillation spectrometer, using LiquifluorTM premixed scintillation solution (New England Nuclear Corp., Boston, Massachusetts). Benzene-U- ^{14}C was obtained from Pathfinder Laboratories Inc., St. Louis, Missouri.

Nitrobenzene-U- ^{14}C

To 85 mg (1 mmole) sodium nitrate in 2.5 ml trifluoroacetic acid, 10 mCi (0.97 mmole) benzene-U- ^{14}C was added. The mixture was stirred at room temperature for 4 hr. After this time, the reaction was quenched by the addition of 10 ml of water, brought to pH > 10 with 3 N sodium hydroxide and the resulting solution extracted with three portions of methylene chloride. The organic extracts were dried over anhydrous magnesium sulfate and evaporated to dryness leaving 110 mg (92%) of radiochemically pure nitrobenzene.

Pentachloronitrobenzene-U- ^{14}C

Aluminum trichloride (930 mg, 7 mmole) was added to the above 110 mg nitrobenzene-U- ^{14}C and thoroughly mixed. After adding 1 ml (2.33 g; 7.8 mmole) of antimony pentachloride, the mixture was stirred at 160° C for 2 hr and then allowed to cool. The reaction was quenched by careful addition of 20 ml 6 N hydrochloric acid and the product extracted with three portions of benzene. The organic extracts were washed once with 6 N hydrochloric acid and twice with water. After drying over anhydrous magnesium sulfate, the benzene was removed

(in vacuo) leaving 221 mg of crystalline residue. Pure pentachloronitrobenzene-(U-¹⁴C) was obtained by preparative TLC on silica gel using hexane as the developing solvent. A total of 156 mg (53% overall), 5.28 mCi at 10 mCi/mole specific activity with a purity of $\geq 98\%$ was obtained. In addition, 50 mg (0.18 mmole, 18% overall), 1.76 mCi of pure hexachlorobenzene-U-¹⁴C was also isolated.

Acknowledgement

Support of this work by the Environmental Protection Agency, Contract No. 68-02-2236, is gratefully acknowledged.

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