NOTES

A FACILE MICROMOLAR REDUCTION OF [1,2,3,4,10-^{14}C]ALDRIN TO 6,7-DIHYDRO[1,2,3,4 10-^{14}C]ALDRIN

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Summary

The preparation of 6,7-dihydro[1,2,3,4,10-^{14}C]aldrin is reported by catalytic reduction of [1,2,3,4,10-^{14}C]aldrin. Modification of previously published conditions afforded the desired product in 97.1% yield as assayed by electron capture gas chromatography. The convenient one vessel reaction proceeds rapidly to give the high purity product in twenty minutes at atmospheric pressure.

Key Words: ^{14}C-aldrin, ^{14}C-6,7-dihydroaldrin, halogenated pesticides, ^{14}C-aldrin reduction

We had previously observed that halogenated pesticides were associated with DNA damage in mammalian cells (1,2). Studies of genetic damage structure-action relationships of this class of pesticides necessitated ^{14}C-labeled derivatives of aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene). Earlier literature reports of the reduction of aldrin to 6,7-dihydroaldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4:5,8-dimethanonaphthalene) and the selective reduction of similar unsaturations in halogenated dienes utilized platinum oxide catalyst or unspecified ratios of palladium catalysts on hundred gram quantities of aldrin (3-6).

The synthetic scheme utilized in our laboratories started with 500 μCi [1,2,3,4,10-^{14}C]aldrin* (76 mCi/mM) which represented a total of 2.40 mg (6.6 μmol) of aldrin. Cold runs required the effective determination of catalyst ratios since excess concentrations of catalyst led rapidly to over-reduction and apparent dehydrohalogenation products as analyzed by flame-ionization and electron-capture gas chromatography.

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Preparation of 6,7-dihydro[1,2,3,4,10-^{14}C]aldrin(1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4:5,8-dimethanonaphthalene.

A solution of 500 μCi [1,2,3,4,10-^{14}C]aldrin (2.40 mg) in 1.0 mL benzene was evaporated to dryness under a stream of dry nitrogen utilizing the "Duraseal" vial (provided by Amersham Corp., Arlington Heights, Illinois) as the reaction vessel. To this was added 5.0 mL methanol, 1.20 mg 10% palladium on carbon (Matheson Coleman and Bell, Norwood, Ohio) and a micro stirring bar. The atmosphere above the solution was charged with hydrogen gas, the reaction vessel stoppered and the mixture stirred vigorously for 20 minutes. The vial was unstoppered, the stirring ceased and the solution rapidly filtered through a cotton plugged Pasteur pipet to remove catalyst. The filtrate was evaporated to dryness under a stream of dry nitrogen, dissolved with exactly 2.40 mL spectral grade benzene, an aliquot taken and diluted appropriately for gas chromatograph assay using the following systems: a) Hewlett-Packard Model 402 gas chromatograph fitted with 6 ft x 1.0 mm glass column 10% SE 30 on Chromosorb P, with oven temperature maintained 185°C b) Hewlett-Packard 5710A gas chromatograph fitted with 6 ft x 1.0 mm glass column 3% OV-1 on Chromsorb W with oven temperature maintained at 185°C. The resulting chromatographic profile indicated the desired product was present in 97.1% yield as determined by planimetry with retention time identical to pure 6,7-dihydroaldrin. All synthetic compounds were compared with standards provided by the U.S.E.P.A. or synthesized in our laboratories. Radiochemical purity was assayed by thin layer chromatography on silica gel in a) cyclohexane/chloroform (4:1) and b) hexane and visualized using a Baird beta camera. Specific activity was determined by counting 5 x 1.0 μL aliquots in Amersham PCS scintillation cocktail with a Beckman Counter Model LS 355.

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