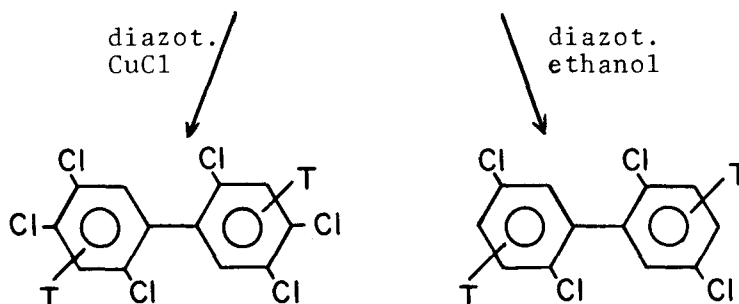


A General Method for the Preparation of Tritiated Polychlorobiphenyls of High Specific Activity: 2,2',5,5'-Tetrachlorobiphenyl- ^3H and 2,2',4,4',5,5'-Hexachlorobiphenyl- ^3H ¹

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We wish to report a general method for preparing tritiated chlorobiphenyls of high specific activity. Incorporation of hydrogen isotope was low, as shown by mass spectrometry, when acid catalyzed deuterium exchange was attempted on hexachlorobiphenyls. Chlorobiphenyls in which amino groups activated this electrophilic exchange process, on the other hand, gave good incorporation. This method is useful for preparing other tritiated chlorobiphenyls since some aminochlorobiphenyls are available commercially (Pfalz & Bauer) and others are easily accessible by simple synthetic procedures such as benzidine rearrangement (e.g. 1,2) or nitration of chlorobiphenyls and subsequent reduction (e.g. 3,4,5). For each labelled aminochlorobiphenyl two chlorobiphenyls can easily be obtained by either removing the amino groups or Sandmeyer reaction.

2,2',5,5'-Tetrachlorobenzidine- ^3H



Synthetic Procedures: Samples prepared from unlabelled material by identical procedures were analytically pure and showed only one peak on gas chromatography (3). Merck silica gel HF-254 and hexane were used for t.l.c.

¹Issued as NRCC No. 12127.

2,2',5,5'-Tetrachlorobenzidine-dihydrochloride-[³H]:
2,2',5,5'-Tetrachlorobenzidine 2 HCl (50 mg), prepared from the free base (Pfalz & Bauer) and hydrogen chloride, was exchanged (New England Nuclear Corp.) by stirring with trifluoroacetic acid (³H) (0.5 ml) and platinum catalyst (25 mg) at 60° overnight. Specific activity: 5.48 mCi/mg.

Preparation of Diazonium Solution: 2,2',5,5'-Tetrachlorobenzidine (100 mg) was stirred and heated to ca. 70° with conc. hydrochloric acid (3 ml), the mixture was cooled and 40 mg of the tritiated material added and diazotized, at 0°, with sodium nitrite (100 mg) in water (0.5 ml). Thirty minutes after the addition was complete, the diazonium solution was filtered and used as described below.

2,2',4,4',5,5'-Hexachlorobiphenyl-[³H]: One half of the diazonium solution described above was slowly added to a solution of cuprous chloride (50 mg) in conc. hydrochloric acid (1 ml). The mixture was stirred for 1 hour at room temperature, the crude hexachlorobiphenyl removed by filtration and washed with conc. HCl and water. The crude material was purified by preparative t.l.c. (R_f = 0.72). Yield 30 mg; m.p. 101-102°; specific activity, 1.9 mCi/mmmole.

2,2',5,5'-Tetrachlorobiphenyl-[³H]: One half of the clear diazonium solution described above was added to 20 ml boiling ethanol and boiling was continued for 15 minutes. The mixture was concentrated to ca. 2 ml, extracted with benzene and the benzene layer, after drying and evaporation purified by preparative t.l.c. (R_f = 0.65). Yield 29.7 mg; m.p. 84-85°; specific activity, 1.9 mCi/mmmole.

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