SYNTHESIS OF ^{14}C-LABELLED POLYCHLOROBIPHENYLS DERIVED FROM THE LABELLED 4-CHLORO-, 2,5-DICHLORO-, 3,4-DICHLORO-, 2,3-DICHLORO-2,4,5-TRICHLORO- AND 2,3,6-TRICHLOROANILINES

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SUMMARY

[^{14}C] Aniline hydrogen sulphate was acetylated, and the acetanilide obtained was chlorinated with N-chlorosuccinimide to 2-chloro, 4-chloro- and 2,4-dichloroacet[^{14}C] anilide. The labelled 2- and 4-chloroacet [^{14}C] anilides were hydrolyzed and treated with aluminium chloride, hydrogen chloride and chlorine in dry dichloromethane to give the major products 2,5-dichloro- and 3,4-dichloro [^{14}C] aniline. The labelled 2,3-dichloro- and 2,3,6-trichloroanilines were obtained as minor products from the chlorination of 2-chloro [^{14}C] aniline, likewise 2,4,5-trichloroaniline was obtained from 4-chloro [^{14}C] aniline. The [^{14}C] anilines prepared were coupled with benzene, 1,4-dichloro-, 1,2-dichloro- or 1,3-dichlorobenzene to give 4-chloro-, 2,3',4',5-tetrachloro-, 2,3,3',4'-tetrachloro-, 3,3',4,4'-tetrachloro-, 2,2',5,5'-tetrachloro-, 2,2',3,3'-tetrachloro-, 2,2',3,5',6-pentachloro-, 2,2',4,4',5-pentachloro- and 2,3',4,5,5'-pentachloro [^{14}C] biphenyl.

3,4-Dichloro [^{14}C] aniline and biphenyls prepared from this aniline were found to be contaminated by bromoanalogues. The origin of these have been studied.

INTRODUCTION

Most polychlorinated biphenyls found in technical mixtures of PCB have been synthesized and characterized as pure compounds (1,2). Some ^{14}C-labelled chlorinated biphenyls have also been prepared (3 - 14) but their structures are often different from the structures of the major constituents of PCB. Mixtures of ^{14}C-labelled PCB with 42%[1], 50%[2] and 54%[1] chlorine are, however, commercially available.

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Whole-body autoradiographic studies of several polychlorobiphenyls have been performed (15 - 20) and in this context a significant accumulation in the bronchial epithelium of the lungs of mice administered certain chlorobiphenyls has been of special interest (19, 21). The structure of the chlorobiphenyls given to mice, which have a strong retention in the lung, could be related to a common chlorine and hydrogen substitution pattern of the biphenyls (19, 21). The compounds accumulated in the lungs were later shown to be methyl sulphones derived from each chlorobiphenyl given to the mice except in one case, 2,2',4,4',5,5'-hexachlorobiphenyl, which was accumulated as such (22). The study also showed comparative amounts of methylsulphonyl-polychlorobiphenyls in lung tissue after treatment with two chlorobiphenyls so far not studied autoradiographically, 2,3',4',5-tetrachlorobiphenyl and 2,2',5,5'-tetrachlorobiphenyl (22). The present paper describes the preparation of these two biphenyls tagged with carbon-14 and in addition eight other labelled chlorobiphenyls (Figure 1).

For the synthesis of ^{14}C-labelled Imugan from [^{14}C] benzene a <u>meta</u>-directing chlorination method was utilized in order to prepare 3,4-dichloro[^{14}C] aniline from 4-chloro[^{14}C] aniline (6). An aromatic amine, aluminium chloride and hydrogen chloride were proposed to form a complex which facilitated bromination and chlorination in the <u>meta</u>-position (23). The 2,5- and 3,4-dichloro[^{14}C]-anilines, prepared by the <u>meta</u>-directing halogenation method, were purified and isolated by preparative thin layer chromatography. Subsequently the Shu Huang-Cadogan coupling reaction (24, 25) between a chloroaniline and a chlorobenzene was utilized for the preparation of the labelled chlorobiphenyls.

RESULTS AND DISCUSSION

The polychlorinated biphenyls <u>1</u>-<u>10</u> in Figure 1 have been synthesized. Uniformly labelled [^{14}C] aniline hydrogen sulphate was used as starting material. The aniline was acetylated in quantitative yield and the acetanilide obtained was then chlorinated with N-chlorosuccinimide (NCS) (12). 2-Chloroacet[^{14}C] anilide (31%), 4-chloroacet[^{14}C] anilide (49%) and 2,4-dichloroacet[^{14}C] anilide (11%) were obtained after isolation using liquid chromatography and preparative TLC. In order to facilitate the separation of 2-chloro- and 2,4-dichloroacetanilide the silica gel of the TLC-plates was impregnated with tetrabutylammonium hydrogen phosphate (26). The second chlorination step was worked out on a semimicro-scale (25 mg chloroaniline) with unlabelled 4-chloroaniline. This reaction step was so sensitive to moisture that even the humidity of the air should be taken into account. After appropriate TLC-separation the amounts of 3,4-dichloro[^{14}C]-aniline (39.5%), 2,4,5-trichloro[^{14}C] aniline (14.5%) and unreacted 4-chloro-[^{14}C] aniline (8.0%) were determined by radioactivity measurements. The chloroanilines thus isolated were subsequently used for coupling with benzene and the

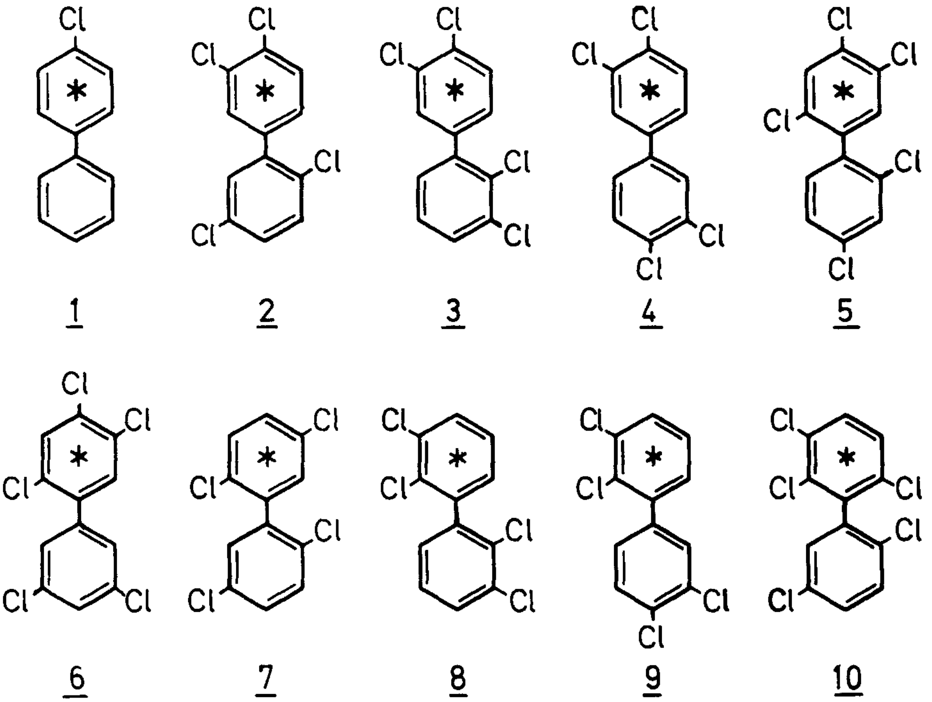

Figure 1.
The structures of the chlorinated biphenyls synthesized. The ^{14}C-labelled phenyl nucleus of each biphenyl is marked.

appropriate chlorobenzenes to form the biphenyls 1 and 2-6 respectively (Figure 1). The chlorobiphenyls 2-4 were found by gas chromatography (GC) to be contaminated with some later eluting compounds even after repeated TLC-purification. The impurities were found to be stable to conc. sulphuric acid and sodium hydroxide (5 M). In the case of 2,3',4',5-tetrachlorobiphenyl, obtained in a pilot preparation from 1,4-dichlorobenzene and 3,4-dichloroaniline, the latter synthesized from 4-chloroaniline, the impurity corresponding to that found in 2 was also present (GC). If instead, commercial 3,4-dichloroaniline was used for the preparation of unlabelled 2,3',4',5-tetrachlorobiphenyl no contamination products were observed. The impurity was shown by gas chromatography - mass spectrometry (GC-MS) to correspond to a bromotrichlorobiphenyl. By GC (flame ionization detector, FID) the purity of 2 was estimated to be about 95%. The content of the major impurity, a bromotrichlorobiphenyl, was estimated to be 4%, assuming equal responses for both compounds.

The 3,4-dichloroaniline used in the pilot preparation was also analysed (MS) and found to contain a bromochloroaniline, most probably 3-bromo-4-chloroaniline. The chlorobiphenyls 3-4 and 5-6 synthesized from 3,4-dichloro- and 2,4,5-trichloro[^{14}C]aniline respectively should likewise contain a minor amount of the corresponding bromopolychlorobiphenyl (for the purity of 3-6 cf Experimental).

The contamination of 3,4-dichloroaniline by a bromochloroaniline was originally overlooked for several reasons the main reason being that the expected byproduct, 2,4,5-trichloroaniline, differed only very slightly in retention time from the unexpected bromochloroaniline.

The origin of the brominated aniline was obviously due to a contamination by bromine or bromide in one or several of the chemicals used in the chlorination step. 4-Bromoacet[^{14}C]anilide, a possible byproduct in the preparation of 4-chloroacet[^{14}C]anilide, due to a contamination with N-bromosuccinimide in the N-chlorosuccinimide used, could be ruled out since the anilide prepared, after hydrolysis, was used for the synthesis of 2,4',5-trichloro[^{14}C]biphenyl (12), which was $>$98% pure (GC-EC) with no peaks at the position corresponding to the 4-bromo-2,5-dichlorobiphenyl. However, the high purity grade chlorine gas ($>$99.5%) was declared by the manufacturer (Matheson Gas Products) to contain traces of bromine ($<$ 40 ppm). The aluminium chloride used was analysed by MS, but no bromide was detected.

In order to study the role of the two gases, chlorine (99.965%) and hydrogen chloride (99.99%) of highest available purity were purchased and used in two further chlorinations.

In one case, the chlorine (99.5%) was used together with hydrogen chloride (99.99%). The resulting dichloroaniline fraction contained as much as 6% bromochloroaniline (GC-MS). From the corresponding reaction with chlorine (99.965%) but technical hydrogen chloride (99.0%) a product containing about 1% bromochloroaniline was obtained.

It is obvious that both gases contribute to the formation of the observed bromoproducts, although the "high purity" chlorine seems to be responsible for the larger amounts. The exact bromine contents of the gases are so far unknown, but it is noteworthy that traces of bromine or bromide in the gases can give as much as 5-10% bromosubstituted products under the conditions prevailing in the reaction described. Most probably, the bromine occurs in the reaction mixture as bromine chloride, known as a powerful brominating agent (27). The formation of a complex $Br^{+}AlCl_4^{-}$ might further contribute to the observed unexpectedly high reactivity of bromine versus chlorine.

The formation of bromocontaining compounds, after treatment with chlorine gas of e.g. waste water, is well known (28). Traces of bromochloro-substituted compounds might also be produced in industrial and laboratory chlorination-processes unless appropriate chemicals of high quality are used. However, to our knowledge no work has dealt with contamination of products such as PCB, hexachlorobenzene or pentachlorophenol by partially brominated analogues. The preparation of 2,5-dichloro[^{14}C]aniline was performed from 2-chloro[^{14}C]-aniline as above except that the high purity gases were used. The 2,5-dichloro-[^{14}C]aniline obtained was coupled with 1,4-dichlorobenzene to give 2,2',5,5'-tetrachloro[^{14}C]biphenyl (7). Two minor products 2,3-dichloro- and 2,3,6-trichloro[^{14}C]aniline from this chlorination step were also isolated and used for the synthesis of 8-10 (Figure 1).

EXPERIMENTAL

[U-^{14}C]Aniline hydrogen sulphate was purchased from The Radiochemical Centre Ltd (Amersham, UK). Chlorine, high purity grade (99.5%) and research grade (99.965%) and hydrogen chloride, technical grade (99.0%) and electronic grade (99.99%), were obtained from Matheson Gas Products (Oevel, Belgium) and dried by conc. sulfuric acid prior to use. Aluminium chloride, N-chlorosuccinimide and 1,4-dichlorobenzene for synthesis (Merck, Darmstadt, West Germany) and 1,2-dichlorobenzene technical grade (Kebo, Stockholm, Sweden) were all purified prior to use. 3-Methylbutyl nitrite, 97% (EGA, Steinsheim, West Germany) was used as such. All other chemicals were of analytical grade. The radioactivity measurements were performed in 5 ml of scintillation fluid (5 g PPO + 50 mg POPOP/l toluene) by an Intertechnique SL-30 liquid scintillation spectrometer. Thin layer chromatography (TLC) was performed on precoated silica gel plates (DC-Fertigplatten, Kiselgel 60 F-254, 0.25 mm thick, Merck, Darmstadt, West Germany). Silica gel (Kiselgel 60, 70-230 Mesh ASTM, Merck) was used for liquid chromatography on columns (i.d. 13 mm). Gas chromatography (GC) was carried out on a Varian 3700 fitted with FID and ECD. A column (2.2 m x 1/8") with 3% SE 30 on Chromosorb W (AW, DMCS, 100-120 mesh) was used with the FID and an OV-17, 5% on Supelcoport (100-120 mesh) with the ECD. Gas chromatography - mass spectrometry (GC-MS) was performed on a HP 5700A gas chromatograph and a HP 5930 A mass spectrometer with an on line computer. All labelled compounds prepared were compared to authentic unlabelled compounds by use of TLC and GC.

3,4-Dichloro[^{14}C]aniline. [^{14}C]Aniline hydrogen sulphate (11.0 mCi, 56 Ci/mol) was acetylated and chlorinated by N-chlorosuccinimide as described earlier (12). The anilide products were isolated within two consecutive separations. 4-Chloroacet[^{14}C]anilide (5.43 mCi) was obtained pure in fraction 3 after a silica gel (7.0 g) column eluted with 5 ml dichloromethane/ethyl acetate (4/1) into fraction 1, then with a new portion (12 ml) into fraction 2 and finally with 28 ml into fraction 3. 2-Chloro- and 2,4-dichloroacet[^{14}C]anilide, from fraction 2, were not separated by this procedure and therefore silica gel plates impregnated with tetrabutylammonium hydrogen phosphate (0.4 M) had to be used

(26). The compounds were eluted using diethyl ether. 2-Chloroacet$[^{14}C]$anilide (3.41 mCi) and 2,4-dichloroacet$[^{14}C]$anilide (1.17 mCi) were obtained.

4-Chloroacet$[^{14}C]$anilide (4.46 mCi, 25 Ci/mol) was hydrolyzed (12) and the free base isolated by extraction with dichloromethane. The organic phase was dried on a sodium sulphate column and the solvent was evaporated to dryness. The 4-chloro$[^{14}C]$aniline was dried in vacuo over potassium hydroxide for 60 min.

Aluminium chloride (211 mg), freshly sublimated, was transferred to a dry three-necked flask (25 ml) and dissolved in dry dichloromethane (8.0 ml). The reaction flask was put in an ultrasonic bath for one minute and the mixture was then stirred for 30 min. A reflux condenser was applied to the flask and dry hydrogen chloride (99.0%) was added to the mixture. 4-Chloro$[^{14}C]$aniline was dissolved in dry dichloromethane (1.0 ml) and transferred to the reaction flask as well as the dichloromethane (2 x 0.5 ml) used to wash the flask, initially containing the aniline. The reaction flask was placed in an oil bath after 5 min and the temperature was raised to 45°C (bath temperature). After hydrogen chloride has been bubbled for 30 min dry chlorine (99.5%) was led in for 5 h. The reaction was stopped after 5 h and the reaction flask transferred to an evaporator for removal of solvent by use of a nitrogen stream. Ice was added under vigorous stirring followed by sodium bisulphite (10 mg). The water phase was extracted with dichloromethane (2 x 3 ml). Sodium hydroxide (5 M, 0.5 ml) was added and the extraction was continued (3 x 2 ml). The combined extracts were evaporated to a volume of 1 ml and the residue was transferred to a silica gel (5.0 g) column. The products were eluted using dichloromethane (20 ml). The solution was evaporated by a stream of nitrogen to a volume of 2.0 ml and transferred in 0.5 ml aliquots to four TLC-plates (20 x 20 cm). The chromatograms were developed in chloroform. The aniline bands with R_f-values 0.19, 0.28 and 0.46 corresponding to 4-chloroaniline, 3,4-dichloroaniline and 2,4,5-trichloroaniline respectively were scraped off and the compounds eluted with dichloromethane. The radioactivity from each eluate were calculated and gave: 4-chloro$[^{14}C]$aniline (366 μCi), 3,4-dichloro$[^{14}C]$aniline (1760 μCi) and 2,4,5-trichloro$[^{14}C]$aniline (648μCi).

2,5-Dichloro$[^{14}C]$aniline. 2-Chloroacet$[^{14}C]$anilide (1.70 mCi, 11.1 Ci/mol) was hydrolyzed (12) and extracted as above. The 2-chloro$[^{14}C]$aniline was dried at atmospheric pressure over phosphorus pentoxide over night. The chlorination step by use of aluminium chloride (220 mg), hydrogen chloride (99.99%) and chlorine (99.965%) was performed as described above. The chloroanilines were separated by means of TLC with chloroform/hexane (2/1) as eluent. The TLC-bands corresponding to 2,5-dichloro$[^{14}C]$aniline (746 μCi), 2,3-dichloro$[^{14}C]$aniline (160 μCi) and 2,3,6-trichloro$[^{14}C]$aniline (112 μCi) were isolated. By GC (FID), the labelled 2,5-dichloroaniline was found to contain 2,4,5-trichloro$[^{14}C]$aniline (14%, 104 µCi).

Polychloro$[^{14}C]$biphenyls. Coupling reactions between the ^{14}C-labelled anilines and the appropriate chlorobenzene were carried out according to Shu-Huang and Cadogan (24, 25). The labelled mono-, di- or trichloroanilines were dissolved in 1,2-, 1,3- or 1,4-dichlorobenzene (3-4 g) at 70°C. The reaction was run at 70°C after the addition of acetic acid and 3-methylbutyl nitrite. A new portion of the nitrite was added after 2 h, the temperature was raised to 100°C and kept there for another 2 h. The excess of dichlorobenzene was evaporated by destillation in a vacuum. The residue was dissolved in hexane and transferred to a silica gel column (5.0 g) and eluted using hexane (20 ml) in order to get rid of polymeric products. The solvent was evaporated and the residue transferred to a silica gel plate impregnated with tetrabutylammonium hydrogen phosphate (0.8 M) (26) and developed in hexane. The biphenyl band(s) were sucked off and the procedure was repeated on an ordinary silica gel plate. The following biphenyls were obtained:

4-Chloro$[^{14}C]$biphenyl (1), (52 µCi) was obtained from 4-chloro$[^{14}C]$aniline (366 µCi, 20 Ci/mol), benzene (3 g), acetic acid (15 µl) and 3-methylbutyl nitrite (50 µl).

2,3',4',5-Tetrachloro$[^{14}C]$biphenyl (2), (168 µCi) was obtained from 3,4-dichloro$[^{14}C]$aniline (400 µCi, 20 Ci/mol), 1,4-dichlorobenzene (3 g), acetic acid (18 µl) and 3-methylbutyl nitrite (50 µl). The purity of 2 was ≥ 95% (GC). The major impurity (≃ 4%) most probably corresponded to 3'-bromo-2,4',5-trichloro$[^{14}C]$biphenyl.

2,3,3',4'-Tetrachloro$[^{14}C]$biphenyl (3), (162 µCi) and 3,3',4,4'-tetrachloro-$[^{14}C]$biphenyl (4) (110 µCi) were obtained from 3,4-dichloro$[^{14}C]$aniline (700 µCi, 20 Ci/mol) 1,2-dichlorobenzene (3 g), acetic acid (30 µl) and 3-methylbutyl nitrite (50 µl). The purity of 3 was ≥95%, contaminated with 4 (≤ 3%) and most probably 3'-bromo-2,3,4'-trichloro$[^{14}C]$biphenyl (≃ 2%). The purity of 4 was ≥ 94%. The major contaminants were 3 (4%) and most probably 3'-bromo-3,4,4'-trichloro$[^{14}C]$biphenyl (≃ 2%).

2,2',4,4',5'-Pentachloro$[^{14}C]$biphenyl (5), (80 µCi) and 2,3',4,5,5'-pentachloro$[^{14}C]$biphenyl (6), (24 µCi) were obtained from 2,4,5-trichloro$[^{14}C]$aniline (648 µCi, 25 Ci/mol), 1,3-dichlorobenzene, acetic acid (25 µl) and 3-methylbutyl nitrite (50 µl). The purity of 5 was ≥ 92% and of 6 ≥ 70%.

2,2',5,5'-Tetrachloro$[^{14}C]$biphenyl (7), (174 µCi) was obtained from 2,5-dichloro$[^{14}C]$aniline (746 µCi, 11 Ci/mol) containing 2,4,5-trichloro$[^{14}C]$aniline (≃ 14%), and reacted with 1,4-dichlorobenzene (4 g), acetic acid (65 µl) and 3-methylbutyl nitrite (100 µl). Two by-products, 2,2',4 , 5,5'-pentachloro$[^{14}C]$-

biphenyl and most probably 2,2',3,4,5'-pentachloro[^{14}C] biphenyl were isolated as a mixture from TLC. The purity of 7 was ≥ 95% (GC).

2,2',3,3'-Tetrachloro[^{14}C] biphenyl (8), (6 µCi) and 2,3,3',4'-tetrachloro [^{14}C] biphenyl (9), (9 µCi) were obtained from 2,3-dichloro[^{14}C] aniline (160 µCi, 11 Ci/mol), 1,2-dichlorobenzene (3 g), acetic acid (12 µl) and 3-methylbutyl nitrite (50 µl). The purity of 8 was ≥90% and of 9 ≥ 92%. The major impurity of 8 and 9 was the corresponding biphenyl, 9 and 8 respectively.

2,2',3,5',6-Pentachloro[^{14}C] biphenyl (10), (12 µCi) was obtained from 2,3,6-trichloro[^{14}C] aniline (112 µCi, 11 Ci/mol), 1,4-dichlorobenzene (3 g), acetic acid (10 µl) and 3-methylbutyl nitrite (50 µl). The purity of 10 was ≥ 96% (GC).

Bromopolychlorobiphenyls. The meta-directing chlorination method was used with 4-chloroaniline as described above. In experiment A, chlorine (99.5%) and hydrogen chloride (99.0%) was used. A minor product eluting after 3,4-dichloroaniline was found by MS to contain a molecular ion at m/z = 205 and an isotopic cluster typical for a bromochloro-substituted compound. The above dichloroaniline was reacted with 1,4-dichlorobenzene according to Shu Huang - Cadogan (24, 25). The 2,3',4',5-tetrachlorobiphenyl fraction obtained after TLC, was analysed and found to be contaminated. The most abundant fragments in the impurity were m/z = 334, 336, 220, 185 and 150 corresponding to $M^{+\cdot}$, $(M + 2)^{+\cdot}$, $(M\text{-}BrCl)^{+}$, $(M\text{-}BrCl_2)^{+\cdot}$ and $(M\text{-}BrCl_3)^{+}$ respectively. In addition the cluster of the molecular ion was in accordance to a bromotrichloro-substituted compound. From the total ion chromatogram of the fraction mainly containing 2,3',4',5-tetrachlorobiphenyl the relative amount of bromotrichlorobiphenyl was calculated to be 4.7%.

In experiment B, chlorine (99.5%) and hydrogen chloride (99.99%) were used. The dichloroaniline obtained was coupled with 1,4-dichlorobenzene as described above.

In experiment C, chlorine (99.965%) and hydrogen chloride (99.0%) were used in the preparation of the dichloroaniline, which was subsequently coupled with 1,4-dichlorobenzene.

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