G-value of about 26 can be calculated from the assumed linear part of the degradation curve for pyridine as solvent. This is not significantly different from the average slope of the degradation curve for dissolution in water within the same dose interval, *i.e.* $0.3 \times 10^{21} - 10^{21}$ eV g^{-1}.

It therefore seems most likely that the dissolution in water is not a reason for the high radiation induced degradation of these crystalline carbohydrates but that the major part or all of the degradation is present already in the solid state. Ahmed *et al.*[2] have inferred a similar conclusion indirectly by means of spectroscopic studies of irradiated lactose samples.

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Polychlorinated Biphenyls

IV.* Synthesis of 2,2′,3,3′,4,4′,5,6′-Octachlorobiphenyl-^{14}C from 3-Nitro-2,2′,3′,4,4′,5,6′-heptachlorobiphenyl-^{14}C and Tetrachloromethane**

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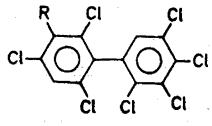
As a part of an investigation concerning the distribution and metabolism in mice and quails of the industrial chemical and environmental pollutant PCB (polychlorinated biphenyls) [1-3] we recently reported the syntheses of some ^{14}C-labelled tetra- and hexachlorobiphenyls.[4,5] The simple syntheses of some unlabelled tetra- and pentachlorobiphenyls were also reported.[6]

The present paper describes the synthesis of 2,2′,3,3′,4,4′,5,6′-octachlorobiphenyl-^{14}C (II) labelled in the 2,3,4,6-substituted ring. Acetylation of aniline-^{14}C hydrogen sulphate followed by chlorination [5] gave 2,4,6-trichloroacetanilide-^{14}C [5] which was nitrated to give 3-nitro-2,4,6-trichloroacetanilide-^{14}C.[7] Hydrolysis of the anilide gave 3-nitro-2,4,6-trichloroaniline-^{14}C, which was coupled with 1,2,3,4-tetrachlorobenzene by the method of Cadogan [8] (*cf.* Refs. 5, 6) to yield 3-nitro-2,2′,3′,4,4′,5′,6-heptachlorobiphenyl-^{14}C (I). The nitroheptachlorobiphenyl I on treatment with tetrachloromethane at 280 – 290° for 70 min gave 2,2′,3,3′,4,4′,5,6′-octachlorobiphenyl-^{14}C (II) (isotope yield from I, 72 %).



I: R = NO_2
II: R = Cl

The labelled compound was chromatographically identical (TLC, GLC) with 2,2′,3,3′,4,4′,5,6′-octachlorobiphenyl as

* Part III, Ref. 5.

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prepared (a) from 2,3,4,6-tetrachloroaniline by a coupling with 1,2,3,4-tetrachlorobenzene according to Cadogan,[8] and (b) from 3-nitro-2,4,6-trichloroaniline by the above method. This compound is reported as a minor component of Aroclor 1260.[9]

The substitution of the nitro group of I for chlorine was achieved through the use of a reaction first described by Ponomarenko.[10–13] The reaction involves treatment of an aromatic nitro compound with a suitable aliphatic chlorine compound, *e.g.* tetrachloromethane, at temperatures around 250 – 300°. Hereby, substitution of nitro groups for chlorine occurs rapidly and in high yields, most probably through a radical displacement reaction.

This type of reaction constitutes a convenient alternative being used as a route to polychlorinated biphenyls of defined structure. The substitution of nitro groups for chlorine is usually carried out by reduction and a subsequent Sandmeyer reaction on the amine. However, yields are moderate, side reactions are often disturbing,[14] and moreover the Sandmeyer reaction is not easily handled on a micro scale.

The Ponomarenko reaction requires well defined conditions (time, temp.) to certify satisfactory yields. In the present case polymerisation reactions sometimes occurred. However, the use of a large excess of tetrachloromethane – in contrast to the molar ratio 1:1 as originally recommended – reduced the effects of these side reactions. Further chlorination of the expected product was also observed when too long reaction times were used.

Experimental. Conditions and equipment were those earlier described.[4–6]

Gas chromatography. The products were characterised by GLC using a Hewlett-Packard 7620A instrument fitted with an EC detector. Glass columns (0.20 × 160 cm) containing 4 % (w/w) SF 96 on Chromosorb W A/W DMCS (100 – 120 mesh) at 200° were used. The gas flow (nitrogen) was about 25 ml/min.

Thin layer chromatography. The reactions were followed by TLC on 0.1 mm layers of silica gel (Kieselgel HF_{254}, Merck) using chloroform, hexane-ethyl acetate (9:1), or hexane as solvent. Preparative TLC was performed on *ca.* 1 mm layers of the same adsorbent.

3-Nitro-2,4,6-trichloroacetanilide-^{14}C. 2,4,6-Trichloroacetanilide-^{14}C synthesised as described in Ref. 5 (2.05 mCi, 25 Ci/mol) was dissolved in sulphuric acid (95 – 97 %, 0.5 ml) at 0° and potassium nitrate (11.1 mg, 0.10 mmol) was added. The mixture was stirred for 1 h at 0°, diluted with ice water (5 ml) and extracted with chloroform (5 × 2 ml). The extracts were filtered through a column (0.8 × 2.5 cm) of magnesium sulphate. After evaporation of solvent the product was used in the next step without purification.

3-Nitro-2,4,6-trichloroaniline-^{14}C. To the above 3-nitro-2,4,6-trichloroacetanilide-^{14}C was added hydrochloric acid (12 M, 1 ml) and acetic acid (0.5 ml) and the mixture was stirred for 3 h at 100°. The acids were evaporated in a vacuum desiccator over sodium hydroxide and silica gel to give crude 3-nitro-2,4,6-trichloroaniline-^{14}C which was used in the following reaction.

3-Nitro-2,2′,3′,4,4′,5′,6-heptachlorobiphenyl-^{14}C. 1,2,3,4-Tetrachlorobenzene (Fluka, m.p. 47° (EtOH), 1.5 g) was added to the 3-nitro-2,4,6-trichloroaniline-^{14}C and the mixture was heated to 70°. Isoamyl nitrite (Riedel-de Haën, pure DAB. 6., 0.1 ml) was added with stirring which was continued for 1 h at 70°. The temperature was then raised to 100° and another portion of isoamyl nitrite (0.05 ml) was added. After 1.5 h at 100° excess tetrachlorobenzene was evaporated *in vacuo* and collected in a cold trap (*cf.* Ref. 5). Activity measurements indicated the presence of a low boiling by-product (0.93 mCi) in the trap, probably 2,4,6-trichloronitrobenzene-^{14}C (TLC). The residue, containing some tetrachlorobenzene, was dissolved in a small amount of chloroform-hexane (1:1) and added to a column (0.8 × 1 cm) of neutral alumina (Merck, activity grade I) which was irrigated with hexane-ethyl acetate (9:1). The eluate was collected on preparative TLC plates (20 × 20 cm) which were eluted twice with hexane-ethyl acetate (9:1). The desired zones were collected and eluted with chloroform. Evaporation of solvent gave 3-nitro-2,2′,3′,4,4′,5′,6-heptachlorobiphenyl-^{14}C, 0.32 mCi, 16 %, as crystals free from 2,4,6-trichloronitrobenzene-^{14}C (TLC).

2,2′,3,3′,4,4′,5,6′-Octachlorobiphenyl-^{14}C. The nitrobiphenyl was transferred to an ampoule (Pyrex glass, volume 2.3 ml) with the aid of carbon tetrachloride (Riedel-de Haën, A.R.). The amount of carbon tetrachloride was adjusted to *ca.* 0.5 ml and the ampoule, placed in a steel autoclave, was heated at 280 – 290° for 70 min in an electric oven. After cooling the solvent was evaporated and the residue dissolved in hexane and added to a column of neutral alumina (0.5 × 1 cm). Elution with 10 ml hexane and evaporation of solvent gave 2,2′,3,3′,4,4′,5,6′-octachlorobiphenyl-^{14}C, 0.23 mCi, as a slowly crystallising oil, overall yield from acetanilide-^{14}C 7.5 %.

Elution of the column with hexane-ethyl acetate (4:1, 10 ml) gave some starting material, 0.02 mCi.

2,3,4,6-Tetrachloroaniline. *m*-Chloroaniline, dissolved in carbon tetrachloride, was chlorinated at *ca.* −30° as described for the synthesis of pentachloroaniline.[15] Yield *ca.* 35 %, m.p. 88−90° (aq. EtOH) (m.p. lit.[16] 88°).

3-Nitro-2,2′,3′,4,4′,5′,6-heptachlorobiphenyl. 3-Nitro-2,4,6-trichloroaniline [7] (*cf.* above) (0.72 g, 3 mmol) and 1,2,3,4-tetrachlorobenzene (5 g) were heated to 70° and isoamyl nitrite (0.6 ml) was added with stirring. After 1 h the temperature was raised to *ca.* 100° and another portion of isoamyl nitrite (0.25 ml) was added. Stirring was continued for 1.5 h whereafter excess tetrachlorobenzene was removed *in vacuo*. The residue was dissolved in chloroform-hexane (1:1, 4 ml) and filtered through a column (2 × 15 cm) of neutral alumina (*cf.* above) which was eluted with hexane-ethyl acetate (9:1). Crystallisation from ethanol gave 3-nitro-2,2′,3′,4,4′,5′,6-heptachlorobiphenyl (0.2 g), m.p. 160−161° (Found: C 32.9; H 0.6; N 3.3; M^+ 437 (7 Cl). $C_{12}H_2Cl_7NO_2$ (440.3) requires C 32.7; H 0.5; N 3.2). λ_{max} (EtOH) 285 nm (ε=1,120), 294 nm (ε=1,100).

GLC as described above showed a retention time of 16.1 min for this compound.

2,2′,3,3′,4,4′,5,6′-Octachlorobiphenyl. (a) The compound was synthesised from 2,3,4,6-tetrachloroaniline and 1,2,3,4-tetrachlorobenzene by the same procedure as the above nitrobiphenyl. Purification on an alumina column which was eluted with hexane, crystallisation from ethanol and sublimation *in vacuo* gave 2,2′,3,3′,4,4′,5,6′-octachlorobiphenyl (0.12 g), m.p. 126−128° (Found: C 33.6; H 0.6; M^+ 426 (8 Cl). $C_{12}H_2Cl_8$ (429.8) requires C 33.5; H 0.5). λ_{max} (EtOH) 285 nm (ε=960), 294 nm (ε=930).

GLC as above showed a retention time of 12.8 min for the octachlorobiphenyl.

(b) The octachlorobiphenyl was also synthesised by the same route as the labelled compound. 3-Nitro-2,2′,3′,4,4′,5′,6-heptachlorobiphenyl (30 mg) and carbon tetrachloride (0.5 ml) were heated in an ampoule (Pyrex glass, volume 2.2 ml) at 280−290° for 80 min. Purification of product was performed as described for the labelled compound and gave 2,2′,3,3′,4,4′,5,6′-octachlorobiphenyl (28 mg), indistinguishable from the biphenyl synthesised by the method (a) above (GLC, TLC, m.p., mixed m.p.).

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