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SHORT PAPER

2-$HC_{12}Cl_9$: a simple synthesis of PCB-206

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A one-pot synthesis is described for polychlorobiphenyl number 206. Addition of C_6Cl_5Li to tetrachlorobenzyne gives 2-$LiC_{12}Cl_9$, which undergoes Li/H exchange with C_6Cl_5H to form 2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenyl

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INTRODUCTION

The chlorinated biphenyls were known before the start of the 20th century and their useful industrial properties, particularly those of good electrical insulation and low flammability, were recognized early.[1,2] Between 1929, when commercial production began, and 1977 after their being banned, about 1.4×10^9 lb (6.36×10^8 kg) of PCBs were produced in the USA alone. In 1966 a report was mentioned in *New Scientist*[3] which drew attention to the widespread occurrence of chlorinated biphenyls in the Swedish environment. Since then their worldwide distribution has been established and, due to their lipid solubility and resistance to degradation, the PCBs have been shown to accumulate in food chains.[1,2]

Although it was well known that polychlorobiphenyls were toxic towards humans, the fact that 209 different PCBs are possible has meant that relatively little is known about the toxicity of each individual chlorobiphenyl. There is thus a twofold requirement for good syntheses of single PCB isomers: as standard reference compounds required both for analysis of natural contaminants which occur as complex mixtures, and also for toxicity studies. Many of the syntheses described in the literature use some kind of coupling procedure for joining the two chlorinated phenyl rings together. Unless crossed-coupling reactions are used in which a mixture of three products is formed, the biphenyls produced this way contain an even number of chlorine atoms. Cadogan coupling of 2,3,4,5-tetrachloroaniline and pentachlorobenzene gives 2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenyl as the major product but the crude reaction mixture has to be subjected to column chromatography on Florisil, followed by thin-layer chromatography (TLC) on silica gel.[4] The use of TLC severely restricts the quantity of material which can be processed. The preparation described here gives only one nonachlorobiphenyl isomer, which is contaminated with pentachlorobenzene; a single recrystallization from a solvent such as toluene is sufficient to give a product somewhat superior in purity to commercially available analytical samples.

The PCB mixture ‘Aroclor 1268’, originally manufactured by Monsanto, contains about 7.7% of 2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenyl;[4] other Aroclors also contain traces of this compound.[4] Thus there is a need to study the toxicity of this PCB, and to have it available as an analytical standard. It was estimated[5] in 1982 that in the USA there were still about 750×10^6 lb (3.41×10^8 kg) of PCBs in service, so the analytical requirement of standard polychlorobiphenyls is going to be with us for many years to come.

Although pentachlorophenyllithium (C_6H_5Li) has been used as a precursor of tetrachlorobenzyne via loss of lithium chloride,[6] no studies seem to have been carried out on the addition of C_6Cl_5Li to tetrachlorobenzyne. Decachlorobiphenyl resulted in low yield when C_6Cl_5Li was coupled using titanium tetrachloride,[7] and coupling of the Grignard reagent C_6Cl_5MgCl with copper(I) iodide has been used to make chlorobiphenyls;[8] however, in Ref. 8 it was stated that no biphenyls were obtained in the absence of CuI even though the reaction shown by Eqn [1] is feasible (X = Cl, Y = halogen).

$$C_6X_5MgY \rightarrow [C_6X_4] \xrightarrow{C_6X_5MgY} 2\text{-}C_6X_5C_6X_4MgY \qquad [1]$$

This route to biphenyl production has been demonstrated[9] for X = F.

We have previously[10] shown that the reaction sequence in Eqn [2],

$$\begin{aligned} C_6F_5Li &\xrightarrow{-LiF} [C_6F_4] \xrightarrow{+C_6F_5Li} 2\text{-}LiC_{12}F_9 \\ &\xrightarrow{C_6F_5H} HC_{12}F_9 + C_6F_5Li \end{aligned} \qquad [2]$$

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gives 2,2′,3,3′,4,4′,5,5′,6-nonafluorobiphenyl in high yield within a few hours at room temperature. However, the observed stability sequence[11] $C_6Cl_5Li > C_6F_5Li > C_6Br_5Li$ means that a longer reaction time and/or higher temperatures are required for the chloro system.

PREPARATION OF 2,2′,3,3′,4,4′,5,5′,6-NONACHLOROBIPHENYL

Pentachlorobenzene (5 g; 0.02 mol) was placed in a three-necked flask provided with a stopper, a dry nitrogen atmosphere and a stirrer; dry diethyl ether was added and the flask cooled to −78 °C before 8.7 cm^3 of 2.31 mol dm^{-3} butyl-lithium (0.02 mol) was dripped in slowly against a positive nitrogen atmosphere using a syringe. The mixture was stirred for 30 min at −78 °C before the addition of a further 5 g of pentachlorobenzene. Stirring was continued as the flask was allowed to warm to room temperature and left for 1–2 days.

After about 2 cm^3 of water had been added, the ether was removed under reduced pressure and most of the excess pentachlorobenzene remaining in the flask was removed by sublimation under vacuum. Recrystallization of the residue from toluene gave the colourless 2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenyl in yields of up to 2 g [Found: C, 31.4; H, 0.2; Cl, 68.9%; calculated for $C_{12}HCl_9$: C, 31.1: H, 0.2; Cl, 68.7%]. The mass spectrum showed an intense isotopomeric cluster of peaks, centred at 464, which represents the parent ion $C_{12}HCl_9^+$; an accurate mass determination on the peak at mass 464 gave $m/z =$ 463.722; calculated for $^{12}C_{12}{}^{1}H^{35}Cl_7{}^{37}Cl_2$, 463.722. There are three isomers of nonachlorobiphenyl; the one prepared in this experiment was identified by comparison of its infrared spectrum with that of a certified commercial analytical sample. This certified commercial sample was shown by capillary GC on a 25 m column to be only about 91.5% pure and contained a second component in 8.2% abundance. Correspondingly, its infrared spectrum possessed three extra peaks compared

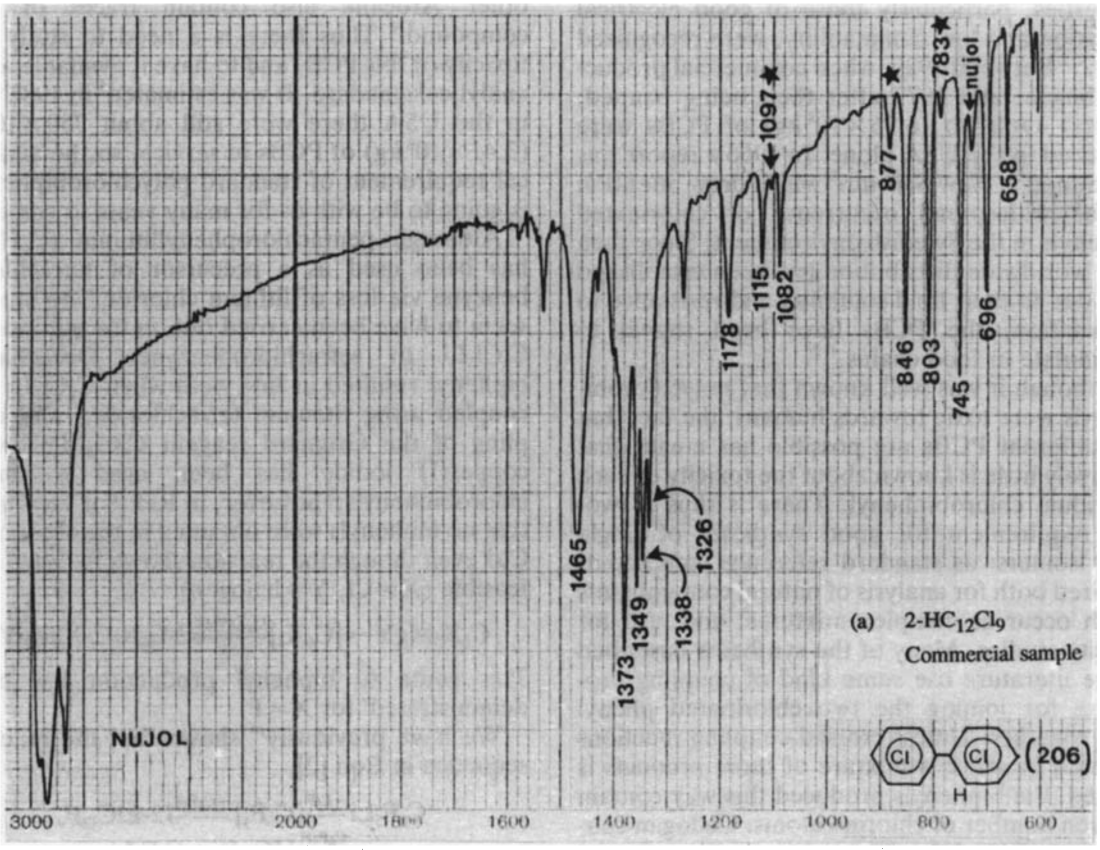


Figure 1(a)

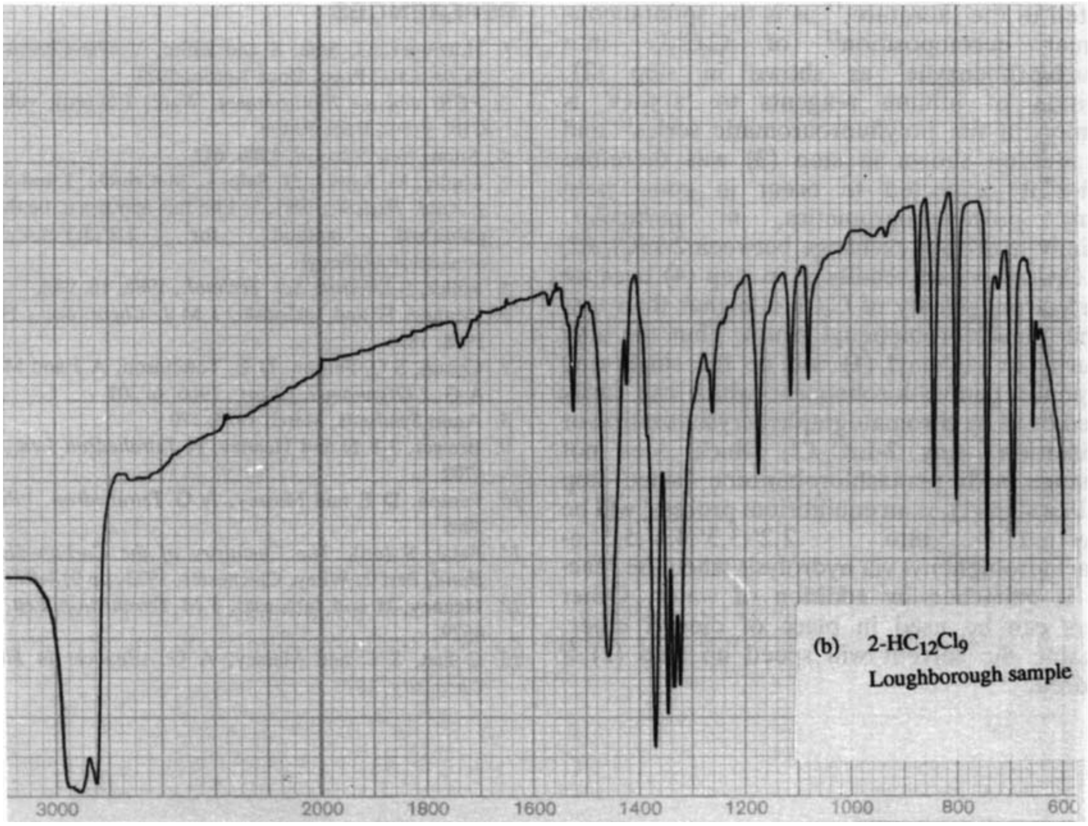
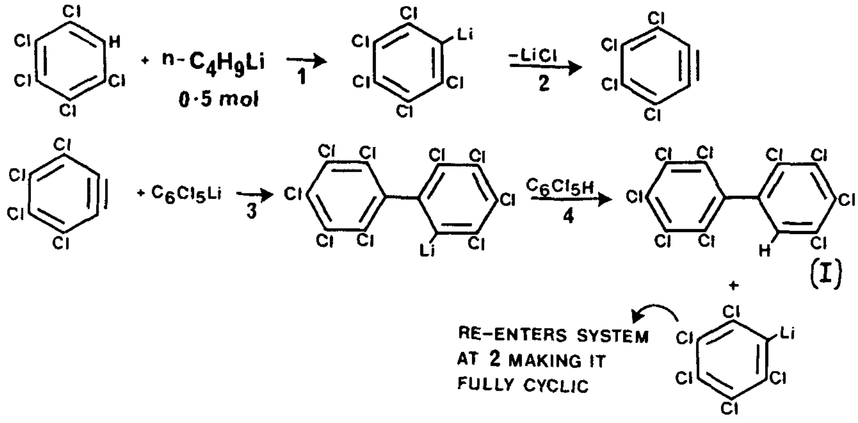


Figure 1(b)

Figure 1 Infrared spectra of two samples of nonachlorobiphenyl: (a) commercial sample; (b) sample prepared in this work.



Scheme 1

with our sample: these are marked with an asterisk on Fig. 1(a) and occur at 1097 cm^{-1}, as a shoulder on the authentic peak at 877 cm^{-1} at 783 cm^{-1}. After one recrystallization our sample was shown by GC to be 96 ± 0.5% pure with no other component present above 1.7% abundance.

The synthesis of PCB-206 is thought to proceed via the sequence of reactions shown in Scheme 1.

The metallation of inexpensive pentachlorobenzene via the method in step (1) is well documented in the literature,[11] as is the spontaneous thermal decomposition[12] of C_6Cl_5Li into 'tetrachlorobenzyne' as shown in step (2). Addition of lithium reagents to 'arynes' is common in the polyfluoroaromatic series[13] and the addition shown in step (3) was therefore confidently expected to occur in good yield among polychloroaromatics, in particular. Lithium–hydrogen exchange between $2\text{-}LiCl_{12}Cl_9$ and C_6Cl_5H occurs readily as in step (4) because the electronegativity of C_6Cl_5 is higher than that of the nonachlorobiphenyl group. Thus the only impurity in biphenyl (**I**) will be the single-ring compound pentachlorobenzene which can easily be removed by chromatography, crystallization or sublimation. Any $2\text{-}LiC_{12}Cl_9$ which does not exchange with pentachlorobenzene [since step (4), like step (1), is an equilibrium process] will be converted into 2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenyl via hydrolysis when the reaction is quenched by addition of water. Other ethers can be used in place of diethyl ether; refluxing the solvent will speed up step (2) if required.

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