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Regioselectivity of dechlorination: reductive dechlorination of polychlorobiphenyls by polymethylhydrosiloxane-alkali metal *,**

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Abstract

Polychlorobiphenyls are completely dechlorinated to biphenyl by a polymethylhydrosiloxane-alkali metal system at ambient conditions. Dechlorination proceeded via the formation of a polychlorobiphenyl radical anion, which cleaved with a regioselectivity similar to that normally observed in nucleophilic substitution of polyhaloarenes.

Introduction

A frequently encountered free radical reaction in organic synthesis is the reduction of organic halides, RX (X; Br or I), by trialkyltin hydride as shown in eqs. 1 and 2 [1]. However, trialkyltin hydrides do not efficiently reduce organic chlorides, particularly aromatic chlorides. Because organotin compounds are toxic, recent studies focussed on replacing tin hydrides by more environmentally acceptable hydrogen transfer agents [2].

$$R'^{\cdot} + R_3SnH \rightarrow R'H + R_3Sn^{\cdot} \tag{1}$$

$$R'X + R_3Sn^{\cdot} \rightarrow R_3SnX + R'^{\cdot} \tag{2}$$

Our research is aimed at determining the scope and utility of polymethylhydrosiloxanes as reducing agents for the dechlorination and destruction of polychlorobiphenyls (PCBs). Polymethylhydrosiloxane (PMHS) is available commercially, is relatively cheap and is less toxic than organotin hydrides. The unique thermal and chemical stability that makes PCBs industrially useful has also made them a threat to the environment. They are toxic, suspected carcinogens, and are resistant to

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* Dedicated to Professor Alwyn G. Davies in recognition of his outstanding work in organometallic/organosilicon chemistry over the last four decades.

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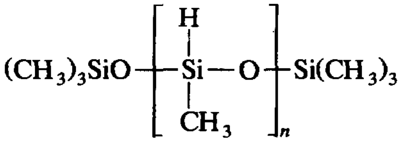
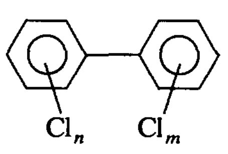
solar and microbial degradation. Chemical [3,4], photochemical [5] and joint chemical-microbial processes for the dechlorination of PCBs have been reported [6]. The present study describes the use of PMHS (I) in conjunction with an alkali metal to dechlorinate PCBs at ambient conditions in tetrahydroguran [3]. The mechanism and regioselectivity of the dechlorination process are investigated.



$$(CH_3)_3SiO\left[\overset{\displaystyle H}{\underset{\displaystyle CH_3}{-Si-}}O\right]_n Si(CH_3)_3$$

I



II $(n+m) = 1-10$

Experimental

Materials and reagents

Biphenyl was obtained from Alfa Products, Danvers, MA. 3-Chlorobiphenyl was obtained from Pfaltz & Bauer, Waterbury, CT. All other polychlorobiphenyl isomers were obtained from Ultra Scientific, Kingstown, RI. Aroclor 1254 was from Chem Service, West Chester, PA. Polymethylhydrosiloxane (MW 2270) was purchased from Petrarch, USA. All solvents were of pesticide grade and were obtained from Fisher Scientific, Montreal.

Dechlorination of 3-chlorobiphenyl by sodium and PMHS (I). A mixture of sodium sand (0.12 g, 5.2 mmol) and 3-chlorobiphenyl (0.98 g, 5.2 mmol) in tetrahydrofuran (25 ml) was stirred for 10 min under nitrogen followed by dropwise addition of **I** (5.0 g) at 0°C. The mixture was stirred for 2 h at room temperature giving a homogeneous yellow solution. Excess methanol was added to residual sodium and the mixture was evaporated to dryness. The white powder obtained was spiked with 4-bromobiphenyl as recovery standard and partitioned between water (50 ml) and hexane (50 ml). The water fraction was washed with hexane (50 ml) and the hexane fraction was washed with water (50 ml). The combined hexane extracts were passed through a silica gel column, concentrated and spiked with 1,2,3-trichlorobenzene as internal standard for GC/MS analysis. The combined water extracts were analysed for chloride ion by either HPLC ion chromatography or by silver nitrate titration to a potentiometric end point.

In the absence of **I** the attempted dechlorination of 3-chlorobiphenyl was carried out under identical conditions except that the reaction time was 12 h.

Dechlorination of Aroclor 1254 with Na and PMHS (I). A mixture of Aroclor 1254 (0.20 g, 54% w/w Cl), sodium sand (1.10 g), and **I** (2.50 g) in THF (25 ml) was stirred for 2 h at room temperature under nitrogen. The reaction products were separated and analysed as described above.

Dechlorination of the Aroclor in the absence of **I** was carried out under identical conditions except that the reaction time was 12 h.

Regioselectivity assessment

Sample aliquots (100 μl) were withdrawn from the reaction mixture at different time intervals (0, 5, 10, 20, 40, 60 and 120 min), diluted with water and adjusted to pH 4 by treatment with nitric acid (0.1 *N*). The acidified samples were spiked with 4-bromobiphenyl as the recovery standard and extracted with hexane (2 × 2 ml). The hexane extract was analysed with GC/MS using 1,2,3-trichlorobenzene as an internal standard. Products were analyzed by GC on a Perkin–Elmer Sigma 2000 capillary gas chromatograph with a 30 m × 0.25 mm DB-5 capillary column (J & W Scientific Inc.) equipped with an electron capture detector, a Perkin–Elmer LC1-100 integrator, and a Perkin–Elmer AS-2000B Autosampler (1 μl, splitless) injection. Argon/methane (5%) was used as the make-up gas and helium as the carrier gas. In cases where high resolution was required to separate various PCB products, a Hewlett-Packard 50 m × 0.2 mm Ultra-1 capillary column was employed. Products were identified by GC/MS (Hewlett Packard 5970 MSD connected to a HP 5890 GC) and by comparison with authentic compounds.

Results and discussion

Reaction of polychlorobiphenyl with sodium in THF

Reaction of 3-chlorobiphenyl with sodium in THF for 12 h gave biphenyl, *m/z* 154 (65%), tetraphenyls, *m/z* 306 (5%), and unidentified polymeric material. All chlorine was accounted for as chloride ion. The reaction of Aroclor 1254 * with sodium under otherwise identical conditions gave < 80% dechlorination with the formation of biphenyl (*ca.* 50%), unidentified polymeric material, and several PCB-solvent-derived products. For example, several mass ions were observed with a base peak (*m/z* 71) characteristic of THF.

The complexity of the above products indicates that the dechlorination process involves free radicals. In contact with sodium, the chlrobiphenyl gives the aryl radical anion through an electron transfer process as shown in eq. 3. In view of the high electronegativity of chlorine, the aryl radical anion will cleave to give the aryl radical and the chloride anion. Subsequent H-abstraction by the aryl radical will give biphenyl as shown in eq. 4 (for simplicity ArCl stands for polychlorobiphenyl). However, in the absence of an efficient hydrogen donor the aryl radical, $\mathrm{Ar}^{\cdot}$, may either dimerize or attack the parent compound to give tetraphenyl, or react with the solvent.

$$\mathrm{ArCl + Na \rightarrow Ar^{\cdot}Cl^{-} + Na^{+}} \tag{3}$$

$$\mathrm{Ar^{\cdot}Cl^{-} \rightarrow Cl^{-} + Ar^{\cdot} \xrightarrow{RH} ArH + R^{\cdot}} \tag{4}$$

$$\mathrm{Ar^{\cdot}\ or\ R^{\cdot} + R^{\cdot}\ or\ Ar^{\cdot} \rightarrow ArR + Ar_2 + R_2} \tag{5}$$

Reaction of polychlorobiphenyl with sodium and PMHS in THF

When the above reactions were repeated in the presence of PMHS (I), under otherwise identical conditions, dramatic differences were observed. For 3-chlorobiphenyl, the reaction was exothermic and complete in less than 2 h. Biphenyl was formed quantitatively (*ca.* 99%) and all chlorine was recovered as $\mathrm{Cl^{-}}$. No

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* Commercially available PCB with 54 wt% Cl, composed of a mixture of 77 chlorobiphenyl congeners, see Fig. 1A.

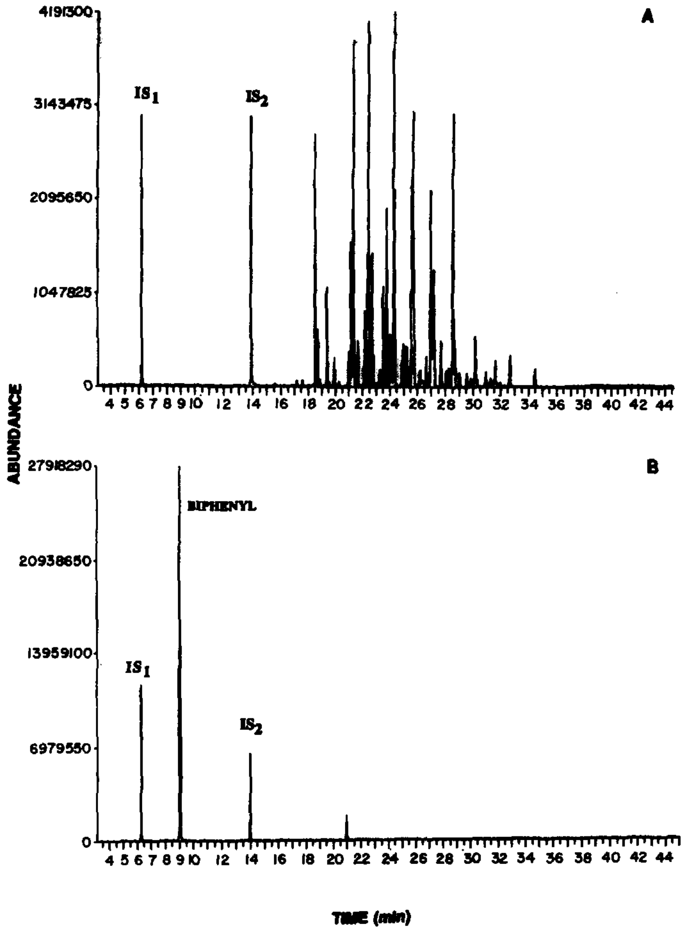


Fig. 1. GC/MS total ion chromatogram of Aroclor 1254 (0.20 g). (A) Before reaction; (B) after reaction with I (2.50 g)/Na (1.10 g) in THF (25 ml). The product is biphenyl. $IS_1 = 1,2,3\text{-}Cl_3$-benzene and IS_2 = 4-Br-biphenyl as internal standards.

biphenyl dimers or any other PCB-solvent-derived products were detected. Similarly, reaction of Aroclor 1254 in the presence of I for 2 h, under otherwise identical conditions, gave biphenyl (*ca.* 95%) as shown in Fig. 1B. Only traces of tetraphenyl (< 0.1%) were observed with no sign of PCB-solvent-derived products, and all chlorine was recovered as Cl^-.

The Aroclor/Na/I reduction should essentially have the same mechanism as described above (eqs. 3 and 4). The only basic difference between the two reductions is that the H-abstraction step by $Ar^{\bullet}$ is dominant in the PMHS reduction. The absence of other competitive reactions by $Ar^{\bullet}$ allowed biphenyl to be formed predominantly (eq. 6). However, I could enhance the reduction process in addition to simply being a hydrogen donor. Recently we have reported that the adsorption efficiency of Aroclor 1254 on the surface of polymeric polysiloxanes, *e.g.*, manosil, could reach 100% [7]. We therefore speculate that the close association between the Aroclor and the hydrosiloxane polymer during the electron transfer process could have made the polymeric hydride the main source of hydrogen to $Ar^{\cdot}$.

$$ArCl \xrightarrow{Na} Ar^{\cdot}Cl^{-} \rightarrow Cl^{-} + Ar^{\cdot} \xrightarrow{PMHS} ArH \qquad (6)$$

Dechlorination of Aroclor was stepwise and selective (*see below*). Simultaneous loss of more than one chlorine from the aryl chloride did not seem to take place. If such a dechlorination mechanism did take place, we might expect benzyne to be formed as an intermediate in the dechlorination process. When dechlorination was attempted in the presence of 2,5-dimethylfuran, a known benzyne addendum, no benzyne adducts were observed. In contrast, simultaneous loss of more than one chlorine has been reported in the electrochemical reduction of polychloroarenes [8].

Finally we found some similarity between the present reduction and that of Birch reduction. When excess Na/PMHS was used in the reduction of Aroclor 1254, products such as phenylcyclohexane and phenylcyclohexadienes were formed. These products are normally formed when biphenyl is reduced with Na/liquid NH_3. The Na/PMHS reduction at ambient conditions may be more convenient than the Na/NH_3 reduction in which special equipment must be used to handle ammonia and to accommodate reaction temperatures as low as −30°C.

Regioselectivity of dechlorination

Extensive product analysis of samples during the course of the Aroclor/Na/I reaction showed the following major products as identified by their GC/MS spectra (*m/z*): 2,2′,5,5′-tetrachlorobiphenyl (**III**, 292), 2,3′,4′,5-tetrachlorobiphenyl (**IV**, 292), 2,3′,5-trichlorobiphenyl (**V**, 256), 3,3′-dichlorobiphenyl (**VI**, 222), 3-chlorobiphenyl (**VII**, 188) and biphenyl (**VIII**, 154) (Fig. 2). The above enriched *meta* products were formed at a rate 1–2 orders of magnitude higher than their *ortho* and *para* counterparts, whereas the statistical distribution of *meta/ortho/para* chlorines in total Aroclor 1254 (77 congeners) is calculated to be 2.08/2.13/1.00 [9]. This indicates that the distribution of the above intermediate products is not statistical, but is rather regioselective, favouring *ortho* and *para* Cl-elimination over that of *meta*. Furthermore, when 2,3′,4′,5-Cl_4BP (**IV**) was dechlorinated under the same conditions, it gave 2,3′,5-Cl_3BP (**V**), 3,3′-Cl_2BP (**VI**) and 3-ClBP (**VII**) as primary products prior to the formation of BP. The results emphasize that dechlorination proceeds in a stepwise, regioselective manner favouring *para* and *ortho* elimination over that of *meta*.

Recently, we found that photoinduced dechlorination of Aroclor 1254 by sodium(methyl)siliconate proceeds with similar regioselectivity [10], and it is suggested that an electron transfer process, involving a photoexcited state of the Aroclor and the siliconate, gives the aryl radical anion, $Ar^{\cdot -}$–Cl, whose subsequent cleavage to eliminate Cl^{-} controls regioselectivity (Scheme 1, path a). Likewise, electrochemical dechlorination of PCBs is reported to proceed through the same intermediate giving similar regioselectivity [8] (Scheme 1, path b). The similar regioselectivity observed in the dechlorination of Aroclors by the Na/PMHS system clearly indicates the involvement of $Ar^{\cdot -}$–Cl as the intermediate in the dechlorination process (Scheme 1, c).

The present trend in regioselectivity is very similar to that observed by Burdon *et al.* in the nucleophilic aromatic substitution of polyhaloarenes [11]. Burdon and

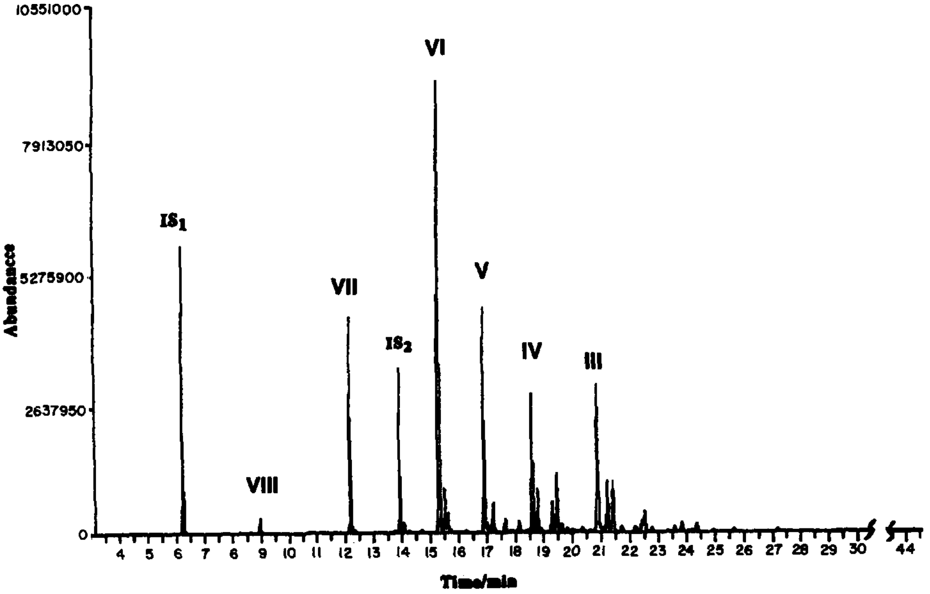
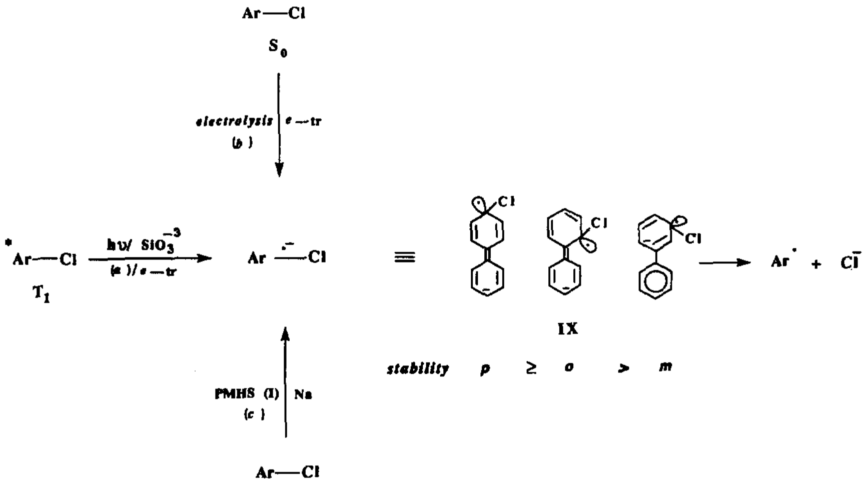


Fig. 2. GC/MS total ion chromatogram showing partially dechlorinated biphenyl products formed after reacting Aroclor 1254 with **I** and Na in THF for 40 min. **III**, 2,2′,5,5′-Cl_4-BP; **IV**, 2,3′,4′,5-Cl_4-BP; **V**, 2,3′,5-Cl_3-BP; **VI**, 3,3′-Cl_2-BP; **VII**, 3-Cl-BP; **VIII**, BP. IS_1 = 1,2,3-Cl_3-benzene and IS_2 = 4-Br-biphenyl as internal standards.

co-workers have rationalized orientation in the dechlorination of polyhaloaromatics by considering the relative stabilities of the Wheland-type intermediate involved in the dechlorination process [11]. Taking into account that chlorines in a π-system are electron-repelling (I_π repulsion theory) and the second aryl group in the aryl radical anion, **IX** (for simplicity only one Cl is shown) is a stabilizing



Scheme 1.

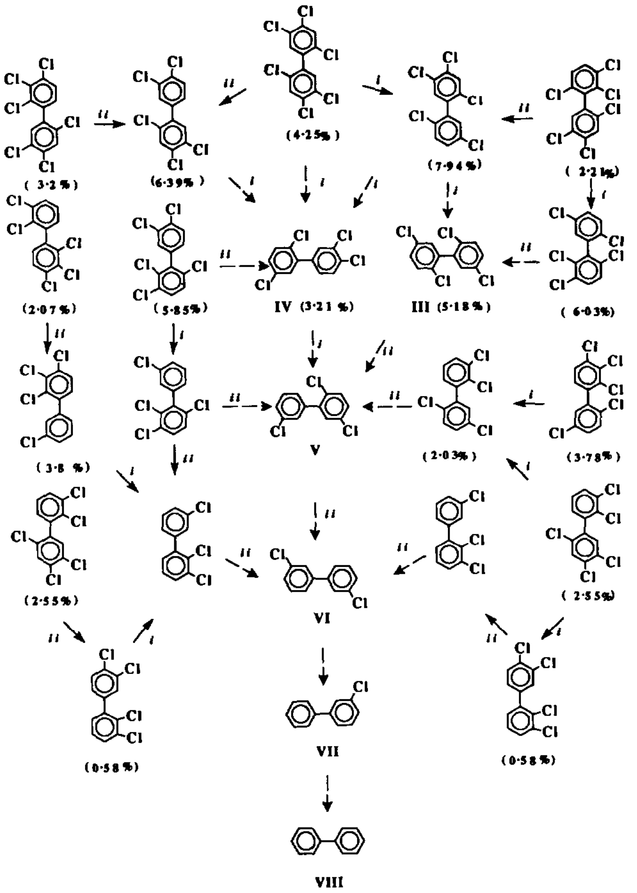


Fig. 3. Constructed dechlorination pathway of Aroclor 1254 of the 16 most abundant congeners of Arochlor 1254. (i) *para* elimination and (ii) *ortho* elimination. Percentage abundance (values in parentheses) are calculated using ref. 9. The structures 2,2′,3′,4,5-Cl_5-BP, 2,3,3′,4′-Cl_4-BP and 2,3,3′-Cl_3-BP are repeated for clarity.

substituent, the aryl radical anion will exhibit the following order of stability (**IX**): *para* > *ortho* > *meta*. In the case of the *para* intermediate an extra stability is added due to the formation of a *para*-quinonoid structure. Based on Burdon model, a reduction pathway was constructed in which only the 16 most abundant congeners of Aroclor 1254 (*meta*/*ortho*/*para* Cl ratio is 1.82/1.82/1.00) were considered (Fig. 3). In Fig. 3, no preferential differentiation between *ortho* (ii) and *para* (i) cleavage is taken into account, whereas, values in parentheses represent the amount (%) of each congener in commercial Aroclor 1254. Remarkably, all the predicted products **III**–**VIII**, drawn horizontally in Fig. 3, match those observed experimentally during the reductions of Aroclor 1254 (Fig. 2). The above model, describing regioselectivity, is qualitative and oversimplified. For a better quantitative assessment, the charge density distribution in all carbons substituted with chlorines in the highest occupied molecular orbital (HOMO) of the radical anion **IX** should be correctly assessed to determine which intermediate possesses the minimum energy (I_π repulsion theory).

The successful use of Na/PMHS as reducing agent for the dechlorination of Aroclor 1254 is a novel application of reduction processes to serve the environment and fight pollution.

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