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A MILD AND EFFICIENT PROCESS FOR DETOXIFYING POLYCHLORINATED BIPHENYLS

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Summary: Polychlorinated biphenyls (PCBs) were effectively dechlorinated to biphenyl under mild conditions using an aqueous solution of sodium hypophosphite in the presence of a palladium catalyst.

Polychlorinated biphenyls (PCBs) have been employed for several decades in a variety of industrial applications. They are non-flammable and have low volatility and good viscosity characteristics at operating temperatures.[1a-b] Thus, they have been used primarily as additives in dielectric, hydraulic and heat transfer fluids. It has been reported that over a half a million tons of PCBs have been manufactured in the United States and it is estimated that 300 million pounds of these are in chemical landfills and about 750 million pounds are still in use.[1b] In the 1960's the first signs of potential environmental problems appeared and subsequently, because of toxicity, environmental persistance and suspected carcinogenicity, the EPA banned the continued manufacture and importation of PCBs and issued regulations governing their storage and disposal. Various techniques for disposing of PCBs have been proposed including a variety of sodium metal reduction procedures,[1] high temperature incineration,[2] and recently, ammonium formate mediated catalytic hydrogenolysis.[3] We herein report the results of our studies on the development of a practical hydrogen transfer process which makes possible the complete destruction of PCBs in an aqueous system at atmospheric pressure under relatively mild conditions.

Previously,[4] we reported on various applications of hydrogen transfer reductions and hydrogenolysis using sodium hypophosphite. In these reports we examined the scope and limitations of this process toward a variety of functional groups such as reduction of olefins, ketones, aldehydes, azides, N-oxides, epoxides and hydrogenolysis of benzyl ethers, alkyl and aryl halides. It was found that aromatic halides (Cl and Br) were amenable to rapid hydrogenolysis as were activated alkyl halides such as benzylic halides or those alpha to carbonyl groups. Simple aliphatic halides were unreactive. We then extended the use of this hydrogen transfer reagent to a variety of polyhalogenated aromatics and PCBs. Both crude PCB oils from transformers and PCB reference standards of Aroclor 1254[5] were investigated. Typically, a sample of PCB such as Aroclor 1254 was diluted with an appropriate solvent (e.g. toluene, tetrahydrofuran or ethanol) and mixed with an excess of base (e.g. sodium carbonate, potassium carbonate or sodium hydroxide) which was used to neutralize any HCl produced. An appropriate catalyst (5% or 10% Pd/carbon) was added, and the reaction mixture was warmed to 50-90°C with vigorous stirring while an aqueous solution of sodium hypophosphite was slowly added and gas evolution was observed.

The reactions were monitored for disappearance of starting materials and appearance of products by gas chromatography and additional sodium hypophosphite was introduced when necessary. When complete, the reactions were cooled, filtered, and organic layers were separated and analyzed. In some cases the aqueous layers were also analyzed for total chloride ion content by silver nitrate titration. As a way of demonstrating the general utility of this process, and because PCBs are frequently diluted with various halogenated benzenes such as trichlorobenzene, we subjected pure samples of chlorobenzene, 1,4-dibromobiphenyl, 4-chloroanisole and 1,2,4-trichlorobenzene to the above conditions. All compounds were completely converted to the respective dehalogenated products. In a few cases, when a very large excess of catalyst was employed at elevated temperatures, some reduction of PCBs to phenylcyclohexane was observed. Initially, this was of some concern, since if reduction were to proceed prior to hydrogenolysis, this could result in the formation of aliphatic halides, which would be unreactive to this system. Careful examination of the reaction products and comparison with reference samples indicated that this was not a problem. Some comparisons between the sodium hypophosphite hydrogen transfer hydrogenolysis and conventional hydrogenolysis using hydrogen were performed. When crude PCB oils were subjected to catalytic hydrogenation at 40 psi in a Parr apparatus using conditions similar to those described above (50°C, Pd/C, excess Na_2CO_3) the major product was identified as biphenyl. Attempts to eliminate the use of excess base resulted in recovery of largely unreacted PCBs in both cases.

In conclusion, this process serves to demonstrate the utility of hydrogen transfer reductions in the detoxification of PCBs, and has the potential for application to other chlorinated waste (such as dioxins). Its advantages are ease of execution, use of an inexpensive hydrogen donor, no need of special hydrogenation equipment and a broad applicability to relatively high concentrations of PCBs.

Experimental

General Procedure: To a solution of Aroclor 1254 (1.0 g) in toluene (25 mL), was added sodium carbonate (8.0 g, 0.08 mol) and 10% Palladium on carbon (0.4 g of 50% water wet material). A 1 mL aliquot of the reaction mixture was taken for a chromatography standard (t = 0) and the reaction mixture was warmed to 90°C with vigorous stirring while a solution of sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$, 3.0 g, 0.03 mol) in water (15 mL) was added dropwise during 1h. The reaction mixture was maintained at 90°C for an additional 3h and another 1 mL aliquot taken and analyzed. At this point the conversion of starting materials to product was greater than 90% complete. An additional charge of sodium hypophosphite (3.0 g, 0.03 mol) in water (15 mL) was added and the temperature maintained at 90°C for an additional hour. At this point, analysis indicated that the reaction was complete. The reaction mixture was cooled and filtered. The catalyst was washed with toluene (10 mL), and the layers were separated. The toluene layer was concentrated to yield biphenyl (0.4 grams, > 85%). Titration of a sample of the aqueous layer with silver nitrate indicated > 95% accountability for the theoretical amount of chlorine.

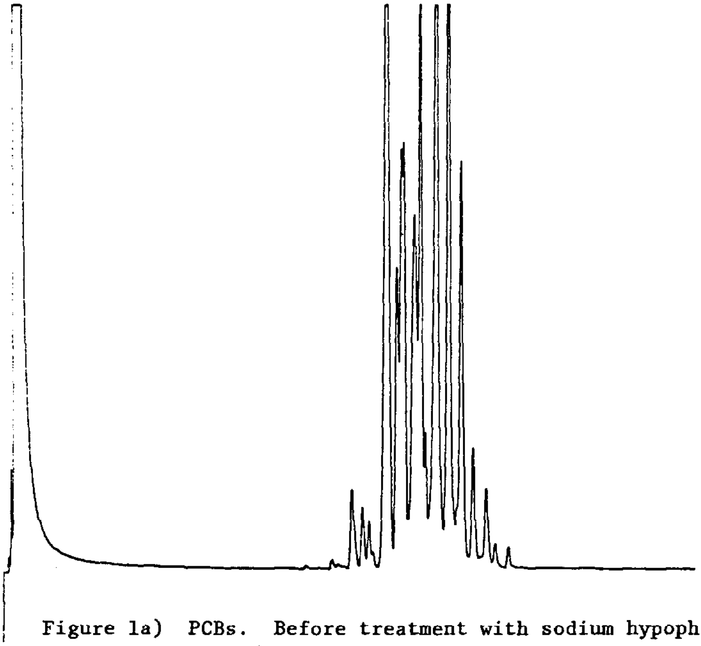

Figure 1a) PCBs. Before treatment with sodium hypophosphite.

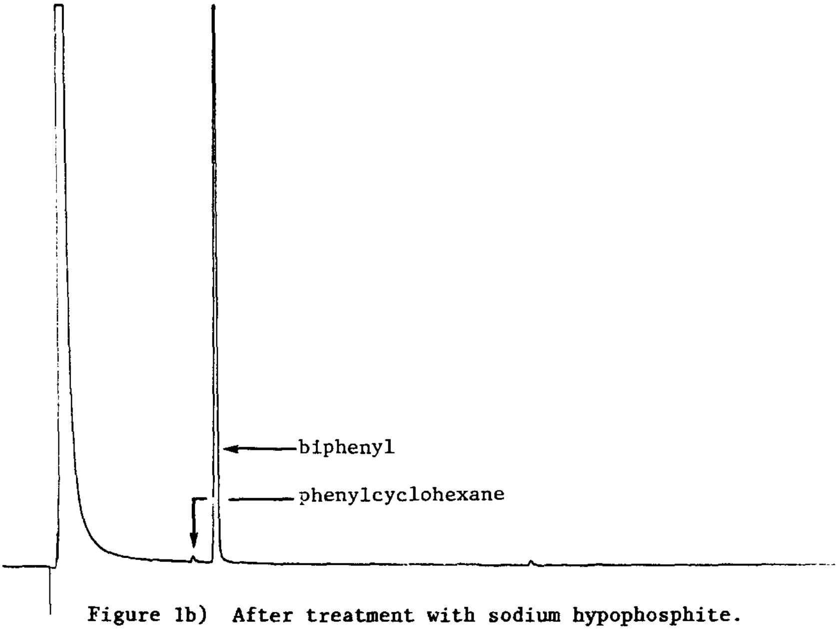

Figure 1b) After treatment with sodium hypophosphite.

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5. Aroclor 1254 is a PCB mixture consisting of 13.8% tetrachlorobiphenyls, 61.9% pentachlorobiphenyls, 23.3% hexachlorobiphenyls and 1.0% heptachlorobiphenyls. This is available from Analabs, North Haven, Conn.

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