Synthesis and Characterization of Polychlorinated Naphthalenes

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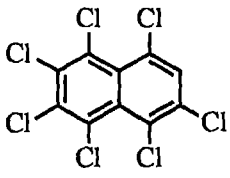
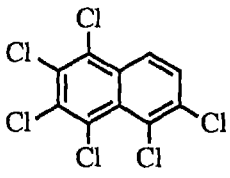
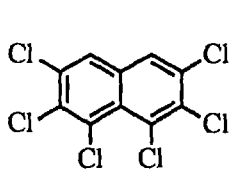
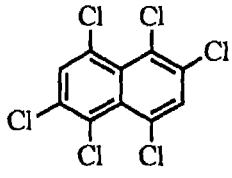
Polychlorinated naphthalenes (PCN's) have been recognized as a distinct and ubiquitous class of the polychlorinated polyaromatic environmental pollutants[1]. However, despite many published reports concerning the physiology, toxicology and some chemistry of these compounds, there exist no adequately documented studies available concerning details of rational syntheses or physico-chemical characterization for purity or structure proof especially for the penta- and hexa- congeners. This situation is in contrast to the availability of many well-characterized isomers in the PCB, PCDD and PCDF series.

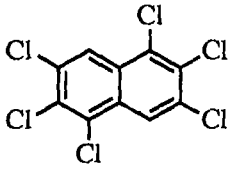
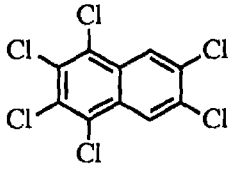
Since it is necessary to have available reasonable supplies of a variety of isomerically pure congeners for any environmental or toxicological studies we have undertaken a research program to systematically prepare and characterize all of the 14 possible pentachloronaphthalene isomers as well as the 10 possible hexachloronaphthalenes.

We consider a synthetic method to be adequate only if it permits preparation of multi-milligram, ca 100-500mg, amounts of isomers that are >95% pure.

The first phase of our investigations has provided appreciable quantities of the following PCN isomers which have been variously reported in the literature with few or no details concerning purity, proof of structure or quantity,

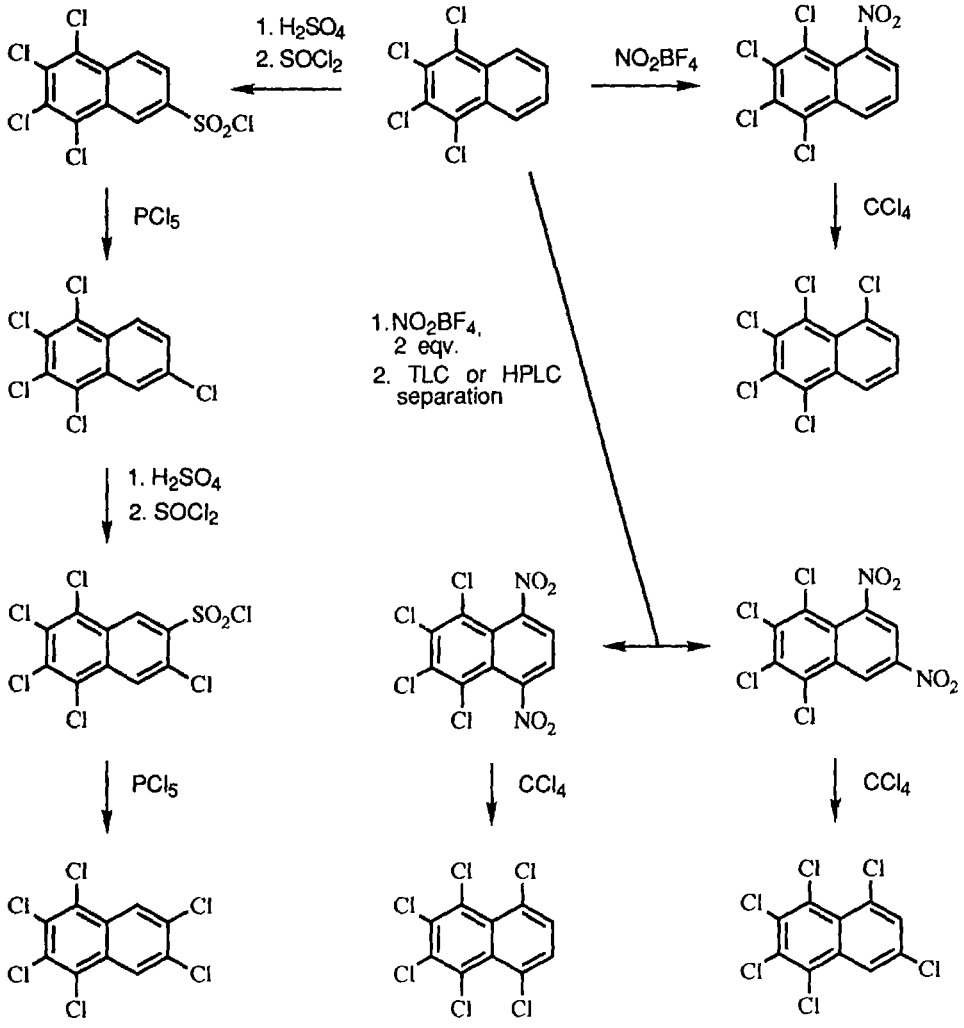
plus the environmentally most interesting pair, i.e.

The next phase of our program has involved a systematic investigation of the stepwise derivatization of lower chlorinated naphthalenic compounds followed by chlorosubstitution of these functionalities.

A typical synthetic series beginning with the commercially available substance, 1,2,3,4-tetrachloronaphthalene, is illustrated below. As can be seen this series allowed us to

synthesize two previously uncharacterized penta- and two hexa- isomers in addition to one of the biologically interesting compounds, 1,2,3,4,6,7-tetrachloronaphthalene, in > 100mg quantity and > 99% purity. All compounds are completely characterized by ^{1}H NMR, ^{13}C NMR, IR, UV, MP, GC/MS and HPLC.



The scheme clearly outlines the two main selective synthetic pathways: nitration followed by Ponomarenko reaction for introduction of chlorine in positions 1,4,5 or 8 or sulfonation followed by reaction with phosphorous pentachloride for substitution in positions 2,3,6 or 7.

We hope that our results will encourage an increased research effort with this somewhat neglected class of environmental pollutants so that a more precise evaluation can be made of all aspects of their environmental impact.

1 Jakobsson E, Ericsson L, Bergman A. Synthesis of hexachloronaphthalenes. *Acta Chem. Scand.* 1992.