PCB

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DEPARTMENT OF MEDICINE & ENVIRONMENTAL HEALTH

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Dr. R. Emmet Kelly
665 South Skinker, Apt. 10D
St. Louis, Missouri 63105

Dear Emmet:

I have enclosed three pages of hand drawn structures of interest in the dioxin and furan fracas. Any material that undergoes strong oxidation that has benzene or phenol in it as a contaminant can end up as a compound of more than one benzene nucleus. What dioxins and furans are are oxygen-bridged benzene nuclei.

In the case of furans it shows a carbon-carbon bridge and a carbon-oxygen-carbon bridge. In the dioxins, it shows two carbon-oxygen-carbon bridges that connect the two benzene nuclei. If you chlorinate phenols and subject them to strong oxidation, you have an almost certainty of producing the chlorinated substituents of one or both of these structures. In the case of the dioxins, the most hazardous, based on rodent toxicology, is the 2,3,7,8-tetrachloro isomer. Since the reactive carbons on both structures are numbered the same, you will find both chlorinated materials with similar chlorine location numbers.

In the case of biphenyl, this is a so-called bis structure where the fusion of the two nuclei is to a single carbon. In this case the reactable carbons are numbered, each nucleus separately, from the common carbon connecting the two nuclei. For example, our famous para-amino biphenyl is actually 4-amino biphenyl. Benzadine, which has an amine group on both tip carbons, is 4,4'-diamino biphenyl.

Practically no organic material is absolutely free of water. The water comes over in the material from process or gets into the material from condensation in storage facilities. If you take an organic aromatic stock and chlorinate it in the presence of oxygen or water the oxidative chlorination that takes place will chlorinate these aromatics and then begin to connect them up by dehydrohalogenation. My Example #10 shows this reaction. When you consider the number of aromatic chlorinations we perform and the fact that small amounts of phenol are in most of these chlorinations, you can readily see how minute quantities of chlorofurans and/or chlorodioxins arise. When the reaction is actually with a chlorophenol, the chances of course are better. In the case of 2,4,5-trichlorophenol which is a precursor of 2,4,5-T, the coupling reaction produces a tetrachlorodioxin plus two moles of hydrochloric acid. In the case of pentachlorophenol,

you will produce octachlorodioxin. The trouhle with pentachlorophenol is that a substantial amount of the material is tetrachlorophenol. You can consequently produce the hexa, hepta and octa moieties. In every case where the dioxin is produced it is possible to produce the corresponding furan. Dioxins and furans and their chlorinated substituents are, in minute quantities, very common as contaminants in aromatic chlorinations and many chloro aromatic oxidations. If one had sufficient skill and analytical equipment, it is possible to find these materials in practically anything that is associated with the parent compounds.

Toxicological research has shown that the 2,3,7,8-tetrachloro dibenzo para-dioxin and certain other 2,3-chlorinated structures are the most toxic of the isomers of the chlorofurans and chlorodioxins. The same research also shows an enormous difference in the toxic response of different species of rodents. It is my view that humans are not particularly susceptible to this toxicology aside from chloracne problems. It is probably true that all isomers from hexa down to the dichloro isomers are chloracnegenic. The hepta and octa isomers are not as toxic nor chloracnegenic, for example, as pentachlorophenol. It is probably the hexa isomer that contributes most to the chloracne seen in the penta worker, and probably the di, tri and tetra isomers in 2,4,5-T workers.

The chlorofurans have not been nearly as well characterized toxicologically as the dioxins. I am sure time will correct this deficiency. It can be assumed on a worst case basis that the chlorofurans are as bad as the corresponding chlorodioxins. Incidently, some of the chlorophenols are more toxic to humans than either the chlorofurans or chlorodioxins.

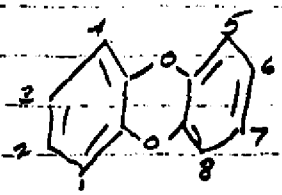
I am sorry I did not supply this information earlier.

Sincerely,

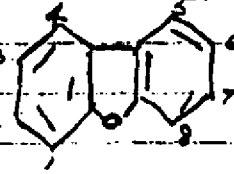
Jack T. Garrett

mlw

1. Basic dioxin structure (dibenzo p-dioxin

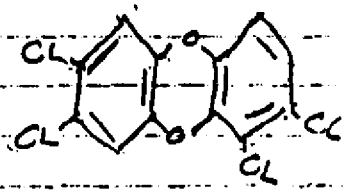


2. Basic Furan structure

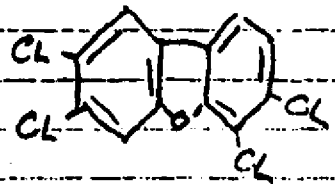


(dibenzofuran)
(Note: Numbers represent Reactable Carbons to Facilitate Naming)

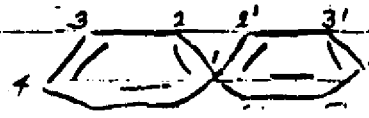
3. 2,3,7,8 Tetrachlorodibenzo paradioxin



4. 2,3,7,8 Tetrachloro dibenzo Furan

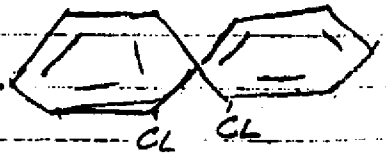


5. diphenyl (or biphenyl)



(numbers of reactive carbons

6. 2,2' dichloro diphenyl (SAME AS 6,6' (or o,o'))

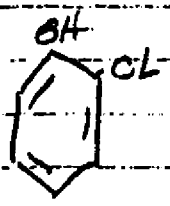


Phenol

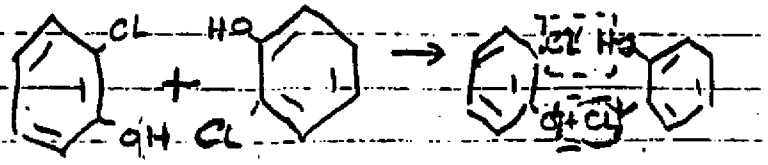
7.

8. p-Chlorophenol

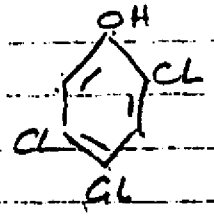
9. o-Chlorophenol



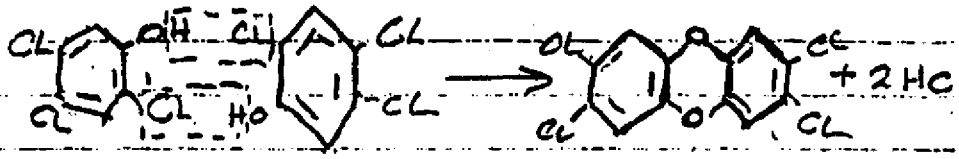
10. Two p-Chlorophenol's in Reaction to produce dioxin



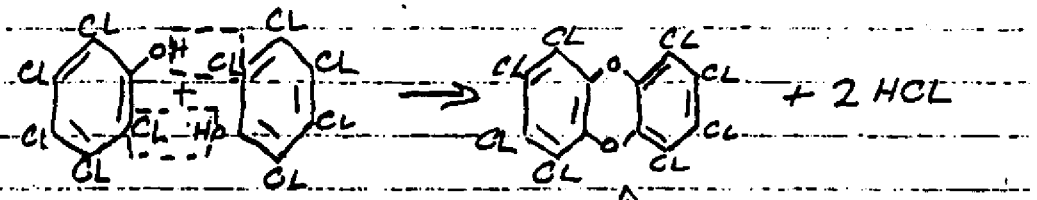
11. 2, 4, 5 Trichlorophenol



12. Two 2, 4, 5 Trichlorophenols in reaction produce 2, 3, 6, 7 – Tetrachloro dibenzo p-dioxin.

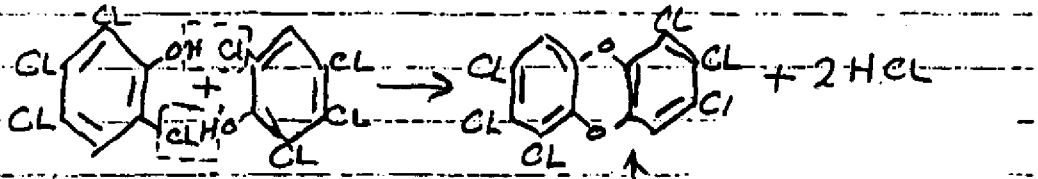


13 Two pentachlorophenols –



↳ octachlorodibenzopdo

14 Two Tetrachlorophenols –



↳ hexachlorodibenzopdio
OR To be determ.