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SUBJECT TO PROTECTIVE ORDER.

HISTORICAL OVERVIEW: 2,4,5-T, Chloracne & 2,3,7,8-TCDD

- 1930s -- Chloracne, a dermatitis characterized by blackheads similar to teen-age acne but often more severe, was noted among workers dealing with chlorinated aromatic hydrocarbons (chloracnegens).
- 1941 -- 2,4-D and 2,4,5-T first synthesized.
- 1944 -- 2,4-D and 2,4,5-T reported as herbicides and marketed by Amchem Products.
- 1947 -- Effectiveness of 2,4,5-T and derivatives against woody plants resistant to 2,4-D established by Dow.
- 1948 -- 2,4,5-T registered for control of weeds on rangelands, fence rows and rights of way.
- 1949 -- Explosion in Monsanto's 2,4,5-trichlorophenol (TCP) unit at Nitro, W.Va. exposed 250 workers to reaction mass causing 122 cases of chloracne, some very severe. TCP is intermediate in 2,4,5-T manufacture.
- 1950 -- Presence of a "highly toxic impurity" in production of TCP recognized by Dow.
- 1957 -- 2,3,7,8-TCDD first implicated as causative agent of chloracne associated with TCP production. (Kimmig and Schultz, Germany)
- 1962 -- U.S. military began spraying 2,4,5-T formulations in Vietnam to take away foliage cover from the enemy.

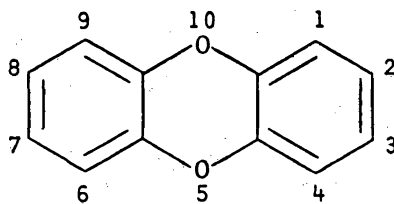
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HISTORICAL OVERVIEW (CONT'D.)

- 1965 -- 2,3,7,8-TCDD recognized by Dow as causative agent of chloracne in TCP wastes. Alerted health authorities and other U.S. 2,4,5-T manufacturers. Shared analytical techniques.
- 1970 -- 2,3,7,8-TCDD's teratogenicity and fetotoxicity first reported in animals. U.S. military stopped spraying Agent Orange in Vietnam. U.S. Dept. of Agriculture suspended uses of 2,4,5-T.
- 1973 -- Vietnamese study linked liver cancer, abortions, and birth defects to Agent Orange spraying.
- 1976 -- Explosion at ICMESA chemical plant in Seveso, Italy released heavy concentration of 2,3,7,8-TCDD in densely populated area. Workers (156) and residents (37,000) exposed. More than 500 treated for presumed toxic symptoms; 134 cases of chloracne. Mortality rate normal to date. Event received worldwide publicity through news media.
- 1978 -- Dow announced chlorinated dioxins found in particulate matter in air emissions from various commercial and domestic combustion processes.
- 1979 -- Suit filed by Vietnam veterans against five U.S. chemical companies that produced Agent Orange. Companies, in turn, filed third party action against U.S. government for its negligent misuse of the chemical.
- 1982 -- Times Beach

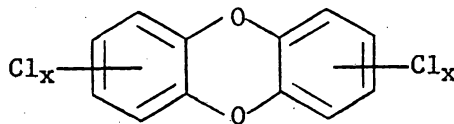
DIOXIN

Chemical Nomenclature: Dioxin = Dibenzo-p-dioxin

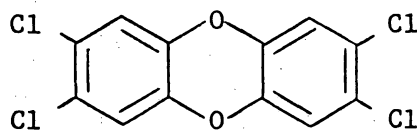


Media: Dioxin = 2,3,7,8-Tetrachlorodibenzo-p-dioxin
= 2,3,7,8-TCDD

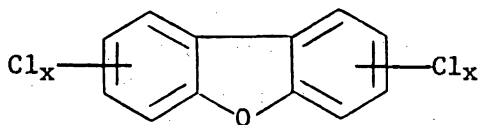
CHLORINATED DIOXINS (CDDs)



- 75 CDDs
- 22 TCDDs
- 2,3,7,8-TCDD - most toxic isomer to the male guinea pig

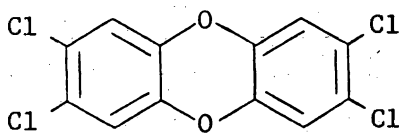


- CDDs 10 to 20 times more toxic than chlorinated dibenzofurans in the rabbit ear test



STRUCTURE AND PHYSICAL PROPERTIES

OF 2,3,7,8-TCDD



Physical State:	White, crystalline solid
Molecular Weight:	322
Melting Point, °C.:	303-305
Decomposition Point, °C.:	980-1000
Solubility:	Water = 2×10^{-8} g./L Benzene = 0.57 g./L <u>o</u> -Dichlorobenzene = 1.4 g./L

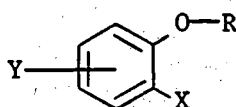
SOURCES AND FORMATION
OF DIOXINS

- Formed during manufacture of chlorophenols, intermediates in synthesis of pesticides. Thus contaminants in chlorophenol derived pesticides.
- Pyrolysis (<750°C) of chlorophenols or chlorophenol derived pesticides.
- Formed in a wide variety of commercial and domestic combustion processes.

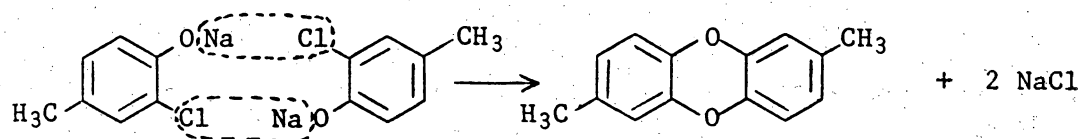
REQUIREMENTS FOR

DIOXIN FORMATION

- Precursor must contain an o-substituted benzene ring with one of the substituents being an oxygen atom attached directly to the ring.



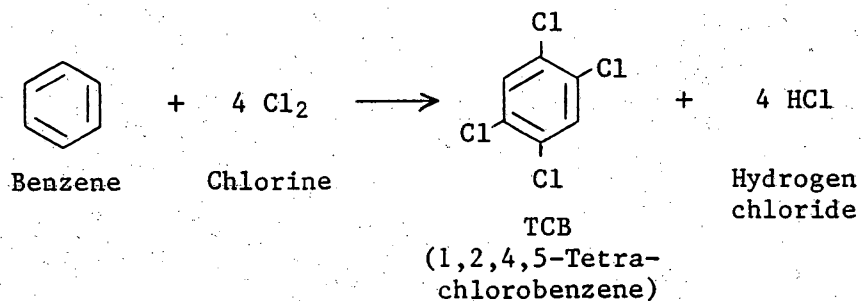
- The two substituents must be able to react with each other to form another compound.



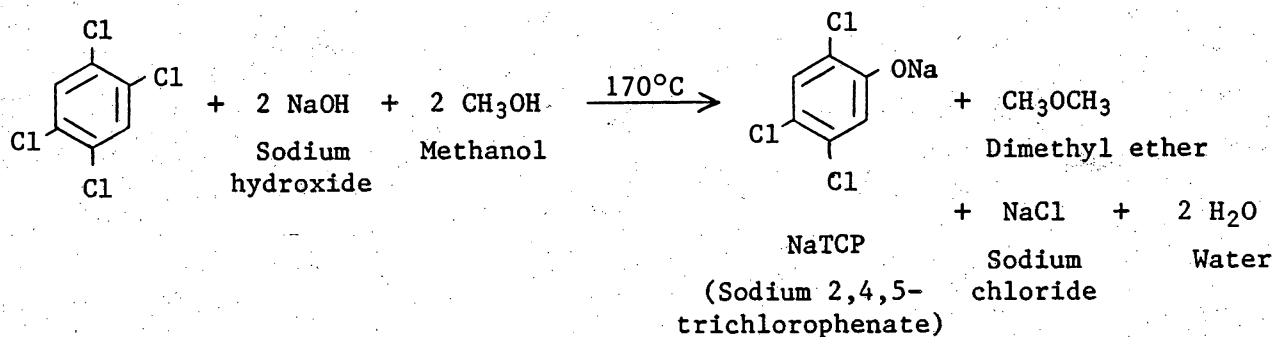
- The reaction is favored by basic conditions (e.g., sodium hydroxide) and temperatures of 180-400°C.
- Presence of a metal catalyst (e.g., copper or iron powder) promotes the reaction.

MANUFACTURE OF 2,4,5-T

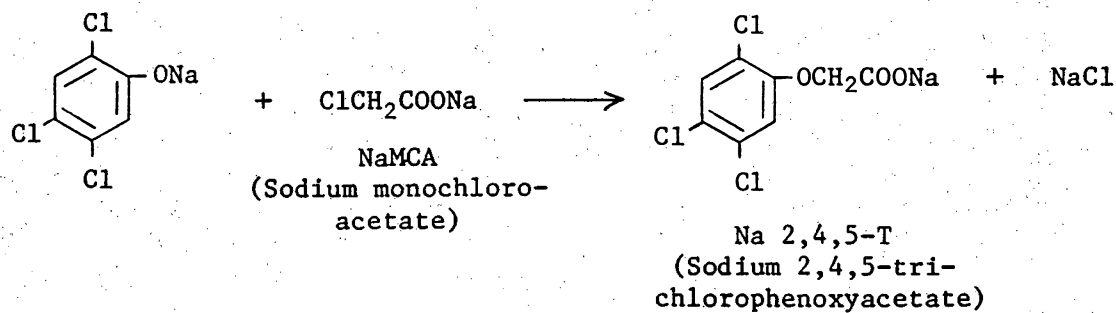
Step 1



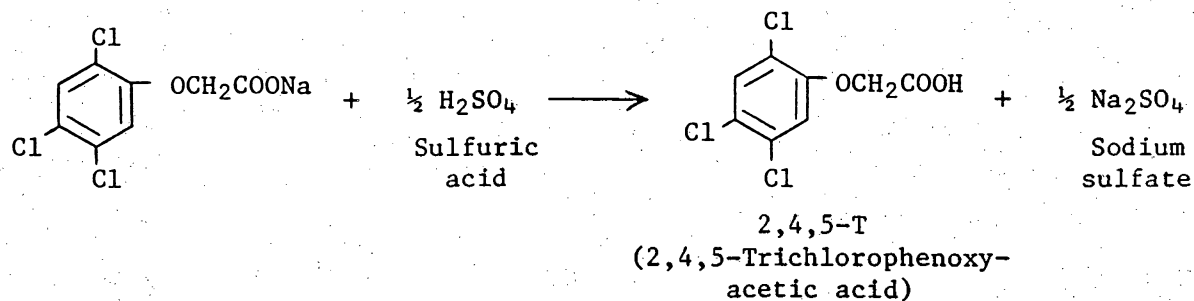
Step 2



Step 3



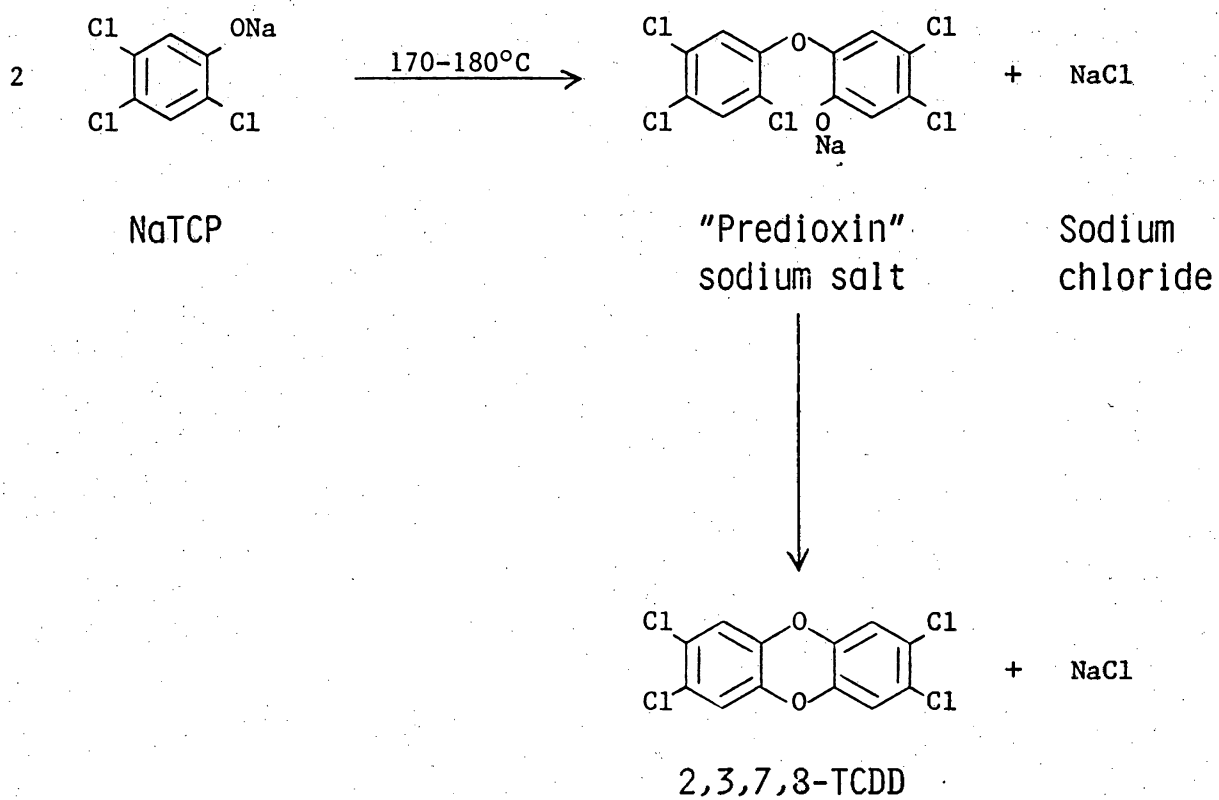
Step 4



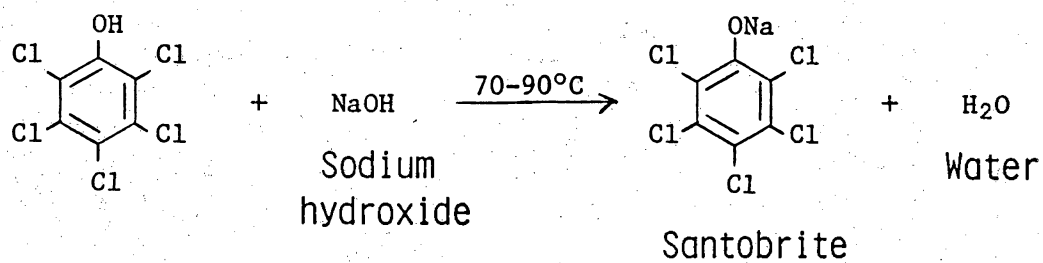
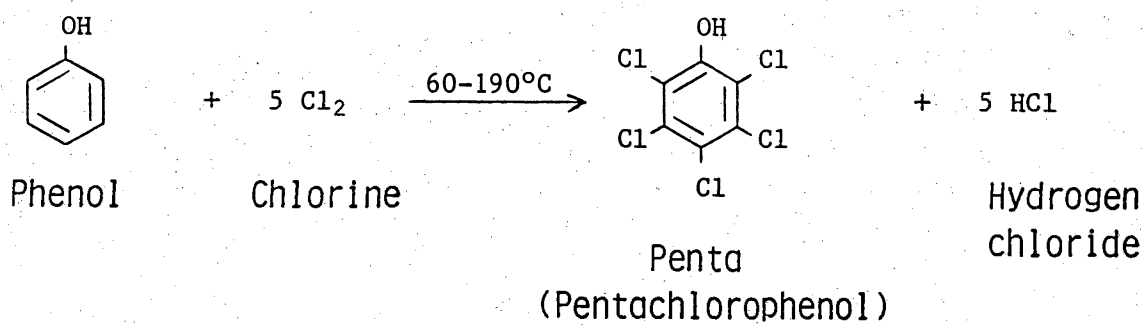
FORMATION OF 2,3,7,8-TCDD

AS SIDE REACTION IN

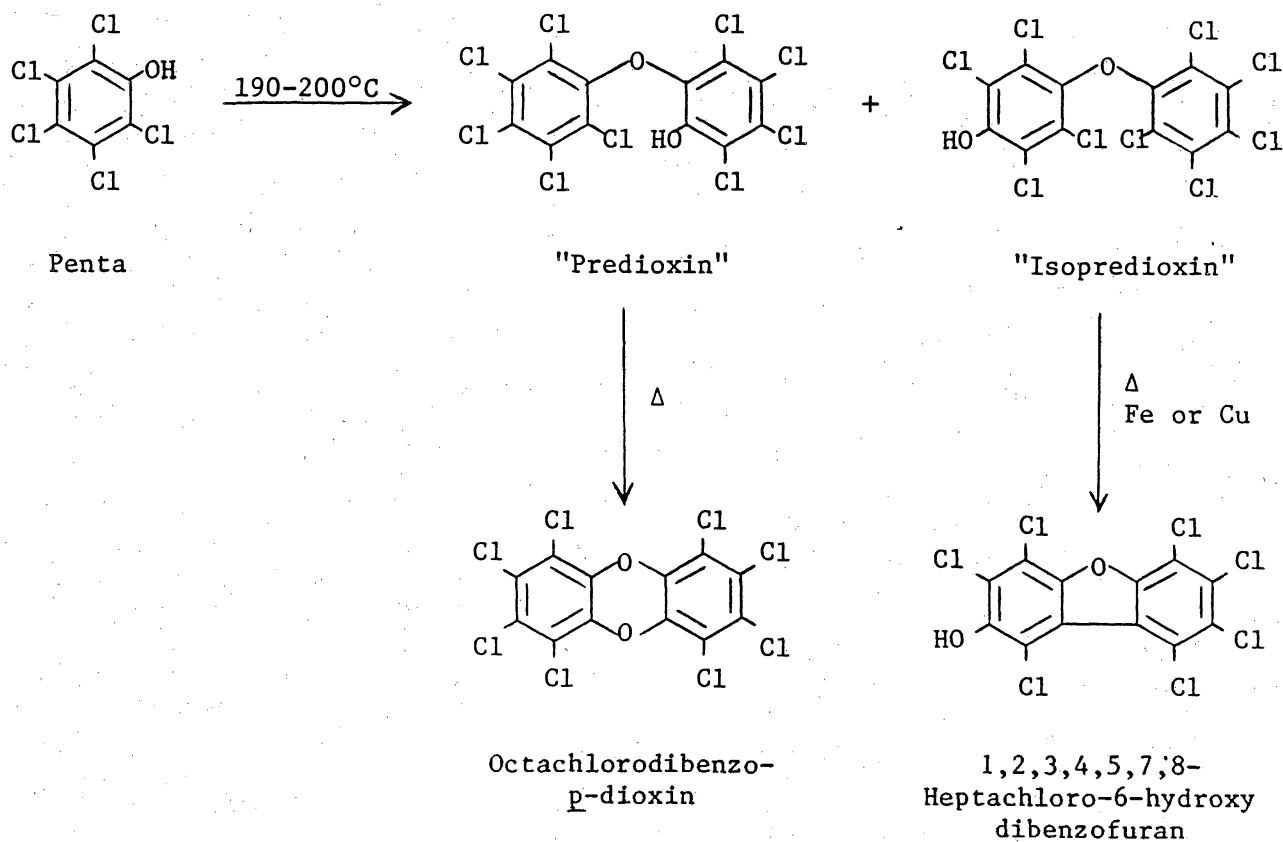
MANUFACTURE OF NaTCP



MANUFACTURE OF
PENTA AND SANTOBRITE



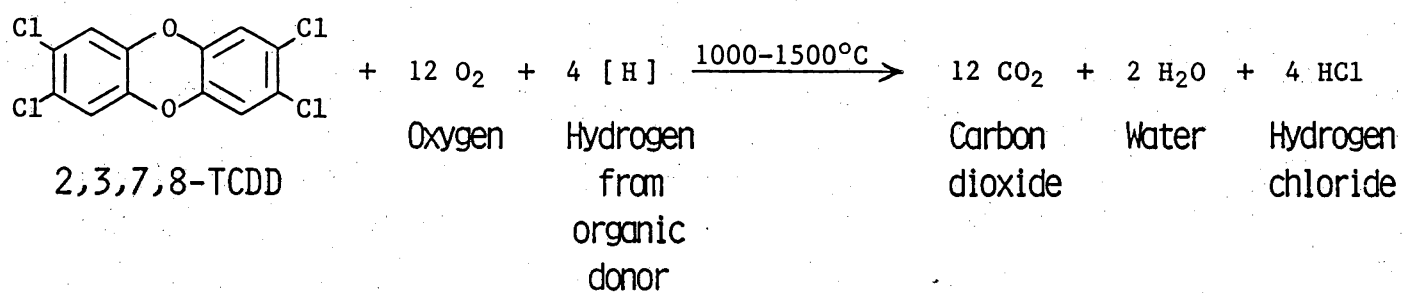
FORMATION OF
CHLORINATED DIBENZO-p-DIOXINS AND
CHLORINATED DIBENZOFURANS
AS SIDE REACTIONS IN
MANUFACTURE OF PENTA



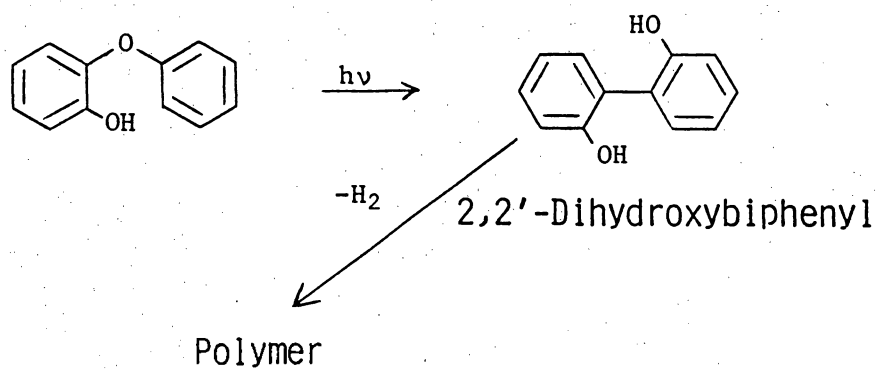
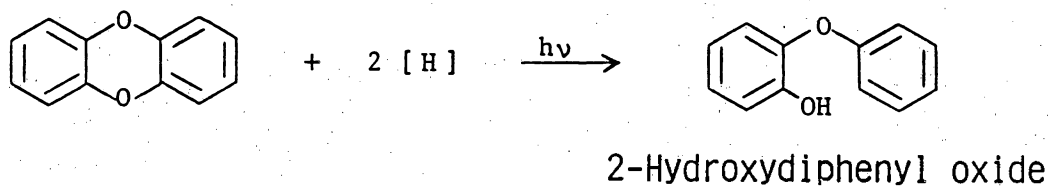
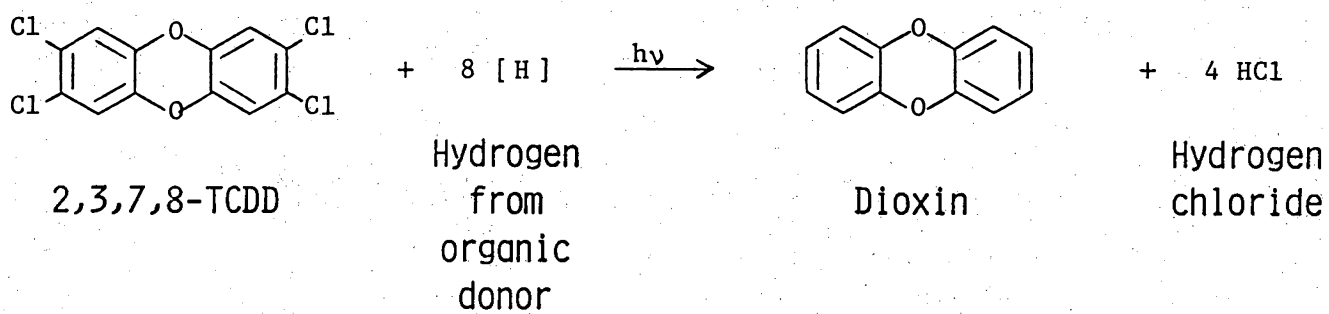
METHODS OF DESTRUCTION
OF CHLORINATED DIOXINS

- Incineration at temperatures of 1000 to 1500° in industrial incinerators. Future: molten salt combustion or microwave plasma destruction.
- Degraded quickly by sunlight or artificial ultraviolet light (photolysis).
- Chemical destruction by ozonolysis, chlorinolysis, catalytic wet oxidation (Zimpro process), and catalytic dechlorination processes.
- Biological destruction by new genetic engineered bacteria may hold future promise.

CHEMISTRY OF INCINERATION OF 2,3,7,8-TCDD



CHEMISTRY OF PHOTOLYSIS OF 2,3,7,8-TCDD



III. HISTORICAL OVERVIEW: PHENOXY HERBICIDES & CHLORACNE

REFERENCE: "The Science of 2,4,5-T and Associated Phenoxy Herbicides", R. W. Bovey and A. L. Young, Wiley, New York, 1980¹

- 1930's Chloracne, a dermatitis characterized by comedones (blackheads) similar to teen-age acne but often more severe, was noted among workers dealing with chlorinated aromatic (benzene-derived) hydrocarbon materials. Components which cause chloracne are termed "chloracnegens".
- 1941 2,4-D and 2,4,5-T first synthesized.
- 1942 Cell elongation in plants by 2,4-D at concentrations first established.
- 1944 Effectiveness and selectivity of 2,4-D on broad-leaf weeds in lawns and the effect on established grasses was established.
- 1947 Effectiveness of 2,4,5-T and derivation of plants resistant to 2,4-D established.
- 1950 Presence of "a highly toxic impurity" in production of TCP recognized by Dow.
- 1957 TCDD first implicated as causative agent for chloracne (Kimmig and Schultz, Germany).
- 1964 Dow recognized waste oils from TCP caused chloracne.
- 1965 TCDD recognized by Dow as causative agent for chloracne in TCP wastes. Alerted health authorities and other 2,4,5-T manufacturers. Shared analytical techniques.
- 1966 Dow able to lower TCDD content of 2,4,5-T to less than 1 ppm.

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