EXPLORATORY AROCLOR CHEMISTRY. PART II. DIPHENOLS BY HYDROLYSIS

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DSW 621363

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		Page No.
I.	PURPOSE	1
II.	SUMMARY	2
III.	CONCLUSIONS	4
IV.	RECOMMENDATIONS	5
V.	DATA AND DISCUSSION	
	Syntheses	
	Evaluation Data	
	Analytical Procedures	
VI.	EXPERIMENTAL DETAILS	
	Apparatus	
	Raw Materials	
	Experiments	
VII.	PATENT STATUS	
VIII.	REFERENCES	
IX.	COST ESTIMATES	
X.	RECOMMENDED PROCESS	
XI.	MATERIAL SPECIFICATIONS	
XII.	ANALYTICAL PROCEDURES	
XIII.	TOXICITY AND HAZARDS	
XIV.	ACKNOWLEDGMENT	
	APPENDIX	

DSW 621364

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Monsanto's main market for Aroclors today is in dielectrics but the use patent for this application expired some years ago. It is apparent that studies of the preparation of new derivatives of Aroclors and other highly chlorinated aromatic materials would constitute a sound exploratory program for Monsanto.

After preparation of a few ethers by reaction of Aroclors with alcohols, attempts were made to obtain Aroclor ethers with ethylene glycol. Instead of etherification, hydrolysis occurred readily (R-15-16-17) and re-kindled interest in Monsanto-based polychlorinated diphenols as chemical intermediates. These can be used to prepare special types of epoxy resins, one of the fastest growing areas in the plastics industry. Currently, most of the epoxy resins are based on bisphenol A. This and other uses for the Aroclors and other halogenated aromatics as chemical intermediates has been suggested in several memos (R-1-5).

Experimental data [illegible] concerns ethylene glycol hydrolysis of eight Aroclors, [illegible], and hexachlorodiphenyl oxide. Study of an Aroclor [illegible] hydrolysis process is reported by J. R. LeBlanc (R-[illegible]).

Promising application leads were [illegible] and reported in R-7 for bis-glycidyl ethers [illegible] and for hydrolyzed Aroclors as curing [illegible] in polyepoxies, as stabilizers for PVC, and as wood preservatives.

The data reported [illegible] part of our exploratory research on chlorinated aromatics carried out between April 1954 and February 1957.

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II. SUMMARY

Alkali-hydrolyses in ethylene glycol of chlorinated compounds such as Aroclors 1271, 1270, 1268, 1262, 1254, 1248, 1168, 5460, hexachlorodiphenyl oxide, hexachlorobenzene, 1,2,4,5-tetrachlorobenzene, p-dichlorobenzene and octachloronaphthalene were investigated. The hydrolysis of Aroclors goes smoothly and rapidly to yield mixtures of isomers. However by this method dihydroxy polychlorobiphenyls are obtained only from Aroclors 1270 and 1271; neither of these Aroclors is now manufactured by Monsanto. The "lower" Aroclors give mixtures of di- and monophenols.

Pilot plant quantities of hydrolyzed Aroclor 1262 and 1268 were prepared using the ethylene glycol process by the Organic Chemicals Division in St. Louis, a direct scale-up of our laboratory procedure (R-8,-9,-11,-12). The hydrolyzed Aroclor 1262 was distilled in the [illegible] plant.

[illegible] of the ethylene glycol process to give di-hydrolyzed [illegible] pilot plant of a methanol-alkali pressure [illegible] R, L-Plant R-[illegible]). This process gives difunctional [illegible] with 1262.

[illegible] of Aroclor 1254 in ethylene glycol gives a mixture of [illegible] dihydroxylated biphenyl.

[illegible] replace more than two chlorines by hydroxyl in Aroclor [illegible] unsuccessful.

Although not competitive with current production processes, ethylene glycol hydrolyses can be used for the preparation of two Monsanto products: pentachlorophenol (95%) from hexachlorobenzene, and 2,4,5-trichlorophenol (80%), thru 2,4,5-T intermediate, from 1,2,4,5-tetrachlorobenzene (R-13).

Hexachlorodiphenyl oxide and p-dichlorobenzene also hydrolyze in polyethylene glycol; the former gives a mixture of the mono- and dihydroxy products, and the latter gives a practically chlorine-free material of unknown composition.

Copper powder fails to catalyze or increase the extent of hydrolysis. Hydrolysis in isopropylbiphenyl or o-nitroethylbenzene as solvents is not promising; the latter decomposed violently and is unsafe for this use.

Qualitatively, superheated steam or fusion with caustic results in chlorine displacement in Aroclor 1262 at 250-300°C.

[illegible] atoms found to be most labile toward hydrolysis are those [illegible] naphthalene. More than four halogen atoms are [illegible] [illegible] hydrolysis. [illegible]

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[illegible]t) this reaction [illegible] practical value.

A model molecule 4,4'-bis(2,6-dichlorophenol) was prepared by chlorination of 4,4'-diphenol. Studies of this model were most helpful in understanding the chemistry of hydrolyzed Aroclors and their glycidyl ethers and for modifications and interpretation of analyses.

Manufacturing cost estimates for hydrolyzed Aroclor 1268 were reported by J. F. Adams of Organic Research, St. Louis (R-14). Of the two the methanolic process is more economic than the ethylene glycol process, and the former gives diphenol from Aroclor 1268. The latter gives diphenol only with Aroclors 1270, 1271, and 5460. Solvent losses in the ethylene glycol process are major cost factors.

The main market foreseen for a di-hydrolyzed Aroclor is as an intermediate for diglycidyl ethers, which, on curing, give epoxy resins (R-7). Dihydroxy Aroclors, although higher in cost than bisphenol A, form epoxy resins having some properties superior to those of the bisphenol A epoxies (R-7).

Development of di-hydrolyzed Aroclor 1268 (methanol process) is now in progress [illegible] the Organic Chemicals Division (R-24). Hydrolyzed Aroclors [illegible] and 1268 are efficient curing agents for glycidyl ethers (R-7).

Hydrolyzed A[illegible] was found [illegible] somewhat less active than [illegible] wood [illegible] preliminary screening; tests are [illegible]. No significant [illegible] resulted from other biological [illegible] evaluations at [illegible] of seven hydrolyzed Aroclor [illegible] (R-7).

Because [illegible] art (R-15,-16,17), only limited patent protection on hydrolyzed Aroclors 5460, 1268 and lower homologs appears likely.

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Aroclors are raw materials for dihydroxypolychlorobiphenyls as promising Monsanto-based chemicals. Di-hydrolyzed Aroclors are intermediates for new epoxy resins (R-6,-7), for which hydroxyl di-functionality is critical. However, products that are less than difunctional can be employed as epoxy resin-drying oil fatty acid formulations, useful in surface coating applications (R-7).

Hydrolysis of Aroclors by the ethylene glycol process goes smoothly, but difunctionality is obtained only with Aroclors 1270 and 1271. Di-hydrolyzed 1268 is produced in the methanolic-alkali process (R-6). Lower-chlorinated biphenyls give mixtures containing mono- and diphenols, using the ethylene glycol process. Aroclor 5460 hydrolyzes to a mixture containing between 2-3 phenolic groups in the molecule. Attempts to replace more than 2 Cl atoms in Aroclor 1270 were unsuccessful.

Ethylene glycol hydrolysis of hexachlorobenzene to pentachlorophenol, and 1,2,4,5-tetrachlorobenzene to 2,4,5-trichlorophenol was demonstrated, but cannot compete with current Monsanto processes for these two materials.

The chlorine atoms most subject toward hydrolysis are those in octachloronaphthalene; at least four halogen atoms are replaced. However, toxicity of the starting compound eliminates this from any further consideration.

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A study of the successful di-hydrolysis of Aroclor 1268 by the methanolic process has been reported by J. R. LeBlanc (R-6). For hydroxyl di-functionality the ethylene glycol process is not recommended for Aroclor 1268 or lower analogs.

Samples of dihydrolyzed Aroclor 1270 and 5460 (when cleared by our patent department) should be prepared for development purposes and evaluated as curing agents for epoxy compounds.

Glycidyl ethers derived from a tri-hydroxy aryl compound might be well accepted by the trade and justify serious consideration by Monsanto. Hydrolyzed perchlorinated terphenyl is a possible candidate.

Recommendations for uses for hydrolyzed Aroclors are given in R-3. Octachloronaphthalene, because of its toxicity, should not be investigated further.

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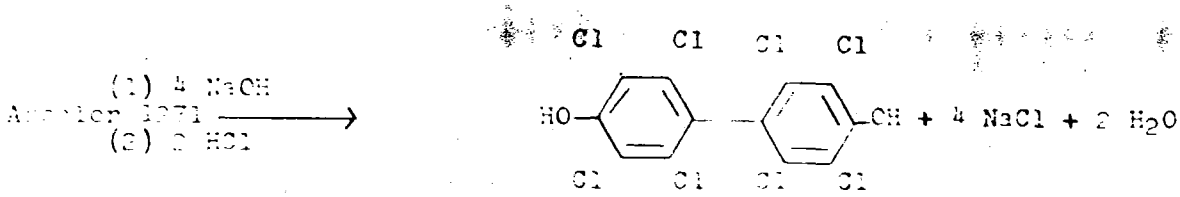
V. DISCUSSION

SYNTHESES Two chloro groups of decachlorobiphenyl (Aroclor 1271) hydrolyze with caustic in ethylene glycol solution at 160° to 200°C; Aroclor 1270 also gives diphenol.



This replacement reaction takes place with the lower chlorinated Aroclors 1268, 1[illegible], [illegible], 1254, and 124[illegible]. However, the yield of [illegible] is directly proportional to chlorine [illegible] Aroclor [illegible] give mixtures contain- [illegible]

[illegible] caustic [illegible] first with ethylene glycol to form the [illegible] C. This may be [illegible] by the water [illegible] distillation. Alth[illegible] necessary for [illegible] water [illegible] boiling point of the [illegible] mixture [illegible] C to 1[illegible] C, and the higher temperature [illegible] substantially.

[illegible] in ethylene glycol always gives diethylene glycol as a [illegible] product (Expt. 3[illegible]). A possible explanation for its formation may [illegible] via nucleophilic displacement of hydroxyl group of ethylene glycol [illegible] upon attack by a β-hydroxyethoxy anion, formed by NaOH removal [illegible] proton.

$$HOCH_2CH_2O^{\ominus} + HOCH_2CH_2OH \longrightarrow HOCH_2CH_2OCH_2CH_2OH + OH^{\ominus}$$

For each chlorine replaced in hexachlorobenzene, 0.52 mole of di- [illegible] glycol was isolated (Expt. 3[illegible]); more may actually form since [illegible] total material recovery of the mono- and diethylene glycol was [illegible] 75.[illegible]%.

No difference was observed between NaOH and KOH as hydrolysis agents, and solid or 50% aqueous caustic are equivalent, removing the water [illegible] in the latter case (Expt. 11 and 12). Neither small amounts of specially prepared copper (R-18) nor the use of a copper stirring blade changed the rate of hydrolysis.

As expected, hydrolysis [illegible] glycol proceeds [illegible] low temperature. Hexachlorobenzene gives pentachlorophenol in 19.2% [illegible] (Expt. [illegible])

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[illegible] of Aroclor 12[illegible] and 12[illegible] [illegible] The caustic [illegible] material is [illegible] than [illegible] the Aroclor charged and [illegible] mainly of iron compounds [illegible] either from the chlorination catalyst or from steel equipment (Expt. 4).

Hydrolyzed Aroclor 1270 and 1271 are best precipitated hot by adding the diphenolate salt solution to dilute HCl at 80-90°C. This yields a product which filters and dries rapidly (Expts. 18-20); precipitation at ice- or room temperature occasionally gave products which filtered slowly and dried very slowly; formation of a hydrate is a possible explanation for this low-temperature behavior. In most of the cases, the isolated hydrolyzed Aroclor 1270 is free of NaCl (Expt. 4). For accurate conclusions based on Cl analysis, NaCl was removed by hot water leaching.

Hydrolyzed Aroclor 1268 and lower analogs melt below 100°C, therefore are best precipitated and washed hot with vigorous stirring; layer separation is fast and complete. The final product dries without foaming at 100-120°C/20 mm. Hydrolyzed Aroclor 1262 and lower homologs were flash-distilled easily at 1-2 mm and showed neither foaming nor thermal decomposition; distillation residues were always low (Expt. [illegible]). The hydrolyzed product [illegible] over a wide range, as expected for a mixture of isomers. The color of the distillate is light yellow.

Directions for the hydrolysis of Aroclor 1262 and 1268 were passed to the Organic Chemicals Division (R-8,-9). They duplicated the procedure in the pilot plant (R-10,-12). The 1262 product was distilled.

Hydrolyzed Aroclor 1268 and all lower analogs hydrolyzed by the ethylene glycol process are mixtures of mono- and dihydroxy Aroclors. Misleading analytical data were obtained with early products. The hydroxyl group determination used at Dayton did not work well, so the OH content was estimated from the C, H and Cl values. Since the Cl contents were all low due to implete peroxide fusion, the calculated OH content was too high, hence indicated diphenol for mixtures of mono- and diphenol. Application of St. Louis analytical procedures for OH group and neutral equivalent were finally used and showed that hydrolyzed Aroclor 1268 and the lower analogs were all mixtures of mono- and dihydroxy Aroclors. J. Herbig, Polymer Evaluation Group, also arrived at this conclusion as a result of comparative studies of curing properties of glycidyl ethers prepared from hydrolyzed Aroclor 1271 and the 1262 analog. Independently, S. E. Gebura at Springfield came to this same conclusion. Because of the inconsistencies between early analytical data and the evaluation data, it was necessary to clarify several points by studies of a model compound of unequivocal phenolic difunctionality. Accordingly, 4,4'-bi-(2,6-dichlorophenol) was prepared by chlorination of 4,4'-diphenol in glacial acetic acid solution. Halogenation was rapid at 40°C, the precipitated material was filtered [illegible] and the filtrate still containing diphenol was re-chlorinated to [illegible] where [illegible] was formed (Expt. [illegible]). The combined

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[illegible] acid giving pure [illegible] conversion (Expt. [illegible]). This product [illegible] good analytical checks for chlorine, OH content, and N.E., using the revised analytical techniques. Concentration of the recrystallization mother liquors gave trichlorinated diphenols.

The original chlorination filtrate contained small amounts of what may be chlorinated quinones, analyzing for between 4 and less than 7 Cl atoms in the molecule (Expt. 49-52). Infrared spectra showed typical quinone absorption at 5.83 microns and a very weak-OH absorption. These minor by-products were not investigated further.

Studies of this model compound led to establishment of reliable analytical methods, and confirmed that a di-functional epoxy compound was required for optimum curing to resins. With this information, efforts were resumed to obtain di-hydrolyzed Aroclors, deemed necessary for the proposed applications. The ethylene glycol process was repeated successfully with Aroclors 1271 and 1270 in larger size batches (Expt. [illegible]). Curing studies of the diglycidyl ethers prepared from these products confirmed their di-functional nature.

Since Aroclor 1270 is no longer manufactured by Monsanto, the decision was made to concentrate our efforts on Aroclor 1268, which is still in interim production. A few runs were made using more drastic conditions, such as higher temperature and longer reaction times (Expt. 28), but the nearest approach was [illegible] of theory di-functionality (Expt. [illegible]). It was concluded from these experiments that even more drastic reaction conditions were needed to [illegible] di-functionality.

A [illegible] under [illegible] methanolic caustic at 1[illegible]°C was made. Although most of the [illegible] was lost by accident, a small amount was recovered and was [illegible]% di-functional (Expt. 37). J. R. LeBlanc subsequently developed a methanol-pressure process giving 100% diphenol from Aroclor 1268 (R-6).

Three runs (Expt. 21-24) on hydrolysis of Aroclor 1271 were made at [illegible]-160°C, each for three-hr. In the first experiment, the water was removed at the rate of formation, while in the second and third experiment the water was not removed. The third experiment was under N[illegible]. [illegible]% of the charged Aroclor reacted to give a mixture of mono- and dihydroxy Aroclor 1271, shown later by OH content. Color of the final product was best for the sample hydrolyzed in the absence of water. Data obtained, however, were insufficient to circumvent prior art information in a Monsanto patent disclosing hydrolysis of Aroclors (R-17).

A reduction in process costs could be obtained if other Monsanto-manufactured products could be made economically by the ethylene glycol hydrolysis process in the same plant. Hydrolysis of 1,2,4,5-tetrachlorobenzene to 2,4,5-trichlorophenol, the 2,4,5-T intermediate, went in 82% conversion (Expt. [illegible]). Data were passed to Nitro (Appendix [illegible]), [illegible] (R-20) [illegible]

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Hydrolysis of hexachlorobenzene goes smoothly to yield pentachlorophenol in 96.5% conversion and very high purity (Expt. 39). The sample was sent to St. Louis for purity determination and found to be superior to their reference sample. Monsanto's Santophen-20 is a mixture of tetra- and pentachlorophenol, prepared by chlorination of chlorophenols. The mixture is claimed to be biologically superior to pentachlorophenol.

One of our earliest investigations was to react p-dichlorobenzene with ethylene glycol in the presence of NaOH. Since no reaction took place at 150°C, part of the dehydrated mixture was heated in a bomb at 250°C for 10 hrs. A brittle, heat stable material, very soluble in water, was isolated. Analyses showed low carbon content (C, 33.55; H, 4.82) practically no chlorine (total 1.13%), and high sodium content (21.51%) The analytical values are most inconclusive (see Expt. 43-44), but no further studies were made.

Undistilled Aroclor 1168 behaves like 1268 on hydrolysis (Expt. 30). Hydrolyzed Aroclor 1268 is a dark brown material. For some applications it should be distilled. In such cases Aroclors 1168 should be used as starting material.

Ethylene glycol hydrolysis of chlorinated terphenyl (Aroclor 5460) gave a quantitative conversion to a mixture of di- and trihydroxypolychloroterphenyl (Expt. 35). In an (Expt. 36) attempt to increase the tri-functionality in the final product by using more caustic, results were inconclusive. Glycidyl ethers derived from hydrolyzed Aroclor 5460 were successfully prepared and cured. Hydrolysis of chlorinated terphenyl by the NaOH methanol pressure process is protected by a Monsanto patent to R. L. Jenkins (R-21).

Octachloronaphthalene and hexachlorodiphenyl oxide were hydrolyzed successfully by the ethylene glycol process. The chlorine atoms in the former compound were found to be the most reactive of any aromatic halogen compound studied to date (Expt. 41). More than four Cl atoms were replaced; the exact Cl content of the final material could not be determined since the product failed to dissolve in the reagent used for the H-8-57 Cl analytical method. Thiolysis and ammonolysis work also showed high chloro group reactivity. However, the toxicity of the octachloronaphthalene precludes further investigation of this as a raw material; it causes severe dermatitis. Hydrolyzed hexachlorodiphenyl oxide is a mixture of mono- and dihydrolyzed material (Expt. 45). The purpose of these two experiments was to broaden the scope of this hydrolysis method.

The ideal hydrolysis solvent from the standpoint of recovery should be water soluble. With this purpose in mind, o-nitroethylbenzene, an excellent solvent for Aroclor 1268, was investigated. It is dangerous

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In this [illegible] exotherm [illegible] at about [illegible]

Aroclor 1268 was dissolved in m(p)-isopropylbiphenyl, then NaOH was added along with less than molar amounts of ethylene glycol. Incomplete hydrolysis took place, and the product formed was much darker and messier than in all other runs (Expt. 46). This solvent is not recommended for further investigation.

Practically no reaction took place on heating Aroclor 1270 in pyridine and NaOH dissolved in ethylene glycol (Expt. 27).

Highly chlorinated biphenyls are soluble in very few solvents stable to NaOH. However, dimethyl sulfoxide is a good solvent for Aroclor 1270 and also dissolves KOH. None of these solvents, however, can compete price-wise with ethylene glycol which, in turn, is more expensive then methanol. It is conceivable that less ethylene glycol than given in Expt. 4 can be used, but the lower limits were not determined.

The recovery of the solvent can be simplified by distilling off part of the solvent after hydrolysis and before adding water to separate the NaCl formed.

Other possiblities exist for hydrolysis of Aroclors; for example, with super-heated steam or by fusion with NaOH. Both syntheses, based on commercial phenol processes, were demonstrated qualitatively in small size experiments made at 300°C using Aroclor 1268 and 1270 (Expts. 48 and 48-A).

EVALUATION DATA Converting hydrolyzed Aroclors to glycidyl ethers was the main objective of this program, and is the subject of a separate report (R-25).

Another potential use for dihydrolyzed Aroclor is as a curing agent for diglycidyl ethers, where it might replace the popular HET anhydride, hexachlorocyclopentadiene maleic anhydride 1 to 1 adduct. HET anhydride possesses flame-retarding properties, but a drawback is its thermal instability; it loses HCl. Hydrolyzed Aroclors are very heat stable and are recommended for further applications. Hydrolyzed Aroclor 1270 is a relatively strong acid, pH 3.5.

Biological toxicant properties of hydrolyzed Aroclors are given in R-7; no outstanding use is indicated.

Bisphenol A is patented for use as a stabilizer for PVC in U. S. 2,[illegible]. Samples of hydrolyzed Aroclor 1242, 1248, 1254, 1262, 1268 and 1270 were submitted for screening as stabilizers for PVC and [illegible]. Evaluation data are pending on these samples [illegible] on 8-[illegible]

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[illegible] PROCEDURES [illegible] hydrolyzed [illegible] especially 1268 [illegible] estimate [illegible] and hydrogen values [illegible] significantly [illegible] when the Aroclor [illegible] hydrolyzed product [illegible] Dayton's OH determination [illegible] product, our early conclusions were based mainly on Cl content, which turned out later to be too low also; this led to high estimates of OH content from which we assumed difunctionality in cases where mixtures of mono- and diphenols existed.

The St. Louis reports on the hydrolysis of Aroclor 1262 and 1268 (R-10, -12) contain a more accurate method for OH determination. Using this method, and the chlorine analysis developed John J. Hawkins at Dayton for highly chlorinated compounds, prior discrepancies in product identity were eliminated.

It was also found that Aroclor 1270 contains 71% Cl; this increases the molecular weight based on Cl content from 480 (Aroclor 1270) to 496.54 and consequently changes the calculated OH and N.E. values for hydrolyzed product. The NE values are more accurate than the OH (R-6). Table I contains the C, H, Cl, OH and NE values for the whole Aroclor series. All calculations are based on Cl as the reference value. It is recommended that a given Aroclor be analyzed since the chlorine content varies from batch to batch. Small chlorine differences give large changes in NE value.

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[illegible] E[illegible] [illegible] ILS

APPARATUS All experiments were conducted in standard taper Pyrex glass equipment. Hydrolysis was carried out in a 3- or 4-necked, round-bottom flask equipped with a stirrer, condenser and thermometer. In cases where the water was removed, a 10" Vigreux column carrying a Dean and Stark trap was used. In some experiments a freshly polished copper blade was used to study the influence of copper metal and the rate of reaction.

All melting points were determined on the Fisher-Johns block.

RAW MATERIALS All Aroclors used are Monsanto products. Aroclor 1271 was received from Anniston via St. Louis as Lot Number K-1583.

Aroclor 1270 represents material (600-700 lbs) from St. Louis sent to Everett and from there to Dayton; this is the only stock in the company. Chlorine content by [illegible] procedure reveals it contains [illegible]% halogen. Consequently its [illegible] molecular weight is [illegible] as shown in Table I. Other raw materials used are listed below:

Hexachlorobenzene		Eastman
1,2,4,5-Tetrachlorobenzene		"
Hexachlorodiphenyl Oxide	Dow X	Dow
Octachloronaphthalene (Halowax [illegible])		Bakelite
p-Dichlorobenzene		Monsanto
m,(p)-Isopropyldiphenyl		Monsanto
o-Ethylnitrobenzene		Monsanto
1,5-Pentanediol		Eastman

All other materials used are stock room items.

EXPERIMENTS

Hydrolysis of Aroclor 1271 and 1270

Expt. 1, 29[illegible] A mixture consisting of Aroclor 1271 ([illegible] mole, 249.5 g), ethylene glycol (4 moles, 248 g), 700 g of diethylene glycol diethyl ether, and 70 ml of toluene was stirred at 160°C all dissolved. The mixture was cooled to 80°C, then 1.2 moles (50 g) of powdered sodium hydroxide was added and reheated. At 130°C water was formed, and 29.2 g of water-ethylene glycol mixture was collected, n_D^{25} 1.36[illegible], during two hours. The pot temperature was increased in the meantime to 155°C.

[illegible] mixture was [illegible] at 15[illegible]°C. The cooled [illegible] with [illegible] and [illegible] (N[illegible]) went into

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[illegible] ...and then diluted ... mm. The material ... toluene and acetone, ... analysis, 32.45% C, 1.82 H; 59.37% Cl. These data check for dihydrolyzed Aroclor 1271 and not for the expected bis β-hydroxyethoxyoctachlorobiphenyl (51.6% Cl calculated). On diluting the wash waters, 2.4 g, mp. 240-45°C, was isolated. Conversion was 89.5% calculated as dihydrolyzed Aroclor 1271.

Expt. 2, 303300, 310401 This experiment was made with the intention of preparing bis(β-hydroxyethoxy)octachlorobiphenyl by first making the monosodium salt of ethylene glycol and then allowing it to react with Aroclor. Excess ethylene glycol (20 moles, 1240 g), was stirred at 150°C with sodium hydroxide (1.1 moles, 44 g), and 80 ml of toluene while the water was collected as formed. Aroclor-1271 (0.5 moles, 249.5 g) was added and this mixture was refluxed at 180°C for 20 hr cooled to 100°C, diluted with 250 ml water, acidified (75 ml HCl), filtered, and washed free of NaCl. A gray powder was isolated, (240 g) mostly soluble in hot 10% NaOH. Part of this material was extracted with ethanol using a Soxhlet; the alcohol soluble material is completely soluble in 5% NaOH and was identified as hydrdyzed Aroclor 1271, mp 215-18°C. The crude ethanol-insoluble material melts at 278-81°C; after recrystallization from benzene it melted at 287°C and was identified as unreacted Aroclor 1271.

Expt. 3, 310402-3, 341402 Hydrolysis of Aroclor 1271 was carried out according to the directions given in (R-17) example using one mole (498.[illegible] g) Aroclor 1271, 4.4 moles KOH (246 g), ethylene glycol (1500 g), and 2 ml water. This mixture was refluxed for 8 hr. at 180°C, filtered, and acidified to isolate 43[illegible] g of a light gray powder, mp 218°C. A recrystallized sample from benzene melted at 243°C. Conversion was 94.5%

Anal. Found (crude): C, 31.54; H, 0.71; res, 9.90; Cl, 59.72
(recryst): C, 33.32; H, 0.72; res, 0.18; Cl, 58.16
Calcd for: $C_{12}H_2Cl_8O_2$: C, 31.36; H, 0.45; Cl, 61.25

The high carbon content of recrystallized product is due to traces of carbon used to purify the product.

Expt. 4, 350204-5 This is considered the best method for hydrolyzing Aroclor 1270.

A mixture of Aroclor 1270 (1.36 moles, 5[illegible]2 g), ethylene glycol (38.[illegible] moles, 2350 g), sodium hydroxide pellets (7 moles, 280 g), and 130 ml toluene was charged to a 5-l, 4-necked flask equipped with a good stirrer, thermometer, 12" Vigreux column carrying a Dean and Stark trap, and a reflux condenser. The flask was heated by means of an electrical heating mantle. Reaction course details are given below:

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Time, min	Hot Temp, °C	H_2O Collected, ml	Vacuum, mm	Remarks
0	20		65	
12	52		65	
19	64		off	
38	80		"	
43	78		65	Solution turned lt yellow
[illegible]	[illegible]		65	
90	108		85	first drop H_2O collected
[illegible]	[illegible]	11	85	Collected 40 ml toluene
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	85	Collected 20 ml toluene
[illegible]	[illegible]	[illegible]	85	Collected 20 ml toluene
[illegible]	[illegible]	112	[illegible]	
[illegible]	[illegible]	[illegible]	85	Kept 5 hr at 200°C
[illegible]	[illegible]	[illegible]	85	No more H_2O was formed

The reaction mixtures was cooled to 80°C, diluted with 2 l of water (60°C), filtered rapidly (25 min.) through a [illegible] filter paper. The filtrate was neutralized to phenolphthalein using 150 ml HCl (1.8 moles). Residue was [illegible]. Total volume of filtrate plus wash water was 4.7 l. Equal parts of this solution were mixed, each over a [illegible] minutes period with stirring, [illegible] l of water and 125 ml of conc. HCl at 80-95°C. Precipitation of the product went smoothly, filtration was very fast (8 min). Residue was washed with 250 ml of hot water, then stirred for 1 hr in 3 l of water at 80°C, filtered and washed with 300 ml of boiling water. Residue dried fast; material was kept over the week-end in vacuum oven to collect 586 g of a light yellow powder. Analyses check very well for dihydroxy Aroclor 2270. Conversion was 95.3%.

Anal. Found: C, 31.41, 31.70; H, 0.66, 0.76; resi, 0.31, 0.64; Cl, 59.83, 60.54 (H-8-57 method) NE, 228.90, 229.70 (acetone as solvent), 231.0, 232.0 (butanol as solvent); OH, 7.26, 7.46

Calcd for [illegible] (Table I): C, [illegible]; H, [illegible]; Cl, 61.25; NE, [illegible]; OH, [illegible]

DSW 621378

STLCOPCB4095408

[illegible] Second Work-Up [illegible] Experiment [illegible]
[illegible] Material [illegible] Sample [illegible]
[illegible] Caustic Insoluble [illegible]
[illegible] Combustion Residue [illegible]

Expt. 4-A, 353892-3 The same charge and reaction conditions reported in detail in Expt. 4 were used in this run. It was noted that when the precipitated hydrolyzed product was suspended in hot water and refluxed, foaming occurs, which can be stopped with a few drops of 2-ethylhexanol. This reflux is unnecessary, however. Total collected product is 613 g, equal to 98.9% conversion.

Anal. Found: C, 31.27; H, 0.71; Cl*, 58.20, 58.07, 58.44, 58.47; OH, 7.33, 7.34.

*Chlorine run by the H-8-57 method.

Expt. 5, 353892-3 The same general procedure and charge was used as in previous expt. The mixture was stirred for 3.6 hr while the temperature increased from 45 up to 200°C, then was kept 6 hr at 200°C. It was diluted with 2 l of water at 80°C and neutralized to pH of 7.5 using 1.29 moles HCl. This solution, (4.6 l) was added to 3.4 l H2O and 250 ml HCl (conc.) and heated at 80°C. A nice precipitation of the phenolic material occurred; this filtered rapidly. It was suspended with stirring in 3 l of water, heated at 80°C, filtered and dried giving 613 g of material, equal to 98.9% conversion.

Anal. Found: C, 31.27; H, 0.71; Cl, 58.20, 58.07, 58.44, 58.47; OH, 10.49, 10.63 (potentiometric titration), 7.33, 7.34.

Expt. 6, 35-601-2 The purpose of this expt. was to hydrolyzed decachlorobiphenyl (Aroclor 1271) and use the product as an intermediate for polyester type fibers. A mixture consisting of Aroclor 1271 (1.2 mole, 599 g, Anniston sample) was stirred at 50°C with 2100 g ethylene glycol and 150 ml of toluene. At this temperature was added in two portions sodium hydroxide pellets (4.92 moles, 197 g). The mixture was heated over 2 hr from 110 up to 200°C while the water formed and toluene were removed azeotropically. The reaction mixture was kept for 1 hr. at 200°C then diluted with 1200 ml of water at 90°C and filtered; (no residue). The filtrate was divided into equal parts, and each added (1.2 hr) to 300 ml HCl plus 400 g ice to give a nice crystalline material. It was filtered, washed with 400 ml of water, then dried at 20°C and finally kept over night in an over (no vacuum) at 60-70°C. Yield was 556 g of a light yellow powder.

Anal. Calcd.: C, 31.36; H, 0.45; Cl, 61.25; OH, 7.36

Found: C, 31.15; H, 1.20; Cl*, 57.27; 57.37; OH, 7.48, 7.72

*Cl was analyzed by the unmodified method.

DSW 621379

STLCOPCB4095409

[illegible] containing Aroclor 1270 [illegible] 750 g), potassium hydroxide (6.75 moles, 378 g), ethylene glycol (2000 g), and [illegible] ml of water was refluxed for 10 hr at 156-160°C, then diluted with 3 l of water and filtered; residue was 36.2 g. Acidification and washing gave 676 g of a very light gray powder, mp 223°C, analyzing 32.48% C; 0.99% H; and 56.62% Cl (a rerun on Cl gave 58.01 and 58.16%); and OH, 6.09, 6.23%. At the time this experiment was made the OH determination by the H-7-46 method did not work (see 315636-8). Conversion was 96.6%.

Expt. 8, 316051 Aroclor 1270 (1.52 moles, 750 g), potassium hydroxide pellets (6.7 moles 375 g), ethylene glycol (2225 g), and 3 ml of water were refluxed at 156-160°C for 12 hr while all dissolved. The batch was diluted with 2 l of water, 1.3 g of residue was filtered off, and the filtrate was added at r.t. to 3 moles of 4 N HCl. The precipitate, still containing KCl, was washed with 4 l of water using a Waring Blender, giving 646 g of product, mp 223°C, analyzing 31.62% C; 0.76% H; 58.99% Cl; and OH (later det.) 6.10, 6.22%. Conversion was 92.6%. The 1.3 g residue contains 29.61% C; 0.51% H; 65.34% Cl. This could be monohydroxy Aroclor 1270; calcd. values are: C, 30.05; H, 0.21; Cl, 67.0.

Expt. 9, [illegible] Similar charge as in expt. 316051. The refluxing period was cut in half to 6 hr. In this case the insoluble residue was [illegible]. Since the acidified (at 20°C) mixture filtered very slowly, product was discarded.

Expt. 10, [illegible] Process studies were the purpose of the following experiments.

Potassium hydroxide was replaced by NaOH in this run. A mixture consisting of Aroclor 1270 (1.6 moles, 793 g), and ethylene glycol (27 moles, 2300 g) was heated up to 78°C. Sodium hydroxide flakes (7.1 moles, 284 g) were added, the temperature rising to 115°C in 7 minutes. After 5 more minutes, heating was started and 120 ml of toluene was added. The pot temperature was increased to 150° during the next 65 minutes. At this point water began to form, and was collected in the Dean and Stark trap. During the next 135 minutes the pot temperature was increased to 192°C and a total of 126 ml of water and ethylene glycol mixture was obtained. The reaction mixture was stirred for 1 more hr at 190-192°C, cooled to 80°C, and diluted with 1100 ml water. This solution was treated with 43 g of charcoal at 60°C. The filtrate was divided into equal volume and each added at room temp. to 450 ml of 5 N HCl and the product was washed. Yield was 690 g, conversion 98.8%.

Anal. Found: C, 29.25; H, 1.21; Cl, 58.50, 58.67 (modified method); OH, 7.67, 7.78; NE, 241, 242.

The OH and N. Eq. values do not check against each other.

DSW 621380

STLCOPCB4095410

heating to 200°C, 50% aqueous sodium hydroxide (5 moles, 400 ml as 50% aqueous solution) was added over 2 hr. Azeotroped water was drained as collected, and the pot temperature was increased to 135°C; neither foaming nor change in color occurred. The temperature was increased to 175°C over the next 75 min while all Aroclor 1270 dissolved. Finally, it was heated up rapidly to 200°C, the toluene was removed completely and the mixture was kept for six hr at 200°C. The solution darkened considerably after 3 hr. Filtration of the diluted solution with 700 ml H_2O gave no residue. The washed precipitate weighed 429.5 g, mp 226°C; conversion was 93.5%.

Anal. Found: C, 31.74; H, 0.85; Cl, 61.04, 61.06 (H-S-37); OH, 7.23, 7.90; rerun 7.09, 7.19.

Expt. 12, 358852-3 This experiment duplicates Expt. 11, the only variation being a 2-hr longer hydrolysis period at 200° (total 8 hr). This is an attempt to increase the OH value of the final product The charge consisted of Aroclor 1270 (1.26 moles, 576 g), ethylene glycol (2000 g), and 60 ml toluene, and the sodium hydroxide (6 moles, 480 ml 50%) was added at 120-130°C pot temperature over 1.5 hr. Total isolated product was 512 g, mp 226°C conversion was 95.6%.

Anal. Found: C, 31.89; H, 0.86; Cl, 60.63, 60.53, 61.35, 60.44; (H-S-57); OH, 7.31, 7.41.

Expt. 13, 353867-8 This experiment is a duplication of Expt. 12. Total collected hydrolyzed material was 528 g, mp 226°C conversion 98.8%.

Anal. Found: C, 31.56; H, 0.77; Cl, 60.76, 60.78 (H-S-57) OH, 6.81, 6.99, rerun 6.77, 6.86.

The caustic-insoluble filtration residue (5.9 g, mp above 314°C) is not unreacted Aroclor 1270, according to infrared absorption. This indicates some C-O-C linkage as well as -OH group. Combustion analysis shows: C, 17.87; H, 2.48; residue 46.31 (inorganic); Cl, 22.48, 22.49 (C-3 [illegible]).

Expt. 14, 353869 This experiment was a duplication of Expt. 13. Analysis gave poor OH values (5.92, 6.82), a rerun gave 7.40, 7.41% OH. The color of the reaction mixture as well as of final product was darker than in the last two experiments. This variation in color was traced to the ethylene glycol used. This was obtained from a different supplier (Matheson Coleman and Bell).

Expt. 15, 353876 A mixture of Aroclor 1270 (1.10 moles, 576 g), sodium hydroxide (six moles, 240 g), ethylene glycol (2200 g), and 10 ml

DSW 621381

STLCOPCB4095411

of water was [illegible] water was not rem[illegible] filtered reaction mixture was [illegible] 2 l of water, [illegible] equal parts, and added to 300 [illegible] 100 g of [illegible] precipitate formed filtered and dried exceptionally slowly [illegible] material weighed 513 g, mp 227°C, conversion 96%.

Anal. Found: OH, 6.39, 6.61.

The color of solution and final product was again very light, as in all experiments where Carbide and Carbon ethylene glycol was used.

Expt. 16, 353878-80 Previous experiment was repeated using exactly the same mole ratio and reaction conditions but an 18% larger charge was used in order to collect replicate data. Again, the filtration and drying step were slow as in the previous experiment. The light-colored product weighed 573 g, conversion 99%.

Anal. Found: OH, 5.94, 6.58, 8.48, 7.96

Expt. 17, 353875 Water was not removed during the hydrolysis step in this run. A mixture consisting of Aroclor 1270 (1.162 moles, 576 g), ethylene glycol (2200 g), sodium hydroxide pellets (6 moles, 240 g), and 10 ml water was refluxed at 162°C for 9 hr. The solution was diluted with 2 l of water at 80°C, filtered off from little residue and acidified cold. The precipitate dried very slowly. It was washedd in 3 l of water, giving 513 g of a very light colored material, mp 227°C, hydroxyl value 6.39, 6.61. These values indicate incomplete difunctionality.

Expt. 18, 353881-2 In this experiment the water was again removed at the rate of formation while the reaction temperature was increased to 198°C. At the same time attempts were made to explain the inconsistency in filtration and drying of the final product. A mixture consisting of Aroclor 1270 (1.16 moles, 576 g), ethylene glycol (2500 g) and 130 ml toluene was stirred at 65°C. The heat was turned off while sodium hydroxide (6 moles, 240 g pellets) was added at once causing the temperature to raise 20°C in the first 5 minutes and 15°C in the next 4. Reaction temperature was gradually increased to 200°C removing the water as it was formed. The mixture was heated for 7 hr at 200°C and diluted with 1-l water at 90°C. Equal parts of the filtrate were added to 300 ml conc. HCl plus ice. Filtration was rapid. When the cake was exposed to air at r.t. for 48 hr it dried slowly; at 40°C in vacuum oven it started to get messy and sticky. This material was suspended in 2 l of water at 80°C, stirred for 2 hr and filtered (fast) to give 501 g, mp 225°, conversion 94.6%.

Expt. 18A, 353884-5 Same charge was used as in Expt. 18. The reaction mixture was heated for a shorter time (5.5 hr) at 200°C. The mixture was acidified cold, filtered and kept on the Buchner funnel over the weekend. Product turned gooey. It was worked up by adding to water under good stirring (slow process). Finally [illegible] g

DSW 621382

STLCOPCB4095412

[illegible] OH, mp 225°C. No [illegible] which was not [illegible]; conversion was 95.9%.

Expt. 19, 353837 The purpose of this experiment was to study further the acidification and filtration steps.

The charge was exactly the same as in the previous run except that the NaOH was added at room temperature. After removing the water and refluxing for 7 hr at 200°C the reaction mixture was diluted with 2.1 of water, filtered and neutralized to phenolphthalein using 90 ml conc. HCl; total filtrate 4.4 l. Part (1.1 liter) of this solution was added over 1.2 hr to 60 ml conc. HCl plus 600 g ice while the container was kept in ice water. Material filtered fast, but the residue contained some sticky material. The filtrate cake kept at r.t. over the weekend, turned hard. Material was ground by hand giving 128 g. of product, mp 226°C.

The next approach was to precipitate the hydrolyzed Aroclor 1270 at 80°C to confirm a test tube observation of clean separation.

Part (370 ml) of the original hydrolyzed Aroclor 1270 solution was added over 23 min to 20 ml of conc. HCl and 200 ml H_2O. The product precipitated in a finely divided form. It was filtered (warm) and dried very rapidly to give 46.5 g, mp 227°C, of a very light-colored material. This improved procedure was confirmed on a larger scale batch when 2.9 l of this solution was added over 2 hr to 140 ml conc. HCl and 1.4 l H_2O heated at 80-85°C. It was filtered hot (very fast), washed with 550 ml of water, and dried (very fast) to collect 354 g as a fine powder. Total combined fractions weighed 528, equal to 98.6% conversion.

Anal. Found: OH, 7.74, 7.79, 7.08, 7.[illegible]9.

Expt. 20, 353890 To confirm the previous observation, Aroclor 1270 (1.26 moles, 623 g), sodium hydroxide (6.5 moles, 260 g), ethylene glycol (2100 g), and 130 ml of toluene were mixed at room temperature and heated to 200°C over a 4-hr period, draining the water as it formed. After 6 hr at 200°C it was diluted with 2.1 l water, filtered while at 80°C, and added over 2 hr to acid solution kept 80°C. Again, filtration and drying went very rapidly, giving 558 g product with 7.28% OH; conversion was 96.2%.

Expt. 21, 354632 The purpose of the next three experiments was to study the rate of hydrolysis and the quality of product in the presence and absence of water. A mixture of Aroclor 1271 (0.15 mole [illegible] g), KOH (0.67 mole, 37.5 g), ethylene glycol (375 g), and 60 ml toluene was heated up to 155°C and kept for 3 hr. At this temperature the water was isolated at the rate it was formed. The reaction mixture [illegible]

DSW 621383

STLCOPCB4095413

ml of H_2O and filtered from 5.3 g residue. The color of the filtrate was 6.5 Gardner. Isolated material was 64 g with mp 234-5°C.

Expt. 23, 334639 In this run with identical charge and reaction conditions, the water was not removed, but hydrolysis was carried out under N_2 to study its affect on the color of the final product. Filtration gave 8.5 g unreacted Aroclor and the color of the filtrate was 2.5 Gardner. Isolated hydrolyzed material weighed 60 g, mp 234-5°C, and its color was lighter than the previous experiments.

Analyses found for the three experiments are practically identical and are tabulated below.

Expt.	Wt. g*	C	H	Cl	OH
21	63.5	31.28	[illegible]	60.12;60.46	6.42;6.51
[illegible]	64.0	31.78	[illegible]	[illegible]	4.43,4.87
23	60.0	31.75	[illegible]	59.41,59.12	5.83,6.05
Calcd.		31.30	[illegible]	61.5	7.40

*Refers to washed and dried hydrolyzed Aroclor 1270

Expt. 24, 228993-9 With the purpose of introducing more than two hydroxyl groups into the Aroclor molecule, a mixture of Aroclor 1270 (0.96 mole, 480 g), sodium hydroxide (8.8 moles, 352 g), ethylene glycol (2000 g), and 130 g toluene was heated under good stirring. At 140°C water began forming, then ceased after 110 min as the pot temperature reached 190°C. Heating was continued for 2 hr at 190-205°C. The next day it was reheated at 210-215°C for 14 hr with removal of some low boilers.

The reaction mixture, much darker than in previous experiments, was diluted with 1200 ml of water and neutralized using 2.93 moles conc. HCl. The residue (122 g) turned red on drying indicating the presence of sodium phenolate. This residue was suspended in 300 ml of water, and 10 ml conc. HCl was added. The suspension was filtered and washed to give 88 g, analyzing C, 3.84; H, 2.24; residue 84.9; Cl, 2.77, [illegible]; the product is a mixture. The original filtrate was acidified at 90° by the usual procedure, but failed to give a clean crystalline precipitate. Finally 78 g of solids were isolated as a gray powder, mp 175-85°C.

Anal. Found: [illegible] H, 1.36 (propriety) Cl, 52.32, 2.50; OH, [illegible]

DSW 621384

STLCOPCB4095414

These elemental values add up to 98.5[illegible] [illegible] the potentiometric end-point was very [illegible] found N. Eq. values of 228.1 and 238.1 are subject to error.

Data are insufficient to indicate that the isolated product is a mixture of di- and trihydroxy Aroclor 1270.

Expt. 25, 353854-7 In another attempt to hydrolyzed more than 2 chlorine atoms, a mixture of Aroclor 1270 (0.48 mole, 240 g,) 1050 g ethylene glycol (1050 g), and 60 ml toluene was stirred at 120°C while NaOH (5 moles, 400 ml 50% aq. solution) was added. The water was distilled off continuously. The reaction mixture was stirred at 200°C for 10 hr then diluted with water. It was filtered (traces of residue), acidified, washed, and dried to give 206.2 g of light gray powder, mp 216-19°C.

Anal. Found: C, 31.07; H, [illegible]; Cl, 58.71, 58.43, 58.48, (H-8-57); OH, 7.28, 7.40.

The analyses check for [illegible]

Hydrolysis of Aroclor 1268

Expt. 26, 310444 A mixture consisting of Aroclor 1268 ([illegible] moles, [illegible] g), KOH [illegible] g), ethylene glycol ([illegible] g), and [illegible] ml of water was refluxed for 8 hr to isolate an alkali-soluble material. For [illegible] of a glycidyl ether of this see 310448.

Expt. 27, 341265 The purpose of this experiment was to try to increase the difunctionality in hydrolyzed Aroclor 1268. A mixture consisting of Aroclor 1268 (0.5 mole, 257 g), sodium hydroxide (2.75 moles, 110 g), ethylene glycol (800 g), 3 g of Cu powder, and 80 ml toluene was heated to 200°C over 1.5-hr; then kept at 200-206°C for 10 hr. The reaction mixture was diluted with 1 liter of water, filtered, and then added to 400 ml 6 N HCl at 80-90°C. The precipitate was washed in a preheated separatory funnel with 2 x 250 ml of boiling water and then heated to 160°C/1 mm to give [illegible] g residue.

Anal. Found: C, 37.81; H, [illegible], 53.5, 53.35; OH 7.64, 7.84.

Combustion analysis of this sample gave 4.78% residue hence results are meaningless; all data above are calculated are residue free material.

Hydrolysis of Aroclor 1168

Expt. 28, [illegible] A mixture consisting of [illegible] Aroclor 1168 [illegible] g, analyzing [illegible]

DSW 621385

STLCOPCB4095415

potassium hydroxide (2.5 moles, 250 g), ethylene glycol (1500 g), 200 ml of water was refluxed for 8 hr. The mixture was heated up to 190°C (pot temperature) and 2.5 moles of water was collected. The reaction mixture was separated while still warm. It was washed (hot) free of ionic chlorine. The residue was heated up to 170°C/0.5 mm (pot temperature) to collect 420 g of dark resin, mp ca. 70°C; conversion was quantitative.

Anal. Found: C, 35.04; H, 1.39 (res. 0.26); Cl, 56.35, 56.83.

Calcd: C, 34.52; H, 0.80; Cl, 57.00.

Hydrolysis of Aroclor 1262

Expt. 29, 316053 A mixture consisting of Aroclor 1262 (1.5 moles, 534 g), potassium hydroxide (6.7 moles, 375 g), and 3 ml of water was refluxed for 8 hr. One more mole KOH was added and the mixture was heated for 2 hr. The mixture was diluted with 2 l of water, filtered, and acidified to form a viscous liquid. This was easily washed at 100°C in a separatory funnel. Total product was 510 g, n_D^{25} 1.6268; conversion was 97%.

Anal. Found: C, [illegible]; H, 2.24; res. 0.20; Cl, 46.82

Calcd: C, 44.22; H, 1.41; Cl, 48.50

NE 308.6 indicating a mixture of mono- and dihydroxy Aroclor 1262.

Expt. 30, 3[illegible]-7 With the object of increasing the difunctionality, higher temperature and longer reaction times were investigated. Aroclor 1262 (1 mole, 387.0 g), sodium hydroxide (5.5 moles, 220 g), ethylene glycol (1100 g), and 120 ml toluene was heated to 195°C while water was removed as it was formed. This mixture was kept at 195-200°C hr, then heated 3 hr at 202-8°C. It was diluted with 1.5 l H_2O, filtered, acidified with 270 ml HCl (conc.), washed to neutrality at 80°C (good layer separation), and finally distilled to collect (1) 266 g, bp 186-215°C/2-4 mm (pot temperature 190-2[illegible]°C) and (2) residue, 21 g.

Anal. Found: (1) C, 41.84; H, 1.85; Cl, 47.66, 47.67; OH, 8.74, 8.75.

(2) C, 46.08; H, 2.76; Cl, 37.07, 37.10.

The sum of C, H, Cl and O values found for (1) adds up to 99.3%. Cl value was rerun by the H-8-57 method. Based on the OH value fraction (1) contains 91.5% dihydroxy compounds.

Hydrolysis of Aroclor 1254

Expt. 31, 316062 Aroclor 1254 (1.75 moles, 565 g), potassium hydroxide (7.83 moles, 438 g), ethylene glycol (1800 g), and 3 ml of water were refluxed at 150°C for 1 hr, then diluted with [illegible]

DSW 621386

[illegible] excess HCl. The bottom organic layer [illegible] water [illegible] 55 g of crude viscous [illegible] at 1.5 mm gave [illegible] 536 g, bp 155-185°C, n_D^{25} 1.6345, of a yellow liquid, and (II) 16 g, bp 186-197°C (pot temp 235°C), of a dark yellow resin.

Anal. Found: (I) C, 45.40; H, 1.62; Cl, 50.23, 50.11.
(II) C, 43.74; H, 2.03; Cl, 47.25.

Calcd: for dihydroxy: C, 50.20; H, 2.44; Cl, 36.3

Hydrolysis of Aroclor 1248

Expt. 32, 234630-1 A mixture consisting of Aroclor 1248 (2.5 moles, 721 g) sodium hydroxide (11 moles, 440 g, flakes), ethylene glycol (24.2 moles, 1500 g), and 150 ml of toluene was refluxed while the water was removed. The mixture was heated for 9 hr at 208-12°C. The color of this mixture was darker than in similar runs using the more highly chlorinated Aroclors. The reaction product was diluted with 1.5 l of hot water, added to a preheated separatory funnel. Very little alkali-insoluble material was obtained. The alkaline solution was added to 500 ml conc. HCl plus 300 ml H_2O heated at 80°C and washed to neutrality. Fractional distillation at 1 mm gave:

	Bp°C	Wt. g	n_D^{25}	Analyses % C	H	Cl	OH
1	113-30	[illegible]	[illegible]				
2	131-5[illegible]	[illegible]8	[illegible]	54.32	4.47	25.31	
3	151-80	180	1.6204	55.65	3.64	30.09	8.29, 8.30
4	181-210	270	1.6387	57.27	3.52	30.63	9.79, 9.92
	Residue	61		58.50	4.24	22.75	
	Anal. Calcd. for monohydroxy;			53.40	2.63	38.00	6.32
	for dihydroxy:			57.20	3.23	26.90	13.51

The various fractions represent a mixture of mono- and di-hydroxy Aroclor 1248. Conversion was 87.2% calculated as mono-hydroxy Aroclor 1248.

Hydrolysis of Aroclor 5460

Expt. 33, 328965-7 A mixture of Aroclor 5460 (1.44 moles, [illegible] 1.20 [illegible] 58.88, 59.04, 58.38 [illegible] moles, [illegible] ethylene glycol [illegible] moles,

DSW 621387

STLCOPCB4095417

[illegible] the water [illegible] stirring [illegible] hr at [illegible] of water, [illegible] residue), and divided into two equal volumes. In one case the solution was added to 400 ml conc. HCl and water (1 to 1) at 50°C. The product precipitated and was easily filtered off, giving 4.3 g, mp. 67-72°C (I).

An attempt to neutralize the second half of the filtrate by adding acid gave a glue-like product. It was redissolved in 4N NaOH and then dropped into excess HCl to isolate 302 g of product (II). Conversion was 94.5% calculated as dihydroxy compound.

Anal. Found: (I) C, 42.61; H, 2.32; Cl, 43.79, 43.97 OH, 9.14, 9.51

(II) C, 42.46; H, 2.44; res. 1.64; Cl, 45.48, 45.68

OH, 8.26, 8.67, 8.18, 8.45.

Compound failed to dissolve completely in reagent used for OH determination.

The NE found for I was 321.3, 324.4; but this value is meaningless since the sample failed to dissolve completely in reagent. The Cl content of sample II was rerun later by the H-8-57 method giving Cl, 46.19, 46.25, 46.72.

Anal. Calcd. for dihydroxy: C, 41.0; H, 1.24; Cl, 51.0; OH, 6.45

trihydroxy: C, 42.5; H, 1.47; Cl, 45.8; OH, 10.[illegible]

The 7.1 g of caustic-insoluble residue was analyzed: C, 30.57; H, 2.92; res 36.00; Cl, 25.3[illegible]; 25.61. Again, this residue is high in inorganic content.

Expt. 34, 341260-1 The purpose of this experiment was to increase the hydroxyl content of the Aroclor 5460 hydrolyzed product by using more caustic and a longer reaction time. A mixture of Aroclor 5460 (0.955 mole, 540 g), sodium hydroxide (6.6 moles, 264 g flakes), ethylene glycol (30 moles, 1860 g), and 130 ml toluene was heated to 200°C over 3.3-hr period, then kept for 5 hr at this temperature. The material was diluted at 90°C with 1.5 l of water, filtered and added to 800 ml HCl water (1 to 1). An oil formed and did not solidify after 48 hr at room temperature. The organic layer was dissolved in 1.5 l of acetone, filtered from NaCl, then concentrated to 1 liter. This solution was added in small portions to water stirred in a Waring Blendor to give a total of 414 g material, mp 80-85°C; conversion was 85.5%.

Anal. Found: C, 45.09; H, 2.45; res. 0.35; Cl, 40.56; 49.92, 40.90;

[illegible]

DSW 621388

STLCOPCB4095418

Calcd for [illegible]

for tetra OH: C, 44.10; H, 1.73; Cl, 40.3; OH, 13.85

Cl determination by the C-8-57 method. The elemental values for C, H, Cl, and O add up to 97.5%. With the exception of OH, the found values indicate close to a tetrahydroxy polychloroterphenyl. Again the product failed to dissolve in the reagent used for OH determination.

Expt. 35, 360228-9 Since incomplete dihydrolysis of Aroclor 1268 occurs in ethylene glycol at reflux temperature, the next step was to hydrolyze under pressure using methanolic alkali. A mixture of Aroclor 1268 (0.33 mole, 151 g), sodium hydroxide flakes (1.58 moles, 63 g), and methanol (14.1 moles, 450 g) was heated for 1 hr at 190°C in a 1 liter bomb (No. 2, heated on the rocker); the pressure increased to 500 psig. The reaction mixture, free of residue, was concentrated to 241 g and then acidified at 90°C to a pH of 2 using 87 ml conc. HCl. This was separated and washed [illegible] times at 90°C until free of ionic chlorine. The organic layer was dried by heating up to 140°C/13 mm. The flask broke in the oil bath and all material was lost.

In order to gain some benefit from this experiment, the wash water was worked up to isolate 2.5 g of hydrolyzed Aroclor 1268 mp [illegible]°C, analyzing 7.64 and 8.24% OH, equal to 95% difunctionality. This is higher in difunctionality than in all previous runs on hydrolysis of Aroclor 1268 and lower homologs.

Difunctional hydrolyzed Aroclor 1268 was obtained by methanolic alkali hydrolysis by J. R. LeBlanc (R-6).

Hydrolysis of hexachlorobenzene

Expt. 36, 328961 The purpose of this experiment was (1) get data on the ethylene glycol recovery, (2) to use hexachlorobenzene as a model molecule, and (3) prepare pentachlorophenol by the hydrolysis of hexachlorobenzene. A mixture of hexachlorobenzene (1 mole, 284.8 g), sodium hydroxide (2.15 moles 86 g flakes), ethylene glycol (3 moles, 930 g), and 110 ml of toluene was refluxed. The water formation started at 103°C pot temperature, and was completed 31 min later at 118°C pot temperature. Pot temperature was increased gradually to 129°C in the next 25 min and then turned off. No more hexachlorobenzene sublimed on the flask, indicating that hydrolysis was complete. The reaction mixture was filtered (no residue) then the ethylene glycol was distilled giving 212 g. The residue was diluted with 1000 ml of water and acidified with conc. HCl (1.2 moles). The mixture is too thick to determine the amount of acid needed for neutralization. The precipitate was filtered off, washed with 250 ml of water and dried to collect 127 g still containing [illegible] The material [illegible] water (1 liter) and filtered [illegible] 2% [illegible] powder equal to 95% conversion [illegible]

DSW 621389

STLCOPCB4095419

Anal. Calcd: C, 27.05; H, [illegible]; Cl, 65.5

Found: C, 27.40; H, 1.25; Cl, 64.72, 65.04

The filtrate was concentrated to collect an additional 445.5 g(II) of ethylene glycol, bp to 187°C, n_D^{25} 1.4291. The semisolid residue was filtered off (mostly NaCl) and the filtrate distilled to collect 54.5 g (bp 120-30°C/20 mm) of diethylene glycol equal to 5.8% of the total ethylene glycol charged.

Anal. Calcd: C, 45.27; H, 9.50; OH, 32.03

Found: C, 45.59; H, 10.16; OH, 31.99, 32.02

Total ethylene glycol recovered was 657.4 g (I + II) is equal to 70.8% of charge.

Expt. 37, 328972-3 The purpose of this experiment was to study the use of ethylene glycol at a much lower temperature (110-115°C) using hexachlorobenzene as model compound. A mixture consisting of hexachlorobenzene (1 mole, 284.8 g) and ethylene glycol (20 moles, 1240 g) was heated up to 180°C without giving complete solution. It was then cooled to 90°C with stirring, and NaOH (1.075 moles, 43 g) and 150 ml of toluene were added. The mixture was heated at 110°C pot temperature, and water began forming. The pot temperature was kept between 114-115°C for 5.5 hr. Most of the water-ethylene glycol mixture (24 ml) was collected during the first hour of heating (total volume 41.2 ml, n_D^{25} 1.3800 to a 49% water-ethylene glycol mixture). This reaction mixture was cooled to 65°C, diluted with 700 ml of water, neutralized to a pH of 8, using 0.79 moles of HCl, and filtered off from 229.5 g equal to 80.8% theory unreacted C_6Cl_6, mp 227°C. Filtrate was acidified to a pH of 2, filtered giving 32 g pentachlorophenol, mp 185°C, analyzing 65.55, 65.59% Cl; calcd. 66.2%. This shows that 19.2% of the hexachlorobenzene charged reacted at 115°C to give pentachlorophenol. No ether-alcohol was formed.

Hydrolysis of octachloronaphthalene

Expt. 38, 353876-7 A mixture consisting of octachloronaphthalene (Halowax 1051-X, 0.5 mole, 202 g), sodium hydroxide (5 moles, 200 g), ethylene glycol (1500 g), and 10 ml of water was heated while it was stirred with a copper stirring blade. The solution turned dark at 130°C. Duration of heating was 8 hr at 156°C. The reaction mixture was diluted with 1 liter of water and filtered from 1.8 g insoluble material, mp 300°C. Neutralization of the filtrate used only 1.25 moles of acid. This solution was dropped into 300 ml HCl conc. to precipitate a very dark product. [illegible] very rapidly to yield 33 g of a brown powder mp 125-[illegible]°C

Anal. Found: C, [illegible]; H, [illegible]; Cl, [illegible]; OH, 7.7[illegible]

DSW 621390

STLCOPCB4095420

[illegible] reagents used [illegible] (and period) the [illegible] add [illegible] up to only 87.08%.

Expt. 39, All details on the hydrolysis of 1,2,4,5-tetrachlorobenzene to 2,4,5-trichlorophenol are given in R-19, these data were for cost comparison with Nitro's hydrolysis process (methanol).

Attempts the Hydrolyze p-Dichlorobenzene

Expt. 40, 294219, 298315 No reaction took place on heating a mixture of p-dichlorobenzene (2 moles, 294 g), sodium hydroxide (4.8 moles, 192 g pellets), ethylene glycol (12 moles 744 g), and 200 ml toluene. After removing the water the mixture was refluxed for 6 hr at 150-160°C. Only starting materials and some diethylene glycol were formed.

Expt. 40. In this experiment copper powder was investigated as a possible catalyst for hydrolysis. A mixture consisting of p-dichlorobenzene (2 moles, 294 g), sodium hydroxide (4.8 moles, 192 g pellets), ethylene glycol (12 moles, 744 g), copper powder (3 g), and 100 ml of toluene was heated up to 150°C and water was collected as it formed. Since the material failed to react on heating for 4 hr at 150°C (no ionic chlorine formation) half of this mixture was heated at 210°C for 12 hr in a bomb on a rocker. The viscous reaction mixture formed was diluted with ethanol, filtered and concentrated to distill off ethylene glycol. A fraction (7 g) boiling at 100-120°C/1 mm. n_D^{25} 1.4812 was identified as diethylene glycol. Anal. Calcd: C, 45.3; H, 9 ---: Found: C, 46.90; H, 9.52. After heating up to 250°/1 mm (bath temperature) 62 g of brittle brown resin was isolated. It is water soluble and forms brittle fibers. Analysis gave inconclusive results.

Anal. Found: C, 33.31; 33.78; H, 4.34, 5.30.

Total: Cl: 1.11, 1.15; Na, 21.20, 21.42

We have no explanation for the low carbon content in a mixture very low (1.13%) in total chlorine.

Hydrolysis of Hexachlorodiphenyl Oxide (Dow 6X)

Expt. 41, 334627, Hexachlorodiphenyl ether (1.5 moles, 566 g), sodium hydroxide (6 moles, 240 g flakes), ethylene glycol (1000 g), and 120 ml toluene was heated up to 200°C over a 1-hr period, while water and low boilers were removed. This mixture was stirred for 5.5 hr at 200-208°C. The dark solution was diluted with [illegible] acidified, washed to neutrality, and distilled as [illegible]

DSW 621391

STLCOPCB4095421

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Analyses C	H	Cl
[illegible]	[illegible]	[illegible]	[illegible]	1.5839	40.44	3.30	40.79
2	116-30	15	67	1.5830	38.13	2.21	49.64
3	131-140	15	116.8	1.5899	36.44	1.95	51.81
4	100-20	1.	24	1.5931	33.86	1.92	53.21
5	121-40	1	28	1.5940	33.99	2.11	52.46
6	141-80	1	9.7	1.5895			
7*	19-220	1	176	1.6305	42.40	2.23	43.12
8**	Residue		489.5				

*OH value found: 8.38, 8.39%

**Combustion residue [illegible]%

Anal. Calcd for dihydroxy tetrachlorodiphenyl ethers:

C, [illegible]; H, 1.[illegible]2; Cl, [illegible]; OH, 10.0

for 2 Dow X6: C, [illegible].18, H, 1.[illegible]; Cl, [illegible].8

Expt. 42, 334615-6 The purpose of this experiment was to hydrolyze Aroclor 1268 using a water insoluble solvent which would simplify the recovery of the solvent. A mixture consisting of Aroclor 1268 (0.5 moles, 227 g), sodium hydroxide flakes (2.1 moles, 84 g), and isopropylbiphenyl (m,p-mixture, 500 g), was heated to 130°C, then 20 g of ethylene glycol was added. This was heated under N_2 220°C for 3 hr while a total of [illegible] ml of water was separated. The black solution was diluted at [illegible]°C with 700 ml of water, filtered (slow, very little residue), diluted with 200 ml of ethylene glycol, and acidified under good stirring. A total of 1.34 moles of NaOH have reacted indicating incomplete reaction. The reaction mixture was quite messy and was discarded.

Expt 43, 323134 o-Ethylnitrobenzene, a Monsanto by-product, is an excellent solvent for Aroclors. A mixture consisting of Aroclor 1268 (1 mole, 454 g), potassium hydroxide (4.4 moles, 247 g), and o-ethylnitrobenzene (700 g) was stirred in a 3-necked flask equipped with Dean and Start trap carrying a condenser and a thermometer and heated slowly. Suddenly, a detonation took place when the pot temperature was close to 100°C, breaking the stirrer and trap, but not the flask. Everything in the flask vaporized. This confirms the danger of using o-nitro-[illegible] benzenes as [illegible]

DSW 621392

STLCOPCB4095422

Expt. [illegible] 229 [illegible] in the [illegible] was [illegible] Rocelin [illegible] at the ACS 1958 [illegible] meeting by replacement reaction of hexachlorobenzene catalyzed by pyridine. A mixture consisting of Aroclor 1270 (0.05 mole, 24.7 g), NaOH (4.4 g powder, dry), pyridine (3.8 moles, 300 g), and ethylene glycol (0.5 mole 31 g, added increase alkali solubility) was refluxed for 4.5 hr, cooled and acidified with 4 moles of conc. HCl. A brown powder (23.4 g) was isolated. A sample of this solid was extracted with aqueous NaOH and acidified to obtain very small amounts of caustic-soluble material analyzing C, 33.59; H, 1.09; Cl, 57.81, 57.75, 58.10; N, 1.46. The product failed to dissolve in the reagent used for H-8-5 chlorine method, therefore, the found values are most likely too low. The caustic-insoluble material is unreacted Aroclor 1270, mp 294°C. Very little or no reaction took place.

Hydrolysis of Aroclor 1268 using steam

Expt. 48, 323:21 Aroclor 1268 (0.5 mole, 227 g) was heated up to 250°C under N_2 using a tubular reactor, 35 by 5 cm with a sintered glass bottom for gas dispersion. When the Aroclor sample was free of HCl at 200-/00°C, steam at 28 -300°C was passed through the mixture. HCl was identified immediately in the off gases in low concentration. Sublimation, temperature control difficulty, and steam rate variation complicated the experiment. The same run was repeated using copper powder (1 g) as catalyst. Again, HCl was detected immediately in the off gas. Both experiments were made only on a qualitative basis.

Expt. [illegible], 32[illegible] A small sample of Aroclor 1268 was heated at [illegible]°C (in test tube) and powdered sodium hydroxide was added. The [illegible] was kept for 5 minutes at 300°C. The reaction product was ground to a fine powder, extracted with water. Acidification with HNO_3 and addition of $AgNO_3$ gave a copious AgCl precipitate. The identical experiment was repeated with Aroclor 1270 with similar results.

Chlorination of 4,4'-biphenol

Expt. [illegible], 33-[illegible]-3, 3-12[illegible] Cured glycidyl ethers derived from hydrolyzed Aroclor failed to show expected properties, this failure could be traced back to the presence of mono hydroxy compound, which would behave as a chain stopper. Studies of a model molecule, 4,4'-bi-(2,6-dichlorophenol), derived from chlorinated 4,4'-bisphenol, were chosen to test intrinsic polymerization character of glycidyl ethers of this chlorinated diphenol type. Halogenation of 4,4'-biphenol was carried out according the general procedure given in R-15. Starting material was from Dow, analyzing C, 78.03; 78.24; H, 5.65, 5.68; OH, 18.30. Calcd: C, [illegible] H, 5.63; OH, 18.30. A mixture consisting of the 4,4'-diphenol [illegible] was stirred in a 1-liter flask with [illegible] at [illegible] Solid obtained [illegible] was dissolved in [illegible]

DSW 621393

STLCOPCB4095423

passed through the [illegible] and the [illegible] precipitated suddenly, was filtered off, and washed with glacial acetic acid; 67 g was obtained, mp 230°C (I). The filtrate and wash solvents were chlorinated further to isolate 27 more g, mp 230-32°C (II). When the filtrate was diluted with 1 liter of water, 12 g of a yellow powder was obtained.

Melting points of fraction I and II check with those given in R-15 for 4,4'-bi(2,6-dichlorophenol); OH values also check very well but Cl values by the C-35-55 method were too low. Reruns on Cl by the H-8-57 method gave the good results given below:

Anal. Calcd: Cl, 43.85; OH, 10.48; NE. 162.

Found: I; Cl, 42.07, 42.30; OH, 10.69, 10.94, NE. 157.7, 158.65

II; Cl, 43.26, 43.64; OH 10.59, 10.60.

The OH values found for I check very well with those calculated (10.76) from the NE found. Fraction III is a brown-orange material, it melts between 60-65°C and analyzes 59.00, 59.11% Cl; infrared shows typical quinone absorption at 5.83 microns and very weak OH content. The Cl content found indicates close to 8 cl atoms in the molecule.

Expt. 48, 341251-2 The previous experiment was repeated using a larger charge, 4.4'-Diphenol (1.5 moles, 279 g) was dissolved in 3400 g of acetic acid and chlorinated at 40°C. The precipitated material was filtered off and washed to give 246 g, mp 205-8°C (I). The filtrate was rechlorinated to give 193 g of product, mp. 237°C (II). The filtrate was diluted with 3 l of water, giving 42 g of red powder mp. 55-60°C (III).

Anal. Found: I, C, 47.90; H, 2.48; Cl, 39.57, 40.18; OH, 10.89, 11.06

II, Cl, 43.12, 43.28; OH, 10.26, 10.33

III, C, 33.46; H, 1.55; Cl, 56.56, 56.93

Fraction I is a mixture of tri- and tetrachloro product, II checks for the tetrachlorodiphenol, while III is again a highly chlorinated quinone type product, red in this experiment and yellow in the previous. Conversion was 95.2%.

Expt. 49, 341255-66 4,4'-Diphenol (1.25 moles, 233 g) was [illegible] acid at 40°C and the chlorination was [illegible] Dehydrochlorination [illegible] solution [illegible] quinone started [illegible] minutes [illegible] The mixture was flushed with N2, filtered and washed

DSW 621394

to give 200 g, mp 221-32°C. Chlorination (1 hr) of the filtrate gave 73 g (II) mp 240-8°C. The filtrate was diluted with water (1 to 1) to give 18.7 g of a yellow material, mp 182-89°C. This material turns red-brown at 162-75°C; it analyzed 44.75, 45.03, 45.27% Cl. Conversion 97.7%.

Expt. 50 Same amount of 4,4'-diphenol (1.25 moles, 233 g) and less solvent (3. kg) was used in this experiment. Chlorination was started at 45°C. After 47 min, all phenolic material was dissolved. Total duration of halogenation was 1.25 hr when the mixture became too viscous for stirring. After flushing with N_2 the product was filtered and washed to give 197 g, mp 231-8°C. The filtrate was rechlorinated (1.5 hr) until no more chlorine reacted as indicated by the color. The solution was flushed with N_2 at 27°C and filtered to isolate 161 g, mp 240°C. Filtrate diluted with water gave 37 g (III) of a red brown material mp. 159-62°C. Conversion 98.0%.

Anal. Found: I C, 46.23; H, 2.12; Cl, 42.56, 42.59; OH, 10.62, 10.81

II Cl, 42.59, 43.17.

III C, 41.40; H, 1.71; Cl, 48.69, 48.96.

Expt. 51, 341272-3 The purpose of this run was to combine chlorination and recrystallization in one batch. 4,4'-Diphenol (1.25 moles, 233 g) and 3.300 kg of acetic acid were stirred at 40°C and then chlorinated. After 17 minutes all went into solution. The thick solution, formed after halogenation for 2 hr, was filtered and washed with 100 ml acetic acid. The semi-dry cake (460 g) was dissolved in 4400 ml of acetic acid, treated with 14 g of charcoal, and filtered over a clay-filter aid cake. The filtrate was concentrated to the point of crystallization. On cooling, 301.5 g of white needles were obtained, mp 245°C (I). Concentration of the filtrate gave 41 g, mp 186°C (II). Chlorination of the original filtrate gave, on dilution with water (1 to 4), 24 g of a red brown product, which got dark at 65°C and melts at 82°C (III).

Anal. Found: I: C, 45.99; H, 2.36; Cl, 41.53; 41.65; OH, 10.16, 10.24

II: C, 37.84; H, 1.42; Cl, 51.37, 51.48.

Recrystallization Studies

Expt. 52, 341268 Crude tetrachlorodiphenol (50 g, 341262 II) was dissolved in 400 ml of 85% ethanol, then treated with 2 g [illegible] filtered, and concentrated to collect the following [illegible]

DSW 621395

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[illegible] procedure was used to recrystallize fraction II from the same experiment (341262). From 161 g were isolated (1) 81 g, mp 241°C; (2) 30 g, mp 242-4°C; (3) 25 g, mp 244-5°C; (4) 10 g, mp 228-30°C. Total 146, equal to 90.8% of charge. Again, fraction (4) was isolated by diluting with H_2O (600 g).

Expt. 54, 341267 Benzene (600 g) was investigated as a solvent to recrystallize crude 4,4'-bi-(2,6-dichlorophenol). Crystallization went very slowly. After keeping at 0°C over week-end there was collected only 12.1 g of light yellow needles, mp 240.5°C.

Expt. 55, 341270 One gram of chlorinated 4,4'-biphenol dissolved in 10 g of hot glacial acetic acid. This gave, on cooling, only 0.72 g of product, mp 240°C. This observation was confirmed by dissolving 300 g crude 4,4'-bi-(2,6-dichlorophenol). (I, Expt. 50) in 3000 ml of acetic acid. Charcoal (10 g) was added and the mixture was refluxed for 1 hr, filtered over a clay cake on an electrically heated Buchner funnel. The filtrate was concentrated to 2270 g total weight whereupon crystallization started. White needles (226 g) were collected with, mp 243°C (I). The filtrate gave on concentration to 181 g, 41 g mp 195°C (II); finally it was concentrated further to 11.8 g which gave 4.5 g (III). The 7.1 g filtrate was diluted with 100 ml of water to collect 1.3 g of residue. Total material recovery 90.8%. Analyses of these four fractions are tabulated below.

No.	C	H	Cl	OH
I	45.66	2.36	42.05, 42.04	10.35, 10.53
II	49.32	2.55	37.27, 37.32	11.10, 11.19
III	48.59	2.68	34.16, 34.21	10.33, 10.33
IV	48.77	3.08	33.07, 33.21	8.32 , 8.32
X	44.49	1.86	43.85	10.48
Y	49.7	2.42	36.7	11.73

X = Calcd. values for 4,4'-bi-(2,6-dichlorophenol)

Y = Calcd. values for 4,4'-trichlorobiphenol.

Data on the preparation of 4,4'-bi-(2,6-dichlorophenol) by the procedure given in Expt. 49 was used by Mr. [illegible] Beck who prepared [illegible]

DSW 621396

STLCOPCB4095426

VIII. PATENT STATUS

Hydrolysis of decachlorobiphenyl to dihydroxyoctachlorobiphenyl is reported in the literature (R-15, -16, - 17.) using both methanol under pressure, and ethylene glycol at atmospheric pressure. Halogenated terphenyls are hydrolyzed under pressure as disclosed in a Monsanto patent (R-21). The ethylene glycol hydrolysis of Aroclor 4560, 1268 and lower homologs are not distinguishable patent-wise over R-17.

A summary of a preliminary study of the patent problems associated with making and selling glycidyl ethers derived from hydrolyzed Aroclors and epichlorohydrin was made by Mr. F. Wellington on March 26, 1956.

Six disclosures were submitted on hydrolysis of Aroclors by various processes as well as on uses for hydrolyzed Aroclors.

Neither a patent nor literature search was made on the subjects covering the disclosures given below:

D-1939 J. Dazzi, 3-8-55; Dimethyl sulfoxide as a solvent for Aroclor 1270 formulations. Reactions of hydrolyzed Aroclors carried out in dimethyl sulfoxide.

D-2003 J. Dazzi, 10-31-55; Hydrolysis of chlorinated biphenyls on contacting with steam.

D-2078 J. Dazzi, 1-23-56; Hydrolyzed chlorinated biphenyls as industrial preservatives.

D-2107 J. Dazzi, 3-27-57; Hydrolyzed Aroclors as bacteriostates for secondary oil recovery waters.

D-2119 J. Dazzi, 3-25-57; Hydrolysis of octachloronaphthalene to polyhydroxy polychloronaphthalene

D-2261 J. Dazzi, 4-8-58; Hydrolysis of chlorinated bi- and terphenyls by caustic fusion.

The four disclosures D-1939, D-1943, D-2050, D-2066 directed to the hydrolysis of various chlorinated biphenyls and terphenyls are too close to the art given in U.S. Patents Nos. 2,240,073 and 2,419,688 as stated in Mr. B. L. Bussard's memo to J. Dazzi, 3-19-58. Four disclosures will be abandoned.

DSW 621397

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DSW 621398

2,4,5-trichlorophenol, Memo, 2-22-56.

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DSW 621399

STLCOPCB4095429

A cost estimate on hydrolyzed Aroclor 1268 was prepared by J. F. Adams of Organic Research on March 6, 1956 (R-14). A recalculation using more recent data was prepared by J. F. Adams on October 11, 1957, Report 57-10-34.

DSW 621400

STLCOPCB4095430

X. PROCESS RECOMMENDED

Only limited process studies were made. Best procedure for preparing dihydrolyzed Aroclor 1270 is given in Expt. no. 4. The model compound 4,4'-bi-(2,6-dichlorophenol) is best prepared and purified by directions reported in Expt. 49.

DSW 621401

STLCOPCB4095431

XI. MATERIAL SPECIFICATIONS

No material specifications were set on any of the products described.

DSW 621402

XII. ANALYTICAL PROCEDURES

Carbon, hydrogen combustions were run at 800°C.

All chlorine analyses run by the sodium peroxide method give low values for highly chlorinated aromatics and their derivatives using the C-25-56 and C-35-55 procedures. The former refers to visual, the latter to automatic titration.

The modified procedure (H-8-57) developed by Dr. J. J. Hawkins uses sodium biphenyl reagent. The ionic chlorine formed is determined by automatic titration.

The modified H-8-57 Cl procedure gives on the average 2-4% higher Cl values than C-35-55 method. This is especially the case for compounds containing more than 45% Cl. The method is limited to compounds which are soluble in dimethoxyethane, the preferred solvent for this procedure.

A critical analytical study on the Aroclor 1270 (sample from the 600 lbs stock, dried at 90°C/2-3 mm) reveals that its real chlorine content is 71.07%, the average value of six determination.

Anal. Found: Cl, 71.00, 71.28, 70.89, 70.98, 71.06, 71.25; C, 29.13; H, 0.35.

Samples 1-4 were dissolved in the solvent using a volumetric flask. Volume samples of this solution were analyzed and gave an average Cl content of 70.0375%. For determination 5 and 6 the sample was weighed out and then added to the solvent; average content found 71.15% Cl. Details are given on 360244, 365127, and 365130. The average Cl content of this Aroclor 1270 batch is taken 71.0%. Consequently, this increases the calculated molecular weight by 15.07 from 481.47 up to 496.54 as shown in Table I.

The molecular weight Z of an Aroclor of known Cl content is calculated by the equation given below.

$$144.12 + (Z \times \text{Cl content}) + 10 - \frac{(Z \times \text{Cl content})}{35.47} = Z$$

Z = unknown molecular weight

[illegible] content refers to value found for the Aroclor

[illegible] corresponds to the 12 [illegible] Aroclor

[illegible] $\frac{(Z \times \text{Cl content})}{35.47}$ [illegible]

35 [illegible] refers to the atomic weight of Cl

DSW 621403

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XIII. TOXICITY AND HAZARDS

No toxicity data have been obtained on products reported here. Octachloronaphthalene causes dermatitis and was withdrawn from the market years ago. The author developed a stubborn skin rash while working over a long period of time with these highly chlorinated aromatics and their derivatives; the dermatitis character suggests strongly that the Halowax, octachloronaphthalene, was the causative agent. No further work on this compound should be done.

DSW 621404

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XIV. ACKNOWLEDGMENT

The modified chlorine procedure developed by Dr. J. J. Hawkins is gratefully appreciated and acknowledged. We thank the Analytical Physical Groups for analysis and identification of material described in this report. Testing of samples by Mr. J. A. Herbig of the Polymer Evaluation Group, by J. L. Schwendeman and J. K. Craver of the Applied Ingenuity Group, and screening by Creve Coeur personnel are gratefully acknowledged.

DSW 621405

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APPENDIX A - NOTEBOOK PAGES, J. DAZZI

294219
227
228

278301-2
315
326-7

303300

310401-3
445-5

316051
053
062
090-1

323102
121
134

328961-3
966-7
927-4
985-6
988-9
993-4
999

334601-2
615-6
627-9
630-4
639
648-9

341251-2
255-7
260-3
267-74
282

347339-40
346-7

353851-4
857
867-9
874-93

360204-5
228-9
244

APPENDIX B - DETAILED LIST OF EXPERIMENTS

Hydrolysis of Ethylene Glycol Process	Expt. No.
1. Hydrolysis of Aroclor 1270 and 1271	1-25
2. Best recommended conditions	4
3. Attempts to prepare trihydroxy Aroclor	4-25
4. Hydrolysis of Aroclor 1268	6-28
5. Hydrolysis of Aroclor 1168 (undistilled)	28
6. Hydrolysis of Aroclor 1262	29-30

DSW 621406

STLCOPCB4095436

8. [illegible] Aroclor 1248 32

9. Hydrolysis of Aroclor 5460 33-34

10. Hydrolysis of hexachlorobenzene 36

Hydrolysis of hexachlorobenzene at 115°C 37

11. Hydrolysis of octachloronaphthalene 38

12. Hydrolysis of 1,2,4,5-tetrachlorobenzene 39

13. Attempts to hydrolyze p-dichlorobenzene 40

14. Hydrolysis of hexachlorodiphenyl oxide, Dow 6X 41

Hydrolysis Using Other than Ethylene Glycol as Solvent

1. Hydrolysis of Aroclor 1268 using methanol under pressure. 35

2. Hydrolysis of Aroclor 1268 using m,p-isopropylbiphyl as solvent. 42

3. Hydrolysis of Aroclor 1268 using o-ethylnitrobenzene as solvent. 43

4. Hydrolysis of Aroclor 1270 using pyridine 44

5. Hydrolysis of Aroclor 1268 using steam, and steam plus copper catalyst 45

6. Hydrolysis of Aroclor 1268 and 1270 by fusion with NaOH 46

Chlorination of 4,4'-biphenol to 4,4'-bi-(2,6-dichlorophenol)

1. Halogenation studies 47-50

2. Chlorination and recrystallization 51

Recrystallization Studies on 4,4'-bi(2,6-dichlorophenol) 52-55

Analysis of Aroclor 1270 (Section XII)

DSW 621407

STLCOPCB4095437

[illegible] DESCRIPTION

Table I - Calculated Analyses for Aroclors and Di-Hydrolyzed Aroclors 1242-5460.

Table II - pH Determination of various phenolic compounds at 25°C.

APPENDIX D - LOT NUMBERS OF SAMPLES SUBMITTED FOR EVALUATION

Hydrolyzed Aroclor	Lot No.	Application	Sent to
1271	L-992	Biol. Tox.	Creve Coeur
	L-1052	Ind. Preserv.	St. Louis
	L-340	Intermediate	Nitro
1270	L-971	PVC Stabilizer	St. Louis
	L-1053	Ind. Preserv.	St. Louis
1268	L-972	PVC Stabilizer	St. Louis
	L-932	Intermediate	Springfield
	L-993	Biol. Tox.	Creve Coeur
	L-977, L-1051	Rubber Chem.	Nitro
1262	L-973	PVC Stabilizer	St. Louis
	L-933	Intermediate	Springfield
	L-994	Biol. Tox.	Creve Coeur
	L-1054	Ind. Preserv.	St. Louis
	L-978	Rubber Chem.	Nitro
1254	L-974	PVC Stabilizer	St. Louis
	L-995	Biol. Tox.	Creve Coeur
	L-979	Rubber Chem.	Nitro
1248	L-975	PVC Stabilizer	St. Louis
	L-996	Biol. Tox.	Creve Coeur
1242	L-976	PVC Stabilizer	St. Louis
	L-997	Biol. Tox.	Creve Coeur

DSW 621408

STLCOPCB4095438

TABLE I

ANALYTICAL DATA CALCULATED FOR AROCLORS

AND DI-HYDROLYZED AROCLORS

Aroclors			Dihydroxy Aroclors			Analysis %		
Number	Mol.Wt.	Cl atoms	% Cl	Mol.Wt.	OH %	N. Eq.	C	H	Cl
[illegible]	498.69	10.00	71.126	461.78	7.36	230.89	31.21	0.43	[illegible]
[illegible]	496.54	9.94	71	459.63	7.40	229.82	31.36	0.45	[illegible]
[illegible]	481.47	9.51	70	444.56	7.65	222.38	32.42	[illegible]	[illegible]
[illegible]	453.85	8.74	68	416.74	8.16	208.37	34.48	0.78	[illegible]
[illegible]	387.29	6.77	62	350.38	9.71	175.19	41.13	[illegible]	[illegible]
[illegible]	323.94	4.93	54	287.03	11.85	143.52	50.21	2.46	[illegible]
[illegible]	288.53	3.91	48	251.62	13.51	125.81	57.28	3.21	[illegible]
[illegible]	260.11	3.08	42	223.20	15.23	111.60	64.57	4.00	[illegible]
[illegible]	215.03	1.94	32	178.13	19.09	89.07	80.91	[illegible]	[illegible]
[illegible]	564.42	9.5[illegible]	[illegible]0	527.[illegible]1	[illegible].[illegible]	263.76	40.98	1.22	[illegible]
[illegible]	[illegible]	[illegible]	60	509.05[3]	10.02[3]	169.68[3]	42.47	1.48	[illegible]

[illegible]ulations are based on assumed Cl content.

[illegible]alues found for material used as Aroclor 1270 see Section XII.

[illegible]culated as trihydroxy Aroclor 5460.

DSW 621409

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TABLE II

pH DETERMINATION OF VARIOUS

PHENOLIC COMPOUNDS AT 25°C

Compounds	pH
Hydrolyzed Aroclor 1270	3.37
Tetrachlorobisphenol A	3.49
Bisphenol A	3.55
4,4'-bi-(2,6-dichlorophenol)	3.60
Hydrolyzed Aroclor 1271 Stock room sample	3.65
Octachlorodiphenyldiethiol	3.75
Pentachlorophenol	3.80
Hydrolyzed Aroclor 5460	3.80

1. The compound was dissolved in dioxane-water 1 to 1 solution. nc standard molecular solutions were used. As standard water, was used, pH 6.2. These measurements were made by Dr. W. J. McCarville and reported on 3/3/74.

DSW 621410

STLCOPCB4095440