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CONFIDENTIAL

EXPLORATORY AROCLOR CHEMISTRY. PART I. ETHERS BY ALCOHOLYSIS. HYDROLYZED AROCLOR DERIVATIVES

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I. PURPOSE

This report relates initial experiments with Aroclors as chemical intermediates. A specific objective was to convert Aroclors, a low cost Monsanto product, to ethers for test as functional fluids and dielectrics.

Also reported is early scouting research on the condensation of hydrolyzed Aroclors (diphenols) with ethylene chlorohydrin, ethyl chloroacetate, and a diisocyanate.

A program covering specific phases of this Aroclor chemistry was submitted in four detailed memos (R-1-3). Later work with hydrolyzed Aroclor 1268, now an Organic Division Development item, is reported elsewhere (R-7).

This report covers part time work carried out between November 1953 and June 1956.

II. SUMMARY

ETHERS Highly chlorinated Aroclors such as 1271, 1270, 1268 and 5460 react smoothly at 170-220°C in the presence of caustic with alcohols such as 2-ethylhexanol and butyl cellosolve to form the corresponding diethers in high yields.

Aroclor 5460 gives a mixture of di- and triethers.

Aroclor 1262 and excess m-cresol gives a mixture of mono-, di-, and tricresyl ethers.

To prepare mono-ether, a large excess of Aroclor 1254 was reacted with 2-ethylhexanol and caustic.

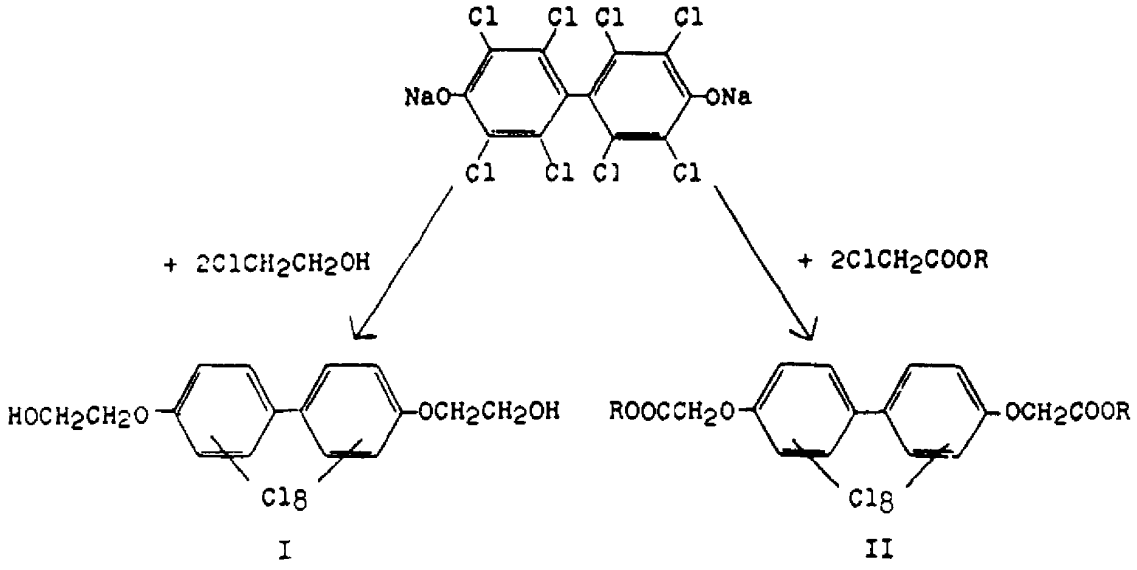
No reaction took place between Aroclor 1270, excess allyl alcohol, and caustic at reflux temperature.

Ethylene glycol fails to form β-hydroxyethyl ether with Aroclor 1271 and 1268. Instead, conversion to the corresponding hydrolyzed Aroclor occurs. This unexpected observation led to our work on polychlorodiphenols from Aroclors, and eventual transfer to Organic Chemicals Division Development.

Glycerol, immiscible with Aroclor 1268, failed to react and only a trace of partly hydrolyzed material was isolated.

Glycols possessing isolated hydroxyl groups, such as 1,5-pentanediol, form an ether alcohol, shown first on 1,2,4-trichlorobenzene, a model compound. The single experiment gave 23% conversion and 49% yield of the 5-(2,4-dichlorophenoxy)pentanol.

HYDROLYZED AROCLOR 1270 DERIVATIVES Scouting research demonstrates that ethylene chlorohydrin and alkyl chloroacetates condense with hydrolyzed Aroclors to yield the corresponding ether alcohol (I) and ether acid (II).



Further studies are needed in order to secure samples sufficiently pure for evaluation in polymer formation.

A new polyurethane was prepared from hydrolyzed Aroclor 1270 and diisocyanatodiphenylmethane.

Eight patent disclosures were submitted on reported Aroclor chemistry.

EVALUATION Replacement of two chlorine atoms in Aroclor by alkoxy groups substantially reduces the viscosity of the material. The 2-ethylhexyl ethers derived from Aroclor 1271 and 1260 showed some promising properties as industrial fluids. Because of the high chlorine content, the flash point of these ethers was very high (630°F).

Mono-2-ethylhexyl ether of Aroclor 1254 represents a new type of dielectric, but pricewise, such chloroethers could never compete with Aroclors. The di-2-ethylhexyl ethers of Aroclor 1271 and 1268 are more symmetrical molecules and consequently have poor dielectric properties. Details are summarized in Table II.

III. CONCLUSIONS

New ethers derived from highly chlorinated Aroclors are readily prepared in high yield using procedures adapted from those specified for preparation of pentachlorophenyl ethers (R-4). Aroclor 1271 and 1270 give diethers, while Aroclor 5460 gives a mixture of di- and triethers. Monoethers of Aroclors may be prepared in low conversion by using excess Aroclor. Ethers can be prepared from Aroclors and phenols and glycols other than 1,2-glycols; ethylene glycol gives hydrolysis only, and glycerol is unreactive.

Dihydroxyoctachlorobiphenyl condenses with ethylene chlorohydrin and with chloroacetates to give the corresponding ether alcohols and ether carboxylic acid derivatives. It is questionable whether they can be purified sufficiently to be good polymer intermediates.

These ethers derived from Aroclor show some promise as functional fluids and dielectrics but have no outstanding advantages.

IV. RECOMMENDATIONS

Continue exploratory work on Aroclor chemistry as suggested in R-2 and 3.

Prepare ethers and thioethers derived from Aroclors and C_{12}-C_{18} alcohols and mercaptans. Evaluate the thioethers as corrosion inhibitors in oil and gasoline.

Reinvestigate the preparation of diallyl ether derived from Aroclor 1268 and 1270 using higher reaction temperature or the method with pyridine catalyst (R-6).

React mercaptobenzothiazole with Aroclors using dimethyl-formamide or dimethyl sulfoxide as solvent.

Investigate the reaction between equal moles of Aroclor 1270 and sodium salts of bisphenol A or dihydroxyoctachlorobiphenyl using dimethyl sulfoxide as solvent.

V. DATA AND DISCUSSION

ETHERS Ethers derived from hexachlorobenzene, the first type of compounds prepared in 1947 by the author as possible polyvinyl chloride plasticizers, were very incompatible. In 1953, some scouting experiments were made on preparing ethers from Aroclor 1270 using the excellent procedure given in R-4 for the preparation of pentachlorophenyl ethers. As expected, this procedure worked well for Aroclors giving di-ethers.

The process consists of heating Aroclor and solid caustic at 160°C with excess (50%) 2-ethylhexanol for 4.5 hr, while the water is distilled off at the rate of formation. Etherification goes rapidly with little coloration. Water extracts the sodium chloride formed and excess NaOH used. No hydrolysis (caustic-soluble material) of Aroclor 1271 takes place at 160°C under conditions used in Expt. 1.

The reaction mixture was neutralized in later experiments before washing. This eliminates emulsion formation.

A sample of crude bis(2-ethylhexyloxy)octachlorobiphenyl (200 g) was distilled over 1.5 hr period to give 198 g, bp 256-267°C/0.25-0.5 mm, without indication of decomposition. The distillate is a rather viscous, yellow, odorless liquid.

Aroclor 1260, containing less reactive chlorine atoms, gave a mixture of mono- and diether at 160°C (expt. 2).

A mixture of di- and tri-butoxyethyl ether is formed on heating Aroclor 5460, caustic, and butyl cellosolve at 160°C for 4.5 hr. (Expt. 3).

No process studies were made on the etherifications of Aroclor 1271, 1260 and 5460 in Expt. 1-3. Minor process variation should increase the conversion. (Expt. 3)

Allyl alcohol failed to react at 110°C with Aroclor 1271, most likely due to too low a reaction temperature (Expt. 6). This experiment should be repeated under pressure allowing a higher reaction temperature. A diallyl ether of Aroclor may be of interest inside Monsanto, especially as a cross-linking agent for polymers.

The mono-ether of Aroclor 1254 was obtained by reaction of equal moles of 2-ethylhexanol and caustic with a large excess (400%) of the Aroclor. Reaction was quite slow, even at 230°C and over a long period (26 hr) Expt. 4). The more highly chlorinated fraction in Aroclor 1254 reacted first, as expected (Expt. 4). Although the mono-ether has a rather low pour point and fair dielectric properties, the process is expensive and gives low conversion.

Preparation of aryl ether of Aroclor 1262 requires much longer reaction times and higher temperatures than for alkyl Aroclor ethers. This was shown in the only experiment tried (No. 5), where Aroclor 1262 reacted with excess m-cresol. The distilled reaction product was a mixture of mono-, di-, and tri-ether. It is conceivable that more than 2 alkyl ether groups can be introduced since in the case of hexachlorobenzene up to 3 chlorine atoms were replaced by 2-ethylhexyloxy groups (R-9) (288805).

No attempts were made to prepare methyl and ethyl ethers of Aroclors. According to R-4, hexachlorobenzene fails to form methyl and ethyl ethers. That this is the case for Aroclor 1271 has to be demonstrated by experiment.

Rocklin (R-6) has an excellent method for the preparation of pentachlorophenyl methyl ether using hexachlorobenzene, methanol and caustic in pyridine. It is conceivable that this method may work for the preparation of methyl or ethyl ethers of Aroclor 1271, 1270, 1268 and 5460.

Ethers derived from unsaturated alcohols such as allyl and propargyl alcohol should also be prepared from Aroclors and hexachlorobenzene by the Rocklin procedure. Unsaturated ethers are not mentioned in his paper (R-6).

No ether alcohol is formed on heating Aroclor 1271 with ethylene glycol and caustic (Expt. 8). Instead, hydrolysis (mono- and di-) takes place. This hydrolysis initiated our studies on hydrolyzed Aroclor, now transferred to the Organic Chemical Division for development (R-7). The mechanism for the unexpected behavior of ethylene glycol is not known.

Glycerol failed to react with Aroclor 1268 at temperatures between 125-170°C (Expt. 9). Glycerol is immiscible with Aroclor which may account for this result. No common solvent was found for this mixture.

To evaluate glycols other than 1,2-glycols, 1,5-pentanediol and 1,2,4-trichlorobenzene were chosen as model compounds. The latter is readily distilled from the reaction mixture. A single experiment at 210°C for 2 hr, gave the desired 5-(2,4-dichlorophenoxy)pentanol in 32.5% conversion and 48.9% yield (Expt. 10). This new ether alcohol is very low melting (-35°C). A part of the 1,2,4-trichlorobenzene (15.7%) hydrolyzed to 2.4-dichlorophenol. It is conceivable that 1,5-pentanediol will also react with Aroclor 1270. Pyridine as a catalyst-solvent (R-6) should be investigated for this reaction.

Neopentyl alcohol and pentaerythritol also should be tried with a model compound, 1,2,4-trichlorobenzene, and then with Aroclors.

No thioethers derived from Aroclors were prepared. By analogy with hexachlorobenzene, syntheses from mercaptans should go smoothly.

DERIVATIVES OF HYDROLYZED AROCLORS The most promising derivatives of hydrolyzed Aroclors are the bis-glycidyl ethers, on which most of our time was spent. This work is reported separately (R-8).

Bis-hydroxyethyl ether of Aroclor 1271 was prepared by condensation of hydrolyzed Aroclor with ethylene chlorohydrin. Reaction was rapid and quantitative (Expt. 11). This ether alcohol is very soluble in most organic solvents. The same general method was used to condense hydrolyzed Aroclor 5460 (mixture of di- and trihydroxy) with ethylene chlorohydrin. No efforts were made to separate isomers. Our main object was to demonstrate a method to prepare β-hydroxyethyl ethers derived from various hydrolyzed Aroclors (Expts. 11 and 12). A possible use for another alcohol derived from Aroclors is as an intermediate for polyesters and alkyd resins. For certain evaluation studies only di-functional material should be used first; this will require extensive purification studies.

Another series of Aroclor derivatives are the carboxylic esters obtained in quantitative conversion by condensing hydrolyzed Aroclor 1271 with ethyl chloroacetate. The product is very soluble in common solvents and failed to crystallize from several solvents tried. The same difficulty was observed when trying to recrystallize the free acid, obtained by hydrolysis of the corresponding ester. Nevertheless, purification of such acids and alcohols should be studied. Our preliminary solubility studies were limited to test tube size experiments.

Use of difunctional acids and alcohols derived from Aroclor will probably be limited to applications where high purity is not required, e.g., alkyds. These compound will probably not be pure enough for "fiber-polymer" types. All our Aroclor derivatives are probably mixtures of isomers and their separation is a problem in itself (R-5). Low-chlorinated, monohydroxy Aroclor condensed with chloroacetic acid gives a product similar to 2,4-D, and should be tested for herbicidal activity.

POLYURETHANES Hydrolyzed Aroclor 1270 reacts with diisocyanatodiphenylmethane to form a polyurethane. Since the starting material used was only partly difunctional, shown later by improved analytical procedures, the urethane formed is low in molecular weight. The value of this new urethane should be determined on a sample derived from di-hydrolyzed Aroclor 1270 or 1268.

NEW SOLVENT FOR AROCLOR 1270 Dimethyl sulfoxide is an excellent solvent for Aroclor 1270. It has the advantage over dimethylformamide of being stable to aqueous alkali; therefore, it should be evaluated as a solvent for reactions of Aroclor 1270 with sodium cyanide, sodium isethionate and pentaerythritol, all which are soluble in dimethyl sulfoxide (Expt. 16).

VI. EVALUATION

Ethers derived from Aroclors are very heat stable and presumably flame-resistant, which suggests their use as industrial fluids, especially where fire retarding properties are required. Data reported by St. Louis are given in Table I. Viscosity properties are poor. A longer alkyl group, combined with a lower Aroclor might overcome the viscosity deficiency. The evaluated ethers possess a very high fire point (625°F); their flash points are between 510-560°F. This early lead on Aroclor ethers as functional fluids led later to preparation of ethers possessing superior properties as functional fluids (R-9). Initial work indicates low breakdown on heating at 350°F for 75 hrs.

Aroclor ethers were also screened as dielectrics. Data are summarized in Table II. Lot number K-779 and K-780 are rather symmetrical molecules, consequently their dipole moments are low. The mono-2-ethylhexyl ether of Aroclor 1254 possesses superior dielectric properties (Lot number 1546-1547). The pour points of these two samples are 10°C and 5°C, respectively, which is rather high.

These few experiments indicate that little chance exists to develop an ether from Aroclor possessing dielectric properties good enough to stand the substantially higher cost of the final product. This work led to the preparation of o-chlorophenyl 2-butoxyethyl ether possessing a pour point of -70°C and a dielectric constant of 7.25 at 25°C. Data on this and other ethers derived from chlorobenzenes is the subject of a special report (R-9). Monsanto has no purification procedure to eliminate all conducting impurities.

General routine biological toxicant evaluation at Creve Coeur of 4,4'-bis-(2-ethylhexyloxy)octachlorobiphenyl (undistilled product, Expt. 1) and 2-ethylhexyl ether of Aroclor 1260 (mixture of mono- and di-ether, Expt. 2) failed to reveal special activity. These two ethers were screened as CP Numbers 8076 and 8077, respectively.

VII. EXPERIMENTAL DETAILS

APPARATUS All experiments were conducted in standard taper, Pyrex glass equipment. The flask was heated by means of a heating mantle. Good stirring was applied to eliminate local overheating. For high vacuum distillations a separately heated 10-inch Vigreux column was used.

A Dean and Stark trap was used in the Expts. 1-10 to separate the water at the rate of formation.

EXPERIMENTS

4,4'-Bis(2-ethylhexyloxy)octachlorobiphenyl - Expt. 1 [288806-8] This experiment was performed after successful preparation of di-2-ethylhexyl ether of hexachlorobenzene (288805, R-9).

A mixture consisting of Aroclor 1271 (1 mole, 499 g), 2-ethylhexanol (6 moles, 780 g), NaOH (3 moles, 120 g as ground pellets), and 35 ml toluene was stirred at 160°C for 4.5 hr. The water was removed at the rate of formation. Etherification was rapid with little change in color. The reaction product was treated with water to remove NaCl and excess NaOH. An emulsion appeared, but disappeared on acidification. The dried reaction mixture was heated at 230°C/0.3 mm to remove 421 g unreacted 2-ethylhexanol, n_D^{25} 1.5686. Conversion 75.9%.

Anal.: C, 47.82; H, 4.51; Cl, 41.07, 41.08.

A sample (200 g) of this ether was distilled at 256-265°C/0.25-0.5 mm to collect: (1) 170 g, bp 255-265, n_D^{25} 1.5576; (2) 38 g, bp 260-67°C/0.5 mm, n_D^{25} 1.5725; and (3) residue, 2.4 g. Duration of distillation was 1.5 hr with no indication of decomposition.

Anal.: Calcd. MW 686; C, 29.00; H, 4.96; Cl, 41.45
Pract. 1. Found: C, 30.31; H, 5.52; Cl, 38.17, 38.28, 38.47.

Some material was lost due to emulsion formation, accounting for lower than expected conversion value.

2-Ethylhexyl ether of Aroclor 1260 - Expt. 2 (288830-1)
A mixture consisting of Aroclor 1260 (1.5 moles, 552 g), 2-ethylhexanol (6 moles, 780 g), NaOH (4 moles, 33% excess), and 60 ml toluene was stirred at 170°C for 6.5 hr while collecting 60 ml of water. The reaction mixture was diluted at 100°C with 400 ml of water, neutralized with 1.07 moles HCl and washed at 80-100°C (good layer separation). The excess alcohol was removed by steam distillation giving 430 g n_D^{25} 1.4380, (2-ethylhexanol, n_D^{25} 1.4300). Residue was stirred at 125-130°C/1 mm to give 727 g, n_D^{25} 1.5500. Conversion was 86.5%. This ether was treated with fine Al_2O_3 at 120°C, filtered and its resistivity was measured and found to be 1 x 10^{12} ohms-cm at 25°C.

Anal. Found: C, 55.54; H, 6.39; Cl, 29.83.

These values indicate it is a mixture of mono and diether of Aroclor 1260. The product is considerably less viscous than Aroclor 1260.

Butoxyethyl ether of Aroclor 5460 - Expt. 3 (328975-77)
Aroclor 5460 (0.96 mole, 540 g) was dissolved in butyl cellosolve (8 moles, 944 g) at 70°C, then 4 moles NaOH flakes was added. A mild exothermic reaction increased the temperature up to 115°C. The pot temperature was gradually increased from 160° up to 160°C over 1.75 hr while collecting 72 ml of water. The mixture was stirred for 4.5 hr at 160°C, cooled, and diluted with 900 ml of water. Acidification to a pH of 8 required 0.68 mole HCl. The organic layer was shaken with NaOH (10%): no hydrolyzed Aroclor was extracted. The final product was heated for 0.6 hr at 210°C/0.3 mm to give 740 g residue, 96% conversion calculated as triether.

Anal. Calcd. ($C_{36}H_{43.3}Cl_{6.44}H_{13.5}$): C, 53.45; H, 4.38; Cl, 29.08
Found: C, 53.63; H, 5.51; H, 5.51; Cl, 28.27, 28.31.

The C, H, and Cl values check for the tri-ether. It is a viscous material and was not further investigated.

Mono 2-ethylhexyl ether of Aroclor 1254 - Expt. 4(303286,303297)
Monoethers of Aroclors are unsymmetrical molecules and therefore should be low melting and might find use as dielectrics and functional fluids. A mixture consisting of Aroclor 1254 (5 moles, 1632.5 g), 2-ethylhexanol (1 mole, 130 g), and one mole NaOH was heated at 230°C for 26 hr, while the water was collected (13 ml) with 2-ethylhexanol, which was returned to the reaction mixture. The washed product was fractionally distilled to give 1374 g unreacted Aroclor, bp 170-210°C/1 mm, analyzing 52.07% Cl. The residue (245 g, n_D^{25} 1.5820) was distilled at 0.6 mm as tabulated below.

Fr. No.	bp, °C	wt,g	n_D^{25}	Anal. Found(%): Cl	C	H
1	200-21	19.2	1.6152	49.06	46.36	2.78
2	225-40	42.4	1.5918	42.33	50.53	3.87
3	241-45	61.0	1.5788	38.72	52.78	4.63
4	245-40	84.3	1.5766	38.01	53.01	4.70
Residue		33.				
Anal. Calcd. for $C_{20}H_{20}Cl_5O$:				39.1	52.8	4.42

Analysis values of fraction 3 and 4 check for a monoether. The residue (33 g) is a dark semisolid.

Fractions 3 and 4 were screened as dielectrics (Table II).

Cresyl ether of Aroclor 1262 - Expt. 5 (343706 gy L. Beck)
A mixture consisting of Aroclor 1262 (1.2 moles, 468 g), m-cresol (5 moles, 518 g), KOH (2.6 moles, 148 g), and 160 ml of toluene was heated under stirring. The water formed was removed at the rate of formation, collecting 60 ml while the mixture was heated at 170°C for 8 hr. Neutralization required 1.2 moles HCl indicating a rather low conversion, therefore, the mixture was not worked up.

The same fresh charge was heated at 200°C for 12 hr in the presence of copper powder as catalyst. After reaction, 400 ml of water was added and the mixture was neutralized with 0.25 mole HCl and washed. Excess cresol was distilled off (208 g) and the residue was fractionally distilled at 1 mm.

Fract.	bp, °C	wt,g	Anal. Found (%): C	H	Cl
1	170-200	85	48.45	2.25	46.95
2	200-240	208	53.32	2.95	40.35
3	24-280	110	57.03	2.97	34.85
4	300-310	61	62.16	4.14	27.80
5	Residue	100	70.87	4.13	14.90
Anal. Calcd. for:					
mono cresyl ether	MW	458.8	49.65	2.25	44.65
di " " "		530.3	57.80	3.26	31.92
tri " " "		601.8	65.80	4.05	21.85

Analyses show that a mixture containing mono, di- and tri-cresyl ethers was formed. All these compounds are very heat stable.

Attempt to prepare the diallyl ether of Aroclor 1271 - Expt. 6 (293303) A mixture consisting of Aroclor 1271 (0.5 mole, 250 g), allyl alcohol (4 moles, 240 g), and 900 ml xylene was refluxed under stirring without dissolving completely. To this was added 1.1 moles of NaOH and 2 g of Cu powder and reflux continued at 110°C while collecting water. Apparently the temperature was too low: practically no reaction took place. The planned run in the bomb at higher temperature was never made.

Attempts to react Aroclors with ethylene glycol - Expt. 7 (288834-5) Aroclor 1260 (1.5 moles, 552 g), ethylene glycol (10 moles, 620 g), NaOH (4 moles), and xylene (150 ml) was heated first at 130°C, then up to 180°C for a total of six hr. The reaction mixture was neutralized using 1.03 moles of HCl, washed, and dried to give 500 g product.

Anal. Found: C, 39.97: H, 2.32; Cl, 45.66; OH, 8.50.

Hydrolysis took place instead of ether formation.

Aroclor 1271 - Expt. 8 (293301-2) A mixture consisting of Aroclor 1271 (0.5 mole, 249.5 g), ethylene glycol (5.2 moles, 248 g), ethylene glycol diethyl ether as solvent (700 g), and 70 ml toluene was stirred at 150-170°C for 10 hr. Reaction product (206 g), mp. 220°C. was identified later as crude hydrolyzed Aroclor 1271 formed in 89.8% conversion. This unsuccessful ether synthesis opened up hydrolysis of Aroclors (R-10).

Anal. Calcd. for $C_{12}H_8O_2Cl_8$: C, 31.20; H, 0.44; Cl, 61.6
Found: C, 32.45; H, 1.32; Cl. 59.37.

Attempted reaction between glycerol and Aroclor 1268 - Expt. 9 (288842-3) Aroclor 1268 (1.33 moles, 600 g), glycerol (6 moles, 552 g), NaOH (3.1 moles), and 200 ml xylene were stirred at 125-170°C over a 5 hr period collecting a total of 70 ml water. Material was washed and neutralized to give 451 g unreacted Aroclor 1268. From the wash waters was isolated 20 g of product.

Anal. Found (%): C, 32.78; H, 1.33; Cl, 62.12.

This was identified later as partly hydrolyzed Aroclor 1268. No common solvent could be found for glycerol and Aroclor 1268.

Glycerol heated with NaOH (mole ratio 2:1) reacts rapidly at 120-140°C to form the sodium salt and water (288848).

Reaction between 1,2,4-trichlorobenzene and 1,5-pentanediol - Expt. 10 (343708, 343713 by L. Beck) 1,2,4-Trichlorobenzene is lower boiling and easier to fractionate than Aroclors or hexachlorobenzene, hence was used as a model compound to reinvestigate the preparation of ether alcohols. 1,5-Pentanediol was used to find out if the distance between the OH groups changes the rate of reaction (hydrolysis only occurred with 1,2-glycol).

A mixture consisting of 1,2,4-trichlorobenzene (0.75 mole, 135.5 g), KOH (0.75 mole, 42 g), excess 1,5-pentanediol (6 moles, 624 g), and 125 ml toluene was stirred at 120°C while collecting the water at the rate of formation. The pot temperature was increased gradually to 210°C and kept 2 hr at this temperature. The salt formed was filtered off (41 g KCl) and the filtrate was neutralized with 0.114 mole HCl and then extracted with ether. The ether solution was treated with caustic to extract 20 g of 2,4-dichlorophenol. The ether solution was distilled to recover 46 g (36% of charge) of 1,2,4-trichlorobenzene and the fractions tabulated below.

Fract.	bp, °C	mm	wt.g	n_D^{25}	Anal. Found(%): C	H	Cl	OH
1	140-150	18	18	1.4645	57.9	10.5	6.9	22.65
2	130-150	0.8	10	1.4782	59.9	9.6	9.00	7.90
3	150-155	0.8	61	1.5255	54.3	6.1	25.8	6.82
4	220-250	0.8	9	1.5281	55.4	6.2	23.9	4.57
Anal. Calcd. for ether alcohol:					53.0	5.6	28.5	6.83

Analytical values for fraction 3 indicate that the desired 5-(2,4-dichlorophenoxy)pentanol was obtained in 32.5% conversion and 48.9% yield.

Reaction between hydrolyzed Aroclors and ethylene chlorohydrin

Hydrolyzed Aroclor 1270 - Expt. 11 (328983-4) Hydrolyzed Aroclor 1270 (0.242 mole, 111 g of partly dihydrolyzed Aroclor, 6.16% OH, calcd. 7.40) was dissolved in NaOH (0.485 mole 2.5 N and stirred at 75°C while ethylene chlorohydrin (0.53 mole, 42.5 g) was added at once. The mixture was heated up to 90-95°C; the solution turned neutral to phenolphthalein

after 10 minutes. It was kept at 90-95°C for 5 hr and then given several hot water washes. No unreacted hydrolyzed Aroclor was found on extraction with caustic. The organic material solidifies on standing and could be ground to a powder (124 g) possessing an mp. of 112°C (not sharp. Conversion was 92.9%.

Anal. Calcd. MW 547.4: C, 35.90; H, 1.83; Cl, 51.6; OH, 6.22
Found: C, 36.92; H, 2.71; Cl, 50.19; 50.83; OH, 6.64, 6.73.

The OH content of starting material was determined 2 years after its preparation when the modified OH method was available.

Hydrolyzed Aroclor 5460 - Expt. 12 (328995-6) The same general procedure as in the previous run was used. Hydrolyzed Aroclor 5460 (121.2 g of mixed di- and tri-hydroxy cpd, 328966-7) was dissolved in NaOH (0.75 mole 2.5 N) and the ethylene chlorohydrin (1 mole 80.4 g) was added at once at 85°C. After 20 more minutes the pH of the mixture turned to 8. It was heated for a total of 3 hr at 85-95°C, and then washed until free of ionic Cl, to give 132 g of a light powder. Conversion was 92.5% calculated as a mixture of di- and tri-ether.

Anal. Calcd. tri-ether: C, 44.95; H, 3.04; Cl, 37.0; OH, 7.98
Cl, 43.6; OH, 5.52
Found: C, 44.21; H, 2.61; Cl, 42.38, 42.44; OH, 5.45, 5.73

Reaction between ethyl chloroacetate and hydrolyzed Aroclors.

Hydrolyzed Aroclor 1271 - Expt. 13 (334605-8) Caustic (0.8 mole 32 g) was dissolved in 900 ml of absolute ethanol and hydrolyzed Aroclor 1271 (0.4 mole, 184.9 g, 7.60% OH) was added. Redistilled ethyl chloroacetate (0.88 mole, 108 g) was added at once at 70°C and the system was refluxed for 14 hr; salt precipitation started after 0.5 hr and total salt formed was 98.2 g(0.84 mole). The ethanol was distilled off at reduced pressure. The semi-solid residue is very soluble in the low normal and branched alcohols and dioxane. No precipitation occurred from ethanol solution kept at -40°C over night. Precipitation using solvents such as pentane, ether, water failed to yield a crystalline precipitate; only oils were formed. The crude ester was dissolved in 800 ml of ethanol and refluxed 10 hr with NaOH (0.9 mole, 9 N). The ethanol-water mixture (750 ml) was distilled off, the residue diluted with 1000 ml of water, and refluxed. The water soluble material was filtered off and the filtrate was acidified to yield 162 g of acid.

Anal. Calcd for ether acid: C, 33.2; H, 1.04; Cl, 49.04; NE, 289.1.
Found: C, 32.72; H, 1.31; Cl, 54.28, 54.55; NE, 311.4,315.8.

The reagent used for Cl analysis failed to dissolve the sample completely.

No solvent was found to purify the material by recrystallization to the point where it could be used as an intermediate for polyester type polymers.

Hydrolyzed Aroclor 1262 - Expt. 14 (334617) A solution consisting of partially dihydrolyzed Aroclor 1262 (212 g, N 221, calcd. as diphenol 176.5, prepared in St. Louis Pilot Plant) was dissolved in 900 g ethanol containing 1.2 moles of NaOH and the system was refluxed. Ethyl chloroacetate (1.32 moles, 160 g) was added over a 68-min period and reflux was continued for 16 hr. Material was isolated as in the previous experiment, then heated up to 120°C at 1 mm under good stirring to give 303 g product.

Anal. Found: 41.55% C, 3.18% H.

Product failed to dissolve in reagent used in the modified H-8-57. The values found indicate, as expected, a mixture of mono- and diester. Infrared analysis, run as No. 5285, was inconclusive due to overlapping of bands for suspected functional groups.

Polyurethane derived from hydrolyzed Aroclor 1270 - Expt. 15 (316088) Equal moles of hydrolyzed Aroclor 1270 (0.015 mole, 6.93 g. 316051, partly dihydrolyzed product) and diisocyanatodiphenylmethane were stirred at 100-110°C for 0.5 hr using 20 g xylene as solvent. Indications were of an incomplete reaction, therefore, 1 drop of N-methylmorpholine was added and stirring was continued for one hr at 120-30°C. A solid precipitated on cooling, was filtered off and washed with hot xylene to give 9.2 g residue (I). Precipitation of the filtrate gave a white powder, 0.6 g (II).

Anal. Calcd. MW $(711.7)_x$: C, 45.52; H, 1.97; Cl, 39.6;N, 3.92
Found: (I) C, 47.30; H, 2.48; Cl, 42.92; N, 3.57
(II) C, 43.89; H, 2.37; Cl, 37.18; N, 2.74

Starting material was not completely difunctional (OH found 6.16%, calcd. 7.82%), therefore, only a low molecular weight polymer could be formed. Product is free of phenolic groups.

Solvent for Aroclor 1270 - Expt. 16 (310432) Aroclor 1270 is insoluble in most organic solvents. As soon as dimethyl sulfoxide (DMS) was announced a sample was ordered (January 1955) from Stepan Chemical Company and found to be an excellent solvent for Aroclor. Furthermore, DMS is stable to caustic and dissolves sodium cyanide, sodium isethionate and pentaerythritol, all compounds slated for reaction with Aroclor 1270 when time allows.

VIII. PATENT SITUATION

Eight patent disclosures were submitted as a result of this work on Aroclor Chemistry.

D-1584 J. Dazzi - Preparation of ethers of chlorinated biphenyls and their uses as functional fluids, 6-3-54.

D-1686 J. Dazzi - Ethers derived from chlorinated biphenyls as new dielectrics, 9-7-54.

D-1838 J. Dazzi - Dimethyl sulfoxide as a solvent for Aroclor 1270 and suggested uses, 3-8-55.

D-1941 J. Dazzi - New halogenated polyurethane derived from hydrolyzed Aroclor 1270, 7-18-55.

D-2051 J. Dazzi - New triethers prepared from chlorinated terphenyl (Aroclor 5460), 12-16-55.

D-2266 J. Dazzi - New synthesis of ether alcohols using 1,2,4-trichlorobenzene and 1,5-pentanediol, 9-14-56.

D-2699 J. Dazzi - New acids derived from hydrolyzed Aroclors and chloroacetic acid, 5-6- 58.

D-2700 J. Dazzi - New ether alcohols derived from hydrolyzed Aroclors and ethylene chlorohydrin, 5-6-58.

Disclosure D-1686 was filed in November 1955 as part of four patent applications on chloroethers as new dielectrics, see Dayton Cases 1658, 1660, 1662 and 1663.

More experimental data are needed in order to widen claims for submitted disclosures.

IX. REFERENCES

1. Dazzi, J. - New epoxy compounds derived from Aroclor, memo to the Idea Review Committee, dated 11-16-54.

2. Dazzi, J. - New organic chlorine (Aroclor) derivatives, memo to the Idea Review Committee, dated 4-26-55.

3. Dazzi, J. - The Aroclors and other halogenated aromatics as chemical intermediates, memo to Dr. C. A. Hochwalt, 1-16-56 Part I; Part II, 12-14-56; Part III, 11-7-57.

4. P. B. Report No. 588 - I. G. Farben (Verdingen 1943) Preparation of pentachlorophenyl ethers.

5. P. B. Report No. 589 - I. G. Farben (Verdingen 1943) Hydrolysis of decachlorobiphenyl.

6. Rocklin, A. L. - Substitution reactions of hexachlorobenzene. J. Org. Chem, 21, 1478-80 (1956).

7. Schwendeman, Craver, Dazzi, LeBlanc, and Herbig, Synthesis and Application studies on Hydrolyzed Aroclors and Derivatives, RD-58-Fin. Rep. No. 1115.

8. Dazzi, J., Exploratory Aroclor Chemistry. Part III. Glycidylation of Hydrolyzed Aroclors, RD-58-Int. Rep. No. 1183.

9. Dazzi, J., New Chloroaryl Ethers and other Exploratory Investigations During 1953-1957, RD-58-Fin. Rep. No. 1180.

10. Dazzi, J., Exploratory Aroclor Chemistry. Part II. Diphenols by Hydrolysis. RD-58-Int. Rep. No. 1182.

X. DESCRIPTION OF RECOMMENDED PROCESS

Not applicable to this report.

XI. COST ESTIMATES

None were prepared on compounds described in this report.

XII. TOXICITY AND HAZARDS

No special toxicity tests were made on compounds described in this report. A skin irritation was the consequence of the author's exposure over several years to Aroclors, octachloronaphthalene and their derivatives.

XIII. ANALYTICAL PROCEDURES

Carbon and hydrogen combustions were run at 800°C. Nitrogen was determined by the Dumas method.

Chlorine analysis was run by C-35-55 method, which gives low values on compounds high in chlorine, such as the Aroclors 1268, 1270, 5460 and their derivatives. The current modified H-8-57 Cl method was developed after the compounds described were prepared.

For the OH determination in Expt. 10 the H-3-56 procedure was used.

XIV. ACKNOWLEDGMENTS

We thank Messrs. A. M. Ellenburg, St. Louis, and A. S. Kenyon, Dayton for measuring the dielectric properties on Aroclor ethers and R. E. Hatton, St. Louis, for evaluating Aroclor ethers as functional fluids.

The assistance of L. H. Beck in carrying out two experiments is acknowledged. We thank the various groups in Dayton for elemental and infrared analyses.

XV. APPENDIX

APPENDIX A - NOTEBOOK REFERENCES

288806
288807
288808
288831
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288842
288843
288848
298301
298302
398303
303286
303287
310432
316088
328975
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APPENDIX B - DETAILED LIST OF EXPERIMENTS

Ethers	Expt. No.
2-Ethylhexyl ether of Aroclor 1271 (diether)	1
2-Ethylhexyl ether of Aroclor 1260 (mixture of mono- and di-)	2
Butoxyethyl ether of Aroclor 5460 (mixture of di- and tri-)	3
2-Ethylhexyl ether of Aroclor 1254 (mono-)	4
m-Cresyl ether of Aroclor 1262 (mono-, di- and tri-)	5
Attempts to prepare allyl ether of Aroclor 1271	6

Ethers (Cont'd.)	Expt. No.
Attempts to react Aroclor 1260 with ethylene glycol to form an ether	7
Attempts to react Aroclor 1271 with ethylene glycol to form an ether	8
Attempt to react Aroclor 1268 with glycerol	9
Preparation of 5-(2,4-dichlorophenoxy)pentanol	10
Reaction Between Ethylene Chlorohydrin and Hydrolyzed Aroclors	
Hydrolyzed Aroclor 1270	11
Hydrolyzed Aroclor 5460	12
Reaction Between Ethyl Chloroacetate and Hydrolyzed Aroclors	
Hydrolyzed Aroclor 1271	13
Hydrolyzed Aroclor 1262	14
Polyurethane Derived From Hydrolyzed Aroclors 1270	15
Dimethyl Sulfoxide Solvent for Aroclor 1270	16

APPENDIX C - TABLES

Aroclor Ethers as Functional Fluids	Table I
Dielectric Properties of Aroclor Ethers	Table II

TABLE I

AROCLOR ETHERS AS FUNCTIONAL FLUIDS[4]

Lot No.		J-1714[1]	J-1715[2,3]
Viscosity, cs.,	210°F	108.9	27.36
	100°F	19200.	1420
Viscosity index		--	-77
Specific gravity 25/25°C		--	1.191
Flash point °F		560	510
Fire point °F		630	625
Pour point °F		--	+ 30

1. J-1714, 4,4'-Bis(2-ethylhexyloxy)octachlorobiphenyl Expt. 1, undistilled.

2. J-1415, 2-Ethylhexyloxytetrachlorobiphenyl, mixture as mono- and di-ether, Expt. 2, undistilled.

3. No breakdown of J-1715 at 350°F for 75 hours.

4. Evaluated by Dr. R. E. Hatton, St. Louis and reported by memo to J. D., 5-12-54.

TABLE II

DIELECTRIC PROPERTIES OF AROCLOR ETHERS

Temp, °C	60 cycles DK	60 cycles PF	1 kc DK	1 kc PF	10 kc DF	10 kc PF	100 kc DK	100 kc PF	Lot Number
100	3.41	1.22	3.43	.17	3.42	.06	3.43	0	K-779
25	3.85	2.5	3.89	1.02	3.77	4.9	3.40	10	
-25	2.96	4.3	2.92	1.2	2.91	1.1	2.89	0.7	
-55	no data								
100	4.01	2.3	3.98	0.1	3.99	0.1	3.98	0	
25	4.70	0.1	4.65	0.2	4.62	2.3	4.20	14.4	K-780
-25	3.11	11.7	2.80	3.9	2.72	1.5	2.67	1.8	
-55	no data								
100	4.41	3.1	4.42	0.18	4.44	0.1	4.04	0	K-1546
25	5.22	0.6	5.24	0.15	5.24	1.4	5.16	9.8	
100	4.84	28.5	4.6	1.8	4.65	0.2	4.61	0	
25	5.50	0.6	5.51	1.4	5.51	1.4	5.23	13.0	K-1547

1) Lot No. K-779, 4,4'-Bis(2-ethylhexyloxy)octachlorobiphenyl, Expt. 1, undistilled.

Lot No. K-780, 2-Ethylhexyloxytetrachlorobiphenyl, mixture of mono- and di-ether, Expt. 2, undistilled.

Lot No. K-1546, 2-Ethylhexyloxy-X,X,X,X,X-pentachlorobiphenyl, Expt. 4, fraction 3.

Lot No. K-1547, 2-Ethylhexyloxy-X,X,X,X,X-pentachlorobiphenyl, Expt. 4, fraction 4.