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SYNTHESIS OF HIGH DIELECTRIC CONSTANT AROCLORS

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R&E RESEARCH DAYTON, OHIO
By: R. G. Schultz and V. R. Gaertner

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D I S T R I B U T I O N

Lion Oil Division

(1)	R. C. Tallman	El Dorado

Organic Division

(2)	L. E. Klein	St. Louis
(3)	T. M. Patrick	St. Louis
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Research and Engineering Division

(6)	Central Technical Files	St. Louis
(7)	V. R. Gaertner	Dayton
(8)	E. W. Gluesenkamp	Dayton
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(10)	F. C. Meyer/E. J. Prill	Dayton
(11)	R. G. Schultz	Dayton
(12)	E. G. Somogyi	St. Louis
(13)	Extra	
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I. INTRODUCTION

In order to protect our market for the Aroclors and/or increase our participation in the electrical industry, it became desirable to provide new dielectric fluids with improved properties (dielectric constant (Dk), pour point, resistivity, power factor, etc.) upon which patent coverage could be obtained. In addition to our earlier approach of fractionating Aroclors, thus improving the isomer distribution (1), it was worthwhile to investigate thoroughly chemical methods of synthesis of high Dk Aroclors or modified Aroclors.

This report describes four approaches to this problem:

1. Chemical modification of production Aroclors to give high Dk products.

2. Separation of high Dk isomers from the Aroclors by chemical means.

3. Syntheses of high Dk Aroclors via "blocked" biphenyls.

4. Exploration of the previously reported Gomberg reaction (1) of o-chlorophenyl radical with o-dichlorobenzene.

The period covered in this report extended from July 1958 to February, 1960.

II. SUMMARY AND CONCLUSIONS

It was found that the Aroclors could be chemically modified by treatment with sodium methoxide in diglyme to introduce one or more methoxyl groups. A significant improvement in Dk (to 7.4) was found with Aroclor 1242 (Dk 5.8), and corresponding increases with Aroclors 1248 and 1254. In the case of Aroclor 1242, slightly less than one methoxyl per molecule was optimum. In other properties (power factor, resistivity, thermal stability, and pour point) the "Methoxyaroclors" are comparable to the parent Aroclors. A disadvantage of the process is the necessity of using the expensive solvent diglyme; results of bomb runs at higher temperatures did not approach those obtained with digylme.

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Since no 3-methoxyl substitution was found on treatment of 2,4'-dichlorobiphenyl with methoxide, a benzyne intermediate in the reaction can be ruled out. The relative amounts of o-, m-, and p-methoxyl substitution in the Methoxyaroclors were determined.

Attempts to separate high Dk isomers from Aroclors by selective chemical substitution reactions were unsuccessful. One method (sulfonation, alkaline extraction, desulfonation) afforded unsulfonated material of somewhat lower Dk (5.3 vs. 5.8 for Aroclor 1242), but, because of the deactivating effect of the chlorines, the sulfonated Aroclor fraction could not be desulfonated.

The use of the nitro group as a "blocking" group in the synthesis of high Dk trichlorobiphenyls was investigated. The trichlorobiphenyl mixture obtained from 4-nitrobiphenyl had a lower Dk (5.0) than Aroclor 1242 (5.8), while that obtained from 2-nitrobiphenyl had a higher Dk (7.0). However, since several consecutive reactions were involved, this increase was uneconomical.

A study of the Gomberg reaction and other methods of production of the o-chlorophenyl radical was undertaken in attempts to improve the earlier yield of high Dk trichlorobiphenyl mixture from orthene. The yields were never over 55% from various expensive starting materials; it was concluded that these very high Dk (10+) Aroclors were non-competitive.

III. RECOMMENDATIONS

No economically feasible method having been devised in this work, no further effort is recommended.

IV. PATENT STATUS

A disclosure on the Methoxyaroclors (D-3149, rated A) was filed.

V. DATA AND DISCUSSION

METHOXYAROCLORS It has been previously reported (2) that the higher Aroclors (Aroclors 1254, 1260, 1270) could be hydrolyzed or converted to ethers by alkoxides. However,

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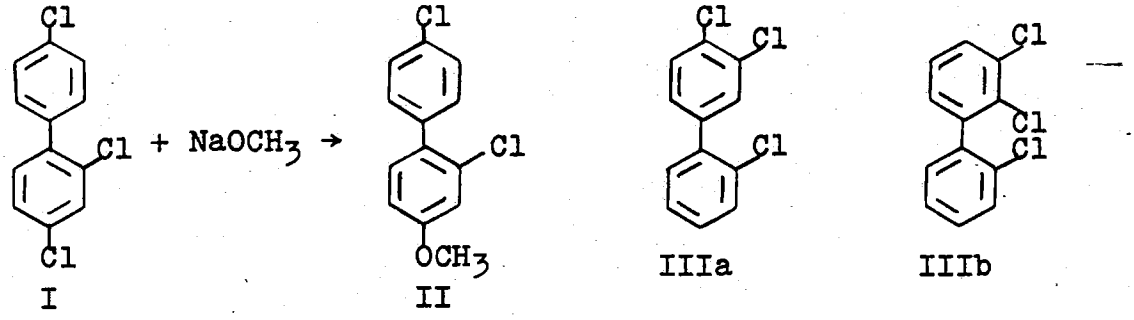
attempts to extend these reactions to the lower Aroclors (Aroclor 1232, 1242, 1248) were much less successful. It has now been found that use of a solvent such as diglyme caused the lower Aroclors to undergo facile nucleophilic aromatic substitution with sodium methoxide without catalysis. Tables I and II (Appendix) detail the scope of the reaction. In general it was found that as the amount of methoxyl substitution increased, the Dk increased (Figure I). No upper limit was found for this pattern in the case of Aroclor 1242, but as the methoxyl content approached 1.0 methoxyl per molecule the pour point of the product began to rise well above the just acceptable -20°C. for Aroclor 1242.

Several generalizations on the reaction can be made. The increase in dielectric constant can be explained by the selective elimination of cancelling C-Cl dipoles. The reaction of a low Dk component of Aroclor 1242 such as 2,4,4'-trichlorobiphenyl (I) with sodium methoxide, assuming selective 4 substitution and a lower moment for CH_3O, would afford a methoxydichlorobiphenyl (II) in which the cancelling effect of Cl-C dipoles would be greatly reduced. This lower dipolar



I II IIIa IIIb

contribution from methoxyl (anisole, 1.16D) than from chlorine (chlorobenzene, 1.56D) will also explain the decrease in Dk (from 10.5 to 9.14) found in the reaction of the Gomberg trichlorobiphenyl mixture (IIIa and IIIb) (Table I, Run 20). In this case all the dipoles are vectorially additive, and introduction of a smaller contribution would be expected to lower the dielectric constant. In the case of Aroclor 1242' (HDK-1), in which a smaller proportion of cancelling dipoles are to be found, a much smaller increase in Dk (from 6.9 to 7.6) is found (Table I, Run 19) as expected.

As might be expected, when higher Aroclors are used (Aroclor 1248, 1254) the displacement reaction is more facile due to the increasing activation by chlorine. In the cases of both Aroclor 1248 (Table I, Run 22) and Aroclor 1254 (Table I, Run 23) more than one methoxyl per molecule is easily introduced with corresponding improvements in Dk. The Methoxyaroclor from Aroclor 1248 (Dk 5.6) had a Dk of 7.9, and that from Aroclor 1254 (Dk 5.0) had a Dk of 6.7. When the substrate

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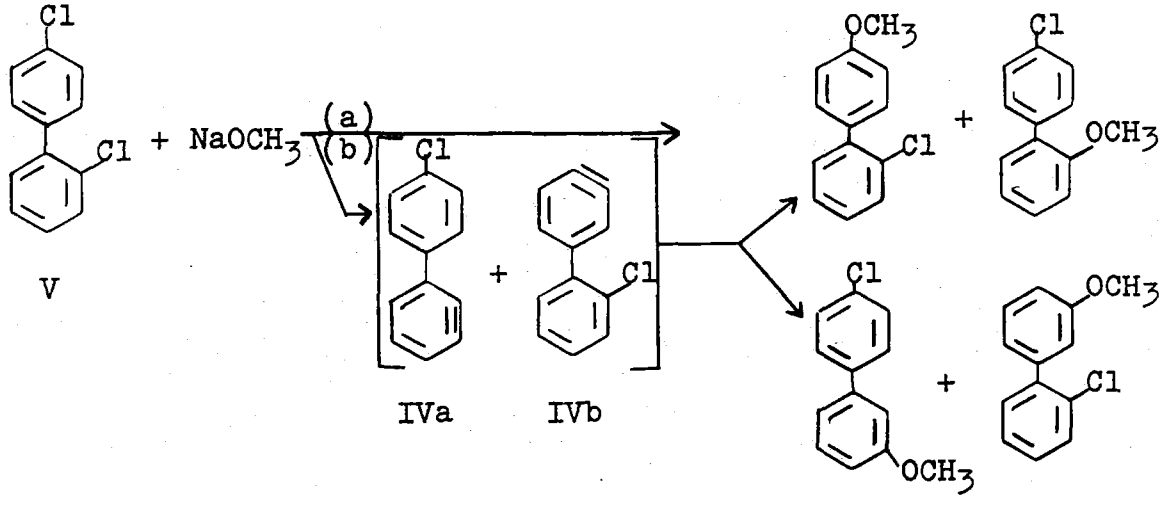
for the reaction is 2,4'-dichlorobiphenyl (where neither chlorine is activated by other chlorines in the same ring), the displacement is very sluggish and goes only partly to completion.

It was found that there was a rough relationship between Dk and index of refraction (Figure I) which was useful for making an estimate of the extent of the reaction prior to elemental analysis. When Dk is plotted against chlorine content a straight-line correlation is also found (Figure I).

It would appear that diglyme or some similar solvent is necessary, since, when no solvent (Table I, Runs 11, 12) or a hydroxylic solvent (Table I, Runs 13, 14, 15, 16) is employed, no displacement results.

In the hope that the expensive diglyme could be replaced, a series of runs was made at higher temperatures in a bomb (Table II). It may be seen that in no case without diglyme did the Dk of the product approach that found with diglyme. It is interesting to note (Table II, Runs 7-11) that catalysts have no effect on this reaction in contrast to their profound effect on the Ullmann diphenyl ether synthesis. Temperature changes (Table II, Runs 3, 4, 5) also had no effect on the reaction.

Some theoretical aspects of these reactions were investigated briefly. One point of interest was whether any reaction occurred via "benzyne" intermediates (IVa and IVb), as is true of sodamide-chloroarene substitutions. This could be determined by the results with 2,4'-dichlorobiphenyl (V) and sodium methoxide (Table I, Run 25). The product obtained, containing an average of 0.41 methoxyl per molecule, was



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dehalogenated according to the palladium-hydrazine method of Mosby (3) and the resulting product analyzed by vapor phase chromatography. The only products found were 66.3% biphenyl (from unreacted 2,4'-dichlorobiphenyl), 2-methoxybiphenyl (13.8%), 4-methoxybiphenyl (15.4%) and some higher boiler (4.5%, probably dimethoxybiphenyl). Since no 3-methoxybiphenyl was found, the benzyne intermediate path (b) may be discounted, the reaction occurring completely by the direct path (a). It is interesting to note that, in this case, where the chlorines are about equally activated, there is very little difference in the reactivities of the 2- and 4-chlorines.

Another point of interest was in the determination of the pattern of methoxyl substitution in the product from Aroclor 1242 and sodium methoxide. A Methoxyaroclor with an average of 0.89 methoxy per molecule was dehalogenated and the vapor phase chromatogram on the resulting product showed there to be biphenyl (39.1%), 2-methoxybiphenyl (26.2%), 3-methoxybiphenyl (9.9%), 4-methoxybiphenyl (17.0%) and high boilers (7.7%). It is somewhat surprising to find a greater amount of 2-chloro than 4-chloro substitution. When the Methoxyaroclor from the Gomberg trichlor (III) (0.86 methoxyl per molecule) was dehalogenated, 31.5% biphenyl, 10.9% 2-methoxybiphenyl, 15.8% 3-methoxybiphenyl, 24.1% 4-methoxybiphenyl and 17.7% high boilers were found.

OTHER SYNTHETIC STUDIES The chemical separation of high Dk isomers from production Aroclors offers another approach to the problem. Economically, one attractive methods to effect this separation would be partial selective sulfonation of the high Dk isomers production Aroclor, presumably in open 4 positions, followed by alkaline extraction. It was found that Aroclor 1242 could be partially sulfonated and the resulting mixture separated into sulfonated and unsulfonated fractions of equal size. The unsulfonated fraction possessed a lower Dk (5.3), as predicted, than that of the starting Aroclor 1242 (Dk 5.8). However, desulfonation of the sulfonated fraction could not be effected by the standard acid hydrolyses. This lack of reactivity can probably be explained by the deactivating effect of the substituent halogens.

Another approach to high Dk Aroclors involved the use of "blocked" biphenyls into which chlorine could be introduced, followed by removal of the blocking group. Three groups were considered as blocking groups: sulfonic acid, nitro, and alkyl. The sulfonic acid group was eliminated from consideration because of the unfavorable results described above in the attempted desulfonation of sulfonated Aroclor 1242, although a successful method of specific monosulfonation of biphenyl was developed (see Appendix).

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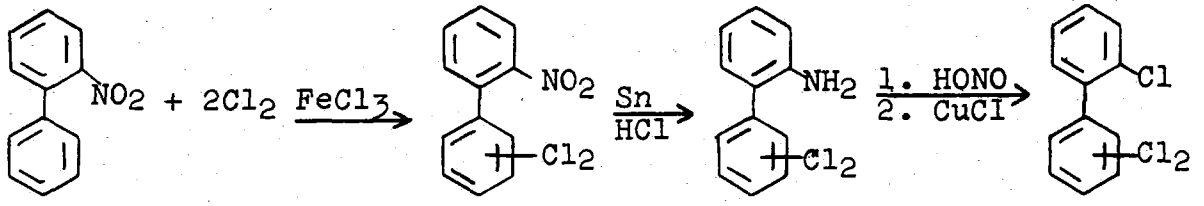
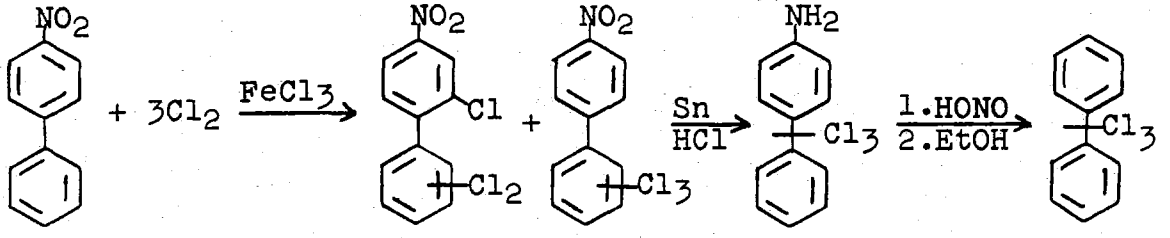
An approach to the use of the 2-nitro- and 4-nitro blocking group in the synthesis of high Dk trichlorobiphenyls is outlined below. 2-Nitrobiphenyl (VI) was dichlorinated to



VI VII VIII IX



X XIa XIb XII XIII

x,x-dichloro-2-nitrobiphenyl (VII). The nitro group was then reduced with tin in hydrochloric acid and the resulting amine (VIII) was diazotized and replaced with chlorine under anhydrous Sandmeyer conditions. The overall yield of 2,x,x-trichlorobiphenyl (IX) from 2-nitrobiphenyl was 56.5%. The dielectric constant at 25° and 100 Kc was 7.21.

4-Nitrobiphenyl (X) was trichlorinated and the resulting x,x,x-trichloro-4-nitrobiphenyl (XI) was reduced with tin and hydrochloric acid to x,x,x-trichloro-4-aminobiphenyl (XII). The amine was diazotized and reduced under anhydrous conditions to x,x,x-trichlorobiphenyl (XIII) having a Dk of 5.0 at 25° and 100 Kc. The overall yield from 4-nitrobiphenyl was 11.6%. Evidently, in this case, little 2,x,x-trichloro-4-nitrobiphenyl (XIa) was formed in the chlorination step. With three chlorines in one ring, cancelling of chlorine dipoles is to be expected.

The last approach using a blocking group was via an alkylbiphenyl. Chlorination of nonylbiphenyl afforded material which analyzed for nonyltrichlorobiphenyl, but on dealkylation, only slightly more than one chlorine per biphenyl molecule was found. Apparently, side chain chlorination is a major factor; this area was abandoned.

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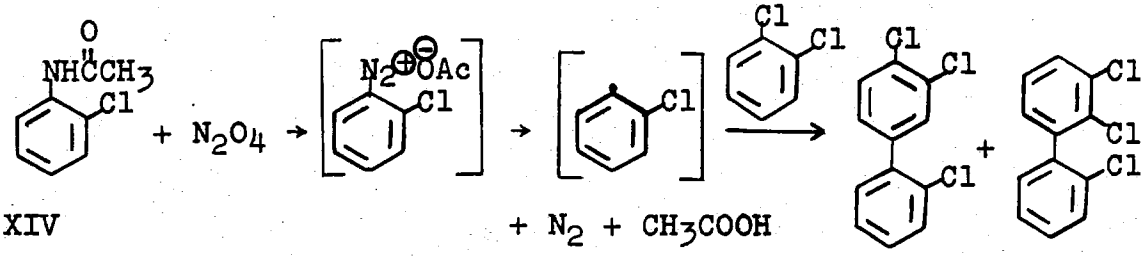
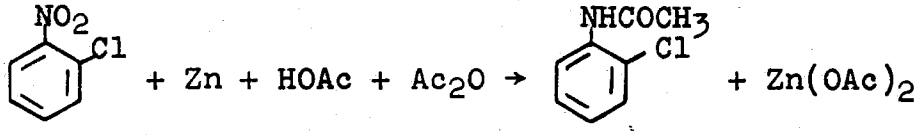
GOMBERG REACTION A study of the previously described (1) Gomberg reaction of o-chloroacetanilide (XIV), dinitrogen tetroxide, and o-dichlorobenzene was undertaken in order to



XIV + N_2 + CH_3COOH IIIa IIIb

determine optimum conditions and yields for the process. One of the first requirements was an economical source of o-chloroacetanilide itself. A one-step reductive acetylation of o-nitrochlorobenzene (XV) to o-chloroacetanilide (XIV) in 91%



XV XIV

yield was developed using zinc dust, acetic acid and acetic anhydride. The results of the Gomberg study are listed in Table III. It may be seen that an excess (200-300% of theoretical) of dinitrogen tetroxide is necessary for optimum yields. A buffer or a base is necessary to react with the nitric acid formed in the nitrosation. From the series of reactions run it appears that potassium carbonate is better in this respect than sodium acetate and that water present in any form (Table III, Run 9) completely supresses the reaction. The use of dinitrogen trioxide in place of dinitrogen tetroxide affords no advantage (Table III, Runs 5, 11). It is apparent that a wash step between nitrosation and decomposition is necessary to remove the excess dinitrogen tetroxide. Omission of the wash step (Table III, Run 3), or use of nitrogen stream and reduced pressure to remove it (Table III, Runs 4, 8) afforded lower yields. There is no advantage in adding the nitrosated anilide to warm orthene (Table III, Run 6) over warming the entire mixture slowly (Table III, Run 5), nor is there any advantage in employing inverse addition in the nitrosation step (Table III, Runs 7, 10). There is no relationship between the volume of nitrogen evolved and the product yield, except that in no case was the yield of product greater than the yield of evolved nitrogen.

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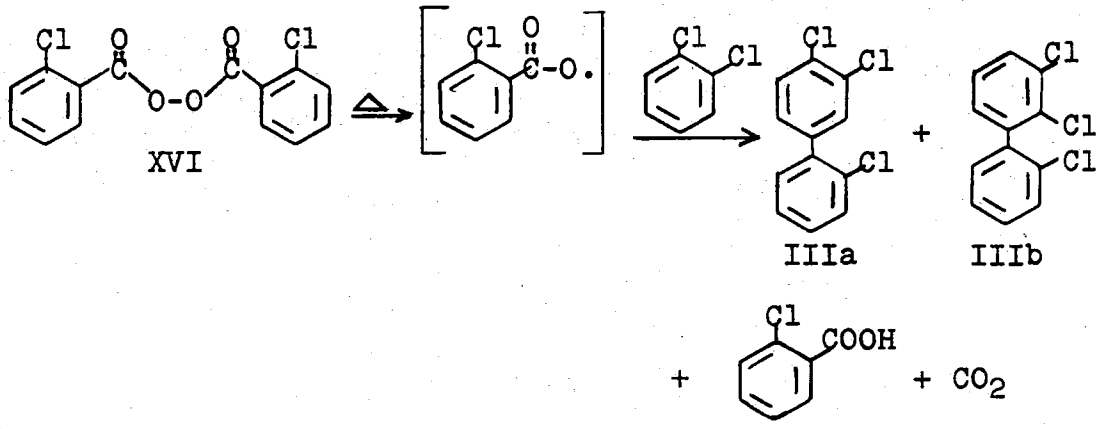
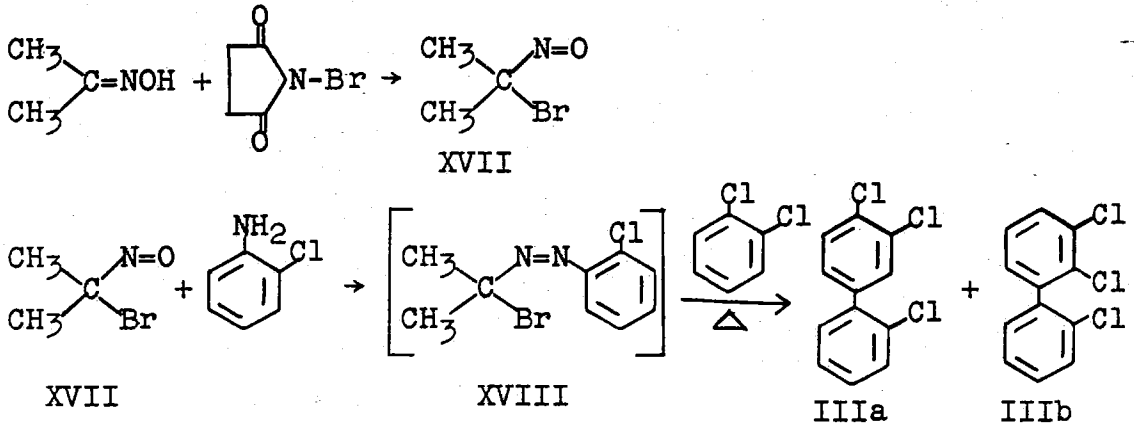
Two other routes to the o-chlorophenyl radical intermediate in the Gomberg reaction were investigated. Decomposition of bis-o-chlorobenzoyl peroxide (XVI) in orthene afforded the Gomberg trichlorobiphenyl mixture (III) in 46% yield.



XVI IIIa IIIb

Production of a mixed haloalkyl arylazo compound and its decomposition in orthene was the second new route to the Gomberg trichlorobiphenyl mixture (III). Reaction of acetone



XVII XVIII IIIa IIIb

oxime with N-bromosuccinimide afforded 2-bromo-2-nitrosopropane (XVII). Reaction of XVII with o-chloroaniline led to the haloalkyl-o-chlorophenyl azo compound (XVIII) which was not isolated, but was decomposed directly in orthene to afford the Gomberg trichlorobiphenyl mixture in 9% overall yield from acetone oxime. This product was identical with that obtained from nitroso-o-chloroacetanilide and orthene.

From a rough cost estimate on the optimum process (Table III, Run 10) it was concluded that the high raw material cost (> $2/lb.) precluded any further interest in this process at this time.

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METHOXYAROCLOR (METHOXYDICHLOROBIPHENYL) (NBP 423639) To a mixture of 40.5 g. (0.75 mole) of sodium methoxide and 500 ml. of diglyme (the dimethyl ether of diethylene glycol) was added 128.5 g. (0.5 mole) of Aroclor 1242. The mixture was heated at reflux (162°) for 22 hours. After cooling, the mixture was filtered and the solids were washed with ether. The filtrates were combined and the ether and diglyme were removed by distillation. The residue was distilled yielding 81.8 g. (64.7%) of methoxyaroclor, b.p. 130-155° at 0.5 mm., n_D^{25} = 1.6075, having a dielectric constant at 100 Kc. and 25° of 7.45 and a pour point of -10°C.

Anal. Found: Cl, 28.78, 28.78.

The introduction of an average of 0.94 methoxyl per Aroclor 1242 molecule is indicated.

Bomb Run (NBP 431176) A mixture of 51.4 g. (0.2 mole) of Aroclor 1242, 10.8 g. (0.2 mole) of sodium methoxide and 20 ml. of diglyme was heated in a bomb for 19 hours at 200°. After cooling, the mixture was filtered and the solids washed with ether. The filtrates were combined, washed with water, dilute acid, dilute base, and water and dried over magnesium sulfate. The ether solution was evaporated and the residue distilled yielding 33 g. (60%) of "methoxyaroclor", b.p. 142-162° at 0.7 mm., n_D^{25} 1.6166, having a dielectric constant of 6.98 at 100 Kc. and 25°.

Anal. Found: Cl, 33.25, 33.24.

Introduction of 0.61 methoxyl per Aroclor molecule is indicated.

Bomb Run (NBP 431172) A mixture of 51.4 g. (0.2 mole) of Aroclor and 42.2 g. (0.2 mole) of 25% sodium methoxide in methanol was heated in a bomb at 200° for 16 hours. The procedure from run above was then followed. The crude product was distilled yielding 31.7 g. (63%) of "methoxyaroclor", b.p. 140-160° at 0.8 mm., n_D^{25} 1.6196, having a dielectric constant of 6.30 at 25° and 100 Kc.

Anal. Found: Cl, 36.31, 36.30.

Introduction of 0.37 methoxyl per Aroclor 1242 molecule is indicated.

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METHOXYAROCLOR FROM AROCLOR 1248 (NBP 431154) A mixture of 73 g. (0.25 mole) of Aroclor 1248, 27 g. (0.5 mole) of sodium methoxide and 250 ml. of diglyme was heated at reflux for 18 hours. After cooling, the mixture was filtered and the solids washed with ether. The filtrates were combined and the ether and diglyme were evaporated. The residue was distilled yielding 48 g. (68%) of "methoxyaroclor", b.p. 142-187° at 0.6 mm. having a dielectric constant of 7.92 at 100 Kc. and 25°C., and a pour point of -1°C.

Anal. Found: Cl, 29.80, 29.80.

Introduction of 1.6 methoxyls per Aroclor 1248 molecule is indicated.

METHOXYAROCLOR FROM AROCLOR 1254 (NBP 431159) A mixture of 81.6 g. (0.25 mole) of Aroclor 1254 and 27 g. (0.5 mole) of sodium methoxide in 250 ml. of diglyme was heated at reflux for 21 hours. After cooling, the mixture was filtered and the solids washed with ether. The filtrates were combined and the ether and diglyme evaporated. The residue was distilled yielding 41.6 g. (52.5%) of "methoxyaroclor", b.p. 160-185° at 0.6 mm., having a dielectric constant of 6.7 at 100 Kc. and 25° and a pour point of +24°C.

Anal. Found: Cl, 39.12, 39.13.

The introduction of 1.47 methoxyls per Aroclor 1254 molecule is indicated.

REACTION OF AROCLOR 1242 WITH SODIUM iso-PROPOXIDE (NBP 423605) Sodium (10 g., 0.44 mole) was added to 200 ml. of isopropyl alcohol and the mixture heated until the reaction was complete. The isopropoxide solution was then added to a solution of 103 g. (0.4 mole) of Aroclor 1242 in 350 ml. of diglyme. The excess isopropyl alcohol was removed by distillation and the diglyme solution then heated at reflux (165°) for ten hours. After cooling the mixture was filtered, the filtrate evaporated to small volume and the residue partitioned between methylene chloride and water. The methylene chloride solution was washed with water, dried over magnesium sulfate and evaporated to small volume. The residue was distilled yielding 78.8 g. (70.4%) of "isopropoxyaroclor", b.p. 118-145° at 0.3 mm., having a dielectric constant of 6.6 at 100 Kc. and 25° and a pour point of -18°C.

Anal. Found: Cl, 32.60, 32.75.

The introduction of 0.54 alkoxyl per Aroclor 1242 molecule is indicated.

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REACTION OF THE GOMBERG TRICHLOROBIPHENYL MIXTURE (III) WITH SODIUM TETRAHYDROFURFURYL ALCOHOLATE (NBP 416024, 416025) The reaction was carried out as described by J. Dazzi, RD-58-Interim Report 1180, p. 21. The product, b.p. 181-191° at 0.2 mm., obtained in 60.4% yield had a dielectric constant of 8.62 at 25° and 100Kc.

Anal. Calc'd. for $C_{17}H_{16}Cl_2O_2$: Cl, 21.94.
Found: Cl, 21.76, 21.80.

REACTION OF 2,4'-DICHLOROBIPHENYL (V) WITH SODIUM METHOXIDE (NBP 423615) A mixture of 43.2 g. (0.19 mole) of 2,4'-dichlorobiphenyl and 10.5 g. (0.19 mole) of sodium methoxide in 200 ml. of diglyme was heated at reflux for 15 hours. After cooling, the mixture was filtered and the filtrate evaporated to small volume. The residue was partitioned between ether and water and the ether solution was washed once with water and dried over magnesium sulfate. The ether was evaporated and the residue distilled yielding 39.2 g. (92.6%) of material, b.p. 116-150° at 0.5 mm.

Anal. Found: Cl, 25.53, 25.53 indicating introduction of an average of 0.41 methoxyl per molecule.

DEHALOGENATION (NBP 431157) To a solution of 4.1 g. (0.018 mole) of the product above (NBP 423615) in 50 ml. of ethanol was added 0.3 g. of 10% palladium on carbon and 15 g. (0.3 mole) of hydrazine hydrate and the mixture was heated at reflux for one-half hour. The mixture was cooled and filtered and the filtrate partitioned between ether and water. The ether solution was washed twice with dilute hydrochloric acid and then with water and was dried over magnesium sulfate. The oily solid resulting after evaporation of the ether was submitted for vapor phase chromatography.

Found: biphenyl (66.3%); 2-methoxybiphenyl (13.8%); 4-methoxybiphenyl (15.4%); and dimethoxybiphenyl (4.5%).

DEHALOGENATION OF THE METHOXYAROCLOR OBTAINED FROM AROCLOR 1242 (NBP 431156) A mixture of 6.2 g. (0.025 mole) of methoxyaroclor (NBP 423644), 12.5 g. (0.25 mole) of hydrazine hydrate and 0.3 g. of 10% palladium on carbon in 50 ml. of ethanol was heated at reflux for one hour. The workup was as described above. The resulting oil was submitted for vapor phase chromatography.

Found: biphenyl (39.1%); 2-methoxybiphenyl (26.2%); 3-methoxybiphenyl (9.9%); 4-methoxybiphenyl (17.0%); high-boiler (7.7%).

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DEHALOGENATION OF MIXTURE (III) OF METHOXYAROCLORS OBTAINED FROM THE GOMBERG TRICHLOROBIPHENYL (NBP 431160) A mixture of 2.0 g. (0.008 mole) of methoxyaroclor (NBP 416026), 10 g. (0.2 mole) of hydrazine hydrate and 0.3 g. of 10% palladium on carbon in 50 ml. of ethanol was heated at reflux for one-half hour. The workup was as described above. The resulting oil was submitted for vapor phase chromatography.

Found: biphenyl (31.5%); 2-methoxybiphenyl (10.9%); 3-methoxybiphenyl (15.8%); 4-methoxybiphenyl (24.1%); dimethoxybiphenyl (17.7%).

SULFONATION OF AROCLOR 1242 (NBP 397567, 397570, 397587, 397597) To a solution of 46.6 g. (0.4 mole) of chlorosulfonic acid in 400 ml. of chloroform was added 103.2 g. (0.4 mole) of Aroclor 1242. After standing at 25° for 4 hours, the solution was mixed with 10% sodium hydroxide. After this extraction, the chloroform solution was washed once with water and dried over sodium sulfate. The chloroform was evaporated and the residue distilled yielding 55 g. (53.3%) of unreacted Aroclor, b.p. 135-150° at 1.0 mm. The dielectric constant of this product at 25° and 100 Kc. was 5.30 as compared to 5.82 observed for Aroclor 1242 under the same conditions.

The sodium hydroxide extract from above was acidified (HCl) and extracted twice with chloroform. Evaporation of the chloroform afforded 44.8 g. (71%) of gummy white solid. This solid was dissolved in 1-liter of 55% (by volume) sulfuric acid and the solution heated at reflux (155°) with a Dean-Stark apparatus being used to collect any steam-volatile organic material produced. After 96 hours refluxing, no trichlorobiphenyls had been produced. Pentane extraction of the cooled reaction mixture also afforded no desulfonated product.

x,x-DICHLORO-2-NITROBIPHENYL (NBP 410861) Chlorine was bubbled into a mixture of 99.5 g. (0.5 mole) of 2-nitrobiphenyl and 1.5 g. of ferric chloride at 50° until a weight increase of 34.5 g. was noted. The reaction mixture was distilled and the fraction, b.p. 165-180° at 0.15-0.30 mm., was collected yielding 120 g. (89.5%) of yellow liquid which was not characterized further.

x,x-DICHLORO-2-AMINOBIPHENYL (NBP 410873) A mixture of 54.6 g. (0.2 mole) of x,x-dichloro-2-nitrobiphenyl and 74.8 g. (0.63 mole) of tin in 1-liter of absolute ethanol was stirred and cooled in an ice bath. Concentrated hydrochloric acid (350 ml.) was added slowly while keeping the temperature below 30° by means of the ice bath. When the addition was complete,

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the mixture was stirred at 25° for 16 hours. The tin that was still unreacted was removed by filtration and washed with ethanol. The filtrates were combined and the ethanol evaporated. The residue was partitioned between ether and aqueous potassium hydroxide and the ether solution washed twice with water and dried over sodium sulfate. The ether was evaporated and the residual oil distilled yielding 39.4 g. (81.3%) of x,x-dichloro-2-aminobiphenyl, b.p. 135-152° at 0.2 mm.

x,x,2-TRICHLOROBIPHENYL (NBP 410876, 410877) To 140 ml. of concentrated sulfuric acid was slowly added with stirring and cooling 13.8 g. (0.20 mole) of sodium nitrite. To this cold solution was slowly added a solution of 39.3 g. (0.165 mole) of x,x-dichloro-2-aminobiphenyl in 150 ml. glacial acetic acid. A solution of cuprous chloride (0.5 mole) in 175 ml. of concentrated hydrochloric acid was prepared as described in the literature (4). The solution of the diazotized amine was added to the cuprous chloride solution and was warmed slowly and finally heated at 80° for 18 hours. Water was then added and the mixture extracted twice with hexane. The hexane extracts were combined, washed thrice with concentrated sulfuric acid, and then with water, 5% potassium carbonate and water and were dried over sodium sulfate. The hexane was evaporated and the residue distilled yielding 33 g. (77.5%) of x,x,2-trichlorobiphenyl, b.p. 125-130° at 0.2 mm.

Anal. Calc'd. for $C_{12}H_7Cl_3$: Cl, 41.30.
Found: Cl, 41.39, 41.18.

The material possessed a dielectric constant of 7.2 at 100 Kc. and 25°.

x,x,x-TRICHLORO-4-NITROBIPHENYL (NBP 410875) Chlorine was bubbled into a mixture of 100 g. 4-nitrobiphenyl (0.5 mole) and 3.2 g. of ferric chloride at 120-150° until a weight increase of 52 g. was noted. The mixture was cooled and poured into methylene chloride. The methylene chloride solution was washed three times with water and then evaporated to give 164 g. of crude x,x,x-trichloro-4-nitrobiphenyl.

x,x,x-TRICHLORO-4-AMINOBIPHENYL (NBP 410878) To a cooled suspension of 164 g. of crude x,x,x-trichloro-4-nitrobiphenyl and 178 g. (1.5 mole) of tin in 2.5-liters of absolute ethanol was slowly added 900 ml. of concentrated hydrochloric acid keeping the temperature below 25°. The mixture was then stirred at 25° for two days. The mixture was evaporated and the residual solids were partitioned between ether and 10% potassium hydroxide. The ether solution was washed with water, dried over sodium sulfate and evaporated yielding 129 g. (94.6%) of crude x,x,x-trichloro-4-aminobiphenyl.

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x,x,x-TRICHLOROBIPHENYL (NBP 410879, 410880) To a solution of 129 g. of crude x,x,x-trichloro-4-aminobiphenyl in 1-liter of 95% ethanol and 225 ml. of benzene was added with stirring 60 ml. of concentrated sulfuric acid. Then 69 g. (1 mole) of sodium nitrite was added. The mixture was warmed slowly to reflux and then heated at reflux for 17 hours. The solvent mixture was evaporated to small volume and the residue partitioned between hexane and water. The hexane solution was washed three times with concentrated sulfuric acid, once with water, twice with 5% potassium carbonate and with water and was dried over sodium sulfate. The hexane was evaporated and the residue distilled yielding 15.0 g. (12.3%) of x,x,x-trichlorobiphenyl, b.p. 110-130° at 0.12 mm. The product possessed a dielectric constant of 5.0 at 100 Kc. and 25°.

o-CHLOROACETANILIDE (XIV) (NBP 405311, 405312) (By reductive acetylation of ONCB) To a mixture of 363 g. of 90% zinc dust (5 moles) in 750 ml. of acetic anhydride was added a solution of 158 g. (1 mole) of o-nitrochlorobenzene in 63 ml. (1.1 mole) of acetic acid and 250 ml. of acetic anhydride. The ONCB was added at such a rate that the temperature was maintained at 50°, the addition requiring six hours. After the addition was complete, the mixture was allowed to cool to 25°, and was then stirred at that temperature for six hours. The reaction mixture was then filtered and the solid washed on the filter with 180 ml. of acetic acid. The filtrates were combined and evaporated to dryness (aspirator). The residual solid was then distilled and the fraction b.p. 110-120° at 0.5-0.6 mm. was collected yielding 154.8 g. (91.4%) of o-chloroacetanilide, m.p. 82-85°.

GOMBERG REACTION (2,3',4'- AND 2,2',3'-TRICHLOROBIPHENYL (III))

From o-Chloroacetanilide (NBP 416010) To a mixture of 400 ml. of o-dichlorobenzene and 138 g. (1 mole) of anhydrous potassium carbonate stirred at 0-5°C. in an ice bath was added 69 g. (0.75 mole) of dinitrogen tetroxide. To this mixture was added with stirring during 30 min. 42.5 g. (0.25 mole) of o-chloroacetanilide dissolved in 450 ml. of o-dichlorobenzene. The mixture was stirred at 0-5°C. for 2 hours, was washed with 500 ml. of ice water containing 34.5 g. (0.25 mole) of potassium carbonate and dried over sodium sulfate.

The o-dichlorobenzene solution was then added to 1150 ml. of o-dichlorobenzene (total vol. o-$C_6H_4Cl_2$, 2 liters) at 25° and slow warming, with stirring, begun. Evolution of nitrogen is first noted at 25-30° and warming is continued at a rate to afford rapid nitrogen evolution. After 3 hours the solution temperature reached 90° and was maintained at this point until no more gas was evolved.

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The o-dichlorobenzene was evaporated and the residue dissolved in 300 ml. hexane and the solution filtered. The hexane solution was washed with 3 portions of concentrated sulfuric acid (total volume 600 ml.). The combined sulfuric acid washes were re-extracted with 200 ml. of hexane. The hexane solutions were combined, washed with water (400 ml.), 2 portions of 10% sodium carbonate (600 ml.) and water (400 ml.), and dried over sodium sulfate. The hexane was evaporated and the residue distilled yielding 33.4 g. (52.5%) of trichlorobiphenyls, (III) b.p. 117-125° at 0.15-0.20 mm.

From Bis-o-chlorobenzoyl Peroxide and o-Dichlorobenzene (NBP 410883, 410884, 410885) The preparation of bis-o-chlorobenzoyl peroxide (XVI) is described in the literature (5). A solution of 31.1 g. (0.1 mole) of bis-o-chlorobenzoyl peroxide in 1.6 liters of o-dichlorobenzene was heated until gas evolution began and warming was continued at such a rate that gas evolution was rapid, but not violent. The solution was then heated at reflux for 4 hours. A test (sodium iodide-acetone) on the solution showed no peroxide remaining. The o-dichlorobenzene was evaporated and the residue taken up in hexane. The hexane solution was washed with conc. sulfuric acid (twice), water, 10% potassium carbonate (twice) and water and was dried over sodium sulfate. The hexane was evaporated and the residue distilled yielding 11.8 g. (46%) of 2,2',3'- and 2,3',4'-trichlorobiphenyl (III), b.p. 120-130° at 0.10-0.15 mm.

From o-Chloroaniline and 2-Bromo-2-nitrosopropane (NBP 405330, 405331, 405332, 405335, 405336) 2-Bromo-2-nitrosopropane (XVII) was prepared as described in the literature (6). The preparation in pentane solution was used without purification or isolation of the product. The solution of 2-bromo-2-nitrosopropane (theo. 15.2 g., 0.1 mole) in 100 ml. pentane was mixed with a solution of 12.7 g. (0.1 mole) of o-chloroaniline in 300 ml. o-dichlorobenzene. The pentane was removed by distillation and the mixture slowly heated to reflux. During the period of warming, the solution changed color from blue → green → yellow → red-brown. The solution was then heated at reflux (160°) for 18 hours. After cooling to 25° the orthene solution was washed with dilute hydrochloric acid twice and with water. After drying over sodium sulfate, the o-dichlorobenzene was evaporated and the residue distilled yielding 2.3 g. (9%) of trichlorobiphenyls (III), b.p. 130-150° at 0.75 mm. A vapor phase chromatogram on the product showed the same peak pattern (retention time and relative size) as obtained from the Gomberg reaction described above.

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VII. TOXICITY AND HAZARDS

The toxicity of the Aroclors has been reported (7). It is expected that the Methoxyaroclors would possess similar toxicity. Diazonium compounds are known to be sensitive and should be handled with according care. Aminobiphenyls have been reported to be carcinogenic so that the nitrobiphenyls and the chloroaminobiphenyls should be treated carefully.

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IX. APPENDIX

LIST OF NOTEBOOK PAGES COVERING WORK REPORTED

397551-397600
401601-401650
405301-405350
410851-410900
416001-416050
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PREPARATION OF SOME SUBSTITUTED BIPHENYLSULFONIC ACIDS

Robert G. Schultz

While there is extensive literature on the sulfonation of biphenyl[1-6], no information is to be found on the direct mono-

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sulfonation of the substituted biphenyls reported herein. The present work stems from the development of a convenient procedure for the specific monosulfonation of biphenyl. It was found that 4-biphenylsulfonic acid is much less soluble in chloroform than is biphenyl so that by taking advantage of this solubility difference, it was possible to preclude any further reaction by precipitation of the monosulfonic acid.

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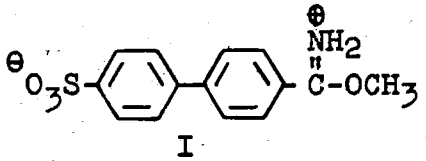
Substituted biphenyls could be sulfonated in a similar manner, the procedure differing mainly in the quantity of chloroform solvent employed. It is expected that in the bromo-, nitro- and cyanobiphenyls sulfonation would occur only in the more active, unsubstituted ring in the 4'-position. In 4-methyl- and 4-t-butylbiphenyl structural assignments are less certain but on the basis of infrared spectra and from steric considerations 4'-substitution also might well be favored.

In the sulfonation of 4-biphenylcarbonitrile it was found that the first mole of chlorosulfonic acid was consumed in complex formation with the nitrile group and only on addition of a second mole of chlorosulfonic acid did sulfonation occur. In order to destroy the excess chlorosulfonic acid present after the completion of this reaction, methanol was added which resulted in the formation of the zwitterion form of methyl 4'-biphenylimidoate-4-sulfonic acid (I).



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EXPERIMENTAL*

*All melting points are corrected. Analyses by Mr. E. M. Hubbard and associates or by Galbraith Laboratories, Knoxville, Tenn. Samples for analysis were dried in an Abderhalden apparatus at 80° and 0.5 mm. for 16 to 24 hours.

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4-Biphenylsulfonic Acid. To a stirred solution of 154 g. (1 mole) of biphenyl in 850 ml. of chloroform was slowly added 144 g. (1.237 mole) of chlorosulfonic acid in 125 ml. chloroform. (The excess chlorosulfonic acid was used to react with the ethanol present as a stabilizer in the chloroform.) During the course of the addition, a temperature increase of 15° was noted. After addition of about 75% of the chlorosulfonic acid precipitation of 4-biphenylsulfonic acid began. The suspension was stirred for 30 minutes after the completion of addition of the chlorosulfonic acid. The precipitate was filtered (sintered glass funnel), washed with 500 ml. chloroform, and dried yielding 187 g. (80%) of 4-biphenylsulfonic acid, m.p. 138-140° (lit.[1] m.p. 138°).

Anal. Calc'd. for $C_{12}H_{10}SO_3$: S, 13.68.
Found: S, 13.91, 13.91.

A second crop (about 15%) of less pure 4-biphenylsulfonic acid could be obtained from the mother liquor.

4'-Bromobiphenyl-4-sulfonic Acid. Prepared as described for 4-biphenylsulfonic acid except that 2 liters chloroform used per mole 4-bromobiphenyl. Yield 97%, m.p. 157-158°.

Anal. Calc'd. for $C_{12}H_9BrO_3S$: C, 46.02; H, 2.89; Br, 25.53.
Found: C, 45.30, 45.46; H, 3.04, 3.34; Br, 25.33, 25.41.

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A copper salt was prepared in 75% yield.

Anal. Calc'd. for $[C_{12}H_8BrO_3S]_2Cu \cdot 1/2\ H_2O$: C, 41.36; H, 2.46; Br, 22.93; S, 9.20; Cu, 9.12. Found: C, 41.30, 41.56; H, 2.55, 2.76; Br, 22.93, 22.83; S, 9.42; Cu, 9.20.

2'-Bromobiphenyl-4-sulfonic Acid. To a solution of 11.6 g. (0.05 mole) of 2-bromobiphenyl in 25 ml. chloroform was slowly added 6.6 g. (0.056 mole) of chlorosulfonic acid in 25 ml. chloroform. After stirring at 25° for one hour 25 ml. hexane was added and the resulting precipitate was filtered, washed with hexane and vacuum dried yielding 13.5 g. (86%) of 2'-bromobiphenyl-4-sulfonic acid, m.p. 58-62°, very hygroscopic. A sample was recrystallized from methylene chloride-hexane and then from carbon tetrachloride, m.p. 62-64°. A sample was dried (Abderhalden) at 25° and 0.5 mm. for 24 hrs. and submitted for analysis.

Anal. Calc'd. for $C_{12}H_9BrO_3S \cdot 2.5\ H_2O$: C, 40.23; H, 3.92.
Found: C, 40.39, 39.91, 40.57; H, 4.35, 4.07, 3.96.

A copper salt was prepared in 86% yield.

Anal. Calc'd. for $[C_{12}H_8BrO_3S]_2Cu \cdot 2H_2O$: C, 39.82; H, 2.78; Br, 22.08; S, 8.86; Cu, 8.77. Found: C, 40.06, 40.16; H, 2.84, 3.11; Br, 22.42, 22.09; S, 8.73, 8.73; Cu, 8.58, 8.57.

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4'-Nitrobiphenyl-4-sulfonic Acid. 4'-Nitrobiphenyl-4-sulfonic acid was prepared as described for 4-biphenylsulfonic acid in 99% yield, m.p. 148-149.5° (dec.). A sample was purified for analysis by precipitation from aqueous solution by acidification with concentrated hydrochloric acid, m.p. 149-150°.

Anal. Calc'd. for $C_{12}H_8NSO_5$: C, 51.60; H, 3.25; S, 11.47; N, 5.01. Found: C, 51.16; H, 3.87; S, 10.97; N, 4.60.

A silver salt was prepared in 38% yield.

Anal. Calc'd. for $C_{12}H_8NSO_5Ag \cdot 1/2\ H_2O$: Ag, 27.30.
Found: Ag, 27.05, 27.25.

4'-Methylbiphenyl-4-sulfonic Acid. 4'-Methylbiphenyl-4-sulfonic acid was prepared as described for 4-biphenylsulfonic acid in 82% yield, m.p. 166-168°, infrared band at 807 cm.$^{-1}$ in Nujol.

Anal. Calc'd. for $C_{13}H_{12}SO_3 \cdot H_2O$: C, 58.62; H, 5.29; S, 12.04.
Found: C, 58.28, 58.13; H, 5.36, 5.29; S, 12.15, 12.21.

A copper salt was prepared in 90% yield.

Anal. Calc'd. for $[C_{13}H_{11}SO_3]_2Cu \cdot H_2O$: C, 54.20; H, 4.19; S, 11.13; Cu, 11.03. Found: C, 54.30, 54.43; H, 4.50, 4.60; S, 11.15, 11.17; Cu, 10.70, 10.81.

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4'-t-Butylbiphenyl-4-sulfonic Acid. 4'-t-Butylbiphenyl-4-sulfonic acid was prepared as described for 2'-bromobiphenyl-4-sulfonic acid in 91% yield, m.p. 127-129°, infrared band at 820 cm.$^{-1}$ in Nujol.

Anal. Calc'd. for $C_{16}H_{18}O_3S \cdot H_2O$: C, 62.31; H, 6.53; S, 10.40.
Found: C, 62.28; H, 6.74; S, 10.94.

A copper salt was prepared in 95% yield.

Anal. Calc'd. for $[C_{16}H_{17}O_3S]_2Cu \cdot 3H_2O$: C, 55.17; H, 5.78; S, 9.21; Cu, 9.13. Found: C, 55.35, 55.23; H, 6.02, 6.05; S, 9.15, 8.97; Cu, 9.09, 9.05.

Methyl-4'-biphenylimidoate-4-sulfonic Acid (I). To a solution of 17.9 g. (0.1 mole) of 4-biphenylcarbonitrile in 60 ml. chloroform was added 24.5 g. (0.21 mole) of chlorosulfonic acid in 15 ml. chloroform. The mixture was stirred at 25° for 2 1/2 hours. An oily solid separated from the chloroform solution. The chloroform was decanted and the residual solid dissolved in 25 ml. methanol. Ether (75 ml.) was added and the resulting bright yellow solid was filtered, washed with ether and dried yielding 17.5 g. (68%) of methyl-4'-biphenylimidoate-4-sulfonic acid (I), m.p. 238-240°, infrared bands at 1670, 1165 and 1030 cm.$^{-1}$ in Nujol.

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Anal. Calc'd. for $C_{14}H_{13}NO_4S$: C, 57.71; H, 4.70; N, 4.81; S, 11.01. Found: C, 56.95, 57.10; H, 4.39, 4.68; N, 4.98, 4.96; S, 10.88, 10.74.

Research and Engineering Division
Monsanto Chemical Company
Dayton 7, Ohio

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TABLE I. METHOXYAROCLORS - ATMOSPHERIC PRESSURE RUNS

Run No.	Substrate (Moles)	Alkoxide (Moles)	Solvent (Vol. in ml.)	Time (hrs.)	Temp. (°C.)	Yield (%)	n_D^{25}	Dk (at 25°C.)	Pour Point (°C.)	$Cl_x(OCH_3)_y$ x	y	NBP
1	Aroclor 1242 (0.5)	$NaOCH_3$ (0.75)	Diglyme (500)	22	160	65	1.6075	7.45	-10	2.06	0.94	423639
2	" (0.5)	" (0.7)	" (500)	21	165	68	1.6078	7.43	-	2.08	0.92	423642
3	" (0.5)	" (1.0)	" (500)	17	160	70	1.6104	7.32	-	2.11	0.89	423644
4	" (0.5)	" (0.75)	" (500)	22	160	72	1.6131	7.20	-10	2.20	0.80	423623
5	" (0.3)	" (0.9)	" (250)	22	160	73	1.6118	7.14	-	2.20	0.80	423632
6	" (0.5)	" (1.0)	" (500)	19	160	73	1.6136	7.05	-	2.26	0.74	423624
7	" (0.5)	" (0.65)	" (400)	12	165	66	-	7.04	-15	2.31	0.69	416036-37
8	" (0.5)	" (0.5)	" (400)	21	160	80	1.6138	6.90	-	2.33	0.67	423621
9	" (0.5)	" (0.5)	" (400)	18	160	86	1.6176	6.34	-	2.71	0.29	423622
10	" (0.5)	" (1.0)	" (400)	1	160	76	1.6194	6.30	-	2.83	0.17	423620
11	" (0.5)	" (0.75)	None	22	165	95	1.6238	5.94	-	3.00	0.00	423627
12	" (0.5)	" (0.5)	"	17	195	78	1.6230	6.00	-	3.00	0.00	431161
13	" (0.2)	" (0.2)	MeOH (25)	18	100	0	-	-	-	-	-	431164
14	" (0.2)	" (0.2)	" (12)	17	130	0	-	-	-	-	-	431165
15	" (0.3)	" (0.35)	Ethylene glycol (250)	20	195	0	-	-	-	-	-	423633
16	" (0.25)	" (0.38)	" (50) Diglyme (200)	23	130	0	-	-	-	-	-	423640
17	" (0.5)	$Mg(OMe)_2$ (0.5)	MeOH (350)	2	70	0	-	-	-	-	-	431182
18	" (0.4)	$NaOCH(CH_3)_2$ (0.44)	Diglyme (350)	10	165	70	-	6.60	-18	2.46	0.54	423605
19	Aroclor 1242' (HDK-1) (0.166)	NaOMe (0.17)	" (175)	4	170	73	-	7.60	-20	-	-	423603
20	Gomberg trichloro-biphenyl (0.25)	" (0.28)	" (200)	18	165	80	-	9.14	+2	2.14	0.86	416026
21	" (0.25)	Na-OCH_2- (0.375)	Toluene (30)	10	155-195	60	-	8.62	-	2.00	1.00	416024-25
22	Aroclor 1248 (0.25)	NaOMe (0.5)	Diglyme (250)	18	165	68	-	7.92	-1	2.40	1.60	431154
23	Aroclor 1254 (0.25)	" (0.5)	" (250)	21	160	52	-	6.70	+24	3.53	1.47	431159
24	2,4'-Dichloro-biphenyl (0.22)	" (0.23)	" (200)	4	160	93	-	-	-	2.96	0.04	423613
25	" (0.19)	" (0.19)	" (200)	40	160	93	-	-	-	2.59	0.41	423615

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TABLE II. METHOXYAROCLORS - BOMB RUNS

Moles of Aroclor 1242	Alkoxide (Moles)	Solvent (Moles)	Catalyst	Time (Hrs.)	Temp. (°C.)	Yield (%)	n_D^{25}	Dk (at 25°)	$\phi\text{-}\phi$ $Cl_x(OCH_3)_y$ x	y	NBP	Run No.
0.2	NaOMe (0.3)	Diglyme 20 ml. (~0.15)	-	16	200	47	1.6140	6.81	2.18	0.82	431180	1
0.2	" (0.2)	" (~0.15)	-	19	200	60	1.6166	6.98	2.39	0.61	431176	2
0.2	" (0.2)	MeOH (0.6)	-	16	200	63	1.6196	6.30	2.63	0.37	431172	3
0.2	" (0.2)	" (0.6)	-	15	225	60	1.6190	6.32	2.65	0.35	431175	4
0.2	" (0.15)	" (0.75)	-	17	175	67	1.6212	6.27	2.80	0.20	431170	5
0.2	" (0.3)	" (0.9)	-	14	200	44	1.6173	6.27	-	-	431177	6
0.2	" (0.3)	" (0.9)	Cu	14	140	78	1.6214	6.30	2.92	0.08	431184	7
0.2	" (0.2)	" (0.6)	Cu	19	200	62	1.6197	6.31	2.67	0.33	431174	8
0.2	" (0.3)	" (0.9)	Cu	18	200	44	1.6176	6.10	2.54	0.46	431187	9
0.2	" (0.3)	" (0.9)	CuCl	14	200	53	1.6184	6.30	2.61	0.39	431188	10
0.2	" (0.3)	" (0.9)	Cupric naphthenate	17	200	49	1.6156	6.30	2.50	0.50	431181	11
0.26	$Mg(OMe)_2$ (0.2)	MeOH (2)	-	14	200	77	1.6242	6.05	3.0	0.0	438162	12

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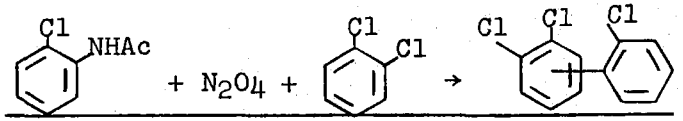
TABLE III. GOMBERG REACTION STUDY



Run No.	Moles o-Chloro-acetanilide	Moles N_2O_4	Volume of Solvent During Nitrosation (ml.)	Volume of Solvent Total (ml.)	Buffer (Moles)	Nitrosation Time (Hrs.)	Nitrosation Temp. (°C.)	Wash Step (b)	Purge Method (b)	Decomposition Temp. at Start (°C.)	Decomposition Highest Temp. (°C.)	Decomposition Total Time (Hrs.)	Decomposition % N_2 of Theory	Yield (%)	NBP
1	0.35	0.39	3500	3500	-	2	-5	Yes	-	25	85	24	(c)	20.6	405314
2	0.30	0.45	500	2000	NaOAc (1.0)	2	0-5	"	-	35	91	8	76.6	39.6	405318
3	0.30	0.32	2300	2300	" (1.0)	1	0	No	-	33	90	12	36	24.2	405322
4	0.30	0.60	2300	2300	" (1.5)	2	0	"	N_2+vacuum	29	100	21	56	26.0	405325
5	0.25	0.75	500	2000	" (1.0)	2	5	Yes	-	(c)	120	20	95	39.7	405334
6	0.25	0.75	500	2000	" (1.0)	2	5	"	-	50 (e)	80	26	62.5(d)	39.0(d)	405344
7	0.25	0.75	500	2000	K_2CO_3 (1.0)	2	5-10	"	-	(c)	115	19	95.6	50	405347
8	0.25	0.75	500	2000	" (1.0)	2	5	No	N_2+vacuum	(c)	58	2	(c)	30	410854
9	0.25	0.75	800	2000	NaOAc·$3H_2O$ (1.0)	2	5	Yes	-	(c)	90	24	2.8	0(f)	416012
10	0.25	0.75	800	2000	K_2CO_3 (1.0)	2	5	"	-	25	94	24	89	52.3(g)	416010
11	0.25	0.75(a)	500	2000	NaOAc (0.61)	1	-5	"	-	33	120	21	60.7	38.8	410898

(a) Nitrosating agent was N_2O_3.

(b) To remove unreacted N_2O_4.

(c) Not recorded.

(d) Some unreacted o-chloroacetanilide was recovered. On basis of unrecovered material, N_2=86% of theory; yield 53.5%.

(e) Diazotized o-chloroacetanilide (cold) was added to warm (50°) orthene.

(f) 86.8% of o-chloroacetanilide was recovered.

(g) Inverse addition in diazotization. o-Chloroacetanilide in orthene was added to N_2O_4 in orthene.

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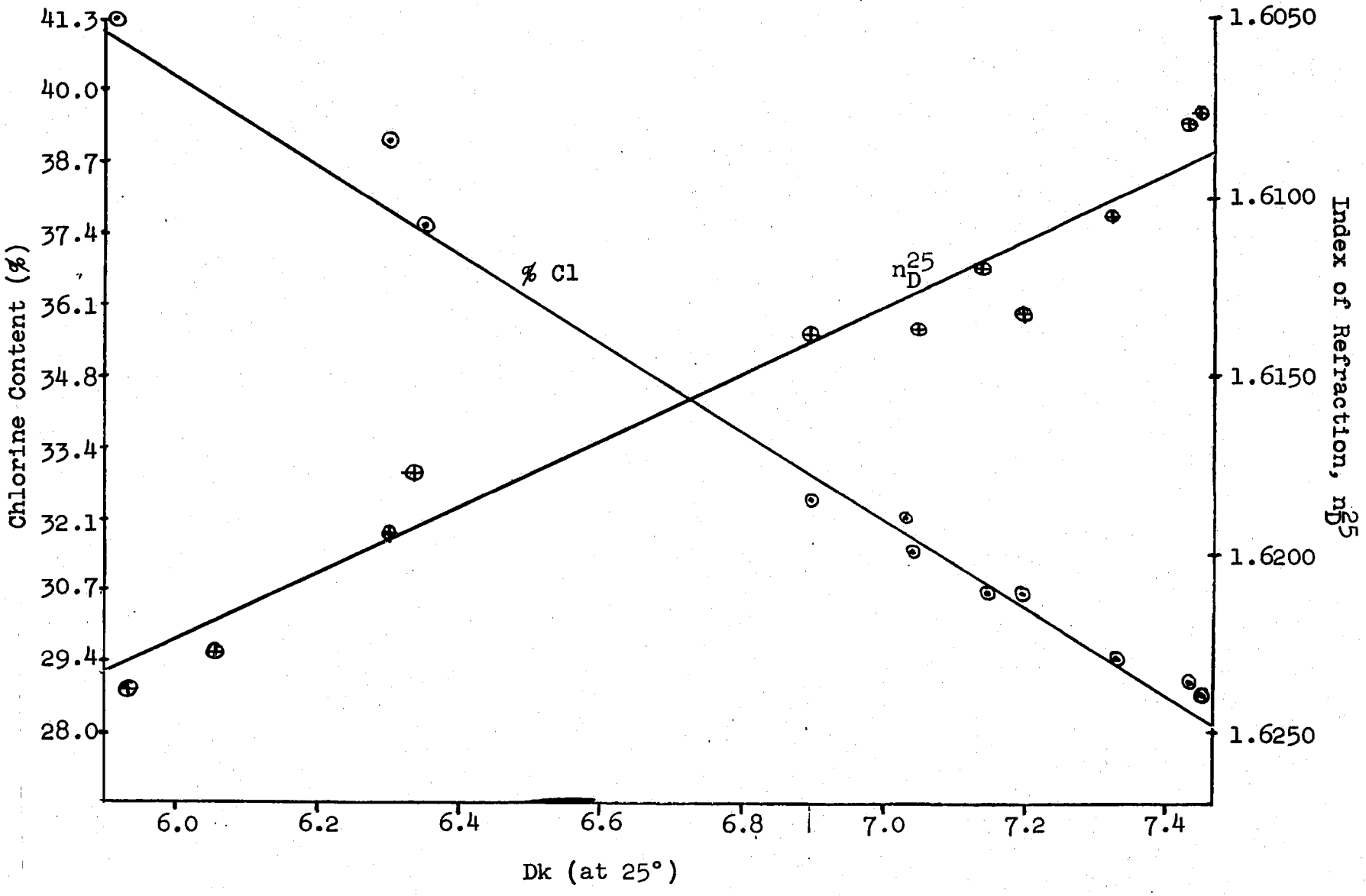
FIGURE I

Relation of Chlorine Content and Index of Refraction to Dielectric Constant in the Methoxyaroclors (NBP 423631)



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