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FINAL REPORT

ON

EXPLORATORY FLUORINATION STUDIES OF BIPHENYL DERIVATIVES

JOB NO. 2-02-750.01-3199

April 19, 1960 H.L. Merten

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MONSANTO CHEMICAL COMPANY
Organic Chemicals Division
St. Louis Research Department

St. Louis Research Report No. 2455

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EXPLORATORY FLUORINATION STUDIES OF BIPHENYL DERIVATIVES

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April 19, 1960 Reported by: H.L. Merten

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INTRODUCTION

This study was undertaken in an effort to explore synthetic routes to obtain fluorinated biphenyl derivatives, and to evaluate such material as potential dielectrics, and as industrial and specialty fluids.

SUMMARY

Decachlorobiphenyl was successfully fluorinated with antimony pentafluoride. The material obtained was a colorless liquid, boiling between 246-247°C., specific gravity of 1.84, and containing about 40% fluorine. The fluorinations were carried out at different molar ratios in an attempt to vary physical properties of the fluorination products. In order to find a substitute for antimony pentafluoride, an expensive chemical, the following reaction systems were investigated using Aroclor 1260, a mixture of chlorinated biphenyls containing about 60% chlorine:

1. antimony trifluoride, antimony pentachloride, —
2. potassium fluoride in dimethylsulfoxide,
3. hydrogen fluoride, potassium fluoride and antimony pentachloride

These experiments were unsuccessful.

In addition, several attempts were made to convert isopropylbiphenyl to the side-chain chlorinated derivative, and then to fluorinate such a material with hydrogen fluoride. Isopropylbiphenyl was chlorinated without a catalyst, with and without actinic light at different temperatures, with and without catalytic amounts of water.

Using actinic light and catalytic amounts of water finally gave a product containing 37% of chlorine, half the amount calculated for a material of the formula $C_{15}H_9Cl_7$.

CONCLUSION

Only the fluorination of decachlorobiphenyl with antimony pentafluoride gave a satisfactory product. The other described reactions were unsuccessful.

Due to the urgency of other projects, further work such as the fluorination of chlorinated isopropylbiphenyl or chlorinated methylbiphenyl was canceled.

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Compared to Monsanto's Aroclor series, fluorinated decachlorobiphenyl failed to exhibit any outstanding dielectric properties significantly better than the chlorinated biphenyls. However, characteristics such as high density, relatively low pour point, and above all, oxidation and thermal resistance are expected to be far superior to that of our Aroclor series.

RECOMMENDATIONS

Fluorinated biphenyl derivatives should exhibit excellent stability against thermal and chemical attack, however, the relatively small nucleus of a fluorine atom would make it necessary to fluorinate alkylated biphenyl derivatives in order to obtain a dipole moment sufficiently high to facilitate a superior dielectric.

It is, therefore, suggested that continuing efforts in this area be directed towards the fluorination of alkylbiphenyl or terphenyl derivatives. Such materials as the chloromethylation products of biphenyl and/or terphenyl could be completely side-chain chlorinated and then be fluorinated with hydrogen fluoride by a relatively simple and cheap procedure, known and described in the literature[4,5].

EXPERIMENTAL WORK

A. Fluorination of Chlorobiphenyl

The successful fluorination of chlorinated ring systems has been described in the literature. The following experiments were carried out in a 1-L Parr autoclave. Different ratios of decachlorobiphenyl and antimony pentafluoride were used in an attempt to introduce just enough fluorine atoms to obtain a high boiling compound or mixture, liquid at room temperature with a pour point not above -5°C.

a. Antimony Pentafluoride

A-78341; 50 g. (0.1 mole) of decachlorobiphenyl and 347 g. (1.6 mole) of antimony pentafluoride were agitated for 2 hours between 180-250°C. The reaction mixture was diluted with chloroform, washed with diluted hydrochloric acid, and was dried. A colorless product distilled between 101-117°C./30 mm. Hg yielding 30 g. (85 wt. percent).

A-93023; 251 g. (0.5 mole) of decachlorobiphenyl and 253 g. (1.25 mole) of antimony pentafluoride were agitated at a temperature between 180-186°C. for 4 hours. The reaction mixture was worked up as described above. A solid material was obtained which was insoluble in glacial acetic acid, Skelly B, ethyl alcohol, toluene, acetone, and dimethylsulfoxide.

A-93024; A similar experiment using a 0.5/2.4 molar ratio gave also a partially solid product.

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A-93025; Using a molar ratio of 0.5/4.0 gave a liquid product, having a specific gravity of 1.84 and a boiling range of 246-247°C. The analysis gave 28.6% Cl, and 43.8% F. The electrical data measured were as follows:

Dk at 25°C.	3.03 (60 c.),	2.99 (1 kc)
Dk at 100°C.	2.67 (60 c.),	2.67 (1 kc)
Diss. Factor at 25°C.	0.24% (60 c.),	0.00% (1 kc)
Diss. Factor at 100°C.	2.60% (60 c.),	0.23% (1 kc)

Several other means of fluorinating were investigated in order to circumvent the use of the rather expensive antimony pentafluoride.

b. Fluorination with antimony trifluoride and antimony pentachloride

A-78338; 356 g. of Aroclor 1260 (ca. 1 mole), 380 g. (2.16 mole) of antimony trifluoride and 38.g. (0.12 mole) of antimony pentachloride were charged into a 1-L Parr autoclave. An exothermic reaction took place when the temperature of the reaction mixture reached 85°C. and climbed to 100°C. without external heating. After 1 hour, this temperature began to drop. With external heat the reaction temperature was maintained at 120°C. for a period of 2 hours. After the reaction mixture was allowed to cool to room temperature, Skelly C was added and the separating solid was washed with water and decomposed with dilute hydrochloric acid. The Skelly solution, and the Skelly extracts, were combined, dried, and passed through a 12" x 1" column of activated alumina. The effluent was stripped of the solvent. The remainder, a colorless liquid, was distilled between 192-204°C./3 mm. Hg pressure. A qualitative analysis failed to indicate any fluorine.

A-78339; A similar experiment as described above was carried out at 250°C. The resulting product was worked up as before and did not contain any fluorine.

c. Fluorination with potassium fluoride and dimethylsulfoxide

A-78325, 78331, 78337; 451 g. of Aroclor 1260 (ca. 1.1 mole), 200 ml. of dimethylsulfoxide, and 169 g. (3 mole) of potassium fluoride (anhydrous) were refluxed for 12 hours. The mixture was allowed to cool to room temperature and filtered. The filter cake was washed with dimethylsulfoxide (200 ml.). The filtrate was distilled using a short column. A total of 390 ml. of solvent were recovered (97%). The remainder was yellow-colored and contained a very small amount of crystalline material; the total distillate was diluted with 250 ml. of Skelly C (the white solid matter remained insoluble) and was passed through a 12" x 1" activated alumina column. The eluates were combined, the Skelly C solvent was stripped off, and the remainder was distilled between 199-216°C./2 mm. Hg pressure. The colorless material showed an apparently lower pour point than the starting material. The qualitative analysis for fluorine was positive.

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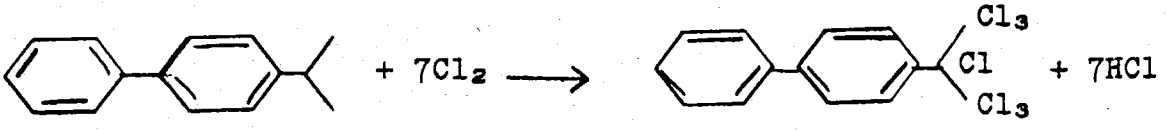
A similar experiment was carried out using 247 g. (0.5 mole) of decachlorobiphenyl, 600 ml. of dimethylsulfoxide, and 320 g. (5.5 mole) of anhydrous potassium fluoride. 92% of decachlorobiphenyl was recovered (A-78336).

d. Fluorination with hydrogen fluoride, potassium fluoride and antimony pentachloride

356 g. (1 mole) of Aroclor 1260 were placed into a 1-L Parr autoclave. After the clave had been cooled with ice, 200 g. (10 mole) of hydrogen fluoride were added. Next, 81 g. (1.4 mole) of anhydrous potassium fluoride were added in small increments while the autoclave was cooled with ice. After the addition of potassium fluoride, about 10 g. of antimony pentachloride were poured into the mixture, the autoclave was closed, the agitation was started and a reaction temperature of 170°C. was maintained for 5 hours. After the mixture was allowed to cool to room temperature, the autoclave was opened, chloroform was added, then water. The chloroform extracts were washed with water until no longer acidic. The chloroform solution was dried with sodium sulfate, filtered and the filtrate was distilled. A colorless product was obtained between 205-225°C./5 mm. Hg pressure. A qualitative analysis failed to indicate any fluorine.

B. Chlorination of Isopropylbiphenyl

The following experiments were carried out in a tubular reactor, equipped with a stirrer, a subsurface gas inlet, reflux condenser and a thermometer.



$C_{15}H_{16}$	70	434	36
196	490		252

Theor. Analysis: Cl: 56.4% (7 chlorines)
Cl: 52.5% (6 chlorines)
Cl: 35.2% (3 chlorines)

Experiment No. 1

A-78347; 674 g. of isopropylbiphenyl and 0.7 g. of ferric chloride were heated to 110°C. with agitation. Chlorine was introduced at such a rate that a temperature between 110-120°C. was maintained without external cooling or heating. After 6 hours, the introduction of chlorine was discontinued and the mixture was blown with air at 80°C. for 3 hours. Then, the mixture was washed with water, diluted with 250 ml. of chloroform, and dried over magnesium sulfate. The filtrate was distilled over 0.1 wt. % of calcium hydroxide. A water white material distilled between 176-211°C. at 10 mm. Hg pressure. (451 g.)

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The distillate was agitated with 1 wt. % of attapulgus earth at 80°C. for 2 hours; the dielectric properties were determined of the filtrate (n_D^{25} 1.5924).

Dk at 25°C.	4.36	(1 kc)	4.38	(60 c.)
Dk at 100°C.	3.79	(1 kc)	3.94	(60 c.)
Diss. Factor	.076%	(1 kc/25°C.)	0.29%	(60 c./25°C.)
Diss. Factor	2.29%	(1 kc/100°C.)	36.2%	(60 c./100°C.)
Resistivity at 100°C.	224×10^9			

Experiment No. 2

A-78349; A similar experiment was carried out without the use of ferric chloride, in order to prevent any aromatic-ring chlorination. A very viscous, brown-colored material was obtained which decomposed during an attempt to distill the material under vacuum.

Experiment No. 3

A-93001; Experiment No. 2 was duplicated except that isopropylbiphenyl was preheated to 220°C. before the introduction of chlorine was started. A temperature of 235-250°C. was maintained during the chlorination. Within 4.5 hours, a gravity of 1.080/25°C. was reached. A sample was dissolved in chloroform, washed with water until neutral, and dried. The solvent was stripped off and a vacuum distillation was attempted but the material decomposed at about 180°C. at a pressure of 10 mm. Hg.

Experiment No. 4

A-93026; 680 g. (3.5 moles) of isopropylbiphenyl and 35.0 g. of water were placed into a tubular reactor, equipped with a stirrer, a gas inlet on the bottom of the tube, a thermometer and a reflux condenser. Three 200-watt bulbs were arranged concentrically 4 in. from the reactor.

The mixture was heated to 90°C., chlorine was introduced and a reaction temperature between 95-100°C. was maintained for 20 hours. About 828 g. of chlorine were introduced, total weight of the crude: 877 g., gain: ca. 198 g. (theor. gain for $C_{15}H_9Cl_7$: 856 g.). The material was agitated with activated alumina (12 g.) at 80-90°C. for 2 hours, filtered and the filtrate was distilled over lime. A total of 16 g. of lime had to be added before the product could be distilled without decomposition. 357.2 g. of a yellow-colored material distilled between 158-220°C. at 1-2 mm. Hg pressure. Spec. Grav.: 1.250/25°C. Analysis: 65.28% C, 4.75% H, 30.11% Cl corresponding to $C_{15}H_{13-14}Cl_{2-3}$.

Experiment No. 5

A similar experiment was carried out using 588 g. of isopropylbiphenyl and 30 ml. of water. The chlorination was performed under actinic light as described previously, but chlorine was introduced at a faster rate (90 g./hr.).

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After 2.5 hours (ca. 590 g. of chlorine) foaming occurred and the reaction temperature dropped gradually to 85°C., although the same chlorine feed rate was maintained. The temperature was raised to 110°C. by external heating, foaming was reduced, but the off-gas became richer on chlorine indicating no or too low a conversion.

The reaction was discontinued after a total of 5 hours, about 200 ml. of carbon tetrachloride were added to the highly viscous material, then the mixture was aerated for 2 hours, washed with water, dried with anhydrous sodium sulfate, filtered, and the solvent was stripped off under reduced pressure. (541 g., theor. gain 953 g.). A sample was distilled at reduced pressure (8 mm. Hg). Three fractions were obtained:

I.	Fraction 175-192°C., n_D 1.6022, 19.0% Cl.	16 wt. %
II.	Fraction 193-220°C., n_D 1.6182, 27.0% Cl.	47 wt. %
III.	Fraction 221-240°C., n_D 1.6288, 37.0% Cl.	29 wt. %
Residue		9 wt. %

DISCUSSION

Fluorination reactions with molecular fluorine are characterized by disruptive and explosive reactions. Since fluorine, the most electro-negative of all elements, has a high nuclear charge, it should react by the radical rather than by the ionical mechanism during the fluorination of an aromatic system. Consequently, fast chain reactions, which actually take place, might well be expected. Another fundamental cause of the violence of these reactions is due to the high heat of formation of hydrogen fluoride (103 kcal.) compared to the heats of formation of hydrogen chloride (23 kcal.)[3]. Since the heat of dissociation of a carbon-carbon bond is about 71 kcal., it can be expected that fluorinations result often in disrupted molecules whereas chlorinations do not.

In addition to these very unfavorable kinetic considerations, it is known that the reactions of fluorine with hydrocarbons are characterized by a high energy of activation. Therefore, gas-phase fluorinations remained unsuccessful until these reactions were performed in small diameter tubes with heat conducting walls, provided by copper gauze(1,2) or in the presence of selected catalysts.

Generally, fluorination reactions were carried out either with fluorine, or with compounds which easily release atomic or molecular fluorine. Combinations of both methods are applied also.

In the course of our study we were restricted to use only fluorine-releasing compounds (antimony pentafluoride, antimony trifluoride, hydrogen fluoride, and potassium fluoride). In order to obtain fluorinated biphenyl compounds, we attempted to substitute the halogens in chlorinated derivatives. However, none of the routes chosen proved successful except the reaction with antimony pentafluoride already described in the literature. The material obtained from the fluorination of decachlorobiphenyl with antimony pentafluoride exhibited a dielectric constant lower than our Aroclor.

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During the second phase of our program we started with an alkylated biphenyl with the intention to chlorinate the side-chain and subsequently substitute the chlorines with fluorine atoms by means of hydrogen fluoride (Ref. 4,5,6).

The purpose of these experiments with alkylated biphenyl derivatives was to obtain a higher dipole moment than that attainable from straight biphenyl. In addition, the substituting fluorination reaction of aliphatic chlorines is known to be considerably easier than the substitution of aromatic chlorine atoms with fluorine.

This work was discontinued at this point because of more urgent projects.

REFERENCES

(1) Bigelow, L.A., J. Am. Chem. Soc., 59, 2073 (1937)

(2) Fredenhagen, Cadenbach, Ber., 67B, 928 (1934)

(3) Bockemueller, Ann., 506, 20 (1933)

(4) I.G. Farben, British Patent 464,859 (1935)

(5) I.G. Farben, British Patent 465,885 (1937)

(6) Murray, R.L., et al., Ind. Eng. Chem. 39, 302 (1947).

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