[(PERHALOALKYL)BENZENES]

Fluorinated derivatives of diethylbenzene

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TECHNICAL bis(pentachloroethyl)benzene, 1,3-bis(pentachloroethyl)benzene, and 1,4-bis(pentachloroethyl)benzene were prepared by photochemical chlorination of the corresponding hydrocarbons. Optimum yields were obtained by conducting the reactions in carbon tetrachloride solution. The chlorinated diethylbenzene was fluorinated with antimony trifluoride or anhydrous hydrogen fluoride at autogenous pressure and with hydrogen fluoride at atmospheric pressure. The latter procedure gave optimum fluorination yields.

THE synthesis of bis(pentafluoroethyl)benzene and bis(chloroperfluoroethyl)benzenes was undertaken to provide liquid fluorine-containing organic compounds for evaluation as heat transfer media and hydraulic fluids. Their preparation was accomplished by first chlorinating diethylbenzene to bis(pentachloroethyl)benzene and subsequently fluorinating the latter compound.

In general, methylbenzenes are converted to the corresponding trichloromethylbenzene by photochemical liquid-phase chlorination (*4*). This process was applied to the chlorination of 1,4-diethylbenzene, 1,3-diethylbenzene, and mixtures of the two. Control of the chlorination was facilitated by conducting the reaction in a solution of carbon tetrachloride or in the presence of water. Slightly higher yields of bis(pentachloroethyl)benzene were obtained when the reaction was conducted in solution. The time required for chlorination was decreased by carrying out the reaction in the absence of a solvent and in the presence of water.

Fluorine was substituted for chlorine in bis(pentachloroethyl)-benzene with either anhydrous hydrogen fluoride or antimony trifluoride at autogenous pressures and in the presence of antimony pentachloride. The fluorination was also conducted at atmospheric pressure with anhydrous hydrogen fluoride and antimony pentachloride. Excellent yields of fluorinated product are obtained in this manner, and many disadvantages encountered with high-pressure equipment are avoided.

Although the positions of halogen atoms in the side chains of bis(chloroperfluoroethyl)benzenes were not determined, it is known that chlorine atoms in allylic positions (*3*) are readily replaced by fluorine, and the first two chlorine atoms replaced by fluorine in each pentachloroethyl group would probably be those on the carbon atoms attached to the benzene ring. The next two chlorine atoms replaced would be those on the beta carbon atom, giving the structure —CF_2CF_2Cl for each side chain of bis(chlorotetrafluoroethyl)benzene. The remaining two chlorine atoms were much more difficult to replace with fluorine, and as a consequence bis(chlorotetrafluoroethyl)benzene occurred in the reaction products in much larger quantities than more highly fluorinated compounds. Physical constants and halogen analyses of the new compounds are summarized in Table I.

m-Diethylbenzene was isolated from a technical mixture of diethylbenzenes by preparation of the sulfonic acid as described by Copenhaver and Reid (*1*). This method was modified by the use of a barium hydroxide slurry instead of a saturated solution for the preparation of the barium diethylbenzenesulfonates. Consequently much time was saved in concentrating the solution before crystallization of barium sulfonates. *m*-Diethylbenzene was found to solidify at −85° C. The melting point of this compound had not been reported previously.

p-Diethylbenzene was prepared by the Clemmensen reduction of *p*-ethylacetophenone, which resulted from a reaction of ethylbenzene with acetic anhydride in the presence of aluminum chloride. The method of Adams and Noller was followed (*2*).

CHLORINATION

Chlorinations were conducted in vertical Pyrex tubes, 5.1 × 129.5 cm., fitted with a gas-dispersion disk (30-mm. diameter, medium porosity) and reflux condenser. A thermometer was suspended in the tube by a glass rod; the bulb was about 5 cm. below the surface of the liquid. Illumination was furnished to the photochemical reaction by mounting the tube between two banks of three 200-watt incandescent bulbs. At the end of the experiment dissolved chlorine and hydrogen chloride were removed from the reaction mixture by aeration. The chlorinated product was poured into a beaker containing equal volumes of methanol and benzene. After cooling, crystals were filtered with suction and washed with cold methanol.

In one instance 344 grams (2.57 moles) of technical diethylbenzenes were poured into the chlorination tube. Chlorine was at first added slowly to allow for a short induction period and was then added at a rate such that no color of free chlorine was detected in the upper portion of the apparatus (approximately 2 moles per hour). During the first 2 hours of reaction the temperature was maintained in the range 20–30° C., and heat liberated by the exothermic reaction was removed by immersing the lower portion of the tube in an ice bath. When the reaction became sluggish, as evidenced by unreacted chlorine in the top of the tube, the reaction mixture was allowed to warm slowly to 120° C. After 2 hours at this temperature chlorine flow was adjusted to maintain an excess at all times, and the temperature was allowed to rise slowly to 145–155° C., where it was maintained for 8 hours. In this manner 800 grams (1.67 moles) of bis(pentachloroethyl)-benzenes were obtained, a yield of 65%.

1,3-Bis(pentachloroethyl)benzene (melting point, 153–155° C.), 1,4-bis(pentachloroethyl)benzene (melting point, 214–216° C.), and technical bis(pentachloroethyl)benzenes were also prepared by chlorination of the corresponding starting materials in carbon tetrachloride at 80° C. The yields were 61, 95, and 65%, respectively.

Technical diethylbenzenes (344 grams, 2.57 moles) were chlorinated in the presence of 25 ml. of water. The temperature rose rapidly to 115–120° C., remained at this level for 4 hours, and then dropped slightly with decreased reaction rate. Gradual evaporation of water allowed the temperature to reach 150–160° C.; this temperature was maintained until chlorine was no longer absorbed. Total chlorination time was 24 hours; the yield of bis(pentachloroethyl)benzenes was 65%.

The purity of bis(pentachloroethyl)benzenes is an important factor in determining conversion and yield obtained upon fluorination. It was found that several recrystallizations of chlo-

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rinated product were necessary to obtain material which could be fluorinated satisfactorily. If crude bis-(pentachloroethyl)benzenes were used, the fluorination reaction produced a considerable amount of carbonaceous material and only small amounts of desired fluorine-containing product.

Table I. Fluorinated Derivatives of Diethylbenzene

Compound	B.P. at 750 Mm., ° C.	M.P., ° C.	d_4^{25}	n_D^{25}	% F		% Cl	
					Calcd.	Found	Calcd.	Found
1,4-$C_6H_4(C_2F_5)_2$	138.5–139.0	17.1	1.5056	1.3590	60.5	60.3	0.0	0.0
1,3-$C_6H_4(C_2F_5)_2$	134.5–135.0	−28.5	1.4938	1.3565	60.5	60.1	0.0	0.0
1,4-$C_6H_4(C_2F_5)(C_2ClF_4)$	164.8–165.2	− 7.5	1.5291	1.3878	51.8	52.4	10.8	10.9
1,3-$C_6H_4(C_2F_5)(C_2ClF_4)$	160.5–161.0	−45.5	1.5219	1.3838	51.5	52.0	10.8	10.8
1,4-$C_6H_4(C_2ClF_4)_2$	193.0–194.0	−13.5	1.5586	1.4140	43.8	44.0	20.5	20.6
1,3-$C_6H_4(C_2ClF_4)_2$	190.0–190.5	No crystals	1.5517	1.4093	43.8	44.1	20.5	20.5

FLUORINATION

Fluorinations of bis(pentachloroethyl)benzenes were conducted both at superatmospheric and at atmospheric pressures. Pressure fluorinations were conducted in a Monel autoclave of 1.5-liter capacity which had been cold-tested at a hydrostatic pressure of 10,000 pounds per square inch. This autoclave was heated with an external electric heater, and means were provided for continuous rocking of the heater. The entire apparatus was located within a shelter of 1/2-inch iron plate to avoid serious injury to the operator in case any part of the system failed.

When hydrogen fluoride was used as fluorinating agent, material to be fluorinated was placed in the autoclave and the head fastened. The catalyst was introduced and the desired amount of hydrogen fluoride distilled into the fluorination equipment from a 600-ml. iron container through suitable pipe fittings. After addition was completed, the autoclave was heated at the desired temperature for a predetermined time. At the end of the reaction, gaseous products were discharged into a scrubber containing 6 *N* sodium hydroxide in quantity equivalent to the amount of hydrogen fluoride charged. Organic material which did not condense in the scrubber passed through a drying tower and into a receiver cooled with dry ice, connected in series with the tower. Liquid reaction product was poured from the autoclave, and antimony salts were removed by dissolving in concentrated hydrochloric acid. The liquids were combined, made alkaline with aqueous sodium hydroxide, and steam-distilled. Water-insoluble distillate was then separated, dried with anhydrous calcium sulfate, and rectified.

Fluorinations at atmospheric pressure were conducted in a nickel reactor of 2-gallon capacity, equipped with a hydrogen fluoride inlet, stirrer, thermocouple well, and air-cooled dephlegmator. The dephlegmator was connected to an air-cooled receiver which, in turn, was connected to a receiver cooled by a solid carbon dioxide-trichloroethylene mixture. The last receiver was vented to the hood. Reaction products were treated for separation and purification as previously described.

In a typical experiment 364 grams (0.76 mole) of bis(pentachloroethyl)benzenes, 648 grams (3.54 moles) of antimony trifluoride, and 30 grams (0.10 mole) of antimony pentachloride were placed in an autoclave and heated to 220° C. over a 12-hour period. The reaction was then heated between 220° and 310° C. during 8 hours and cooled from 310° to 280° C. during 5.25 hours. After purification as already described, the product was rectified under reduced pressure. Rectification produced 14 grams (0.045 mole) of bis(pentafluoroethyl)benzenes, 29 grams (0.088 mole) of (chlorotetrafluoroethyl)(pentafluoroethyl)benzenes, and 65 grams (0.187 mole) of bis(chlorotetrafluoroethyl)benzenes. Conversions to these compounds were 5.9, 11.6, and 24.6%, respectively.

1,3-Bis(pentachloroethyl)benzene and 1,4-bis(pentachloroethyl)benzene were also fluorinated separately with antimony trifluoride at temperatures in the range 315–330° C. 1,3-Bis(pentafluoroethyl)benzene, 1-(chlorotetrafluoroethyl)-3-(pentafluoroethyl)benzene, and 1,3-bis(chlorotetrafluoroethyl)benzene were obtained in yields of 17.2, 16.6, and 14.7%, respectively; 1,4-bis(pentafluoroethyl)benzene, 1-(chlorotetrafluoroethyl)-4-(pentafluoroethyl)benzene, and 1,4-bis(chlorotetrafluoroethyl)benzene were obtained in yields of 20.0, 9.2, and 9.0%, respectively.

A fluorination with anhydrous hydrogen fluoride under superatmospheric pressure was conducted as follows: Four hundred eighty grams (1.0 mole) of technical bis(pentachloroethyl)benzenes and 100 grams (0.33 mole) of antimony pentachloride were placed in an autoclave, and 450 grams (22.5 moles) of anhydrous hydrogen fluoride added. The autoclave was heated for 48 hours; the maximum temperature was 244° C. and the pressure, 3000 pounds per square inch. Rectification of the product gave 15.0 grams (0.048 mole) of bis(pentafluoroethyl)benzenes, 43.0 grams (0.13 mole) of (chlorotetrafluoroethyl)(pentafluoroethyl)benzenes, and 172.0 grams (0.49 mole) of bis(chlorotetrafluoroethyl)benzene. Conversions to these compounds were 5.0, 13.0, and 42.0%, respectively.

Fluorination with anhydrous hydrogen fluoride and antimony pentachloride at atmospheric pressure was found to be more satisfactory. In an example of this procedure, 2655 grams (5.7 moles) of technical bis(pentachloroethyl)benzenes and 2270 grams (7.7 moles) of antimony pentachloride were sealed in the reactor, and the temperature was raised to about 100° C. Hydrogen fluoride (2320 grams, 116 moles) was bubbled into the reactor at the rate of 300 grams per hour. After addition of hydrogen fluoride, the reaction mixture was heated at 200° C. for 12 hours with continuous stirring. Product rectification yielded 330 grams (1.27 moles) of bis(chlorotetrafluoroethyl)benzenes, 363 grams (1.07 moles) of (chlorotetrafluoroethyl)(dichlorotrifluoroethyl)benzenes, 120 grams (0.32 mole) of bis(dichlorotrifluoroethyl)benzenes, and 93 grams (0.23 mole) of (dichlorotrifluoroethyl)(trichlorodifluoroethyl)benzenes. Conversions to these compounds were 22.2, 18.8, 5.6, and 4.1% of theoretical, respectively.

For most runs rectification data were not required, and the compositions of the products were determined from chlorine and fluorine analyses. In one experiment 3000 grams (6.26 moles) of bis(pentachloroethyl)benzenes were introduced into the reactor, followed by 3050 grams (10.2 moles) of antimony pentachloride and 2000 grams (100 moles) of hydrogen fluoride. Analysis of the 2018 grams of fluorinated bis(pentachloroethyl)benzenes produced showed 39.8% fluorine and 28.2% chlorine present. The analysis of an average composition of $C_{10}H_4Cl_3F_7$ is 37.6% fluorine and 29.3% chlorine. The yield, calculated on this basis, was 5.6 moles, or 89% of theoretical. In some experiments conversions to a mixture containing approximately 7 fluorine and 3 chlorine atoms per molecule were as high as 90% of the theoretical.

The compounds were purified by careful rectification in a column packed with glass helices.

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[(PERHALOALKYL)BENZENES]

Fluorinated derivatives of p-ethyltoluene

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1-(PENTACHLOROETHYL)-4-(trichloromethyl)benzene was prepared by liquid-phase photochemical chlorination of 1-chloromethyl-4-ethylbenzene and photochemical chlorinolysis of *p*-isopropyltoluene. The latter method gave the highest conversion to the desired chlorinated product. 1-(Pentachloroethyl)-4-(trichloromethyl)benzene was fluorinated with anhydrous hydrogen fluoride or antimony trifluoride under autogenous pressures and with hydrogen fluoride at atmospheric pressure. The latter procedure gave optimum yields of fluorinated products.

IN CONTINUING the investigation of polyfluoro organic compounds as heat transfer media, certain fluorinated derivatives of *p*-ethyltoluene were prepared. Since neither *p*-ethyltoluene nor any of its chlorinated derivatives was available commercially, it was necessary to prepare the desired intermediate, 1-(pentachloroethyl)-4-(trichloromethyl)benzene. This compound was made either by photochemical chlorination of 1-chloromethyl-4-ethylbenzene or of *p*-cymene.

1-(Pentachloroethyl)-4-(trichloromethyl)benzene was fluorinated with either antimony chlorofluorides or antimony pentachloride and anhydrous hydrogen fluoride. When the latter method was used, ring chlorination occurred during fluorination, and fluorinated derivatives of *p*-ethyltoluene containing chlorine atoms in the ring were produced. This chlorination probably resulted from the action of antimony pentachloride at the higher final temperature, where partial reduction of the antimony salts occurred to liberate active chlorine which reacted with the aromatic nuclei.

The purity of 1-(pentachloroethyl)-4-(trichloromethyl)benzene was of prime importance. Yields and conversions to identifiable fluorinated materials varied from 0 to about 90%, depending on the nature of the starting material. The presence of other chlorinated products in the 1-(pentachloroethyl)-4-(trichloromethyl)benzene led to the formation of tar and carbonaceous solids with correspondingly lower yields and conversions to fluorinated products. In experiments involving 1-(pentachloroethyl)-4-(trichloromethyl)benzene, a melting range of less than 1° C. was required for high conversions to fluorinated substances.

In assigning positions to the halogen atoms, it was assumed that the chlorine atoms in allylic positions were readily replaced by fluorine atoms. The remaining chlorine atoms to be substituted were those on the beta carbon atom of the ethyl side chain. These atoms were more difficultly replaced; in some instances they required a temperature in the range 300–350° C. Physical constants of the new compounds are summarized in Table I.

CHLORINATION

1-Chloromethyl-4-ethylbenzene was prepared by the chloromethylation of ethylbenzene according to the procedure described for the chloromethylation of toluene by Braun and Nelles[1]. The conversions to 1-(chloromethyl)-4-ethylbenzene were about 95% and the yields about 98%, based on starting ethylbenzene.

A vertical glass tube 54 mm. in diameter and 100 cm. in length was used for chlorinations. A chlorine-dispersion disk (30 mm. in diameter and of medium porosity), was located at the bottom of the tube and a water-cooling coil within the reaction zone. A Hopkins condenser was placed vertically at the top of the tube, and the lower section of the chlorination tube was wrapped with resistance wire connected to a variable transformer for temperature control. Temperatures were measured by a thermocouple inserted in a well. Light was furnished by two 40-watt fluorescent lamps placed on either side of the tube. Six hundred eighteen grams (4.0 moles) of 1-(chloromethyl)-4-ethylbenzene were placed in the chlorination apparatus. Chlorine was bubbled into the reaction mixture at the rate of 2.5 moles per hour. After an induction period of several minutes the temperature rose rapidly, but passage of water through the cooling coil maintained the reaction temperature at 15–20° C. for 8 hours. At the end of this time excess chlorine was observed in the chlorination tube. Cooling was discontinued and the temperature elevated slowly to 100° C. The reaction mixture was heated at 135–140° C. for 8 hours; then the chlorine flow was stopped, and excess chlorine and hydrogen chloride were removed by aeration. The temperature was not permitted to fall below 100° C. during aeration to prevent crystallization of the product in the chlorination tube.

The product was crystallized by pouring it into equal volumes of benzene and methanol while it was hot. Two additional recrystallizations from benzene-methanol solvent were necessary to obtain a product with a melting range of less than 1° C. The yield was 93% and conversion 65%. By repeated crystallizations, a sample of pure 1-(pentachloroethyl)-4-(trichloromethyl)benzene (melting point, 115.0° C.) was obtained.

Similarly 500 grams (3.7 moles) of 1-isopropyl-4-methylbenzene were placed in the chlorination apparatus, and chlorine was bubbled in at the rate of 2 moles per hour. The reaction temperature during the first 30 hours of chlorination was maintained at 20° C. The temperature was increased to 100° C., maintained at this level for 24 hours, and finally increased to 140° C. After a few hours at this temperature carbon tetrachloride was observed to be refluxing. The reaction was continued at 140° C. for 48 hours, total reaction time being 102 hours. Chlorine flow was stopped and the reaction mixture aerated. The product was crystallized from a benzene-methanol solvent in a manner already described; 1200 grams of product were obtained, a yield and conversion of 80%.

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