oratory for financial support which made this work possible. Halogen analyses were made by M. H. Danzig, A. M. Ribley, and M. D. Kinzie, to whom the authors extend their appreciation.

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ABSTRACTED from doctoral theses of R. E. Leech, E. M. Hodnett, and M. R. Frederick, submitted to the faculty of Purdue University.

Fluorinated derivatives of p-ethyltoluene

E. T. McBee and O. R. Pierce

N 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. 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.

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 $300-350^{\circ}$ 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 Nelles¹. The conversions to 1-(chloromethyl)-4-ethylbenzene were about 95%and the yields about 98%, based on starting ethylbenzene.

¹ Braun, J. v., and Nelles, J., Ber., 67, 1094 (1934).

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 con-Temperatures were measured by a thermocouple introl. serted 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%.

Compound	B.P. M.P.,					Mol. Wt.		% Cl		% F	
	° C.	Mm.	° C.	n_{D}^{20}	d_{4}^{26}	Theoretical	Found	Theoretical	Found	Theoretical	Found
$4-CCl_3C_6H_4C_2Cl_5$			115.0 •			396		71.7	71.7	0.0	0.0
$4-CF_3C_6H_4C_2F_5$	128.5 - 128.7	746	-8.3	1.3690	1.4572	264	264	0.0	0.0	57.6	57.5
$4-CF_3C_6H_4C_2F_4Cl$	159.0 - 159.2	746	-13.0	1.4005	1.5291	280.5	277	12.6	12.6	47.4	47.7
$4-CF_3C_6H_4C_2F_3Cl_2$	187.9 - 188.1	751	-2.4	1,4313	1.5184	297	294	23.9	23.8	38.4	38.2
$4-CF_2C_6H_4C_2F_2Cl_3$	217.0 - 217.2	751	27.5		1.5610	313.5	310	34.0	33.8	30.3	30.7
$4-CF_3C_2H_3ClC_2F_4Cl$	184.8-185.0	751	No crystals	1.4275	1.5631	315	315	22.5	22.2	42.2	42.6
$4-CF_3C_6H_2Cl_2C_2F_4Cl$	211.0 - 211.2	751	1.2	1.4539	1.6586	349.5	342	30.5	30.4	38.6	38.5
4-CF ₃ C ₆ HCl ₃ C ₂ F ₄ Cl	229.9 - 230.1	751	1.0	1.4828	1.7420	384	381	37.0	36.9	34.6	34.4
4-CF ₃ C ₆ Cl ₄ C ₂ F ₄ Cl	263.0-263.2	751	56.0			418.5		42.4	42.4	31.8	31.9
4-CF ₃ C ₆ H ₃ ClC ₂ F ₅	154.0 - 154.2	748	а	1.3980	1.5436	298.5	296	11.9	11.8	50.9	51.1

FLUORINATION

The apparatus in which atmospheric pressure fluorination experiments with hydrogen fluoride were conducted consisted of a nickel vessel of 3-liter capacity equipped with a sealed stirrer, an inlet tube for hydrogen fluoride, and a thermocouple well. An electrical heater was placed around the vessel. A 3.5-foot length of 1-inch nickel pipe was attached to the reactor and served as dephlegmator. Exit gases from the reaction vessel passed through the dephlegmator, an air-cooled nickel trap, and then a similar trap immersed in a bath of trichloroethylene and dry ice.

Fluorinations at superatmospheric pressures were conducted in a 1-liter iron autoclave lined with nickel. The autoclave was provided with a cylindrical electric heater, equipped to allow constant rocking of the apparatus, as described in the second paper of this series (page 395).

Fluorination with antimony trifluoride and antimony pentachloride at atmospheric pressures caused complete halogen exchange. In this process 792 grams (2.0 moles) of 1-(pentachloroethyl)-4-(trichloromethyl)benzene and 1050 grams (5.9 moles) of powdered antimony trifluoride were mixed thoroughly and placed in a 3-liter three-neck glass flask equipped with a reflux condenser, mercury-seal stirrer, and thermometer. Antimony pentachloride (92 grams, 0.3 mole) was added to the flask, and the mixture heated at 165° C. for 7 hours with constant stirring. The contents of the flask were then cooled, and the liquid product was decanted from solid antimony salts, washed with dilute hydrochloric acid and aqueous sodium hydroxide, and steamdistilled. Four hundred twenty-six grams of crude fluorinated product were obtained, dried with calcium sulfate, and rectified. Three distinct fractions were obtained from the rectification: 11 grams of 1-(pentafluoroethyl)-4-(trifluoromethyl)benzene, 281 grams of 1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, and 107 grams of 1-(dichlorotrifluoroethyl)-4-(trifluoromethyl) benzene. The yield and conversion were 69%.

Decreased amounts of fluorinating agent and lower reaction temperatures produced increased amounts of less highly fluorinated compounds. For example, 792 grams (2.0 moles) of 1-(pentachloroethyl)-4-(trichloromethyl)benzene and 534 grams (3.0 moles) of powdered antimony trifluoride were thoroughly mixed and placed in a suitably equipped 3-liter, three-neck flask. Eighty grams (0.27 mole) of antimony pentachloride were added to the flask, and the mixture was heated at 110° C. for 7 hours with constant stirring. The flask and contents were then cooled, and the liquid organic products decanted and treated as described previously. Three hundred ninety-eight grams of crude fluorinated product were obtained. Rectification of the product yielded 28 grams of 1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, 208 grams of 1-(trichlorodifluoroethyl)-4-(trifluoromethyl)benzene, and 125 grams of 1-(trichlorodifluoroethyl)-4-(trifluoromethyl)benzene. The yield and conversion were 60%.

Fluorination with antimony trifluoride and antimony pentachloride at superatmospheric pressure and relatively high reaction temperatures (300–350° C.) were required to obtain increased amounts of 1-(pentafluoroethyl)-4-(trifluoromethyl)benzene. The use of a mixture of 1-(perchlorofluoroethyl)-4-(trifluoromethyl)benzenes as starting material rather than 1-(pentachloroethyl)- 4-(trichloromethyl)benzene obviated lower yields because of the extensive pyrolytic decomposition when the latter compound was fluorinated at the higher temperatures required. A mixture of antimony trifluoride and antimony pentachloride was used as fluorinating agent to eliminate the higher pressures necessary with anhydrous hydrogen fluoride.

Seven hundred fifteen grams of a mixture containing 281 grams (1.0 mole) of 1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, 297 grams (1.0 mole) of 1-(dichlorotrifluoroethyl)-4-(trifluoromethyl)benzene, and 135 grams (0.43 mole) of 1-(trichlorodifluoroethyl)-4-(trifluoromethyl)benzene, 400 gram (2.26 moles) of antimony trifluoride, and 81 grams (0.27 mole) of antimony pentachloride were placed in the autoclave and heated at 325° C. for 48 hours with continuous rocking. At the end of this time the autoclave was cooled to room temperature, and liquid products were decanted from solid antimony salts. The crude fluorinated product was treated as described previously, and 511 grams were obtained. Rectification yielded 128 grams of 1-(pentafluoroethyl)-4-(trifluoromethyl)benzene. Conversion to this compound was 20% and the yield 72%. The yield was comparatively low because of some pyrolytic decomposition during the reaction, even with the partially fluorinated starting materials.

Fluorination with anhydrous hydrogen fluoride and antimony pentachloride at superatmospheric pressure was investigated, since this process appeared to offer economic advantages. Three hundred ninety-six grams (1.0 mole) of 1-(pentachloroethyl)-4-(trichloromethyl)benzene and 66 grams (0.22 mole) of antimony pentachloride were placed in the autoclave. Anhydrous hydrogen fluoride (400 grams, 20.0 moles) was then distilled into the autoclave from a small container and the reaction mixture heated at 175° C. for 24 hours. Contents of the autoclave were agitated by rocking throughout the entire reaction period. The autoclave was then cooled to room temperature, and gases present were passed into aqueous sodium hydroxide. The reaction product was removed from the autoclave, washed with aqueous sodium hydroxide, and steam-distilled. Two hundred thirteen grams of fluorinated product were obtained. The distillate was dried with calcium sulfate and rectified, and three separate fractions were obtained: 70 grams of 1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, 89 grams of 1-(dichlorotrifluoroethyl)-4-(trifluoromethyl)benzene, and 16 grams of 1-(trichlorodifluoroethyl)-4-(trifluoromethyl)benzene. These represented a yield and conversion of 55%.

Fluorination with anhydrous hydrogen fluoride and antimony pentachloride at atmospheric pressure followed by a distillation of the product from the antimony salts was investigated in an attempt to produce substantial quantities of 1-(pentafluoroethyl)-4-(trifluoromethyl)benzene. 1-(Pentachloroethyl)-4-(trichloromethyl)benzene (1584 grams, 4 moles) and 1560 grams (5.3 moles) of antimony pentachloride were placed in the nickel reactor. Anhydrous hydrogen fluoride (1584 grams, 79.2 moles) was added at 100 ° C., and the temperature of the reaction mixture was increased to 240 ° C. for distillation of the fluorinated product. Products were treated as described in the second paper of this series, 1060 grams of fluorinated product being produced. The steam distillate was dried with calcium sulfate and rectified to yield 20 grams of 1-(pentafluoroethyl)-4-(trifluoromethyl)benzene, 505 grams of 1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, 350 grams of chloro-1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, and 147 grams of dichloro-1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene; this represented a yield and conversion of 85%.

Concurrent chlorination and fluorination were obtained by adding chlorine to the reaction mixture during fluorination. In this process 1-(pentachloroethyl)-4-(trichloromethyl)benzene (1482 grams, 3.75 moles) and 1482 grams (5.0 moles) of antimony pentachloride were placed in the reactor. Twelve hundred grams (60.0 moles) of anhydrous hydrogen fluoride were added as in the preceding example. After addition, 426 grams (6.0 moles) of chlorine were bubbled into the mixture over a period of 0.5 hour, the temperature rising to 120 °C. Hydrogen fluoride (382 grams, 19.1 moles) was passed into the reaction mixture during 1 hour: the reaction mixture was then heated at 250 °C. for 3 hours. During this period part of the product distilled into the receivers. The crude fluorinated product was treated as above, 1191 grams being obtained. Rectification of the product yielded 224 grams of 1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, 283 grams of chloro-1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, 385 grams of dichloro-1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, 184 grams of trichloro-1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene, and 52 grams of tetrachloro-1-(chlorotetrafluoroethyl)-4-(trifluoromethyl)benzene. The yield and conversion were 85%.

The compounds were purified by rectification in a Podbielniak Hyper-Cal column.

ACKNOWLEDGMENT

The authors wish to acknowledge the financial assistance of the United States Army Air Forces Matériel Center and Ethyl Corporation and gratefully acknowledge the analytical work of A. M. Ribley.

ABSTRACTED from a doctoral thesis of O. R. Pierce, to be submitted to the faculty of Purdue University.

[(PERHALOALKYL)BENZENES]

Fluorinated derivatives of p-isopropyltoluene and isopropylbenzene

E. T. McBee and O. R. Pierce

ISOPROPYLBENZENE and *p*-iscpropyltoluene were chlorinated photochemically in the liquid phase to produce the corresponding (heptachloroisopropyl)benzene and 1-(heptachloroisopropyl)-4-(trichloromethyl)benzene. These chlorinated hydrocarbons were fluorinated with anhydrous hydrogen fluoride or antimony trifluoride under autogenous pressure and with hydrogen fluoride at atmospheric pressure. Optimum yields of fluorinated product were obtained with the latter procedure. Physical constants and halogen analyses are reported.

N EVALUATION of the properties of fluorinated branchedchain alkylbenzenes was desired, especially as compared to those of the straight chain analogs. For this reason fluorinated derivatives of p-isopropyltoluene and isopropylbenzene were prepared.

The chlorinated intermediates, 1-(heptachloroisopropyl)-4-(trichloromethyl)benzene and (heptachloroisopropyl)benzene, were obtained by photochemical chlorination of the corresponding hydrocarbon at temperatures ranging from 150° to 200° C. These compounds were fluorinated according to several different procedures: (a) with mixed trivalent and pentavalent antimony halides, and (b) with anhydrous hydrogen fluoride and pentavalent antimony chlorofluorides. The latter prepared from equal weights of anhydrous hydrogen fluoride and antimony pentachloride were found to give best yields and conversions at atmospheric pressure fluorinations. Procedure b was also productive of fluorinated derivatives containing chlorine atoms substituted in the ring.

In assigning positions to halogen atoms, it was assumed that chlorine atoms in allylic positions were readily replaced by fluorine. The remaining chlorine atoms were substituted by fluorine with more difficulty, requiring reaction temperatures of 300° to 350° C. in some instances.

The 1-(heptachloroisopropyl)-4-(trichloromethyl)benzene used as starting material for fluorinations melted at $128^{\circ} \neq 0.5^{\circ}$ C. High purity was important for good yields and conversions; quantities of unidentifiable tars were produced from fluorination of impure samples. As (heptachloroisopropyl)benzene could not be isolated in a pure state, yields and conversions on fluorination were relatively low. Large samples of 1-(heptafluoroisopropyl)-4-(trifluoromethyl)benzene, (heptafluoroisopropyl)benzene, and (chlorohexafluoroisopropyl)benzene were prepared from partially fluorinated derivatives of 1-(heptachloroisopropyl)-4-(trichloromethyl)benzene and (heptachloroisopropyl)benzene, since these compounds undergo less decomposition. A mixture of antimony trifluoride and antimony pentachloride as fluorinating agent was more suitable for the preparation of these compounds than anhydrous hydrogen fluoride, since lower reaction pressures were required.

The apparatus and techniques are described in the third paper of this series (page 397).

CHLORINATION

(Heptachloroisopropyl)-4-(trichloromethyl)benzene was prepared by placing 600 grams (4.47 moles) of p-cymene (boiling range, 175–177°C.) in the chlorination apparatus and bubbling chlorine into it at the rate of 2.5 moles per hour. After an induction period of about 5 minutes the reaction occurred rapidly. The reaction temperature was adjusted as follows: 20° for 8 hours, 100° for 15 hours, 150° for 8 hours, and 175°C. for 5 hours. Near the end of this period it was observed that a liquid, later identified as carbon tetrachloride formed by chlorinolysis, was refluxing. Chlorine introduction was discontinued, and excess chlorine and hydrogen chloride were removed by aeration at 100°C. The products were poured while hot into 500 ml. of equal volumes of benzene and methanol. Upon cooling a solid separated and was removed by filtration. Repeated crystallizations from a benzene-methanol mixture yielded 1290 grams (2.7