Preparation of Fluoro- and Bromofluoroaryl Compounds by Copyrolysis of Bromofluoroalkanes[*]

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Pyrolysis of tribromofluoromethane yields chiefly hexafluorobenzene. Copyrolysis of this material with several bromine-containing compounds was studied at 540 °C and under several atmospheres' pressure of nitrogen gas. The addition of bromine or dibromodifluoromethane has very little effect on the pyrolysis products of tribromofluoromethane. Copyrolysis with carbon tetrabromide or bromoform yields increased amounts of bromopentafluorobenzene and dibromotetrafluorobenzene at the expense of hexafluorobenzene. The addition of relatively small amounts of 1,1,1-tribromo-2,2,2-trifluoroethane gives a significant yield of octafluorotoluene.

1. Introduction

Synthesis of hexafluorobenzene by the pyrolysis of tribromofluoromethane has been described and investigated by several workers [1–4][1]. The original synthesis [1] was carried out at atmospheric pressure and 640 °C. In a previous study of this reaction in our laboratory [2], we explored the effects of pressure and temperature. On increasing the pressure to 4 atm, optimum yields were obtained near 540 °C, and the maximum yields were somewhat greater than at atmospheric pressure. A secondary product from the pyrolysis of tribromofluoromethane was bromopentafluorobenzene[2,3]. Since this material has great value in synthesis work [5], it was of interest to find means of increasing the relative yield of this product. A conceivable approach to this aim would be to increase the concentration of bromine in the reaction or to introduce carbon tetrabromide or bromoform into the reaction. Introduction of other compounds, it was anticipated, could also lead to the synthesis of various derivatives of hexafluorobenzene or related compounds.

2. Materials

The tribromofluoromethane, obtained from Columbia Organic Chemicals, Inc., was dried over anhydrous calcium sulfate and filtered through glass wool. The carbon tetrabromide, bromoform, and bromine were reagent grades and were used without further purification. The 1,1,1-trifluoroethane was a research sample.[2] The dibromodifluoromethane was obtained as a byproduct in the pyrolytic preparation of hexafluorobenzene.

The tribromotrifluoroethane was prepared by first converting CF_3CH_3 to CF_3CHBr_2 by thermal reaction with Br_2 in a hot-tube apparatus [6]. Then, in a one-liter, three-necked flask equipped with an efficient stirrer and a reflux condenser, a mixture of 242 g (1 mole) of CF_3CHBr_2, 135 g of KOBr (prepared from 112 g of KOH and 160 g of Br_2), and 300 ml of water was cooled for 3 hr in a bath maintained at 15 °C. The mixture was stirred vigorously and irradiated with a 350-watt bulb throughout the reaction. When the exothermic reaction had subsided and the contents of the flask had cooled, the product solidified. The aqueous layer was decanted. The slightly yellow product, 1,1,1-tribromo-2,2,2-trifluoroethane, was briefly dried in air and sublimed. The yield was 257 g (80%).

3. Experimental Procedures

The pyrolysis experiments were carried out as described previously [2]. However, the apparatus used was newly constructed and designed to handle 2 liters of reactants or about 5 kg of tribromofluoromethane. A diagram of the apparatus is shown in figure 1. The pyrolysis tube, platinum 89 percent and ruthenium 11 percent, 76 cm long, 0.95 cm ID, and 1.15 cm OD, was silver-soldered to brass fittings at each end. The reservoir and traps were constructed of welded stainless steel and connected via copper tubing and brass fittings. The only nonmetal component of the apparatus was a thick-walled, hard-glass, solenoid valve which controlled the input of liquid CBr_3F mixtures into the furnace. This glass valve was connected with two glass inner 10/30 standard tapers to two outer 10/30 tapers machined out of brass and silver soldered to copper tubing. The taper joints were waxed together with poly(chlorotrifluoroethylene) wax.

The reservoir was filled with the reactants. Then, after closing the system and bringing the furnace to the desired temperature, set on an indicating, proportioning controller operating from a thermocouple, the pressure of N_2 gas in the system was adjusted, using the reducing valve on the gas cylinder. The flow of N_2, which had been prepurified, was adjusted by bleeding through a brass, blunt-needle valve at the exhaust end of the apparatus. Finally an electric timer was switched on, which periodically allowed pulses of liquid CBr_3F mix-

tures to enter the furnace. After the reservoir was emptied the apparatus was shut down and the pressure allowed to drop to atmospheric. The products were drained from the first trap, which was operated at room temperature. Very little material was found in the second trap, which was operated at -78 °C, but its use tended to prevent corrosion of the exhaust valve. The products were worked up as described previously [1–4].

4. Results

Mixtures of CBr_3F with CBr_4, with $CHBr_3$, with Br_2, with CBr_2F_2, and with CF_3CBr_3 were pyrolyzed under conditions listed in table 1. The last three columns in the table give the total amount of recovered material, the weight percent of debromination, and the total weight of products other than bromine. The conditions used were approximately the optimum ones for the production of C_6F_6. The experiments with the first three substances listed were carried out to explore the possibility of syn-thesizing greater amounts of C_6BrF_5 and $C_6Br_2F_4$. After pyrolysis, the material was first treated to remove Br_2 and then distilled. The fractions collected were analyzed, using a mass spectrometer.

Results from the copyrolysis of CBr_3F with CBr_4 are given in table 2, along with boiling points, weights, and analyses of the fractions. Quantitative results, when given, are expressed in mole percent. A few compounds are merely listed when found in trace amounts. The addition of CBr_4 decreases the yield of C_6F_6 and increases the yields of C_6BrF_5 and $C_6Br_2F_4$. However, the major material was the $C_6Br_2F_4$ and not the more desirable C_6BrF_5.

Table 3 gives the results from copyrolysis of the CBr_3F with $CHBr_3$. Surprising amounts of C_6BrF_5 and $C_6Br_2F_4$ are produced. From $CHBr_3$ it was initially conceivable that C_6HF_5 or even $C_6H_2F_4$ could be a product. However, no products containing hydrogen were detected, excluding the HBr which was qualitatively evident in the exhaust gases.
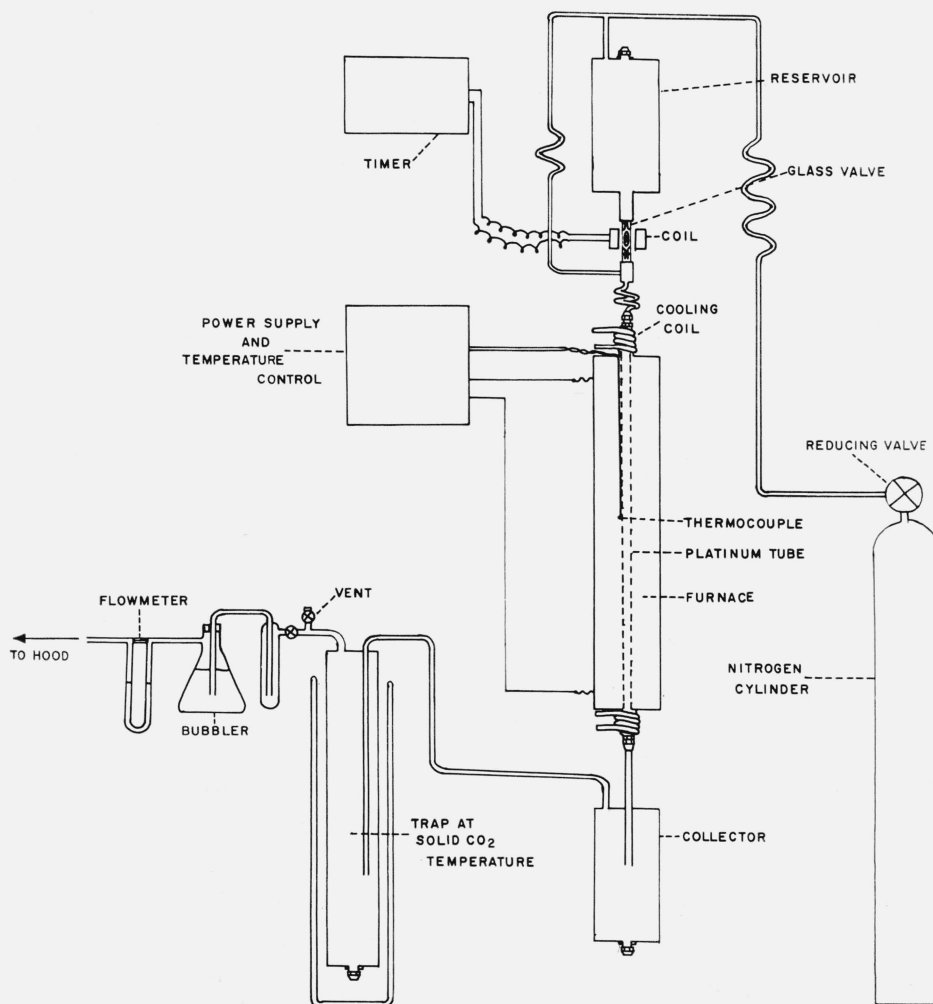

FIGURE 1. *Apparatus for pyrolysis of bromofluorocarbon liquids under pressure.*

TABLE 1. *Pyrolysis of bromofluorocarbon mixtures*

Mixtures	Weight	Moles	Temperature	Pressure	N₂ flow	Time	Recovered material (including Br₂)	Br₂ removal	Products (other than Br₂)
	g		$°C$	atm	cm^3/min	hr	$\%$	$\%$	g
CBr₃F _____ CBr₄ _____	2981 756	11 2.2	540	18	25	5	98	87	652
CBr₃F _____ CBr₄ _____	7859 1307	29 3.8	540	18	25	7	67	87	1721
CBr₃F _____ CBr₄ _____	4490 1100	16.5 3.3	545	3.5	25	5.2	98.5	69.8	740
CBr₃F _____ CHBr₃ _____	4065 759	15 3.1	560	10	25	11.3	95	96	769
CBr₃F _____ Br₂ _____	3400 1360	12.5 8.5	540	10	50	11	70	49ᵃ	416 9C₆F₆ 197CBr₃F 210Residue
CBr₃F _____ CBr₂F₂ _____	2710 420	10 2	540	10	25	5	77	68	420 84C₆F₆ 210CBr₃F 126Residue
CBr₃F _____ CF₃CBr₃ _____	1900 210	10.7 1	560	10	25	4	98	74	793

ᵃ Does not include the added bromine.

TABLE 2. *Fractional distillation of products from the pyrolysis of* CBr₃F/CBr₄ *mixtures*

Boiling range	Pressure	Weight of fraction	Analysis of fraction
$°C$	mm	g	*Mole %*
25 to 90	at 760	139	C₆F₆ (80%), CBrFCBrF (10%), CBr₂F₂
90 to 120	at 760	848	CBr₃F (90%), C₃Br₄F₂, C₆BrF₅
120 to 145	at 760	160	C₆BrF₅ (79%), C₂Br₄F₂ (20%), C₇BrF₇
85 to 95	at 25	218	C₆Br₂F₄ (90%), C₂Br₄F₂, C₆BrF₅
88 to 98	at 10	61.5	C₆Br₂F₄ (50%), C₂Br₄ (10%)
>100	at 10	268	Not analyzed.

Br₂ seemed to lower the extent of reaction; CBr₂F₂ appeared to have no significant effect. These materials are products from the pyrolysis of CBr₃F itself.

Copyrolysis with CF₃CBr₃ gave a significant yield of C₆F₅CF₃, as anticipated (see table 4). This material was also found in the pyrolysis products along with C₆F₆ [3] at 800 °C. However, under the conditions used here it is evident that it is produced as a result of the copyrolysis. This material is difficult to separate from the mixture in which it is produced.

TABLE 3. *Fractional distillation of products from the pyrolysis of* CBr₃F/CHBr₃ *mixtures*

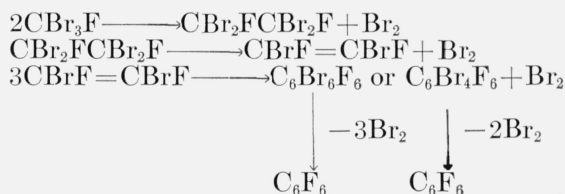| Boiling range at 760 mm	Weight of fraction	Analysis of fraction
$°C$	g	*Mole %*
45 to 100	69.4	C₆F₆ (70%), CHFBr₂ (20%)
100 to 125	510.4	CBr₃F (90%), C₂Br₃F
125 to 140	69.1	C₆BrF₅ (60%), CHBr₃ (30%), C₇BrF₇, C₆HBrF₄
140 to 175	39.7	C₄Br₃F₃, C₃Br₃F₃, C₈BrF₇
175 to 200	94.8	C₆Br₂F₄, C₂Br₄F₂

Unfortunately, our supply of CF₃CBr₃ was quite limited, and experiments with greater ratios of this material to CFBr₃ were not carried out. It is evident, however, that greater ratios would produce such substances as perfluoroxylenes.

TABLE 4. *Fractional distillation of products from the pyrolysis of* CBr₃F/CF₃CBr₃ *mixtures*

Boiling range at 760 mm	Weight of fraction	Analysis of fraction
$°C$	g	*Mole %*
50 to 95	51.2	C₆F₆ (66%), C₆F₅CF₃ (5%), C₆F₄Br₂
95 to 106	51.7	CBr₃F (85%), C₇F₈ (10%), C₆F₆ (5%)
106 to 110	302.9	CBr₃F (90%), C₇F₈ (5%), C₂Br₃F₃
>110	401	Not analyzed.

5. Discussion

The results obtained here are compatible with the type of mechanism assumed previously for this pyrolysis. The stages of reaction can be visualized thus:

$$2CBr_3F \longrightarrow CBr_2FCBr_2F + Br_2$$
$$CBr_2FCBr_2F \longrightarrow CBrF{=}CBrF + Br_2$$
$$3CBrF{=}CBrF \longrightarrow C_6Br_6F_6 \text{ or } C_6Br_4F_6 + Br_2$$

$$-3Br_2 \downarrow \qquad \downarrow -2Br_2$$

$$C_6F_6 \qquad\qquad C_6F_6$$

No perhalocyclohexanes have been isolated. The effect of pressure in enhancing the yield can be explained on this type of mechanism [2] without $CF \equiv CF$ as an intermediate. The intermediate, $CBrF = CBrF$, was found in the products in trace amounts, but no evidence was found for $CF \equiv CF$ as an intermediate. The $C_6Br_6F_6$ or the $C_6Br_4F_6$ shown are presumed to be extremely unstable; a Fischer-Hirshfelder model of these compounds indicates large steric effects. No evidence exists for the formation of such compounds from C_6F_6 and Br_2, although the $C_6Cl_6F_6$ has been made [1]. The chlorine derivative thermally decomposes near 250 to 300 °C.

It has been reported that $CF \equiv CF$ forms a dimer, presumably tetrafluorocyclobutadiene [7]. So far, no evidence exists for these compounds from the pyrolysis reaction of CBr_3F. However, $CF \equiv CH$ does trimerize to 1,2,4-trifluorobenzene [8], and hexafluoro-2-butyne trimerizes to hexa(trifluoromethyl)benzene [9].

6. References

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