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THE FLUORINATION OF BENZENE OVER MANGANESE TRIFLUORIDE

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SUMMARY

Fluorination of benzene, in the vapour phase, over manganic fluoride at 300° has given undecafluorocyclohexane (3.5%); 1*H*-, 3*H*- and 4*H*-nonafluorocyclohexene (3.3, 0.2 and 1.6%, respectively); 1*H*/2*H*- and 1*H*/4*H*-decafluorocyclohexane (1.1 and 6.2%, respectively); 1*H*,4*H*-hexafluorocyclohexa-1:4-diene (4.0%); 1*H*,2*H*- and 1*H*,4*H*-octafluorocyclohexene (0.04 and 15.8%, respectively); fluoro- (3.9%), *p*-difluoro- and 1,2,4-trifluoro-benzene; 1*H*,4*H*/2*H*-, 1*H*/2*H*,4*H*- and 1*H*,2*H*/4*H*-nonafluorocyclohexane; and 1*H*,3*H*/4*H*-, 1*H*,4*H*/5*H*- and 1*H*, 2*H*,4*H*- (8.0%) heptafluorocyclohexene.

INTRODUCTION

An earlier investigation[1] of the manganic fluoride fluorination of benzene in the vapour phase at 200–350° described a complex product which was partially separated by fractional distillation to give perfluorocyclohexane, monofluorobenzene (VIII), an octafluorocyclohexene and 1*H*,2*H*,4*H*-heptafluorocyclohexene (XVII).

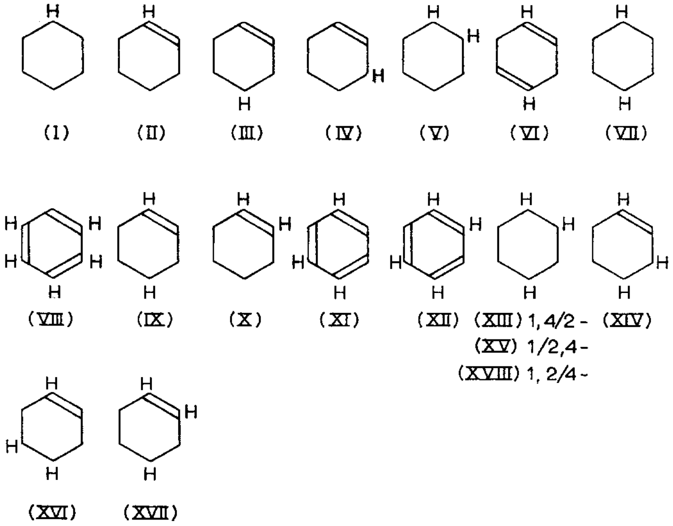
In the intervening period of time a detailed study of fluorocyclohexanes in this Department has resulted in the characterisation of many highly fluorinated cyclohexanes and cyclohexenes. Therefore, the separation and identification of the products of the manganic fluoride fluorination was greatly facilitated.

RESULTS AND DISCUSSION

The fluorination and isolation procedure, like that of the earlier work[1], involved removal of unchanged benzene by sulphonation and distillation of the mobile liquid residue into a series of multi-component fractions.

The separation of pure compounds necessitated the use of preparative-scale GLC, a technique not available in the previous study[1]. However, considerable difficulty was still experienced in obtaining complete separation of pure compounds. Thus, fractions J, K and L (Table 1) each gave a GLC component which was a mixture of several compounds, which were tentatively identified by their retention volumes. The estimates of the yields of pure compounds from the total fluorination product are accordingly less reliable as indications of their practical significance as synthetic precursors.

All of the pure compounds isolated (see Fig. 1) have been described previously[1–13] and were identified by a comparison of IR spectra with those of authentic specimens, as follows: undecafluorocyclohexane[3](I), 1*H*-[4], 4*H*-[6] and 3*H*-[6] nonafluorocyclohexene ((II)–(IV), respectively), 1*H*/2*H*-[5] and 1*H*/4*H*-[8] decafluorocyclohexane (V) and (VII), respectively), 1*H*,4*H*-hexafluorocyclohexa-1:4-diene[7] (VI), 1*H*,2*H*-[10] and 1*H*,4*H*-[1] octafluorocyclohexene ((X) and (IX), respectively), fluoro-, *p*-difluoro- and 1,2,4-trifluoro-benzene ((VIII), (XII) and (XI), respectively) 1*H*,4*H*/2*H*-[9], 1*H*/2*H*,4*H*-[9] and 1*H*,2*H*/4*H*-[13] nonafluorocyclohexane ((XIII), (XV) and (XVIII), respectively) and 1*H*,3*H*/4*H*-[11], 1*H*,4*H*/5*H*-[12] and 1*H*,2*H*,4*H*-[1] heptafluorocyclohexene ((XIV), (XVI) and (XVII), respectively).



(All unmarked substituents are fluorine)

Fig. 1. Products of the manganic fluoride fluorination of benzene.

The products so obtained differ from those obtained by the fluorination of benzene with cobaltic fluoride[2], ceric fluoride[14] and potassium cobaltifluoride complex[11] principally in the variation in the proportions of polyfluorocyclohex-enes and -anes. Thus, under comparable conditions at 300°, perfluorocyclohexane is the principal product of the fluorination of benzene with cobaltic fluoride, whereas C_6F_{12} forms only approximately 15–20% of the product using manganic trifluoride. Nonetheless the overall pattern of products obtained suggests a common mechanism of fluorination[2,15]. The gradation in fluorinating power observed, *viz.*, $CoF_3 > MnF_3 > CeF_4$ is in accord with the oxidation potentials of Co^{II}/Co^{III}, Mn^{II}/Mn^{III} and Ce^{III}/Ce^{IV}. However, the differences in product proportions may be reduced by adjustments in the conditions of fluorination. Thus, cobaltic fluoride and an excess of benzene vapour at 60–150° in a counter-current reactor[16] gives a product more like that obtained using the milder fluorinating agents.

EXPERIMENTAL

Preparative-scale gas–liquid chromatography

The GLC tubes for preparative scale work were (i) Unit A, 35 mm diam. × 488 cm packed with dinonylphthalate/celite, (1:2), (ii) Unit B, 75 mm diam. × 488 cm packed with dinonylphthalate/celite, (1:2), (iii) Unit C, 35 mm diam. × 488 cm packed with silicone gum 301/celite, (1:5) and (iv) Unit D, 35 mm diam. × 488 cm packed with KelF oil/celite (1:4). The nitrogen flow rate and temperature used are quoted where reference to the column is made. Separated components were collected in traps cooled in liquid air and removed by vacuum distillation for GLC analysis and spectral measurements. Pure components were identified by a comparison of the IR spectra with those of authentic samples.

Fluorination of benzene

The fluorination of benzene was carried out as previously described[2] in a tubular nickel reactor 10 cm diam. × 122 cm containing 3 kg of manganic fluoride. In a typical fluorination, benzene (100 ml) was added at a rate of 25 ml h^{-1} to the reactor which was heated to 300°. At the end of the addition the reactor was swept out with nitrogen. The product (160 g) was collected in a trap cooled in solid CO_2 and washed with water. Manganic trifluoride was regenerated by passing elemental fluorine into the reactor at 300° until a steady stream of fluorine emerged from the outlet.

Fluorinated product

The combined products (1286 g) from a number of fluorinations were stirred with conc. H_2SO_4 (500 g) for 24 h at 0° to remove unchanged benzene. The organic layer (1122 g) was washed with sodium bicarbonate solution and water, and dried. The polyfluoride mixture and ether (500 ml) was fractionally distilled using a 120 cm vacuum-jacketted column containing Dixon gauze rings. After removal of two initial fractions, ether/dodecafluorocyclohexane azeotrope and ether, the following fractions were taken (Table 1).

TABLE 1

Fraction	Boiling range (°C)	Yield (g)	Composition																	
			(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)	(XIV)	(XV)	(XVI)	(XVII)	(XVIII)
A	38–57.5	11.6	+	+																
B	57.5–62	60.1	+	+																
C	62–68.5	60.2	+	+	+	+	+	+		+										
D	68.5–74	39.6		+		+	+	+	+	+	+									
E	74–76	78.0						+	+	+	+									
F	76–79	41.2						+	+	+	+									
G	79–83	20.3							+		+									
H	83–85.2	138.5								+	+		+	+						
I	85.2–87	52.5								+	+		+	+						
J	87–90.5	59.1									+	+	+	+	+	+				
K	90.5–102	52.9									+				+	+		+	+	
L	102–104.8	42.1														+	+	+	+	+
M	104.8–112.2	18.1														+		+	+	
Residue		201.8																	+	
Weight % in original product mixture:			3.5	3.3	1.6	0.2	1.1	4.0	6.2	3.9	15.8	0.04	*	*	*	*	*	8.0	*	

* Estimation prevented by incomplete GLC separation.

A portion (135 g) of the crude product mixture before sulphonation was fractionally distilled with ether, the ether/C_6F_{12} azeotrope collected (42 g) and the distillation residue weighed (114 g). The azeotrope was separated by preparative scale GLC (Unit B, 85°, 75 l h^{-1} N_2) to give ether (18.5 g) and perfluorocyclohexane (15 g), both identified by IR spectroscopy. Under comparable conditions, the fluorination of benzene by CoF_3 gave a product shown by analytical GLC to consist principally of C_6F_{12}.

Analytical GLC showed that all the fractions were multi-component mixtures, and these were separated into pure components by preparative-scale GLC.

Fraction A: A sample (3 g) of fraction A was separated (Unit A, 80°, 18 l h^{-1} N_2) into (i) undecafluorocyclohexane[3] (1.6 g) and (ii) 1*H*-nonafluorocyclohexene[4] (0.6 g) and (iii) ether (trace).

Fraction B: A sample (4.8 g) of fraction B was separated (Unit A, 80°, 18 l h^{-1} N_2) into (i) undecafluorocyclohexane (1.9 g) and (ii) 1*H*-nonafluorocyclohexene (2.0 g).

Fraction C: A sample (6.0 g) of the fraction was separated (Unit A, 80°, 14 l h^{-1} N_2) into seven components. These were (i) undecafluorocyclohexane (0.2 g), (ii) 1*H*-nonafluorocyclohexene (0.3 g), (iii) 1*H*/2*H*-decafluorocyclohexane[5] (0.9 g), (iv) 4*H*-nonafluorocyclohexene[6] (1.6 g), (v) 3*H*-nonafluorocyclohexene[6] (0.2 g), (vi) 1*H*,4*H*-hexafluorocyclohexa-1,4-diene[7] (0.1 g) and (vii) monofluorobenzene (2.1 g).

Fraction D: A sample (5.6 g) of fraction D was separated (Unit A, 80°, 16 l h^{-1} N_2) into (i) 1*H*-nonafluorocyclohexene (trace), (ii) 1*H*/2*H*-decafluorocyclohexane (0.3 g), (iii) 3*H*-nonafluorocyclohexene (0.1 g), (iv) 1*H*, 4*H*-hexafluorocyclohexa-1,4-diene (1.6 g), (v) 1*H*/4*H*-decafluorocyclohexane[8] (0.8 g) (vi) monofluorobenzene (1.4 g) and (vii) 1*H*, 4*H*-octafluorocyclohexene[1] (0.2 g).

Fraction E: A sample (5.7 g) of the fraction was separated (Unit A, 90°, 18 l h^{-1} N_2) into (i) 1*H*,4*H*-hexafluorocyclohexa-1,4-diene (1.1 g), (ii) 1*H*/4*H*-decafluorocyclohexane (1.3 g); (iii) monofluorobenzene (0.4 g) and (iv) 1*H*,4*H*-octafluorocyclohexene (0.8 g).

Fraction F: From a sample (5.1 g) of the fraction was separated (Unit A, 90°, 20 l h^{-1} N_2) (i) 1*H*,4*H*-hexafluorocyclohexa-1,4-diene (0.6 g), (ii) 1*H*/4*H*-decafluorocyclohexane (2.0 g), (iii) monofluorobenzene (0.1 g) and (iv) 1*H*,4*H*-octafluorocyclohexene (1.2 g).

Fraction G: A sample (4.9 g) of fraction G was separated (Unit A, 96°, 18 l h^{-1} N_2) into two components. These were identified as (i) 1*H*/4*H*-decafluorocyclohexane (2.1 g) and (ii) 1*H*,4*H*-octafluorocyclohexene (1.2 g).

Fraction H: From a sample (15.1 g) of fraction H was separated (Unit B, 85°, 75 l h^{-1} N_2) (i) 1*H*,4*H*-octafluorocyclohexene (5.1 g) and (ii) mixture h (2.5 g).

Fraction I: A sample (20 g) of the fraction was separated (Unit B, 95°, 70 l h^{-1} N_2) into (i) 1*H*,4*H*-octafluorocyclohexene (11.0 g) and (ii) mixture h (6.0 g).

Mixture h: A sample (2 g) of the combined mixtures h obtained from fractions H and I was separated (Unit D, 60°, 10 l h^{-1} N_2) into (i) monofluorobenzene (0.1 g), (ii) *p*-difluorobenzene (0.1 g), (iii) 1,2,4-trifluorobenzene (0.2 g) and (iv) a mixture (0.9 g) containing components (i), (ii) and (iii).

Fraction J: Fraction J was a complex mixture not fully resolvable into pure components on any of the GLC column packings available. From the fraction (20 g) was obtained (Unit B, 85°, 75 l h^{-1} N_2) (i) 1*H*,4*H*-octafluorocyclohexene (4.7 g) and (ii) mixture j. Separation of mixture j (Unit D, 55°, 10 l h^{-1} N_2) gave (i) 1*H*,4*H*/2*H*-nonafluorocyclohexane[9] (0.2 g), (ii) 1*H*,2*H*-octafluorocyclohexene[10] (0.1 g) and (iii) mixture j_1 (7.6 g). Mixture j_1 was not separable into pure compounds, but by analytical GLC the components were tentatively identified as *p*-difluorobenzene, 1,2,4-trifluorobenzene, 1*H*,4*H*/2*H*-nonafluorocyclohexane and 1*H*:3*H*/4*H*-heptafluorocyclohexene[11].

Fraction K: A sample (34.7 g) of the fraction was separated (Unit B, 100°, 75 l h^{-1} N_2) into (i) 1*H*,4*H*-octafluorocyclohexene (0.6 g), (ii) 1*H*,4*H*/2*H*-nonafluorocyclohexane (1.7 g), (iii) 1*H*:3*H*/4*H*-heptafluorocyclohexene (2.8 g) (iv) 1*H*:4*H*/5*H*-heptafluorocyclohexene[12] (0.4 g) (v) 1*H*,2*H*,4*H*-heptafluorocyclohexene[1] (1.7 g) and (vi) a mixture (13.8 g) of components similar in composition to fraction K.

Fraction L: A sample (27.3 g) of fraction L was separated (Unit B, 85°, 65 l h^{-1} N_2) into (i) 1*H*:3*H*/4*H*-heptafluorocyclohexene (1.7 g), (ii) 1*H*,2*H*,4*H*-heptafluorocyclohexene (2.0 g), (iii) 1*H*/2*H*,4*H*-nonafluorocyclohexane[9] (1.6 g) and (iv) a mixture. From the mixture was obtained (Unit A, 85°, 20 l h^{-1} N_2) (i) 1*H*:4*H*/5*H*-heptafluorocyclohexene (0.6 g), (ii) 1*H*,2*H*/4*H*-nonafluorocyclohexane[13] (0.2 g) and (iii) a mixture (12.2 g) which was not investigated further.

Fraction M: A sample (11.8 g) of the fraction was separated (Unit B, 85°, 75 l h^{-1}) into (i) 1*H*:3*H*/4*H*-heptafluorocyclohexene (0.4 g), (ii) 1*H*:4*H*/5*H*-heptafluorocyclohexene (0.4 g) and (iii) 1*H*,2*H*,4*H*-heptafluorocyclohexene (5.6 g).

Distillation residue: Gas–liquid chromatography analysis of the distillation residue showed the presence of a major component. A sample (20 g) of the residue was separated (Unit B, 110°, 75 l h^{-1} N_2) to give 1*H*,2*H*,4*H*-heptafluorocyclohexene[1] (4.1 g).

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