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THE FLUORINATION OF BENZENE OVER CERIUM TETRAFLUORIDE

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Abstract—Benzene has been fluorinated over cerium tetrafluoride at temps between 250° and 480°. From the product obtained by fluorination at 480° there were isolated 1*H*-nona,- and 1*H*, 4*H*-octa-fluorocyclohexene 1*H*-hepta and 1*H*,4*H*-hexa-fluorocyclohexa-1,4-diene, 1*H*-hepta- and 1*H*,4*H*-hexa-fluorocyclohexa-1,3-diene, benzene and mono-, *o*- and *p*-di-, 1,2,4-tri-, 1,2,4,5-tetra- and 1,2,3,4-tetra-fluorobenzene.

THE efficacy of cerium tetrafluoride as an exhaustive fluorinating agent has not been established hitherto. The fluorinations of hydrocarbon oils, hexachlorobutadiene (to yield chlorofluorobutanes) and dichlorodecafluorocyclohexane have been described,[1] but there are no studies of simple hydrocarbons. However, it seemed to be mild, and hence possibly selective, in action. This paper describes the products obtained from the fluorination of benzene over cerium tetrafluoride at 480° in a stirred reactor of design similar to those previously used[2] for reactions with cobaltic fluoride. Cerium tetrafluoride was prepared from the trifluoride by reaction *in situ* with elemental fluorine at 450–500°: below this temperature the tetrafluoride was not formed.

The fluorination of benzene was carried out by passing the vapour over heated cerium tetrafluoride. The product, which was collected in a trap cooled in solid carbon dioxide and then washed with water to remove hydrofluoric acid, was subjected to a preliminary GLC analysis using a dinonylphthalate/celite stationary phase. This showed that at temperatures below 400° little fluorination occurred, though above 410° an increasing reaction took place. A chromatogram of the products obtained by fluorination at 480° showed the presence of eleven components, benzene itself (No. 8) being ca. 30% of the mixture. Seven components had retention times less than, and three greater than that of benzene. It was hoped to minimize complications arising during the distillation due to azeotope formation[3] between benzene and cyclic fluoro compounds by sulphonation of the reaction product. However, this was not completely satisfactory since the chromatogram of the sulphonated product suggested, unexpectedly, that components with retention times greater than that of benzene were also being removed. In view of this only part of the product was so treated. The product was then fractionally distilled, but the fractions taken (a–f) were still complex (Table 1). They were separated into simpler mixtures (1–9) by preparative scale GLC using dinonylphthalate: celite as stationary phase. Mixtures 1–8 corresponded to benzene and the 7 components with shorter retention times and mixture 9 the remaining 3 components observed on the chromatogram of the untreated fluorination product. Table 1 gives details.

Separation of components 1 to 8 which contained the products with retention times equal to or less than that of benzene, resulted in the identification, by a comparison of IR spectra with those of authentic samples, of the following as constituents of the fluorination product: 1*H*-nonafluorocyclohexene (I), 1*H*,4*H*-octafluorocyclohexene (II) 1*H*-heptafluorocyclohexa-1,4-diene (III) 1*H*,4*H*-hexafluorocyclohexa-1,4-diene (IV), 1*H*-heptafluorocyclohexa-1,3-diene (V), and benzene (VI). Compounds I, III, IV and V have not previously been obtained from a fluorination product. In addition, the previously unknown diene, 1*H*,4*H*-hexafluorocyclohexa-1,3-diene (VII) was obtained. This was characterized by elemental analysis, which was correct for $C_6H_2F_6$, and the UV spectrum which was typical of a 1,3-diene. The mass spectrum confirmed a mol wt of 188, with a cracking pattern typical of a 1,3-diene in which the H atoms were not present on adjacent C atoms. The proton and fluorine NMR spectra were also consistent with the proposed structure. The 1,4-orientation of the H atoms was confirmed by the fluorination over cobalt trifluoride at 80° of component 7 obtained by preparative scale GLC. This component contained only the unknown diene (VII) and 1*H*,4*H*-octafluorocyclohexene (II); the product of its fluorination contained only 1*H*, 4*H*/- and 1*H*/4*H*-decafluorocyclohexane, confirming the *para* orientation of the H atoms in the diene (VII).

TABLE 1

Fraction	Boiling range	Weight obtained (g)	Weight separated (g)	Weights of components obtained (g)								
				1	2	3	4	5	6	7	8	9
a	63·0–64·5	2·4	2·4	0·2	0·2	0·7	0·1	0·1	0·6	—	0·1	—
b	64·5–71·0	4·1	3·6			1·2	0·2	0·4	0·7	—	0·2	—
c	71·0–72·0	5·6	4·8					0·3	2·8	0·1	1·0	—
d	72·0–77·0	21·0	7·8						1·0	3·0	1·8	0·5
e	77·0–83·0	23·2	11·1							5·3	0·8	1·5
f	83·0–84·0	3·6	3·4							1·8	0·2	0·7

The remaining components (having retention times greater than that of benzene) contained aromatic compounds which were isolated by further preparative scale GLC separation of an unsulphonated portion of the original fluorinated product. The compounds identified were monofluorobenzene, (VII), *o*-(IX) and *p*-difluorobenzene (X), 1,2,4,5-(XII) and 1,2,3,4-tetrafluorobenzenes (XII) all known compounds, by comparisons of IR spectra with those of authentic samples. No tetrafluorobenzenes have been previously isolated from a direct fluorination process.

The products obtained by the fluorination of benzene with cerium tetrafluoride differ markedly from those obtained using cobalt trifluoride. The former gave a mixture of approximate composition 40% unsaturated alicyclics, 10% fluoro aromatics, 30% benzene, with 20% unidentified residue. No saturated fluorocarbons were obtained, in contrast with fluorinations over cobalt trifluoride at 150–200°, where the principal products are fluorocyclohexanes containing only traces of fluorocyclo-alkene and -aromatic compounds.[4] Thus cerium tetrafluoride is a mild fluorinating agent.

EXPERIMENTAL

Preparative scale gas–liquid chromatography. The units used were (i) Unit A, 13 mm diam × 200 cm packed with dinonylphthalate/celite (1:2), (ii) Unit B, 35 mm diam × 488 cm, packed with dinonyl phthalate/celite (1:2) (iii) Unit C, 35 mm diam × 488 cm packed with Kel F oil/celite (1:4), (iv) Unit D, 13 mm diam × 200 cm packed with tricresyl phosphate/celite (1:3), and (v) Unit E, 75 mm diam × 488 cm packed with dinonylphthalate/celite (1:2). Products were collected in traps cooled in liquid N_2, and removed by vacuum distillation for GLC analysis and spectral measurements.

Preparation of cerium tetrafluoride. "Analar" grade cerous fluoride hemihydrate was dehydrated by heating for 24 hr at 150° in a stream of HF. Elemental F was then passed over the cerous fluoride, initially at 230° for 3 hr, then at 470° for 4 hr, according to the method described.[5] It was subsequently found that regeneration of ceric fluoride which had been used to fluorinate benzene could be achieved by passing F at 450–500° until F was detected issuing from the end of the reactor.

Fluorination reactor. This consisted of a nickel tube (5 cm diam × 46 cm) fitted with a stirrer rotating at 4 rpm, and was similar to those described.[2] It was charged with cerous fluoride (150 g). Benzene was added dropwise (2·3–15 g/hr), and the products collected in a trap cooled in solid CO_2.

Preliminary fluorination results. Benzene (4·3 g samples) was passed over ceric fluoride at temps between 250–400° at flow rates of 4·0 g/hr and 2·3 g/hr. The product ($\approx$4 g) was shown by GLC to consist largely of benzene, and contained only small amounts of fluorinated products. Above 400° fluorination proceeded to an increasing extent, and at 480° the product contained substantial amounts of fluorinated compounds together with unchanged benzene. The variation in the wt of product with input rate using 3·5 g samples of benzene at 480° was as follows [input rate (g/hr) and yield (g) respectively in each case]: 5·8, 5·7; 7·0:5·9; 8·4:5·6; 10·5, 5·1; 11·1, 4·8; 15·0, 4·5. The proportion of benzene in the product (by GLC) diminished with decreasing input rate.

Fluorination of benzene. Benzene (96 g) was fluorinated using 3·5 g samples (input rate 10 g/hr), over cerium tetrafluoride at 480°. At the end of each addition, N_2 (10l./hr) was passed for 15 min to purge the reactor of products. F (10 g/hr) was then passed through the reactor at 480° for 45–60 min until a steady stream of F was issuing from the outlet, when the reactor was purged of F by the passage of N_2 (10l./hr) for 15 min. The product of fluorination was washed with water to remove HF, and the organic layer separated to yield a mixture of hydrofluorocarbons and benzene (136 g). GLC (dinonylphthalate stationary phase) showed the presence of 11 components in the reaction mixture.

Sulphonation of the product. Fuming H_2SO_4 (20% SO_3, 70 g) was added slowly (150 min) at 0° to a portion (70·1 g) of the mixture of hydrofluorocarbons and benzene, and the mixture stirred for a further 60 min. The reaction mixture was separated and the organic layer washed with $NaHCO_3$aq and water to yield a product (38·5 g).

Fractional distillation. Sulphonated product (38 g) and untreated product (65 g) were combined and fractionally distilled from P_2O_5. Fractions were taken at suitable temp intervals and separated by GLC The results are given in Table 1.

The distillation residue (23·9 g) was a yellow oil containing only small amounts of components 7, 8 and 9, together with other compounds having a long retention time on GLC (silicone gum/celite, 120°).

Separation of components. Samples of the fractions obtained by distillation were separated by preparative scale GLC. The following conditions were used for the separation of fractions (i) fraction a, unit A, 92°, N_2 flow rate 5·4 l./hr; (ii) fractions b and c, unit B, 75°, N_2 flow rate 14 l./hr; (iii) fraction d, unit B, 80° N_2 flow rate 14 l./hr; (iv) fraction e, unit B, 86°, N_2 flow rate 14 l./hr; (v) fraction f, unit A, 90°, N_2 flow rate 5 l./hr. The results of the separations are given in Table 1.

Identification of components. By GLC analysis (dinonyl phthalate/celite) component 1 was shown to be a mixture (3 peaks) and components 2 was also a mixture (2 peaks), the individual peaks having very similar retention times. These mixtures were not further investigated. Components 3 and 4 were found to be I (b.p. 64°)[6] and III (b.p. 67°) respectively by a comparison of IR spectra.[7] Components 6 and 8 were identified as IV (b.p. 75°) and VI respectively by a comparison of IR spectra.[8] Components 5 and 7 were shown by GLC (Kel F oil/celite and Tricresylphosphate/celite stationary phases respectively) to be mixtures.

Separation of component 5. A sample (0·75 g) was separated by preparative GLC (Unit C, 65°, N_2 flow rate 10 l./hr) into V (0·3 g), identified by the IR spectrum,[9] and an unidentified component (0·2 g).

Separation of component 7. A sample (2·6 g) was separated by preparative GLC (Unit D, 72°, N_2 flow rate 5 l./hr) into II (0·85 g) (b.p. 86°) identified by a comparison of the IR spectrum,[9] and 1H, 4H-*hexafluorocyclohexa*-1,3-*diene* (VII) (1·6 g, b.p. 83°).

Characterization of 1H,4H-*hexafluorocyclohexa*-1,3-*diene.* The compound (Found: C, 38·4; H, 1·2.

$C_6H_2F_6$ requires: C, 38·3; H, 1·1%), showed an absorption max at 252 mμ (ε = 6400) in the UV consistent with a 1,3-diene structure. Mass spectrometry indicated a mol wt of 188, and a breakdown pattern consistent with a 1,3-diene in which the H atoms were not present on adjacent C atoms. The proton NMR spectrum consisted of 1 signal corresponding to a vinylic proton (τ = 4·24 ppm from TMS) and the F spectrum consisted of two signals in the ratio 2:1 with chemical shifts of 115·95 ppm and 121·8 ppm (from CCl_3F internal standard).[10]

Fluorination of component 7. Component 7 (1·8 g), in a stream of N_2 (10 l./hr), was fluorinated over cobalt trifluoride at 80° to give a product (0·7 g) containing two compounds. These were separated by preparative GLC (Unit B, 76°, N_2 flow rate 5l./hr) into 1*H*,4*H*/-decafluorocyclohexane (0·05 g), and 1*H*/4*H*-decafluorocyclohexane (0·15 g) identified by a comparison of IR spectra with those of authentic samples.[11]

Identification of component 9. A sample of the fluorination mixture (106 g) before sulphonation was separated in portions by preparative GLC (Unit E, 100°, N_2 flow rate 65 l./hr) into components 1–8 (66·7 g) and component 9 (10·3 g). The latter (10·2 g) was further separated by GLC (Unit A, 92°, N_2 flow rate 5·4 l./hr) into 3 parts, components 9a (5·4 g), 9b (1·7 g) and 9c (1·2 g).

Identification of component 9a. A sample (0·95 g) was further separated by GLC (unit C, 70°, N_2 flow rate 10 l./hr) into 3 compounds which were identified as (i) VI (trace from component 8), (ii) VIII (0·45 g) and (iii) XII (0·50 g), identified by a comparison of IR spectra with those authentic samples.

Identification of component 9b. A sample (1·4 g) was separated by GLC (Unit C, 70°, N_2 flow rate 10 l./hr) into (i) 9a (0·2 g), (ii) XIV (0·3 g) and (iii) XI (0·9 g) which was identified by the IR spectrum. The mixture XIV (0·3 g) was separated by GLC (Unit C, 70°, N_2 flow rate 10 l./hr) into (i) 9a and XI (0·1 g) and (ii) X (0·1 g) identified by the IR spectrum.

Identification of component 9c. A sample (0·55 g) was separated by GLC (Unit C, 70°, N_2 flow rate 10 l./hr) into (i) IX (0·2 g), (ii) XIII (0·1 g) and (iii) an unidentified mixture (0·05 g). Both pure components were identified by a comparison of IR spectra with those of authentic samples.

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