

## FLUORINATION WITH COMPLEX METAL FLUORIDES PART III.\* THE FLUORINATION OF BENZENE OVER POTASSIUM HEXAFLUORONICKELATE(IV)

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### SUMMARY

Fluorinations of benzene over potassium hexafluoronickelate(IV) at temperatures of 120–350° have given mixtures of fluorocyclohexanes containing small amounts of fluorocyclohexenes and fluorobenzenes. Benzene was recovered unchanged after contact with potassium trifluoronickelate(II) at elevated temperatures.

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### INTRODUCTION

The profound differences in behaviour shown by cobalt trifluoride<sup>2</sup>, the alkali metal tetrafluorocobaltates(III)<sup>3,4</sup> and potassium hexafluorocobaltate(III)<sup>5</sup> as fluorinating agents for organic compounds in the vapour phase have prompted investigations into the uses of other complex fluorides for this purpose.

As part of a systematic study of complex fluorides of other transition metals, we report the fluorination of benzene with potassium hexafluoronickelate(IV).

### RESULTS

The bright red potassium hexafluoronickelate(IV) may be prepared by the elemental fluorination of anhydrous potassium tetrachloronickelate(II)<sup>6</sup> or a 1:1 mixture of potassium fluoride and potassium trifluoronickelate(II). The latter compound is unreactive towards fluorine and towards organic substrates at elevated temperatures. Preliminary experiments showed that at temperatures above 100° potassium hexafluoronickelate(IV) is an efficient fluorinating agent for benzene, and that the reagent is regenerated reproducibly with elemental fluorine at tempera-

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\* For Part II, see ref. 1.

tures above 200°. At temperatures above 250°, benzene is converted almost entirely to dodecafluorocyclohexane; as the temperature is lowered, multicomponent mixtures are produced until at 100° benzene is recovered unchanged. Potassium hexafluoronickelate(IV) is reduced by an excess of benzene to the yellow potassium tetrafluoronickelate(II). It is believed that this is the first example of the use of a high-valency nickel compound as an exhaustive fluorinating agent, although such reactivity has been hinted at recently<sup>7</sup> and speculations about mechanisms involved in electrochemical fluorination have envisaged such a possibility<sup>8</sup>.

The fluorination and isolation procedures, like those of earlier work<sup>2</sup>, involved the distillation of the crude products accumulated from several fluorinations into a series of multicomponent fractions; most components were common to more than one fraction. Samples of all the components, all known compounds, were isolated from selected fractions by gas-liquid chromatography and identified by comparison of their spectra (IR and/or <sup>1</sup>H and <sup>19</sup>F NMR) with those of authentic samples. The composition of each fraction (Table 1) was then determined by retention volume measurements based on gas-liquid chromatograms. The products identified are listed in Figure 1 where the preponderance of saturated compounds should be noted.

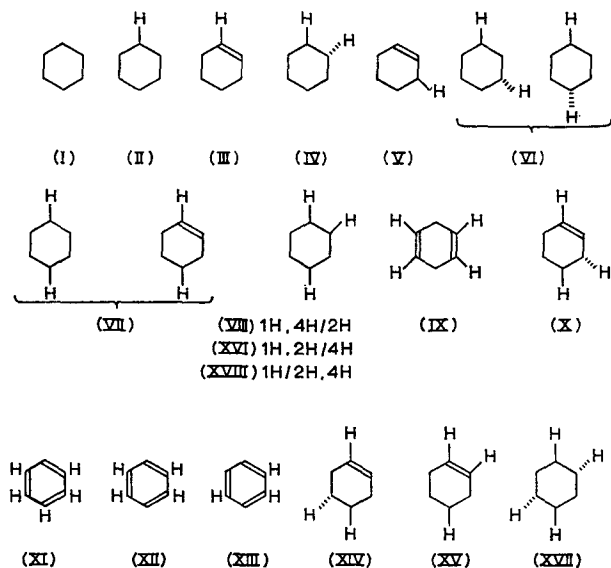


Fig. 1. Products of the fluorination of benzene by potassium hexafluoronickelate(IV). (All unmarked bonds are to fluorine.)

The products thus obtained do not differ significantly from those obtained from the fluorination of benzene with cobalt trifluoride<sup>2</sup>. Fluorination of benzene with either potassium hexafluoronickelate(IV) or cobalt trifluoride in the same

reactor under comparable conditions showed that the former reagent is more reactive; lower temperatures were required to bring about the same degree of fluorination. This is consistent with the high oxidation potential predicted for nickel(IV) compounds and supports the recently proposed cation-radical theory<sup>9</sup> of fluorination for organic compounds. The reduction of hexafluoronickelate(IV) to the tetrafluoronickelate(II) was expected since complex nickel(III) fluorides are not prepared easily. Thus this reagent provides an example of a "2-electron oxidant" (*cf.* lead tetrafluoride fluorinations<sup>10</sup>) but this appears to be of little significance in the fluorination process described.

To date, potassium hexafluoronickelate(IV) offers no practical advantage over cobalt trifluoride, but since the presence of complex fluoronickelates in the electrochemical fluorination process has been suggested<sup>8,11</sup> the fluorination of other organic compounds is being studied.

#### EXPERIMENTAL

##### *Gas-liquid chromatography*

Analytical and preparative gas-liquid chromatography experiments were performed using a Pye 105 chromatograph [Column 1, 8 mm diam.  $\times$  9 m, packed with dinonyl phthalate/celite (1:2); Column 2, 8 mm diam.  $\times$  9 m, packed with di-isodecyl phthalate/Chromosorb P (1:3)].

##### *Preparation of potassium hexafluoronickelate(IV)*

###### *Method A*

Dehydration of an intimate mixture (2:1) of potassium chloride and nickel chloride hexahydrate by azeotropic distillation with toluene gave potassium tetrachloronickelate(II)<sup>6</sup> (2 kg) which when treated with elemental fluorine for 4 days at 300° gave potassium hexafluoronickelate(IV) (*ca.* 1.8 kg).

###### *Method B*

Fluorination of an intimate mixture (1:1) of potassium fluoride and potassium trifluoronickelate(II) with elemental fluorine at 300° gave potassium hexafluoronickelate(IV).

Samples from both preparations were examined by X-ray powder photography ( $CoK\alpha$  radiation). The X-ray powder patterns were indexed for face-centred cubic cells with a lattice constant 8.07 Å (*lit.* value<sup>12</sup>: 8.10 Å).

##### *The reduction of potassium hexafluoronickelate(IV)*

Benzene was passed over potassium hexafluoronickelate(IV) in a tubular nickel reactor (5.7 cm diam.  $\times$  45.7 cm, Reactor 1) at 300° until samples of the effluent vapours were shown to be unchanged benzene by gas-liquid chromatography and IR spectroscopy. A sample of the exhausted reagent was shown to be

potassium tetrafluoronickelate(II) by X-ray powder photography ( $\text{CuK}\alpha$  radiation). The powder pattern was indexed for a tetragonal unit cell with lattice constants,  $a = 4.007 \text{ \AA}$ ,  $c = 13.04 \text{ \AA}$  (lit. values<sup>13</sup>:  $a = 4.006 \text{ \AA}$ ,  $c = 13.076 \text{ \AA}$ ).

#### *Fluorination of benzene*

The fluorination of benzene was carried out as described previously<sup>2</sup> in a tubular nickel reactor (10 cm diam.  $\times$  122 cm) containing potassium hexafluoronickelate(IV) (*ca.* 1.8 kg). In a typical fluorination, benzene (50 ml) was added at a rate of  $25 \text{ ml h}^{-1}$  in a stream of nitrogen ( $8 \text{ l h}^{-1}$ ) to the heated reactor ( $120\text{--}200^\circ$ ). At the end of the addition, the reactor was swept out with nitrogen ( $15 \text{ l h}^{-1}$ ) for 1 h. The product (80–85 g) was collected in a nickel trap cooled in solid  $\text{CO}_2$ , warmed to room temperature and washed free of HF with water. The fluorinating agent was regenerated by passing elemental fluorine into the reactor at  $200\text{--}300^\circ$  until a steady stream of fluorine emerged from the outlet.

The combined products from a number of fluorinations were washed with sodium bicarbonate solution and water and dried ( $\text{MgSO}_4$ ). The polyfluoride mixture (800 g) and ether (200 ml) was distilled using a vacuum-jacketed column (120 cm) containing Dixon gauze rings; the fractions listed in Table 1 were taken.

Analytical gas-liquid chromatography showed that all fractions were multi-component mixtures and some of these were separated into pure components by gas-liquid chromatography. All compounds were known and were identified by comparison of their IR spectra, measured on a Perkin-Elmer 257 grating IR spectrophotometer, with those of authentic samples<sup>14</sup>. The composition of the remaining fractions was estimated by retention volume measurements taken from gas-liquid chromatograms.

*Fraction 1*: A sample (2.55 g) was separated (Column 2,  $75^\circ$ ,  $5 \text{ l h}^{-1} \text{ N}_2$ ) into (i) dodecafluorocyclohexane (1.02 g) and (ii) ether (0.48 g).

*Fraction 4*: A sample (1.07 g) was separated (Column 1,  $92^\circ$ ,  $5.3 \text{ l h}^{-1} \text{ N}_2$ ) into (i) dodecafluorocyclohexane (trace), (ii) undecafluorocyclohexane (0.52 g), (iii) 1*H*-nonafluorocyclohexene (trace), (iv) ether (0.15 g) and (v) benzene (0.08 g).

*Fraction 5*: A sample (0.93 g) was separated (Column 1,  $92^\circ$ ,  $5.3 \text{ l h}^{-1} \text{ N}_2$ ) into (i) dodecafluorocyclohexane (trace), (ii) undecafluorocyclohexane (0.03 g), (iii) 1*H*-nonafluorocyclohexene (trace), (iv) ether (0.13 g), (v) 1*H*/2*H*-decafluorocyclohexane (0.18 g), (vi) 3*H*-nonafluorocyclohexene (0.02 g) and (vii) a mixture (0.13 g), mainly benzene plus two unidentified compounds.

*Fraction 6*: A sample (0.68 g) was separated (Column 2,  $109^\circ$ ,  $5 \text{ l h}^{-1} \text{ N}_2$ ) into (i) 1*H*/3*H*- and 1*H*/4*H*-decafluorocyclohexane (0.31 g), (ii) a mixture (trace) and (iii) benzene (0.11 g).



*Fraction 9*: A sample (1.80 g) was separated (Column 2, 127°, 5 l h<sup>-1</sup> N<sub>2</sub>) into (i) a mixture (0.09 g) of 1*H*,4*H*-octafluorocyclohexene and 1*H*/4*H*-decafluorocyclohexane, (ii) mainly 1*H*,4*H*/2*H*-nonafluorocyclohexane (0.18 g), (iii) 3,3,6,6-tetrafluorocyclohexa-1,4-diene (0.27 g) and (iv) a mixture (0.68 g). This mixture (0.6 g) was further separated (Column 1, 97°, 5 l h<sup>-1</sup> N<sub>2</sub>) into (i) benzene (0.08 g) and (ii) monofluorobenzene (0.18 g).

*Fraction 10*: A sample (1.79 g) was separated (Column 1, 99°, 5.3 l h<sup>-1</sup> N<sub>2</sub>) into (i) a mixture (trace) of 1*H*,4*H*-octafluorocyclohexene and 1*H*/4*H*-decafluorocyclohexane, (ii) mainly 1*H*,2*H*/4*H*-nonafluorocyclohexane (0.20 g), (iii) mainly 3,3,6,6-tetrafluorocyclohexa-1,4-diene (0.77 g) (peaks (ii) and (iii) overlap) and (iv) a mixture (0.14 g; 70:30) of *p*-difluorobenzene and 1,2,4-trifluorobenzene identified by <sup>19</sup>F NMR spectroscopy<sup>15</sup>.

*Fraction 13*: A sample (4.32 g) was separated (Column 1, 97°, 5.5 l h<sup>-1</sup> N<sub>2</sub>) into (i) 1*H*,4*H*/2*H*-nonafluorocyclohexane (0.09 g), (ii) 1*H*,3*H*/4*H*-heptafluorocyclohexene (0.06 g), (iii) a mixture (trace), (iv) mainly 1*H*,4*H*/5*H*-heptafluorocyclohexene (0.15 g), (v) 1*H*,2*H*,4*H*-heptafluorocyclohexene (0.41 g), (vi) 1*H*,2*H*/4*H*-nonafluorocyclohexane (0.69 g) m.p. 34.5° (lit. value<sup>16</sup>: 34–35°) and (vii) 1*H*/2*H*,4*H*-nonafluorocyclohexane (0.89 g).

*Fraction 16*: This was mainly 1*H*,4*H*/2*H*,5*H*-octafluorocyclohexane.

*Fraction 17*: This was not separated, but analysis by gas-liquid chromatography and IR spectroscopy indicated the presence of stereoisomers of 1*H*,2*H*,4*H*,5*H*-octafluorocyclohexanes.

*The fluorination of benzene with potassium hexafluoronickelate(IV) and cobalt trifluoride (a comparative study)*

A tubular nickel reactor (Reactor 1) was packed with either potassium hexafluoronickelate(IV) (430 g) or cobalt trifluoride (200 g). Aliquots of benzene (5 ml) were fluorinated in the usual way over a range of temperatures; typical yields are recorded in Table 2.

TABLE 2

RESULTS OF FLUORINATION OF BENZENE WITH POTASSIUM HEXAFLUORONICKELATE(IV) AND COBALT TRIFLUORIDE

Temperature (°C)	Wt. of fluorocarbon (g)	
	K <sub>2</sub> NiF <sub>6</sub>	CoF <sub>3</sub>
340–360	5.5–6.0	7–9
240–260	6–7	8
150–160	3.5	6–7

Each product was examined by gas-liquid chromatography. The low yields from the potassium hexafluoronickelate(IV) fluorinations are disturbing since in all cases a higher degree of fluorination than that obtained with cobalt trifluoride was indicated. Some lowering of the yield would be expected if the benzene had been degraded to simple aliphatic fluorocarbons.

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