

FLUORINATION WITH COMPLEX METAL FLUORIDES
PART II.* THE FLUORINATION OF BENZENE,
TETRAHYDROFURAN AND CYCLOHEXANONE WITH SILVER
DIFLUORIDE AND POTASSIUM TETRAFLUOROARGENTATE(III)

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SUMMARY

Potassium tetrafluoroargentate(III) and silver difluoride have similar reactivities as fluorinating agents for benzene in the vapour phase. The products are mainly polyfluorocyclohexanes, together with some decafluorocyclohexene and traces of octafluorocyclohexa-1,4-diene. No polyfluoroaromatic species were found in the products. Fluorination of tetrahydrofuran and cyclohexanone gave breakdown products which showed no evidence of oxygen retention.

INTRODUCTION

Silver difluoride has been used as an exhaustive fluorinating agent for organic compounds in either the liquid² or the vapour³ phase.

Little has been published since these initial investigations, possibly due to a report⁴ that the silver difluoride formed a low-melting eutectic mixture with the monofluoride to which it is reduced by the organic compound. However, stirred reactors of a type previously described⁵ have been used in the current study and the reagent has been found to be a free-flowing powder at all times. Potassium tetrafluoroargentate(III) has not previously been used as a fluorinating agent.

RESULTS

Silver difluoride was initially prepared *in situ* in the reactor by the direct fluorination of silver oxide. Potassium tetrafluoroargentate(III) was prepared *in*

* For Part I, see ref. 1.

situ by the direct fluorination of a 2:1 mixture of potassium chloride and silver oxide, as previously described⁶. Fluorination of organic compounds results in the reduction of the tetrafluoroargentate(III) to the known potassium trifluoroargentate(II), identified by an X-ray powder photograph⁷. Both reagents were regenerated without trouble from their lower-valency reduced analogue and both were sufficiently reactive to attack the nickel body of the reactor. The silver difluoride was eventually found to have become contaminated with *ca.* 10% nickel difluoride whilst the potassium tetrafluoroargentate(III) contained a trace of potassium hexafluoronickelate(IV) (identified by its colour) at the conclusion of the fluorination studies.

The products obtained from small-scale fluorinations of benzene were separated by preparative-scale GLC in most cases but otherwise the product composition was determined by measuring retention times and peak areas of each component on the analytical GLC traces of the crude product mixture. The combined products from a series of large-scale fluorinations of benzene with silver difluoride were fractionally distilled. The fractions rich in one component were then separated by preparative GLC and the component identified by its infrared spectrum. The compositions of unseparated fractions were estimated by peak area measurement on the appropriate analytical GLC trace. The product compositions of the various fluorinations of benzene with either reagent are summarised in Table 1.

The contact time of the organic and inorganic reagents seems to have little effect on the composition of the products in view of the close agreement, both qualitative and quantitative, between the small-scale and large-scale silver difluoride fluorinations at 180–260°. This may be due to the considerable reactivity of the reagent, since work with lithium tetrafluorocobaltate(III), a milder fluorinating agent, has shown a marked dependence of the fluorination products on reactor geometry⁸.

The presence of decafluorocyclohexene and octafluorocyclohexa-1,4-diene in the products is unexpected. These could have originated from dehydrofluorination of undecafluorocyclohexane, followed by defluorination of decafluorocyclohexene, or by fluorination of hexafluorobenzene. The latter possibility is suggested by recent work which has shown that hexafluorobenzene may be isolated as a product from the fluorination of benzene with caesium tetrafluorocobaltate(III)⁹.

Fluorination of hexafluorobenzene at 250° gave only dodecafluorocyclohexane, irrespective of the reagent used. However, at 120°, potassium tetrafluoroargentate(III) gave a small amount of decafluorocyclohexene as well as the dodecafluorocyclohexane noted previously, while silver difluoride gave only a trace of dodecafluorocyclohexane plus decafluorocyclohexene and octafluorocyclohexa-1,4-diene. Fluorination of decafluorocyclohexene at 250° with either reagent gave dodecafluorocyclohexane. Potassium tetrafluoroargentate(III) at 250° gave dodecafluorocyclohexane as the product from the fluorination of undecafluorocyclo-

TABLE 1
PERCENTAGE PRODUCT COMPOSITION OF BENZENE FLUORINATIONS

Component	Silver difluoride		Potassium tetrafluoroargentate(III)		
	300-380° ^a	180-260°	220-260° ^b	100-160° ^a	100-160° ^a
Dodecafluorocyclohexane	47	trace	0.6	—	—
Decafluorocyclohexene	5	1	0.9	—	—
Octafluorocyclohexa-1,4-diene	—	trace	—	—	—
Undecafluorocyclohexane	27	13	17.4	trace	trace
1H/2H-Decafluorocyclohexane	3	8	6.6	—	2
1H/3H-Decafluorocyclohexane + 1H/4H-decafluorocyclohexane	5	13	15.1	—	3
1H,4H-Decafluorocyclohexane	2	trace	—	—	3
1H,4H/2H-Nonafluorocyclohexane	4	16	13.5	13	16
Benzene	3	2	4.7	50	5
Unresolved polyfluorocyclohexanes	4	46	41.2	37	29
					74
					8
					—
					10
					9
					8
					3
					16
					4
					2

^a Percentage composition estimated on peak area; components identified by GLC enrichment techniques.
^b 2 kg reactor (B).

hexane, together with some unconverted starting material. Silver difluoride under the same conditions gave only a 25% yield of dodecafluorocyclohexane, the remaining 75% of the product consisting of unreacted undecafluorocyclohexane.

In some early fluorination experiments with silver difluoride, it was claimed that hexafluoroacetone could be produced from acetone¹⁰. In order to investigate further the possibility of oxygen retention during fluorinations with silver reagents, some preliminary experiments were undertaken with tetrahydrofuran and cyclohexanone. With tetrahydrofuran, irrespective of the reagent employed and despite the use of low temperatures (*ca.* 100°), only small amounts of very volatile products (probably a mixture of polyfluorobutanes) were obtained. Some intractable polymeric material was also formed. Fluorination of cyclohexanone with either silver reagent gave reasonable yields of multicomponent mixtures of fluorohydrocarbons. There was no spectroscopic (infrared, mass spectrometry) evidence for the presence of fluoro-ketones, acid fluorides *etc.* in the products. In view of the complexity of the products in each case, and because of the lack of evidence for oxygen retention in them, no further investigations were made.

DISCUSSION

The products formed on fluorination of benzene may all be accounted for by the recently published cation-radical theory of high-valency metal fluoride fluorination¹¹. Indeed, the isolation of decafluorocyclohexene and octafluorocyclohexa-1,4-diene lends some support to the proposal in the cation-radical theory that a separate pathway to hexafluorobenzene may be operative, especially since they arise from the fluorination of hexafluorobenzene with silver difluoride. Whilst no octafluorocyclohexa-1,4-diene was isolated from fluorinations with potassium tetrafluoroargentate(III), the decafluorocyclohexene which is produced cannot have arisen from dehydrofluorination of undecafluorocyclohexane since this, under fluorination conditions in the reactor, is converted to dodecafluorocyclohexane.

Potassium tetrafluoroargentate(III) is marginally more reactive than silver difluoride as a fluorinating agent, almost certainly because of the higher oxidation state of silver in the complex. The two reagents are both slightly less reactive than the more commonly used cobalt trifluoride (higher temperatures are required to produce similar product compositions), but more reactive than potassium tetrafluorocobaltate(III). Indeed, it seems that the complex salts of a given transition metal atom are generally less reactive than the corresponding binary salts, even though the metal is in the same oxidation state. Thus potassium hexafluorocobaltate(III) does not fluorinate benzene¹² while potassium tetrafluorocobaltate(III) is a milder fluorinating agent than cobalt trifluoride. The situation is similar with the silver salts, where silver difluoride is an effective fluorinating agent while potassium trifluoroargentate(II) [the product formed when organic material is

fluorinated by potassium tetrafluoroargentate(III)] does not fluorinate benzene. There is as yet no satisfactory explanation of these observations.

EXPERIMENTAL

Gas-liquid chromatography

Crude fluorination products and separated components were examined by analytical GLC using a glass column, 0.4 cm diam. \times 1.83 m, packed with diisodecyl phthalate on Chromosorb P in a 1:2 ratio (Unit I). The column was maintained at 75° and the nitrogen flow rate was 1 l h^{-1} .

Preparative-scale GLC was used to separate some of the crude fluorination products and some of the fractions from the distillations. Two columns were used in this case: Unit II consisted of a copper tube, 35 mm diam. \times 4.88 m, packed with dinonyl phthalate on Chromosorb P in a 1:2 ratio and Unit III consisted of a copper tube, 75 mm diam. \times 4.88 m, packed with dinonyl phthalate on Chromosorb P in a 1:2 ratio. Both tubes were used at 95° with nitrogen flow rates of 15 l h^{-1} and 60 l h^{-1} respectively. Separated components were collected in traps cooled in liquid air.

Infrared spectra

Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrometer and compared with the spectra of authentic samples¹³.

Fluorination apparatus

Small-scale fluorinations were undertaken in a stirred nickel reactor (Reactor A) of a type previously described⁵, length 45.7 cm, internal diameter 5.7 cm, holding *ca.* 200 g of either silver difluoride or potassium tetrafluoroargentate(III). The 2 kg reactor (Reactor B) used in the large-scale silver difluoride fluorinations was 1.22 m long and had an internal diameter of 7.6 cm.

Small-scale fluorinations

Aliquots of benzene (5.0 ml, 4.4 g) were dripped into Reactor A following the standard procedure⁵, with a carrier gas flow of nitrogen (*ca.* 1 l h^{-1}). The input time for the aliquot varied between 5 and 30 min but did not significantly affect the character of the products, as shown by analytical GLC (Unit I). After all the aliquot had been dripped into the reactor, the system was purged with nitrogen for a further 0.5 h. The products were collected in a glass trap cooled in liquid air. After allowing the trap and contents to warm up to room temperature, the products were washed with water. The inorganic reagents were regenerated by passage of fluorine through the reactor, followed by purging with nitrogen. The average recoveries from fluorinations of the aliquots with both reagents are shown in Table 2.

TABLE 2

AVERAGE RECOVERIES (g) FROM FLUORINATION OF BENZENE ALIQUOTS

Fluorinating agent	Temperature range (°C)		
	100-160	180-260	300-380
KAgF ₄	6.5	9.6	8.9
AgF ₂	4.4	8.1	5.4

Large-scale fluorinations

Aliquots of benzene (50 ml, 44 g) were dripped into Reactor B over periods varying between 40 and 90 min. After all the aliquot had passed into the reactor, a purging stream of nitrogen (*ca.* 10 l h⁻¹) was passed through the reactor for 2 h. The products were collected in a copper trap cooled with crushed solid carbon dioxide. After the nitrogen purge, the trap was disconnected from the reactor and allowed to warm up to room temperature when the products were washed with water, separated from the aqueous layer and stored in the refrigerator. The reagent was regenerated by passage of fluorine through the reactor followed by a purging stream of nitrogen.

The products from 15 such fluorinations (1243 g) were combined and 100 ml of ether were added in order to separate the dodecafluorocyclohexane in the product mixture as the azeotrope. The combined distillation mixture was dried (magnesium sulphate) and then distilled from a small amount of phosphorus pentoxide. Fifteen fractions were collected and their boiling ranges, weights and the components present in them are recorded in Table 3.

TABLE 3

THE SEPARATION OF THE PRODUCT OF THE FLUORINATION OF BENZENE WITH SILVER DIFLUORIDE

Fraction No.	Boiling range (°C)	Weight (g)	Component ^b									
			(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	
1	26-30	14.8 ^a	+									
2	30-34	38.4 ^a		+								
3	34-57	6.3 ^a			+	+						
4	57-60	33.7			+	+						
5	60	120.1			+	+						
6	60-67	80.5			+	+	+					
7	67-73	50.1				+	+	+				
8	73-76	34.8					+		+			+
9	76-78	45.7					+		+	+		+
10	78-88	102.8							+	+		+
11	88-98	144.1								+		+
12	98-103	49.3								+	+	+

(continued)

TABLE 3 (continued)

Fraction No.	Boiling range (°C)	Weight (g)	Component ^b									
			(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	
13	103–114	97.4									+	+
14	114–117	23.6										+
15 ^c	>117	74.1										+

^a Contains ether, weight not included in fraction weight.

^b Component (I), dodecafluorocyclohexane; (II), decafluorocyclohexene; (III), undecafluorocyclohexane; (IV), benzene; (V), 1*H*/2*H*-decafluorocyclohexane; (VI), 1*H*/3*H*- and 1*H*/4*H*-decafluorocyclohexane; (VII), 1*H*,4*H*/2*H*-nonafluorocyclohexane; (VIII), 1*H*,2*H*/4*H*-nonafluorocyclohexane and (IX), a mixture of unidentified polyfluorocyclohexanes.

^c Fraction No. 15 consisted of the pot residue.

Fluorination of hexafluorobenzene, decafluorocyclohexene and undecafluorocyclohexane

Aliquots of hexafluorobenzene (6.0 g), decafluorocyclohexene (6.5 g) and undecafluorocyclohexane (5.0 g) were fluorinated in Reactor A in the usual manner. (Undecafluorocyclohexane was sublimed into the reactor in a current of nitrogen (1 l h⁻¹)). The composition of the product mixtures was determined either by preparative-scale GLC separation (Unit II) or by GLC enrichment techniques coupled with peak area estimation on an analytical GLC trace (Unit I) of the crude product. The results are summarised in Table 4.

TABLE 4

RESULTS OF THE FLUORINATION OF HEXAFLUOROBENZENE, DECAFLUOROCYCLOHEXENE AND UNDECAFLUOROCYCLOHEXANE

Compound	Reagent	Temp. (°C)	Average yield (g)	Composition (%)			
				C ₆ F ₁₂	C ₆ F ₁₁ H	C ₆ F ₁₀	1,4-C ₆ F ₈
C ₆ F ₆	KAgF ₄	250	5.9	100	—	—	—
C ₆ F ₆	KAgF ₄	120	6.0	80	—	20	—
C ₆ F ₆	AgF ₂	250	5.5	100	—	—	—
C ₆ F ₆	AgF ₂	120	5.2	3	—	57	40
C ₆ F ₁₀	KAgF ₄	250	3.8	100	—	—	—
C ₆ F ₁₀	AgF ₂	250	3.3	100	—	—	—
C ₆ F ₁₁ H	KAgF ₄	250	2.0	56	44	—	—
C ₆ F ₁₁ H	AgF ₂	250	3.6	25	75	—	—

Fluorination of tetrahydrofuran and cyclohexanone

Aliquots of tetrahydrofuran (10 ml) and cyclohexanone (6 ml) were fluorinated at temperatures of 90–220° over silver difluoride and potassium tetrafluoroargentate(III) in the usual manner except that the products were passed

through a NaF/HF scrubber before condensing in the collection vessel. With tetrahydrofuran, the liquid product (0–0.2 g) always contained lumps of brown polymeric material. Cyclohexanone gave good recoveries (6–7 g) of a volatile liquid, which was shown by analytical GLC (Unit I), infrared spectroscopy and mass spectrometry to be a multicomponent mixture of hydrofluorocarbons.

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