Fluorination with Complex Metal Fluorides. Part I. Fluorinations of Benzene, Fluorobenzene, and *p*-Difluorobenzene with a Potassium Cobaltifluoride Complex

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Benzene, fluorobenzene, and *p*-difluorobenzene have been fluorinated in the vapour phase with a potassium cobaltifluoride complex to yield a number of known and new fluorocyclohexenes which have been fully characterised.

The fluorination of hydrocarbons in the vapour phase by transition-metal fluorides is well known.[1] Cobaltic fluoride has been used most frequently to give products which are mixtures of saturated fluoro- or fluorohydrocarbons, and in most cases olefins occur only as minor constituents. The present investigation stems from our earlier work [1,2] on cobaltic fluoride and is concerned with the use of a complex cobaltifluoride as the fluorinating agent. There are few reports [3] of the use of complex metal fluorides for this purpose, and a potassium cobaltifluoride complex was chosen initially to compare its fluorinating ability with that of the parent cobaltic fluoride. The reagent was prepared by treatment of potassium trifluorocobaltate with elemental fluorine in a conventional stirred-bed apparatus.[1] The structure of the reagent is being investigated;[4] it is probably potassium tetrafluorocobaltate.[5]

Benzene was fluorinated as previously described for cobaltic fluoride.[2] After each fluorination of hydrocarbon the reagent was regenerated by treatment with elemental fluorine. The products from a number of runs were combined and partially separated by fractional distillation into six fractions as shown in the Table.

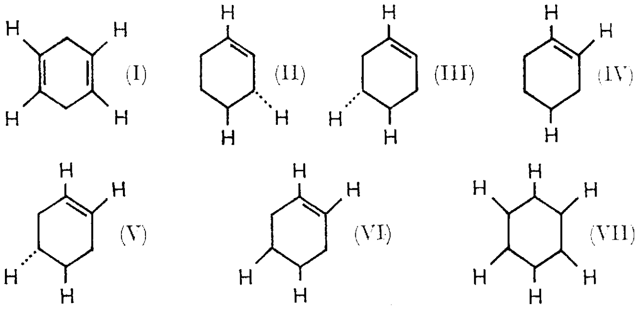
Fraction	B.p. range	Yield (g.)	Composition
(1)	44—86	160	Benzene + perfluorocyclohexane and -hexene
(2)	88—99	33	(I) + (II)
(3)	100—110	83	(II) + (III) + (IV)
(4)	110—120	33	(IV) + (V)
(5)	120—126	171	(V) + (VI)
(6)	140—175	95	(V) + (VI) + (VII)

Overall yields (approx.). Compound (I) (8%), (II) (8%), (III) (6%), (IV) (12%), (V) (35%), (VI) (5%), and (VII) (0·5%)

Each fraction was then separated into its components by preparative gas chromatography.

The lowest-boiling fraction was shown to be a complex mixture containing benzene and traces of dodecafluorocyclohexane and decafluorocyclohexene and was not further investigated.

The second fraction was separated into two major components and a trace of an unidentified olefin. The first component (I) had an analysis which corresponded to the molecular formula $C_6H_4F_4$ and mass spectrometry indicated a molecular ion at 152. There was no significant u.v. spectrum and the i.r. spectrum showed weak signals in the region 1700—1800 $cm.^{-1}$ characteristic of HC=CH, and a C–H stretching band at 3100 $cm.^{-1}$ indicative of vinylic hydrogen atoms. The ^1H n.m.r. spectrum was deceptively simple, being a quintuplet (J 2·3 Hz) at τ 4·25 ($SiMe_4$ by substitution). The ^{19}F n.m.r. spectrum was a strikingly similar quintuplet at 91·6 p.p.m. (relative to CF_3CO_2H) (J 2·3 Hz). Oxidation of (I) by potassium permanganate in acetone [6] afforded an acid isolated as di-anilinium and bis-*S*-benzylthiuronium salts identical to authentic samples of the salts derived from difluoromalonic acid; no other



All unmarked bonds are fluorine

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[2] A. K. Barbour, H. D. Mackenzie, M. Stacey, and J. C. Tatlow, *J. Appl. Chem.*, 1954, 347; R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1963, 281.

[3] W. Klemm, G.P. 813,847/1951. B. Cornils, M. Rasch, and G. Schiemann, *Chem.-Ztg.*, 1968, **92** (5), 137.

[4] A. J. Edwards, R. G. Plevey, and M. Steward, unpublished results.

[5] R. D. Peacock, personal communication.

[6] J. Burdon and J. C. Tatlow, *J. Appl. Chem.*, 1958, **8**, 293.

acid could be detected. The aforegoing results indicate component (I) to be 3,3,6,6-tetrafluorocyclohexa-1,4-diene.

The second component (II) had an analysis which was consistent with the molecular formula $C_6H_3F_7$ and showed a molecular-ion peak at 208 in its mass spectrum. The u.v. spectrum showed no significant absorption whilst the i.r. spectrum showed strong bands at 1715 (CF=CH)[7] 2980 (C–H) and 3100 cm.$^{-1}$ (=CH–). The ^{19}F n.m.r. spectrum showed five groups of peaks in the ratio 2 : 2 : 1 : 1 : 1. The ^{1}H n.m.r. spectrum was complex but was not inconsistent with the proposed structure. Oxidation of (II) with potassium permanganate in acetone afforded an acid, the bis-*S*-benzyl thiuronium salt of which was identical to that from DL-*threo*-2*H*,3*H*-hexafluoroadipic acid[8] and not identical to the *erythro*-salt.

Fluorination of (II) as previously described[9] at 85° afforded mainly 1*H*,4*H*/2*H*-nonafluorocyclohexane.[8] Dehydrofluorination of (II) with aqueous potassium hydroxide afforded 1*H*,4*H*-hexafluorocyclohexa-1,3-diene[10] and pentafluorobenzene. The above evidence all indicates (II) to be 1*H* : 3*H*/4*H*-heptafluorocyclohexene.

Separation of the third fraction afforded three compounds, a further quantity of (II), 1*H* : 4*H*/5*H*-heptafluorocyclohexene (III)[8] and 1*H*,2*H*,4*H*-heptafluorocyclohexene (IV)[11] all identified by a comparison of their i.r. spectra.

Similarly, the fourth fraction gave a further quantity of (IV) and 1*H*,2*H* : 4*H*/5*H*-hexafluorocyclohexene (V)[12] identified by their i.r. spectra.

The fifth fraction consisted of two components, compound (V) and another compound the analysis for which was also consistent with the molecular formula $C_6H_4F_6$ and which showed a parent-ion peak at 180. The i.r. spectrum showed bands at 3090 (=C–H), 2930 (C–H), and 1675 cm.$^{-1}$ (CH=CH). The ^{19}F n.m.r. spectrum showed three groups of peaks in the ratio 1 : 1 : 1, two groups being part of an AB system due to CF_2 groups and the third due to CHF groups. Oxidation of (VI) with potassium permanganate afforded an acid isolated as di-anilinium and bis-*S*-benzyl thiuronium salts identical to authentic samples of the salts derived from *meso*-3*H*,4*H*-hexafluoroadipic acid.[11] Dehydrofluorination of (VI) gave 1*H*,2*H*,4*H*-pentafluorocyclohexa-1,4-diene.[13] These data clearly indicate compound (VI) to be a stereoisomer of (V) namely 1*H*,2*H* : 4*H*,5*H*/-hexafluorocyclohexene. Defluorination of a mixture of (V) and (VI) gave the expected fluorobenzenes.

When set aside, fraction 6 gave a crystalline solid, (VII), which was filtered off, and a residual filtrate rich in (VI). Analysis of (VII) indicated that it had an empirical formula corresponding to $C_6H_6F_6$. The mass spectrum of (VII) gave a parent ion at 192 and a cracking pattern which indicated the presence of CHF groups only. The ^{1}H and ^{19}F n.m.r. spectra also indicated that only CHF groups were present. The compound was resistant to oxidation and could not be dehydrofluorinated under a variety of conditions. These facts suggest that compound (VII) is a 1,2,3,4,5,6-hexafluorocyclohexane very probably with the all-*trans*-1*H*,3*H*,5*H*/2*H*,4*H*,6*H*-structure.

The above results clearly show that fluorination of benzene with the potassium cobaltifluoride complex gives products significantly different from the polyfluorocyclohexanes obtained with cobaltic fluoride. The mixture is much simpler and the products are nearly all unsaturated. Further, there is a marked preponderance of 1*H*,2*H*,4*H*,5*H*-hexafluorocyclohexenes (35—50% of the mixture). This could be important since these two compounds represent a good source of 1,2,3,4-tetrafluorobenzene.

A proposed addition–elimination mechanism[1] for fluorination with high-valency metal fluorides, which accounts for the specific orientation of residual hydrogen atoms within the isolated fluorocyclohexanes, postulates that compounds (I)—(VI) are intermediates in this reaction. Recently compound (I) has been detected in trace quantities among the products of cobaltic fluoride[14] and ceric fluoride[10] reactions.

Two other proposed intermediates in this mechanism were fluorobenzene and *p*-difluorobenzene, both of which are present in trace amounts among the products from the cobaltic fluoride reaction.

Fluorinations of fluorobenzene and *p*-difluorobenzene with the potassium cobaltifluoride complex were therefore carried out; the products showed analytical g.l.c. traces which were almost identical to that from benzene.

Separation of an aliquot from each fluorination afforded compounds (I)—(VI) in similar amounts to those obtained in the fluorination of benzene; compound (VII) was not detected.

The results would suggest therefore that the proposed mechanism in which fluorobenzene, *p*-difluorobenzene, and 3,3,6,6-tetrafluorocyclohexa-1,4-diene are intermediates is plausible. Further, this potassium cobaltifluoride shows considerable promise as a milder and more selective fluorinating agent than cobaltic fluoride and further results obtained from the fluorination of other organic compounds will be reported later.

EXPERIMENTAL

Apparatus.—Fluorinations were carried out in horizontal stirred-bed reactors as previously described.[1] Preparative g.l.c. utilised columns (488 × 7·5 cm.) packed with dinonyl

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[7] J. Burdon and D. H. Whiffen, *Spectrochim. Acta*, 1958, **12**, 139.

[8] J. A. Godsell, M. Stacey, and J. C. Tatlow, *Tetrahedron*, 1958, **2**, 193.

[9] D. E. M. Evans, J. A. Godwell, R. Stephens, J. C. Tatlow, and E. H. Wiseman, *Tetrahedron*, 1958, **2**, 183.

[10] A. Hudson and A. E. Pedler, unpublished results.

[11] R. Stephens, J. C. Tatlow, and E. H. Wiseman, *J. Chem. Soc.*, 1959, 148.

[12] E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1959, 159.

[13] E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1960, 3800.

[14] B. M. Potts and A. E. Pedler, unpublished results.

phthalate–Kieselguhr (1 : 2) (unit A) or silicone elastomer 301–Kieselguhr (1 : 6) (unit B) and columns (488 × 3·0 cm.) packed with Kel-F oil K.F.3–Kieselguhr (1 : 4) (unit C), or dinonyl phthalate–Kieselguhr (1 : 2) (unit D).

Preparation of the Complex.—Solutions of potassium fluoride dihydrate (56·4 g.) in water (100 ml.) and cobaltous chloride (25·9 g.) in water (100 ml.) were heated to 100°, then slowly mixed and further heated at 100° for 15 min. The precipitate of potassium trifluorocobaltate (28 g.) was filtered off and washed with ethanol. The trifluorocobaltate was fluorinated at 280° until no more fluorine was absorbed to give a new complex, probably potassium tetrafluorocobaltate.[5] This is formed reproducibly and is regenerated by reaction with fluorine after the fluorination of organic compounds. The structure has not, as yet, been precisely determined.

Fluorination of Benzene.—Benzene (53 g.) was passed during 2·5 hr. over a stirred bed of the complex cobaltifluoride (2 kg.) at 280°.[1] The product (92 g.) was flushed from the reactor with nitrogen (25 l./hr.) and collected in a nickel trap cooled in solid carbon dioxide. In subsequent fluorinations the yields varied in the range 85—95 g. The product (590 g.) from several runs was dried over phosphoric oxide and fractionally distilled through a vacuum-jacketed column (122 × 2·5 cm.) packed with Dixon gauze rings to yield six fractions as shown in the Table.

Separation and Characterisation of Fractions.—*Fraction* (1). This was shown to be a complex mixture of many components amongst which were identified benzene and small amounts of dodecafluorocyclohexane and decafluorocyclohexene by analytical g.l.c. and i.r. spectroscopy.

Fraction (2). A portion (22·7 g.) was separated (unit A, 100°, N_2, 30 l./hr.) into 2(i) a complex mixture (6·6 g.) similar to fraction (1), 2(ii) a mixture (3·3 g.), and 2(iii) (0·4 g.) shown to be pure 1H : 3H/4H-*heptafluorocyclohexene* (II), b.p. 100° (Found: C, 34·5; H, 1·6. $C_6H_3F_7$ requires C, 34·6; H, 1·5%), *M* (mass spec.), 208, $\nu_{max.}$ 1715 (CF=CH–), 2980 (C–H), and 3100 cm.$^{-1}$ ($=\overset{|}{C}-H$).

Oxidation of (II) (0·5 g.) with potassium permanganate (1·3 g.) in acetone (60 ml.) at 15° afforded on working up as previously described [6] bis-(*S*-benzylthiuronium) DL-*threo*-2*H*,3*H*-hexafluoroadipate (0·4 g.), m.p. 229° (lit.,[8] m.p. 225°) (Found: C, 45·4; H, 4·5. Calc. for $C_{22}H_{24}F_6N_4O_4S_2$: C, 45·1; H, 4·1%).

Fluorination of (II) (1·1 g.) over cobaltic fluoride (130 g.) at 85° afforded, after separation (unit D, 100°, N_2 18 l./hr.), mainly 1*H*,4*H*/2*H*-nonafluorocyclohexane [8] (0·4 g.), m.p. 43° identified by i.r. spectroscopy.

Treatment of (II) (15·3 g.) with potassium hydroxide (15·0 g.) in water (30 ml.) at 100° for 3 hr. afforded a mixture (10·2 g.) which on separation (unit D, 100°, N_2 20 l./hr.) gave 1*H*,4*H*-hexafluorocyclohexa-1,3-diene (1·8 g.) [10] and pentafluorobenzene (3·5 g.) with i.r. spectra identical to those of authentic samples.

Subfraction 2(ii) was further purified (unit C, 70°, N_2 15 l./hr.) to remove a trace of an unidentified compound to yield 3,3,6,6-*tetrafluorocyclohexa*-1,4-*diene* (I) (3·0 g.), b.p. 100° (Found: C, 47·3; H, 2·7; F, 49·9. $C_6H_4F_4$ requires C, 47·4; H, 2·6; F, 50·0%), *M* (mass spec.), 152, $\nu_{max.}$ 1700—1800 (CH=CH–) and 3100 cm.$^{-1}$ ($=\overset{|}{C}-H$). ^{1}H N.m.r. showed a quintuplet at τ 4·25 (*J* 2·3 Hz) and ^{19}F n.m.r. showed a quintuplet at 91·6 p.p m. (*J* 2·3 Hz).

Oxidation of (I) (0·3 g.) with potassium permanganate (1·0 g.) in acetone (50 ml.) for 3 hr. at 56° afforded as above [6] di-anilinium difluoromalonate (0·4 g.), m.p. 159—160° and bis-(*S*-benzylthiuronium)difluoromalonate, m.p. 183—184°, identified by i.r. spectroscopy.

Fraction (3). Separation of fraction (3) (9·5 g.) (unit A, 102°, N_2 46 l./hr.) gave 3(i) 1*H* : 3*H*/4*H*-heptafluorocyclohexene (II) (1·9 g.), 3(ii) 1*H* : 4*H*/5*H*-heptafluorocyclohexene (III) (1·8 g.), b.p. 105° (lit.,[8] b.p. 104°) and 3(iii) 1*H*,2*H*,4*H*-heptafluorocyclohexene (IV) (2·4 g.), b.p. 107° (lit.,[11] b.p. 106°) identified by i.r. spectroscopy.

Fraction (4). Separation of fraction (4) (6·0 g.) (unit A, 102°, N_2 46 l./hr.) gave 4(i) 1*H*,2*H*,4*H*-heptafluorocyclohexene (IV) (2·9 g.) and 4(ii) 1*H*,2*H* : 4*H*/5*H*-hexafluorocyclohexene (V) (2·0 g.) identified by i.r. spectroscopy.

Fraction (5). Separation of fraction (5) (10·1 g.) (unit A, 90°, N_2 55 l./hr.) gave 5(i) 1*H*,2*H* : 4*H*/5*H*-hexafluorocyclohexene (V) (6·0 g.), b.p. 120—121° (lit.,[13] b.p. 121—122°) with an i.r. spectrum identical with that of an authentic sample and 5(ii) 1*H*,2*H* : 4*H*,5*H*/-hexafluorocyclohexene (VI) (0·5 g.) b.p. 127° (Found: C, 38·0; H, 2·1. $C_6H_4F_6$ requires C, 37·9; H, 2·0%), *M* (mass spec.), 180, $\nu_{max.}$ 1675vw (–HC=CH–), 2930 (C–H), and 3090 cm.$^{-1}$ (=C–H).

Oxidation of (VI) (0·5 g.) with potassium permanganate (1·0 g.) in acetone (50 ml.) at 56° for 15 min. afforded di-anilinium-*meso*-3*H*,4*H*-hexafluoroadipate (0·33 g.), m.p. 201° (lit.,[11] m.p. 201°) and bis-(*S*-benzylthiuronium)-*meso*-3*H*,4*H*-hexafluoroadipate, m.p. 228—229° (lit.,[11] m.p. 228°). A m.p. depression was observed on admixture with the corresponding salts of DL-3*H*,4*H*-hexafluoroadipic acid.

Dehydrofluorination of (VI) (3·0 g.) with potassium hydroxide (3·0 g.) in water (6 ml.) at 100° for 2 hr. afforded after separation (unit D, 90° N_2 15 l./hr.) 1*H*,2*H*,4*H*-pentafluorocyclohexa-1,4-diene (0·9 g.) and unchanged (VI) (0·8 g.) identified by i.r. spectroscopy.

Fraction (6). When set aside fraction (6) afforded a precipitate of needle-like crystals (2·4 g.) shown to be a 1,2,3,4,5,6-*hexafluorocyclohexane* (VII), m.p. 123—124° (sealed tube) (Found: C, 37·2; H, 2·8. $C_6H_6F_6$ requires C, 37·5; H, 3·1%), *M* (mass spec.), 192, $\nu_{max.}$ 2920 cm.$^{-1}$ (C–H). The filtrate was mainly (VI) with some (V) identified by analytical g.l.c.

Defluorination of (V) *and* (VI).—Defluorination by pyrolysis at 380° over iron gauze of fraction (5) (4·5 g.) afforded after separation (unit C, 55° N_2 15 l./hr.) *p*-difluorobenzene (1·5 g.) and 1,2,4-trifluorobenzene (1·0 g.) identified by i.r. spectroscopy.

Fluorination of Fluorobenzene.—Fluorobenzene (30 ml.) was passed over the potassium cobaltifluoride complex (2 kg.) at 275° during 1 hr. The product (60·3 g.) was worked up as described above. Separation (unit B, 90° N_2 50 l./hr.) of a portion (16·7 g.) of the mixture gave (i) a mixture (0·33 g.), (ii) a second mixture (1·1 g.) further purified (unit C, 70° N_2 15 l./hr.) to give 3,3,6,6-tetrafluorocyclohexa-1,4-diene (I) (0·8 g.), (iii) 1*H* : 3*H*/4*H*-heptafluorocyclohexene (II) (0·6 g.), (iv) a mixture (0·5 g.) of fluorobenzene and mainly 1*H* : 4*H*/5*H*-heptafluorocyclohexene (III), (v) 1*H*,2*H*,4*H*-heptafluorocyclohexene (IV) (0·7 g.), (vi) 1*H*,2*H* : 4*H*/5*H*-hexafluorocyclohexene (V) (4·2 g.), and (vii) 1*H*,2*H* : 4*H*,5*H*/-hexafluorocyclohexene (VI) (0·4 g.), all with i.r. spectra identical to those of authentic samples.

Fluorination of p-*Difluorobenzene.*—The difluorobenzene (10 ml.) was passed over the potassium cobaltifluoride complex (130 g.) at 275° during 1 hr. The product (8·2 g.) was separated (unit D, 100° N_2 22 l./hr.) to give (i) a mixture

(0·5 g.), (ii) 3,3,6,6-tetrafluorocyclohexa-1,4-diene (I) (0·4 g.), (iii) 1*H*,3*H*/4*H*-heptafluorocyclohexene (II) (0·5 g.), (iv) a mixture (0·3 g.) of *p*-difluorobenzene and mainly 1*H*,4*H*/-5*H*-heptafluorocyclohexene (III), (v) 1*H*,2*H*,4*H*-heptafluorocyclohexene (IV) (0·7 g.), (vi) 1*H*,2*H* : 4*H*/5*H*-hexafluorocyclohexene (V) (2·3 g.), and (vii) 1*H*,2*H* : 4*H*,5*H*/-hexafluorocyclohexene (VI) (0·5 g.). All components were identified by i.r. spectroscopy.

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