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POLYFLUOROCYCLOALKENES—VII[1]

FLUORINATION OF AROMATIC POLYFLUORO-COMPOUNDS BY COBALTIC FLUORIDE

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Abstract—Cobaltic fluoride fluorination in the vapour phase of a series of polyfluoroaromatic compounds has given polyfluoro cycloalkenes in many cases and negligible amounts of fragmentation products in all cases. The reaction provides a useful route to some otherwise difficultly accessible polyfluoro-olefins.

Vapour-phase fluorination of aromatic hydrocarbons with cobaltic fluoride gives almost exclusively the saturated polyfluoro-carbons,[2] e.g., benzene, toluene, benzotrifluoride, naphthalene, *o*-, *m*- and *p*-xylene, all give negligible amounts of unsaturated products. However, we have now shown that, under comparable conditions polyfluoro aromatics often give almost exclusively polyfluoro-olefins, in agreement with the anticipated electrophilic character of cobaltic fluoride. The degree of fluorination attained, however, increased with increase in temperature; but the value of the process lies in the formation of polyfluoro-olefins which are otherwise difficult to prepare.

A range of aromatic polyfluoro compounds was examined as set out in the Table; some fluorinations were carried out at various temperatures but no attempt was made to establish the optimum conditions for the formation of the various olefins obtained.

Benzene and *p*-xylene were fluorinated in the same reaction vessel and both gave complex mixtures similar to those obtained in the earlier work.[2] Hexafluorobenzene and cobaltic fluoride at 100° gave dodecafluorocyclohexane (8†), decafluorocyclohexene (90) and octafluorocyclohexa-1,4-diene (2). Pentafluorobenzene gave 1H-undecafluorocyclohexane (28), 1H-, 3H- and 4H-nonafluorocyclohexene (53, 8 and 11, respectively). 1,2,3,4-Tetrafluorobenzene gave 1H-undecafluorocyclohexane (5), 1H-nonafluorocyclohexene (5), 1H/2H- and 1H,2H/-decafluorocyclohexane (7 and 5, respectively) and 1H,2H-octafluorocyclohexene (77). 1,2,3,5-Tetrafluorobenzene gave undecafluorocyclohexane (8), 1H-nonafluorocyclohexene (5), 1H/3H- and 1H,3H/-decafluorocyclohexane (44 and 10, respectively) and 1H,5H- and 1H,3H-octafluorocyclohexene (17 and 15, respectively). 1,2,4,5-Tetrafluorobenzene gave 1H/4H-decafluorocyclohexane (28) and 1H,4H-octafluorocyclohexene (70). Octafluorotoluene and cobaltic fluoride at 80°

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† These figures are the approx. percentages of the total product.

[1] Part VI, G. Camaggi and R. Stephens, *Tetrahedron*, 1189 (1966).

[2] M. Stacey and J. C. Tatlow in *Advances in Fluorine Chemistry* (Edited by M. Stacey, J. C. Tatlow, and A. G. Sharpe) p. 176. Butterworths, London (1960).

gave 1-trifluoromethylnonafluorocyclohexene (82), 1-trifluoromethylheptafluorocyclohexa-1,4-diene (15) and 1- or 2-trifluoromethylheptafluorocyclohexa-1,3-diene (2). Decaflouro-*p*-xylene was fluorinated at 110° to give 1,4-bis(trifluoromethyl)-octafluorocyclohexene (30) and 1,4-bis(trifluoromethyl)hexafluorocyclohexa-1,4- and -1,3-diene (45 and 25, respectively).

1,4-Bis(trifluoromethyl)hexafluorocyclohexa-1,4- and -1,3-diene were characterized by elemental analysis, mass spectrometry and IR, ^{19}F NMR and UV spectroscopy. Both were readily defluorinated by iron gauze at 340° to give decafluoro-*p*-xylene.

Decafluoro-*o*-xylene and cobaltic fluoride at 120° gave 1,2-bis(trifluoromethyl)-octafluorocyclohexene (80) and 1,2-bis(trifluoromethyl)hexafluorocyclohexa-1,4-diene (17). Both compounds were characterized by elemental analysis, mass spectrometry and IR and ^{19}F NMR spectroscopy.

When the latter olefins were passed over iron gauze at 340° each gave decafluoro-*o*-xylene as the sole product.

Decafluoro-*m*-xylene and cobaltic fluoride at 100° gave a liquid product which displayed absorptions characteristic of fluorinated double bonds, but the monoene and diene components were inseparable mixtures of 1,3- and 1,5-bis(trifluoromethyl)-octafluorocyclohexene (84) and 1,3-bis(trifluoromethyl)hexafluorocyclohexadienes (14), respectively.

Octafluoronaphthalene and cobaltic fluoride at 160° gave hexadecafluorobicyclo-(4.4.0)-dec-1-ene (98) and *cis*- and *trans*-octadecafluorodecalin (2). The former olefin was characterized by elemental analysis, mass spectrometry and ^{19}F NMR spectroscopy; its IR spectrum was transparent between 4000 and 1460 cm^{-1} but the presence of unsaturation was confirmed by its rapid reaction with potassium permanganate in acetone.

Pentafluorobromobenzene and cobaltic fluoride at 100° gave trace amounts of dodecafluorocyclohexane and decafluorocyclohexene, undecafluorocyclohexyl bromide (74) and an inseparable mixture of bromononafluorocyclohexenes (25) (IR spectroscopy indicated the presence of the known[3] 1-bromo isomer). Pentafluorotoluene under identical conditions gave methyl undecafluorocyclohexane (10), 1-methylnonafluorocyclohexene (26), fluoromethylundecafluorocyclohexane (26), and 1-(difluoromethyl)nonafluorocyclohexene (29). The last named was characterized by elemental analysis, mass spectrometry, IR, ^{1}H NMR and ^{19}F NMR spectroscopy.

Pentafluoroanisole and cobaltic fluoride at 117° gave an entirely saturated product of essentially the same composition as that obtained in the analogous fluorination of 1-methoxy-nonafluorocyclohexene;[4] *viz.*, trifluoromethyl-, difluoromethyl-, fluoromethyl- and methyl-undecafluorocyclohexyl ether (4, 36, 54 and 4, respectively). The absence of 1-methoxynonafluorocyclohexene cannot be explained at present.

In all cases where fluorinations were carried out at various temperatures it was found that the degree of fluorination was increased by increase of temperature, e.g., octafluorotoluene at 150° gave perfluoromethylcyclohexane (5) and 1-trifluoromethylnonafluorocyclohexene (95); pentafluoroanisole at 235° gave trifluoromethyl-, difluoromethyl- and fluoromethyl-undecafluorocyclohexyl ether (41, 54 and 4, respectively).

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[3] S. F. Campbell and R. Stephens, *J. Chem. Soc.* 7367 (1965).

[4] A. B. Clayton, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 7370 (1965).

COBALTIC FLUORIDE FLUORINATIONS

Compound	(g)	Temp	Duration of addition	Duration of N_2 purge (25 l./hr)	Total product (g)
Benzene	(5·6)	100°	10 min	45 min	11·7
Hexafluorobenzene	(6·0)	100	10	45	6·4
Pentafluorobenzene	(5·1)	100	10	60	5·8
1,2,3,4-Tetrafluorobenzene	(5·4)	100	10	45	6·3
1,2,3,5-Tetrafluorobenzene	(5·3)	100	10	45	6·8
1,2,4,5-Tetrafluorobenzene	(3·1)	100	10	60	3·3
Octafluorotoluene	(4·8)	80	10	45	5·3
Octafluorotoluene	(5·2)	100	11	45	5·7
Octafluorotoluene	(5·2)	150	15	45	5·6
p-Xylene	(5·8)	150	10	45	11·9
Decafluoro-*p*-xylene	(11·4)	110	20	60	11·5
Decafluoro-*p*-xylene	(6·9)	120	10	45	6·9
Decafluoro-*p*-xylene	(5·7)	150	10	45	5·5
Decafluoro-*o*-xylene	(6·5)	90	10	120	6·6
Decafluoro-*o*-xylene	(10·1)	115	15	60	10·8
Decafluoro-*o*-xylene	(5·1)	120	6	45	5·1
Decafluoro-*o*-xylene	(9·1)	130	15	45	9·8
Decafluoro-*m*-xylene	(5·0)	100	5	60	5·0
Decafluoro-*m*-xylene	(7·8)	100	15	60	8·2
Decafluoro-*m*-xylene	(5·3)	115	10	45	5·4
Octafluoronaphthalene	(5·0)	160	15	45	4·6
Octafluoronaphthalene	(2·7)	160	10	45	3·2
Pentafluorobromobenzene	(6·5)	100	8	120	7·5
Pentafluorobromobenzene	(5·3)	130	5	45	5·8
Pentafluorotoluene	(5·2)	100	10	60	6·1
Pentafluorotoluene	(5·4)	150	10	120	6·3
Pentafluoroanisole	(5·4)	100	15	45	2·7
Pentafluoroanisole	(4·9)	110	15	45	6·2
Pentafluoroanisole	(5·3)	117	15	60	5·0
Pentafluoroanisole	(4·9)	125	15	35	5·8
Pentafluoroanisole	(5·1)	235	10	90	5·9

EXPERIMENTAL

Techniques. Analytical gas chromatography was carried out, except as otherwise stated, using columns 2 m × 4 mm diam. packed with dinonyl phthalate–kieselguhr (1:2) used at 100° and N_2 flow-rate ca. 1 l./hr. For preparative work a column 488 cm × 35 mm (Column A) and one 488 cm × 75 mm (Column B), with the same packing as the analytical column, were used. IR spectra were measured on a Perkin-Elmer Infracord spectrometer over the range 4000–650 cm^{-1}. The ^{19}F NMR spectra were measured on a Varian HR instrument at 94·1 Mc/s; the figures quoted are chemical shifts (δ) and are in ppm from trifluoroacetic acid as external reference. The H NMR spectra were measured on a Varian instrument at 60 Mc/s, and the figures quoted are chemical shifts (δ) in ppm from TMS as external reference. Mass spectra were measured on an AEI MS9 instrument.

Fluorination procedure. Fluorinations were carried out in a stream of N_2 (25 l./hr) in a small stirred CoF_3 reaction vessel made of Ni (48 cm × 5 cm diam; it contained ca. 150 g CoF_3).[5] The product was collected at −190° and, after warming to room temp, was washed with water and dried ($MgSO_4$).

Products from cobaltic fluoride fluorinations

Hexafluorobenzene. Analytical gas chromatography (63°, N_2 0·5 l./hr) revealed one major and 2 minor components and a portion (4·8 g) of the total product was separated by GPC (Column A,

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[5] J. Burdon, T. M. Hodgins, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 2382 (1965).

70°, N_2 15 l./hr) to give: (i) a mixture of dodecafluorocyclohexane and decafluorohexene (3·8 g); (ii) a mixture of decafluorocyclohexene and octafluorocyclohexa-1,4-diene (0·1 g). Further separation of fraction (i) (3·5 g) gave dodecafluorocyclohexane (0·2 g) and decafluorocyclohexene (2·1 g); all the fractions had appropriate IR spectra.

Pentafluorobenzene. Analytical GPC (65°, N_2 0·7 l./hr) revealed 2 major and 4 minor components. A portion (4·5 g) of the total product was separated by GPC (Column A, 68°, N_2 15 l./hr) to give: (i) unidentified component (trace); (ii) undecafluorocyclohexane (1·0 g); (iii) 1H-nonafluorocyclohexene (1·9 g) containing a small amount of (ii); (iv) mainly 4H-nonafluorocyclohexene (0·4 g) containing very small amounts of (ii) and (iii); (v) mainly 3H-nonafluorocyclohexene (0·3 g) containing very small amounts of (ii) (iii) and (iv); (vi) pentafluorobenzene (0·1 g); all fractions displayed appropriate IR spectra.

1,2,3,4-*Tetrafluorobenzene.* Analytical GPC (74°, N_2 0·5 l./hr) revealed one major and 5 minor components. A portion (5·2 g) of the total product was separated (Column B, 80°, N_2 30 l./hr) to give: (i) unidentified fluorocarbon (<0·1 g); (ii) undecafluorocyclohexane (0·2 g); (iii) 1H-nonafluorocyclohexene (0·2 g); (iv) 1H/2H-decafluorocyclohexane (0·3 g); (v) an unidentified component (0·1 g); (vi) 1H,2H-octafluorocyclohexene (3·1 g); (vii) 1H,2H-decafluorocyclohexane (0·2 g); all fractions displayed correct IR spectra.

1,2,3,5-*Tetrafluorobenzene.* Analytical GPC (70°, N_2 0·5 l./hr) revealed one major and 4 minor components which were separated by this technique to give undecafluorocyclohexane (0·5 g), 1H-nonafluorocyclohexene (0·3 g), 1H/3H-decafluorocyclohexane (2·6 g), 1H,5H-octafluorocyclohexene (1·0 g), 1H,3H-octafluorocyclohexene (0·9 g) and 1H,3H/-decafluorocyclohexane (0·6 g); all fractions had correct IR spectra.

1,2,4,5-*Tetrafluorobenzene.* Analytical GPC (70°, N_2 1·0 l./hr) revealed 2 major and 3 minor components which were separated by this technique (Column A, 78°, N_2 15 l./hr) to give: (i) dodecafluorocyclohexane (trace); (ii) undecafluorocyclohexane (trace); (iii) 1H-nonafluorocyclohexene (trace); (iv) 1H/4H-decafluorocyclohexane (0·9 g); (v) 1H,4H-octafluorocyclohexene (2·2 g); all fractions displayed correct IR spectra.

Octafluorotoluene (CoF_3 *at* 80°). Analytical GPC (90°, N_2 1·0 l./hr) revealed 2 major and one trace component. A portion (4·8 g) was separated by this technique (Column A, 63°, N_2 8 l./hr) to give: (i) 1-trifluoromethylnonafluorocyclohexene (3·3 g) with a correct IR spectrum; (ii) a mixture of (i) and 1-trifluoromethylheptafluorocyclohexa-1,4-diene (0·9 g), λ_{max} 2100 Å (ε 288 in hexane) with an appropriate[6] IR spectrum; (iii) 1- or 2-trifluoromethylheptafluorocyclohexa-1,3-diene containing very small amounts of (i) and (ii) (0·1 g), λ_{max} 2550 Å (ε 4280 in hexane).

*Decafluoro-*p*-xylene* (CoF_3 at 110°). Analytical GPC (86°, N_2 0·6 l./hr) revealed 3 components. A portion (11·3 g) was separated by GPC (Column A, 70°, N_2, 9 l./hr) to give: (i) 1,4-bis(trifluoromethyl)octafluorocyclohexene containing a trace of 1,4-bis(trifluoromethyl)decafluorocyclohexane (3·1 g) with a correct IR spectrum[7]; (ii) 1,4-*bis*(*trifluoromethyl*)*hexafluorocyclohexa*-1,4-*diene* (4·5 g). (Found: C, 29·4; F, 70·5. C_8F_{12} requires: C, 29·6; F, 70·4%), λ_{max} 2050 Å (ε, 370 in hexane), ν_{max} 1730 cm^{-1} (—CF=C(CF_3)—), mass spectrometry gave a large peak at 324 (C_8F_{12}), the ^{19}F NMR spectrum consisted of three bands at −17·35, 28·21 and 35·79 in the approximate relative intensity ratio of 3:2:1, respectively; (iii) 1,4-bis(*trifluoromethyl*)*hexafluorocyclohexa*-1,3-*diene* (2·5 g). (Found: C, 29·3; F, 70·5%), λ_{max} 2490 Å (ε, 5720 in hexane), ν_{max} 1720 and 1698 cm^{-1} (—C(CF_3)=CFCF=C(CF_3)-system), mass spectrometry gave a large peak at 324 (C_8F_{12}), the ^{19}F NMR spectrum consisted of 3 bands at −17·50, 35·05 and 43·48 in the approximate relative intensity ratio of 3:2:1, respectively.

Defluorination of 1,4-*bis*(*trifluoromethyl*)*hexafluorocyclohexa*-1,4-*diene.* This diene (1·0 g) was passed, during 5 min, over Fe gauze at 340° in the manner described previously[8] to give decafluoro-*p*-xylene (0·8 g) with a correct IR spectrum.

Defluorination of 1,4-*bis*(*trifluoromethyl*)*hexafluorocyclohexa*-1,3-*diene.* In the manner described previously, this diene (0·9 g) gave decafluoro-*p*-xylene (0·8 g) with a correct IR spectrum

Decafluoro-o-xylene (CoF_3 at 120°). A portion (4·4 g) of the total product (5·1 g) was separated by GPC (Column A, 70°, N_2 10 l./hr) to give: (i) 1,2-bis(trifluoromethyl)octafluorocyclohexene

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[6] S. F. Campbell, R. Stephens and J. C. Tatlow, unpublished work.

[7] E. Nield, R. Stephens and J. C. Tatlow, unpublished work.

[8] B. Gething, C. R. Patrick and J. C. Tatlow, *J. Chem. Soc.* 1576 (1961).

(3·1 g). (Found: C, 26·8; F, 73·5. C_8F_{14} requires: C, 26·5; F, 73·5%), ν_{max} 1700 cm^{-1} (very weak, —C(CF_3)=C(CF_3)—), λ_{max} 2000 Å (ε, 262 in hexane), mass spectrometry gave a large peak at 362 (C_8F_{14}), the ^{19}F NMR spectrum consisted of 3 bands at −18·27, 35·53 and 59·55 in the approximate relative intensity ratio of 3:2:2, respectively; (ii) intermediate fraction (0·3 g) containing (i) and (ii); (iii) 1,2-*bis(trifluoromethyl)hexafluorocyclohexa*-1,4-*diene* (0·5 g). (Found: C, 29·5; F, 71·0%), ν_{max} 1795 cm^{-1} (—CF=CF—), λ_{max} 2050 Å (ε, 418 in hexane), mass spectrometry gave a large peak at 324 (C_8F_{12}), the ^{19}F NMR spectrum consisted of 3 bands at −18·26, 28·47 and 80·00 in the approximate relative intensity ratio of 3:2:1, respectively.

Defluorination of 1,2-*bis(trifluoromethyl)octafluorocyclohexene*. In the manner described previously, this olefin (1·0 g) gave decafluoro-*o*-xylene (0·7 g) with a correct IR spectrum.

Defluorination of 1,2-*bis(trifluoromethyl)hexafluorocyclohexa*-1,4-*diene*. In the same way, this diene (0·16 g) gave decafluoro-*o*-xylene (0·11 g) with a correct IR spectrum.

Decafluoro-m-*xylene* (CoF_3 at 100°). A portion (7·2 g) of the total product (8·2 g) was separated by GPC (Column A, 85°, N_2 15 l./hr) to give: (i) a mixture of the suspected 1,3- and 1,5-bis(trifluoromethyl)octafluorocyclohexene together with a small amount of perfluoro-1,3-dimethylcyclohexane (5·8 g). (Found: C, 26·5; F, 73·1%), ν_{max} 1720 cm^{-1} (—CF=C(CF_3)—), mass spectrometry gave a top mass peak at 381 (C_8F_{15}) and a large peak at 362 (C_8F_{14}); (ii) a mixture of 1,3-bis(trifluoromethyl)-hexafluorocyclohexadienes (1·0 g). (Found: C, 29·2; F, 70·8%), ν_{max} 1770, 1730 and 1680 cm^{-1} (—CF=C(CF_3)— systems), λ_{max} 2550 Å (ε, 1960 in hexane), mass spectrometry gave a large peak at 324 (C_8F_{12}).

Octafluoronaphthalene (CoF_3 at 160°). A portion (2·6 g) of the total product (4·6 g) was separated by GPC (Column A, 90°, N_2 13 l./hr) to give: (i) *hexadecafluorobicyclo*(4.4.0)-*dec*-1-*ene* (1·9 g). (Found: C, 28·6; F, 72·1. $C_{10}F_{16}$ requires: C, 28·3; F, 71·7%), mass spectrometry gave a large peak at 424 ($C_{10}F_{16}$), the ^{19}F NMR spectrum consisted of 2 bands of equal intensity at 34·87 and 59·19; (ii) hexadecafluorobicyclo(4.4.0)-dec-1-ene containing about 5% of octadecafluorodecalin (0·3 g), as shown by IR spectroscopy and GPC (75°, N_2 0·5 l./hr).

Pentafluorobromobenzene (CoF_3 at 100°). A portion (6·6 g) of the total product (7·5 g) was separated by GPC (Column A, 86°, N_2 12 l./hr) to give: (i) dodecafluorocyclohexane (a trace) with correct IR spectrum; (ii) decafluorocyclohexene (a trace) with a correct IR spectrum; (iii) undecafluorocyclohexyl bromide (4·0 g). (Found: C, 20·1; Br, 21·9; F, 58·3. Calc. for C_6BrF_{11}: C, 20·0; Br, 22·1; F, 57·9%), mass spectrometry gave a large peak at 360 (C_6BrF_{11}); (iv) a mixture of bromononafluorocyclohexenes [and a trace of (iii)] (1·4 g) which were not resolved by several stationary phases (*viz*., kel-F oil-, tricresyl phosphate-, silicone-gum-, benzyl diphenyl—celite). (Found: C, 22·5; Br, 25·1. C_6BrF_9 requires: C, 22·3 Br, 24·7%), ν_{max} 1760 (—CF=CF—) and 1700 cm^{-1} (—CF=CBr—), λ_{max} 2150 Å (ε 1200 in hexane).

Pentafluorotoluene (CoF_3 at 100°). A portion (4·9 g) of the total product (6·1 g) was separated by GPC (Column A, 70°, N_2 17 l./hr) to give: (i) an unidentified component (trace); (ii) methyl undecafluorocyclohexane (0·4 g) with a correct IR spectrum; (iii) a mixture of three components (2·7 g); (iv) 1-methylnonafluorocyclohexene (1·1 g) with a correct IR spectrum. A portion (1·0 g) of fraction (iii) was then separated by GPC (a column 488 cm × 35 mm diam packed with kel-F-oil–kieselguhr 1:4, 85°, N_2 10 l./hr) to give: (i) 1-*(difluoromethyl)nonafluorocyclohexene* (0·3 g). (Found: C, 28·7; H, 0·4. C_7HF_{11} requires: C, 28·6; H, 0·3%), ν_{max} 1720 cm^{-1} (—CF=C(CF_2H)—), mass spectrometry gave a large peak at 294 (C_7HF_{11}), the ^{19}F NMR spectrum consisted of 5 bands centred at 33·74, 42·1 (doublet; —CHF_2), 43·86 (vinylic F), 44·53 and 58·41; in the approximate relative intensity ratio of 2:2:1:2:4, respectively, the ^{1}H NMR spectrum was a triplet (J_{HF} = 52 c/s) centred at 6·2; (ii) a mixture of two components (0·3 g); (iii) fluoromethylundecafluorocyclohexane (0·4 g) with a correct IR spectrum.[8]

Pentafluoroanisole (CoF_3 at 117°). A portion (6·2 g) from the combined products (9·3 g) of two experiments was separated by GPC (Column A, 99°, N_2 15 l./hr) to give: (i) trifluoromethyl undecafluorocyclohexyl ether (0·2 g); (ii) an unidentified component (0·1 g); (iii) difluoromethyl undecafluorocyclohexyl ether (1·8 g); (iv) methyl undecafluorocyclohexyl ether (0·2 g); (v) fluoromethyl undecafluorocyclohexyl ether (2·7 g); fractions (i) and (iii)–(v) all had correct IR spectra.

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[8] W. J. Feast, R. Stephens and J. C. Tatlow, unpublished work.