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Short Communication

A synthesis of 1,2,3,4-tetrafluorobenzene by KF fluorination

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The fluorination of 1,2,3,4-tetrachlorobenzene with potassium fluoride and/or cesium fluoride in dimethyl sulfone (DMSO$_2$) was reported to proceed to 2,3,4-trifluorochlorobenzene[1], with only a trace (0.7%) of 1,2,3,4-tetrafluorobenzene being detected. Two of the probable intermediates (2,3,6-trifluorochlorobenzene and 2,3-dichloro-1,4-difluorobenzene[1]) were not found amongst the products. On the presumption that these compounds were not detected because of their high reactivity toward the exchange reaction, they were synthesized by unequivocal methods to determine if they might be prime source materials for the preparation of 1,2,3,4-tetrafluorobenzene. This assumption was given prior support by the synthesis of 1,2,3,5-tetrafluorobenzene in yields of 44% from the intermediate 2,6-dichloro-1,4-difluorobenzene[1].

The synthesis of 1,2,3,4-tetrafluorobenzene in yields exceeding 26% from 2,3,6-trifluorochlorobenzene (Table 1) by reaction with a potassium fluoride–cesium fluoride mixture in dimethyl sulfone is reported here. Due to the high reactivity of this compound, it is possible to realize a 16.4% conversion using potassium fluoride alone. The isomeric 2,3,4-trifluorochlorobenzene, which is the only trifluoro analog isolated from the fluorination of the corresponding tetrachloro compound, could not be converted to 1,2,3,4-tetrafluorobenzene by using potassium fluoride–cesium fluoride mixtures or even by cesium fluoride alone in yields in excess of 2.5%.

The fluorination of 2,3-dichloro-1,4-difluorobenzene[1] *via* the halogen-exchange reaction gave a 22.6% yield of 1,2,3,4-tetrafluorobenzene (Table 1). The reactive 2,3,6-trifluorochlorobenzene was the only possible intermediate in this synthesis. Since poor fluorination yields to the tetrafluoro level were obtained from 3,4-dichloro-1,2-difluorobenzene (1.8%) and from 2,4-dichloro-1,3-difluorobenzene (1.3%), 3,6-dichloro-1,2-difluorobenzene was not subjected to the halogen-exchange reaction. Low yields in all three cases would be expected as the unreactive 2,3,4-trifluorochlorobenzene is the most likely intermediate.

Experimental

The potassium fluoride used in these experiments was dried at 120 °C for 24 h and quickly powdered in a warm mortar. The cesium fluoride was heated at 120 °C for 24 h prior to use[1].

TABLE 1

TETRAFLUOROBENZENE BY KF FLUORINATION

$C_6H_2X_4$ /mol	KF /mol	CsF /mol	$DMSO_2$ /g	Temp. /°C	Time /h	Method	Product/mol % yield $Cl_2C_6H_2F_2$	$ClC_6H_2F_3$	$C_6H_2F_4$
I. 2,3-Dichloro-1,4-difluorobenzene[a]									
0.33	1.32	—	600	265	3.5	A	18.4	47.5	6.0
0.33	0.99	0.11	600	265	3.0	A	—	30.2	22.6
0.25	0.75	0.25	455	265	2.3	A	—	39.0	18.2
II. 3,4-Dichloro-1,2-difluorobenzene[a]									
0.15	0.45	0.1	300	265	3.5	B	3.8	25.9	1.8
III. 2,4-Dichloro-1,3-difluorobenzene[a]									
0.15	0.45	0.1	300	265	3.5	B	18.0	20.7	1.3
IV. 2,3,4-Trifluorochlorobenzene[a,b]									
0.08	0.31	—	200	265	5.5	B	—	29.0	1.9
0.08	0.31	—	100	225	5.5	B	—	76.0	1.0
0.08	—	0.1	100	225	5.5	B	—	51.5	2.5
V. 2,3,6-Trifluorochlorobenzene									
0.08	0.31	—	200	265	5.5	B	—	27.6	16.4
0.33	0.89	0.1	600	265	2.0	B	—	37.1	25.5
0.33	0.89	0.19	650	270	1.5	B	—	18.5	26.3
0.17	—	0.25	300	225	3.5	B	—	29.0	11.5

[a] Lit. ref. 1.

[b] B.p. 131 °C; data not given in ref. 1.

Fluorination

The polyhalobenzene was added to a heated mixture (200 °C) of dimethyl sulfone and metal fluoride in a Parr reactor. The solid polyhalobenzene was added directly (method A in Table 1), and the liquid polyhalobenzenes were injected with slight nitrogen pressure (method B in Table 1) into the closed autoclave. The reaction mixtures were allowed to react under autogenous pressure and were stirred at the temperatures and time intervals indicated in Table 1. Products were removed from the reactor by distillation, collected in an ice-cooled trap and finally steam-distilled. Yields were determined by chromatographic analysis as described in ref. 1.

2,3,6-Trifluorochlorobenzene (nc)

2-Chloro-3,4-difluoroaniline[2] (1.0 mol) in 800 cm^3 of 50% HBF_4 was diazotized with 1.1 mol of sodium nitrite in 120 cm^3 of water (5–10 °C, acetone–Dry Ice bath). After cooling to −55 °C (to decrease the solubility), the diazonium fluoborate was collected on a filter and washed with diethyl ether. Thermal decomposition gave a 67% yield of crude product. A similar Schiemann reaction on 2,4-difluoro-3-chloroaniline[3] gave yields not exceeding 31.5%. Distillation (annular Teflon spinning-band column) gave pure 2,3,6-trifluorochlorobenzene, b.p. 132 °C (Found: C, 43.54; H, 1.36; Cl, 21.15; F, 34.11%. $C_6H_2ClF_3$ requires C, 43.27; H, 1.21; Cl, 21.29; F, 34.23%).

The dimethyl sulfone ($DMSO_2$) was obtained from the Crown Zellerbach Corporation, Camas, Washington.

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