Superacid-promoted synthesis of polychlorinated dibenzofurans

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Experimental section

All reagents were purchased from commercial suppliers and used as received. However, triflic acid was distilled immediately prior to its use. Products were purified using silica gel chromatography and standard procedures with 100% hexanes as the mobile phase.¹⁷ Calculations were done using the Gaussian 09 program suite.¹⁸ Geometry optimizations were done without constraints at the indicated level of theory. Frequency calculations were done on all structures and each was determined to have zero imaginary frequencies. Energy values were calculated from optimized structures and corrected for zero point energies. *Caution! Polychlorodibenzofurans are exceedingly toxic substances. Their handling should only be done by trained individuals with adequate personal protective and safety equipment.*

Procedure for the Synthesis of Dibenzofurans. Under an inert atmosphere, a solution is prepared containing triflic acid (1 mL, 11 mmol), arene (1 g, ca. 8 mmol), and co-solvent (1 mL of CH₂Cl₂ or CF₃CH₂OH) *o*-Chloranil (0.15 g, 0.6 mmol). The mixture is cooled to -30 °C and a solution of *o*-chloranil **5** (in 2 mL co-solvent) is added slowly with stirring. The resulting mixture is allowed to slowly warm to room temperature overnight. Following this reaction period, the mixture is poured over ice and the solution is extracted three times with chloroform. The organic extracts are then washed twice with water and twice with brine solution. Following a drying regiment with anhydrous Na₂SO₄, the organic solvent is removed and the crude product is subject to chromatography with hexanes.

1,2,3,4-Tetrachlorodibenzo[*b,d*]furan (**6**). White solid, mp 164-166 °C (hexanes; lit., 169-170 °C).¹⁹ ¹H NMR (CDCl₃, 500 MHz): δ, 7.43-7.49 (m, 1H), 7.58-7.63 (m, 1H), 7.65 (d, *J*=8.0 Hz, 1H), 8.33 d, *J*=4.5 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ, 112.7, 116.5, 121.4, 122.0, 123.6, 124.9, 125.6, 127.8, 131.0, 135.0, 150.9, 156.6. Low resolution MS (EI), 308/306/304 (M⁺), 243/241, 206, 171/173, 153, 121. High resolution mass spectrum (EI), calcd for C₁₂H₄Cl₄O, 303.9016, found, 303.9013.

1,2,3,4,7-Pentachlorodibenzo[*b,d*]furan (**7**). White solid, mp 153-155 °C (hexanes). ¹H NMR (CDCl₃, 300 MHz): δ, 7.35 (dd, *J*=1.8, 8.4 Hz, 1 H), 7.58 (d, *J*=1.8 Hz, 1 H), 8.16 (d, *J*=8.4 Hz, 1 H). ¹³C NMR (CDCl₃, 75 MHz): δ, 113.0, 116.2, 123.7, 124.7, 125.9, 127.7, 131.1, 135.1, 150.8, 156.5. Low resolution MS (EI), 344/342/340/338 (M⁺), 279/277/275, 205/207, 170, 138, 120. High resolution mass spectrum (EI), calcd for C₁₂H₃Cl₅O, 337.8627, found, 337.8635.

1,2,3,4,7,8-Hexachlorodibenzo[*b,d*]furan (**8**; obtained as a mixture with **9**). ¹H NMR (CDCl₃, 500 MHz): δ, 7.81 (s, 1H), 8.42 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ, 113.8, 121.3, 122.6, 123.8, 128.5, 132.0, 133.5, 151.2, 154.7. Low resolution MS (EI), 378/376/374/372 (M⁺), 313/311/309, 243/241/239, 187, 155, 138. High resolution mass spectrum (EI), calcd for C₁₂H₂Cl₆O, 371.8237, found, 371.8236.

7-Bromo-1,2,3,4-Tetrachlorodibenzo[*b,d*]furan (**10**). White solid, mp 202-205 °C (hexanes). ¹H NMR (CDCl₃, 300 MHz): δ, 7.52 (dd, *J*=5.7, 1.2 Hz, 1H), 7.77 (d, *J*=1.2 Hz, 1H), 8.11 (d, *J*=5.7 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ, 115.6, 116.6, 121.8, 122.1, 122.6, 123.9, 125.6, 127.6, 127.8, 127.8, 131.2, 150.8, 156.6. Low resolution MS (EI), 388/386/384/382 (M⁺), 279/277/275, 207/205, 192, 160, 135, 120, 102, 85. High resolution mass spectrum (EI), calcd for C₁₂H₃BrCl₄O, 381.8121, found, 381.8111.

7-Fluoro-1,2,3,4-Tetrachlorodibenzo[*b,d*]furan (**11**). White solid, mp 176-178 °C (hexanes). ¹H NMR (CDCl₃, 300 MHz): δ, 7.22 (dt, *J*=2.5, 9.0 Hz, 1H), 7.38 (dd, *J*=2.5, 8.5 Hz, 1H), 8.29 (dd, *J*=5.5, 9.0 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ, 100.1 (d, *J*_{C-F}= 26.3 Hz), 112.4 (d, *J*_{C-F}= 23.8 Hz), 116.4, 119.0, 122.2, 124.0 (d, *J*_{C-F}= 2.5 Hz), 125.4, 127.7, 130.4, 151.2, 156.9 (d, *J*_{C-F}= 12.5 Hz), 163.2 (d, *J*_{C-F}= 248 Hz). Low resolution MS (EI), 326/324/322 (M⁺), 263/261/259, 191/189, 162, 130, 112. High resolution mass spectrum (EI), calcd for C₁₂H₃FCl₄O, 321.8922, found, 321.8925.

Procedure for the Chlorination of Dibenzofurans 6 and 8/9. The dibenzofuran (ca. 0.050 g, 0.2 mmol) is dissolved in 1 mL of CHCl_3 and *N*-chlorosuccinimide (0.16 g, 1.2 mmol) is added. To this solution, 2 mL (23 mmol) of triflic acid is added. The mixture is stirred for 24 hr at room temperature, after which it is poured over about 10 g of ice. The aqueous phase is extracted twice with CHCl_3 and the combined organic extracts are then washed with water and a brine solution (twice). The mixture is dried with sodium sulfate and analyzed by GC-MS and GC-FID.

Results from chlorination of compound **6** (relative yields):

Results from chlorination of compound **8** (relative yields):

^1H NMR

^{13}C NMR (CDCl_3 with acetone impurity)

¹H NMR

^{13}C NMR (CDCl_3 with acetone impurity)

(5:1 ratio)

^1H NMR

Proton

^{13}C NMR (CDCl_3 with acetone impurity)

^1H NMR

^{13}C NMR (CDCl_3 with acetone impurity)

^1H NMR

^{13}C NMR (CDCl_3 with acetone impurity)

Computation methods:

Calculations were done using the *Gaussian09W* program package.¹ Geometry optimizations were done using density function theory (DFT) and the hybrid functional B3LYP at the 6-311G** level.^{2,3} Vibrational analyses were performed at the B3LYP/6-311G** level of theory. Zero-point-energy corrections are unscaled.

Literature Citations:

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(2) (a) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785

(3) Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, 72, 650.

Compound 5

Imaginary Freq. = 0

Point Group C1

B3LYP 6-311G (d,p) optimized structure:

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.982103	-0.693880	-0.056974
2	6	0	0.498923	-0.765039	-0.056464
3	6	0	1.277449	0.583234	-0.056922
4	6	0	0.475439	1.830348	-0.058090
5	6	0	-0.879345	1.785340	-0.058548
6	6	0	-1.620391	0.501970	-0.057900
7	17	0	1.371340	3.303785	-0.058828
8	17	0	-1.798761	3.249486	-0.060003
9	17	0	-3.348080	0.566321	-0.058288
10	17	0	-1.810348	-2.206386	-0.056258
11	8	0	2.480089	0.567381	-0.056184
12	8	0	1.113850	-1.798675	-0.055956

Energy + ZPE = -2219.954618 Hartree

Ion **12a** Imaginary Freq. = 0 Point Group C1

B3LYP 6-311G (d,p) optimized structure:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.483032	0.329105	-0.000005
2	6	0	0.857309	1.567319	-0.000005
3	6	0	-0.664497	1.694848	0.000023
4	6	0	-1.461917	0.450730	0.000004
5	6	0	-0.815874	-0.750936	0.000003
6	6	0	0.658784	-0.809819	0.000018
7	17	0	-3.148015	0.630625	-0.000009
8	17	0	-1.701104	-2.215306	-0.000017
9	17	0	1.390295	-2.325180	0.000026
10	17	0	3.197808	0.248387	-0.000022
11	8	0	-1.108104	2.815370	0.000023
12	8	0	1.510473	2.675646	-0.000008
13	1	0	0.877295	3.429452	0.000029

Energy + ZPE = -2220.262610 Hartree

Ion **12b** Imaginary Freq. = 0 Point Group C1

B3LYP 6-311G (d,p) optimized structure:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.458758	0.301953	-0.000004
2	6	0	-0.892437	1.566507	-0.000030
3	6	0	0.624013	1.742765	0.000009
4	6	0	1.445873	0.489998	-0.000036
5	6	0	0.841052	-0.734959	-0.000016
6	6	0	-0.616418	-0.826534	0.000009
7	17	0	3.121675	0.708676	0.000003
8	17	0	1.769162	-2.177707	0.000027
9	17	0	-1.324885	-2.354632	-0.000007
10	17	0	-3.185253	0.176586	-0.000025
11	8	0	1.090294	2.845239	-0.000056
12	8	0	-1.542969	2.681801	0.000053
13	1	0	-2.510411	2.545594	0.000457

Energy + ZPE = - 2220.256963 Hartree

Ion **13a**

Imaginary Freq. = 0

Point Group C1

B3LYP 6-311G (d,p) optimized structure:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.486109	0.334732	-0.000081
2	6	0	0.799689	1.541655	0.000019
3	6	0	-0.710426	1.587206	0.000179
4	6	0	-1.478579	0.395052	0.000141
5	6	0	-0.790712	-0.809979	0.000026
6	6	0	0.721526	-0.845836	-0.000059
7	17	0	-3.172218	0.514544	0.000254
8	17	0	-1.624443	-2.258616	0.000027
9	17	0	1.485904	-2.316708	-0.000222
10	17	0	3.198272	0.354299	-0.000227
11	8	0	-1.296547	2.717535	0.000063
12	8	0	1.316360	2.724052	0.000121
13	1	0	-0.710360	3.505917	-0.000038
14	1	0	2.298478	2.754571	0.000083

Energy + ZPE = -2220.397251 Hartree

Ion **13b**

Imaginary Freq. = 0

Point Group C1

B3LYP 6-311G (d,p) optimized structure:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.475612	0.364629	0.000012
2	6	0	0.757392	1.574679	0.000028
3	6	0	-0.757394	1.574679	-0.000274
4	6	0	-1.475613	0.364629	-0.000130
5	6	0	-0.758334	-0.826436	0.000113
6	6	0	0.758335	-0.826435	-0.000087
7	17	0	-3.185708	0.441759	-0.000203
8	17	0	-1.556255	-2.288118	0.000242
9	17	0	1.556258	-2.288118	-0.000148
10	17	0	3.185707	0.441763	0.000069
11	8	0	-1.265480	2.743687	0.000358
12	8	0	1.265478	2.743686	-0.000091
13	1	0	2.249799	2.761346	-0.000082
14	1	0	-2.249801	2.761347	0.000637

Energy + ZPE = - 2220.399788 Hartree