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DETERMINATION OF STRUCTURES OF TRI- AND TETRABROMODIBENZOFURANS FORMED IN BROMINATION OF DIBENZOFURAN

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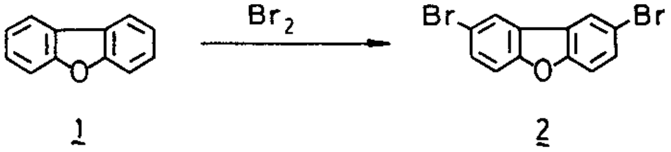
Abstract —— Dibenzofuran reacted with bromine in the presence of Fe powder to afford tri- and tetrabromodibenzofurans and their structures were determined.

There are many investigations concerned with polychlorodibenzofurans (PCDF) which have been reported to be more poisonous compounds than polychlorobiphenyls (PCB). Although polybromodibenzofurans also seem to be poisonous compounds, there are few information about the problems. There might be one of reasons that structures of polybromodibenzofurans have not yet been confirmed so far. Only 2,8-dibromodibenzofuran was obtained by bromination of dibenzofuran (1).[1]

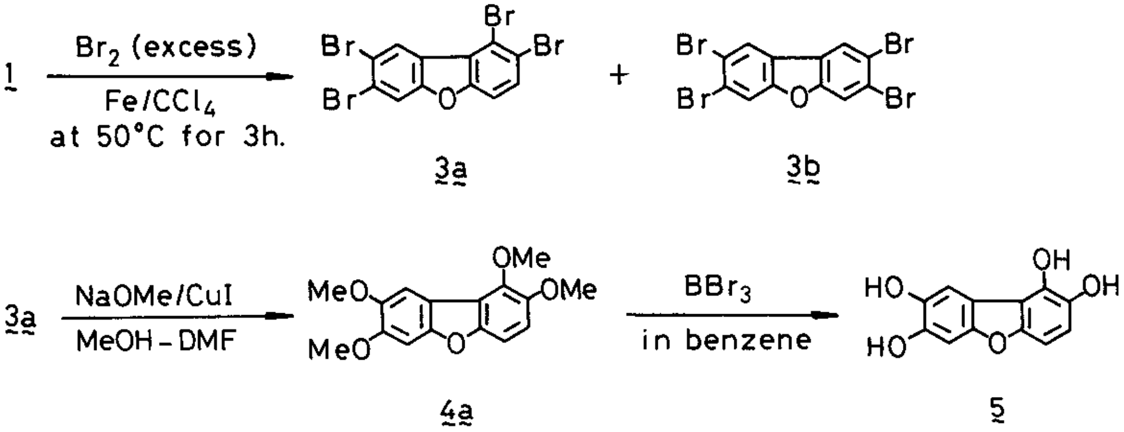


We wish to report the determination of tri- and tetrabromodibenzofurans obtained in bromination of 1.

RESULTS AND DISCUSSION

When 1 was treated with excess bromine in the presence of Fe powder in CCl_4 solution at 50°C for 3 h, a mixture of 1,2,7,8-tetra-(3a) and 2,3,7,8-tetrabromodibenzofurans (3b) were obtained together with a small amount of tribromodibenzofurans (6). These compounds, 3a and 3b were isolated from the mixture by chromatographic method.

Treatment of **3a** with sodium methoxide according to the reported method[2] afforded 1,2,7,8-tetramethoxydibenzofuran (**4a**) in 31% yield, which upon treatment with BBr_3 in benzene afforded the known 1,2,7,8-tetrahydroxydibenzofuran (**5**).[3]



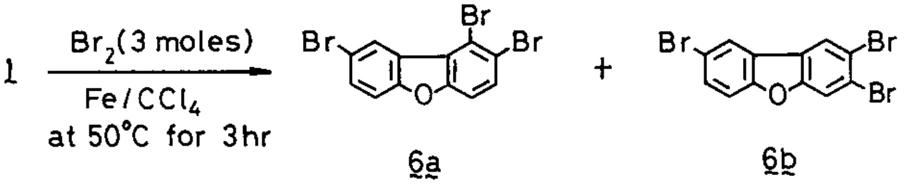
Scheme 1

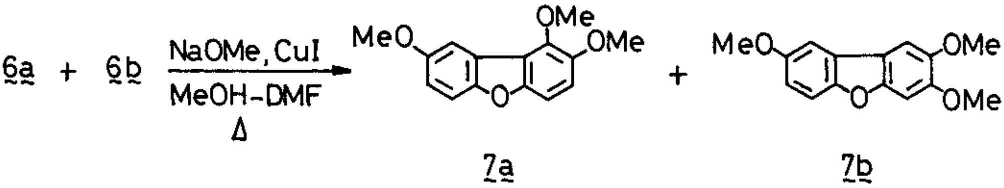
These conversions and spectral data (^{1}H-NMR spectrum) of compound **4a** supported strongly the structure proposed for compound **3a**.

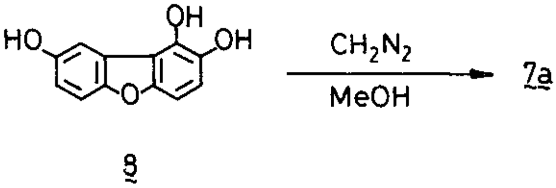
Bromination of **1** with three equivalents of bromine gave a mixture of 1,2,8-tribromo- (**6a**) and 2,3,8-tribromodibenzofurans (**6b**) together with a small amount of **2** and **3**. Unfortunately, separation of the both compounds **6a** and **6b** from the mixture was unsuccessful. The mixture of **6a** and **6b** were converted into a mixture of 1,2,8-tri- (**7a**) and 2,3,8-trimethoxydibenzofuran (**7b**) in 72% yield. One of the products, **7a** was isolated from the mixture by preparative GC method and also prepared by methylation of the known compound, 1,2,8-trihydroxydibenzofuran (**8**)[3] with diazomethane.

It was found that bromination of **2** afforded a mixture of **6a** and **6b**, and that bromination of the mixture of **6a** and **6b** gave a mixture of **3a** and **3b**. From these results and spectral data of the mixture of **3a** and **3b**, the structure of **3b** was confirmed as 2,3,7,8-tetrabromodibenzofuran though **3b** could not be isolated.

$$\mathbf{2} \xrightarrow{Br_2} \mathbf{6a} + \mathbf{6b} \xrightarrow{Br_2} \mathbf{3a} + \mathbf{3b}$$







EXPERIMENTAL SECTION

All melting points are uncorrected. IR spectra were measured by a Nippon Bunko IR-A spectrometer as KBr pellets or films. ^{1}H-NMR spectra were determined with a Nihon Denshi JEOL FT-100 spectrometer with Me_4Si as an internal standard. Mass spectra were determined by using a Nihon Denshi JMS-O1SA-2 mass spectrometer at 70 eV with a direct inlet. Gas chromatographic analyses were carried out by means of a Yanagimoto Yanaco G180 (30% high-vacuum silicon grease; 2 m; carrier gas, nitrogen 1 Kg/cm^2).

Tetrabromination of 1.

To a mixture of 1 (2 g, 12 mmol) and Fe powder (0.8 g) in carbon tetrachloride (80 ml) was added bromine (8.5 g, 53 mmol) and stirred for 3 h at 50°C. The reaction mixture was added to an aqueous $Na_2S_2O_3$ solution and extracted with chloroform. The organic layer was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave the residue, which was washed with a small amount of benzene to give a mixture of 3a and 3b (5.0 g, 87%). NMR spectroscopy indicated that the ratio of 3a and 3b was about 1/1.7. The mixture of 3a and 3b was chromatographed three times on Al_2O_3 using benzene as an eluent to give 3a and 3b. Tribromodibenzofurans (6) were obtained as compounds soluble in benzene in 2% yield.

3a: Colorless needles (benzene); yield 490 mg (8.5%); mp 240.5~242°C; IR (KBr) 1420, 1400, 1200, 905, 890, 875, 800 cm^{-1}; NMR ($CDCl_3$) δ 7.38 (1 Hz, d, J = 9 Hz), 7.72 (1H, d, J = 9 Hz), 7.86 (1H, s), 8.72 (1H, s); mass spectrum, m/e 480, 482, 484, 486, 488 (M^+). Anal. Calcd for $C_{12}H_4OBr_4$: C, 29.79; H, 0.83. Found: C, 29.79; H, 0.87.

3b: Colorless needles (benzene); yield 620 mg (11%); mp 301~302°C; IR (KBr) 1420, 1380, 1185, 1080, 890, 860 cm^{-1}; NMR ($CDCl_3$) δ 7.84 (2H, s), 8.12 (2H, s); mass spectrum, m/e 480, 482, 484, 486, 488 (M^+). Anal. Calcd for $C_{12}H_4OBr_4$: C, 29.79; H, 0.83. Found: C, 29.81; H, 0.86.

Preparation of **4a**.

To 50 ml of methanol was added slowly 2.4 g (104 mmol) of sodium, to a solution of which were added **3a** (300 mg, 0.62 mmol), CuI (0.9 g, 4.7 mmol) and DMF (50 ml). After stirring for 36 h under reflux, the reaction mixture was poured into a large amount of ice-water and extracted with benzene. The benzene solution was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave the residue, which was recrystallized from hexane to give **4a** as colorless prisms (hexane); yield 55 mg (31%); mp 82~82.5°C; IR (KBr) 2940, 2840, 1460, 1250, 880, 845, 820, 785 cm^{-1}; NMR ($CDCl_3$) δ 3.88, 3.92, 3.96, 4.06 (each 3H, s), 6.89 (1H, d, J = 8 Hz), 7.01 (1H, s), 7.12 (1H, d, J = 8 Hz), 7.51 (1H, s); mass spectrum, m/e 288 (M^+). Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.59; H, 5.62.

Preparation of **5**.

To a solution of **4a** (20 mg, 0.07 mmol) in benzene (10 ml) was added a solution of BBr_3 (700 mg, 2.8 mmol) in benzene (3 ml) and the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with ether. The organic layer was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave crude **5** as colorless needles (benzene); yield 11 mg (69%); mp ca.250°C (dec.) [lit.[3] ca.250°C (dec.)].

Tribromination of 1.

To a mixture of **1** (2 g, 12 mmol) and Fe powder (0.8 g) in carbon tetrachloride (180 ml) was added bromine (6.3 g, 39 mmol) and stirred for 3 h at 50°C. The reaction mixture was added to an aqueous $Na_2S_2O_3$ solution and extracted with chloroform. The organic layer was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave the residue, which was chromatographed on Al_2O_3 using a 5:1 mixture of hexane and benzene as an eluent to give **2** (190 mg, 5%), **3** (115 mg, 2%) and a mixture of **6a** and 6b (3.57 g, 74%).

Mixture of 6a and 6b: colorless prisms (benzene); mp 144~148.5°C; IR (KBr) 1460, 1425, 1195, 1050, 1020, 875, 800 cm^{-1}; NMR ($CDCl_3$) δ 7.32~7.60 (m), 7.81~8.09 (m); mass spectrum, m/e 402, 404, 406, 408 (M^+).

Preparation of 7a.

To 200 ml of methanol was added slowly 10.2 g (0.44 mmol) of sodium, to a solution of which were added the mixture of 6a and 6b (4.1 g, 10 mmol), CuI (3.4 g, 18 mmol) and DMF (200 ml). After stirring for 36 h under reflux, the reaction mixture was poured into a large amount of ice-water and extracted with benzene. The benzene solution was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave the residue (1.88 g, 72%), whose gas chromatography indicated that the ratio of 7a and 7b was about 1/1.2. Compound 7a was isolated from the residue by column chromatography on silica-gel (Wako, C-300) using benzene as an eluent and gas chromatography.

7a: pale yellow oil; yield (210 mg, 8%). IR (NaCl) 2930, 2830, 1500, 1480, 1250, 1220, 1055, 770 cm^{-1}; NMR ($CDCl_3$) δ 3.92, 3.94, 4.09 (each 3H, s), 6.99 (1H, dd, J = 9.5, 2.5 Hz), 7.02 (1H, d, J = 9 Hz), 7.18 (1H, d, J = 9 Hz), 7.38 (1H, d, J = 9.5 Hz), 7.59 (1H, d, J = 2.5 Hz); mass spectrum, calcd for $C_{15}H_{14}O_4$ (M^+) m/e 258.0891, found (M^+) 258.0891.

Reaction of 8 with diazomethane.

To a solution of 8 (6 mg, 0.03 mmol) in methanol (3 ml) was added an ethereal solution (3 ml) of diazomethane at 0°C and the mixture was stirred for 20 min at room temperature. The reaction mixture was evaporated in vacuo to leave the residue, whose gas chromatography indicated that 7a was formed in 76% yield.

Bromination of 2.

To a mixture of 2 (500 mg, 1.5 mmol) and Fe powder (200 mg) in carbon tetrachloride (50 ml) was added bromine (300 mg, 1.9 mmol) and the mixture was stirred for 3 h at 50°C. The reaction mixture was added to an aqueous $Na_2S_2O_3$ solution and extracted with chloroform. The organic layer was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave the residue, which was chromatographed on silica-gel (Wako, C-300) using a 2:1 mixture of benzene and hexane as an eluent to give a mixture of 6a and 6b: yield 410 mg (66%).

Bromination of the mixture of **6a** and **6b**.

To the mixture of 6a and 6b (0.3 g, 0.7 mmol) and Fe powder (150 mg) in carbon tetrachloride (50 ml) was added bromine (140 mg, 0.9 mmol) and the workup gave a mixture of **3a** and **3b**: yield 290 mg (81%).

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