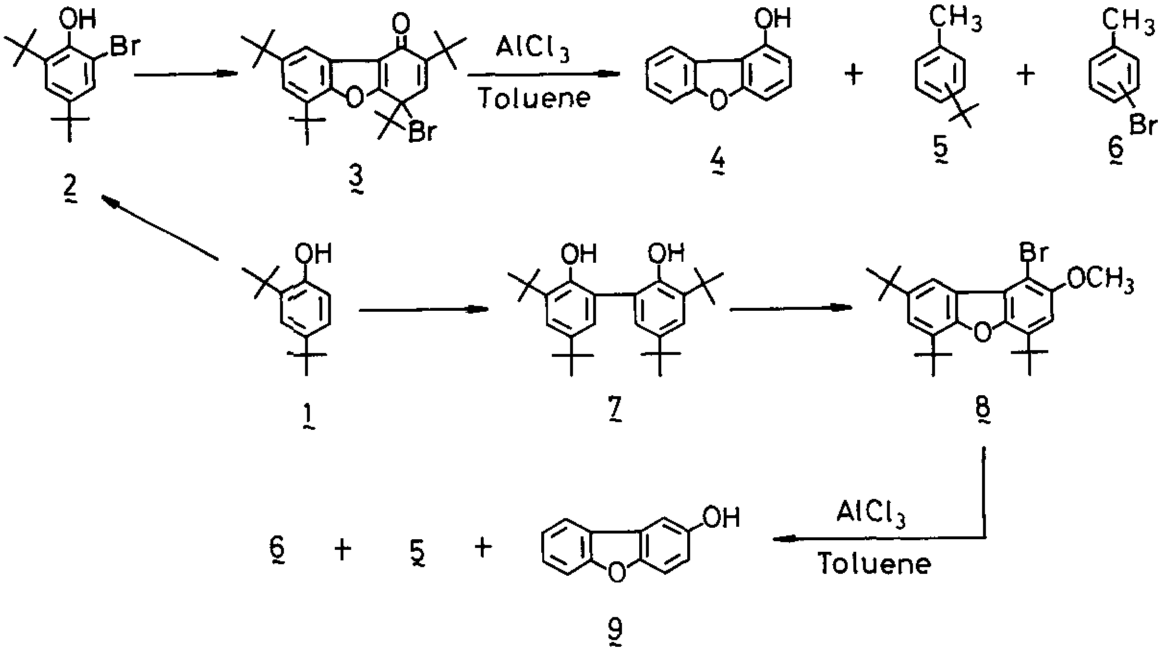
SELECTIVE PREPARATION. 39. PREPARATION OF SOME CHLORODIBENZOFURANS FROM 1-HYDROXY- AND 2-HYDROXYDIBENZOFURAN[1]

Masashi Tashiro* and Haruo Yoshiya
Research Institute of Industrial Science and Department of Molecular
Science and Technology, Graduate School of Engineering Sciences,
Kyushu University 86, Sakamoto, Kasuga, Kasuga-shi 816, Japan

Abstract —— Some chlorodibenzofurans such as 1-chloro-, 2-chloro-, 1,2,4-trichloro- and 1,2,3-trichlorodibenzofurans were prepared from 1-hydroxy- and 2-hydroxydibenzofuran.

It has been previously reported that 1-hydroxy-(4)[2] and 2-hydroxydibenzofurans (9)[3] were easily prepared from 2,4-di-tert-butylphenol (1) (Scheme 1).



Scheme 1

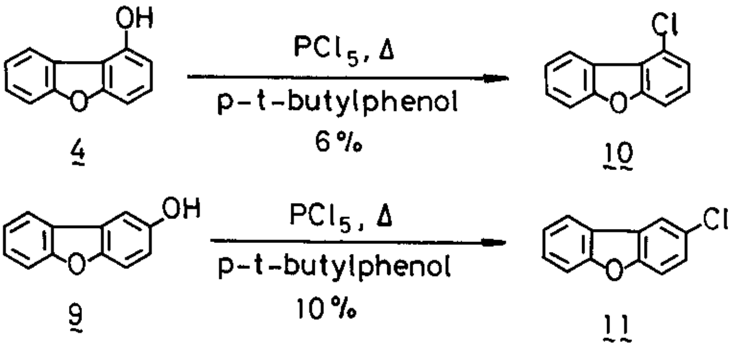
It was also known that some aryl chlorides were prepared from the corresponding phenolic compounds by heating with a mixture of PCl_5 and p-tert-butylphenol.[4]

$$\mathrm{ArOH} \xrightarrow[\text{p-t-butylphenol}\ \Delta]{PCl_5} \mathrm{ArCl}$$

These results suggest that some chlorodibenzofurans might be selectively prepared from hydroxydibenzofurans such as 4 and 9.

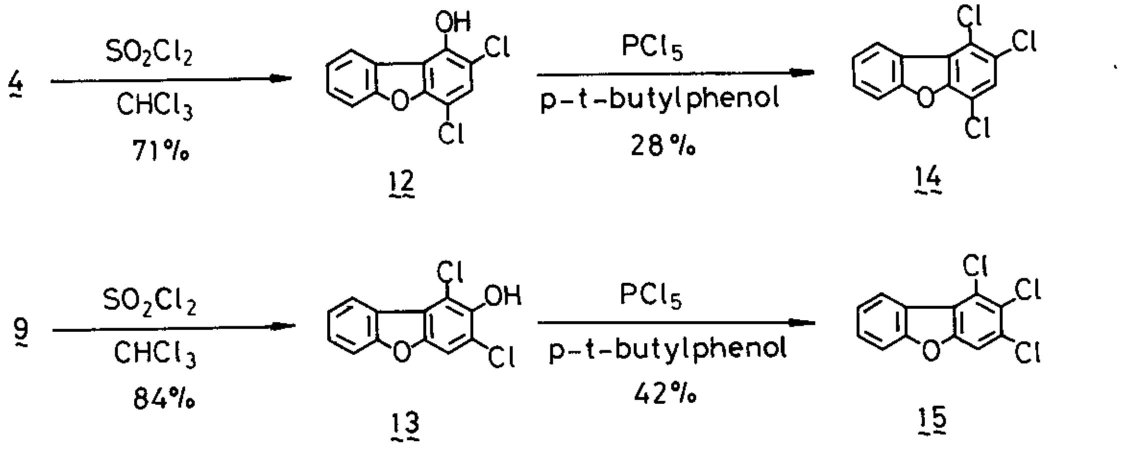
RESULTS AND DISCUSSION

When compounds 4 and 9 were treated with PCl_5 and p-tert-butylphenol according to the reported method,[4] the expected 1-chloro-(10) and 2-chlorodibenzofuran (11) even in very low yields were obtained, respectively.

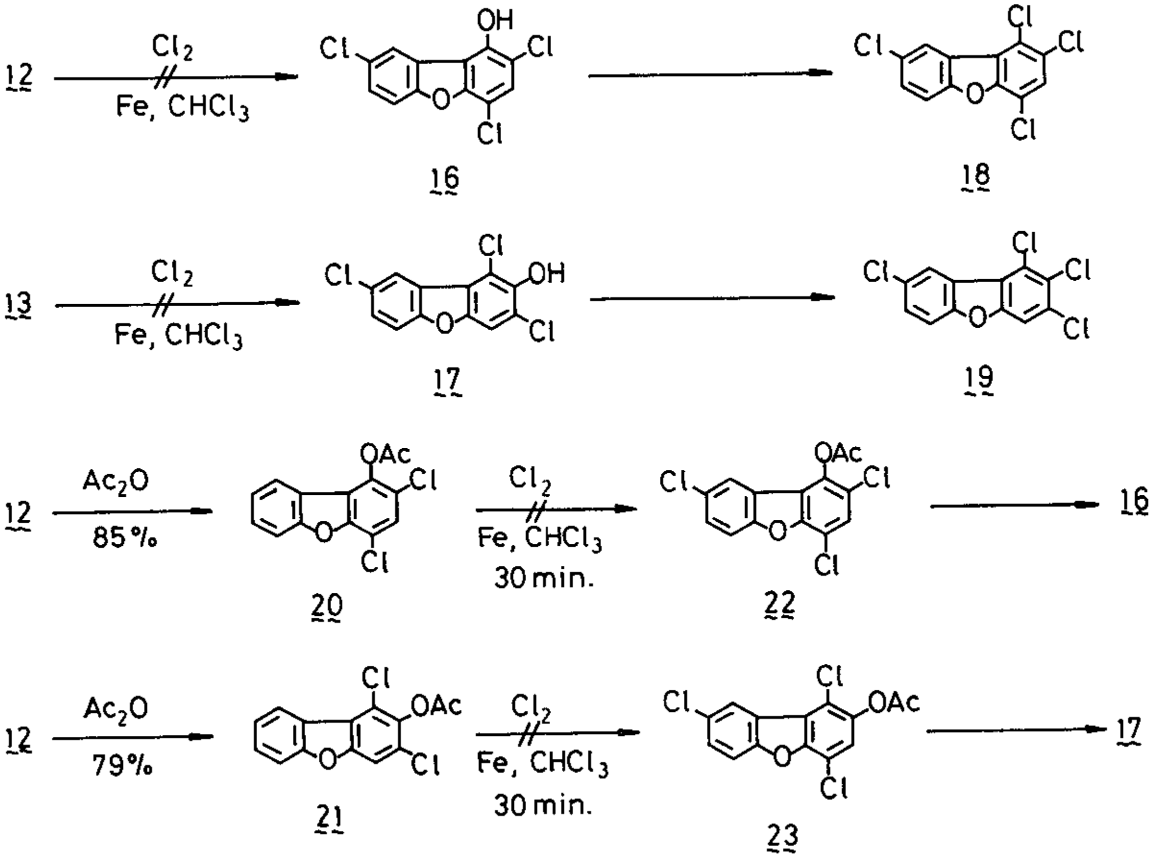


Similar chlorination of 1-hydroxy-2,4-dichloro-(12) and 2-hydroxy-1,3-dichlorodibenzofurans (13), which were easily prepared by treatment of 4 and 9 with sulfuryl chloride, afforded the desired 1,2,4-trichloro-(14) and 1,2,3-trichlorodibenzofurans (15) in 28% and 42% yields, respectively (Scheme 2).

Further chlorination of 12 and 13 with chlorine was attempted in order to obtain tetrachlorodibenzofurans 18 and 19 (Scheme 3). However, the expected chlorinated compounds 16 and 17 were not obtained but only tarry materials and unidentified compounds which might be oxidized compounds were formed. To avoid such oxidation during chlorination, the acetates 20 and 21 were chlorinated with chlorine under similar conditions, however, the expected compounds were not obtained but the starting materials were recovered.



Scheme 2



Scheme 3

All products described above 10, 12, 13, 14, 15, 20 and 21 except 11 were unknown compounds. Preparation of 10, 14 and 15 by this method seems to be of interest because such chlorodibenzofurans can not be synthesized in direct chlorination of dibenzofuran.

EXPERIMENTAL SECTION

All melting points are uncorrected. IR spectra were measured by a Nippon Bunko IR-A spectrophotometer as KBr pellets. ^{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-01SA-2 mass spectrometer at 70 eV with a direct inlet.

Preparation of 1-Chloro-(10) and 2-Chlorodibenzofurans (11). -Typical Procedure-

A mixture of PCl_5 (420 mg, 2 mmol) and p-tert-butylphenol (900 mg, 6 mmol) was heated at 140°C for 4 h and cooled to room temperature. Compound 9 (370 mg, 2 mmol) was added to the above mixture, which was then heated at 280°C for 20 min. The reaction mixture was poured into a large amount of ice-water and extracted with ether. The organic layer was washed with 10% NaOH solution and water. The ether solution was dried over Na_2SO_4 and evaporated in vacuo to leave the residue, which was chromatographed on silica-gel using hexane as an eluent to give 11 as colorless prisms (hexane); yield 41 mg (10%); mp 99.5~101°C (lit.[5] 101~101.5°C); IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 7.29~7.52 (5H, m), 7.82~7.92 (2H, m); mass spectrum, m/e 202, 204 (M^+).

10: This compound was characterized only by GC mass analysis [m/e 202, 204 (M^+)].

Chlorination of Hydroxydibenzofurans. -Typical Procedure-

To a solution of 9 (1.7 g, 10 mmol) in chloroform (70 ml) was added sulfuryl chloride (3.5 g, 26 mmol) and the mixture was stirred for 12 h at room temperature. The reaction mixture was poured into a large amount of water. The organic layer was washed with water, dried with Na_2SO_4 and evaporated in vacuo to leave the residue, which was recrystallized from hexane to give 13 as colorless needles; yield 1.99 g (84%); mp 164.5~166°C; IR (KBr) ν_{OH} 3450 cm^{-1}; NMR ($CDCl_3$) δ 5.78 (s, 1H), 7.24~7.54 (4H, m), 8.19~8.29 (1H, m); mass spectrum, m/e 252, 254, 256 (M^+). Anal. Calcd for $C_{12}H_6O_2Cl_2$: C, 56.95; H, 2.39. Found: C, 56.90; H, 2.54.

12: colorless prisms (hexane); mp 147~148.5°C; IR (KBr) ν_{OH} 3400 cm^{-1}; NMR ($CDCl_3$) δ 6.03 (1H, s), 7.02~7.64 (4H, m), 8.03~8.14 (1H, m); mass spectrum, m/e 252, 254, 256 (M^+). Anal. Calcd for $C_{12}H_6O_2Cl_2$: C, 56.95; H, 2.39. Found: C, 56.72; H, 2.47.

Preparation of Trichlorodibenzofurans (**14** and **15**) from Dichlorohydroxydibenzofurans (**12** and **13**). -Typical Procedure-

A mixture of PCl_5 (265 mg, 1.3 mmol) and p-tert-butylphenol (570 mg, 3.8 mmol) was heated at 140°C for 4 h and cooled to room temperature. Compound **15** (320 mg, 1.3 mmol) was added to the above mixture, which was then heated at 280°C for 20 min. The reaction mixture was poured into a large amount of ice-water and extracted with ether. The organic layer was washed with 10% NaOH solution and water. The ether solution was dried with Na_2SO_4 and evaporated in vacuo to leave the residue, which was chromatographed on silica gel using hexane as an eluent to give **15** as colorless needles (hexane); yield 160 mg (42%); mp 140~140.5°C: IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 7.29~7.60 (4H, m), 8.24~8.36 (1H, m); mass spectrum, m/e 270, 272, 274, 276 (M^+). Anal. Calcd for $C_{12}H_5OCl_3$: C, 53.08; H, 1.86. Found: C, 53.05; H, 1.87.

14: colorless needles (hexane); mp 126~127°C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 7.32 ~7.71 (4H, m), 8.30~8.42 (1H, m); mass spectrum, m/e 270, 272, 274, 276 (M^+). Anal. Calcd for $C_{12}H_5OCl_3$: C, 53.08; H, 1.86. Found: C, 52.87; H, 2.07.

Acetylation of **12** and **13**. -Typical Procedure-

To a solution of **13** (760 mg, 3 mmol) in acetic anhydride (5 ml) was added a drop of conc. H_2SO_4 and the mixture was stirred for 2 h at 80°C. The reaction mixture was poured into water. The formed crystals were collected, washed with water and recrystallized from hexane to give **21** as colorless prisms; yield 750 mg (85%); mp 155.5~156.5°C; IR (KBr) $\nu_{C=O}$ 1770 cm^{-1}; NMR ($CDCl_3$) δ 2.43 (3H, s), 7.25~7.52 (4H, m), 8.16~8.27 (1H, m); mass spectrum, m/e 294, 296, 298 (M^+). Anal. Calcd for $C_{14}H_8O_3Cl_2$: C, 56.98; H, 2.73. Found: C, 57.07; H, 2.86.

20: colorless prisms (hexane); mp 167.5~168.5°C; IR (KBr) $\nu_{C=O}$ 1770 cm^{-1}; NMR ($CDCl_3$) δ 2.55 (3H, s), 7.26~7.81 (5H, m). Anal. Calcd for $C_{14}H_8O_3Cl_2$: C, 56.98; H, 2.73. Found: C, 56.73; H, 2.82.

REFERENCES

1. Part 38. M. Tashiro, Y. Fukuda and T. Yamato, to be published.
2. M. Tashiro, H. Yoshiya and G. Fukata, Synthesis, 495 (1980).
3. M. Tashiro, H. Yoshiya and G. Fukata, Heterocycles, **14**, 1955 (1980).
4. D. G. Coe, H. N. Rydon and B. L. Tonge, J. Chem. Soc., 323 (1957).
5. K. Oita, R. G. Johnson and H. Gilman, J. Org. Chem., **20**, 657 (1955).

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