described for 8. The residue was separated by preparative TLC (silica gel; chloroform–ethyl acetate, 1:2 v/v). From the fraction at $R_f \sim 0.5$ was isolated the isoxazolidine **15** as a white solid after trituration with cold diisopropyl ether: yield 25%; mp 113–114 °C (diisopropyl ether); partial decomposition during TLC accounts for the low yield; ^{1}H NMR $\delta \sim 7.5$ (br s, 1 H, NH), 7.22 (s, 5 H, Ph H), 5.12 (d, 1 H, J = 5.4 Hz, H-5), 3.46 (d, 1 H, J = 5.4 Hz, H-4), 3.31 (s, 3 H, OCH_3), 3.3–2.7 and 2.2–1.8 (m, 4 H, NCH_2), 1.69 (d, 3 H, J = 1.2 Hz, CH_3), 0.83 (t, 6 H, $NCCH_3$); ^{13}C NMR δ 170.5 (s, C=O), 107.0 (d, C-5), 70.5 (s, C-3), 64.9 (d, C-4); mass spectrum, m/e 292.178 (M^+; calcd 292.179).

Anal. Calcd for $C_{16}H_{24}N_2O_3$: C, 65.73; H, 8.27; N, 9.58. Found: C, 65.78; H, 8.30; N, 9.56.

General Procedure for the Oxidation of 1-Hydroxyazetidines to Four-Membered Cyclic Nitrones 1b, 16, and 17 with HgO. The 1-hydroxyazetidine (1 mmol) was added to a suspension of yellow HgO (0.43 g, 2 mmol) in 10 mL of dry dichloromethane. This suspension was stirred at 25 °C for 3 h in the case of **2b** and for 5 h in the case of **3** and **4**. Oxidation of azetidine **2a** was carried out at 30 °C for 24 h. After the reaction was complete, Hyflo was added to the mixture, and the solution was filtered. The dichloromethane was removed under reduced pressure, and the residue was dissolved in acetone (**2b** and **4**) or ethyl acetate (**2a** and **3**) and filtered through Florisil to remove any traces of mercury salts. The filtrate was concentrated under reduced pressure, and in the case of **2b** and **4** the residue was triturated with diisopropyl ether to yield the known cyclic nitrone **1b** in yields of 76% and 73%, respectively.

***N*,*N*-Diethyl-4-cyano-2,3-dihydro-2-methyl-3-phenyl-2-azetecarboxamide 1-oxide (16)** was prepared according to the general procedure from **2a**. The residue was triturated with diisopropyl ether to give **16** as a white solid: yield 80%; mp 119.5–121.5 °C (chloroform/petroleum ether); ^{1}H NMR δ 7.37 (s, 5 H, Ph H), 4.35 (s, 1 H, H-3), 3.5–2.1 (m, 4 H, NCH_2), 2.00 (s, 3 H, CH_3), 0.88 and 0.63 (t, 6 H, $NCCH_3$); ^{13}C NMR δ 163.5 (s, C=O), 118.2 (s, C=N), 108.2 (s, C≡N), 94.0 (s, C-2), 52.5 (d, C-3); mass spectrum, m/e 285.147 (M^+; calcd 285.148).

Anal. Calcd for $C_{16}H_{19}N_3O_2$: C, 67.35; H, 6.71; N, 14.73. Found: C, 67.29; H, 6.64; N, 14.70.

2-[(Diethylamino)methyl]-2,3-dihydro-2,4-dimethyl-3-phenylazete 1-oxide (17) was prepared according to the general procedure from **3** and isolated as a pale yellow oil in a purity of >95%: yield 83%; ^{1}H NMR δ 7.5–7.0 (m, 5 H, Ph H), 3.80 (q, 1 H, J = 1.7 Hz, H-3), 2.60 and 2.33 (AB, 2 H, J = 14.6 Hz, CH_2), 2.3–2.0 (m, 4 H, NCH_2), 2.07 (d, 3 H, J = 1.7 Hz, CH_3), 1.64 (s, 3 H, CH_3), 0.72 (t, 6 H, $NCCH_3$); ^{13}C NMR δ 146.0 (s, C=N), 86.4 (s, C-2), 54.5 (d, C-3), 53.8 (t, CH_2N); mass spectrum, m/e 261.196 ($M^+ + 1$, calcd for $C_{16}H_{25}N_2O$ 261.197).

X-ray Crystal Structure Analysis of 13b. The crystals of **13b** are monoclinic, space group $P2_1/c$. The unit cell dimensions are a = 17.647 (5) Å, b = 14.358 (4) Å, c = 13.943 (4) Å, β = 111.99 (3)°. With eight molecules in the unit cell the calculated density is 1.19 g cm^{-3}. Reflexions were measured by using Mo Kα radiation (Philips PW1100 diffractometer, graphite monochromator, $3 < \theta < 20°$, θ–2θ scan mode, scan speed 0.025° s^{-1}, scan width (θ) 1.3°, total number of reflexions measured 3212). The unit cell contains two independent molecules. The crystal structure determination and refinement was based on 2191 reflexions having a net intensity greater than the standard deviation from counting statistics. The structure was determined by MULTAN[41] and refined by ORFLS.[42] The parameters refined were the scale factor, isotropic extinction parameter, and positional and isotropic thermal parameters of the nonhydrogen atoms (total number of parameters 170). The final R factor was 13.7%. Figure 1 was prepared by ORTEP.[43]

Acknowledgment. We thank Mr. T. W. Stevens for recording the mass spectra and Mrs. J. L. M. Vrielink and Mrs. J. M. Visser for recording the NMR spectra. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

Registry No. 1a, 78602-07-0; **1b**, 75909-31-8; **1c**, 80954-52-5; **2a**, 82238-36-6; **2b**, 82264-40-2; **3**, 83152-70-9; **4**, 82238-35-5; **5a**, 78602-08-1; **5b**, 78602-09-2; **6a**, 83152-71-0; **6b**, 83152-72-1; **7**, 83152-73-2; **8**, 83152-74-3; **9**, 37928-17-9; **13a**, 83152-75-4; **13b**, 83198-86-1; **15**, 83152-76-5; **16**, 82238-37-7; **17**, 83152-77-6.

Supplementary Material Available: Lists of cell parameters, atomic coordinates, thermal parameters, bond distances, and bond angles (4 pages). Ordering information is given on any current masthead page.

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Selective Preparation. 37. Bromination of 2,2′-Dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl and Preparation of Hydroxydibenzofurans[1]

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Treatment of 2,2′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (**3**) with excess bromine in alcohols afforded the 2-alkoxy-1-bromo-4,6,8-tri-*tert*-butyldibenzofurans **6a,b** in 68% and 44% yields, respectively. When compound **6a** was treated with $AlCl_3$ in boiling toluene, 2-hydroxydibenzofuran (**14**) was obtained in 79% yield together with bromotoluenes (**15**) and *tert*-butyltoluenes (**10**). However, at room temperature, this reaction afforded 1-bromo-2-methoxy-4-*tert*-butyldibenzofuran (**16**) in 74% yield. Furthermore, it was found that $AlCl_3$–CH_3NO_2-catalyzed reaction of **6a** in toluene gave 1-bromo-2-methoxy-4,6-di-*tert*-butyldibenzofuran (**17**) in 71% yield together with **10**. From **6a** were obtained 1,2,8-trihydroxy- (**26**) and 1,2,7,8-tetrahydroxydibenzofuran (**27**) in several steps.

It has been previously reported that[3] although oxidation of 2-bromo-4,6-di-*tert*-butylphenol with potassium hexacyanoiron(III) afforded 1,4-dihydro-4-bromo-2,4,6,8-tetra-*tert*-butyl-1-oxodibenzofuran similar oxidation of the

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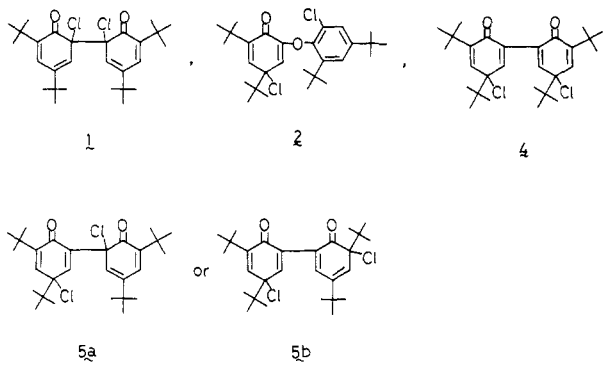
2-chloro analogue gave cyclohexadienones **1** and **2**. On



the other hand, chlorination of 2,2′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (**3**) with sulfuryl chloride gave a mixture of the cyclohexadienones **4** and **5**.[3]

In connection with these studies we have undertaken the bromination of **3** in order to obtain more detailed information on the products as well as the reaction mechanism.

Results and Discussion

Bromination of 2,2′-Dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (3). Bromination of **3** with excess bromine (3.5 mol/mol of **3**) in alcohols such as methanol and ethanol gave the corresponding 1-bromo-2-alkoxy-4,6,8-tri-*tert*-butyldibenzofurans **6** in 68% and 44% yields, respectively, but none of the cyclohexadienones expected in view of the reaction described above.

Bromination of **3** with 0.6 equiv of bromine in methanol afforded 2-methoxy-4,6,8-tri-*tert*-butyldibenzofuran (**7a**) together with a large amount of recovered **3**. It was also found that bromination of **7a** in methanol with bromine produced the expected **6a** in 95% yield. This finding suggests that compound **7a** is an intermediate for the formation of **6a** in the bromination of with excess bromine.

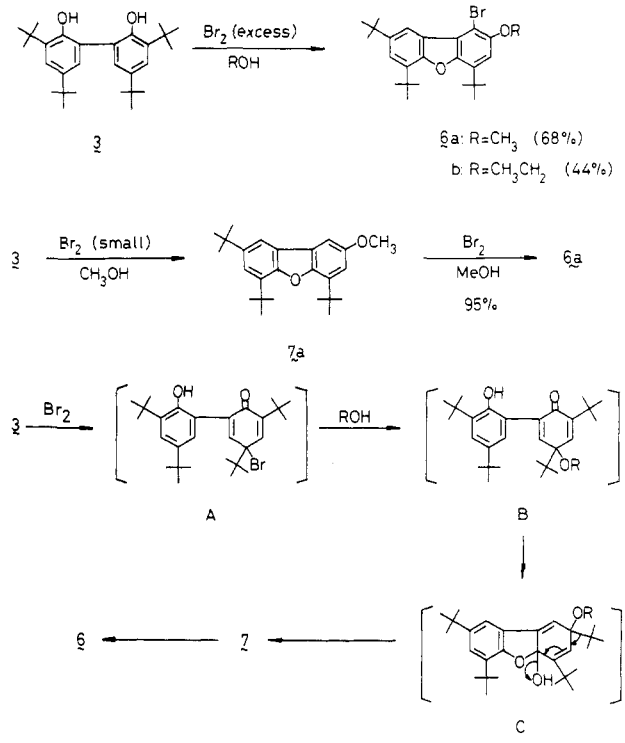
On the basis of these results, the mechanism of formation of **6** from **3** is proposed as shown in Scheme I.

Preparation of Hydroxydibenzofurans. Recently, the *tert*-butyl group has been used as a positional protective function for selective preparation of some aromatic compounds.[4] By this method 1-hydroxy- (**9**) and 1-hydroxy-4-methoxydibenzofuran (**12**) were prepared[3,5] (Scheme II).

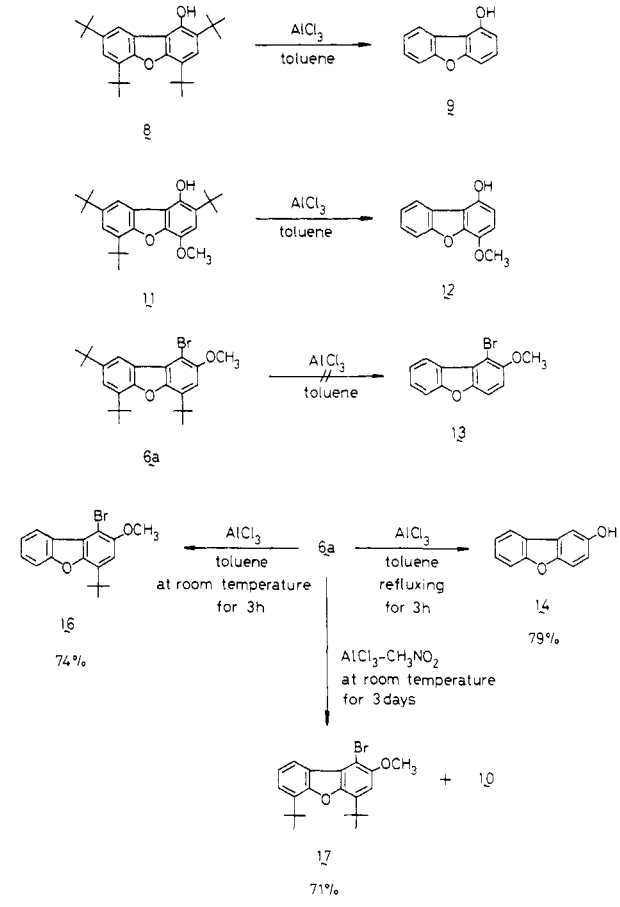
The products of these reactions depended upon the reaction conditions. The expected product **13** was not obtained in all cases. When **6a** was treated with $AlCl_3$ catalyst in boiling toluene for 3 h, the known[6] 2-hydroxydibenzofuran (**14**) was obtained in 79% yield together with *tert*-butyltoluenes (**10**) and bromotoluenes (**15**), but not the expected **13**. The formation of **15** suggests that transbromination occurred in this reaction. The reaction of **6a** with $AlCl_3$ and toluene at room temperature gave 1-bromo-4-*tert*-butyl-2-methoxydibenzofuran (**16**) together with only **10**. The $AlCl_3$–CH_3NO_2 catalyst, which is known to be weaker than $AlCl_3$ itself,[7] gave **17** by cleavage of only one of the *tert*-butyl groups from **6a**.

As mentioned above, the expected compound **13** was not obtained in the transalkylation of **6a**; however, the formation of **14** in only one step from **6a** should be valuable for the synthetic investigation of dibenzofuran chemistry.

Scheme I



Scheme II



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(5) Tashiro, M.; Yoshiya, H.; Fukata, G. *Synthesis* **1980**, 495.

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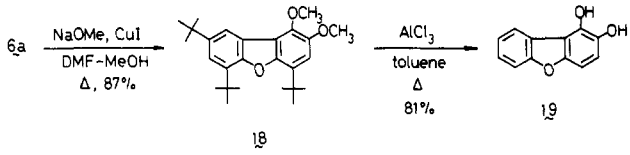
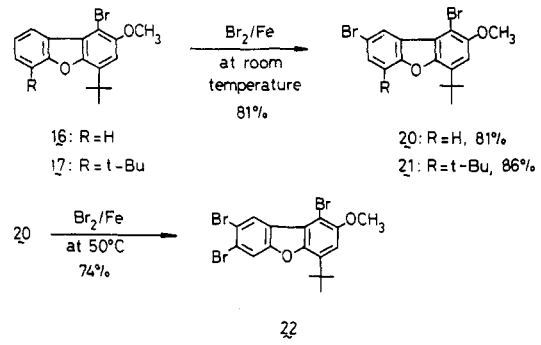
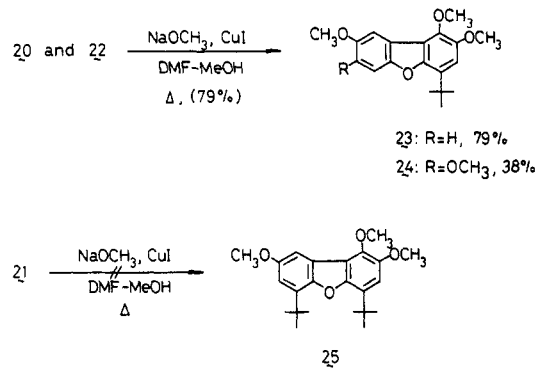
Scheme III



Scheme IV



Scheme V



It is well-known that treatment of aryl halides with NaOR in DMF–MeOH afforded the corresponding alkyl aryl ethers.[8]

$$\mathrm{ArX} + \mathrm{NaOR} \xrightarrow[\text{DMF-MeOH}]{\text{CuI}} \mathrm{ArOR}$$

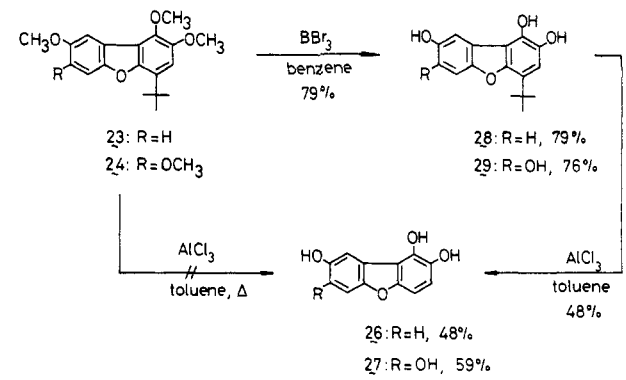
From this fact and results described above, a preparative route for 1,2-dihydroxydibenzofuran (**19**) from **6a** might be expected as shown in Scheme III.

Indeed, the expected **19** was obtained in good yield. This suggests that hydroxydibenzofurans might be easily prepared from the corresponding bromo derivatives by same manner. So bromination of **16** and **17** was carried out in order to obtain the corresponding bromo derivatives, and the results are summarized in Scheme IV.

The bromination of both **16** and **17** in the presence of Fe powder at room temperature afforded the expected dibromides **20** and **21** in good yields, respectively. At 50 °C, bromination of **20** under the same conditions gave the tribromide **22**.

Although treatment of **20** and **22** with $NaOCH_3$ in DMF–MeOH afforded the corresponding trimethoxy (**23**) and tetramethoxy derivatives (**24**), respectively, similar treatment of **21** did not give the expected product **25**, but the starting material **21** was recovered in almost quantitative yield (Scheme V). Unfortunately, it is not yet clear why such a difference was obtained.

Scheme VI



The $AlCl_3$-catalyzed transalkylation of **23** and **24** was carried out in order to obtain the corresponding trihydroxy- (**26**) and tetrahydroxydibenzofuran (**27**). Although these reactions gave only a mixture of the complex reaction products, the transalkylation of **28** and **29**, prepared by treatment of **23** and **24** with BBr_3 in benzene, yielded the expected **26** and **27**, respectively (Scheme VI).

Although compounds **19**, **26**, and **27** were unstable, they could be converted easily to the corresponding stable acetates **30–32** by treatment with acetic anhydride.

The structures of all compounds presented in this work were confirmed by their spectral data, elemental analyses, and the chemical conversions described above.

Experimental Section

All melting points are uncorrected. IR spectra were measured by a Nippon Bunko IR-A spectrometer as KBr pellets. ^1H 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-O1SG-2 mass spectrometer at 75 eV with a direct inlet. Gas chromatographic analyses were carried out by means of a Yanagimoto Yanaco G-180 (30% high-vacuum silicon grease; 2 m; carrier gas, helium at 50 mL/min).

Preparation of 1-Bromo-2-methoxy-4,6,8-tri-*tert*-butyldibenzofuran (6a). A suspension of **3** (20 g, 48.8 mmol) in methanol (500 mL) was heated to reflux until **3** had completely dissolved and allowed to cool to room temperature. A solution of bromine (27 *g*, 169 mmol) in methanol (10 mL) was added slowly to the mixture. After the mixture was stirred for 1 h at room temperature, the precipitate formed was filtered off, washed with methanol, and then dried. Recrystallization from methanol gave **6a**: colorless plates; yield 14.78 g (68%); mp 138–140 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.44, 1.57, 1.59 (each 9 H, s), 3.99 (3 H, s), 7.05 (1 H, s), 7.52, 8.57 (each 1 H, d, J = 2 Hz); mass spectrum, m/e 444, 446 (M^+).

Anal. Calcd for $C_{25}H_{33}O_2Br$: C, 67.41; H, 7.47. Found: C, 67.26; H, 7.51.

Preparation of 1-Bromo-2-ethoxy-4,6,8-tri-*tert*-butyldibenzofuran (6b). To a solution of **3** (2.05 g, 5 mmol) in ethanol (50 mL) was added a solution of bromine (2.8 g, 17.5 mmol) in ethanol (2 mL). After being stirred for 1 h at room temperature, it was worked up as described above to give **6b**: colorless plates (ethanol); yield 1.01 g (44%); mp 139.5–140.5 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.44, 1.56, 1.59 (each 9 H, s), 1.53 (3 H, t, J = 6 Hz), 4.15 (2 H, q, J = 6 Hz), 6.97 (1 H, s), 7.43, 8.48 (each 1 H, d, J = 2.5 Hz); mass spectrum, m/e 458, 460 (M^+).

Anal. Calcd for $C_{26}H_{35}O_2Br$: C, 67.97; H, 7.68. Found: C, 68.12; H, 7.74.

Bromination of 3 with a Small Amount of Bromine in Methanol. A solution of bromine (500 mg, 3 mmol) in methanol (2 mL) was added slowly to a solution of **3** (2.05 g, 5 mmol) in methanol (50 mL). After being stirred for 1 h at room temperature, the reaction mixture was evaporated in vacuo to leave a

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residue. The residue was crystallized from methanol to give the mixture of **7a** and **3**, which were detected by GC analysis.

7a: colorless prism (methanol); mp 161–162.5 °C (lit.[9] mp 162–163 °C).

Bromination of 7a in Methanol. To a solution of **7a** (510 mg, 1.4 mmol) in methanol (15 mL) was added slowly a solution of bromine (300 mg, 1.9 mmol) in methanol (2 mL). After being stirred for 30 min at room temperature, the reaction mixture was evaporated in vacuo to leave the residue, which was crystallized from methanol to give **6a**, yield 590 mg (95%).

Preparation of 2-Hydroxydibenzofuran (14). To a solution of **6a** (1.5 g, 3.4 mmol) in dry toluene (60 mL) was added finely powdered $AlCl_3$ (4 g, 30 mmol). After being stirred at reflux temperature for 3 h, it was poured into a large amount of ice–water and extracted with 10% aqueous NaOH solution. The alkaline extract was acidified with 10% aqueous HCl solution and extracted with benzene. The benzene solution was dried over Na_2SO_4 and evaporated in vacuo to leave a residue, which was recrystallized from hexane to give **14**: colorless needles; yield 490 mg (79%); mp 133.5–134.5 °C (lit.[6] mp 134 °C); IR (KBr) ν_{OH} 3250 cm^{-1}; NMR ($CDCl_3$) δ 4.8 (1 H, br), 6.98 (1 H, dd, J = 8.5, 2.5 Hz), 7.24–7.65 (5 H, m), 7.84–7.97 (1 H, m); mass spectrum, m/e 184 (M^+). *tert*-Butyltoluenes (**10**) and bromotoluenes (**15**) were detected by GC analysis.

Preparation of 1-Bromo-4-*tert*-butyl-2-methoxydibenzofuran (16). To a solution of **6a** (1.5 g, 3.4 mmol) in dry toluene (60 mL) was added finely powdered $AlCl_3$ (1.2 g, 9 mmol) at room temperature. After the reaction mixture was stirred for 3 h, it was poured into a large amount of ice–water and extracted with benzene. The benzene solution was dried over Na_2SO_4 and evaporated in vacuo to leave a residue, which was crystallized from hexane to give crude **16**: colorless prisms (hexane); yield 830 mg (74%); mp 150–151 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.55 (9 H, s), 3.97 (3 H, s), 7.06 (1 H, s), 7.26–7.71 (3 H, m), 8.58–8.72 (1 H, m); mass spectrum, m/e 332, 334 (M^+).

Anal. Calcd for $C_{17}H_{17}O_2Br$: C, 61.27; H, 5.14. Found: C, 61.19; H, 5.18.

Preparation of 1-Bromo-4,6-di-*tert*-butyl-2-methoxydibenzofuran (17). To a solution of **6a** (1.5 g, 3.4 mmol) in dry toluene (60 mL) was added a solution of $AlCl_3$ (1.35 g, 10.1 mmol) in nitromethane (3 mL) at room temperature. After the reaction mixture was stirred for 3 days, it was poured into a large amount of ice–water and extracted with benzene. The benzene solution was dried over Na_2SO_4 and evaporated in vacuo to leave the residue, which was crystallized from methanol to give crude **17**: colorless plates (methanol); yield 930 mg (71%); mp 148.5–149.5 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.56 (18 H, s), 3.95 (3 H, s), 6.98 (1 H, s), 7.24–7.43 (2 H, m), 8.46 (1 H, dd, J = 7.5 Hz); mass spectrum, m/e 388, 390 (M^+).

Anal. Calcd for $C_{21}H_{25}O_2Br$: C, 64.78; H, 6.47. Found: C, 64.53; H, 6.50.

Preparation of 4,6,8-Tri-*tert*-butyl-1,2-dimethoxydibenzofuran (18). To 15 mL of methanol was added slowly 0.8 g (34.8 mmol) of sodium. To the solution were added **6a** (4.45 g, 11.2 mmol), CuI (1.3 g, 6.8 mmol), and DMF (15 mL). After being stirred for 5 h at reflux temperature, the reaction mixture was poured into a large amount of water. The precipitate formed was filtered off and washed with water. The precipitate was extracted with ether, dried over Na_2SO_4, and evaporated in vacuo to leave a residue, which was recrystallized from methanol to give **18**: colorless prisms; yield 3.85 g (87%); mp 140.5–141.5 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.43, 1.55, 1.59 (each 9 H, s), 3.96, 4.08 (each 3 H, s), 7.03 (1 H, s), 7.48, 8.08 (each 1 H, d, J = 2 Hz); mass spectrum, m/e 396 (M^+).

Anal. Calcd for $C_{26}H_{36}O_3$: C, 78.84; H, 9.15. Found: C, 78.85; H, 9.25.

Preparation of 1,2-Dihydroxydibenzofuran (19). To a solution of **18** (1.98 g, 5 mmol) in dry toluene (70 mL) was added finely powdered $AlCl_3$ (2.70 g, 20 mmol). After being stirred at reflux temperature for 2 h, it was poured into a large amount of ice–water and extracted with ether. The ether solution was washed with water, dried over Na_2SO_4, and evaporated in vacuo to leave the residue, which was crystallized from hexane to give crude **19**: colorless prisms (hexane); yield 810 mg (81%); mp 141–142.5 °C; IR (KBr) ν_{OH} 3450 cm^{-1}; NMR ($CDCl_3$) δ 4.62, 5.88 (each 1 H, br), 6.93 (2 H, s), 7.22–7.55 (3 H, m), 8.02–8.13 (1 H, m); mass spectrum, m/e 200 (M^+).

Anal. Calcd for $C_{12}H_8O_3$: C, 71.99; H, 4.03. Found: C, 72.03; H, 4.11.

Bromination of 16. To a solution of **16** (16.6 g, 50 mmol) in carbon tetrachloride (400 mL) were added Fe powder (4 g) and bromine (9.5 g, 59 mmol) at room temperature. After being stirred for 20 min, it was poured into 5% aqueous $Na_2S_2O_3$ solution and extracted with chloroform. The chloroform solution was dried over Na_2SO_4 and evaporated in vacuo to leave a residue, which was recrystallized from hexane to give **20**: colorless needles; yield 16.7 g (81%); mp 232–233.5 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.53 (9 H, s), 3.96 (3 H, s), 7.01 (1 H, s), 7.40 (1 H, d, J = 8 Hz), 7.57 (1 H, dd, J = 8, 2 Hz), 8.66 (1 H, d, J = 2 Hz); mass spectrum, m/e 410, 412, 414 (M^+).

Anal. Calcd for $C_{17}H_{16}O_2Br_2$: C, 49.54; H, 3.91. Found: C, 49.65; H, 3.94.

Bromination of 17. Compound **17** was treated and worked up as described above to give **21**: 86% yield; colorless needles (hexane–benzene); mp 250.5–251 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.55, 1.56 (each 9 H, s), 3.95 (3 H, s), 7.02 (1 H, s), 7.47, 8.57 (each 1 H, d, J = 2 Hz); mass spectrum, m/e 466, 468, 470 (M^+).

Anal. Calcd for $C_{21}H_{24}O_2Br_2$: C, 53.87; H, 5.17. Found: C, 54.06; H, 5.21.

Bromination of 20. To a solution of **20** (9.3 g, 22.6 mmol) in carbon tetrachloride (200 mL) were added Fe powder (2 g) and bromine (4.3 g, 27 mmol) at 50 °C. After being stirred for 40 min, it was worked up as described above to give **22**: colorless needles (hexane); yield 8.2 g (74%); mp 234–235.5 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.51 (9 H, s), 3.93 (3 H, s), 7.00 (1 H, s), 7.82 (1 H, s), 8.73 (1 H, s); mass spectrum, m/e 488, 490, 492, 494 (M^+).

Anal. Calcd for $C_{17}H_{15}O_2Br_3$: C, 41.58; H, 3.08. Found: C, 41.41; H, 3.12.

Preparation of 4-*tert*-Butyl-1,2,8-trimethoxydibenzofuran (23). To 80 mL of methanol was added slowly 4.36 g (0.19 mmol) of sodium. To the solution were added **20** (2.55 g, 6.2 mmol), CuI (1.4 g, 7.3 mmol), and DMF (80 mL). After being stirred for 15 h at reflux temperature, the reaction mixture was poured into a large amount of water and extracted with benzene. The benzene solution was washed with water, dried over Na_2SO_4, and evaporated in vacuo to leave a residue, which was recrystallized from hexane to give **23**: colorless prisms; yield 1.54 g (79%); mp 76.5–77.5 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.53 (9 H, s), 3.84 (3 H, s), 3.89 (3 H, s), 4.05 (3 H, s), 6.95 (1 H, dd, J = 8, 2.5 Hz), 6.97 (1 H, s), 7.37 (1 H, d, J = 8 Hz), 7.61 (1 H, d, J = 2.5 Hz); mass spectrum, m/e 314 (M^+).

Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.69; H, 7.09.

Preparation of 4-*tert*-Butyl-1,2,7,8-tetramethoxydibenzofuran (24). To a solution of sodium (1.93 g, 84 mmol) in methanol (30 mL) were added **22** (0.92 g, 1.9 mmol), CuI (0.64 g, 3.4 mmol), and DMF (20 mL). After being stirred for 1 day at reflux temperature, the reaction mixture was worked up as described above to give **24**: colorless prisms (hexane); yield 250 mg (38%); mp 65–66 °C; IR (KBr) ν_{OH} none; NMR ($CDCl_3$) δ 1.52 (9 H, s), 3.92, 3.95, 3.97 (each 3 H, s), 6.89 (1 H, s), 7.09 (1 H, s), 7.54 (1 H, s); mass spectrum, m/e 344 (M^+).

Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.77; H, 7.00.

Preparation of 4-*tert*-Butyl-1,2,8-trihydroxydibenzofuran (28). To a solution of **23** (1.56 g, 5 mmol) in benzene (60 mL) was added a solution of BBr_3 (13 g, 53 mmol) in benzene (10 mL) at room temperature. After being stirred for 1 h, it was poured into a large amount of ice–water and extracted with ether. The ether solution was washed with water, dried over Na_2SO_4, and evaporated in vacuo to leave a residue, which was recrystallized from benzene to give **28**: colorless needles; yield 1.06 g (79%); mp 178–181 °C dec; IR (KBr) ν_{OH} 3310 cm^{-1}; NMR (Me_2SO-d_6) δ 1.41 (9 H, s), 6.76 (1 H, dd, J = 8.5, 2.5 Hz), 6.80 (1 H, s), 7.33 (1 H, d, J = 8.5 Hz), 7.41 (1 H, d, J = 2.5 Hz), 8.90 (2 H, br), 9.14 (1 H, br); mass spectrum, m/e 272 (M^+).

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.82; H, 5.94.

(9) Becker, H. D. *J. Org. Chem.* **1969**, *34*, 1198.

Preparation of 4-*tert*-Butyl-1,2,7,8-tetrahydroxydibenzofuran (29). To a solution of **24** (0.7 g, 2 mmol) in benzene (30 mL) was added a solution of BBr_3 (7.1 g, 28 mmol) in benzene (5 mL) at room temperature. After being stirred for 1 h, it was worked up as described above to give **29**: colorless needles (benzene); yield 435 mg (76%); mp 235–238 °C dec; IR (KBr) ν_{OH} 3400 cm^{-1}; NMR (Me_2SO-d_6) δ 1.43 (9 H, s), 6.70 (1 H, s), 6.91 (1 H, s), 7.38 (1 H, s), 8.78 (4 H, br); mass spectrum, m/e 288 (M^+).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.66; H, 5.63.

Preparation of 1,2,8-Trihydroxydibenzofuran (26). To a solution of **28** (500 mg, 1.8 mmol) in dry toluene (50 mL) was added finely powdered $AlCl_3$ (1.7 g, 12.7 mmol) at room temperature. After being stirred for 1 h, it was poured into a large amount of ice–water and extracted with ether. The ether solution was washed with water, dried over Na_2SO_4, and evaporated in vacuo to leave a residue, which was crystallized from hexane to give crude **26**: colorless needles (benzene); yield 190 mg (48%); mp 230–240.5 °C dec; IR (KBr) ν_{OH} 3400 cm^{-1}; NMR (Me_2SO-d_6) δ 6.77 (1 H, dd, J = 8.5, 2.5 Hz), 6.78 (1 H, d, J = 8.5 Hz), 6.88 (1 H, d, J = 8.5 Hz), 7.29 (1 H, d, J = 8.5 Hz), 7.39 (1 H, d, J = 2.5 Hz), 9.04 (1 H, br), 9.18 (1 H, s), 9.19 (1 H, br); mass spectrum, m/e 216 (M^+).

Preparation of 1,2,7,8-Tetrahydroxydibenzofuran (27). To a solution of **29** (290 mg, 1 mmol) in dry toluene (40 mL) was added finely powdered $AlCl_3$ (1.1 g, 8 mmol) at room temperature. After being stirred for 2 h, it was worked up as described above to give **27**: colorless needles (benzene); yield 137 mg (59%); mp ca. 250 °C dec; IR (KBr); 3320 cm^{-1}; NMR (Me_2SO-d_6) δ 6.75 (2 H, s), 6.88 (1 H, s), 7.35 (1 H, s), 8.89, 8.96, 9.02, 9.15 (each 1 H, s); mass spectrum, m/e 232 (M^+).

Acetylation of 19. Typical Procedure. A solution of **19** (500 mg, 2.5 mmol) in acetic anhydride (5 mL) was heated at 80 °C for 3 h. The reaction mixture was poured into ice–water, and the precipitate formed was filtered off and washed with water. The precipitate was recrystallized from hexane to give **30**: colorless needles; yield 560 mg (79%); mp 133.5–134.5 °C; IR (KBr) ν_{OH} none, $\nu_{C=O}$ 1770–1750 cm^{-1}; NMR ($CDCl_3$) δ 2.32, 2.46 (each 3 H, s), 7.17–7.57 (5 H, m), 7.68–7.78 (1 H, m); mass spectrum, m/e 284 (M^+).

Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.26. Found: C, 67.69; H, 4.29.

31: colorless needles (hexane–benzene); yield 83%; mp 199–201 °C; IR (KBr) ν_{OH} none, $\nu_{C=O}$ 1770–1745 cm^{-1}; NMR ($CDCl_3$) δ 2.31, 2.33, 2.46 (each 3 H, s), 7.05–7.56 (5 H, m); mass spectrum, m/e 342 (M^+).

Anal. Calcd for $C_{18}H_{14}O_7$: C, 63.16; H, 4.12. Found: C, 62.94; H, 4.15.

32: colorless needles (hexane–benzene); yield 82%; mp 203–204.5 °C; IR (KBr) ν_{OH} none, $\nu_{C=O}$ 1775–1760 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (9 H, s), 2.46 (3 H, s), 7.24 (1 H, d, J = 8 Hz), 7.43 (1 H, d, J = 8 Hz), 7.44 (1 H, s), 7.56 (1 H, s); mass spectrum, m/e 400 (M^+).

Anal. Calcd for $C_{20}H_{16}O_9$: C, 60.00; H, 4.03. Found: C, 59.91; H, 3.98.

Registry No. **3**, 6390-69-8; **6a**, 77139-38-9; **6b**, 77139-39-0; **7a**, 19566-63-3; **14**, 86-77-1; **16**, 77139-41-4; **17**, 77139-40-3; **18**, 83025-50-7; **19**, 83025-51-8; **20**, 83025-52-9; **21**, 83025-53-0; **22**, 83025-54-1; **23**, 83025-55-2; **24**, 83025-56-3; **26**, 83025-59-6; **27**, 83025-60-9; **28**, 83025-57-4; **29**, 83025-58-5; **30**, 83025-61-0; **31**, 83025-62-1; **32**, 83025-63-2.

Synthesis and Chemistry of 2,2,5,5-Tetramethylthiolane-3,4-dione. A Route to Bicyclo[2.1.0]pentyl-1-sulfonium Intermediates

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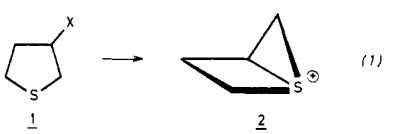
The reaction of sodium sulfide with 2,5-dibromo-2,5-dimethylhexane-3,4-dione affords in good yield 2,2,5,5-tetramethylthiolane-3,4-dione (**3a**). This material has been converted to a variety of derivatives, including 2,2,5,5-tetramethyl-3-diazothiolane-4-one (**3b**) and the corresponding sulfone derivative. Compound **3b** on treatment with electrophiles undergoes rapid substitution by the electrophile at the diazo carbon. The reaction of **3b** with bromine was shown, however, to follow an indirect course involving the formation of a bicyclo[2.1.0]pentyl-1-sulfonium ion as probable intermediate; this is opened reversibly by attack of bromide at sulfur at lower temperature, whereas irreversible attack at carbon adjacent to carbonyl occurs at higher temperatures. Evidence for an ylidic variant of the 1-thiabicyclo[2.1.0]pentyl structure was obtained from the thermal decomposition of **3b**. No trace of a Wolff rearrangement product was obtained. In contrast, the sulfone **18**, derived from **3b** by oxidation, on thermolysis afforded 3,3-dimethyl-4-(2-propenyl)oxathiolan-5-one 2-oxide (**47**). This product was shown, by means of trapping experiments, to arise from the ketene derived by normal Wolff rearrangement of **18** without participation of sulfur. Various other transformations, including 1,3-dipolar cycloadditions, of **3b** and other derivatives, were investigated.

Introduction

Reorganizations of the carbon skeleton of a suitably functionalized thiolane (**1**) could be triggered through bicyclo[2.1.0]pentyl-1-sulfonium intermediates (**2**), obtained by sulfur participation in departure of a leaving group (eq 1). There have been, however, few synthetic



1 2 (1)

applications of the route shown in eq 1.[1] This is all the more remarkable because in other cyclic and alicyclic systems participation of sulfur β to a leaving group leading to a thiiranium ion is a common event.[2] The attractive-

(1) Such intermediates have been invoked in, for example, the solvolysis of the addition product of sulfur dichloride to 1,4-cyclohexadiene: Corey, E. J.; Block, E. *J. Org. Chem.* **1966**, *31*, 1663. Kinetic evidence for the generation of bicyclic thiiranium intermediates has also been obtained from solvolysis studies of some sulfur-containing steroids: Tsuji, T.; Komeno, K.; Itani, H.; Tanida, H. *J. Org. Chem.* **1971**, *36*, 1648. There is also evidence for a stable bicyclo[2.1.0]pentyl-1-sulfonium ion: Černý, J. V.; Poláček, J. *Collect. Czech. Chem. Commun.* **1966**, *31*, 1831. We thank a referee for this latter reference.

(2) Streitwieser, Jr., A. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962.

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