

Baker Laboratory, Cornell University

## Benzodioxoles, Naphthodioxins and Dibenzodioxepins

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The preparation of five-, six- and seven-membered ring oxygen heterocycles containing O-M-O grouping where M = silicon (1-6), germanium (4, 5, 7) and tin (3, 7-9) by various routes from aromatic diols has been reported from this Laboratory. This communication describes the synthesis of the hitherto unknown carbon analogues of these systems, including the first report of the spiro-ring system bis(2,2'-biphenylenedioxy)methane (10).

The phosphorus pentoxide promoted condensation of dihydric phenols with ketones (11) was found to give high yields of product for the alkyl-substituted heterocycles. 2,2'-Biphenylenediphenylmethane was obtained from the dichloromethane in pinene (12). The product crystallizes directly from pinene on the steam bath soon after the onset of an exothermic reaction accompanied by many changes in color and opacity of the solution (13). 1,8-Naphthalenedioxydiphenylmethane was prepared similarly. 2,2'-Dihydroxybiphenyl and thiophosgene reacted in aqueous sodium carbonate to liberate carbon dioxide and precipitate 2,2'-biphenylenethionocarbonate. Heating the thionocarbonate (m. p. 83.5-85.0°) *in vacuo* resulted in its conversion to the spiro-derivative (m. p. 339.5-340.0°). The analogous spiro-silicon (1,4) and germanium (4, 7) heterocycles are also high melting (m. p. 315 and 340° respectively). This novel condensation apparently proceeds in preference to the

Schönberg rearrangement (14),  $\text{ROCOR} \xrightarrow{\Delta} \text{ROCSR}$ , known to occur on heating diphenylthionocarbonate, and lends weight to the suggestion that the rearrangement proceeds via a cyclic transition state (15) which would be impossible to form in the biphenylene case.

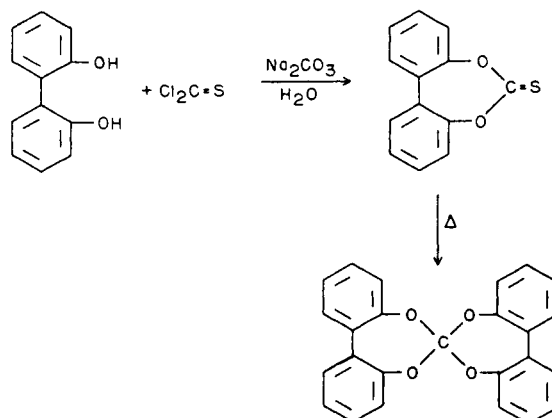
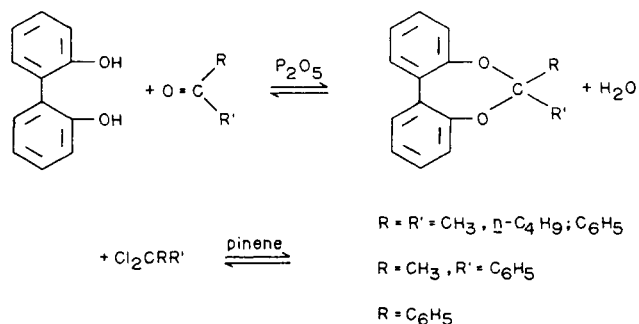
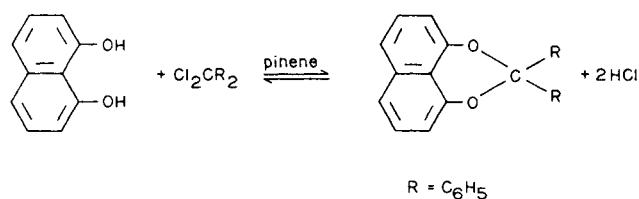
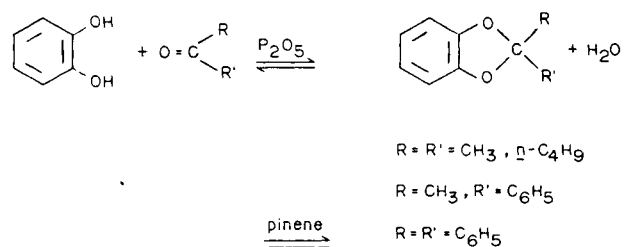
The proposed structures are consistent with infrared and n.m.r. spectra and analytical data. The thionocarbonate exhibits the two strong bands in the 1370-1280  $\text{cm}^{-1}$  region said to be characteristic of

the  $\text{-OCO}$  grouping (16), which disappear on heating *in vacuo*.

## EXPERIMENTAL (17)

*o*-Phenylenedioxydi-*n*-butylmethane.

5-Nonanone (0.035 mole) was heated with an equimolar amount of catechol to 80°. Phosphorus pentoxide (0.4 mole) was added in portions over 0.25 hour with rapid shaking. The solution darkened as the temperature rose. At the conclusion of the reaction (ca. 0.5 hour) the brown mixture was poured into 10% sodium carbonate solution and steam distilled. The product separated on standing from the distilland



as an orange oil and was distilled at 145-146°/18 mm and 134-135°/8 mm,  $n_D^{20} = 1.4875$ . The infrared spectrum contained prominent absorptions at 1460s, 1220s, 1140m, 1080m, 1040m, 1000m, 820m, 785m and 730s  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{15}\text{H}_{22}\text{O}_2$ : C, 76.87; H, 9.46; Mol. Wt., 234. Found: C, 76.97; H, 9.65; Mol. Wt., 228.

#### *o*-Phenylenedioxyethylphenylmethane.

Acetophenone (1.0 mole) was treated similarly with catechol at 90°. The product separated as a yellow oil from the steam distillate and was fractionated at 154.0-155.0°/15 mm;  $n_D^{20} = 1.5715$ . The infrared spectrum contained prominent absorptions at 1460s, 1220s, 900s, 920sh, 865m, 800m, 765s, 730m and 695  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{14}\text{H}_{12}\text{O}_2$ : C, 79.22; H, 5.70; Mol. Wt., 212. Found: C, 79.42; H, 5.79; Mol. Wt., 214.

#### *o*-Phenylenedioxydimethylmethane (11).

This compound (b.p., 178.0-179.0°/750 mm;  $n_D^{20} = 1.5040$ ) was prepared similarly from acetone. The infrared spectrum contained prominent absorptions at 1460s, 1220s, 970m, 838m, 815m and 735s  $\text{cm}^{-1}$ .

#### 2,2'-Biphenylenedioxydi-*n*-butylmethane.

A solution of 2,2'-dihydroxydiphenyl and 5-nonanone (0.176 mole of each) was treated similarly at 80° with excess phosphorus pentoxide. Some 5-nonanone was recovered on steam distillation of the neutralized reaction mixture. The product separated from the distillate and was distilled using a steam-heated column heat at 158°/1 mm to give a white solid, melting point 56.8-57.0°. Final purification was achieved through slow sublimation at 84° *in vacuo*. The infrared spectrum contained prominent absorptions at 1240s, 1200m, 1040m, 960m, 755m, 715m and 508m  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{21}\text{H}_{26}\text{O}_2$ : C, 81.24; H, 8.44; Mol. Wt., 310. Found: C, 81.33; H, 7.90; Mol. Wt., 307.

#### 2,2'-Biphenylenedioxyethylphenylmethane.

Acetophenone was treated similarly with 2,2'-dihydroxydiphenyl (0.4 mole of each) at 75° with excess phosphorus pentoxide. Steam distillation recovered a trace of acetophenone and left a tan residue. Recrystallization from petroleum ether-ethanol gave white plates, m.p. 100.3-100.5°. Final purification was accomplished through slow sublimation at 94° *in vacuo*. The infrared spectrum contained prominent absorptions at 1240s, 1190m, 1125s, 1010s, 930m, 945m, 905m, 753s, 765m, 720m and 700s  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{O}_2$ : C, 83.30; H, 5.59; Mol. Wt., 288. Found: C, 83.42; H, 5.60; Mol. Wt., 287.

#### 2,2'-Biphenylenedioxydimethylmethane.

This compound, prepared previously by transketalization (18), was obtained from acetone, m.p. 75.2-76.0°. The infrared spectrum contained prominent absorptions at 1240s, 1190s, 1195sh, 1120m, 970m, 890m, 810m, 760s, 765s, 715m, and 550m  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{15}\text{H}_{14}\text{O}_2$ : C, 79.60; H, 6.20; Mol. Wt., 226. Found: C, 79.57; H, 6.31; Mol. Wt., 234.

#### 1,8-(Naphthalenedioxy)diphenylmethane.

To 1,8-dihydroxynaphthalene (0.03 mole) at 93° dissolved in 55 ml. of pinene and 75 ml. of benzene was added dichlorodiphenylmethane (0.03 mole) dropwise with stirring under a nitrogen atmosphere. The brown solution of diol in benzene became red immediately upon addition. The reaction was allowed to continue for seven hours between 85° and 95°, then cooled overnight. A red solid separated upon cooling in ice and was collected and sublimed twice (m.p. 204-205°). The infrared spectrum contained prominent absorptions at 1620s, 1065m, 945s, 875m, 862s, 800s, 815sh, 745m and 568  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{23}\text{H}_{16}\text{O}_2$ : C, 85.10; H, 4.97; Mol. Wt., 324. Found: C, 85.05; H, 4.89; Mol. Wt., 320.

#### 2,2'-Biphenylenedioxydiphenylmethane.

This compound, previously prepared by transketalization (18), was obtained similarly and recrystallized from ethanol to give white crystals, m.p. 169.5-169.6°. The infrared spectrum contained prominent absorptions at 1240s, 1190s, 1210s, 1100m, 1050m, 1020s, 995m, 960m, 765s, 755sh, 725m, 710m, 695m and 650m  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{25}\text{H}_{18}\text{O}_2$ : C, 85.70; H, 5.17; Mol. Wt., 350. Found: C, 85.69; H, 5.20; Mol. Wt., 352.

#### *o*-Phenylenedioxydiphenylmethane.

This compound, (m.p. 93.0-93.2°), was prepared in analogous fashion in pinene. The infrared spectrum contained prominent absorptions at 1240s, 1050m, 1015m, 950m, 940sh, 915m, 810m, 780m, 738s, 750sh and 695s  $\text{cm}^{-1}$ .

#### 2,2'-Biphenylenethionocarbonate.

2,2'-Dihydroxybiphenyl (0.217 mole) was placed with sodium carbonate (0.43 mole) in 400 ml. of water and thiophosgene (0.217 mole) added dropwise under nitrogen with vigorous stirring. An ice bath was used to dissipate the heat evolved and stirring was continued for three hours. The pink precipitate was filtered, washed with 500 ml. of water, and subjected to Soxhlet extraction with benzene. Pale orange crystals from the benzene were dried at 56° *in vacuo* and sublimed to give a sulfur-containing white solid at 90° *in vacuo* (m.p. 83.5-85.0°). The infrared spectrum contained prominent absorptions at 1450m, 1295s, 1265s, 1245m, 1200sh, 1175sh, 1150s, 1095m, 775sh, and 765s  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{13}\text{H}_8\text{O}_2\text{S}$ : C, 68.40; H, 3.53; Mol. Wt., 228. Found: C, 69.35; H, 3.88; Mol. Wt., 226.

#### Bis(2,2'-biphenylenedioxy)methane.

2,2'-Biphenylenethionocarbonate was heated for a prolonged period in the absence of air to give an evil-smelling liquid in the cold trap. Sublimation of the white solid residue at 240° *in vacuo* gave sulfur-free, white crystals, m.p. 339.5-340.0°, whose infrared spectrum lacked the characteristic thiocarbonyl absorptions but contained prominent absorption bands at 1450m, 1200m, 1160sh, 1120s, 1070s, 1040m, 760s and 720m  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{25}\text{H}_{18}\text{O}_4$ : C, 79.93; H, 4.25. Found: C, 79.63; H, 5.87.

#### Acknowledgment.

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