[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# A Synthesis of Homologs of Dioxane

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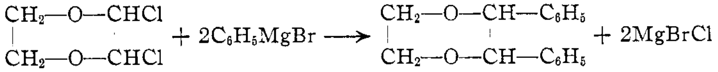
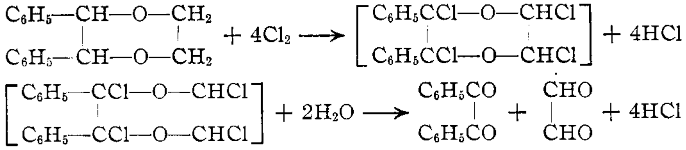
**A. Diphenyldioxane.**—The excellent work on the chlorination of dioxane by Böeseken and his co-workers[1] provides a convenient starting material for a synthesis of the homologs of dioxane. 2,3-Dichlorodioxane is readily obtained in large yield by chlorination of dioxane. As the two chlorine atoms which it contains are alpha to oxygen atoms, they should be reactive to the Grignard reagent. This was found to be the case. Two moles of phenylmagnesium bromide react smoothly with one mole of 2,3-dichlorodioxane to yield 60% of the 2,3-diphenyldioxane.



$$\begin{array}{l} CH_2\text{—}O\text{—}CHCl \\ | \qquad\qquad | \\ CH_2\text{—}O\text{—}CHCl \end{array} + 2C_6H_5MgBr \longrightarrow \begin{array}{l} CH_2\text{—}O\text{—}CH\text{—}C_6H_5 \\ | \qquad\qquad | \\ CH_2\text{—}O\text{—}CH\text{—}C_6H_5 \end{array} + 2MgBrCl$$

The structure of the product was proved by chlorination and hydrolysis to benzil.



$$\begin{array}{l} C_6H_5\text{—}CH\text{—}O\text{—}CH_2 \\ \qquad\quad | \qquad\quad | \\ C_6H_5\text{—}CH\text{—}O\text{—}CH_2 \end{array} + 4Cl_2 \longrightarrow \left[\begin{array}{l} C_6H_5CCl\text{—}O\text{—}CHCl \\ \quad | \qquad\qquad | \\ C_6H_5CCl\text{—}O\text{—}CHCl \end{array}\right] + 4HCl$$

$$\left[\begin{array}{l} C_6H_5\text{—}CCl\text{—}O\text{—}CHCl \\ \qquad\quad | \\ C_6H_5\text{—}CCl\text{—}O\text{—}CHCl \end{array}\right] + 2H_2O \longrightarrow \begin{array}{c} C_6H_5CO \\ | \\ C_6H_5CO \end{array} + \begin{array}{c} CHO \\ | \\ CHO \end{array} + 4HCl$$

The intermediate tetrachlorodiphenyldioxane was not isolated, but its formation was indicated by the hydrolysis products, benzil and glyoxal, which were identified.

**B. Tetrachlorodioxanes.**—In a previous note[2] we confirmed the results of Butler and Cretcher on the symmetrical tetrachlorodioxane, m. p. 143–144°, and also on the unsymmetrical product, b. p. 93–95° at 11–12 mm. In addition we obtained a new symmetrical tetrachlorodioxane of m. p. 70°. This gave two molecular equivalents of glyoxal-*p*-nitrophenylosazone after hydrolysis with water and treatment with *p*-nitrophenylhydrazine.

**C. Catecholdioxane.**—The catechol derivative of dichlorodioxane which we mentioned previously[2] has since been described by Böeseken.[3] He also has obtained only one isomer whereas two would be predicted on the basis of the condensation with glycol. However, in the majority of condensations described so far, only one isomer is obtained, so that glycol is the exception rather than the rule. This might be explained by assuming that the 2,3-dichlorodioxane is not a mixture of *cis* and *trans* isomers but rather the pure *cis* isomer.

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[1] Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931).

[2] Summerbell and Christ, THIS JOURNAL, **54**, 3777 (1932).

[3] Böeseken, Tellegen and Henriquez, *ibid.*, **55**, 1284 (1933).

## Experimental

**I. Diphenyldioxane.**—(a) An ethereal solution of the phenylmagnesium bromide was prepared in the usual manner using 16 g. of magnesium, 104 g. of phenyl bromide and 300 cc. of ether; 52 g. of dichlorodioxane dissolved in 100 cc. of ether was then added slowly over a period of one and one-half hours. The reaction mixture was decomposed with water at 0° and enough sulfuric acid added to dissolve the magnesium hydroxide. The ether layer was separated and the ether distilled off. The viscous liquid remaining could not be crystallized. Upon distillation under reduced pressure the liquid solidified in the condenser. After three crystallizations from petroleum ether 48 g. of pure product was obtained, m. p. 49°, yield 60%.

*Anal.* Calcd.: mol. wt., 240; C, 80; H, 6.67. Found: mol. wt., 231; C, 79.75; H, 6.66.

(b) **Proof of Structure.**—6.1 g. of diphenyldioxane was chlorinated for a period of twenty-four hours at a temperature of 125°. The mixture was then hydrolyzed by boiling with water. The resulting product was extracted with petroleum ether and 1.6 g. of benzil finally crystallized out, m. p. 95°. A mixed m. p. with an authentic specimen gave 95°. A small amount of the diphenyldioxane was recovered. On treating the water solution from the hydrolysis with phenylhydrazine a very slight amount of the osazone of glyoxal was obtained, m. p. 167–168°, mixed m. p. 167°.

**II. Tetrachlorodioxanes.**—One hundred grams of the 2,3-dichlorodioxane was chlorinated for a period of twenty hours at a temperature of 115°. The product was distilled under reduced pressure; 52 g. of dichlorodioxane was recovered and 38 g. of the liquid unsymmetrical tetrachlorodioxane of b. p. 93–95° at 11–12 mm. described by Butler and Cretcher was obtained. Upon cooling the last fractions from the distillation a solid mass of crystals was obtained. Upon fractional crystallization using petroleum ether, 15 g. of the needle-like crystals of the symmetrical tetrachlorodioxane of Butler and Cretcher having a m. p. of 143° was obtained. Using very slow crystallization about 4 g. of a new symmetrical product of m. p. 70° was obtained. It had a crystalline form entirely different from the needles mentioned above and could easily be separated by picking out by hand. The crystals are large, flat and slightly elongated and are apparently orthorhombic and occur in aggregates.

*Anal.* Calcd. for $C_4H_4O_2Cl_4$: mol. wt., 226; Cl, 62.81. Found: mol. wt., 232; Cl, 62.86.

Upon decomposing 0.3550 g. with water in a sealed tube and treating with *p*-nitrophenylhydrazine, 1.01 g. of the *p*-nitrophenylosazone was obtained.

## Summary

1. A new synthesis of 2,3-disubstituted dioxanes is reported.
2. 2,3-Diphenyldioxane is described for the first time.
3. A new symmetrical tetrachlorodioxane was obtained.

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