collected: $n^{20}D$ 1.4632; $d^{20}_4$ 1.2115; *MR* (obsd.), 31.05; *MR* (calcd.), 31.24.

*Anal.* Calcd. for $C_5H_9O_2Cl$: C, 43.92; H, 6.63; Cl, 25.93. Found: C, 43.76; H, 6.75; Cl, 25.88.

**Hydrolysis of 4-Chloromethyl-1,3-dioxane.**—A solution of 20 g. of 2,4-dinitrophenylhydrazine in 800 cc. of approximately 2 *N* hydrochloric acid was prepared and 14 g. of 4-chloromethyl-1,3-dioxane warmed with this solution on a steam-bath for one hour. A voluminous precipitate of formaldehyde-2,4-dinitrophenylhydrazone was formed. After recrystallization from alcohol this melted at 166° either alone or mixed with an authentic sample. The liquid was set aside at room temperature for three days for the precipitation to be complete. The precipitate was collected and the filtrate was made just alkaline with aqueous sodium hydroxide. The solution was evaporated to dryness on a steam-bath. The solids were extracted with 300 cc. of dry acetone, dried over anhydrous potassium carbonate and distilled to evaporate the solvent. The residue, which was colored red, was distilled under reduced pressure to yield 5 g. of a liquid, b. p. 50° (1 mm.); $n^{20}D$ 1.4486; $d^{20}_4$ 1.090. It had an ether-like smell, was miscible with water, alcohol and ether and did not contain any chlorine. The physical properties agreed with those reported for **3-hydroxytetrahydrofuran.** Parisielle[4] reported the following physical constants: $n^{18}D$ 1.4478; $d^{18}$ 1.07.

*Anal.* Calcd. for $C_4H_8O_2$: C, 54.53; H, 9.04. Found: C, 54.44; H, 9.14.

**The phenylurethan** was recrystallized twice from carbon tetrachloride and twice from 50% ethanol; m. p. 120.6° (lit.[2] m. p. 120°).

**Preparation of 3-Hydroxytetrahydrofuran.**—4-Chloromethyl-1,3-dioxane (137 g.), 100 cc. of absolute methanol and 18 g. of concentrated sulfuric acid were placed in a flask fitted with a 60-cm. air-condenser which was connected to another water-cooled condenser set downward for distillation. The flask was heated gently to allow the liquid to reflux very slowly. Methylal (b. p. 42°) started to collect in the receiver attached to the second condenser. After adding 35 g. of sodium acetate, the liquid was heated to boiling and filtered. The filtrate was distilled first at 20 mm. to remove the methyl alcohol and acetic acid. Further fractionation at 0.5 mm. yielded 40 g. of 3-hydroxytetrahydrofuran, b. p. 46–48° (0.5 mm.), and 25 g. of another liquid which was evidently the unstable 4-chloro-1,3-butylene glycol, b. p. 90–95° (0.5 mm.).

The second fraction was dehydrohalogenated to 3-hydroxytetrahydrofuran by refluxing for half an hour with 50 cc. of pyridine and 100 cc. of diisopropyl ether. The ether and the pyridine were removed by distillation. The residue was fractionated at 1 mm. The fraction boiling between 49–50° (16 g.) was collected.

**Acetolysis of 4-Chloromethyl-1,3-dioxane.**—Ten drops of concentrated sulfuric acid were added to a mixture of 68 g. of 4-chloromethyl-1,3-dioxane and 52 cc. of acetic anhydride. There was considerable heat evolved. The mixture was heated on a steam-bath for six hours and allowed to stand at room temperature overnight. It was then shaken with 2 g. of sodium acetate, filtered and distilled at 20 mm. Two principal fractions were collected, one up to 140° (20 g.) and the other between 140–142° (86 g.). The latter proved to be the diacetate of 2-oxa-3-chloromethyl-1,5-pentanediol: $n^{20}D$ 1.4474; $n^{20}_4$ 1.196; *MR* (calcd.), 53.58; *MR* (obsd.), 53.38.

*Anal.* Calcd. for $C_9H_{15}O_5Cl$: C, 45.29; H, 6.34; Cl, 14.87; sapn. equiv., 119.4. Found: C, 45.34; H, 6.14; Cl, 14.80; sapn. equiv., 122.0.

The first fraction appeared to be a mixture of methylene diacetate, the diacetate of 4-chloro-1,3-butylene glycol and the diacetate of 2-oxa-3-chloromethyl-1,5-pentanediol.

**Attempted Replacement of Chlorine.**—Since the chloromethyldioxane is a primary alkyl chloride, it was surprising to find it so resistant for replacement reactions. Attempts to replace the chlorine by cyanide using boiling alcoholic sodium cyanide, sodium cyanide in ethyl carbitol at 100° and cuprous cyanide in boiling benzene failed, since a major part of the starting material was recovered unchanged in each case. A similar result was obtained in attempting to replace the chlorine by iodine using sodium iodide in boiling acetone.

DEPARTMENT OF CHEMISTRY
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RECEIVED APRIL 10, 1950

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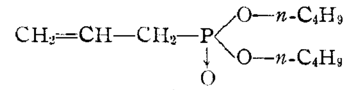
# Anomalous Reaction of Allyl Bromide with Sodium Dibutyl Phosphite

BY WALTER H. C. RUEGGEBERG, JACOB CHERNACK AND IRA M. ROSE

During the course of preparation of some alkane dibutyl phosphonates from alkyl halides and sodium dibutyl phosphite, it was desired to prepare dibutyl-1-propene-3-phosphonate (I) from allyl bromide.

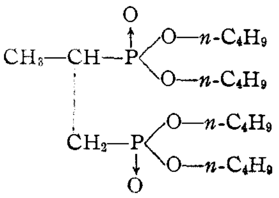


$$CH_2{=}CH{-}CH_2{-}\underset{\overset{\downarrow}{O}}{P}\begin{matrix}\diagup O{-}n\text{-}C_4H_9\\ \diagdown O{-}n\text{-}C_4H_9\end{matrix}$$

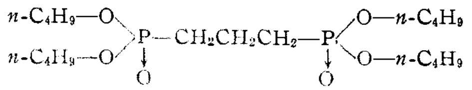
(I)

It has already been shown in the published literature by Kosolapoff[1] that the *n*-alkane phosphonic acid esters can be prepared in good yield by this type of reaction. However, when one mole of allyl bromide was added to one mole of sodium dibutyl phosphite in benzene solution, the reaction mixture yielded a high boiling compound which from analytical results was clearly one containing two phosphorus atoms per allyl unit.

It is believed that the compound formed is either propane bis-(dibutyl phosphonate)-1,2 (II) or propane bis-(dibutyl phosphonate)-1,3 (III).



II



$$\begin{matrix}n\text{-}C_4H_9{-}O\diagdown\\ n\text{-}C_4H_9{-}O\diagup\end{matrix}\underset{\overset{\downarrow}{O}}{P}{-}CH_2CH_2CH_2{-}\underset{\overset{\downarrow}{O}}{P}\begin{matrix}\diagup O{-}n\text{-}C_4H_9\\ \diagdown O{-}n\text{-}C_4H_9\end{matrix}$$

III

## Experimental

The apparatus used for the synthesis of the unexpected diphosphonic acid ester consisted of an all glass still equipped with a 1-l., 3-neck round-bottom flask as still kettle (bearing a dropping funnel and stirring device), a 24-inch column packed with $^1/_8$-inch glass helices and a total reflux-partial take off fractionation head protected from atmospheric moisture by means of a calcium chloride trap. One mole of sodium methoxide (purity 98.5% obtained from the Mathieson Alkali Works) and 500 ml. of C. P. benzene were placed in the kettle and heated to re-

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[4] Parisielle, *Ann. chim.*, [8] **24**, 367 (1911).

[1] Kosolapoff, THIS JOURNAL, **67**, 1180 (1945); U. S. Patent **2,397,422**.

flux. A small amount of methanol was removed at the head of the column as an azeotropic mixture with benzene. Subsequently, one mole of dibutyl hydrogen phosphite (b. p. 103–104° at 6.5 mm.) was added to the hot mixture and methanol was removed at the head of column again as an azeotrope with benzene (b. p. 58–59°). Analysis of the distillate showed that only 75–80% of the theoretical amount of methanol could be recovered in this way. The clear benzene solution of sodium dibutyl phosphite was allowed to cool to room temperature and one mole of freshly distilled allyl bromide was added dropwise over a period of 1.5 hours to the benzene solution with stirring keeping the temperature between 50–60°. A precipitate of sodium bromide appeared five minutes after the addition of allyl bromide had begun. After addition was complete, the mixture was heated at 60° for an additional 2.5 hours. The cooled reaction mixture was poured into 500 ml. of water, the benzene layer separated and washed again with 150 ml. of water. The benzene layer was again separated and benzene together with residual water were removed by distilling at normal pressure.

The residual yellowish-orange liquid was fractionated and yielded the diphosphonate as the main fraction (96 g.) boiling at 231–232° at 7 mm. pressure which possessed the following characteristics: $n^{20}_D$, 1.4495; $d^{20}_4$, 1.028; *MR* calcd., 111.44; *MR* found, 111.90; mol. wt. calcd. for either II or III, 428.5; mol. wt. found, 409. *Anal.* Calcd. for $C_{19}H_{42}O_6P_2$: C, 53.3; H, 9.8; P, 14.5. Found: C, 53.2; H, 9.9; P, 14.7.

TECHNICAL COMMAND
ARMY CHEMICAL CENTER, MARYLAND

RECEIVED JUNE 2, 1950

## Structure of the Silver Perchlorate–Benzene Complex[1]

BY R. E. RUNDLE AND JEANNE H. GORING

Benzene acts as a Lewis base under a number of circumstances, but it is as yet unknown whether the acid is bonded to one carbon, or by $\pi$-bonds, to two, or as more often suggested,[2] equally to six carbons. The problem is interesting due to possible implications in organic reaction mechanisms.[3] We have examined the silver perchlorate–benzene complex to aid in settling this question.

Crystals, $AgClO_4 \cdot C_6H_6$, prepared by crystallization of $AgClO_4$ from benzene, are orthorhombic, $a_0 = 7.96$, $b_0 = 8.34$, $c_0 = 11.7$ Å., $\rho_{obsd.} = 2.4$, $Z = 4$, space group Cmcm, Cmc or C2cm. Patterson and, subsequently, Fourier projections on (100), (010) and (001) have been made. On Fouriers, carbon and oxygen peaks are resolved, leading to the structure of Fig. 1, based on Cmcm. Ag and Cl are in 4(c) with $y_{Ag} = 0.04$, $y_{Cl} = 0.44$. Benzene centers are in 4(a) with the normal to the ring making an angle of about 40° with $c_0$. Bond lengths C–C and Cl–O appear normal. The complete structure, after refinement, will be published elsewhere.

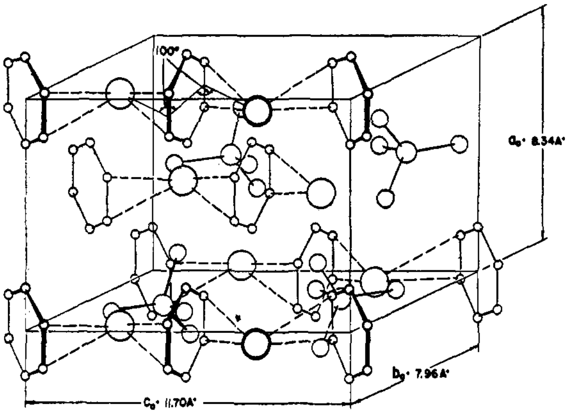

Fig. 1.—Structure of the silver perchlorate–benzene complex.

Definite, though weak, Ag–benzene interactions are indicated by Ag–C distances of 2.6 Å., leading to an electron density of 0.15 pair per bond by Pauling's rule and radii.[4] Each silver is bonded equally to two carbons of each of two rings, lying above and below the rings, suggesting $\pi$-bonding. The perchlorates are pushed away from one side of $Ag^+$ to make room for benzene.

Benzene may act differently with other Lewis acids or with $Ag^+$ in solution. But if the silver positions in the crystals are influenced by the availability of $\pi$-electrons from benzene, as appears to be the case, then the axial position cannot be materially more favorable than a position over two carbon atoms, and it may be considerably less favorable.

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[1] Paper No. 106 from the Institute for Atomic Research and the Department of Chemistry, Iowa State College, Ames, Iowa. Work performed in the Ames Laboratory, Atomic Energy Commission.

[2] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

[3] See, for example, the speculation of M. Dewar in "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949.

[4] L. Pauling, THIS JOURNAL, **69**, 542 (1947).

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RECEIVED JUNE 16, 1950

## A Methoxyl-containing Lignin-like Component of the Mold *Trametes Pini*[1]

BY WALTER J. SCHUBERT AND F. F. NORD

Information on the occurrence of lignin in fungi is scanty, and it has been stated that definite proof for the presence of true lignin in fungi is not available. However, since lignin is characteristically resistant to concentrated mineral acids, residues obtained in this way from fungi have arbitrarily been considered as "lignin," without supporting analytical data. For example, 25% of the weight of the mycelium of *Polyporus fomentarius* was designed as "lignin,"[2a] although this material did not contain the characteristic methoxyl groups.[2b] Similarly, high percentages of fuming HCl-resistant "lignin-like" materials, have been claimed to be present in certain "bracket" fungi,[3] but no methoxyl determinations were reported on the products. On

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[1] For the previous communication of this series, see reference (5b). Contribution No. 202 from the Department of Organic Chemistry and Enzymology, Fordham Univ.

[2] F. O. Kucher, Dissertation, München, 1929. Cited by L. Kalb in G. Klein's "Handbuch der Pflanzenanalyse," Springer, Wien, 1932, (a) Vol. III, No. 1, p. 191; (b) *ibid.*, p. 201.

[3] C. Thom and M. Phillips, *J. Wash. Acad. Sci.*, **22**, 237 (1932).