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: $n^{20}\text{D}$, 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

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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 π-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., $\rho_{\text{obsd.}} = 2.4$, $Z = 4$, 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 $y_{\text{Ag}} = 0.04$, $y_{\text{Cl}} = 0.44$. 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.

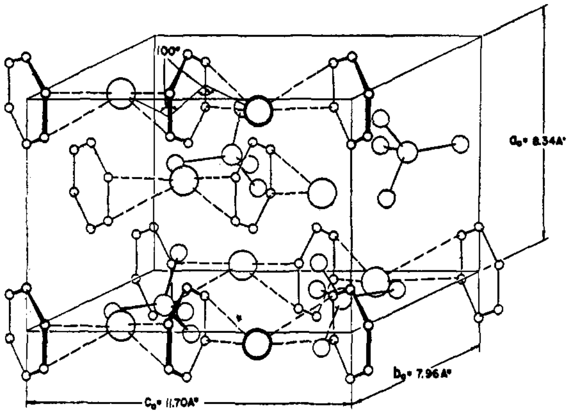

Fig. 1.—Structure of the silver perchlorate–benzene complex.

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 π-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 π-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).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

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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).