disagreement with the adjacent charge rule.[4] Since the P–S distance is considerably less than the double bond value of 1.95 Å., and since the P–O distance is also considerably shorter than the single bond value of 1.76 Å.,[3] it is probable that structure III represents to the first approximation the bonding arrangements, with considerable contributions of structures such as IV and V. Structures such as I and II probably do not contribute appreciably since these would tend to increase the P–S distance to the single bond value. It would appear that structure V must contribute to the resonance system if the shortening of the P–S bond below the double bond value is to be explained simply. Structures VI and VII could also result in a shortening of the P–S distance by a formal charge effect.

A comparison of the P=O and P=S distances in various other phosphorus compounds is instructive.

Compound	P=O	Compound	P=S
P_4O_{10}	1.39[2]	$P_4O_6S_4$	1.85
$POCl_3$	1.58[5]	$PSCl_3$	1.94[6]
$POFCl_3$	1.54[5]		
POF_2Cl	1.55[5]		
POF_3	1.56[5]		

It is evident from the above table that the P=O and P=S bond type in P_4O_{10} and $P_4O_6S_4$, respectively, is different from that in the phosphoryl and thiophosphoryl halides, and the inclusion of structure V may be considered justifiable.

(4) Pauling and Brockway, This Journal, **59**, 13 (1937).
(5) Brockway and Beach, ibid., **60**, 1836 (1938).
(6) Beach and Stevenson, J. Chem. Phys., **6**, 75 (1938).

The O–P–O valence angle of 101.5° is close to the value of the phosphorus angle in several other compounds, the decrease below the tetrahedral value of 109°28′ being explainable by a greater degree of p orbital character than in normal sp^3 tetrahedral bonds. The change of the O–P–O angle from 99° in $P_4O_6{}^2$ to 101.5° in $P_4O_6S_4$ and P_4O_{10} indicates that increasing the coördination of the phosphorus atom from three to four tends to make the valence angles become more like those of the tetrahedral $PO_4{}^{---}$.

Acknowledgment.—The author wishes to acknowledge the helpful criticisms of Professor Linus Pauling.

Summary

The structure of $P_4O_6S_4$ has been determined by electron diffraction in the gas phase. The molecule consists of four P atoms at (a, a, a), (a, ā, ā), (ā, ā, a), and (ā, a, ā); six O atoms at (±b, 0, 0), (0, ± b, 0), and (0, 0, ± b); and four S atoms at (c, c, c), (c, c̄, c̄), (c̄, c̄, c) and (c̄, c, c̄). The valence angles and the principal interatomic distances are: P–O = 1.61 ± 0.02 Å., P–S = 1.85 ± 0.02 Å., P–P = 2.85 ± 0.03 Å., O–P–O = 101.5 ± 1°, P–O–P = 123.5 ± 1°, and O–P–O = 116.5 ± 1°. Single-double bond and double-triple bond resonance is considered to be the cause of the shortening of the P–O and P–S bond distances below the single and double bond values, respectively.

Structure of Gossypol. XIX.[1] Synthesis of 1,2-Dihydroxy-3-isopropyl-6-benzoic Acid

BY ROGER ADAMS AND MADISON HUNT

By the vigorous action of hydrobromic acid on gossic (I) or apogossypolic acid (II),[2] a dihydroxy isopropyl benzoic acid is obtained which might be, on the basis of formula I for gossic acid, the 6-, 5-, or 4-carboxylic acid (II, III, or IV) of 1,2-dihydroxy-3-isopropylbenzene.

If the postulated formula for apogossypolic acid (V), however, is correct, then the structure

(1) For previous paper see Adams, Hunt and Morris, This Journal, **60**, 2972 (1938).
(2) Adams, Morris, Butterbaugh and Kirkpatrick, ibid., **60**, 2191 (1938).

with the carboxyl group in the 6-position (II) is excluded since both gossic and apogossypolic acids degrade to the same product.

In order to confirm this assumption, the synthesis of 1,2-dihydroxy-3-isopropyl-6-benzoic acid (II) has been undertaken. The dihydroxy acid was not identical with the dihydroxy monobasic acid obtained from gossic or apogossypolic acid. Thus, it may be deduced that the dihydroxy monocarboxylic acid from the natural source has either formula III or IV.
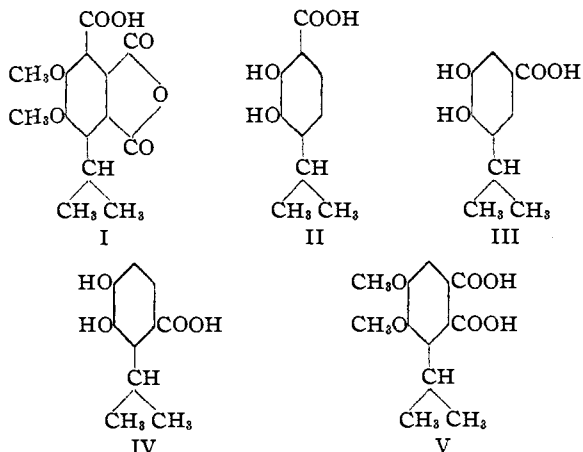
The 1,2-dihydroxy-3-isopropyl-6-benzoic acid was prepared from 1,2-dimethoxy-3-isopropylbenzene (VI)[1] by conversion to the lithium derivative (VII), carboxylation to the acid (VIII) and demethylation to the dihydroxy compound (II).
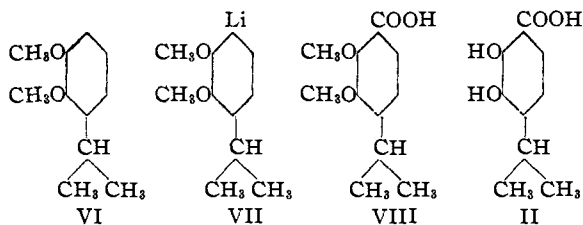
Butyllithium proved to be satisfactory for conversion of compound VI to VII. Since anisole and its derivatives or analogs[3] are converted by the action of alkyl- or aryllithium to lithium derivatives with the metal ortho to the ether linkage and since no exception to this orientation has been reported, the assumption that formula VII is correct for the compound obtained from 1,2-di-

(3) Wittig, Pockels and Dröge, *Ber.*, **71**, 1903 (1938); **72**, 89 (1939); For analogous sodium derivatives see Challenger and Miller, *J. Chem. Soc.*, 894 (1938); Gilman and Begg, THIS JOURNAL, **61**, 106, 109 (1939).

methoxy-3-isopropylbenzene (VI) is entirely justified. The 6-position for the carboxyl group is thus established.

Experimental

1,2-Dimethoxy-3-isopropyl-6-benzoic Acid.—A solution of 1.8 g. of *n*-butyl chloride in 8 cc. of dry ether was refluxed for two hours with 0.28 g. of lithium. To the butyllithium thus formed was added a solution of 1.8 g. of 1,2-dimethoxy-3-isopropylbenzene[1] in 10 cc. of dry benzene. The reaction mixture was heated to distil off the ether and then refluxed for five hours. An excess of dry-ice was then added. After an hour, the mixture was poured into cold dilute hydrochloric acid. The benzene layer was separated and extracted with aqueous sodium bicarbonate. The alkaline solution was acidified with hydrochloric acid and an oil separated which solidified on standing; yield, 0.32 g. It was purified by crystallization from aqueous ethanol and then sublimed at 120° (4 mm.) as white crystals, m. p. 72–73° (corr.).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.26; H, 7.20. Found: C, 63.93; H, 7.33.

1,2-Dihydroxy-3-isopropyl-6-benzoic Acid.—A suspension of 0.025 g. of 1,2-dimethoxy-3-isopropyl-6-benzoic acid in 2 cc. of 48% aqueous hydrobromic acid was refluxed for an hour. The mixture was cooled and the solid filtered and dried; yield, 0.014 g. This product was purified by several crystallizations from a mixture of ether and petroleum ether (b. p. 60–110°) as white crystals, m. p. 153° (corr.).

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.19; H, 6.17. Found: C, 60.96; H, 6.27.

Summary

1,2-Dimethoxy-3-isopropyl-6-benzoic acid was prepared by treatment of 1,2-dimethoxy-3-isopropylbenzene with butyllithium and carbonation of the product. Demethylation gave 1,2-dihydroxy-3-isopropyl-6-benzoic acid. This latter product proved not to be identical with the dihydroxy monocarboxylic acid obtained by the action of hydrobromic acid on gossic or apogossypolic acid.