were prepared and the cell was filled in a glove bag or drybox filled with argon. Spectral grade solvents were used. In order to obtain spectra in the gas phase, the compounds were transferred by expansion into an evacuated quartz cell of 10-mm path length, fitted with a stopcock and conical joint.

Preparation of Compounds.—Most of the trivalent vinyl derivatives used in this study were prepared by treating the corresponding alkylhalophosphines and -arsines with vinylmagnesium bromide or vinyllithium. Standard procedures were followed.[14-16] The alkyldivinylarsines were prepared by the reaction of divinyliodoarsine with the appropriate alkylmagnesium bromide. Divinylheptafluoropropylarsine was prepared by the reaction of divinyliodoarsine and heptafluoropropyl iodide in the presence of mercury, following the procedure of Cullen.[17]

Divinyliodoarsine was prepared by heating a mixture of tributylvinyltin and arsenic triiodide at 130° for 24 hr, following a procedure similar to that used in the preparation of divinylbromoarsine.[15] Oxidation of the trivalent compounds was accomplished in hexane or dioxane solution by heating at 50° with manganese dioxide for 24 hr.[16]

All compounds and intermediates prepared in this study gave the correct analyses for carbon and hydrogen (and halogen where appropriate). The correct ratio of vinyl to alkyl hydrogens was established with nmr spectroscopy. The boiling points and analyses for the vinyl derivatives used in this study are given in Table II.

Registry No.—$(CH_3)_2AsC_2H_3$, 13652-14-7; $(C_2H_2)_5$-AsC_2H_3, 13652-15-8; n-$(C_4H_9)_2AsC_2H_3$, 13652-16-9; $CH_3As(C_2H_3)_2$, 13652-17-0; $C_2H_5As(C_2H_3)_2$, 13652-18-1; n-$C_4H_9As(C_2H_3)_2$, 13699-66-6; n-$C_3F_7As(C_2H_3)_2$, 13652-19-2; $(C_2H_3)_3As$, 13652-20-5; $(C_2H_5)_2PC_2H_3$, 13652-21-6; n-$(C_4H_9)_2PC_2H_3$, 13652-22-7; C_2H_5P-$(C_2H_3)_2$, 13652-23-8; n-$(C_4H_9)P(C_2H_3)_2$, 13652-24-9; $(C_2H_3)_3P$, 3746-01-8; $(C_2H_5)_2As(O)C_2H_3$, 2234-92-6; n-$C_4H_6As(O)(C_2H_3)_2$, 13652-27-2; n-$(C_4H_9)_2P(O)C_2H_3$, 4569-33-9; $(C_2H_3)_3PO$, 13699-67-7.

Acknowledgment.—Acknowledgment is made to the Research Corporation for a Frederick Gardner Cottrell Grant.

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Reaction of Hydrogen Disulfide with Phthaloyl Chloride

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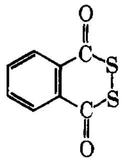
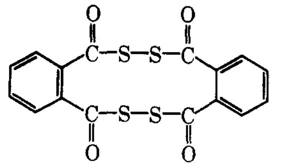
Only a few reactions of hydrogen disulfide, H_2S_2, with organic compounds are reported in the literature. Hydrogen disulfide reacts with aromatic aldehydes to give disulfide derivatives, $[ArCH(OH)]_2S_2$, or dithiocarboxylic acids, ArCSSH, depending on reaction conditions.[1-3] Hydrogen disulfide and acid chlorides react to form acyl or aroyl disulfides, RC(O)SSC(O)R.[4] Reaction of hydrogen disulfide and 1-pentene formed a mixture of diamyl sulfide, diamyl disulfide, diamyl trisulfide, higher amyl sulfides, and other products.[5] The reaction of hydrogen disulfide with isoprene, styrene, and α-methylstyrene was studied in connection with vulcanization processes.[5]

Results and Discussion

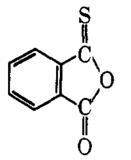
We have confirmed the ready reactivity of hydrogen disulfide with aromatic aldehydes and with acid chlorides. The reaction of hydrogen disulfide and phthaloyl chloride was studied in detail. Instead of the expected disulfide products I and II, thionphthalic anhydride (III) was formed. Isolation and purification of III proved to be tedious and difficult because it readily rearranged to thiophathalic anhydride (IV).



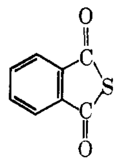
I



II



III



IV

Early preparations of III were always contaminated by IV and, in spite of good elemental analysis, spectral data indicated that a mixture was in hand.

When purified by sublimation, thionphthalic acid (III) is a red solid with a characteristic ABCD nmr pattern which differentiates it from the isomeric previously prepared *white* thiophthalic anhydride (IV) which has a typical A_2B_2 nmr pattern. Other pertinent information on III is reported in the Experimental Section.

Experimental Section

Hydrogen disulfide was prepared by the method of Bloch and Hohn[6] as modified by Walton and Parson.[7] Properties of our hydrogen disulfide were in agreement with properties reported earlier. Analysis of the purity of hydrogen disulfide was made by observation of nmr spectra at 60 Mc/sec. When pure, only a single sharp absorption at 3.08 ppm downfield from tetramethylsilane was observed.[8]

Thionphthalic Anhydride (III).—In a 50-ml erlenmeyer flask at 25° were mixed 2.82 g (13.9 mmoles) of phthaloyl chloride, 1.34 g (20.2 mmoles) of hydrogen disulfide, and 10 mg of zinc chloride. The reaction mixture was maintained at 25°. The reaction mixture changed from light yellow to pink and evolved gases vigorously after 0.75 hr. Gases evolved were identified as hydrogen sulfide and hydrogen chloride by moistened lead acetate paper and formation of silver chloride. After about 1.5 hr, the pink solution became deep red and solidified. Based on spectral analysis to be described later, this crude red solid was thionphthalic anhydride contaminated with small but spectrally significant amounts of thiophthalic anhydride and phthalic anhydride.

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[2] F. Hohn and I. Bloch, *ibid.*, **82**, 486 (1911).

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Sublimation of the crude red solid at 1-mm pressure and *less than* 50° gave purified thionphthalic anhydride, mp 91–96°, rearranging and reacting on melting.

Anal. Calcd for $C_8H_4O_2S$: C, 58.50; H, 2.45; S, 19.55. Found: 58.38; H, 2.51; S, 18.82.

The sublimed red thionphthalic anhydride (III) was shown by its infrared spectrum to be free of phthalic anhydride and thiophthalic anhydride.[9] An absorption at 8.68 μ (1155 cm^{-1}) may be assigned as a thiocarbonyl stretching frequency.[10]

The ultraviolet spectrum of III in cyclohexane had absorptions with the extinction coefficients stated as follows: 2350 A, 6666; 2873 A, 6620; 2945 A, 6764; 3147 A, 4611; and 3279 A, 3888. On the same Cary ultraviolet spectrophotometer, Model 20, phthalic anhydride showed absorbancies at 2479 A (1179), 2857 A (461), and 2948 A (567); thiophthalic anhydride showed absorbancies at 2464 A (2153), 2906 A (1834), and 2960 A (1742). The nmr spectrum of III observed in carbon disulfide solution at 60 Mc/sec on a Varian A-60 spectrometer had a complex absorption pattern in the region characteristic for phenyl hydrogens with the most intense absorption at 8.0 ppm downfield from tetramethylsilane. The complex splitting pattern was definitely not A_2B_2 and appeared to be ABCD. In contrast, under the same conditions, phthalic anhydride and thiophthalic anhydride gave nmr spectra with an A_2B_2 pattern for the phenyl protons.

Attempts to purify III by crystallization or by column chromatography led to rearrangement of III to thiophthalic anhydride. Oxidation of III by aqueous basic potassium permanganate gave a quantitative yield of phthalic acid which was identified by mixture melting point with an authentic sample, mp 192–193°, and by superimposable infrared spectra.

Thiophthalic Anhydride (IV).—This white compound was prepared for analytical comparisons from phthaloyl chloride and hydrogen sulfide by the method described by Chakravarti and had mp 113–114° in agreement with the literature.[11]

Registry No.—III, 13699-68-8; hydrogen disulfide, 13465-07-1; phthaloyl chloride, 88-95-9.

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[9] The spectra of these compounds are available in the Master's Thesis submitted to San Diego State College by Mr. Dodd-Wing Fong in partial fulfillment of the Master's Degree. This paper is taken in part from that thesis.

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Reaction of Triphenylphosphine Dihalides with Grignard and Organolithium Reagents

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In 1931, Grignard and Savard[2] reported the synthesis of pentasubstituted phosphorus compounds by the reactions given in eq 1. Blount,[3] noting the importance of the pentasubstituted compounds in solving certain problems related to "valency and stereochemistry," attempted to repeat Grignard's work. He was not able to isolate the products reported by Grignard.

$$\begin{tikzcd} (\mathrm{C_6H_5})_3\mathrm{P{=}O} + \mathrm{PCl_5} \arrow[r] & (\mathrm{C_6H_5})_3\mathrm{PCl_2} + \mathrm{POCl_3} \arrow[d, "2\mathrm{RMgX}"] \\ (\mathrm{C_6H_5})_3\mathrm{PR_2}' + 2\mathrm{Mg(OH)X} & (\mathrm{C_6H_5})_3\mathrm{P(MgX)_2} + 2\mathrm{RCl} \arrow[l, "2\mathrm{R'OH}"'] \end{tikzcd} \quad (1)$$

He attributed his lack of success to the destruction of the triphenylphosphine dihalide when Grignard's procedure was followed; that is, when the dihalide was washed with water and aqueous sodium bicarbonate, it was converted to the phosphine oxide.

When Blount repeated this work with an authentic sample of triphenylphosphine dichloride, he was still unable to isolate pentasubstituted phosphorus compounds. He suspected that alkyltriphenylphosphonium halides were formed; however, he was not able to confirm this. He concluded that "the substance was either very complicated or very impure."

In a subsequent publication,[4] he reported that the product was indeed an alkyltriphenylphosphonium salt and that the anomalous evidence obtained from the first reaction was due to "the peculiar depression in the melting point of ethyltriphenylphosphonium iodide upon exposure to air."

The reaction of an organometallic compound with a trialkyl or triarylphosphine dihalide to give tetrasubstituted phosphonium salts could be a particularly attractive route to these materials. Generally these salts are simply prepared by allowing the appropriate trisubstituted phosphine to react with an alkyl halide; however, this method is not satisfactory for most aryl halides or alkyl halides which do not undergo S_N2 or S_N1 reactions. Examples of these are some tertiary halides, highly hindered halides, and certain bicyclic halides. It seemed of interest, therefore, to investigate in some detail the reactions of triphenylphosphine dihalides with Grignard and organolithium reagents.

Reaction of triphenylphosphine dibromide with butyllithium at −10° (eq 2) for 4 hr afforded as major

$$(\mathrm{C_6H_5})_3\overset{+}{\mathrm{P}}\mathrm{X}\;\mathrm{X}^- + \mathrm{RM} \longrightarrow (\mathrm{C_6H_5})_3\mathrm{P} + \mathrm{RX} + \mathrm{MX} \quad (2)$$

$$\mathrm{X} = \mathrm{Cl, Br};\; \mathrm{M} = \mathrm{Li, Mg}$$

products triphenylphosphine (88%), triphenylphosphine oxide (12%), and butyl bromide. Similar results were obtained when butylmagnesium bromide was allowed to react with the dibromide. Triphenylphosphine dichloride was allowed to react with butyllithium. The major products were triphenylphosphine and butyl chloride. Reactions of the dichloride with phenyllithium afforded triphenylphosphine and chlorobenzene as major products.

These results show quite clearly that under the conditions used little or no phosphonium salt is being formed and the major mode of reaction involves displacement on halogen. Blount[4] did not describe his reaction conditions in detail; however, in general it appears that he added a slurry of triphenylphosphine dichloride in benzene to a large excess (5 moles) of the Grignard, which was probably in ether. No cooling was used and the reaction was exothermic. After the addition, the mixture was heated under reflux for 2 hr.

Repetition of Blount's experiment using methylmagnesium iodide resulted in an excellent yield of triphenylmethylphosphonium iodide (eq 3). When

$$(\mathrm{C_6H_5})_3\overset{+}{\mathrm{P}}\mathrm{Cl} + \mathrm{Cl}^- + \mathrm{CH_3MgI} \longrightarrow (\mathrm{C_6H_5})_3\overset{+}{\mathrm{P}}\mathrm{CH_3} + \mathrm{I}^- \quad (3)$$

triphenylphosphine dichloride was allowed to react with phenylmagnesium bromide under the same condi-

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[1] F. J. G. wishes to acknowledge his gratitude to the American Cyanamid Co. for a Junior Educational Award and to the Hatco Chemical Division of W. R. Grace Co. for a fellowship.

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