The Electronic Spectra of Vinylphosphines and -arsines

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In recent years, the ultraviolet spectra of several tertiary arylphosphines and -arsines have been investigated[1,2] and attempts made to determine the effect of any π bonding between the central atom and the aryl groups. However, the conclusions have been contradictory, with varying assignments made on the observed peaks. Recently the ultraviolet spectra of some ethynylphosphines have been recorded.[3] We wish to report the results of an investigation of the ultraviolet spectra of a number of vinylphosphines and -arsines and offer some tentative conclusions based upon the appearance of some interesting trends.

Each of the trivalent derivatives exhibits a single peak in the ultraviolet region above 220 mμ, together with a second, intense absorption at shorter wavelengths which shows no maximum above 200 mμ.[4] The longer wavelength absorption peak disappears upon oxidation of the trivalent derivatives. The absorption maxima for these longer wavelength bands are listed in Table I.

The data demonstrate rather clearly the dependence of $\lambda_{\max}$ on the electron-donating ability (inductive effect) of the groups attached to the central atom. For each series of compounds, $R_nM(C_2H_3)_{3-n}$, the wavelength of maximum absorption increases with R in the order $CH_3 < C_2H_5 \leqslant C_4H_9$. Moreover, successive replacement of alkyl groups by vinyl groups results in a decrease of $\lambda_{\max}$ in every case. In the spectrum of the one perfluoralkyl compound investigated, the absorption maximum was lowered so much by the electron-withdrawing group that it appears only as a region of inflection on the intense, short-wavelength peak.

The sensitivity of the observed transition energy to the electron density on the central atom and the disappearance of the observed band upon coordination of the lone pair of electrons (*via* oxidation) strongly suggest that the transition responsible for the longer wavelength band involves an electron from the nonbonded orbital on the central atom. The relative transition energies are then influenced most importantly by the effect of the attached groups on the ionization energy of the lone pair of electrons. However, this does not seem to be either a Rydberg or an $n \rightarrow \sigma^*$ transition of the type postulated for PH_3 and AsH_3.[5] Although only a few alkylphosphine or alkylarsine spectra have been investigated (Table I),[6] there is no evidence of any maximum above 210 mμ in the spectrum of any saturated derivative.[7] Thus it appears likely that the π orbitals on the vinyl groups also play a role in this transition.

The above data are consistent with the type of electron-transfer mechanism described by Cullen and Hochstrasser[2] for the arylarsines. In this case an electron would be removed from the nonbonded orbital on the central atom and transferred to the empty π^* orbital on *one* of the vinyl groups. The small but usually noticeable blue shift in the absorption maxima, upon substitution of a hydroxylic solvent for isooctane, is analogous to the observation of Cullen and Hochstrasser.[2]

The effective disappearance of the longer wavelength absorption maximum, upon oxidation of the trivalent compounds, would appear to eliminate the possibility that the band is actually an ethylene $\pi \rightarrow \pi^*$ transition sufficiently shifted by some interaction involving the d orbitals on the central atom ($\pi \rightarrow \pi^*$ transitions for C_2H_4 are listed at 165 and 200 mμ).[8] If anything, oxidation would increase the availability of the empty d orbitals by increasing the electronegativity of the central atom. However, in the type of charge-transfer excited state described above, dative π bonding between the negatively charged vinyl group and a vacant d orbital on the positively charged central atom is now possible. This would serve to stabilize the charge-transfer state. Thus a decreasing tendency from P to As toward $d\pi$–$p\pi$ bonding might explain the lower transition energies observed for the vinylphosphines relative to the corresponding arsines. Although there is no large body of evidence on the relative tendencies of third and fourth row elements toward $d\pi$–$p\pi$ bonding, some recent studies have indicated that the Ge and As 4d orbitals are weaker π acceptors (toward $p\pi$ orbitals) than the Si and P 3d orbitals, respectively.[9]

Matsen[10] has discussed the bathochromic effect of a substituent bearing a lone pair of electrons on the ethylene $\pi \rightarrow \pi^*$ transition. This effect is due primarily to a conjugative interaction between the nonbonded orbital of the substituent (containing the lone pair) and the π orbital of the vinyl group. It is highly unlikely that the absorption maximum observed in this study is due to the lowest energy ethylene $\pi \rightarrow \pi^*$ transition shifted to longer wavelengths by such an effect. A bathochromic shift of *ca.* 30–45 mμ would have to be

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(1) (a) H. Schindlbauer, *Monatsh. Chem.*, **94**, 99 (1963); (b) G. P. Schiemenz, *Tetrahedron Letters*, 2729 (1964); (c) H. Goetz, F. Nerdel, and K. H. Wiechel, *Ann.*, **665**, 1 (1963); (d) H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952); (e) H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954); (f) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952); (g) C. N. R. Rao, J. Ramachandran, and A. Balasubramanian, *Can. J. Chem.*, **39**, 171 (1961).

(2) (a) W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectry.*, **5**, 118 (1960); (b) W. R. Cullen, B. R. Green, and R. M. Hochstrasser, *J. Inorg. Nucl. Chem.*, **27**, 641 (1965).

(3) (a) C. Charrier, M-P. Simonnin, W. Chodkiewicz, and P. Cadiot, *Compt. Rend.*, **258**, 1537 (1964); (b) C. Charrier, W. Chodkiewicz, and P. Cadiot, *Bull. Soc. Chim. France*, 1002 (1966).

(4) The vacuum ultraviolet spectra of dibutylvinylphosphine and its oxide have been measured [E. M. Popov, E. N. Tsvetkov, Chung-Yu-Chang, and T. Ya. Medved, *J. Gen. Chem. USSR*, **32**, 3199 (1962)] and absorption maxima have been reported at 182 and 179 mμ for the two compounds, respectively.

(5) (a) D. P. Stevenson, G. M. Coppinger, and J. W. Forbes, *J. Am. Chem. Soc.*, **83**, 4350 (1961); (b) C. M. Humphries, A. D. Walsh, and P. A. Warsop, *Discussions Faraday Soc.*, **35**, 148 (1963).

(6) See also M. Halmann, *J. Chem. Soc.*, 2853 (1963).

(7) Although earlier workers had reported a weak band between 220 and 230 mμ in the spectrum of PH_3 [G. H. Cheesman and H. J. Emeleus, *J. Chem. Soc.*, 2847 (1932); H. Melville, *Nature*, **129**, 546 (1932)], this observation has not been verified in subsequent studies.[5]

(8) F. A. Matsen in "Technique of Organic Chemistry," Vol. 9, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 647.

(9) (a) J. Singh and A. B. Burg, *J. Am. Chem. Soc.*, **88**, 718 (1966); (b) T. D. Goldfarb and S. Sujishi, *ibid.*, **86**, 1679 (1964); (c) J. E. Griffiths and K. B. McAfee, *Proc. Chem. Soc.*, 456 (1961); (d) J. E. Griffiths and M. Onyszchuk, *Can. J. Chem.*, **39**, 339 (1961); (e) A. W. Johnson, *J. Org. Chem.*, **25**, 183 (1960).

(10) See ref 8, pp 649–651.

TABLE I

ULTRAVIOLET SPECTROSCOPIC DATA

Arsenic derivatives			Phosphorus derivatives		
Compound	Solvent[a]	λ_{max}[b] ($\epsilon_{max} \times 10^{-3}$),[c] mμ	Compound	Solvent[a]	λ_{max}[b] ($\epsilon_{max} \times 10^{-3}$),[c] mμ
$(CH_3)_2AsC_2H_3$	I	231 (3.07)			
$(CH_3)_2AsC_2H_3$	M	230 (3.03)			
$(CH_3)_2AsC_2H_3$	G	225			
$(C_2H_5)_2AsC_2H_3$	I	235 (2.81)	$(C_2H_5)_2PC_2H_3$	I	244 (2.71)
$(C_2H_5)_2AsC_2H_3$	M	234 (2.83)	$(C_2H_5)_2PC_2H_3$	M	242 (2.76)
$(C_2H_5)_2AsC_2H_3$	G	230	$(C_2H_5)_2PC_2H_3$	G	239
n-$(C_4H_9)_2AsC_2H_3$	I	236 (2.45)	n-$(C_4H_9)_2PC_2H_3$	I	246 (2.60)
$CH_3As(C_2H_3)_2$	I	228 (4.50)	n-$(C_4H_9)_2PC_2H_3$	M	245 (2.63)
$CH_3As(C_2H_3)_2$	M	227 (4.45)			
$CH_3As(C_2H_3)_2$	G	223			
$C_2H_5As(C_2H_3)_2$	I	230 (4.27)	$C_2H_5P(C_2H_3)_2$	I	237 (5.20)
$C_2H_5As(C_2H_3)_2$	M	229 (4.02)	$C_2H_5P(C_2H_3)_2$	M	236 (5.23)
$C_2H_5As(C_2H_3)_2$	G	225	$C_2H_5P(C_2H_3)_2$	G	231
n-$C_4H_9As(C_2H_3)_2$	I	231 (3.99)	n-$C_4H_9P(C_2H_3)_2$	I	238 (5.13)
n-$C_4H_9As(C_2H_3)_2$	M	230 (4.04)	n-$C_4H_9P(C_2H_3)_2$	M	237 (5.25)
n-$C_3F_7As(C_2H_3)_2$	I	*Ca.* 215–220[d]			
n-$C_3F_7As(C_2H_3)_2$	G	*Ca.* 215–220[d]			
$(C_2H_3)_3As$	I	227 (4.98)	$(C_2H_3)_3P$	I	235 (6.41)
$(C_2H_3)_3As$	M	227 (4.65)	$(C_2H_3)_3P$	M	234 (6.48)
$(C_2H_3)_3As$	G	222	$(C_2H_3)_3P$	G	229
$(C_2H_5)_3As$	I	208 (11.7)	n-$(C_4H_9)_3P$	I	204 (11.2)
$(C_2H_5)_3As$	M	207 (10.4)	n-$(C_4H_9)_3P$	M	203 (11.4)
$(C_2H_5)_3As$	G	206			
$(C_2H_5)_2As(O)C_2H_3$	M[e]	...	n-$(C_4H_9)_2P(O)C_2H_3$	I	*Ca.* 200[d]
n-$C_4H_9As(O)(C_2H_3)_2$	M[e]	...	$(C_2H_3)_3PO$	M[e]	...

[a] Isooctane (I), methanol (M), gas (G). [b] Owing to the broadness of the peak near the maximum, λ_{max} is reported only to the nearest mμ. [c] Intensity data for the gas phase spectra were not obtained because of the lack of a suitable pressure measuring device. [d] Region of inflection. [e] Most of the oxides obtained were insoluble in isooctane.

postulated in this case and this would seem to be unusually large. By way of comparison, the ultraviolet spectra of simple enamines show no absorption maxima higher than 225–235 mμ.[11] This is in spite of the generally recognized importance of 2p–2pπ overlap between nitrogen and the attached unsaturated group.

In order to minimize the effect of any oxidation of the samples, the spectra were taken on solutions of relatively large concentration (*ca.* 0.02–0.05 *M*). The effective path length of the solution cell was reduced by means of a quartz insert. Despite the sensitivity of many organophosphines and -arsines to oxidation,[12] we believe the results obtained from the measurements in solution are reliable for the following reasons.

1. The absorption intensities were obtained with good precision. The maximum deviation of any value of ϵ_{max} from the average of three determinations (obtained from three different solutions of the same compound) was ±3%. In almost all cases the deviation was less.

2. The spectra obtained on samples in the gas phase followed the same trends as the spectra obtained on the solutions (although λ_{max} for the gas phase spectra was generally lowered by *ca.* 5 mμ from the corresponding solution spectra).[13]

3. The spectra obtained on the oxides showed no absorption in the region above 220 mμ.

TABLE II

VINYL DERIVATIVES PREPARED FOR THE PRESENT STUDY

Compound	Bp (mm) or mp, °C	Calcd, % C	Calcd, % H	Found,[a,b] % C	Found,[a,b] % H
$(CH_3)_2AsC_2H_3$	79–80 (760)	36.38	6.87	36.57	6.84
$(C_2H_5)_2AsC_2H_3$	58 (39)	45.01	8.19	45.27	8.24
n-$(C_4H_9)_2AsC_2H_3$	86–87 (10)[c]	55.55	9.78	55.58	9.68
$CH_3As(C_2H_3)_2$	102 (760)	41.69	6.29	41.94	6.36
$C_2H_5As(C_2H_3)_2$	54 (40)	45.59	7.01	45.74	7.07
n-$C_4H_9As(C_2H_3)_2$	64 (18)[d]	51.62	8.12	51.49	8.10
n-$C_3F_7As(C_2H_3)_2$[e]	44 (40)	28.21	2.02	28.41	2.17
$(C_2H_3)_3As$	49–50 (40)[f]	46.18	5.81	46.32	5.70
$(C_2H_5)_2PC_2H_3$	48 (54)[g]	63.14	9.71	63.05	9.80
n-$(C_4H_9)_2PC_2H_3$	38 (0.7)[h]	69.73	12.28	69.77	12.33
$C_2H_5P(C_2H_3)_2$	48 (54)[i]	62.05	11.28	61.88	11.40
n-$(C_4H_9)P(C_2H_3)_2$	49–50 (11)	67.58	10.63	67.58	10.42
$(C_2H_3)_3P$	44 (50)[j]	64.28	8.09	64.44	8.20
$(C_2H_5)_2As(O)C_2H_3$	95–96[k]	40.93	7.44	41.04	7.50
n-$C_4H_9As(O)(C_2H_3)_2$	66–67[k]	47.54	7.48	47.40	7.27
n-$(C_4H_9)_2P(O)C_2H_3$	37–38[k,l]	63.81	11.24	63.79	11.18
$(C_2H_3)_3PO$	99–101[k]	56.25	7.08	55.77	7.04

[a] Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y., and by Galbraith Laboratories, Inc., Knoxville 21, Tenn. [b] Carbon and hydrogen analyses for the known vinyl derivatives were obtained in order to ascertain the purity of the compounds. The values are included in this table. [c] Lit.[15] bp 85–86° (10 mm). [d] Lit.[15] bp 56° (12 mm). [e] *Anal.* Calcd for $C_7H_6F_7As$: F, 44.61. Found: F, 44.45. [f] Lit.[15] bp 45–46° (41 mm). [g] Bp 125° (744 mm) reported by D. J. Foster, British Patent 870,425 (1961). [h] Lit.[16] bp 48–49° (2 mm). [i] Bp 121° (751 mm) reported by D. J. Foster, British Patent 870,425 (1961). [j] Lit.[14a] bp 58° (100 mm). [k] Uncorrected. [l] Lit.[16] mp 37.5–38°.

Experimental Section

Spectra.—All ultraviolet spectra were obtained on a Cary Model 14 recording spectrophotometer. The solution spectra were measured with a standard rectangular quartz cell fitted with a quartz insert to reduce the path length to 0.0649 mm (calibrated with standard potassium chromate). All solutions

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[11] G. Opitz, H. Hellmann, and H. W. Schubert, *Ann.*, **623**, 112 (1959).

[12] However, experiments on the reaction of vinylarsines with air showed them to be remarkably insensitive to air oxidation.

[13] This is analogous to observations made on the n → π* transitions of acetone and nitromethane; see N. S. Baylis and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954), for a discussion of these refractive index dependent shifts.

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.

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[14] (a) H. D. Kaesz and F. G. A. Stone, *J. Org. Chem.*, **24**, 635 (1959); (b) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961); (c) C. Screttas and A. F. Isbell, *J. Org. Chem.*, **27**, 2573 (1962).

[15] L. Maier, D. Seyferth, F. G. A. Stone, and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 5884 (1957).

[16] M. I. Kabachnik, Chung-Yu-Chang, and E. N. Tsvetkov, *Dokl. Akad. Nauk SSSR*, **135**, 603 (1960); *Chem. Abstr.*, **55**, 12272 (1961).

[17] W. R. Cullen, *Can. J. Chem.*, **38**, 439 (1960).

Reaction of Hydrogen Disulfide with Phthaloyl Chloride

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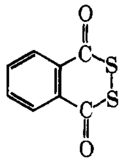
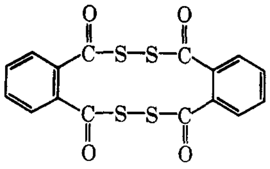
Only a few reactions of hydrogen disulfide, H_2S_2, with organic compounds are reported in the literature. Hydrogen disulfide reacts with aromatic aldehydes to give disulfide derivatives, $[ArCH(OH)]_2S_2$, or dithiocarboxylic acids, ArCSSH, depending on reaction conditions.[1-3] Hydrogen disulfide and 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

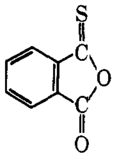
We have confirmed the ready reactivity of hydrogen disulfide with aromatic aldehydes and with acid chlorides. The reaction of hydrogen disulfide and phthaloyl chloride was studied in detail. Instead of the expected disulfide products I and II, thionphthalic anhydride (III) was formed. Isolation and purification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



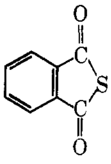
I



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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[1] I. Bloch, F. Hohn, and G. Bugge, *J. Prakt. Chem.*, **82**, 473 (1911).

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

[3] G. Bugge and I. Bloch, *ibid.*, **82**, 512 (1911).

[4] I. Bloch and M. Bergmann, *Chem. Ber.*, **B53**, 961 (1920).

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[6] I. Bloch and F. Hohn, *Chem. Ber.*, **41**, 1961, 1971, 1975 (1908).

[7] J. H. Walton and L. B. Person, *J. Am. Chem. Soc.*, **43**, 2539 (1921).

[8] H. Schmudbaur, M. Schmidt, and W. Siebert, *Chem. Ber.*, **97**, 3374 (1964).