was heated at 45–65° for 24 hr. The Grignard complex was hydrolyzed with saturated ammonium chloride and the organic products were extracted with ethyl ether. Distillation gave 4.3 g (37%) of **2a**: bp 73–75° (0.5 mm); $n^{20}{}_{\mathrm{D}}$ 1.4803; $\bar{\nu}$ 3300, 3070, 1650 (w), 1032, 730, 652.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.60; H, 11.47.

4-(3-Cyclohexenyl)butyl Acetate (2c).—A mixture of **2a** (1.5 g, 9.8 mmol), 4.0 g of acetic anhydride, and 8 ml of pyridine was heated under reflux for 5 min. The mixture was poured on ice and the organic products were taken up in ether. Distillation gave 1.2 g (61%) of **2c**: $n^{20}{}_{\mathrm{D}}$ 1.4638; $\bar{\nu}$ 3025, 1740, 1650 (w), and 1240; nmr (CCl_4), δ 1.2–2.2 (m), 1.92 (s, 3, CH_3CO), 4.01 (t, J = 6.3 cps), 5.63 (s).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.29; H, 10.25.

Acetolyses.—A sample of **1b** was prepared in 87% yield by the method of Tipson:[8] $\bar{\nu}$ 3020, 1360, 1190, 1175, 955, 930, 653. The crude **1b** (7.16 g, 24.4 mmol) was dissolved in 500 ml of anhydrous acetic acid containing 2.1 g (25.6 mmol) of dry sodium acetate. The solution was stirred at 113–114° for 94 hr. About 500 ml of water was added to the cooled solution, and the organic products were extracted with several portions of hexane. The combined hexane extracts were washed with sodium bicarbonate and then dried and concentrated. The residue weighed 4.16 g (108% calculated as **1c**). Aside from a small amount of hexane, this contained **1c** and two trace components (*ca.* 5% total). Analysis was made by glpc on a 6-ft Carbowax 1500 column at 156° using helium as a carrier gas. Distillation of the crude acetolysis mixture gave 3.52 g (78.5%) of **1c** identical in infrared and nmr spectra with those of the sample prepared directly from **1a**.

Similarly a sample (1.23 g) of **2b** was heated at 113–114° for 72 hr. The organic products were isolated as described above and, after removal of the hexane, 1.0 g (128% calculated as **2c**) of residual material was recovered. This was analyzed by glpc at 171° on a 10-ft UCON nonpolar column, and was found to consist of hexane, **2c**, and two trace components. Exclusive of the hexane, the composition of this mixture was 96% **2c** and 4% trace components. The main component was identified as **2c** by use of an internal standard.

Registry No.—**1a,** 16626-54-3; **1b,** 16626-55-4; **1c,** 16626-56-5; **2a,** 16626-57-6; **2b,** 16626-58-7; **2c,** 16626-59-8; 3-cyclohexenylcarbinyl chloride, 2555-08-0.

[8] S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

The Electronic Spectra of Some Air-Sensitive Phosphorus Ylides[1,2]

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Air-sensitive alkylidenephosphoranes (phosphinemethylenes, phosphorus ylides) are important in organic synthesis, but very few physical properties have been obtained[3] for these compounds. Recently, proton[4] and phosphorus[5] nuclear magnetic resonance data have been reported.

We report here the ultraviolet-visible spectra in hexane solution of seven of these air-sensitive compounds (Table I). Each of the spectra consists of two main absorptions in the region (200–600 mμ) examined, *viz.*, a structured band centered about 265 mμ and a broad peak at longer wavelength in the 340–400-mμ range. The 265-mμ peak is constant within experimental error for all the compounds in this study. It is due to the benzene absorption and has been discussed previously[6] for the somewhat analogous compound, triphenylphosphine oxide.

TABLE I

ULTRAVIOLET MAXIMA AND ^{31}P CHEMICAL SHIFTS FOR SOME AIR-SENSITIVE PHOSPHORUS YLIDES

Compound[a]	λ_{max}, mμ		δ (ppm) *vs.* 85% H_3PO_4[b]
$(C_6H_5)_3P{=}O$	266		−25.5[c]
$(C_6H_5)_3P{=}CH_2$	265	341	−20.3
$(C_6H_5)_3P{=}CHCH_3$	265	374	−14.6
$(C_6H_5)_3P{=}CHCH_2CH_3$	265	378	−12.2
$(C_6H_5)_3P{=}CH(CH_2)_2CH_3$	264	375	−12.6
$(C_6H_5)_3P{=}CH(CH_2)_4CH_3$	264	377	−12.2
$(C_6H_5)_3P{=}C(CH_3)_2$	265	386	−11.3
$(C_6H_5)_3P{=}C(CH_2)_5$	265	391	−6.4

[a] Registry no. are given in descending order: 791-28-6, 3487-44-3, 1754-88-7, 16666-78-7, 3728-50-5, 16666-79-8, 16666-80-1, 16666-81-2. [b] See ref 5. [c] In dimethyl sulfoxide. Literature values, −23.0 to −27.0: V. Mark, *et al.*, "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 285.

The long-wavelength peak varies as the alkylidene group changes, and it is the absorption of interest. It is seen that the substitution of a methyl group for a methylene hydrogen in the parent compound, methylenetriphenylphosphorane, gives rise to a bathochromic shift of 33 mμ. Substitution of longer chain alkyl groups causes only slight further shifts of several millimicrons to longer wavelengths. Substitution by another methyl for the second methylene hydrogen causes an additional bathochromic shift of 12 mμ.

In the case of the resonance-stabilized, charge-delocalized ylides, the more extensive the conjugated system becomes, the greater is the bathochromic shift.[7]

At first glance, these data seem contradictory, *i.e.*, both increasing electron-withdrawing (by delocalization of the methylenic negative charge) character and electron-releasing (by induction of alkyl substituents) character of the groups cause shifts to longer wavelengths. However in the case of the resonance-stabilized ylides, the substituent on the methylene carbon contains a chromophore and extensive conjugation serve to lower the π^* energy levels. The phosphorus in this case probably contributes only slightly as an auxochrome by participating in the conjugation,[7] and the transition is undoubtedly $\pi \rightarrow \pi^*$ (or $n \rightarrow \pi^*$ depending on the nature of the substituent). Further evidence for this slight participation by phosphorus in the resonance-stabilized ylides is provided by their

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[1] Supported by the National Science Foundation uuder Grant No. GP 4483.

[2] Taken from the M.S. Thesis of J. H. Ambrus, University of Maryland, 1966.

[3] A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 76–79.

[4] H. J. Bestmann and J. P. Snyder, *J. Amer. Chem. Soc.*, **89**, 3937 (1967), and references cited therein.

[5] S. O. Grim, W. McFarlane, and T. J. Marks, *Chem. Commun.*, 1191 (1967).

[6] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 500.

[7] H. Fischer and H. Fischer, *Chem. Ber.*, **99**, 658 (1966).

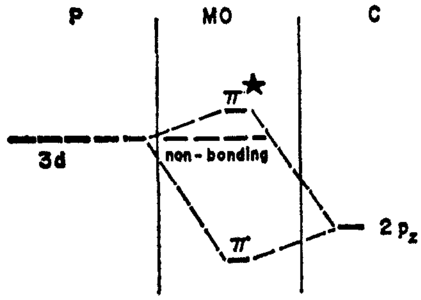

Figure 1.—Simple energy level diagram for nonconjugated phosphorus ylides.

phosphorus-31 chemical shifts, which are very similar to those of the corresponding phosphonium salts from which they are derived.[3,5]

In the colored air-sensitive ylides, the methylene carbon–phosphorus bond system must be the chromophore. A simple energy level diagram is given in Figure 1. If phosphorus is bonded to the four attached atoms by sp^3 hybrids and carbon is bonded to its three attached atoms by sp^2 hybrids and if the methylene carbon–phosphorus bond is taken as the x axis with the carbon sp^2 hybrids lying in the xy plane, then the remaining carbon p orbital has the same π symmetry as the d_{xz} orbital[3] of phosphorus and can combine to form a π bonding and an antibonding orbital. The transition could be $\pi \rightarrow 3d$ or $\pi \rightarrow \pi^*$. The $\pi \rightarrow d$ transition represents an electronic transfer from a molecular orbital mainly on carbon to an empty nonbonding 3d orbital of phosphorus. This would not be greatly different from the $\pi \rightarrow \pi^*$ transition, which is the transition from the molecular orbital mainly on carbon to the antibonding orbital composed mainly of the 3d orbital of phosphorus. The usual methods for differentiating between $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, for example, are of limited use for discriminating between $\pi \rightarrow \pi^*$ and $\pi \rightarrow d$. First, two methods,[8] *viz.*, the magnitude of the extinction coefficients and the shift of wavelength with change in solvent polarity, are experimentally very difficult in this case because of the great reactivity of the compounds (see Experimental Section). Second, apparently $\pi \rightarrow d$ transitions have not been discussed previously; so there is no mention of selection rules for such transitions.

Although the intensity of the long-wavelength peak in fresh solution is an order of magnitude less than the intensity of the benzene absorption, any decomposition of the ylide would result in loss of the long-wavelength peak intensity with no decrease in the benzene absorption. Because of the air-sensitive nature of the compounds, reliable values for the extinction coefficients were not obtained.

In either case, $\pi \rightarrow d$ or $\pi \rightarrow \pi^*$, substitution by alkyl groups would tend to destabilize the π bond (raise the π-energy level) of these compounds with a large proportion of carbanionic character, and thereby lower the transition energy so that increased alkyl substitution leads to bathochromic shifts.

It should be pointed out that, with free rotation about the phosphorus–methylene carbon bond, the dxz and dxy orbitals of phosphorus would become equivalent and the bonding and antibonding orbitals would contain equal amounts of these orbitals. Also, in this symmetry for phosphorus, the remaining 3d orbitals would not be degenerate. For simplicity, this is not shown in the figure.

The quantitative correlation between changes in λ_{max} and the phosphorus chemical shifts is interesting (see Table I), with both being related to the inductive effect. The most significant changes in the λ_{max} occur for one and two methyl substitutions on the methylene carbon, whereas larger alkyl groups cause a less significant change. Ths phosphorus chemical shifts have been discussed briefly previously.[5] The rather unexpected chemical shift of the cyclohexyl derivative is not understood at present.

Experimental Section

Spectra of the solutions in 1-cm quartz cells were recorded with a Cary Model 14 spectrometer.

Preparation of Phosphonium Salts.—*n*-Alkyltriphenylphosphonium bromides were prepared by the direct reaction of triphenylphosphine and the alkyl bromide in refluxing benzene. *sec*-Alkyltriphenylphosphonium salts were prepared in a Carius tube from the alkyl bromide and triphenylphosphine without solvent at 140°. All bromides gave acceptable analyses, except the cyclohexyl compound which is extremely hygroscopic. It was converted into the hexafluorophosphate for analysis.

Cyclohexyltriphenylphosphonium Bromide.—Triphenylphosphine (10 g, 0.038 mol) and bromocyclohexane (6.1 g, 0.038 mol) were placed in a 25 × 320 mm medium-walled Pyrex tube. After degassing, the contents were cooled to −78° and the tube was sealed. The Carius tube was heated in an oven at 140° for 24 hr. After cooling the tube was opened in a glove bag filled with N_2. The contents of the tube were dissolved in a minimum amount of isopropyl alcohol and then reprecipitated by the addition of diethyl ether. The solid was separated by decantation, then washed with ether and the mixture decanted again. While ether-wet, the solid was removed from the glove bag and transferred to a vacuum oven and dried at 60° (5 torr). Nitrogen was released into the oven and the flask containing the cyclohexyltriphenylphosphonium bromide, mp 273–276°, was quickly stoppered.

Preparation of Alkylidenephosphoranes.—A 100-ml, three-necked flask, equipped with Dry Ice condenser, mechanical ground glass stirrer, and stopper, was flushed with nitrogen and insulated with asbestos cloth, and 30–40 ml of ammonia was introduced. A small crystal of $Fe(NO_3)_3 \cdot 9H_2O$ was added, followed by sodium (0.12 g, 0.005 g-atom). The mixture was stirred until the blue color had disappeared and the Na had been converted into $NaNH_2$. Finely powdered phosphonium salt (0.005 mol) was added at once and the mixture was stirred for 10 min. The bright color characteristic of the alkylidenephosphoranes appeared immediately. The insulation was removed; the Dry Ice condenser was replaced by an adaptor with a three-way stopcock for N_2 inlet and NH_3 outlet to a Hg bubbler; the stopper was replaced by a dropping funnel with 50 ml of degassed hexane; and the mixture was stirred as the NH_3 evaporated. After the NH_3 had evaporated, the hexane was added and after stirring for a few minutes the mixture was allowed to settle. Several drops of the solution was added *via* syringe to the quartz cells which had previously been almost filled with degassed hexane. The spectra were recorded immediately. After a short time the long-wavelength band began to decrease in intensity and usually disappeared after several hours. For this reason, it was difficult to estimate the extinction coefficient for the long-wavelength band, although it was generally about one-tenth the intensity of the 265-mμ band when the spectra were recorded immediately after preparation of the sample.

Registry No.—Cyclohexyltriphenylphosphonium bromide, 7333-51-9.

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