Elution with 1% methanol–chloroform gave 300 mg of the dienone **9** as colorless needles (from ethanol): mp 265–267°; ir ($CHCl_3$) 3510, 1660, 1630 cm^{-1}; nmr τ ($CDCl_3$) 6.80 (3 H, s, NMe), 6.13 (3 H, s, OMe), 3.73 (1 H, d, J = 10 Hz, H_α), 2.92 (1 H, d, J = 10 Hz, H_β), 3.39, 2.55 (2 H, each s, Ar H); mass spectrum (70 eV) m/e 299 (M^+) and 256 ($M^+ - 43$).

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68. Found: C, 68.49; H, 5.59; N, 4.95.

(b) To a stirred solution of 1 g of **7** in 50 ml of chloroform was added dropwise 1.5 g of vanadium oxytrichloride at room temperature. After the mixture had been stirred for 4 hr, the excess of vanadium oxytrichloride was decomposed with water, and the separated chloroform layer was washed with water, dried over Na_2SO_4, and evaporated to give 0.5 g of a brownish syrup, which was chromatographed on 10 g of silica gel. Elution with chloroform gave 20 mg of the enone **8** as colorless prisms, mp 269–271°, whose spectroscopic data were identical with those of the authentic sample **8**. Removal of the eluent with 1% methanol–chloroform (20 ml) afforded 25 mg of the dienone **9** as colorless needles, mp 265–267°, and, finally, successive elution with the same eluent gave 100 mg of the starting material **7** as colorless needles, mp 167–169°.

In this case when the above reaction was carried out for a short time (2 hr), the para-coupled compound **9** was not observed.

(±)-Galanthamine (1) and (±)-Epigalanthamine (2).—To a stirred suspension of 50 mg of lithium aluminum hydride in 20 ml of tetrahydrofuran was added dropwise a solution of 22 mg of **8** in 50 ml of tetrahydrofuran at room temperature. The mixture was refluxed on a water bath for 10 hr. The mixture was then decomposed with 20% sodium hydroxide solution. The inorganic substance was removed by filtration and the solvent was evaporated to give 18 mg of a colorless syrup which was chromatographed on 0.6 g of alumina. Elution with ethyl acetate–benzene (1:1) gave 13 mg of (±)-galanthamine (**1**) as colorless needles (from ether), mp 121–123°, whose spectroscopic data and chromatographic behavior were identical with those of the authentic (±)-galanthamine and natural (−)-galanthamine. Subsequent elution with ethanol–chloroform (1:9) gave a small amount of material whose chromatographic data were identical with those of authentic (±)-epigalanthamine, but the substance could not be isolated in the pure state.

Registry No.—**1**, 23173-12-8; **7**, 28129-09-1; **8**, 28129-07-9; **9**, 27994-91-8; **11**, 28129-10-4.

Acknowledgment.—We thank Professor S. Uyeo, Kyoto University, and Dr. A. Brossi, Hoffmann-La Roche, Inc., for a gift of natural galanthamine. We also thank Mr. S. Hirata for mass spectral determination, Miss A. Kawakami and Miss C. Yoshida for microanalysis, and Miss Y. Tadano for the nmr measurements.

Spectral Effects Attributable to Conjugation with Trivalent Phosphorus among Some 2-Phospholenes[1]

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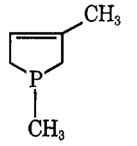
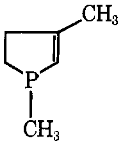
Received September 15, 1970

Synthetic work in this laboratory with phospholenes has made available pairs of isomers which differ in the position of the double bond. In compiling spectral data for these compounds, we have observed consistent differences which can be associated with conjugation of phosphorus with the double bond of the 2-phospholene system. The differences to be described have apparently not been reported upon previously; in part, this may be due to nonavailability of a series of vinylic–allylic models, although the differences appear particularly strong in our cyclic compounds. The existence of a conjugative effect for trivalent phosphorus and the relative importance of utilization of its d or p orbitals have remained points of uncertainty; the opinion has been expressed that there may be a weak involvement of the lone pair on phosphorus in delocalization,[2] but the view has also been taken that acceptance of electrons in the d orbitals of phosphorus may be more significant.[3]

The spectral differences we have encountered so far (infrared and ^{31}P and ^{1}H nmr) are particularly well displayed by the isomeric 1,3-dimethylphospholenes (Ia[4] and Ib[5]). The conjugative effect is clearly revealed by characteristics of the C=C stretching band in the ir spectra. For the allylic isomer Ia, this band appears at 1658 cm^{-1}, while the vinylic isomer Ib has a band of considerably greater intensity at lower frequency (1613 cm^{-1}). The frequency and intensity differences are those expected for diminished double-bond character and polarization in the vinylic isomer through delocalization involving phosphorus. The low electronegativity of phosphorus suggests that the effect is not due to induction. Enamines exhibit similar intensification of the C=C absorption,[6] but apparently this has not been previously observed for vinylphosphine derivatives. In the Raman spectrum, the C=C absorption of di-n-butylvinylphosphine is at considerably lower frequency than that of 1-hexene, but the relative intensities are similar.[7] This observation was interpreted to indicate that little, if any, p_π–p_π conjugation prevails among vinylphosphines.[3]



Ia



Ib

That the conjugative effect is in the direction to endow phosphorus with some positive character is suggested by the nmr spectra of compounds Ia and Ib. The ^{31}P signal for the vinylic compound is at considerably lower field than that of the allylic isomer (Ia, +32.6; Ib, +15.2). Acyclic vinylphosphines do not exhibit appreciable chemical shift differences from their saturated counterparts; for example, trivinylphosphine has a value of +20.7 ppm,[8] while that of triethylphosphine is +20.4 ppm.[9] It is apparent that the phospholene system is unique; in view of the conjugative effect

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(1) Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute.

(2) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967, p 3.

(3) E. N. Tsvetkov, D. I. Lobanov, M. M. Makhamatkhanov, and M. I. Kabachnik, *Tetrahedron*, **25**, 5623 (1969).

(4) L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, **33**, 1034 (1968).

(5) D. K. Myers and L. D. Quin, *ibid.*, **36**, 1285 (1971).

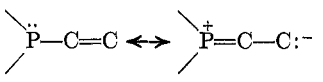
(6) N. J. Leonard and V. W. Gash, *J. Amer. Chem. Soc.*, **76**, 2781 (1954).

(7) E. M. Popov, E. N. Tsvetkov, C. Chung-yu, and T. Y. Medved, *Zh. Obshch. Khim.*, **32**, 3255 (1962).

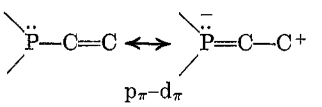
(8) L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Amer. Chem. Soc.*, **91**, 3308 (1969).

(9) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 249 (1967).

clearly seen in its ir spectrum, it is reasonable to attribute the strong deshielding in the vinylic isomer to reduced electron density on phosphorus as a result of p_{π}–p_{π} conjugation. Had the conjugative effect been of the type p_{π}–d_{π}, electron density on phosphorus would have been increased.



p_{π}–p_{π}



p_{π}–d_{π}

It is possible that bond angle differences prevail about phosphorus in the phospholene isomers and may contribute to the shift differences. The present state of knowledge of ^{31}P chemical shifts of phosphines unfortunately does not permit an evaluation of the importance of this factor at this time.

The ^{1}H nmr spectra also show differences possibly attributable to conjugation. The P-CH_3 signal of Ib (δ 1.23 ppm) is downfield relative to that of Ia (δ 1.14 ppm), an effect again explicable on the basis of increased positive character at phosphorus. Differences in the chemical shift of the vinylic proton may also be associated with conjugation; the signal for Ib is 0.2 ppm downfield from that of Ia (Ia, δ 5.70; Ib δ 5.90 ppm). However, the vinyl proton is α to phosphorus in Ib, and β in Ia, and some of the difference in the chemical shift may be associated with the proximity of the proton to phosphorus. As has been discussed elsewhere, there is an enormous difference in P–H coupling constants for the vinylic proton in 2- and 3-phospholenes (*e.g.*, 7 Hz for Ia,[4] 42 Hz for Ib[5]). Any relevance of this difference to the conjugative effect, and modification of bonding at phosphorus, cannot be established at this time.

The concept of p_{π}–p_{π} conjugation therefore seems capable of explaining the spectral differences noted for these phospholene derivatives. For *acyclic* trivalent phosphorus systems, however, it has recently been argued that weak d_{π}–p_{π} interaction is operative and that p_{π}–p_{π} conjugation is negligible.[3] The geometry of the cyclic compounds may be responsible for the more well-defined p_{π}–p_{π} conjugation observed; the opportunity for overlap is possibly greater when the orbitals to participate are not associated with the freely rotating atoms of an acyclic system.

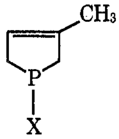
Some of the spectral differences discussed above have also been observed for other isomeric phospholenes (Table I). Thus, the ^{31}P signal for 1-benzyl-2-phospholene (IIb) is at lower field by 23.5 ppm than that of the 3 isomer, and in their ^{1}H nmr spectra, the benzylic CH_2 of IIb is downfield (δ 2.85 ppm) from that of IIa (δ 2.72 ppm). Conjugation is also indicated for the vinylic isomer of the 1-phenyl-3-methylphospholenes (III) by both the infrared effect and the downfield shift in the ^{31}P signal of 22.6 ppm. The cyclic phosphinous halides (IV and V) likewise exhibit both effects, although the magnitude of the ^{31}P shift is much less than that seen for the tertiary phosphines. This may be due to π bonding of halogen with phosphorus, a feedback mechanism acting in addition to p_{π}–p_{π} conjugation and partly compensating for the positivity developing on phosphorus through the latter mechanism. Finally, in the rather special case of the 1-alkylphospholes, some properties have also been interpreted to be consistent with electron delocalization from phosphorus.[8,10]

Table I

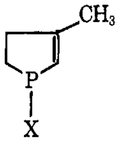
Spectral Data for Phospholenes

Compound	$\nu_{C=C}^{neat}$, cm^{-1} [a]	δ (^{31}P), ppm[b]
Ia	1658	+32.6
Ib	1613	+15.2
IIa[c,d]	. . .[e]	+23.4
IIb[c,d]	. . .[e]	0.0
IIIa	1660	+18.6
IIIb	1618	−4.0
IVa	1655	−127.5
IVb	1601	−132.5
Va[c]	1655	−120.5
Vb[c]	1601	−130.6

[a] Obtained with a Perkin-Elmer Model 237 spectrophotometer. [b] Obtained with Varian V-4300B spectrometer at 19.3 MHz, 85% H_3PO_4 as standard. [c] Values obtained on a mixture of isomers. [d] ^{1}H nmr spectrum (neat) contained benzyl CH_2 signals (slightly broadened singlets) at 2.72 (IIa) and 2.85 ppm (IIb). [e] Not well separated from phenyl bands.



IIIa, X = C_6H_5
IVa, X = Cl
Va, X = Br



IIIb
IVb
Vb

Experimental Section

The synthesis of the following compounds has been reported elsewhere: Ia,[4] Ib,[5] IIa,[4] IIb,[4] IVa,[5] IVb.[5] A mixture of compounds Va and Vb (3:7) was also available from earlier work[5] and was used directly in this study.

1-Benzyl-3- (and -2-) phospholene.—A solution of benzylphosphonous dichloride (26.0 g, 0.135 mol) and butadiene (7.67 g, 0.142 mol) in 40 ml of cyclohexane (containing 0.2 g of copper stearate as polymerization inhibitor), after standing several months, had precipitated 15.1 g of cycloadduct. This was hydrolyzed by addition to ice, and the resulting phospholene oxide was extracted with chloroform and distilled: 5.2 g (20%), bp 151–159° (0.3 mm). Gas chromatography showed a ratio of 1-benzyl-3-phospholene oxide to 1-benzyl-2-phospholene oxide of 1:2. The oxide mixture was placed in 100 ml of dry benzene; the solution was cooled to 0° and reduced by treatment with 14 g of trichlorosilane in 20 ml of benzene, added over a 20-min period. After the solution was stirred for 30 min at room temperature and refluxed for 2 hr, it was cooled and treated with 100 ml of 30% NaOH. Layers were separated, and the aqueous layer was extracted with benzene. Distillation gave 2.7 g, bp 68–72° (0.25 mm), of 1-benzyl-3-phospholene (IIa) and 1-benzyl-2-phospholene (IIb). Spectral properties for the mixture, which was not separated, are recorded in Table I. The major product (about 75%) was IIb, which has been prepared by a different route.[10]

Registry No.—Ia, 15450-84-7; Ib, 28273-45-2; IIa, 28278-52-6; IIb, 28278-53-7; IIIa, 28278-54-8; IIIb, 28278-55-9; IVa, 28278-56-0; IVb, 28273-36-1; Va, 28273-34-9; Vb, 28278-59-3.

Acknowledgment.—Compounds IIa and IIb were prepared by Mr. John F. Engel in connection with another study.[10]

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[10] P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, **92**, 5779 (1970).