Chemiluminescence of Lithium Phosphides

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Abstract: The chemiluminescence of a series of lithium phosphides, most of which were prepared for the first time, has been characterized. Sensitivity of the emissions of the solid salts to change in the organic group, particularly the shift to longer wavelength obtained with the di-α-naphthylphosphide relative to phenyl, indicates that the chemiluminescence is of molecular rather than crystal origin. Factors affecting the relationship of phosphide chemiluminescence to molecular structure are discussed. Comparison of chemiluminescence and fluorescence data obtained on several phosphides and intermediate and final oxidation products indicates that electronically excited phosphide molecules are the major emitters. The lithium salts of dicyclohexyl- and diphenylphosphine oxides were discovered to be chemiluminescent, and a structure for these salts in the crystalline state is suggested based on a study of infrared spectra. In some instances a minor component was detected in the phosphide chemiluminescence spectra, and this emission is attributable to the lithium salt of the phosphine oxide in the case of cyclohexyl, but not in the case of phenyl. Mechanistic aspects of the oxidation and chemiluminescence of lithium phosphides are discussed.

In 1959, Issleib and Tzschach reported that lithium dicyclohexylphosphide (LHP = R_2PLi; R = cyclohexyl) yields an "extremely" strong yellow-green chemiluminescence with traces of oxygen.[1] This was followed by reports in 1961 that compounds of the type $R(Li)P(CH_2)_nP(Li)R$ chemiluminesce as intensely as LHP when R = cyclohexyl and n = 5,[2] and only weakly when R = phenyl.[3] Chemiluminescence spectra were not reported, and no further investigation of the chemiluminescence of these compounds has been published. The subject of phosphide chemiluminescence has been overlooked in recent reviews of chemiluminescent reactions,[4] and is characterized to date by relative obscurity.

The present work was undertaken to determine the effect of the organic group on lithium phosphide emission characteristics, to identify possible emitting species, and to gain some insight into the mechanism of the chemiluminescent oxidation.

Results and Discussion

Synthesis and Chemiluminescent Characteristics of Lithium Phosphides. LHP was originally prepared[1] by the action of phenyllithium on $(C_6H_{11})_2PH$ obtained by $LiAlH_4$ reduction of $(C_6H_{11})_2P(S)P(S)(C_6H_{11})_2$. The disulfide was prepared from cyclohexyl Grignard reagent and $PSCl_3$. We have found it more convenient, however, to prepare the phosphine *in situ* by $LiAlH_4$ reduction of the phosphinous chloride, $(C_6H_{11})_2PCl$, formed from PCl_3 and cyclohexyl Grignard reagent. With one exception, all other phosphines employed in this work were similarly prepared from PCl_3, or from $(C_2H_5)_2NPCl_2$ by hydrochlorinolysis of the P–N bond. Di-α-naphthylphosphine was obtained from the tertiary phosphine *via* cleavage with potassium, and hydrolysis of the resulting potassium phosphide. Lithium dicyclopentylphosphide could not be obtained from phenyllithium and the secondary phosphine, and was unlike LHP in this respect. The compound was obtained using the more basic n-butyllithium, and in general, all phosphides were prepared with this reagent. The following represent the reaction sequences employed in the preparation of the phosphides.

$$PCl_3 \xrightarrow{RMgX} R_2PCl \xrightarrow{LiAlH_4} R_2PH \xrightarrow{n\text{-BuLi}} R_2PLi$$
$$R = C_5H_9\text{–}, C_6H_{11}\text{–}, C_7H_{13}\text{–}, C_6H_5\text{–}, p\text{-}CH_3C_6H_4\text{–}, sec\text{-}C_4H_9\text{–}, t\text{-}C_4H_9\text{–}$$

$$(C_2H_5)_2NPCl_2 \xrightarrow{RMgX} R_2PN(C_2H_5)_2 \xrightarrow{HCl} R_2PCl \xrightarrow[2.\ n\text{-BuLi}]{1.\ LiAlH_4} R_2PLi$$
$$R = n\text{-}C_4H_9\text{–}, p\text{-}CH_3OC_6H_4\text{–}$$

$$PCl_3 \xrightarrow{RMgX} R_3P \xrightarrow{K} R_2PK \xrightarrow{H_2O} R_2PH \xrightarrow{n\text{-BuLi}} R_2PLi$$
$$R = \alpha\text{-}C_{10}H_7\text{–}$$

Lithium diphenylphosphide was discovered to be a strong emitter when precipitated from petroleum ether. This compound was previously isolated as the dioxanate, and as such did not exhibit chemiluminescence.[1] The unsolvated di-p-tolyl- and anisylphosphides and, in the alkyl series, n-butyl-, *sec*-butyl-, and *tert*-butylphosphides also were obtained from petroleum ether, and their chemiluminescence was observed. The substituted phenylphosphides were comparable to phenyl in emission intensity, while the alkylphosphides were generally weaker. The *tert*-butylphosphide showed solubility in ethyl ether, and did not chemiluminesce when precipitated from that solvent due to cocrystallization with solvent. Lithium dicyclopentylphosphide, however, was found to be insoluble in ether, like LHP, and chemiluminesced strongly when formed in that solvent. Lithium dicycloheptylphosphide, precipitated from petroleum ether, proved to be a weaker emitter, while the α-napthylphosphide was the weakest of the phosphides prepared in this work.

Besides the requirement that the phosphide molecule be unsolvated if it is to chemiluminesce, the presence of a suitable cyclic group on phosphorus apparently is necessary if the phosphide is to be a strong emitter. Table I summarizes the chemiluminescence data

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(1) K. Issleib and A. Tzschach, *Chem. Ber.*, **92**, 1118 (1959).

(2) K. Issleib and G. Döll, *ibid.*, **94**, 2664 (1961).

(3) K. Issleib and F. Krech, *ibid.*, **94**, 2656 (1961).

(4) K. D. Gundermann, *Angew. Chem., Int. Ed. Engl.*, **4**, 566 (1965); F. McCapra, *Quart. Rev., Chem. Soc.*, 20, 485 (1966); J. W. Haas, Jr., *J. Chem. Educ.*, **44**, 396 (1967); V. Ya. Shlyapintokh, O. N. Karpukhin, L. M. Postnikov, V. F. Tsepalov, A. A. Vichutinskii, and I. V. Zakharov, "Chemiluminescence Techniques in Chemical Reactions," translation from Russian, Consultants Bureau, New York, N. Y., 1968, Chapter 1.

Table I. Chemiluminescence of R_2PLi

R	Color of emission	Relative intensity[a]	Major emission λ_{max}, mμ	Minor emission λ_{max}, mμ
Cyclopentyl	Yellow	Strong	544	479
Cyclohexyl (LHP)	Yellow–green	Very strong	531	463
Cycloheptyl	Blue–green	Medium	507	*b*
α-Naphthyl	Orange	Extremely weak	580	*b*
Phenyl	Yellow	Strong	558	470
p-Tolyl	Yellow	Strong	555	*b*
p-Anisyl	Yellow	Strong	545	*b*
tert-Butyl	Yellow–green	Medium	532	*b*
n-Butyl	Blue–green	Very weak	500	*b*
sec-Butyl	Light blue	Weak	456	520

[a] Visual comparison. The compounds were exposed under dry nitrogen to traces of oxygen. The di-α-naphthylphosphide was visually chemiluminescent only when exposed to air. [b] Not detected.

obtained on the new phosphides as well as LHP.[5] LHP and the cyclopentylphosphide produced an unusual type of chemiluminescence spectrum consisting of two broad bands, one, strong (major emission), the other, weaker and sometimes appearing as a shoulder (minor emission). Of the remaining phosphides, the minor emissions were detected in the case of phenyl and *sec*-butyl, but were either too weak to be detected or were absent in the other cases. With phenyl, the minor emission was barely detectable, while with *sec*-butyl, the emission was nearly as intense as the major (but weak) emission. LHP, exposed under dry nitrogen to traces of oxygen, was found to chemiluminesce with intensities comparable to that displayed by tetrakis(dimethylamino)ethylene[6] in air. The duration of the emission of the aromatic phosphides was noticeably shorter than that of LHP.

The sensitivity of the wavelength of the emitted light to change in structure of the organic group can be seen in the data in Table I. Shifts of the major emission band of over 20 and 35 mμ to longer wavelength were obtained in going from cycloheptyl to cyclohexyl and cyclopentyl, respectively. The wavelengths obtained for phenyl and *p*-tolyl were nearly identical, while the wavelength for α-naphthyl was red-shifted over 20 mμ, and that for *p*-anisyl was blue-shifted over 10 mμ with respect to phenyl. Proceeding from *sec*-butyl to *n*- and *tert*-butyl produced red shifts of approximately 45 and 75 mμ, respectively.

The importance of delocalization may be seen in the shift obtained with α-naphthyl relative to phenyl. The lower emission intensity of the naphthylphosphide, moreover, is attributable, in part at least, to a slower rate of oxidation due to extended delocalization of the phosphorus lone pair. Emission of the *p*-anisylphosphide at shorter wavelength than the phenylphosphide accords with the effect observed in the ultraviolet absorption of benzene[7] when two substituent groups of the same directive influence are disposed para to each other and are electronically opposed.

Resonance effects such as hyperconjugation involving the phosphorus 3d orbitals should also be important. Although the increased wavelength of the emission of the cyclopentylphosphide over the cyclohexylphosphide (Table I) is in accord with the polar substituent (σ^*) constants for cyclopentyl and -hexyl (-0.20 and -0.15, respectively[8]), the increase may be due to the effect of delocalizable "π" electrons of cyclopentyl, as compared to the lesser effect of the hyperconjugative type of resonance interaction presumably shown by cyclohexyl,[9] and presumably minimal in the case of cycloheptyl. Indeed, no simple correlation is seen to exist between characteristics of the emissions (Table I) and the polar substituent constants for the alkyl and cycloalkyl groups since the wavelength for *tert*-butyl (σ^* value, -0.32[8]) was practically the same as that obtained for the cyclohexyl group (σ^* value, -0.15[8]).

In the alkyl series, where the predicted increase in wavelength would be $n\text{-}C_4H_9 < sec\text{-}C_4H_9 < t\text{-}C_4H_9$ based on their σ^* values (-0.13, -0.21, and -0.32, respectively[8]), emission occurred at lowest wavelength in the case of *sec*-C_4H_9 (Table I). The behavior displayed by this series, moreover, cannot be attributed solely to steric or hyperconjugative effects. Rather, the effect exerted on the chemiluminescence by the organic group attached to phosphorus is likely a combination of resonance and steric effects superimposed on inductive effects to which the σ^* constants are essentially related. Electron releasing groups should enhance phosphorus lone-pair participation. Steric effects would alter the bond angles (thus the hybridization of phosphorus), and could thereby affect the chemiluminescent oxidation. An optimum combination of such effects would appear to be responsible for the fact that the chemiluminescence of LHP is characterized by greatest intensity and longest duration.

Origin and Mechanism of Phosphide Chemiluminescence. The sensitivity of the chemiluminescence of lithium phosphides to change in the organic group, particularly the demonstrated effect of delocalization (above), indicates that in common with organic molecules, the light emission observed is molecular rather than crystal luminescence. The major emissions in the chemiluminescence spectra of several phosphides were found to coincide with the fluorescence emissions of the solid phosphides (Table II). It thus appears that phosphide oxidation produces electronically excited molecules capable of energy transfer to unoxidized phosphide molecules which become the emitters. The nature of the emitters, whether discrete, excited phosphide molecules, or di- or tetrameric aggregates, is unknown.

Although no esr signals have been detected,[10] lithium phosphide oxidation may proceed *via* formation of a peroxyphosphoranyl diradical, analogous to the scheme proposed for the air oxidation of secondary phosphines to phosphine oxides,[11] to produce the phosphinyl-

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[5] K. Issleib and F. Krech, *J. Organometal. Chem.*, **13**, 283 (1968), have reported the preparation of lithium di-*tert*-butylphosphide in petroleum ether without mentioning that the compound chemiluminesces.

[6] H. E. Winberg, J. R. Downing, and D. D. Coffman, *J. Amer. Chem. Soc.*, **87**, 2054 (1965), and references cited therein and in ref 4.

[7] L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).

[8] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

[9] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 254.

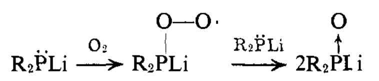
[10] Early in this work, a stable esr signal (*g* value = 2.007) was detected upon oxidation of several phosphides prepared with *n*-butyllithium. The signal was not reproducible, however, on generating LHP or $(C_6H_5)_2PLi$ with *n*-butyllithium of a different lot obtained commercially, or with phenyllithium.

Table II. Chemiluminescence and Fluorescence of Lithium Salts of Phosphorus Compounds

Compound	Chemiluminescence λ_{max}, mμ	Fluorescence λ_{max}, mμ
$(C_6H_{11})_2PLi$ (LHP)	531,[a] 463[b]	530
$(C_6H_{11})_2POLi$[c]	460	460
$(C_6H_{11})_2P(O)OLi$		443
$(C_6H_5)_2PLi$	558,[a] 470[b]	555
$(C_6H_5)_2POLi$[d]	520	520
$(C_6H_5)_2P(O)OLi$		440
$(CH_3OC_6H_4)_2PLi$	545[a]	540
(*sec*-$C_4H_9)_2PLi$	456,[a] 520[b]	460
(*sec*-$C_4H_9)_2P(O)OLi$		442
(*t*-$C_4H_9)_2PLi$	532[a]	532
(*t*-$C_4H_9)_2P(O)OLi$		445

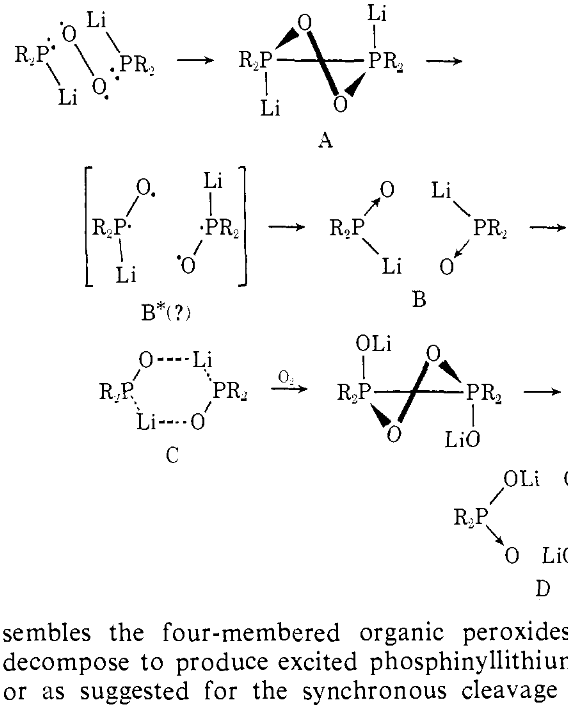
[a] Major emission. [b] Minor emission. [c] Lithium salt of dicyclohexylphosphine oxide (see proposed structure C, Scheme I). [d] Lithium salt of diphenylphosphine oxide (see proposed structure C, Scheme I).

lithium in an electronically excited state. A more attractive possibility, however, is the intermediacy of a cyclic peroxide, such as the four-membered peroxide (A) depicted in Scheme I. This peroxide, which resembles the four-membered organic peroxides, may decompose to produce excited phosphinyllithium (B*), or as suggested for the synchronous cleavage of the organic intermediates,[12] may cleave to produce two phosphinyllithium molecules (B), one of which is formed in an excited electronic state.



$$R_2\ddot{P}Li \xrightarrow{O_2} R_2\overset{O-O\cdot}{\overset{|}{P}}Li \xrightarrow{R_2\ddot{P}Li} 2R_2\overset{O}{\overset{\uparrow}{P}}Li$$

Scheme I



In search of evidence for the intermediacy of $R_2P(O)Li$, exposure of LHP, a light-yellow powder, to traces of oxygen produced a white solid which exhibited only the minor component (λ_{max} 460 mμ) of the chemiluminescence spectrum of LHP. This intermediate was suspected of being either $R_2P(O)Li$ or R_2POLi (R = cyclohexyl) contaminated with $R_2P(O)OLi$, the ultimate product of the controlled oxidation of the phosphide, and was prepared by an alternate route from dicyclohexylphosphine oxide and *n*-butyllithium. The solid product not only chemiluminesced with a blue emission visible to the eye at 460 mμ, but also fluoresced at that wavelength, the spectra coinciding with the minor chemiluminescence emission of LHP (Table II). An ir study (discussed below) indicated the ground-state structure to be closest to C (Scheme I) which may be viewed as a special form of $R_2\ddot{P}OLi$ existing in the crystal lattice, in which lithium ion is intermolecularly coordinated to both oxygen and phosphorus. Two phosphinyllithium molecules derived from peroxide A, and in close proximity to each other (B), may interact to produce C.

Electronically excited C is apparently responsible for the minor emission in the chemiluminescence spectrum of LHP. The chemiluminescence of C itself is attributable to energy transfer from an electronically excited species produced on oxidation of C. If excited C were identical with excited phosphinyllithium (B*),[13] then B* would appear capable of arising both before and after the formation of C during phosphide oxidation. Thus B* ($\equiv$C*) could proceed to the ground state two ways: by energy transfer to phosphide and by photon emission. If electronically excited C possessed a structure different from B*, and B* were the precursor of LHP*, then radiation would appear to be the only pathway available to excited C to return to the ground state. In another possible situation in which excited C rather than B* (C* $\not\equiv$ B*) is the precursor of LHP*, some fraction of electronically excited C would return to the ground state by energy transfer to phosphide, while the remaining fraction would return by radiation. No evidence is at hand to preclude these or other alternatives.

Fluorescence measurements (Table II) indicate that it is energetically possible for excited C (R = C_6H_{11}– and C_6H_5–) to serve as the precursor of R_2PLi^*, while a similar situation may not obtain for the more energetic (*sec*-$C_4H_9)_2PLi$. Although C* (R = C_6H_5–) has been found to be weakly chemiluminescent, the emission has not been detected during oxidation of $(C_6H_5)_2PLi$, and it is apparent from the data in Table II that this species is not responsible for the minor component of the phosphide chemiluminescence spectrum, contrary to the case of C* (R = C_6H_{11}–) and LHP. The data in Table II also indicate that it is energetically feasible for the lithium phosphinate (D, R = C_6H_{11}–, C_6H_5–, *sec*- and *t*-C_4H_9–), formed in an excited state in a manner analogous to B (Scheme I), to serve as precursor of electronically excited C, phosphide, or other emitter. In any case, further investigation is necessary before definite assignments can be made.

Infrared Spectra and the Structure of C. In view of the uncertainty surrounding the equilibrium, $R_2P(O)H \rightleftharpoons R_2POH$, and the problem of structure arising upon salt formation,[14] resolution of the question whether $R_2P(O)Li$ or R_2POLi exists in the crystalline

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(11) M. M. Rauhut and H. A. Currier, *J. Org. Chem.*, 26, 4626 (1961).

(12) E. H. White and D. F. Roswell, *Accounts Chem. Res.*, 3, 54 (1970), and references therein.

(13) The structure, $R_2P(O)Li$, is readily discerned in C (Scheme I) if lithium ion is more closely associated with phosphorus; R_2POLi, if lithium ion is more closely associated with oxygen. In general, it is intended in Scheme I to convey how phosphide oxidation might proceed within the constraints of the relatively rigid crystal lattice.

(14) L. D. Quin and R. E. Montgomery, *J. Inorg. Nucl. Chem.*, 28, 1750 (1966).

state was sought in infrared spectra taken from Nujol mulls. The ir spectrum of the lithium salt of dicyclohexylphosphine oxide showed significant differences with respect to the phosphine oxide. Besides the band at 4.40 μ in the P–H region, absorptions in the phosphoryl region [8.27 (m), 8.52-μ centered triplet (s)] were eliminated.[15] A broad, unsymmetrical band of very strong intensity (λ_{max} 11.33 μ) appeared in the region, 10.60–11.60 μ. The lithium salt of diphenylphosphine oxide also showed instructive differences with respect to its phosphine oxide. The absorption at 4.25 μ in the P–H region and several bands [8.30 (m), 8.44 (s), 8.62 μ (m)] in the P → O region were completely removed. A moderately broad band of strong intensity (λ_{max} 10.90 μ) appeared in the region, 10.60–11.40 μ.

Quin and Montgomery[14] have observed a similar effect on forming the silver salt of diphenylphosphine oxide. In that instance, the ir spectrum was taken from a KBr pellet, and it was reported that a strong, broad band appeared in the region, 9.50–10.50 μ. This absorption, however, was not perceptible in the spectrum obtained from a Nujol mull of the silver salt prepared in the present work[16] according to the published procedure.[14] A moderately broad peak of strong intensity appeared, instead, at 10.55 μ. The lithium salt thus absorbed at a wavelength 0.35 μ *longer* (30 cm^{-1} *lower*) than the silver salt.[17]

As in the case of the silver salt,[14] the removal of the characteristic phosphoryl absorption bands precludes assignment of the structure, $R_2P(O)M$, to the lithium salts. The appearance of the long-wavelength bands points, instead, to a structure in which the metal atom is bonded to phosphorus through the oxygen atom. However, structures analogous to $(C_6H_5)_2P{-}O{-}Ag$ or $[(C_6H_5)_2PO]^-Ag^+$[14] appear not to be applicable to the lithium salts in view of the fact that the long-wavelength band of the lithium salt of diphenylphosphine oxide is at a wavelength even longer than that of the silver salt. A structure such as C, in which the lithium atoms are bonded to both ends of the P–O moiety *via* intermolecular coordination, could account for the additional stretching of the P–O bond.

Experimental Section

General. Melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or on a Hewlett-Packard F & M 185 carbon, hydrogen, nitrogen analyzer. *n*-Butyllithium (approximately 2 *M* in *n*-hexane) was obtained commercially. Solvents [ethyl ether, petroleum ether (bp 30–55°)] were dried over $LiAlH_4$. Infrared spectra were obtained on Nujol mulls or neat compounds using a Perkin-Elmer 21 infrared spectrophotometer. Solid samples were examined for esr signals with a Varian 4500 electron spin resonance spectrometer. Precipitation and other manipulations of air-sensitive materials were done in a Whittaker, Mark V-A, controlled atmosphere system. The chamber was evacuated to 1 μ, then back-filled with Baker (99.997%) nitrogen.

Emission Spectra. Chemiluminescence and fluorescence spectra were obtained from solid samples using a Perkin-Elmer MPF-2A fluorescence spectrophotometer. The samples for fluorescence were excited by 370- or 400-mμ lines of a high-pressure xenon lamp using Corning filter 7-54 with maximum transparency at 370 mμ.

Phosphinous Chlorides. $(C_6H_5)_2PCl$ was obtained commercially. $(C_6H_{11})_2PCl$, $(C_5H_9)_2PCl$, $(C_7H_{13})_2PCl$, (*sec*-$C_4H_9)_2PCl$, (*t*-$C_4H_9)_2PCl$,[18] (*n*-$C_4H_9)_2PCl$,[19] (*p*-$CH_3C_6H_4)_2PCl$,[20] and (*p*-$CH_3OC_6H_4)_2PCl$[21] were prepared by reactions similar to those described in the literature.

Secondary Phosphines. The following phosphines were prepared by reduction of the appropriate phosphinous chloride *in situ* with an excess of $LiAlH_4$, and purified by distillation through a 13-cm Vigreux column, at the following temperatures and pressures: (*n*-$C_4H_9)_2PH$, 45–47° (1 mm) [lit.[22] 68–70° (14 mm)]; (*sec*-$C_4H_9)_2PH$, 39–40° (6 mm) [lit.[23] 162–165°]; (*t*-$C_4H_9)_2PH$, 44–47° (15 mm) [lit.[24] 38–40° (13 mm)]; $(C_6H_{11})_2PH$, 81–82° (0.5 mm) [lit.[25] 105–108° (3 mm)]; $(C_6H_5)_2PH$, 98–100° (1 mm) [lit.[26] 100–102° (1.5 mm)]; $(C_5H_9)_2PH$, 76–78° (0.8 mm); $(C_7H_{13})_2PH$, 100–102° (0.5 mm); (*p*-$CH_3C_6H_4)_2PH$, 112–114° (0.5 mm); (*p*-$CH_3OC_6H_4)_2PH$, 145–148° (0.15 mm) (a solid at room temperature). (α-$C_{10}H_7)_2PH$, purified by distillation as above, 200–204° (0.1 mm), was obtained from tri-α-naphthylphosphine, mp 263–265° [lit.[27] 263–265°], by a published procedure.[28]

The infrared spectra of the phosphines showed P–H stretching in the region of 4.40 μ.

$(C_5H_9)_2PH$ and methyl iodide in ethanol gave the methiodide, mp 156–159° (ethanol–ether). *Anal.* Calcd for $C_{11}H_{22}PI$: C, 42.32; H, 7.10. Found: C, 42.17; H, 6.99.

$(C_7H_{13})_2PH$ and methyl iodide in ethanol gave the methiodide, mp 129–131° (ethanol–ether). *Anal.* Calcd for $C_{15}H_{30}PI$: C, 48.92; H, 8.21. Found: C, 48.82; H, 8.20.

(*p*-$CH_3C_6H_4)_2PH$ was air oxidized to produce the phosphine oxide, mp 93–96° (unrecrystallized) [lit.[18] 94–96°].

(*p*-$CH_3OC_6H_4)_2PH$ and methyl iodide in ethanol yielded a yellow precipitate which could not be recrystallized from ethanol or ethanol–ether. Air was bubbled through a solution of the phosphine in ether, and after evaporation of the solvent the remaining oil was taken up in hot ethanol. Water was added up to the cloudpoint, and cooling caused crystallization of the phosphinic acid, mp 177–178° [lit.[29] 179–180°].

(α-$C_{10}H_7)_2PH$ and methyl iodide in ethanol gave the methiodide, mp 229–231° (ethanol). *Anal.* Calcd for $C_{21}H_{18}PI$: C, 58.75; H, 4.45; I, 29.56. Found: C, 58.81; H, 4.94; I, 29.47.

Lithium Phosphides. The phosphides were precipitated by the dropwise addition of *n*-BuLi in hexane to the appropriate phosphine in oxygen-free petroleum ether. The products were collected on a filter and washed with petroleum ether. Chemiluminescence data are given in Table I. Some fluorescence data are shown in Table II. Oxidation of $(C_6H_{11})_2PLi$ and $(C_6H_5)_2PLi$ produced no detectable esr signal.[10]

Although $(C_6H_{11})_2PLi$ precipitated from solution when C_6H_5Li was used in place of *n*-BuLi, $(C_5H_9)_2PLi$ could not be obtained in the same manner. Both phosphides were also obtained using *n*-BuLi with ethyl ether as solvent in place of petroleum ether, and were chemiluminescent. (*t*-$C_4H_9)_2PLi$, a yellow, chemiluminescing solid when precipitated from petroleum ether, showed partial solubility in ethyl ether, and precipitated, on forming in that solvent, as a white, etherated,[6] nonluminescing solid, gradually turning yellow with loss of solvent on standing.

Lithium Phosphinates. The products obtained by the slow oxidation of solid $(C_6H_{11})_2PLi$ and $(C_6H_5)_2PLi$ under nitrogen containing traces of oxygen produced infrared spectra with strong bands near 8.80 and 9.50 μ consistent with the phosphinate structure.[30] Acidification of aqueous solutions of the respective salts with hydro-

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(15) The lithium salt of the phosphine oxide showed a sharp band of medium intensity at 8.50 μ, a band also shown by dicyclohexylphosphine.

(16) The spectrum obtained from a KBr pellet in this work was similiar to that taken in Nujol.

(17) The spectra of the lithium and silver salts were very similar in all other respects.

(18) W. Voskuil and J. Arens, *Recl. Trav. Chim. Pays-Bas*, **82**, 302 (1963).

(19) K. Issleib and W. Seidel, *Chem. Ber.*, **92**, 2681 (1959).

(20) R. Montgomery and L. Quin, *J. Org. Chem.*, 30, 2393 (1965).

(21) K. S. Yudina, T. Ya. Medved, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1889 (1966).

(22) H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **98**, 1681 (1965).

(23) A. R. Stiles, F. F. Rust, and W. E. Vaughan, U. S. Patent 2,803,597 (1957); *cf.*, *Chem. Abstr.*, **52**, 2049*p* (1958).

(24) H. Hoffman and P. Schellenbeck, *Chem. Ber.*, **99**, 1134 (1966).

(25) H. Niebergall and B. Langenfeld, *ibid.*, **95**, 64 (1962).

(26) W. Kuchen and H. Buchwald, *ibid.*, **91**, 2871 (1958).

(27) W. Tefteller, Jr., R. A. Zingaro, and A. F. Isbell, *J. Chem. Eng. Data*, **10**, 301 (1965).

(28) K. Issleib and H. Völker, *Chem. Ber.*, **94**, 392 (1961); *Chem. Abstr.*, **55**, 15428*d* (1961).

(29) G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **71**, 369 (1949).

(30) N. Colthup, L. Daly, and S. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 300.

chloric acid precipitated the phosphinic acids, $(C_6H_{11})_2P(O)OH$, mp 140–141° [lit.[31] 140–141.5°], and $(C_6H_5)_2P(O)OH$, mp 192–194° [lit.[32] 193–195°]. The lithium salts were precipitated by the dropwise addition of *n*-BuLi in hexane to the acids in petroleum ether and benzene, respectively. The ir spectra were the same as before.

The fluorescence wavelengths of the precipitated salts, together with those of the phosphinates obtained by the slow oxidation of solid $(sec\text{-}C_4H_9)_2PLi$ and $(t\text{-}C_4H_9)_2PLi$, as above, are given in Table II. The butylphosphinates also showed strong bands in the region of 8.80 and 9.50 μ characteristic of the phosphinate structure.

Lithium Salts of Dicyclohexyl- and Diphenylphosphine Oxides. Dicyclohexylphosphine oxide, mp 74–76° [lit.[33] 76–77°], was prepared by air oxidation of the phosphine, by a procedure similar to that described in the literature,[11] and was isolated in anhydrous form by distillation at 142–143° (0.2 mm) through a 13-cm Vigreux column. Its ir spectrum showed principal peaks at 4.40 (ms), 7.56 (m), 7.74 (m), 7.87 (m), 8.27 (ms), 8.45–8.52–8.58 (s, triplet), 8.95 (m), 9.29 (m), 9.59 (m), 10.00 (m), 10.58 (s), 10.69 (m), 10.95–11.02 (w, doublet), 11.35 (m), 11.85 (m), 12.20 (m), 13.33 (m), 13.65 μ (w). Diphenylphosphine oxide, mp 51–53° [lit.[11,32] 53–56°; lit.[34] 51–53°], was prepared from diethyl phosphite and phenylmagnesium bromide as described in the literature.[32] The ir spectrum was essentially the same as the published spectrum.[32]

The lithium salts were precipitated by the dropwise addition of *n*-BuLi in hexane to the phosphine oxides in oxygen-free petroleum ether. The products were collected on a filter and washed with petroleum ether. Chemiluminescence and fluorescence data are given in Table II.[35] The ir spectrum of the cyclohexyl derivative contained principal peaks at 7.75 (m), 7.89 (m), 8.50 (m), 9.04 (m), 10.04 (ms), 10.45 (ms), 11.33 (vs), 11.77 (s), 12.30 (m), 13.40 (m), 13.85 μ (m). The phenyl derivative showed principal peaks at 6.30 (w), 6.97 (ms), 9.15 (m), 9.38 (w), 9.78 (w), 10.04 (w), 10.54 (m), 10.90 (s), 13.42 (ms), 13.60 (ms), 14.41 μ (s).

Slow oxidation of the solid lithium salts of the oxides under nitrogen containing traces of oxygen produced the phosphinates as confirmed by ir spectra identical with those obtained upon slow oxidation of the corresponding phosphides, above.

Silver Salt of Diphenylphosphine Oxide. Diphenylphosphine oxide was prepared as above. Formation of the salt with silver nitrate in 60% ethanol according to the published procedure[14] yielded a hydrate which was dried overnight at 70° *in vacuo*. The ir spectrum of the anhydrous salt showed principal peaks at 6.29 (w), 6.95 (ms), 9.08 (m), 9.37 (w), 9.75 (w), 10.03 (w), 10.55 (s), 13.42 (m), 13.57 (ms), 14.42 μ (s). Taken on a KBr pellet, the ir spectrum contained principal peaks at 3.35 (w), 6.80 (w), 7.01 (ms), 7.28 (w), 8.95 (w), 9.15 (m), 10.62 (s), 13.62 (ms), 14.51 μ (s).

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(35) On generating the lithium salt of dicyclohexylphosphine oxide in ethyl ether, the salt chemiluminesced at 490 mμ instead of 460 mμ, probably due to solvation.

Theoretical Interpretation of the Circular Dichroism of Adenine Nucleosides[1]

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Abstract: We present calculations of the rotational strength of α- and β-deoxyadenosine as a function of sugar–base torsion angle. Our method does not use perturbation theory, but calculates the rotational strength directly from extended Hückel wave functions for the entire nucleoside. Our calculated results show n–π^* transitions to have rotational strengths comparable in magnitude with those of π–π^* transitions. The geometric feature most influential in determining Cotton effects is the sugar–base torsion angle; sugar puckering and furanose substituents are less important. Comparison of our results with those of coupled oscillator theories indicates that one-electron effects and effects of n–π^* transitions are not negligible. For adenine nucleosides, we find agreement with recent experimental data for the four longest wavelength CD bands (270–225 nm) if we assume the nucleosides to be in the anti conformation with the torsion angle near 0°. Departures from enantiomeric behavior of α and β anomers are ascribed to deviations from mirror image relations in the sugar–base torsion angle. We predict adenine nucleosides in syn conformations to have circular dichroism curves quite different from that of deoxyadenosine. Cotton effects arising from interaction of the sugar with the base are large enough to be significant in polynucleotides for certain values of the torsion angle such as that in B form DNA.

The optical activity of polynucleotides is reasonably well understood, at least on a qualitative theoretical basis, and a number of useful empirical techniques have been developed based on this understanding.[2a] Unfortunately, no comparable theoretical basis has yet been developed for mononucleosides. Some empirical rules relating nucleoside optical activity to conformation have been proposed but they have limited applicability.[2a]

The reason for our poorer understanding of the optical activity of mononucleosides over that of their polymers lies in the different nature of the perturbation giving rise to the Cotton effects in the two cases. In oligonucleotides and polymers it is the interaction of similar chromophores (base–base interaction) which dominates the CD spectrum, while in mononucleosides it is the weak perturbation of the nonchromophoric sugar on the nucleoside base which gives rise to the observed Cotton effects.

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