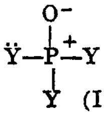
Communications TO THE EDITOR

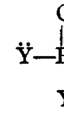
Ultraviolet Absorption Spectra of Tri-2-pyrrylphosphine Oxides: Evidence for $d\pi$-$p\pi$ Bonding

Sir:

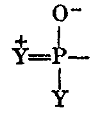
The occurrence of π-bonding involving overlap of a phosphorus *d*-orbital with a *p*-orbital of an adjacent atom has been firmly established for a number of tetracovalent phosphoryl compounds (I).[1] This bonding is conventionally expressed in terms of canonical structures such as II and III.



$\ddot{Y}-\overset{O^-}{\underset{\downarrow Y}{P}}\overset{+}{-}Y$ (I)

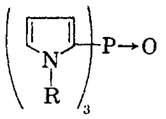


$\ddot{Y}-\overset{O}{\overset{\|}{\underset{\downarrow Y}{P}}}-Y$ (II)



$\overset{+}{\ddot{Y}}=\overset{O^-}{\underset{\downarrow Y}{P}}-Y$ (III)

Such $dp\pi$ bonding has only been observed in instances in which anti-bonding electrons of electronegative atoms, primarily oxygen, nitrogen, and sulfur, are donated to the empty phosphorus *d*-orbital. In no instance has a comparable interaction utilizing a π-bond system such as benzene been demonstrated. In an intensive study, Jaffe, Freedman, and Doak[2,3] examined the ultraviolet absorption spectra of triphenylphosphine oxide and a number of phenylphosphonates and found evidence for only very weak $d\pi$-$p\pi$ bond formation, i.e., bathochromic shifts of <10 mμ relative to the parent arene. Berlin and Butler have recently commented that an appreciable interaction might well be expected to occur in triarylphosphine oxides in which the aryl substituents contained powerful electron donating groups.[4] We now wish to report the first two cases in which such bonding occurs; in each the strong electron donor properties of the pyrrole π-system[5] is utilized.



IV. R=H
V. R=CH_3

Tri-2-pyrrylphosphine oxide (IV) has an intense band in the ultraviolet at 237.5 mμ (log ϵ 4.06) and the *N*-methyl analog (V) has a similar band at 248 mμ (log ϵ 4.11).[6] The parent structures pyrrole[7] and *N*-methyl pyrrole[8] show no such intense bands; their absorption drops smoothly from 225 mμ to 300 mμ (pyrrole[7] has two weak maxima at 262, 268 mμ; log ϵ 0.92, 0.92). A substituent acting only inductively would be expected to produce no change in the general appearance of the spectrum, though slight bathochromic shifts and hyperchromic effects are expected.[2] The appearance of a new and intense band in the spectra of IV and V is indicative of a conjugative interaction between the phosphoryl group and the π electrons of the pyrrole ring. For pyrroles containing substituents capable of conjugation in the 2- position (e.g. carbonyl and phenyl) two intense bands are observed at 228–252 mμ (log ϵ 3.57–3.70) and 263–289.5 mμ (log ϵ 4.10–4.22),[9,10] designated as bands A and B, respectively, by Andrisano and Pappalardo.[9] For example, pyrrole-2-carboxylic acid has maxima at 228, 258 mμ (log ϵ 3.65, 4.10).[9] Since only a single band is observed in the spectra of IV and V, it is probable that this band is related to band B; the hypsochromic shift observed for IV and V relative to the 2-carbonyl substituted pyrroles indicates the degree of conjugation to be much weaker in IV and V However, the pronounced change in the general appearance of the spectrum relative to pyrrole and *N*-methyl pyrrole and the development of intense bands at 237.5 and 248 mμ indicates $d\pi$-$p\pi$ bonding to be appreciable in these structures and much more pronounced than the weak interactions reported for phenyl phosphoryl structures.

More complete studies of the absorption characteristics and chemical properties of IV, V,

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[1] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience, New York, 1958; H. Finegold, *J. Am. Chem. Soc.*, **82**, 2641 (1960); L. Larsson, *Svensk Kem. Tidskr.*, **71**, 336 (1959).

[2] H. H. Jaffe, *J. Chem. Phys.*, **22**, 1430 (1954).

[3] H. H. Jaffe and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952); L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 6221 (1955).

[4] K. D. Berlin and G. B. Butler, *Chem. Revs.*, **60**, 243 (1960).

[5] A. R. Katritzky, *Quart. Revs.* (London), **13**, 353 (1959).

[6] The spectra of these compounds were determined as dilute solutions (C = 5 × 10^{-5} M) in 95% ethanol employing a Cary Model 14 spectrophotometer. Satisfactory analytical data and substantiation of structure have been obtained for IV and V (R. A. Polsky, M. S. thesis, University of Pittsburgh, 1961) and will be reported elsewhere.

[7] K. Ladenburg and C. R. Noller, *J. Am. Chem. Soc.*, **63**, 1240 (1941).

[8] L. C. Craig, L. Michaelis, S. Granich, and W. A. Jacobs, *J. Biol. Chem.*, **154**, 293 (1944).

[9] R. Andrisano and G. Pappalardo, *Gazz. chim. ital.*, **85**, 1430 (1955).

[10] B. Elpern and F. C. Nachod, *J. Am. Chem. Soc.*, **72**, 3379 (1950).

and a number of 2-pyrrylphosphonate structures are in progress and will be reported in detail.

This study was supported in part by a research grant (CY-5338) from the National Cancer Institute, Public Health Service and by an American Cancer Society Institutional Grant to the University of Pittsburgh.

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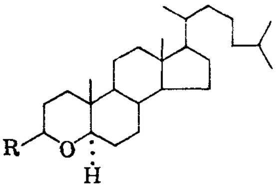
Received July 24, 1961

Steroids and Related Natural Products. VI. Diborane Reduction of Lactones to Cyclic Hemiacetals[1,2]

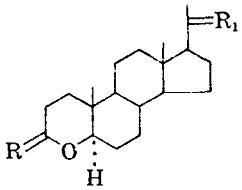
Sir:

Several carbohydrate lactones have been reduced, under carefully controlled conditions, to cyclic hemiacetals by sodium or potassium borohydride.[3] A few examples of lactone → cyclic hemiacetal conversion using lithium aluminum hydride have also been reported.[4]

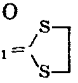
We now wish to report a new and convenient procedure for reducing lactones to cyclic hemiacetals using diborane.[5,6] This useful reduction reaction has been applied to synthesis of several unusual oxasteroids. In a typical experiment, the diborane prepared from sodium borohydride (0.2 g.) and boron trifluoride etherate (1 g.), in diglyme, was passed (over 3 hr.) into a solution of 3-oxo-4-oxa-5α-cholestane (0.39 g.)[7] in tetrahydrofuran at room temperature. Following addition of ethyl ether and water, the crude product was isolated. Chromatographic separation led to 3β-hydroxy-4-oxa-5α-cholestane (Ia, 0.28 g.); m.p. 197–199°, $[\alpha]_D^{22}$, + 106° (chloroform). *Anal.* Calcd. for $C_{26}H_{46}O_2$: C, 79.94; H, 11.87; O, 8.19. Found: C, 79.61; H, 11.52; O, 8.58. The cyclic hemiacetal structure (I) was confirmed by chromic acid oxidation to 3-oxo-4-oxa-5α-cholestane and transformation to 3β-methoxy-4-oxa-5α-cholestane (Ib, m.p. 106–107°, *Anal.* Calcd. for $C_{27}H_{48}O_2$: C, 80.14; H, 11.96; O, 7.91. Found: C, 80.45; H, 11.85; O, 7.47.) by hydrobromic acid–methanol.



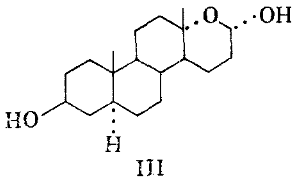
Ia. R = OH
b. R = OCH_3
c. R = H



IIa. R = R_1 = O
b. R = O, R_1 =



c. R = O, R_1 = H_2
d. R = ⋅—OH, R_1 = H_2
H



III

Conversion of 3,20-dioxo-4-oxa-5α-pregnane (IIa)[8] to 20-ethylene-thioketal derivative IIb (m.p. 237–239°, *Anal.* Calcd. for $C_{22}H_{34}O_2S_2$: C, 66.96; H, 8.69; S, 16.30. Found: C, 66.70; H, 8.58; S, 16.54.), followed by Raney nickel desulfurization gave 3-oxo-4-oxa-5α-pregnane (IIc); m.p. 188–190°, $[\alpha]_D^{23}$, + 107° (chloroform), (*Anal.* Calcd. for $C_{22}H_{32}O_2$: C, 78.89; H, 10.59. Found: C, 78.38; H, 10.33.). Diborane reduction of lactone IIc (0.3 g.) provided hemiacetal IId (0.2 g.); m.p. 161–163°, $[\alpha]_D^{23}$, + 69° (chloroform). *Anal.* Calcd. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44; Active H, 0.33. Found: C, 77.93; H, 11.11; O, 10.79; Active H, 0.25.

Diborane reduction of 3β-hydroxy-17-oxo-17a-

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[1] Part V; G. R. Pettit, B. Green, and W. J. Bowyer, *J. Org. Chem.*, **26**, 2879 (1961).

[2] This investigation was supported by PHS Research Grant CY-4074(C2) from the National Cancer Institute, Public Health Service, and National Science Foundation Research Grant G-9585.

[3] These studies have been reviewed by E. Schenker, *Angew. Chem.*, **73**, 81 (1961).

[4] *Cf.*; G. E. Arth, *J. Am. Chem. Soc.*, **75**, 2413 (1953); J. Schmidlin, G. Anner, J. R. Billeter, K. Heusler, H. Ueberwasser, P. Wieland, and A. Wettstein, *Helv. Chim. Acta*, **40**, 1034 (1957); and H. Obara, *Nippon Kagaku Zasshi*, **82**, 58 (1961).

[5] While reaction between diborane and γ-butyrolactone has been observed, the product was not described: H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1135 (1957). Interestingly, bis-3-methyl-2-butylborane has been reported to reduce both γ-butyrolactone and γ-valerolactone to hydroxyaldehydes: H. C. Brown and D. B. Bigley, *J. Am. Chem. Soc.*, **83**, 486 (1961).

[6] Several aspects of diborane chemistry and toxicology have been described by J. Cueilleron and P. Guillot, *Bull. soc. chim. France*, 2044 (1960). The potential value of this interesting substance in organic synthesis is illustrated by a number of recent investigations. For example, see: J. Kollonitsch, *J. Am. Chem. Soc.*, **83**, 1515 (1961); H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961); H. C. Brown and C. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1002 (1961); H. C. Brown, C. Verbrugge, and C. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1001 (1961); W. Jeffers, *Chem. and Ind. (London)*, 431 (1961); R. Köster and G. Griaznov, *Angew. Chem.*, **73**, 171 (1961); N. Nöth and G. Mikulaschek, *Chem. Ber.*, **94**, 634 (1961); H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961); M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 367 (1961); ref. 3; and a review prepared by H. C. Brown, *Organometallic Chemistry*, H. Zeiss, Ed., Reinhold Publishing Corp., New York, 1960, p. 150.

[7] A. Salamon, *Z. physiol. Chem.*, **272**, 61 (1941). Conclusive evidence for the structure and stereochemistry of the lactone prepared by this procedure will be presented in a subsequent communication.

[8] G. R. Pettit and T. R. Kasturi, *J. Org. Chem.*, **26**, 986 (1961).