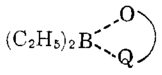
of R but not of R′ and Q, presumably within the limits of the capability of the chelate ring. The B^{11} chemical shift value is invariant at -15 p.p.m. for R′, Q = CH_3, CH_3; C_6H_5, C_6H_5; CH_3, OC_2H_5. (A similar lack of effect on alteration of the chelate ring in the F_2B series is also noted.) As might be expected the methyl, methylene H^1 resonances are unaltered by chelate substitution in these series.

It is interesting, but not surprising, therefore that the B^{11} chemical shift for the R′, Q = CF_3, CF_3 derivative is shifted downfield (-20.3 p.p.m.), suggesting that the CF_3 group has affected the limit of the donating ability of the carbonyl.

On the other hand, when the basic structure (**5**) (ring size or heteroatom) of the chelate is altered, effects on both B^{11} and H^1 n.m.r. of the CH_3CH_2B unit are seen.



5

With respect to the CH_3CH_2 data, there seems to be a unique opportunity for it to serve as a probe to ascertain the electronegativity of the B unit. Dailey and Shoolery[21] have shown that the chemical shift difference, $\tau_{CH_3} - \tau_{CH_2}$, was approximately linearly dependent on the electronegativity of the atom in the substituent which was directly bonded to the ethyl group. In the present case, the ethyl group in the acetylacetonates is a quartet–triplet multiplet, while in the 8 hydroxyquinoline and pyrrolidone products it is a singlet. Similar results have been reported where the boron atom (trigonal) was attached to a nitrogen atom.[22]

One other area of this investigation that has not been adequately explained and which deserves attention is the observation that the B^{11} resonance of the diethylboron derivatives is a function of the chelate ring size. In the five- and six-membered chelate (hydroxyquinoline and acetylacetone) rings the B^{11} resonance is 14.5 p.p.m. downfield from $BF_3 \cdot (C_2H_5)_2O$ and in the four-membered ones[23,24] (acetate and pyrrolidone) it is 47 p.p.m. downfield. For reference, trigonal triethylborane has a shift of -84 p.p.m.

It is felt that this approach of using an incipient organometal cation as a pseudo-metal ion in which charge properties and hybridization can be altered without affecting size and in which probes may be placed on the metal atom involved will permit a more detailed study of chelating agents. It is hoped that this preliminary study will excite work in other laboratories.

Acknowledgment.—The authors express their appreciation to the following agencies for financial support during this investigation: Army Research Office (Durham), and the National Science Foundation. We are indebted to Dr. R. Schaeffer and Dr. Litzow, Indiana University, Bloomington, Ind., for their assistance and cooperation in obtaining the B^{11} nuclear magnetic resonance spectra, and to Anderson Chemical Division, Stauffer Chemical Co., for supplying the triethylborane. The authors are also grateful to Dr. W. Kitching for some of the polarographic data.

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(21) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

(22) S. J. Brois, *Tetrahedron Letters*, **7**, 345 (1964).

(23) Diethylboron acetate shows one C–O absorption. Its molecular weight in benzene could not be determined due to its air sensitivity. However, derivatives involving homolog acids were monomeric. It is assumed that the diethylboron derivative is monomeric.

(24) The tables also show data for compounds which are dimeric in benzene; for example the products derived from the acetamide and 2-pyridone reactions. The exact structures of these materials are unknown.

Notes

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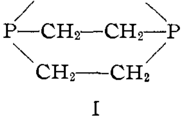
Polycyclic Group V Ligands. II. 2,6,7-Trioxa-1,4-diphosphabicyclo[2.2.2]octane and Derivatives[1]

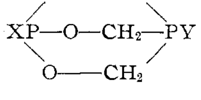
BY K. J. COSKRAN AND J. G. VERKADE

Received May 24, 1965

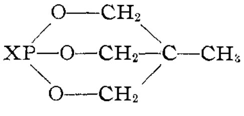
In 1959, Mann[2] reported the synthesis of 1,4-diphosphabicyclo[2.2.2]octane (I). We wish to report the synthesis of the analogous compound, 2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane (IIa) in which the bridgehead phosphorus atoms are chemically different. Also reported are the 1,4-dioxo (IIb), the 1-sulfo (IIc), and the 1-sulfo-4-oxo (IId) derivatives of IIa. These compounds were synthesized in order to evaluate their donor properties with a variety of Lewis acids. Although Mathews has reported the synthesis of the phosphonium salt $[CH_3CH_2P(CH_2CH_2)_3COH]Br$,[3] compound IIc and $P(CH_2O)_3CH$, the orthoformate analog



I



IIa, X = nothing, Y = nothing
IIb, X = O, Y = O
IIc, X = S, Y = nothing
IId, X = S, Y = O



IIIa, X = nothing
IIIb, X = O
IIIc, X = S

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(1) For part I in this series see J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

(2) R. C. Hinton and F. G. Mann, *J. Chem. Soc.*, 2835 (1959).

(3) D. A. Mathews, *Dissertation Abstr.*, **24**, 977 (1963).

of IIa,[4] represent the first examples of monodentate bicyclic phosphine ligands.

Experimental[5]

Research quantities of tetrakis(hydroxymethyl)phosphonium chloride were obtained as a gift from Hooker Chemical Corp., Niagara Falls, N. Y., and recrystallized from 1-propanol. All other reagents were used without further purification. Infrared spectra were obtained in potassium bromide pellets and carbon tetrachloride solutions and recorded on a Perkin-Elmer Model 21 double-beam spectrometer using sodium chloride optics. Proton n.m.r. spectra were obtained in approximately 15% solutions on Varian Associates Model HR-60 and Varian A-60 spectrometers. Tetramethylsilane and Tiers' salt were used as internal standards. The P^{31} n.m.r. spectra were obtained in approximately 30% dimethyl sulfoxide solutions with 85% aqueous phosphoric acid as an external standard. Melting points were taken in capillaries and are uncorrected. Analyses for carbon, hydrogen, and sulfur were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of $P(CH_2OH)_3$.—The triol was prepared according to the method of Grayson,[6] wherein a solution of 4.0 g. (0.10 mole) of sodium hydroxide dissolved in 100 ml. of absolute ethanol was added all at once to a stirred solution of 19.0 g. (0.1 mole) of $[P(CH_2OH)_4]Cl$, dissolved in 175 ml. of absolute ethanol at room temperature. The solution was allowed to stir for 15 min. after which it was filtered and the ethanol removed under vacuum to give quantitative yields of the product in the form of a colorless sirup.

Anal. Calcd. for $C_3H_9O_3P$: C, 29.03; H, 7.25. Found: C, 29.04; H, 6.97.

Preparation of $P(CH_2O)_3P$.—The 0.1 mole of $P(CH_2OH)_3$ prepared in the previous reaction was dissolved in 50 ml. of tetrahydrofuran with vigorous stirring. To the stirred solution was added dropwise 12.4 g. (0.100 mole) of trimethyl phosphite, and the mixture was refluxed for approximately 12 hr. Tetrahydrofuran was removed under vacuum, leaving a viscous solution from which 5.32 g. (35% yield) of clear colorless crystals, melting at 75–76°, were obtained upon sublimation at approximately 0.1 mm. and 50°.

Anal. Calcd. for $C_3H_6O_3P_2$: C, 23.67; H, 3.95. Found: C, 23.62; H, 4.02.

When the reaction was carried out without the presence of a solvent, an uncontrollable exothermic reaction took place. No product could be recovered from the decomposed reaction mixture.

Preparation of $OP(CH_2O)_3PO$.—To 0.3262 g. (2.200 mmoles) of $P(CH_2O)_3P$ dissolved in 5.0 ml. of absolute ethanol, 0.354 ml. (4.40 mmoles) of 30% hydrogen peroxide was added dropwise with stirring. The reaction mixture, which became quite warm, was cooled, producing 0.3100 g. (95% yield) of needle-like crystals melting at 210–213°.

Anal. Calcd. for $C_3H_6O_5P_2$: C, 19.58; H, 3.27. Found: C, 19.49; H, 3.28.

Preparation of $P(CH_2O)_3PS$.—An intimate mixture of 0.9016 g. (5.900 mmoles) of $P(CH_2O)_3P$ and 0.1898 g. (5.900 mg.-atoms) of sulfur was placed in a sealed tube and heated to 110°. After 20 min. at this temperature the yellow color of the sulfur disappeared and the resulting white solid was taken up in acetone from which 0.8147 g. (75% yield) of colorless, needle-like crystals was obtained on cooling, having a melting point of 235–237°.

Anal. Calcd. for $C_3H_6O_3P_2S$: C, 19.57; H, 3.27; S, 17.39. Found: C, 19.57; H, 3.30; S, 17.44.

Preparation of $OP(CH_2O)_3PS$.[6a]—To a stirred solution of 0.4837 g. (2.630 mmoles) of $P(CH_2O)_3PS$ in 150 ml. of absolute ethanol was slowly added 2.1 ml. (26 mmoles) of 30% hydrogen peroxide. The solution was boiled for 5 min. after which it was cooled to 0° overnight. The white powder which formed was filtered and dissolved in boiling acetonitrile. Cooling the solution to 0° produced 0.4317 g. (82% yield based on $P(CH_2O)_3PS$) of small colorless crystals which decomposed at about 210°.

Anal. Calcd. for $C_3H_6O_4P_2S$: C, 18.00; H, 3.00; S, 16.00. Found: C, 17.55; H, 3.24; S, 15.63.

Results and Discussion

Evidence for the formulation of IIa, IIb, IIc, and IId as the bicyclic structure stems from the proton n.m.r. data which are summarized in Table I. The spectrum of IIa consists of a straightforward A_2XY pattern for the six equivalent hydrogens. The assignment of J_{PCH} = 9.3 c.p.s. is based upon a similar value (J_{PCH} = 8.3 c.p.s.) observed in the orthoformate analog of IIa, $P(CH_2O)_3CH$.[4] The value of 2.7 c.p.s. for J_{POCH} is in line with the value observed in $P(OCH_2)_3CCH_3$ (J_{POCH} = 1.8 c.p.s.).[7]

TABLE I

PROTON CHEMICAL SHIFTS (P.P.M. *vs.* $Si(CH_3)_4$)

Compound	H^1	J_{PCH}, c.p.s.	J_{POCH}, c.p.s.	Solvent
$C_3H_6O_3P_2$ (IIa)	4.45	9.3	2.7	CCl_4
$C_3H_6O_5P_2$ (IIb)	5.28	7.8 or 8.7[a]	7.8 or 8.7[a]	D_2O[b]
$C_3H_6O_3P_2S$ (IIc)	5.20	7.8	7.8	DMSO
$C_3H_6O_4P_2S$ (IId)	5.15	8.3 or 8.9[a]	8.3 or 8.9[a]	DMSO

[a] The near equivalence of these coupling constants precluded their assignment. [b] Tiers' salt used as internal standard.

Rather large values of J_{PCH} have been observed before in alkylphosphines, but primarily when a strongly electron-withdrawing group has been substituted for an alkyl group on the phosphorus atom[8] or in trialkylphosphine oxides.[9] In contrast to the observation that J_{PCH} increases upon oxidation of a trialkylphosphine to the corresponding oxide,[9] oxidation of IIa to IIb or IId results in a decrease in J_{PCH}. However, J_{POCH} increases from IIa to IIb as observed earlier in IIIa and IIIb[7] and in open-chain phosphites and phosphates.[10] It is interesting in this respect, however, that in IIc J_{PCH} decreases from its value in IIa to equal J_{POCH} (7.8 c.p.s.) in spite of the fact that the "phosphine" phosphorus has not changed oxidation state. The small decrease in J_{PCH} upon oxidation of IIa to IIb, IIc, or IId is not readily explained at this time, but the relatively large value of J_{PCH} in IIa may be interpreted in terms of the following considerations. The magnitude of J_{PCH} in trialkylphosphines, such as trimethylphosphine, has been attributed to the per cent s character in the hybridized orbitals of phosphorus.[9,11] The P–C bond in alkylphosphines consists of primarily p character while the phosphorus lone pair is primarily s in character.[9,11] This deviation from perfect sp^3 hybridization in trimethylphosphine is supported by the observation that the

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[4] E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, to be published.

[5] All preparations were carried out under a flush of dry nitrogen.

[6] M. Grayson, German Patent 1,151,255; *Chem. Abstr.*, **60**, 554*g* (1964).

[6a] This paragraph added Sept. 7, 1965.

[7] J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King *Inorg. Chem.*, **4**, 83 (1965).

[8] G. Mavel, *J. chim. phys.*, **59**, 683 (1962).

[9] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

[10] R. C. Axtman, W. E. Shuler, and J. H. Eberly, *J. Chem. Phys.*, **31**, 851 (1959).

[11] H. A. Bent, *Can. J. Chem.*, **38**, 1235 (1960).

C–P–C bond angle is 98.9°.[12] In IIa, strain in the bicyclic structure would be minimized if the bond angles in the rings were near the tetrahedral angle. Such an increase in the C–P–C bond angle would give rise to an increase in s character in the P–C bond and consequently larger P–C–H coupling would be realized.

The downfield proton chemical shift observed upon oxidation of IIa as well as the small differences in proton chemical shift among IIb, IIc, and IId parallels that found previously for the polycyclic phosphite compounds IIIa, IIIb, and IIIc.[7]

The P^{31} n.m.r. data in Table II lend further support for the formulation of IIa, IIb, and IIc.[13] The chemical shifts observed for the bicyclic compounds IIIa, IIIb, and IIIc, also shown in Table II, are seen to agree well with the shifts obtained for the analogous phosphorus atom in IIa, IIb, and IIc. Moreover, the P^{31} chemical shift for the "phosphine" phosphorus in IIc lies close to the value observed for the analogous phosphorus nucleus in IIa. If the sulfur atom were bound to the "phosphine" phosphorus, a negative chemical shift such as that observed for trimethylphosphine sulfide (−48.0 p.p.m.)[14] would be expected.

TABLE II

P^{31} CHEMICAL SHIFTS IN DIMETHYL SULFOXIDE (P.P.M. *vs.* 85% AQUEOUS H_3PO_4)

Compound	P^{31}[P-$(CH_2)_3$]	P^{31}[PO_3]	J_{PCH}, c.p.s.	J_{POCH}, c.p.s.
$C_3H_6O_3P_2$ (IIa)	+67.0	−90.0	8.9	2.6
$C_3H_6O_5P_2$ (IIb)	− 6.4	+18.1	...[a]	...[a]
$C_3H_6O_3P_2S$ (IIc)	+ 70.6	−51.8	Not observed	
$C_3H_6O_4P_2S$ (IId)[b]				
$C_5H_9O_3P$ (IIIa)		−91.5[c]		2[c]
$C_5H_9O_4P$ (IIIb)		+7.9[c]		7[c]
$C_5H_9O_3PS$ (IIIc)		−57.4[c]		6[c]

[a] Values are indistinguishable within experimental error. [b] Insufficient solubility. [c] J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962).

Because of the high symmetry of these molecules the infrared spectra contain relatively few bands. Weak fundamental C–H stretching and deformation bands at 2920 and 1429 cm.$^{-1}$, respectively, are evident in the spectrum of IIa, while strong bands at 1046 and 963 cm.$^{-1}$ may be due to C—O and P—O modes. The spectrum of IIb is similar except for a strong phosphate P═O mode at 1325 cm.$^{-1}$ and a strong phosphine P═O mode at 1220 cm.$^{-1}$, while IIc exhibits a strong band at 807 cm.$^{-1}$ which may be due to the P═S stretching frequency. In IId the P═S and P═O modes appear at 807 and 1215 cm.$^{-1}$, respectively. Complete assignment of these and other bands will be the subject of a future publication.

It is not surprising that the 1,4-dioxo compound (IIb) is formed rather easily. Various attempts to prepare a monooxo compound of IIa have thus far been unsuccessful. In view of the apparent ease with which trialkylphosphine sulfides are produced under fusion conditions,[15] it is worthy of note that only a monosulfide is formed wherein the sulfur atom is bonded to the "phosphite" phosphorus even in the presence of a 100% excess of sulfur.

Acknowledgments.—The authors are grateful for the generous support of the National Science Foundation in the form of a grant (GP-2328) to J. G. V. and a Graduate Assistantship to K. J. C.

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[12] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960).

[13] The long-range P^{31}–P^{31} coupling constants will be discussed elsewhere.

[14] M. L. Nielsen, J. V. Pustinger, Jr., and J. Strobel, *J. Chem. Eng. Data*, **9**, 167 (1964).

[15] R. A. Zingaro and R. E. McGlothlin, *ibid.*, **8**, 226 (1963).

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Preparation and Properties of Di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II)

BY J. A. BERTRAND AND ROY I. KAPLAN

Received June 1, 1965

Several complexes containing both methoxide and β-dicarbonylate ions have been reported[1,2]; these can be represented by the general formula $MA(OCH_3)(CH_3OH)_x$. A beryllium complex,[1] with A representing the anion of 3-nitro-2,4-pentanedione and $x = 0$, was reported to have a molecular weight corresponding to a mixture of dimeric and trimeric species; cobalt(II) complexes,[2] with A representing the anion of salicylaldehyde, *o*-hydroxyacetophenone, or 2,4-pentanedione and $x = 1$, were found to have much higher associations. Complexes of nickel(II) and magnesium(II),[2] prepared by the same method used for cobalt(II), were analogous to the cobalt(II) complexes; however, copper(II) complexes prepared by the same method did not separate from solution as large crystals as did the other complexes, the solids did not lose weight on heating, and analyses indicated a formula similar to the beryllium complex. We have investigated the copper(II) complex of 2,4-pentanedione further and report here the results of those investigations.

Experimental

Preparation of Di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II).—A 1.8-g. (0.007 mole) sample of bis(2,4-pentanedionato)copper(II) was dissolved in 350 ml. of refluxing methanol and 0.39 g. (0.007 mole) of potassium hydroxide was added dropwise to the refluxing solution. The solution was refluxed for 2 hr. and filtered while hot. The compound was obtained as a violet, microcrystalline solid.

Anal. Calcd. for $C_6H_{10}O_3Cu$: C, 37.2; H, 5.6. Found: C, 37.1; H, 5.3.

The compound is soluble in acetonitrile, chloroform, dichloromethane, nitromethane, and pyridine.

Spectral Measurements.—Spectra in the visible and ultraviolet were obtained with a Carey Model 14 spectrophotometer. Chloroform was used as solvent.

The infrared spectrum was obtained with a Perkin-Elmer

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[1] R. M. Klein and J. C. Bailar, Jr., *Inorg. Chem.*, **2**, 1189 (1963).

[2] J. A. Bertrand and D. Caine, *J. Am. Chem. Soc.*, **86**, 2298 (1964).