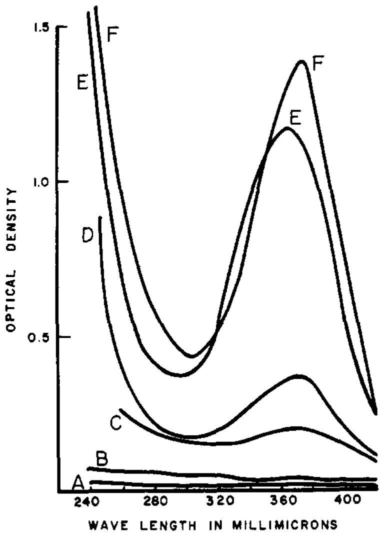


Figure 1. Ultraviolet spectra taken in 0.1 N NaOH at a dilution of 1:40 of reaction mixtures consisting of 1 mmole of 2-aminoimidazole sulfate, 5 mmoles of sodium nitrite, and 100 ml. of water: (A) 16 hr. at room temperature and then heated 2 hr. on steam bath; (B) 16 hr. at room temperature; (C) 1 hr. at room temperature and then heated 1 hr. on the steam bath; (D) 1 hr. at room temperature in the presence of 5 mmoles of $CuSO_4$; (E) heated 1 hr. on the steam bath in the presence of 5 mmoles of $CuSO_4$; (F) 16 hr. at room temperature in the presence of 5 mmoles of $CuSO_4$.

cating Plate column.[9] The ethyl acetate extract was evaporated to 200 ml. and cooled to give 5.34 g. (40%) of crude 2-nitroimidazole, $\lambda_{\max}^{0.1N\,NaOH}$ 373 mμ (ϵ 12,600). This material was purified first by sublimation and then by crystallization from ethanol to give 4.2 g. of pale yellow crystals, m.p. 287–288° dec., $\lambda_{\max}^{0.1N\,NaOH}$ 374 mμ (ϵ 12,750). *Anal.* Calcd. for $C_3H_3N_3O_2$: C, 31.86; H, 2.67; N, 37.16. Found: C, 32.28; H, 2.60; N, 36.98. It was identified with natural azomycin[2,10–12] by mixture melting point, by ultraviolet and infrared spectra, and by its *in vitro* antibacterial spectrum against 19 microorganisms. 1-Methyl-2-nitroimidazole, m.p. 102–103°, identical with the product obtained by Gallo, *et al.*,[11] by methylation of azomycin, was prepared from the corresponding amino compound by a variation of our method. Modifications of our procedure have been applied successfully to the preparation of other homologs of 2-nitroimidazole and to nitro derivatives of related heterocyclic systems. Details of this work will be reported later.[13]

Acknowledgment. The authors wish to express their appreciation to Dr. Arnold Brossi for helpful suggestions and continued interest.

[9] A. Karr, *Am. Inst. Chem. Engrs. J.*, **5**, 446 (1959).

[10] G. C. Lancini, N. Maggi, and P. Sensi, *Farmaco* (Pavia) *Ed. Sci.*, **18**, 300 (1963).

[11] G. G. Gallo, C. R. Pasqualucci, P. Radaelli, and G. C. Lancini, *J. Org. Chem.*, **29**, 862 (1964).

[12] We gratefully acknowledge the gift of a sample of natural azomycin which we obtained from Lepetit S.p.A., Milan, Italy.

[13] After the present investigation was essentially completed, the formation of 2-nitroinosine (as a by-product in yields up to 5%) by treatment of guanosine with nitrous acid was described [R. Shapiro, *J. Am. Chem. Soc.*, **86**, 2948 (1964)].

Alden G. Beaman, William Tautz,
Thomas Gabriel, Robert Duschinsky
Hoffmann-La Roche Research Division
Nutley 10, New Jersey
Received December 2, 1964

A Pyrolytic Synthesis of Ylides. Isolation of Trimethylphosphinetrimethylsilylmethylene

Sir:

The usual routes to ylides are reactions of onium salts with strong bases such as lithium alkyls in suitable solvents. It has now been found that the novel, distillable ylide, trimethylphosphinetrimethylsilylmethylene (I) can be prepared by a solid state pyrolytic route which appears to involve a five-coordinate silicon transition state.

$$(CH_3)_3Si\overset{-}{\bar{C}}H\overset{+}{P}(CH_3)_3 \longleftrightarrow (CH_3)_3\overset{-}{\bar{Si}}{=}CH\overset{+}{P}(CH_3)_3 \longleftrightarrow (CH_3)_3SiCH{=}P(CH_3)_3$$

I

Heating trimethylsilylmethyltrimethylphosphonium chloride (II), $(CH_3)_3SiCH_2P(CH_3)_3Cl$, under vacuum produces I and trimethylsilyl chloride as the volatile products and leaves a residue of tetramethylphosphonium chloride. These observations can be rationalized by a mechanism in which the chloride ion attacks the silicon site leading to rearrangement and decomposition into trimethylsilyl chloride and trimethylphosphinemethylene (III), and the latter product then abstracts a proton from II to form tetramethylphosphonium chloride and ylide I. The presence of finite amounts of intermediate trimethylphosphinemethylene was confirmed by a pyrolysis in the presence of acetone vapor which produced small yields of isobutylene.[1]

Trimethylphosphinetrimethylsilymethylene (I) is a colorless liquid boiling at 70–75° (14 mm.), freezing at −36°. Its ^1H n.m.r. spectrum at 60 Mc. has three resonances, a low-field doublet (chemical shift of −1.20 p.p.m. from external tetramethylsilane, A_{PCH} = 13 c.p.s.) a singlet (0.27 p.p.m.), and a high-field doublet (1.03 p.p.m., A_{PCH} = 8 c.p.s.). The integrated intensities of the peaks were in the ratio of 9:9:1, respectively, in excellent agreement with an assignment of the low-field doublet to CH_3P protons, the singlet to CH_3Si protons, and the high-field doublet to the methylenic proton. The high-field position of the methylenic proton can be explained by the decreased electronegativity of the methylenic carbon atom owing to its partial negative charge and by an enhanced paramagnetic contribution of the neighbor-anisotropy effect.[2] The infrared spectrum of I as a liquid shows the following absorptions in cm.$^{-1}$: 2950 (s), 2900 (m), 1430 (m, sharp), 1305 (w, sharp), 1285 (m), 1250 (w), 1235 (m), 1150 (s), 1000 (s), 930 (s), 825–875 (s), 750 (m, doublet), 710 (w), 675 (w), and 635 (w).

The chemical reactivity of I is intermediate between that of III and highly stable ylides containing carbonyl groups conjugated with the methylenic carbon. Some of the latter type may be obtained from water solution.[3]

---

[1] Isobutylene is the expected product of a Wittig reaction of acetone with III: see S. Trippett and D. M. Walker, *Chem. Ind.* (London), 933 (1960).

[2] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 176.

[3] J. A. Ford, Jr., and C. V. Wilson, *J. Org. Chem.* **26**, 1433 (1961); F. Ramirez and S. Dershowitz, *ibid.*, **22**, 41 (1957).

The reaction of I with air, water, or halogenated hydrocarbons is quite vigorous. A controlled hydrolysis in dilute hydrochloric acid gave a mixture of II and tetramethylphosphonium chloride. The formation of the latter salt is reasonable in view of the fact that II is attacked in boiling water (very rapidly when basic) to form hexamethyldisiloxane and tetramethylphosphonium chloride.

The phosphonium salt II was obtained by heating equimolar amounts of chloromethyltrimethylsilane and trimethylphosphine in a sealed tube at 40° for several days. Traces of unchanged material were removed under vacuum to leave the pure chloride as a white crystalline solid.

Anal. Calcd. for $(CH_3)_3SiCH_2P(CH_3)_3Cl$: Cl (ionic), 17.8. Found: Cl (ionic), 17.9.

For analysis, the hexafluorophosphate salt was precipitated from an aqueous solution of the chloride and recrystallized from acidified water. It is a white crystalline solid.

Anal. Calcd. for $(CH_3)_3SiCH_2P(CH_3)_3PF_6$: C, 27.3; H, 6.5; P, 20.1. Found: C, 28.0; H, 6.6; P, 19.2.

The chloride salt was pyrolyzed at 180° under vacuum over a period of several hours, during which time the volatile material was passed through a series of traps cooled to 0, -78, and $-196°$, respectively. The contents of the $-78°$ trap were transferred to a short-pass still and redistilled to give pure trimethylsilyltrimethylphosphinemethylene.

Anal. Calcd. for $(CH_3)_3SiCHP(CH_3)_3$: P, 19.1; Si, 17.3. Found[4]: P, 18.5; Si, 17.7.

A gas-phase molecular weight determination (18.5 mg. in 306.5 ml. exerted 22.6 mm. pressure at 88.4°) supported the monomeric composition, mol. wt. 165.3 (calcd. 162.3).

Acknowledgment. This work was supported in part by a grant from the University of South Dakota General Research Funds. The author is grateful to Dr. Earl L. Muetterties of the Du Pont Company for obtaining the n.m.r. spectrum and for assistance with elemental analyses.

---

[4] Carbon and hydrogen values by combustion analysis were low, apparently owing to rapid combustion. In an attempt to bring about slow combustion, the sample exploded and destroyed the combustion tube. The values found were: C, 48.6, 49.9, 50.0 (calcd., 51.8); H, 11.2, 11.8, 11.7 (calcd., 11.8).

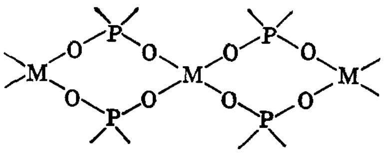
N. E. Miller
Chemistry Department, University of South Dakota
Vermillion, South Dakota

Received October 31, 1964

Inorganic Coordination Polymers. Cobalt(II) and Zinc (II) Di-*n*-butylphosphinates[1]

Sir:

A particular class of inorganic polymers, the so-called "coordination polymers," having a skeleton formed by metal atoms interconnected by ligand molecules, has recently attracted considerable interest.[2] Bridged polymeric structures of the type have been proposed for Co(II), Zn(II), and Be(II) tetrahedral complexes with dimethyl-, diphenyl- and methylphenylphosphinic acids.[3,4] Molecular weight determinations of the zinc methylphenylphosphinate by ebulliometry in benzene have been reported.[3] However, the difficulty of obtaining solutions of the dimethyl and diphenyl derivatives in solvents which do not attack the polymeric bonds has seriously impaired their physicochemical characterization.



In our laboratory di-*n*-butylphosphinates (di-*n*-BP) of Co(II) and of Zn(II), which are soluble in most organic solvents, have been prepared and display polymeric properties. We wish to report here some preliminary results on their characterization.

The di-*n*-butylphosphinate of Co (Co(di-*n*-BP)) was obtained by allowing pure sodium di-*n*-butylphosphinate to react with $CoCl_2$ in water at about 60°. The di-*n*-butylphosphinic acid was prepared according to Kosolapoff.[5] On standing the blue-colored complex precipitated in an almost quantitative yield. The sample dissolved in water gives pink solutions, from which it was recrystallized on heating.

Anal. Calcd. for $Co[(C_4H_9)_2PO_2]_2$: C, 46.49; H, 8.78; P, 14.99. Found: C, 45.96; H, 8.84; P, 14.77.

Zinc di-*n*-butylphosphinate was prepared by stirring an aqueous solution of $Zn(AcO)_2$ with a solution of di-*n*-butylphosphinic acid in benzene. The white precipitate, formed during the evaporation of the benzene layer, was collected and washed with ethanol. The reduced viscosity of both Co(di-*n*-BP) and Zn(di-*n*-BP) in benzene or carbon tetrachloride exhibits a peculiar dependence on concentration.

Typical results are reported in Figure 1, which show that the $[\eta]$ values are low, but the reduced viscosity of the solutions rises quite steeply with concentration. In the case of Zn(di-*n*-BP), gel formation occurred beyond a concentration of about 0.8% in benzene. This behavior may be explained in terms of an aggregation of relatively short chains of the coordination polymers which does not exert any influence on the absorption spectrum of Co(di-*n*-BP) in the 400–700-mμ region since for a wide range of concentrations in CCl_4 no departure from Beer's law could be detected. A study is being carried out on this effect also with the aid of infrared spectra on CCl_4 solutions of both cobalt and zinc phosphinates. Crystals of Co(di-*n*-BP) were obtained by heating a water solution of the compound which appeared as twinned monoclinic prisms elongated along the *b* axis. Attempts to grow single crystals suitable for an accurate X-ray structure analysis so far have been unsuccessful.

The powder diffraction pattern of the residue obtained from evaporation of a benzene or carbon tetrachloride solution is identical with that of the crystal grown from water solutions. The Zn(di-*n*-BP) was

---

[1] This work was supported by the Consiglio Nazionale delle Ricerche (C.N.R.), Rome, Italy.

[2] B. P. Block, "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press Inc., London, 1962, p. 447.

[3] B. P. Block, S. H. Rose, C. W. Schaumann, E. S. Roth, and J. Simkin, *J. Am. Chem Soc*, **84**, 3200 (1962).

[4] G. E. Coates and D. S. Golightly, *J. Chem. Soc.*, 2523 (1962).

[5] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **72**, 5508 (1950).