

Figure 1. Spectra of dilute solutions of nickel(II) ions in molten  $\text{ZnCl}_2$ - $\text{CsCl}$  mixtures at  $400^\circ$ . Each spectrum is labeled with the mole percentage of zinc chloride in the solvent salt.

solvent. In the limit of pure zinc chloride as solvent there is a mixture of tetrahedral and octahedral entities.

The tetrahedral spectra in the two ranges, 50–72 and 92–100 mole % zinc chloride, have significantly different band energies and correspond to different entities.

The tetrahedral–octahedral equilibrium that occurs between about 50 and 70 mole %  $\text{ZnCl}_2$  appears to be of the same type as is found for solute nickel(II) in lithium chloride–potassium chloride and magnesium chloride–potassium chloride melts.<sup>2,3</sup> The second equilibrium, which occurs in pure zinc chloride and neighboring compositions as solvents, is almost certainly associated with the tendency of molten zinc chloride to form chloride-bridged polymers in which zinc is tetrahedrally coordinated.<sup>4</sup> We propose that the tetrahedral nickel(II) species in pure zinc chloride consists of a nickel ion occupying a zinc site within a polymer unit, while the octahedral species is a nickel ion at interpolymer positions. Addition of  $\text{CsCl}$  to molten  $\text{ZnCl}_2$  breaks chloride bridges and destroys the polymer structure,<sup>5</sup> thereby increasing the density of interpolymer positions and, hence, the concentration of octahedrally coordinated nickel(II).

The effect of temperature was studied from 300 to  $600^\circ$ . For melts containing 50–62 mole %  $\text{ZnCl}_2$ , with increasing temperature the equilibrium shifts in favor of four-coordinate nickel just as it does when  $\text{LiCl-KCl}$  and  $\text{MgCl}_2\text{-KCl}$  are the solvents. For melts containing higher zinc chloride concentrations, the behavior is more intricate than this, but it appears

(2) J. Brynestad, C. R. Boston, and G. P. Smith, *J. Chem. Phys.*, in press.

(3) J. Brynestad and G. P. Smith, *ibid.*, in press.

(4) D. E. Irish and T. F. Young, *ibid.*, **43**, 1765 (1965).

(5) J. R. Moyer, J. C. Evans, and G. Y.-S. Lo, *J. Electrochem. Soc.*, **113**, 158 (1966).

that with increasing temperature the fraction of nickel ions at zinc sites in 100%  $\text{ZnCl}_2$  decreases as expected because of the breakup of the polymer network.

The results reported here are taken from an extensive study of nickel(II) ions in solvents ranging in composition from pure  $\text{CsCl}$  to pure  $\text{ZnCl}_2$ . This research will be reported in detail in subsequent publications.

**Acknowledgment.** The work described here was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

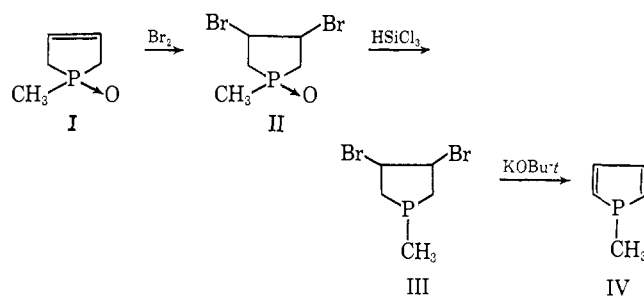
W. Ewen Smith, Jorulf Brynestad, G. Pedro Smith  
Metals and Ceramics Division  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37830  
Received July 27, 1967

### 1-Methylphosphole<sup>1</sup>

Sir:

The extent of delocalization of the phosphorus electron pair in phospholes into an aromatic system has not yet been defined<sup>2</sup> even though the ring system has been known since 1959.<sup>3</sup> Molecular orbital calculations suggest a considerable degree of conjugation energy ( $1.49\beta$ ; cf. to  $1.37\beta$  for pyrrole) for the parent compound.<sup>4</sup> The phospholes characterized to date all bear several substituents, one<sup>5</sup> or more<sup>3,6</sup> of which are phenyl groups. A phenyl substituent, with conjugative effects of its own, is undesirable when attempting to define the electronic character of the parent ring system. We have accomplished a synthesis of a phosphole (IV) bearing but a single methyl substituent; the existence of "aromatic character" for the phosphole system can be expected to be reliably manifested in the properties of this type of simple derivative.

Phospholene derivatives (dihydrophospholes) are now readily available<sup>7</sup> and are potential starting materials for phosphole syntheses.



(1) Supported by Research Grant CA-05507, National Cancer Institute, U. S. Public Health Service.

(2) R. F. Hudson, "Structure and Mechanism in Organo-phosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 28–32.

(3) E. H. Braye and W. Hübel, *Chem. Ind. (London)*, 1250 (1959) [see also E. H. Braye, W. Hübel, and I. Capier, *J. Am. Chem. Soc.*, **83**, 4406 (1961)]; F. C. Leavitt, T. A. Manuel, and F. Johnson, *ibid.*, **81**, 3163 (1959) [see also F. G. Leavitt, T. A. Manuel, F. Johnson, L. U. Maternas, and D. S. Lehmann, *ibid.*, **82**, 5099 (1960)].

(4) D. A. Brown, *J. Chem. Soc.*, 929 (1962).

(5) G. Märkl and R. Potthast, *Angew. Chem.*, **79**, 58 (1967).

(6) I. G. M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes, *J. Chem. Soc.*, 2184 (1965).

(7) W. B. McCormack, U. S. Patents 2,663,736 and 2,663,737 (Dec 22, 1953). The subject has been reviewed: L. D. Quin in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1967, Chapter 3.

1-Methyl-3-phospholene 1-oxide (I)<sup>8</sup> was converted to its dibromide (II).<sup>8</sup> This was reduced to the phospholane (III) by a 3-hr reflux of a benzene solution of the oxide (0.153 mole) and trichlorosilane<sup>9</sup> (0.43 mole). After acid hydrolysis and basification with sodium bicarbonate, the product was extracted continuously with pentane. By an iodine titration the yield in this step was found to be about 65%. Some III crystallized from a concentrated solution and had mp 47.5–49°. The benzyl bromide salt, recrystallized from ethyl acetate, had mp 171.5–172.5°. *Anal.* Calcd for C<sub>12</sub>H<sub>16</sub>Br<sub>2</sub>P: C, 33.52; H, 3.75; P, 7.20. Found: C, 33.56; H, 3.75; P, 7.40. The proton nmr spectrum (CDCl<sub>3</sub>) of III was in accord with the structure [3 H doublet ( $J = 4$  cps) at  $\delta$  0.70 ppm, 4 H multiplet at 1.87, 2 H multiplet at 3.98].

III was dehydrohalogenated in pentane with 3 molar equiv of potassium *t*-butoxide at room temperature overnight. The cooled mixture was hydrolyzed with sodium bicarbonate solution and extracted with pentane. By gas chromatography the yield of IV was 24%. Some 1-methyl-3-phospholene was present as an impurity, but was largely extracted with 0.5 *N* hydrochloric acid without affecting IV. The phosphole in neat or concentrated form is sensitive to prolonged heating, and fractionation is accompanied by considerable loss. However, a sample of 87.8% purity (pentane as the main impurity) was obtained as the heart-cut in a rapid, direct distillation of the residue left from removing the solvent at 300 mm with a spinning-band column. The sample was collected at 82–85° (317 mm) in a receiver chilled in Dry Ice. As it discolors slightly at room temperature, forming a small amount of insolubles, the sample is best preserved at low temperatures. It readily formed a methiodide, which was recrystallized (low recovery) from methanol-ethyl acetate, mp 190–194° dec. *Anal.* Calcd for C<sub>6</sub>H<sub>10</sub>IP: C, 30.02; H, 4.20; P, 12.91; I, 52.87. Found: C, 30.15; H, 4.39; P, 12.63; I, 52.63.

The 60-Mc proton nmr spectrum (external standard) of IV (87.8%) consists of a methyl signal as an apparent singlet (any PCH coupling must be less than about 1 cps) at  $\delta$  1.36 ppm and a 4 H multiplet for the vinyl protons at 6.51–7.52 ppm. The multiplet is being analyzed as A<sub>2</sub>B<sub>2</sub> in an A<sub>2</sub>B<sub>2</sub>X system where P<sup>31</sup> is X; coupling parameters will be reported elsewhere. Preliminary calculations suggest that the  $\alpha$  and  $\beta$  protons differ in chemical shift by about 8 cps, and that  $J_{AX} + J_{BX} = 54$  cps. The P<sup>31</sup> nmr spectrum at 40.5 MHz is an 11-line pattern at +121 ppm relative to external P<sub>4</sub>O<sub>6</sub> standard (*cf.* +154.3 ppm for 1-methyl-3-phospholene).

The  $\alpha$ - and  $\beta$ -proton multiplet, centered at 7.09 ppm, is at markedly lower field than in vinylphosphines. For comparison, data reported<sup>10</sup> for neat trivinylphosphine (recalculated to  $\delta$ ) place the  $\alpha$  proton at 6.66, and the  $\beta$  protons at 5.69 (*trans* to P) and 5.56 ppm (*cis* to P). Also the vinyl proton in neat 1-phenyl-3-methyl-2-phospholene is observed at  $\delta$  5.68 ppm (internal TMS).<sup>11</sup> The ring protons of IV resonate in the

range characteristic of those of aromatic systems (*e.g.*, for neat thiophene,  $\alpha$  and  $\beta$  are at 7.04 and 6.92 ppm, respectively, to internal TMS<sup>12</sup>). A similar downfield position for the  $\beta$  protons of 2,5-dimethyl-1-phenylphosphole (6.39 ppm)<sup>5</sup> and of 1,2,5-triphenylphosphole (7.1–7.6 ppm, unresolved from phenyl protons)<sup>6</sup> has been observed.

The ultraviolet spectrum of 1-methylphosphole in iso-octane ( $\lambda_{\max}$  286 m $\mu$  (log  $\epsilon$  3.88); intense end absorption at 200 m $\mu$ ) resembles that of 1-methylpyrrole ( $\lambda_{\max}$  280 m $\mu$  (log  $\epsilon$  2.06) and 214 m $\mu$  (log  $\epsilon$  3.77)). The mass spectrum shows a strong molecular ion at *m/e* 98 and a breakdown pattern similar to that of 1-methylpyrrole.

Although IV quaternizes with the usual ease and has an exceptionally strong phosphine odor, its basicity appears to be abnormally low for a tertiary phosphine. As noted, it is not extracted from pentane by 0.5 *N* hydrochloric acid. It is extracted by 4 *N* hydrochloric acid, but with chemical change, as it is not recovered on basification. A dilute (10<sup>-4</sup> *M*) solution in 0.01 *N* hydrochloric acid is also unstable, as seen by the gradual reduction in the absorbance at 285 m $\mu$ . The phosphole differs from other tertiary phosphines also in not forming a complex with carbon bisulfide. These chemical properties, as well as the proton nmr and ultraviolet spectral properties, may be indicative of the expected<sup>3</sup> extensive electron delocalization of an aromatic system. A final judgment in this matter, however, must await the results of other experiments on the properties of the system and a comparison of the properties with vinylic, but nonaromatic, phosphines.

**Acknowledgment.** We thank Dr. Charles Moreland, North Carolina State University, Raleigh, N. C., for obtaining the P<sup>31</sup> nmr spectrum of IV and for preliminary calculations on its proton nmr parameters.

(12) T. F. Page, Jr., T. Alger, and D. M. Grant, *J. Am. Chem. Soc.*, **87**, 5333 (1965).

Louis D. Quin, Jay G. Bryson  
Department of Chemistry, Duke University  
Durham, North Carolina 27706  
Received June 9, 1967

### The Solvolysis of (7-Cycloheptatrienyl)methyl 3,5-Dinitrobenzoate. An Example of Cyclopropane Participation Initiated by Valence Tautomerism

*Sir:*

Extensive investigation has demonstrated that carbon-carbon bonding electrons of various types can function as nucleophilic neighboring groups in intramolecular displacement reactions.<sup>1-14</sup> Some evidence

(1) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; *Chem. Rev.*, **56**, 571 (1956).

(2) B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

(3) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).

(4) J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(5) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms 1965," Interscience Publishers, Inc., New York, N. Y., 1966, Chapter 1; B. Capon and C. W. Rees, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **61**, 222 (1964).

(6) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(7) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959), and references therein cited.

(8) L. D. Quin, J. A. Peters, C. E. Griffin, and M. Gordon, *Tetrahedron Letters*, 3689 (1964).

(9) H. Fritzsche, U. Hasserodt, and F. Korte, *Ber.*, **98**, 171 (1965).

(10) W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1963).

(11) L. D. Quin and T. P. Barket, unpublished results.