Table II. Relative Intrinsic Viscosity of DNA-Reporter Complexes to Free DNA[a,b]

Reporter	$(\eta)/(\eta_0)$
1	1.26
2	1.30
3	0.97
4	0.97
$(CH_3)_3N^+(CH_2)_3N^+(CH_3)_3$	0.98

[a] The intrinsic viscosities of free DNA, (η_0), and the DNA-reporter complex, (η), were calculated using the equation $\eta_{sp}/c = (\eta) + k'(\eta)^2c$ and assuming that the value of the Huggins constant, k', is the same for DNA and the DNA-reporter complex. This assumption is justifiable and has been recently shown by P. D. Ross and R. L. Scruggs [*Biopolymers*, **2,** 79 (1964)] to apply for DNA and DNA-dye complexes under similar ionic strength conditions. [b] Viscosity measurements were carried out using 1.13×10^{-3} *M* in poise/liter of DNA and 1.0×10^{-4} *M* in reporter molecule in 0.025 *M* sodium phosphate buffer (pH 6.50) at 25° using a Zimm viscometer. Under these conditions, the reporter molecules are fully bound to DNA as evidenced by spectrophotometric titration studies.

and induced circular dichroism of the 4-nitroaniline transition on binding to DNA (Table I). In addition, the pmr signals of the a-, b-, and c-alkyl protons of **3** and **4** are clearly discernible in the presence of DNA at 32° with only a slight broadening and an upfield chemical shift.[6] In line with these results, the intrinsic viscosity of the DNA-bound reporters **3** and **4** is slightly decreased (Table II). A similar decrease of the intrinsic viscosity of DNA is observed with the diammonium salt **5**, $(CH_3)_3N^+(CH_2)_3N^+(CH_3)_3 \cdot 2Br^-$. The mode of binding of **3** and **4** to DNA seems to be external electrostatic binding to the phosphodiester chain with the 4-nitroaniline ring freely tumbling in solution. Thus, intercalation between base pairs of DNA by **3** and **4** is inhibited presumably due to either (a) the absence of an H-bond donor or (b) steric hindrance by the nonplanar *N,N*-dialkylcarboxamido substituent of **3** and **4**. We favor the latter alternative since the requirement for a hydrogen bond donor at the 2 position of the 4-nitroaniline ring is not essential for the intercalation process. For example, it has been shown that the unsubstituted, the 2-cyano-, and the 2-nitro-substituted 4-nitroaniline labeled diamines intercalate between base pairs in DNA as evidenced by the absorption, induced circular dichroism, proton magnetic resonance, and viscosity studies.[7] It should be noted that the results of the preliminary binding studies of these reporters to DNA show that the reporter molecules **1** and **2** are bound approximately 10–15-fold more strongly than **3** and **4**.[8] This is in line with the proposed binding modes of these molecules described above. Further work along this area is in progress.

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[6] It should be noted that the alkyl protons of the *N,N*-dialkylcarboxamido group of **3** and **4** are not equivalent at 32° due to the restricted rotation about the amide group. At 90°, however, coalescence of the pmr signals is obtained (Figure 1c and d).

[7] (a) F. Passero, E. Gabbay, B. L. Gaffney, and T. Kurucsev, *Macromolecules*, **3,** 158 (1970); (b) E. Gabbay, *J. Amer. Chem. Soc.*, **91,** 5136 (1969); (c) B. L Gaffney, Ph.D. Thesis, Rutgers, 1969.

[8] Binding data were obtained by competitive binding studies using a cation exchange resin technique: A. DePaolis, Ph.D. Thesis, Rutgers, 1971.

[9] Recipient of a U. S. Public Health Service Career Development Award from the National Institutes of Health.

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Some Novel Reactions of Vinyl Isocyanide with Organophosphorus and Organoarsenic Compounds

Sir:

Recently the base-catalyzed addition of phosphorus–hydrogen bonds across the vinyl double bonds of vinylphosphines to give polytertiary phosphines with PCH_2CH_2P units was reported.[1] This communication reports base-catalyzed additions of phosphorus–hydrogen bonds to vinyl isocyanide[2] which provide routes not only to a phosphine isocyanide with a PCH_2CH_2NC unit but also to the first derivative of the 3-azaphosphole heterocyclic system.

Reaction of diphenylphosphine with excess vinyl isocyanide in boiling benzene for ~20 hr in the presence of ~10% potassium *tert*-butoxide catalyst resulted in addition of the phosphorus–hydrogen bond across the vinyl double bond to give a 53% yield of slightly yellow viscous liquid, $(C_6H_5)_2PCH_2CH_2NC$: bp 139–142° (0.05 mm) (*Anal.* Calcd for $C_{15}H_{14}NP$: C, 75.4; H, 5.9; N, 5.9; P, 12.9; mol wt, 239. Found: C, 75.1, 75.7; H, 6.2, 5.7; N, 5.6, 5.3; P, 13.1; mol wt, 238 (osmometer in benzene solution)). The infrared spectrum of neat $(C_6H_5)_2PCH_2CH_2NC$ exhibited a strong ν_{CN} frequency at 2154 cm⁻¹ confirming the presence of an isocyanide group. The proton nmr spectrum of $(C_6H_5)_2PCH_2CH_2NC$ in $CDCl_3$ exhibited the usual aromatic proton resonance at τ 2.74 as well as two resonances at 6.72 (quartet, 8-Hz separation) and 7.66 (triplet, 8-Hz separation) arising from the nonequivalent methylene groups. The mass spectrum of $(C_6H_5)_2PCH_2CH_2NC$ did not exhibit a molecular ion. Instead the highest *m/e* ion was $(C_6H_5)_2PC_2H_3^+$ formed by elimination of HCN from the molecular ion. Other ions frequently found in the mass spectra of $(C_6H_5)_2PR$ derivatives[3,4] were also observed (*e.g.*, $(C_6H_5)_2PH^+$, $C_{12}H_8P^+$, $C_{12}H_{10}^+$, $C_{12}H_8^+$, $C_8H_7P^+$, $C_8H_6P^+$, $C_6H_6P^+$, $C_6H_5P^+$, and $C_6H_4P^+$). The arsenic analog $(C_6H_5)_2AsCH_2CH_2NC$, a liquid, bp 153° (2 mm), was similarly prepared in 31% yield from diphenylarsine and excess vinyl isocyanide and characterized by elemental analyses, molecular weight determination, and infrared and proton nmr spectra.

The compounds $(C_6H_5)_2ECH_2CH_2NC$ (E = P or As) are the first known compounds containing both an isocyanide group and a tertiary phosphorus or arsenic atom. All of these functionalities coordinate with transition metals to form extensive series of com-

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[1] R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, **91,** 5191 (1969).

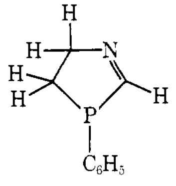
[2] D. S. Matteson and R. A. Bailey, *ibid.*, **90,** 3761 (1968).

[3] D. H. Williams, R. S. Ward, and R. G. Cooks, *ibid.*, **90,** 966 (1968).

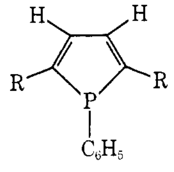
[4] R. Colton and Q. H. Porter, *Aust. J. Chem.*, **21,** 2215 (1968).

plexes.[5,6] However, the linear hybridizations of both the carbon and nitrogen atoms of the isocyanide group direct the lone pair on the isocyanide carbon atom so that it cannot coordinate with the same metal atom as the lone pair on the phosphorus or arsenic atom. This prevents the compounds $(C_6H_5)_2ECH_2CH_2NC$ from acting as bidentate chelating ligands. Accordingly the reaction between the norbornadiene complex $C_7H_8Cr(CO)_4$ and either $(C_6H_5)_2ECH_2CH_2NC$ derivative (E = P or As) in benzene at room temperature did *not* give monometallic $[(C_6H_5)_2ECH_2CH_2NC]Cr(CO)_4$ but instead gave good yields of yellow cyclohexane-insoluble diethyl ether soluble solids of approximate compositions $[(C_6H_5)_2ECH_2CH_2NC]_4Cr_3(CO)_{12}$ (E = P or As).[7] The infrared spectra of these compounds exhibited the expected[8] ν_{CO} frequencies for a *cis*-$L_2Cr(CO)_4$ derivative indicating that the stereochemistry of the nor-$C_7H_8Cr(CO)_4$ had been retained in this reaction. We tentatively formulate the $[(C_6H_5)_2ECH_2CH_2NC]_4Cr_3(CO)_{12}$ derivatives with *cis*-$Cr(CO)_4$ groups bridged by $(C_6H_5)_2ECH_2CH_2NC$ ligands with additional monodentate $(C_6H_5)_2ECH_2CH_2NC$ ligands as end groups.

The reaction of phenylphosphine with excess vinyl isocyanide in boiling tetrahydrofuran[9] in the presence of ~15% potassium *tert*-butoxide catalyst did *not* give the expected phosphine-diisocyanide $C_6H_5P(CH_2CH_2NC)_2$. Instead a very pale yellow air-sensitive viscous liquid, bp 64° (0.07 mm), of composition $C_9H_{10}NP$ was obtained in ~90% yield (*Anal.* Calcd for $C_9H_{10}NP$: C, 66.4; N, 6.1; N, 8.6; P, 19.0; mol wt, 163. Found: C, 66.3; H, 6.0; N, 8.5; P, 19.0; mol wt, 186 (osmometer in benzene); 163 (mass spec)). The infrared spectrum of $C_9H_{10}NP$ showed the absence of any ν_{CN} frequency around 2100 cm^{-1} that could be attributed to an isocyanide group. This indicates that the isocyanide group was destroyed in the reaction. The proton nmr spectrum of $C_9H_{10}NP$ ($CDCl_3$ solution) exhibited olefinic (τ 1.73 (doublet of triplets, J_1 = 56 Hz, J_2 = 2 Hz)), aromatic (τ 2.78 (unsymmetrical multiplet)), and two methylene resonances (multiplets at τ 5.8 and 8.1) of relative intensities 1:5:2:2. On this basis we formulate $C_9H_{10}NP$ as 4,5-dihydro-1-phenyl-3-azaphosphole (I). As far as we can ascertain,[10] this is the first simple derivative of the 3-azaphosphole system that has been prepared. However, somewhat similar phospholes of the type II have been previously prepared[11] by an analogous base-catalyzed addition of phenylphosphine to the 1,3-diynes RC≡C—C≡CR (R = CH_3, C_6H_5, etc.),



I



II

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(5) For a review of metal isocyanide complexes see L. Malatesta, *Progr. Inorg. Chem.*, **1**, 283 (1959).

(6) For a review of metal complexes of tertiary phosphines and arsines see G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).

(7) These formulas were established by analyses for at least five elements and molecular weight determinations in benzene solution with a vapor pressure osmometer.

(8) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(9) This reaction failed to give any product when carried out in benzene rather than tetrahydrofuran solution under otherwise the same conditions.

(10) The 3-azaphosphole ring system is not listed in the Second Edition of the Ring Index or its first three supplements.

(11) G. Märkl and P. Potthast, *Angew. Chem., Int. Ed. Engl.*, **6**, 86 (1967).

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Book Reviews

Markov Chains and Monte Carlo Calculations in Polymer Science. Edited by GEORGE G. LOWRY, Department of Chemistry, Western Michigan University, Kalamazoo, Mich. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1970. xi + 329 pp. 16 × 23.5 cm. $19.75.

According to the preface, this book has been "... written primarily for the polymer chemist who is not an expert in mathematical theories but who wants to be conversant with the topics treated." It is this reviewer's opinion that the editor and other contributors have been successful in producing a book useful to such a reader; they have presented good introductory accounts of the two mathematical methods cited and have clearly discussed their application to a variety of problems in polymer science.

In the first of these methods, Markoffian chain models, the overall probability of a sequence of events is derived from conditional probabilities which are characteristic of each single event and the outcome of a finite number of preceding events. (An obvious example of such a calculation would be the use of such derived, general relationships in the prediction of chemical composition of a copolymeric chain from the conditional probabilities which characterize the chemical combination of the various types of monomers and growing chain ends.) In contrast, the Monte Carlo method is essentially the simulation of a process or system by means of statistical "experiments" performed by applying appropriate mathematical operations to set of random numbers. (The Monte Carlo approach to the copolymer composition problem would be the direct use of the conditional probabilities to define intervals over the range of the random number, each interval corresponding to a possible outcome, *viz.*, choice of monomer to be added to a growing chain. The chain of representative composition is then generated merely by letting each choice be determined by the interval to which each random number is assigned on the basis of its magnitude.)

The first chapter, by G. G. Lowry, is a short introduction which includes definitions, general concepts, and a brief survey of current applications. These are worthwhile features, but the "reference" section on vectors and matrices is almost totally useless. If, for