TABLE II

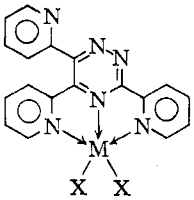
ELECTRONIC ABSORPTION SPECTRA OF I AND ITS COORDINATION COMPLEXES

Compound	λ_{max} (log ϵ)[a]				
I	244 (4.20)	284 (4.39)	382 (3.02)		
IIIa	242 (4.48)	285 (4.63)	380 (sh,[c] 4)	550 (3.65)	590 (sh, 3)
IIIb	. . .[b]	279 (4.62)	392 (3.96)		
IIIc	249 (4.42)	281 (4.54)	413 (3.85)		
IIId	. . .[b]	278 (4.63)	390 (3.98)		
IIIe	250 (sh, 4)	279 (4.58)	389 (3.89)		
IVa	. . .[b]	274 (4.22)	391 (3.79)		
IVb	. . .[b]	275 (4.36)	390 (3.90)		

[a] λ given in mμ, ε is the molar extinction coefficient. [b] Continuous absorption instead of a discernible peak was observed throughout this region. [c] Shoulder.

the latter structure, I would be a bidentate chelate group.

The ligand I can form 1:1 complexes with zinc(II) and copper(II) salts and the dichlorozinc(II), the dichlorocopper(II), and the dibromocopper(II) complexes (IVa, b, c, respectively) are described. Conductivity data indicate that these complexes probably have a trigonal-bipyramidal structure in their solutions in nitrobenzene.[8] The conductivity data also indicate that hydrolysis of these species to di-univalentel ectrolytes occurs in aqueous solution.



IVa, M = Zn(II); X = Cl
IVb, M = Cu(II); X = Cl
IVc, M = Cu(II); X = Br

The electronic absorption spectrum of I has peaks at [mμ (log ε)]: 244 (4.20), 284 (4.39), and 382 (3.02). These may be assigned to two $\pi-\pi^*$ transitions (244 and 284 mμ) and one $n-\pi^*$ transition (382 mμ). The absorption bands in the spectra of the complexes III and IV are principally due to the transitions of the ligand (Table II). Generally, the 244 and 382 mμ bands are shifted to longer wave lengths and the 284 mμ band to shorter wave lengths. In the iron(II) complex IIIa, all shifts are reversed. In addition, charge-transfer bands of the ferroin system are present at [mμ (log ε)] 550 (3.65) and 590 sh (3).[9]

The magnetic moments of IIIa and IIIb indicate that I is a strong-field ligand like terpyridine. Because I is of suitably lower symmetry than terpyridine, its octahedral complexes should exist in enantiomorphous forms. The optical activity of such complexes will be the subject of a future communication.

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Substitution Pattern in Phenoxyphosphonitrilates

BY C. T. FORD, F. E. DICKSON, AND I. I. BEZMAN

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In the cyclic compound, hexachlorotriphosphonitrile, $(\mathrm{NPCl_2})_3$, progressive substitution of chlorine by other groups such as amino, aryl, or aryloxy can take place either geminally or around the ring. In two recent papers[1,2] we have demonstrated that proton magnetic resonance spectra can be used to determine both positional and *cis–trans* configurations of a series of dimethylaminotriphosphonitriles. We now report the extension of this procedure to delineation of the substitution pattern in the formation of phenoxy esters of $(\mathrm{NPCl_2})_3$ and present evidence that it is nongeminal.

Two reaction schemes were carried out as shown below.

$$(\mathrm{NPCl_2})_3 \xrightarrow[\mathrm{C_6H_6}]{\mathrm{KOC_6H_5}} \underset{\mathrm{I}}{\mathrm{P_3N_3Cl_3(OC_6H_5)_3}} \xrightarrow[\mathrm{THF}]{\mathrm{HN(CH_3)_2(g)}} \underset{\mathrm{II}}{\mathrm{P_3N_3[N(CH_3)_2]_3(OC_6H_5)_3}} \qquad (1)$$

$$(\mathrm{NPCl_2})_3 \xrightarrow[(\mathrm{C_2H_5})_2\mathrm{O}]{\text{aq. }\mathrm{HN(CH_3)_2}} \underset{\mathrm{III}}{\mathrm{P_3N_3[N(CH_3)_2]_3Cl_3}} \xrightarrow[\mathrm{C_6H_5CH_3}]{\mathrm{KOC_6H_5}} \underset{\mathrm{IV}}{\mathrm{P_3N_3[N(CH_3)_2]_3(OC_6H_5)_3}} \qquad (2)$$

In the first scheme, $(\mathrm{NPCl_2})_3$, $\mathrm{C_6H_5OH}$, and KOH in a 1:4:4 mole ratio were refluxed in $\mathrm{C_6H_6}$ for 2 hr., during which time the stoichiometric amount of $\mathrm{H_2O}$ required for formation of $\mathrm{KOC_6H_5}$ was azeotroped out. Washing the product with dilute KOH and $\mathrm{H_2O}$, drying, decolorizing, and removing solvent gave a water-white oil whose analysis indicated it to be compound I in 93% yield. Into a solution of the oil (I) in tetrahydrofuran at reflux was bubbled anhydrous dimethylamine, and a precipitate of $\mathrm{HN(CH_3)_2 \cdot HCl}$ in stoichiometric quantity for complete replacement of the chlorine was formed in 6 hr. The residual solution was stripped of THF to give an oil which was dissolved in petroleum ether, decolorized, concentrated, and chilled to give a crystalline product, compound II, in 30% yield and melting at 90–92°.

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In the second scheme, compound III, prepared as previously described,[2] was refluxed in toluene for 7 days in the presence of sufficient KOC_6H_5 to react with all the chlorine. The reaction product was washed with dilute KOH and H_2O and dried over $CaSO_4$, and the solvent was distilled off. The residue was an oil which was dissolved in *n*-hexane and decolorized. By concentrating and chilling the residual solution, compound IV was obtained in 60% yield, melting at 90–92°.

Anal. Calcd. for compound I: C, 41.52; H, 2.90; Cl, 20.43; N, 8.07; P, 17.85. Found: C, 38.92; H, 2.80; Cl, 20.76; N, 8.31; P, 18.38. Calcd. for compound III: C, 19.29; H, 4.86; Cl, 28.48; N, 22.50; P, 24.88. Found: C, 19.18; H, 4.61; Cl, 28.56; N, 22.85; P, 24.86. Calcd. for compounds II and IV: C, 52.74; H, 6.09; N, 15.38; P, 17.01. Found (compound II): C, 52.57; H, 6.11; N, 15.58; P, 16.85. Found (compound IV): C, 52.70; H, 6.37; N, 15.43; P, 16.95.

The melting point of a mixture of compounds II and IV was undepressed and their infrared spectra were superimposable. Because the configuration of compound III had been established previously[2] by H^1 n.m.r. spectra as that in which each $-N(CH_3)_2$ group is attached to a separate P atom and in a *trans* arrangement with respect to the PN ring, the identity of compounds II and IV was sufficient to establish the configuration of compound I, with the reservation that no configurational changes take place in the formation of compounds II and IV.

As further confirmation of the structure of compounds II and IV, their H^1 n.m.r. spectra were obtained on a Varian A-60 n.m.r. spectrometer in 20% deuterated chloroform solution with tetramethylsilane as an internal reference. The spectrum of each compound consisted of two sets of doublets in the ratio of 2:1. The high-field doublet had a chemical shift of 138.8 c.p.s. from TMS while that of the low-field doublet was 154.2 c.p.s. The coupling constant in each case was 12.5 ± 0.1 c.p.s., a value taken to be indicative of the $\equiv P(OC_6H_5)N(CH_3)_2$ grouping. The outside possibility that a $-N(CH_3)_2$ group migrated during formation of II and IV is contraindicated by the previously-established J'_{PH} value of 11.8 c.p.s. for the $\equiv P[N(CH_3)_2]_2$ grouping. Both spectra were identical and confirmed that both reaction routes produced the same compound. The fact that there are two doublets in a ratio of 2:1 indicates that the $-N(CH_3)_2$ groups are in a *cis-cis-trans* configuration about the ring and that no rearrangement takes place when III is converted to IV.

In addition to this evidence for the nongeminal substitution pattern in the formation of phenoxy esters of $(NPCl_2)_3$, some intimation of this was given by the fact that only 3 of the 4 moles of KOC_6H_5 reacted in the synthesis of compound I. Evidently, the formation of $\equiv P(Cl)(OC_6H_5)$ deactivates the remaining Cl so that the second $-OC_6H_5$ substitution takes place on another $\equiv PCl_2$ group. This pattern is similar to that observed for strongly basic amines such as H_2NCH_3 and $HN(CH_3)_2$.[3,4]

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Decomposition of the Adducts of Diethylamine and Isopropylamine with Nitrogen(II) Oxide

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It has been demonstrated[1–3] that nitric oxide behaves as a Lewis acid toward a large number of primary and secondary amines and some diamines. The products are diamagnetic and their infrared and nuclear magnetic resonance spectra support the formulation $R_2NH_2^+R_2NN_2O_2^-$ for secondary amines and $RNH_3^+RNHN_2O_2^-$ for primary amine products. Products of widely varying stability are obtained. It was observed[2] that the diethylamine–nitric oxide addition compound in a closed bottle undergoes slow decomposition over a period of several days in the presence of air, producing a brown oil. The compound has a slight vapor pressure at room temperature and if left on the desk top will eventually disappear. However, it can be stored indefinitely at −78° or under ether at room temperature. It was of interest to study the decomposition of the diethylamine–nitric oxide addition compound in the presence and absence of oxygen. This study was also extended to the decomposition of the isopropylamine–nitric oxide product in the presence of oxygen.

Experimental

Purification of Materials.—Matheson commercial grade nitric oxide was used directly in the high pressure preparation of the nitric oxide products. In the atmospheric pressure method nitric oxide was purified by bubbling through 10 *M* potassium hydroxide and dried by passing through columns of sodium hydroxide pellets. The amines were purified by distillation from anhydrous barium oxide.

Preparation of $(C_2H_5)_2NH_2^+(C_2H_5)_2NN_2O_2^-$ and $(CH_3)_2CHNH_3^+$-$(CH_3)_2CHNHN_2O_2^-$.—The compounds were prepared by both high pressure and atmospheric pressure methods as described in earlier publications[1,2] and were checked by means of elemental analyses.

Decomposition of $(C_2H_5)_2NH_2^+(C_2H_5)_2NN_2O_2^-$.—A weighed sample (11.2 g.) was placed in a loosely-capped bottle and al-

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