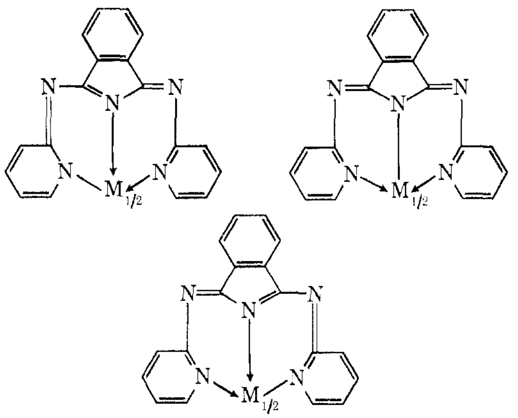
cal forms that can be written for the deprotonated analog (VII).



VII

More interesting, perhaps, is that deprotonation can be brought about by altering the anion associated with the transition metal salt. In contrast to the perchlorate salt which gives rise to the protonated complex (V), the transition metal chloride or acetate derivative in conjunction with two ligand molecules yields the deprotonated species (VI) directly. A possible explanation for this phenomenon is the extreme acidity of the amino proton which requires the presence of the least basic anion for its retention. In the case of the copper(II) system, spontaneous deprotonation occurs even in the presence of the perchlorate ions. Thus, the reaction of copper(II) perchlorate with 1,3-bis(2-pyridylimino)isoindoline does not result in the precipitation of the protonated cationic species as was the case with the other metal analogs. Rather, in about 2 days, a green, crystalline solid forms which is the deprotonated complex.

The transformation of the cationic complexes into their neutral counterparts is accompanied by alterations in both chemical and physical properties. Changes in color, increased solubility in organic solvents, transformation to nonconductors, and the disappearance of the infrared absorption arising from the N–H stretch accompany the formation of the neutral species. In contrast is the consistency exhibited by the magnetic moments of the divalent iron, cobalt, and nickel complexes which indicate that the octahedral array is retained after deprotonation. This is further confirmed by spectral studies on the nickel(II) derivatives in the visible and near-infrared regions in which it is noted that the absorptions remain nearly constant in both position and intensity (Table II). Unfortunately, in the spectra obtained from DMF solutions, no d–d transitions could be observed below 650 mμ owing to the onset of strong charge-transfer bands.

The reaction of nickel acetate with 1,3-bis(2-pyridylimino)isoindoline in a 1:1 molar ratio results in the separation of a small amount of a complex of the general formula $M(L\text{-}H)(C_2H_3O_2)$. The nonconducting nature of this complex indicates that the acetate anion is coordinated to the nickel. The magnetic moment of 3.01 BM and the positions of absorptions in the visible and near-infrared regions make it difficult to assess the structure of this complex in a definitive manner. However, a five-coordinate molecule, in which the acetate anion is bonding in a bidentate fashion, is a possibility. A transformation to an octahedral arrangement, probably through the coordination of solvent molecules, is noted when the complex is dissolved in dimethylformamide. We are still in the process of assessing this structure.

Acknowledgment.—The authors wish to thank the microanalytical section at Olin Mathieson for their adept handling of the samples reported herein.

Contribution from the
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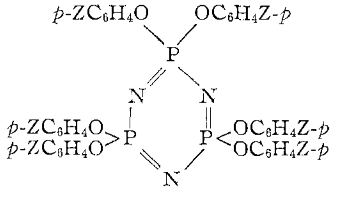
Aminophenoxy- and Isocyanatophenoxyphosphonitriles

By Gerhard Ottmann, Henry Lederle,
Haywood Hooks, Jr., and Ehrenfried Kober

Received September 20, 1966

By virtue of their structural relationship to thermally stable trimeric and tetrameric aryloxy substituted phosphonitriles[1,2] and to polymers obtained by condensation of cyclic phosphonitrilic chlorides with polyfunctional aromatic compounds,[3,4] aminophenoxy- and isocyanatophenoxy-substituted cyclic phosphonitriles are attractive intermediates for the formation of thermally stable, fire-resistant fluids and polymers. Since reactions of cyclic phosphonitrilic chlorides with bifunctional compounds such as *p*-aminophenol or hydroquinone[4] lead inevitably to the formation of highly cross-linked polymers, other routes for the preparation of polyfunctional aminophenoxy- and isocyanatophenoxyphosphonitriles had to be found.



I, Z = NO_2
II, Z = NH_2
III, Z = NCO
IV, Z = $NHCOOCH_3$
V, Z = $NHCOOC_4H_9$

The accessibility of 2,2,4,4,6,6-hexakis(*p*-nitrophenoxy)phosphonitrile (I) in high yield by a recently reported procedure[5] encouraged us to attempt the synthesis of 2,2,4,4,6,6-hexakis(*p*-aminophenoxy)phosphonitrile (II) by hydrogenation of I. Although the PN nucleus of cyclic phosphonitrilic chloride does not survive hydro-

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genolysis and is completely cleaved by reducing agents,[6] one could expect that complete phenoxy substitution would render the PN ring less vulnerable to hydrogenation and thus would permit exclusive conversion of the nitro groups to amino groups. We found indeed that catalytic hydrogenation of 2,2,4,4,-6,6-hexakis(*p*-nitrophenoxy)phosphonitrile (I) with Raney nickel does not attack the PN nucleus to any appreciable extent. 2,2,4,4,6,6-Hexakis(*p*-aminophenoxy)phosphonitrile (II) was obtained in high yields using aniline as solvent.

Phosgenation of 2,2,4,4,6,6-hexakis(*p*-aminophenoxy)phosphonitrile (II) in refluxing *o*-dichlorobenzene, utilizing a high dilution factor to suppress reaction between amino and isocyanato groups, and recrystallization of the crude reaction product gave pure 2,2,4,-4,6,6-hexakis(*p*-isocyanatophenoxy)phosphonitrile (III) in 46% yield. Higher polymeric PN compounds of the urea type were obtained as by-products, but not further identified. All six isocyanato groups of compound III reacted readily with methanol and 1-butanol to give the expected hexamethyl- and hexabutylcarbamates (IV, V) in quantitative yields. With glycols such as diethylene glycol, high polymeric urethanes were obtained.

Experimental Section

2,2,4,4,6,6-Hexakis(*p*-aminophenoxy)phosphonitrile (II).—A 1000-ml stirring autoclave was charged with 77.0 g of 2,2,4,4,6,6-hexakis(*p*-nitrophenoxy)phosphonitrile,[5] 550 g of aniline, and 10 g of Raney nickel catalyst. The vigorously agitated mixture was hydrogenated under 1000-psig hydrogen pressure at 80–90° until no further pressure drop was recorded (~3–4 hr). The reaction mixture was filtered, and most of the aniline solvent was removed by distillation *in vacuo*. The residue was diluted with ether to yield a gummy precipitate from which the liquid layer was decanted. The gum was treated with 250 ml of 2 *N* sulfuric acid and filtered. The solid filter cake was then added to 500 ml of 2 *N* sodium hydroxide and, with stirring, heated to 80–100° for 15 min. After filtration, the crude compound II was washed with water to neutrality, dried *in vacuo* over P_2O_5, and finally recrystallized from *o*-dichlorobenzene; yield 37.0 g (60%) of pure II, mp 189–190°. Additional amounts of II were obtained by working up the mother liquors. *Anal.* Calcd for $C_{36}H_{36}N_9O_6P_3$: C, 55.17; H, 4.63; N, 16.11; P, 11.80. Found: C, 55.17; H, 4.91; N, 16.11; P, 11.61.

2,2,4,4,6,6-Hexakis(*p*-isocyanatophenoxy)phosponitrile (III).—Phosgene was passed into 250 ml of boiling *o*-dichlorobenzene at a rate of approximately 10 g/hr. To this mixture was slowly added a hot solution of 20 g of 2,2,4,4,6,6-hexakis(*p*-aminophenoxy)phosphonitrile (II) in 1500 ml of *o*-dichlorobenzene over a period of 4.5 hr. After complete addition, heating and slow passage of $COCl_2$ was continued overnight. The solution was then filtered from 6.5 g of insoluble material. The solvent was distilled *in vacuo* to render 17 g of a brown solid which was recrystallized, first from toluene and then from acetonitrile, to yield 11 g (46%) of pure III, mp 149–150°. *Anal.* Calcd for $C_{42}H_{24}N_9O_{12}P_3$: C, 53.68; H, 2.57; N, 13.42; P, 9.90. Found: C, 53.85; H, 2.60; N, 13.16; P, 9.24.

The hexamethylcarbamate (IV), mp 148°, was prepared from III and boiling methanol in 98% yield. *Anal.* Calcd for $C_{48}H_{48}N_9O_{18}P_3$: C, 50.93; H, 4.27; N, 11.13; P, 8.22. Found: C, 50.73; H, 4.25; N, 11.02; P, 8.22.

The hexa-*n*-butylcarbamate (V), mp 163.5–164°, was prepared from III and *n*-butyl alcohol in quantitative yield. *Anal.* Calcd for $C_{66}H_{84}N_9O_{18}P_3$: C, 57.26; H, 6.12; N, 9.11; P, 6.72. Found: C, 57.24; H, 6.12; N, 9.15; P, 6.67.

Acknowledgment.—This work was partly supported by the U. S. Navy, Bureau of Ships, under Contract NObs 90092.

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CONTRIBUTION FROM THE CHEMISTRY RESEARCH SECTION,
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Tautomerism Exchange in $B_3H_7 \cdot N(CH_3)_3$ and $B_3H_7 \cdot THF$

BY MOREY A. RING, EDWARD F. WITUCKI,
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Received July 1, 1966

Hydrogen tautomerism in boron hydride like compounds was first deduced from the nmr spectrum of aluminum borohydride.[1] Discovery of hydrogen tautomerism in many other boron hydrides and derivatives followed.[2,3] The B^{11} nmr spectrum of $B_3H_7 \cdot O(C_2H_5)_2$ indicated that all borons were identical (single chemical shift value)[4] and that hydrogen tautomerism was taking place (all borons were equally spin–spin coupled to all seven protons).[2] In order to account for the single chemical shift value it is necessary to assume that rapid Lewis base exchange is taking place (possibly synchronized with the hydrogen tautomerism).

Lewis base exchange would not be expected when the ligand is a much stronger Lewis base than the solvent. In this case, the B^{11} nmr spectrum of a $B_3H_7 \cdot LB$ (LB = Lewis base) should show at least one nonequivalent boron. In order to check this, we obtained the B^{11} nmr spectra of $B_3H_7 \cdot N(CH_3)_3$ in benzene and in ether and the spectra of $B_3H_7 \cdot THF$ (tetrahydrofuran) in benzene and in THF.

Trimethylamine triborane ($B_3H_7 \cdot N(CH_3)_3$) was prepared according to the method of Graybill, Ruff, and Hawthorne.[5] The THF adduct was synthesized by a slight modification of the method of Kodama.[6] B^{11} nmr spectra were obtained with Varian nmr spectrometers, Models V-4300 (12.83 Mc) and DP-60 (19.3 Mc). Chemical shifts and coupling constants were determined using boron trichloride, boron triethyl, and aqueous sodium borohydride as external standards. The spectrum of trimethylamine triborane in benzene is compatible with the superposition of two octets, both with *J* values of about 35 cps. One octet appears to be centered about 35 cps upfield and is half the intensity

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