using a model containing the species $H_5(PO_4)_2^-$, $H_4(PO_4)_2^{2-}$, $H_3(PO_4)_2^{3-}$, $CaH_3(PO_4)_2^-$, and Ca_2H_2-$(PO_4)_2^0$ in addition to those used here. Childs' values for K_x and K_y are both smaller than those reported here as well as others discussed above. This is consistent with the use of more species in his model. It was not necessary for us to assume these additional species in order to obtain constancy in the K_{sp} for CaHPO₄. Precipitation might account for the apparent presence of the other calcium phosphate ion associations given by Childs. A calculation of ion activity products for the solutions of higher pH given by Childs in his Table VI shows that these solutions were supersaturated with respect to the solids CaHPO₄·2H₂O, CaHPO₄, Ca₂H₈(PO₄)₆·5H₂O, β-Ca₃(PO₄)₂, and Ca₅(PO₄)₃OH. One or more of these may have formed as a colloidal precipitate which was not detected.

The value for the standard heat of solution of CaHPO₄ reported in this work is about half the average value, $\Delta H = -9515$ cal mol⁻¹, calculated by Mooney and Meisenhelter[17] from the value of K_{sp}' given for 25° by ref 2 and their solubility measurement at 90°. The solubility constant at 90° was based on a pH measured at 25°. In view of the uncertainties in both solubility constant values and the large temperature range over which the calculation was made, great reliance cannot be given to this value of ΔH. A value of -9515 cal mol⁻¹ would yield a much larger variation in solubility with temperature than would be consistent with our experimental errors.

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Phosphonitrilic Compounds. X.[1] Synthesis of Spirophosphazenes with Five-, Six-, and Seven-Membered Exocyclic Rings at Phosphorus

BY H. R. ALLCOCK* AND E. J. WALSH

Spirocyclophosphazenes are formed when 1,8-dihydroxynaphthalene and a base react with (NPCl₂)₃ or 4 or when 2,2'-dihydroxybiphenyl and base react with (NPCl₂)₄. However, catechol (1,2-dihydroxybenzene) and base interact with (NPCl₂)₄ to yield a phosphorane (II), rather than the spirophosphazene formed with (NPCl₂)₃. These differences are ascribed to the effects of ring strain when five-membered exocyclic rings are present.

Introduction

In an earlier paper[2] we reported the synthesis of tris(o-phenylenedioxy)cyclotriphosphazene (I) by the interaction of hexachlorocyclotriphosphazene, (NPCl₂)₃, with catechol in the presence of triethylamine or pyridine as hydrohalide acceptors.

I

II

(H base)⊕
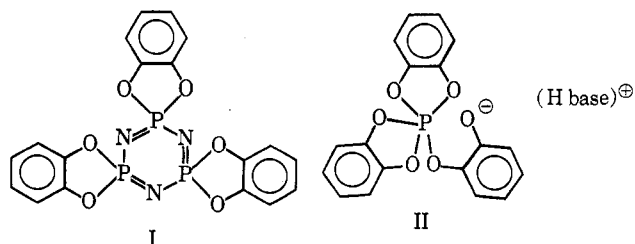
A number of other spirocyclic trimers analogous to I have also been prepared in which the side units were 2,3-dioxynaphthyl, 2,2'-dioxybiphenyl, toluene-3,4-di-

thio, or o-phenylenediamino.[3] Aliphatic spiro derivatives have also been described.[4,5] During our earlier work we encountered difficulty with the preparation of spirocyclic cyclotetraphosphazenes derived from octachlorocyclotetraphosphazene, (NPCl₂)₄. Thus, the interaction of (NPCl₂)₄ with catechol and triethylamine yielded a phosphorane (II) rather than a spirophosphazene.[2] Similar results were observed with high polymeric (NPCl₂)ₙ.[2] This behavior was in marked contrast to the brief report by other investigators[5,6] that the tetrameric analog of I could be prepared from (NPCl₂)₄ and catechol in pyridine solution, a result that we have so far been unable to repeat. It was of some interest, therefore, to attempt the synthesis of cyclotetraphosphazenes with five-, six-, and seven-membered exocyclic dioxyaryl side groups and to ascertain the influence of exocyclic ring size on the ease of cyclization.

(1) Part IX: H. R. Allcock, M. T. Stein, and J. A. Stanko, *J. Amer. Chem. Soc.*, **93**, 3173 (1971).
(2) H. R. Allcock, *ibid.*, **85**, 4050 (1963); **86**, 2591 (1964).
(3) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).
(4) M. S. Chang and A. J. Matuszko, *Chem. Ind. (London)*, 410 (1962).
(5) R. Pornin, *Bull. Soc. Chim. Fr.*, 2861 (1966).
(6) J. Parrod and R. Pornin, *C. R. Acad. Sci.*, **258**, 3022 (1964).

To this end, we have reexamined the reaction between $(NPCl_2)_4$ and catechol under a variety of different conditions and have also studied the reaction between $(NPCl_2)_4$ and 1,2-bis(trimethylsilyloxy)benzene. A new spirocyclic trimer and tetramer with six-membered exocyclic units at phosphorus and a spirocyclic tetramer with seven-membered rings at phosphorus have also been synthesized. Infrared, ultraviolet, and X-ray powder data for these compounds have been obtained.

Results and Discussion

**The Reaction between $(NPCl_2)_4$ and Catechol.—** Attempts have been made to synthesize tetrakis(o-phenylenedioxy)cyclotetraphosphazene by the following procedures: (a) the interaction of $(NPCl_2)_4$ with catechol in tetrahydrofuran in the presence of triethylamine, (b) the reaction of $(NPCl_2)_4$ with catechol in pyridine solution using conditions specified in the literature,[5,6] (c) an interaction of $(NPCl_2)_4$ and catechol in tetrahydrofuran in the presence of anhydrous sodium carbonate, (d) treatment of $(NPCl_2)_4$ with the disodium salt of catechol in tetrahydrofuran, and (e) the interaction of $(NPCl_2)_4$ with 1,2-bis(trimethylsilyloxy)benzene. In no case was the spirocyclic tetramer obtained. The principal products from reactions a and b were the triethylamine and pyridine salts of 2-(o-hydroxyphenoxy)-2,2'-spirobi(1,3,2-benzodioxaphosphole) (II). Data from the reaction between catechol and $(NPCl_2)_4$ in pyridine at $-15°$ indicated that catechol is consumed faster than the chlorophosphazene, and analysis of the final reaction products showed that 25% of the original $(NPCl_2)_4$ remained unreacted but that only a trace of unreacted catechol remained. Thus, it appears that the fully or partly substituted tetramer reacts faster with the catecholate anion than does $(NPCl_2)_4$, and this explains the preparative difficulties encountered. When sodium carbonate was used as a base or the disodium salt of catechol was employed, partly substituted, uncyclized phosphazenes were detected (see Experimental Section). These were exceedingly unstable in contact with atmospheric moisture. Phosphazene ring degradation occurred even when $(NPCl_2)_4$ was treated with 1,2-bis(trimethylsilyloxy)benzene, since the principal products isolated were trimethylchlorosilane and a material believed to be 2-(trimethylsilyloxyphenoxy)-2,2'-spirobi(1,3,2-benzodioxaphosphole). These results provide a striking contrast to the behavior of the cyclic trimeric system under similar circumstances. Thus, in the trimeric case, formation of phosphorane II accompanies the formation of spirophosphazene I when tertiary amines are present, but the phosphorane is not the predominant product.

Reactions between $(NPCl_2)_3$ or $(NPCl_2)_4$ and 1,8-Dihydroxynaphthalene.— Both trimeric and tetrameric spirocyclophosphazenes were prepared with six-membered exocyclic rings at phosphorus. Thus, $(NPCl_2)_3$ reacted with 1,8-dihydroxynaphthalene and sodium carbonate in tetrahydrofuran to yield tris(1,8-dioxynaphthyl)cyclotriphosphazene (III), and $(NPCl_2)_4$ interacted with 1,8-dihydroxynaphthalene and triethylamine in tetrahydrofuran to give tetrakis(1,8-dioxynaphthyl)cyclotetraphosphazene (IV). Both of these compounds are stable, white, crystalline solids. The molecular structures were confirmed by microanalyses and by infrared, ultraviolet, and mass spectral data[7]

III

IV
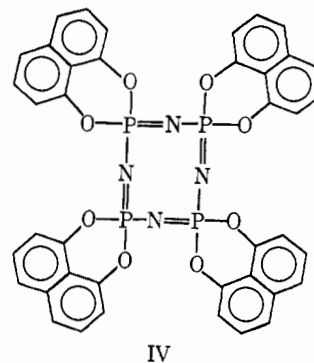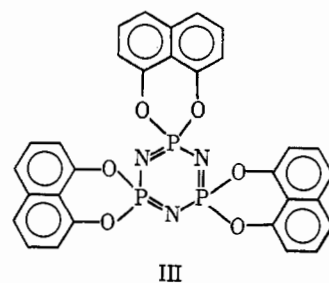
(see spectral data section and Experimental Section). No obvious differences were discernible in the relative stabilities of these two compounds. Certainly IV is a much more stable species than the elusive o-dioxyphenyl tetramer discussed above, presumably because of the lower ring strain in the exocyclic units of IV. It is also interesting that no phosphorane was detected during formation of IV, a fact which confirms the role of exocyclic ring strain in favoring phosphorane formation.[8]

The Reaction between $(NPCl_2)_4$ and 2,2'-Dihydroxybiphenyl.— The reaction between $(NPCl_2)_3$ and 2,2'-dihydroxybiphenyl in the presence of sodium carbonate to yield tris(2,2'-dioxybiphenyl)cyclotriphosphazene has been reported previously.[3] The corresponding tetramer (V) has now been prepared by the interaction of $(NPCl_2)_4$ with 2,2'-dihydroxybiphenyl and triethylamine in tetrahydrofuran. Thus, formation of the

V
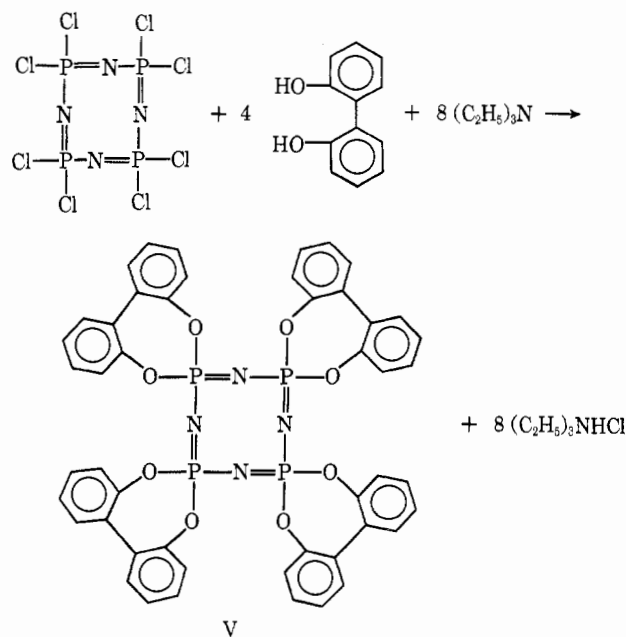
(7) X-Ray single-crystal studies on III–V are in progress.
(8) H. R. Allcock and R. L. Kugel, *J. Amer. Chem. Soc.*, **91**, 5452 (1969).

seven-membered ring occurs in the tetrameric system as well as in the trimer. However, ring closure is apparently a very slow step. Replacement of one chlorine per phosphorus occurs rapidly even at −15° to yield half of the expected triethylamine hydrochloride, but detectable ring closure does not take place until the temperature is raised above 0°. This effect was also observed during the synthesis of IV. The structural examination of V is discussed in the following section.

Infrared, Ultraviolet, and Mass Spectral Data.— Infrared spectra showed the following principal bands (in cm^{-1}): III, 1610 (triplet), 1210 (P=N), 1170, 1045, 920 (P—O—Ar), 850, 840 (P—O—Ar), 812, 787 (Ar), 750 (Ar), 649 (Ar); IV, 1620 (triplet, Ar), 1345, 1245 (P=N), 1180, 1041, 910 (doublet, P—O—Ar), 792 (Ar), 745 (Ar), 649 (Ar); V, 1320, 1244 (P=N), 1200–1177 (doublet), 1100, 960 (P—O—Ar), 935, 848 (P—O—Ar), 790 (Ar), 777, 764, 750 (Ar), 735, 714 (Ar). By contrast, the trimeric analog of V shows a P=N stretch at 1175 cm^{-1}. The tetrameric P=N bands of IV and V can be compared with those of [NP(OCH$_2$CF$_3$)$_2$]$_4$ at 1280 cm^{-1} and [NP(OC$_6$H$_5$)$_2$]$_4$ at 1270 cm^{-1}. Thus, the spectra are consistent with the expected structures.

Ultraviolet data for dioxane or tetrahydrofuran solutions are as follows (in mμ): III, 325 (m), 318 (sh), 311, 305 (sh), 292.5 (λ_{max}, log ϵ = 4.38), 283 (sh); IV, 325 (m), 318 (sh), 311, 305 (sh), 292.5 (λ_{max}, log ϵ = 4.49), 283 (sh); V, 286 (w), 243 (λ_{max}, log ϵ = 4.80). The spectra of III and IV are similar to that of 1,8-naphthalenedioxyphosphoric acid, C$_{10}$H$_6$O$_2$P(O)OH, which shows maxima at 325 (m), 318 (sh), 310 (w), and 391.8 mμ (s), and the spectrum of V is similar to that of the analogous cyclic trimer, (NPO$_2$C$_{12}$H$_8$)$_3$, and to the spectrum of 2,2'-dimethoxybiphenyl.[3] It seems clear that the aromatic ligands in the cyclophosphazenes are responsible for the observed absorptions. The similarities between the ultraviolet spectra of the trimeric and tetrameric 1,8-dioxynaphthyl derivatives, III and V, indicates that the skeletal degree of polymerization has little influence on the π-orbital levels of the ligands. This observation also applies to the spectra of the trimeric[3] and tetrameric (V) 2,2'-dioxybiphenyl derivatives.

The mass spectrum of III at 330° and 70 eV showed a parent peak at 609 mass units and fragmentation peaks at ~596, 398, 354, 315, and 203 mass units. The last corresponds to a monomer unit. Compound IV was studied at 350° and 70 eV, and the parent peak at 812 mass units was observed. Species V, examined under the same conditions, showed a parent peak at 916 mass units and a peak at 732 mass units which corresponds to the loss of a biphenylenedioxy fragment from the parent ion.

Implications of the Preparative Data.— The following facts are apparent from this work. (1) Although tris-(o-phenylenedioxy)cyclotriphosphazene (I) is readily formed by the interaction of (NPCl$_2$)$_3$ with catechol in the presence of base, the corresponding tetrakis(o-phenylenedioxy)cyclotetraphosphazene has not been prepared by this technique. (2) Phosphoranes of structure II appear to be formed much more readily when (NPCl$_2$)$_4$ interacts with catechol and base than when (NPCl$_2$)$_3$ is a reagent. (3) These differences between cyclic trimers and tetramers are not apparent

when six- or seven-membered arylenedioxy rings are formed at phosphorus. No phosphoranes were detected from these reactions.

The five-membered ring at phosphorus in I or in its tetrameric analog is expected to be strained. Attention has already been drawn to this in connection with the anomalously high rate of hydrolysis of I[9] and the facile degradation of I to a phosphorane in the presence of o-aminophenol.[8] By contrast, no strain of this type is expected in III–V or in the trimeric analog of V. Thus, the formation of phosphorane II is associated with a release of ring strain during the conversion of a cyclophosphazene to a phosphorane. In the latter structure, the angles at phosphorus can more nearly approximate to the 90° expected in a trigonal-bipyramidal arrangement. In the presence of catechol and base, the tetramer may be more sensitive than the trimer to degradation to phosphorane II because of its greater skeletal flexibility, which allows it to tolerate more easily the conformational changes required during conversion to the phosphorane.

Experimental Section[10]

Materials.— Hexachlorocyclotriphosphazene (Hooker Chemical Co.) was purified by two recrystallizations from n-heptane to give a material melting at 112.5–113.5°. Octachlorocyclotetraphosphazene, mp 122–123° (Alfa Inorganics), was used as received. Catechol, mp 104.5° (Eastman), was recrystallized from a chloroform–petroleum ether mixture and then dried at 25° in a vacuum oven for 12 hr. 2,2'-Dihydroxybiphenyl (Aldrich) was recrystallized from a chloroform–pentane mixture and then dried under vacuum for 12 hr at 25°. 1,8-Dihydroxynaphthalene was prepared by alkaline fusion of the sodium salt of 1-hydroxy-8-naphthylsulfonic acid (Eastman) by the method of Bender and Lawler.[11] Triethylamine (Eastman) was distilled from potassium hydroxide pellets and then stored over molecular sieves. Pyridine (Fisher reagent) was distilled from phosphorus pentoxide and stored over molecular sieves. Anhydrous sodium carbonate (Baker and Adamson reagent) was dried at 105° for 12 hr in a vacuum oven. Sodium hydride (Pfaltz and Bauer), as a 50% dispersion in oil, was used as received. 1,2-Bis(trimethylsilyloxy)benzene was prepared by the method of Licht and Kriegsmann[12] from 1,2-dihydroxybenzene (11.0 g, 0.1 mol), hexamethyldisilazane (41 ml, 0.2 mol), and trimethylchlorosilane (0.5 ml). The mixture was boiled at reflux for 4 hr until no more ammonia was evolved, and the products were fractionally distilled to yield 25 g (98%) of the clear, liquid 1,2-bis(trimethylsilyloxy)benzene, bp 236–238° (lit.[12] bp 238°).

Molecular Weight Determination.— The new spirocyclotetraphosphazenes reported here were too insoluble to allow colligative molecular weight methods to be applied. Accordingly, mass spectral measurements provided the most critical estimates of these values. A second technique, based on ultraviolet spectroscopy was also used according to the method of Cunningham, Dawson, and Spring.[13] Application of this method requires an assumption of the degree of polymerization, n, of the phosphazene. Evidence that the compounds were tetramers (n = 4) was obtained from the position of the P=N infrared bands in the 1220–1280-cm^{-1} region. The ϵ values used were those of the appropriate cyclic phosphates.

Tris(1,2-dioxyphenyl)cyclotriphosphazene (I) (Using Sodium Carbonate as a Base).— A stirred mixture of (NPCl$_2$)$_3$ (50.0 g, 0.145 mol), catechol (47.6 g, 0.432 mol), and anhydrous sodium carbonate (91.6 g, 0.864 mol) was allowed to react in boiling

(9) H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.*, **91**, 3102 (1969).

(10) Infrared spectra were recorded on a Beckman IR5A spectrometer, ultraviolet spectra were measured on a Cary Model 15 spectrometer, and mass spectrometric data were obtained with the use of an AEI MS 9 spectrometer. Microanalyses were by Schwarzkopf Laboratories. X-Ray powder data were obtained with the use of an 11.46-cm diameter Enraf-Nonius camera using nickel-filtered, Cu Kα radiation.

(11) M. L. Bender and J. T. Lawler, *ibid.*, **85**, 3011 (1963).

(12) K. Licht and H. Kriegsmann, *Z. Chem.*, **12**, 462 (1965).

(13) K. G. Cunningham, W. Dawson, and F. S. Spring, *J. Chem. Soc.*, 2305 (1951).

tetrahydrofuran (500 ml) for 3 hr within a nitrogen atmosphere. Longer reaction times decreased the yield of spirophosphazene. The mixture was then cooled to 25° and the solid components were filtered off using a sintered-glass funnel and then washed with aqueous 5% hydrochloric acid (1 1.) followed by distilled water (3 1.). The insoluble residue was dried under vacuum for 6 hr at 25° and then recrystallized from xylene to yield crystals of I (40.0 g, 60% yield), mp 245°.

The Reactions between $(NPCl_2)_4$ and Catechol. (a) In Pyridine.—A solution of catechol (52.5 g, 0.48 mol) in dry pyridine (80 ml) was added dropwise to a stirred solution of $(NPCl_2)_4$ (46.4 g, 0.10 mol) in pyridine (250 ml). The temperature was maintained at −15° by an ice–salt bath during the addition and for an additional 16 hr thereafter. The precipitate was then filtered off in a cooled sintered-glass funnel with precautions taken to maintain the temperature of the products below −10°. The solid was dried, first by suction and then in a vacuum oven at 40° for 4 hr. It was then washed successively with distilled water (500 ml) at ice temperature, with 0.05 N hydrochloric acid (500 ml) and again with distilled water (500 ml). The white residue was dried in a vacuum oven at 60° for 4 hr to give 3 g of a product which did not melt below 360°. Its infrared spectrum was identical with that of an independently synthesized sample of octahydroxycyclotetraphosphazene, $[NP(OH)_2]_4$, with no aromatic bands being evident. Removal of the pyridine from the original filtrate by vacuum distillation yielded a pale yellow residue. This material was dried at 60° in a vacuum oven and then extracted with boiling heptane to yield unreacted $(NPCl_2)_4$ (8.4 g). The heptane-insoluble residue was then extracted with methylene chloride which, after solvent evaporation, yielded a pure sample of tris(o-dioxyphenyl)cyclotriphosphazene (I) (1.85 g), mp 238–240°. This compound was identified by infrared and mass spectral evidence.[2] It was assumed to have been formed from the ∼4% $(NPCl_2)_3$ impurity present in the original tetramer. The remaining insoluble residue was washed with absolute ethanol and then sublimed at 180° (1 mm) to yield a hygroscopic crystalline material (40.2 g), mp 250–260°. This was identified as the pyridine salt of phosphorane II. Thus, the infrared spectrum was very similar to that of the known triethylamine salt of II,[2] but the triethylammonium bands were replaced by those for the pyridinium ion. The pyridine salt of II was converted to the triethylamine derivative when heated in triethylamine. A mass spectrum at 70 eV of the pyridine salt showed a similar fragmentation pattern to that of the triethylamine derivative but with a parent peak at 435 mass units compared to the calculated value of 435 for the pyridine salt of II. No tetrameric analog of I was found.

(b) With Triethylamine in Tetrahydrofuran.—To a solution of $(NPCl_2)_4$ (5.0 g, 0.0108 mol) in dry tetrahydrofuran (150 ml) was added a solution of triethylamine (8.70 g, 0.0865 mol) and catechol (4.75 g, 0.0435 mol) in tetrahydrofuran (150 ml). The addition took place during 2 hr. After completion of the reaction (see the following conditions), the solid components were filtered off and dried in a vacuum oven. The filtrate was either freeze-dried or evaporated under vacuum at 35°. After a 12-hr reaction at 25°, phosphorane II (2.3 g) and triethylamine hydrochloride (8.8 g) were filtered off. A complex tarry mixture was isolated from the filtrate. After a 4-hr reaction at 0°, the precipitate contained triethylamine hydrochloride (5.6 g, 62%), and vacuum evaporation of the filtrate at 35° yielded phosphorane II (3.4 g). When the solvent was removed by freeze-drying, an unstable, partly substituted phosphazene was isolated. Infrared spectra of this product showed bands at 1250 cm⁻¹ (P–N ring) and 3400 cm⁻¹ (OH), in addition to aromatic bands. Residual halogen was present. After an 8-hr reaction at −10 to −15°, the precipitate consisted of triethylamine hydrochloride (8.82 g, 96%). The filtrate, when freeze-dried, yielded a rubbery, chlorine-containing material. Sublimation of this product yielded phosphorane II, triethylamine hydrochloride, and ammonium chloride. After only a 2-hr reaction using the above conditions, smaller amounts of triethylamine hydrochloride (4.7 g, 52%) were isolated. The lability and hydrolytic instability of the tetrahydrofuran-soluble products obtained from these reactions prevented their detailed structural identification.

(c) With Disodium Catecholate in Tetrahydrofuran.—Disodium catecholate was prepared from catechol and sodium or sodium hydride in tetrahydrofuran. Sodium (3.0 g, 0.03 mol) was dissolved in a solution of dry catechol (8.0 g, 0.0725 mol) in oxygen-free, dry tetrahydrofuran (150 ml). To this solution was added $(NPCl_2)_4$ (7.5 g, 0.0162 mol) in tetrahydrofuran (100 ml).

The mixture was heated to reflux temperature for 2 hr, during which time the brown color of disodium catecholate disappeared and a white solid precipitated. The precipitate was filtered off. It was soluble in water. Solvent was removed from the filtrate in a rotary evaporator to yield a hygroscopic, white solid (VI), mp 170–190°, which contained chlorine and showed hydroxyl bands, aromatic bands, and a P–N ring vibration band at 1250 cm⁻¹ in the infrared spectra. When heated, it evolved catechol and hydrogen chloride, leaving a water-soluble, chlorine-free, hygroscopic white solid (VII), mp 275°. No characteristic cyclophosphazene bands could be detected in the infrared spectra of VII. Similar products were obtained when disodium catecholate was prepared from catechol and a stoichiometric amount of 50% sodium hydride dispersion in oil. After an 8-hr reaction at 25° or a 3-hr reaction at 65°, the precipitate was filtered off and extracted with warm benzene. Evaporation of the benzene yielded VII. Sublimation of the residue from the benzene extraction yielded VI. Both VI and VII were also isolated from the tetrahydrofuran filtrate. Identification of VI and VII was difficult because of their hygroscopic character, and only brief exposure to the atmosphere yielded sodium o-hydroxyphenylphosphate. Attempts to derivatize the hydroxyl groups of VI and VII with acetyl chloride or acetyl chloride–pyridine mixtures gave mixtures of gums and tars. Treatment of VII with triethylamine yielded the triethylamine salt of phosphorane II, identified by infrared data.[2] The evidence is consistent with the belief that VI is a phosphazene with noncyclized ligands or a cyclolinear oligomer in which two or more partly substituted tetramer rings are linked by catechol bridging units. Compound VII appears to be a phosphorane, possibly the sodium salt of II, or a phosphorane precursor.

(d) With Sodium Carbonate in Tetrahydrofuran.—A mixture of $(NPCl_2)_4$ (10 g, 0.0216 mol), catechol (9.65 g, 0.0875 mol), and sodium carbonate (20.0 g, 0.188 mol) in tetrahydrofuran (500 ml) was stirred at temperatures between 0 and −10° for 5 hr and then filtered at the same temperature. The solid filtered off was soluble in water (principally sodium carbonate and sodium chloride). Removal of solvent from the filtrate yielded a white hygroscopic solid, mp 192°. This material contained chlorine and showed an infrared spectrum identical with that of VI. When heated under vacuum, hydrogen chloride and a material with an infrared spectrum identical with that of VII and a similar melting point (276–276.5°) were formed.

Reaction of $(NPCl_2)_4$ with 1,2-Bis(trimethylsilyloxy)benzene.—This reaction constituted an unsuccessful attempt to prepare tetrakis(o-phenylenedioxy)cyclotetraphosphazene by a nonbasic detrimethylchlorosilylation process. A solution of octachlorocyclotetraphosphazene (10.0 g, 0.0214 mol) and 1,2-bis(trimethylsilyloxy)benzene (25 g, 0.1 mol) in dry tetrahydrofuran (300 ml) was boiled at reflux for 72 hr. No precipitate formed and no trimethylchlorosilane was evolved. The tetrahydrofuran was removed by distillation and the residue was boiled at reflux at 235° for 72 hr during which time trimethylchlorosilane was evolved. The pale brown solid, which crystallized slowly from this mixture, was filtered off and was washed with n-heptane (50 ml) and with ether (20 ml). The white, solid residue did not melt below 340°. Its infrared spectrum was devoid of a P=N stretching band, but a strong P—O band was found at 1265 cm⁻¹. Many features of the spectrum were reminiscent of phosphorane derivatives such as II. A mass spectrum showed a prominent peak at 458 amu, with a metastable peak formed by loss of a 2-trimethylsilyloxyphenoxy group. The compound was, therefore, tentatively assigned the structure of 2-trimethylsilyloxyphenoxy-2,2'-spirobi(1,3,2-benzodioxaphosphole) (mol wt 458).

Tris(1,8-dioxynaphthyl)cyclotriphosphazene (III).—A mixture of 1,8-dihydroxynaphthalene (7.3 g, 0.045 mol), anhydrous sodium carbonate (12.0 g, 0.113 mol), and hexachlorocyclotriphosphazene (5.0 g, 0.0144 mol) in dry tetrahydrofuran (100 ml) was allowed to react at reflux temperature for 8 hr with vigorous stirring. The mixture was then cooled to room temperature and filtered. The brown residue was washed successively with 2 vol % hydrochloric acid (1500 ml) and then with distilled water (1500 ml). The resultant brown solid was dried in a vacuum oven at 50° for 8 hr and then recrystallized from xylene to yield tan crystals of **tris(1,8-dioxynaphthyl)cyclotriphosphazene (III)** (7.1 g, 78% yield), mp 358–359°. *Anal.* Calcd for $C_{30}H_{18}O_6N_3P_3$: C, 59.10; H, 2.96; N, 7.06; mol wt 609. Found: C, 58.71; H, 2.99; N, 6.92; mol wt 603 (ultraviolet spectra), 609 (mass spectra).

SILYL(TRANSITION METAL) HYDRIDES   *Inorganic Chemistry, Vol. 10, No. 8, 1971* 1647

Tetrakis(1,8-dioxynaphthyl)cyclotetraphosphazene (IV).—A solution of 1,8-dihydroxynaphthalene (7.15 g, 0.044 mol) and triethylamine (13.0 ml, 0.093 mol) in dry tetrahydrofuran (250 ml) was added dropwise to a stirred solution of octachlorocyclotetraphosphazene (5.0 g, 0.0108 mol) in tetrahydrofuran (250 ml). The solution was stirred for 4 hr at 25° and the solid dispersion (8.4 g) was filtered off and was found to consist of triethylammonium chloride (8.2 g, 60%) and 0.2 g of a material which was recrystallized from cyclohexanone to give IV. The filtrate was boiled at reflux for an additional 8 hr and the solvent was removed in a rotary evaporator. The brown residue was washed with acetone (1000 ml) and the insoluble portion was recrystallized from cyclohexanone to yield an additional 3.2 g of **tetrakis-(1,8-dioxynaphthyl)cyclotetraphosphazene (IV)** (total yield 3.4 g, 27%). The compound did not melt below 360°. *Anal.* Calcd for $C_{40}H_{24}O_8N_4P_4$: C, 59.2; H, 2.96; P, 15.25; mol wt 812. Found: C, 59.20; H, 2.92; P, 15.20; mol wt 808 (ultraviolet spectra), 812 (mass spectra). The use of sodium carbonate in place of triethylamine gave the same product but in much lower yields.

Tetrakis(2,2′-dioxybiphenyl)cyclotetraphosphazene (V).—A solution of 2,2′-dihydroxybiphenyl (8.2 g, 0.044 mol), octachlorocyclotetraphosphazene (5.0 g, 0.0108 mol), and triethylamine (12.5 ml, 0.09 mol) in dry tetrahydrofuran (300 ml) were stirred together at 0°. Triethylammonium chloride precipitated from solution immediately after the reactants were mixed. After a 2-hr reaction at 0°, the mixture was filtered to yield triethylammonium chloride (6.2 g, 50% yield), but continued stirring of the filtrate at 0° for 8 hr yielded no further precipitate. An additional 172-hr reaction at 25° yielded a white precipitate. This was dried in a vacuum oven at 30° and then sublimed at 165° (0.5 mm) for 100 hr. The sublimate was triethylammonium chloride, and the residue was recrystallized from dimethylacetamide to yield **tetrakis(2,2′-dioxybiphenyl)cyclotetraphosphazene (V)** (3.0 g, 30.2% yield). The compound did not melt below 340°. Use of sodium carbonate as a base in this reaction yielded no identifiable product. *Anal.* Calcd for $C_{48}H_{32}O_8N_4P_4$: C, 62.80; H, 3.49; N, 6.11; P, 13.55; mol wt 916. Found: C, 62.64; H, 3.69; N, 6.42; P, 13.22; mol wt 924 (ultraviolet spectra), 916 (mass spectra).

Influence of the Base.—In view of the similarities normally observed between phosphazene cyclic trimers and tetramers, it is surprising that bases such as triethylamine and sodium carbonate have specific influences for reactions of trimers and tetramers. Thus, while triethylamine gives high yields of tetramer IV, the use of sodium carbonate in place of triethylamine gave the same product but in much lower yields. By contrast, sodium carbonate is a good base for the formation of the analogous trimer III. Sodium carbonate was not effective for the synthesis of V, even though it is the preferred reagent for formation of the analogous trimer.[3] Sodium carbonate can be used to prepare I in higher yields than with triethylamine. Thus, it appears that sodium carbonate is an excellent reagent for the synthesis of spirocyclotriphosphazenes but that an organic base, such as triethylamine, is preferred for synthesis of the spirotetramers. These differences may be connected with the extreme insolubility of the aryloxyspiro tetramers and their uncyclized sodium salt precursors. This pattern does not extend to derivatives in which two independent substituents are present at phosphorus, where sodium carbonate is effective for both trimers and tetramers.

X-Ray Diffraction Data.—The following are d spacings (in Å), with estimated intensities in parentheses: III, 13.23 (vs), 10.61 (vs), 7.78 (m), 6.80 (s), 6.29 (vs), 5.82 (s), 5.25 (w), 4.71 (s), 4.56 (s), 4.37 (s), 4.00 (s), 3.89 (m), 3.80 (s), 3.59 (m), 3.49 (w), 3.40 (vs), 3.28 (m), 3.19 (s), 2.62 (w); IV, 10.59 (w), 9.49 (vs), 8.30 (w), 7.48 (s), 6.72 (vs), 5.41 (w), 5.15 (m), 4.85 (w), 4.57 (w), 4.14 (w), 3.97 (s), 3.82 (w), 3.72 (s), 3.59 (s), 3.45 (s), 2.61 (m), 2.52 (w), 2.42 (w), 2.32 (w), 2.21 (w), 2.09 (w), 1.98 (w), 1.88 (w), 1.77 (w), 1.66 (w), 1.40 (m), 1.37 (w), 1.23 (w), 1.14 (m); V, 10.49 (s), 8.80 (vs), 7.16 (vs), 6.24 (w), 5.78 (w), 5.01 (s), 4.77 (s), 4.55 (w), 4.32 (w), 4.12 (s), 3.88 (m), 3.70 (w), 3.57 (s), 3.48 (vs), 3.18 (vs), 2.98 (w), 2.66 (s), 2.51 (w), 2.06 w), 1.96 (w), 1.91 (w), 1.76 (m).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Silicon–Transition Metal Chemistry. II.[1] Anions Derived from Silyl(transition metal) Hydrides and Related Compounds

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The anions $Cl_3SiFe(CO)_4^-$, $(C_6H_5)_3SiFe(CO)_4^-$, $Cl_3SiMn(CO)_2C_5H_5^-$, and $Cl_3SiMn(CO)_2C_5H_4CH_3^-$ have been prepared from the parent hydrides as triethylammonium or tetraethylammonium salts. The acidity of the hydrides decreases in the order $Cl_3SiFeH(CO)_4 > (C_6H_5)_3SiFeH(CO)_4 > Cl_3SiMnH(CO)_2C_5H_5 > (C_6H_5)_3SiMnH(CO)_2C_5H_5$. Reactions of the anions with $(C_6H_5)_nSnCl_{4-n}$ ($n = 0, 1, 2$) lead to stable derivatives such as cis-$Cl_3Sn(Cl_3Si)Fe(CO)_4$ and trans-$C_6H_5Cl_2Sn(Cl_3Si)$-$Mn(CO)_2C_5H_4CH_3$ as well as bis-substituted tin compounds. Bases such as $(C_2H_5)_3N$, CH_3CN, or Cl^- reversibly displace $Cl_3SiFe(CO)_4^-$ from $(Cl_3Si)_2Fe(CO)_4$.

Introduction

Transition metal hydrides, like the common mineral acids, are known to cover a wide range of acidities.[2] For example, cobalt tetracarbonyl hydride[3] and manganese pentacarbonyl hydride[4] have K_a values of 1.0 and 0.8 × 10⁻⁷, respectively, and the anions of these acids are useful synthetic reagents. Furthermore, it

has been shown that the acidity of metal carbonyl hydrides is markedly affected by altering the ligands.[5]

We have described the photochemical synthesis of a number of silyl-substituted transition metal hydrides which also exhibit a wide range of acidities.[1,6] Thus the compound $(Cl_3Si)_2FeH(CO)C_5H_5$ is a strong acid in acetonitrile.[7] We report here a study of the weaker

(1) Part I: W. Jetz and W. A. G. Graham, *Inorg. Chem.*, **10**, 4 (1971).
(2) It is unfortunate from a semantic point of view that so many of the compounds formally classified as hydrides are in fact protonic acids.
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(4) W. Hieber and G. Wagner, *Z. Naturforsch. B*, **13**, 339 (1958).
(5) W. Hieber and E. Lindner, *Ber.*, **94**, 1417 (1961).
(6) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 3375 (1969).
(7) The results of a detailed study of this compound will be submitted shortly. An nmr study has established $K_a = 2.6 × 10^{-3}$ in acetonitrile, intermediate between the dissociation constants of perchloric and hydrobromic acids in that solvent.