

polar solvents, such as pure CDCl_3 , chlorophyll is aggregated, and as a consequence the signal of the C-10 hydrogen is broadened and shifted to an extent which makes detection difficult, even in deuteriochlorophyll.⁴ Mathewson, Richards, and Rapoport,⁵ who have studied hydrogen exchange in chlorophyll, *Chlorobium* chlorophyll 660, and bacteriochlorophyll, make no mention of exchange at C-10 and report exchange only at the δ positions. Because conditions for observing the C-10 proton resonance can now be specified, we have been able to show that both the C-10 and δ protons are exchangeable, with exchange at C-10 much the faster.

The exchange with CD_3OD was studied in tetrahydrofuran, CCl_4 , and CDCl_3 . Exchange of the δ and C-10 protons is qualitatively the same in these three solvents. Tetrahydrofuran is particularly convenient, since the state of aggregation of the chlorophyll and the chemical shift of the C-10 proton vary less than is the case in CDCl_3 or CCl_4 . The results are shown in Table I. The "rate constant" for exchange of the other protons in chlorophyll and pheophytin is apparently smaller than 10^{-9} under these conditions.

TABLE I
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR HYDROGEN EXCHANGE AT C-10 AND δ POSITIONS IN TETRAHYDROFURAN SOLUTIONS AT 38°C ^a

Compd.	Concn., ^b moles/l.	k^c for C-10 exchange, sec. ⁻¹	k^c for δ exchange, sec. ⁻¹	$k_{\text{C-10}}/k_{\delta}$
Chlorophyll <i>a</i>	0.185	3×10^{-4}	2×10^{-6}	150
Chlorophyll <i>b</i>	0.178	2×10^{-4}	5×10^{-6}	40
Pheophytin <i>a</i>	0.096	$>1 \times 10^{-3}$	$<10^{-9}$	$>10^6$

^a The half-time of the exchange in seconds was obtained by integration of Varian A-60 n.m.r. spectra. ^b CD_3OD concentration in all cases, 9.1 moles/l. ^c k is calculated as a pseudo-first-order rate constant from $k = \ln 2/t_{1/2}$.

The pseudo-first-order rate constants for exchange at the δ position in chlorophylls *a* and *b* have relative rates that are quite comparable with those reported by Mathewson, *et al.*⁵ Exchange at the C-10 position was in every case at least two orders of magnitude

(5) J. H. Mathewson, W. R. Richards, and H. Rapoport, *Biochem. Biophys. Res. Commun.*, **13**, 1 (1963).

faster than that of the δ and supports the chemical considerations which indicated that active hydrogen in chlorophyll was located at C-10.⁶

That exchange at the δ position in pheophytin under the conditions above is much slower than in the magnesium-containing chlorophyll derivatives reflects the effect of the central magnesium atom on the localization energy at the methine bridge. On the other hand, the exchange at C-10 in pheophytin was evidently faster than in the chlorophyll derivatives and is comparable to the rate of exchange in 2-carbethoxycyclopentanone.

The preparation of a pyro series of chlorophyll derivatives, in which the carbomethoxy group at C-10 has been replaced by a hydrogen atom,⁷ makes it possible to compare the behavior of the δ and C-10 positions in pyrochlorophyll *a* or methyl pyrochlorophyllide *a* undergoes facile exchange, the two C-10 hydrogen atoms in the pyrochlorophyllide show no measurable exchange in 2.5 months in an 11% $\text{CD}_3\text{OD}-\text{CDCl}_3$ mixture. On the other hand, when pyropheophytin *a* is heated with a mixture of pyridine and D_2O , the C-10 protons exchange and the δ position is scarcely affected. Exchange at C-10 in chlorophyll will be facilitated by either acids or bases, but exchange at the δ position probably proceeds primarily by electrophilic substitution.

(6) (a) H. Fischer and S. Goebel, *Ann.*, **522**, 168 (1936); (b) S. Aronoff, *Encyclopedia Plant Physiol.*, **5**, 234 (1960); (c) W. Vishniac and I. A. Rose, *Nature*, **182**, 1089 (1958).

(7) F. C. Pennington, H. H. Strain, W. A. Svec, and J. J. Katz, to be published.

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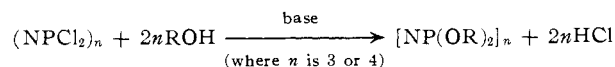
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New Reactions of Phosphonitrilic Chloride Trimer. Substitution and Cleavage Reactions with Catechol and Triethylamine¹

Sir:

Cyclic trimeric and tetrameric phosphonitrilic chlorides react with alcohols or phenols in the presence of base, or with their alkali metal salts, to yield alkyl or aryl phosphonitrilates.²⁻⁸ Dihydroxy compounds have



also been employed to prepare a cyclized aliphatic phosphonitrilate⁹ and to prepare phosphonitrilate polymers.¹⁰

In the present investigation, phosphonitrilic chloride trimer (I) was treated with catechol and triethylamine

(1) Presented to the Symposium on Inorganic Polymers, University of Western Ontario, Sept., 1963.

(2) D. R. Dishon, *J. Am. Chem. Soc.*, **71**, 2251 (1949).

(3) M. Yokoyama and F. Yamada, *Kogakuin Daigaku Kenkyu Hokoku*, **7**, 62 (1959); *Chem. Abstr.*, **54**, 19458 (1960).

(4) C. Hamalainen and J. D. Guthrie, *Textile Res. J.*, **26**, 141 (1956).

(5) R. Ratz and M. Hess, *Ber.*, **84**, 889 (1951).

(6) B. W. Fitzsimmons and R. A. Shaw, *Chem. Ind. (London)*, 109 (1961).

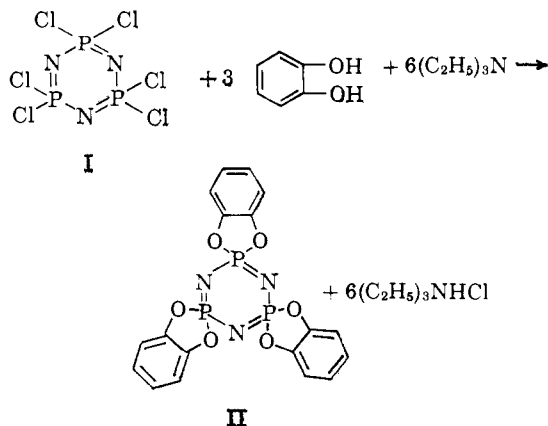
(7) N. Yokoyama, *J. Chem. Soc. Japan*, **80**, 1192 (1959).

(8) R. F. W. Ratz and C. J. Grundmann, U. S. Patent 2,876,248 (1959).

(9) M. S. Chang and A. J. Matuszko, *Chem. Ind. (London)*, 410 (1962).

(10) C. A. Redfarn, U. S. Patent 2,866,773 (1958).

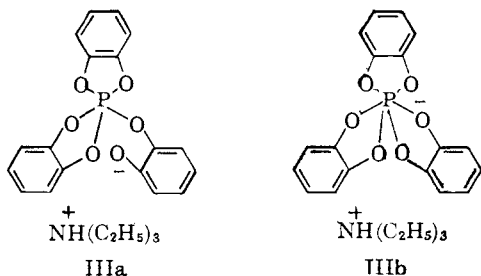
in tetrahydrofuran to yield tris(*o*-phenylenedioxy)-phosphonitrile trimer (II). Polymers and an unusual salt-like by-product (III) were also formed in this reaction.



The arylphosphonitrilate (II) is a white, crystalline solid, m.p. 244–245°, which sublimes without appreciable decomposition at 230° (0.05 mm.). *Anal.* Calcd. for $C_{18}H_{12}N_3O_6P_3$: C, 47.0; H, 2.63; N, 9.15; P, 20.3. Found: C, 46.85; H, 2.85; N, 9.16; P, 20.3. The molecular weight was shown by mass spectrometry to be 459. This compound appears to be less stable to thermal rearrangement than the hexaphenoxy analog, $[NP(OC_6H_5)_2]_3$,⁵ and this behavior undoubtedly reflects a release of steric strain in ring cleavage reactions of II.

The by-product (III) was also formed quantitatively when II was treated with 6 equivalents of catechol and 3 equivalents of triethylamine in toluene. The evolution of ammonia in this reaction indicated an unusual cleavage of the phosphorus–nitrogen ring system. Treatment of III with strong base yielded triethylamine and phenolic residues. *Anal.* Calcd. for $C_{24}H_{28}NO_6P$ (III) after purification by sublimation: C, 63.0; H, 6.17; N, 3.06; P, 6.79. Found: C, 62.8; H, 6.32; N, 3.16; P, 6.95. Infrared spectra of the solid indicated the presence of the groups: NH (3200 cm^{-1}), *o*-substituted aryl (1600, 1500, 1100, 1060, 1040, and 750 cm^{-1}), O-aryl (1250 cm^{-1}), and O–P–O (830 and 735 cm^{-1}). The ultraviolet spectrum of this material in acetonitrile solution was similar to that of II but was displaced 15 $m\mu$ toward the visible. The λ_{max} and log ϵ values (in parentheses) for III were 290 $m\mu$ (sh) (4.07), 284 $m\mu$ (4.17), 280 $m\mu$ (sh) (4.14), and 227 $m\mu$ (sh) (4.17). A mass spectrum of this product at 300° showed considerable fragmentation, but triethylamine was identified as one of the species formed. X-Ray powder diffraction patterns were consistent with a hexagonal, two-molecule unit cell, in which each unit had a molecular weight of 457. The n.m.r. spectra of this material in dimethylformamide indicated a methyl to phenyl proton ratio of 3 to 4.

This evidence suggests that possible structures for this compound are those depicted in IIIa and IIIb.



The ultraviolet spectrum indicates that structure IIIa predominates in solution. However, structure IIIb appears to exist in the crystalline state. The X-ray and infrared evidence can be correlated with the high symmetry of this form. The strong, sharp NH peak (3200 cm^{-1}) is indicative of a larger charge separation than would be expected for structure IIIa. This is consistent with steric shielding of the negatively charged site in a similar manner to that demonstrated for the tetraphenylborate ion.¹¹ The observed stability of the solid salt is also more compatible with structure IIIb than with the triethylamine salt of a phenol.

Other examples of hexavalent phosphorus anions have been restricted to the $(PF_6)^-$ ion and the $(PCl_6)^-$ ion in phosphorus pentachloride.¹² The unique structure and stability of IIIb in the solid state can be attributed to the fact that the sterically hindered counterions are separated in the crystal lattice. Under these circumstances, the negative charge can be stabilized more readily on phosphorus than on oxygen.

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(11) P. Chevalier and C. Sandorfy, *Can. J. Chem.*, **38**, 2524 (1960).

(12) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 238 and 805.

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Tetrahedral Tetrachlorocopper(II) Complex in Molten Salt Solutions

Sir:

The absorption spectra of solutions of copper(II) chloride in melts of cesium chloride and tributyl-2,4-dichlorobenzylphosphonium chloride (Phosphon¹) indicate the presence of tetrahedral, or mildly distorted tetrahedral, $CuCl_4^{2-}$ complexes. The importance of this result lies in the fact that only a few examples of tetrahedral, or distorted tetrahedral, copper(II) complexes are known,^{2,3} and of these only the distorted bromo complex has been found previously³ in liquid solutions. Tetracoordinated chlorocopper(II) complexes have been reported to occur in liquid solvents with excess chloride ions,⁴ but a comparison of their spectra with those reported below shows that they are not tetrahedral.

Measurements were made with a Cary Model 14H spectrophotometer over the wave number range of 4000–27,000 cm^{-1} . Copper(II) chloride when dissolved in molten Phosphon at 128° was found to have a d–d band at 8000 cm^{-1} with a molar extinction coefficient, ϵ , of 79 l./mole-cm. and the lowest energy charge-transfer band at 22,200 cm^{-1} ($\epsilon = 732$ l./mole-cm.). In molten cesium chloride as solvent the d–d band was also at 8000 cm^{-1} ($\epsilon = 1$ /mole-cm.), while the lowest-energy charge-transfer band was a shoulder

(1) Kindly donated by the Virginia-Carolina Chemical Co.

(2) (a) L. Helmbold and R. F. Krub, *J. Am. Chem. Soc.*, **74**, 1176 (1952); (b) E. Prince, *Acta Cryst.*, **13**, 544 (1957); (c) B. Morosin and E. C. Lingafelter, *ibid.*, **13**, 807 (1960); (d) B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, **65**, 50 (1961); (e) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

(3) J. C. Barnes and D. N. Hume, *Inorg. Chem.*, **2**, 444 (1963).

(4) See, for example: (a) J. Bjerrum, *Dan. Mat. Fys. Med.*, **22**, No. 18 (1946); (b) J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954); (c) C. J. Ballhausen, *Dan. Mat. Fys. Med.*, **29**, No. 4 (1954); (d) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).