[CONTRIBUTION FROM THE ENERGY DIVISION, OLIN MATHIESON CHEMICAL CORPORATION]

The Chemistry of Decaborane. Iodination Studies[1]

BY MANNY HILLMAN[1c]

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Two iododecaboranes, m.p. 117–119° (I) and 98.5–100° (II), and two diiododecaboranes, m.p. 260.5–261° (III) and 153–155° (IV), were obtained by direct iodination of decaborane. Compound I was shown to be the 2-iodo isomer by iodination to the 2,4-diiodo isomer (III)[2,3] and to a new diiodo derivative (IV). Compound II was iodinated to give IV. The position of substitution in II and one of the substitution positions in IV was assigned as the 5 position on the basis of deuterium tracer studies.

Introduction

The study of the chemistry of decaborane, a strikingly unusual compound, recently has received increased attention in many laboratories. The halogen derivatives appeared to be most readily available for an initial investigation and this first report deals with the iodo derivatives of decaborane.

Stock,[2] in connection with his early work on the chemistry of boranes, reported the isolation of two halodecaboranes from a reaction of the appropriate halogen and decaborane in a sealed tube. These were a dibromodecaborane and a diiododecaborane. By means of a preliminary crystal structure determination, R. Schaeffer[3] has shown that the iodine atoms in the diiododecaborane were in the 2 and 4 positions,[4] in agreement with the predictions of Lipscomb.[6]

R. Schaeffer[7] also has mentioned the existence of other halogenated decaboranes and by means of nuclear magnetic resonance (n.m.r.) spectroscopy has shown that iododecaborane, m.p. 118°, has the iodine atom in the 2 position and suggested that iododecaborane, m.p. 72°, might have the iodine atom in the 5 position. No preparative methods have been given.

Experimental[8]

Synthetic Experiments. Iodination of Decaborane.—A mixture of 1.00 g. (8.20 mmoles) of decaborane and 2.082 g. (8.20 mmoles) of iodine were heated in a 200 ml. sealed tube at 110–120° for 25 hr. The tube was cooled and opened and the contents were removed. A sample of the crude product was saved for the determination of the product distribution by quantitative infrared analysis. Recrystallization from heptane gave 1.14 g. of a yellow solid, m.p. 68–107°. A second recrystallization gave 0.630 g. of pale yellow needles, m.p. 112–116°. Several additional recrystallizations raised the m.p. to 117–119°. Mass spectrometric analysis indicated that this compound was a monoiododecaborane and the n.m.r. spectrum showed that it was the 2-iododecaborane. The infrared spectrum[9] (KBr pellet) had the following bands (cm.$^{-1}$): 662, 693, 712, 720, 744, 760, 787, 800, 813, 824, 841, 868, 882, 894, 922, 950, 1000, 1045, 1103, 1478, 1518, 1634(H_2O?), 1893, 2580, 3430 (H_2O).

The mother liquors were combined and evaporated to dryness. This product was accumulated from several experiments until a reasonable quantity was obtained. Recrystallization from pentane gave a yellow powder, m.p. 70–79°. The n.m.r. spectrum was similar to that of the low melting isomer reported by R. Schaeffer.[7] Sublimation at 70–80° under a pressure less than 1μ, and then further crystallizations from pentane or hexane gave well defined crystals of reasonable size. Repeated crystallization from pentane coupled with manual separation of the needle-shaped 2-iododecaborane from the block-shaped crystals gave finally a sample of II, m.p. 92–98°. Further recrystallization raised the melting point to 98.5–100°. The mass spectrum indicated that this was a monoiododecaborane. The infrared spectrum[9,10] (KBr pellet) contained these various bands (cm.$^{-1}$): 700, 717, 742, 748, 761, 796, 813, 825, 853, 915, 923, 934, 971, 995, 1029, 1104, 1473, 1520, 1561, 1577, 1626, 1634(H_2O?), 1901, 1940, 2580, 3430 (H_2O).

Diiodination of Decaborane.—In approximately two equal portions in separate 560 ml. sealed tubes, a total of 4.34 g. (35.6 mmoles) of decaborane and 18.1 g. (71.2 mmoles) of iodine were heated at 110° for 24 hr. The product, 12.8 g. of a yellow solid, was recrystallized from 80 ml. of benzene to give 2.96 g. of 2,4-diiododecaborane, m.p. 250–254°. Evaporation of the benzene to 35 ml. gave an additional 0.54 g., m.p. 245–249°. Several additional recrystallizations raised the melting point to 260.5–261°. The infrared spectrum[9] (KBr pellet) contained these bands (cm.$^{-1}$): 687, 703, 734, 749, 783, 796, 849, 893, 902, 932, 993, 1039, 1084, 1464, 1515, 1575, 1632(H_2O?), 1894, 2570, 2620, 3440 (H_2O).

Evaporation of the benzene solution to dryness and then recrystallization of the residues from 60 ml. of heptane gave 4.92 g. of a yellow solid with a wide melting point range starting at 133°. Five additional recrystallizations from hexane and a sublimation before the final recrystallization at 130–140° and 1μ gave small yellow crystals of IV, m.p. 153–155°. The purification during recrystallization seemed to cause the disappearance of the 687, 703 and 851 cm.$^{-1}$ bands in the infrared spectrum. The mass spectrum suggested the material was a diiododecaborane and the n.m.r. spectrum indicated that one iodine atom was in the 2-position and that the other was similar to the iodine in II. The infrared spectrum (KBr pellet) contained these several bands (cm.$^{-1}$): 667, 694, 712, 723, 750, 780, 804, 824, 851 (very weak), 878, 911, 920, 953, 988, 1029, 1094, 1470, 1513, 1564, 1634 (H_2O?), 1890, 2580, 3430 (H_2O).

Anal. Calcd. for $B_{10}H_{12}I_2$: B, 28.92; H, 3.23. Found: B, 29.20; 29.97; H, 3.94, 3.51.

The mother liquor from the heptane recrystallizations was evaporated to dryness and the residue was subjected to a fractional crystallization from hexane. Three fractions were obtained which, besides containing bands in their infrared spectra attributable to the known iododecaboranes, contained new bands. Sample I showed the following new bands (cm.$^{-1}$): 689, 741, 761, 775, 813, 842, 920, 935, 982, 1020, 1460, 1515, 1563, 2545, 2584. Sample II showed these new bands (cm.$^{-1}$): 699, 712, 789, 813, 862, 915, 969,

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(1) (a) Presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959; (b) supported by Air Force Contract 33(600)-33920; (c) The Hot Laboratory, Brookhaven National Laboratory, Upton, L. I., N. Y.

(2) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

(3) R. Schaeffer, THIS JOURNAL, **79**, 2726 (1957).

(4) For nomenclature see G. W. Schaeffer, Abstracts of Papers of the 133rd National ACS Meeting, San Francisco, California, April 14, 1958, 2-L, as illustrated by Shapiro, Lustig and Williams.[5]

(5) I. Shapiro, M. Lustig and R. E. Williams, THIS JOURNAL, **81**, 838 (1959).

(6) W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

(7) R. Schaeffer, J. N. Shoolery and R. Jones, THIS JOURNAL, **80**, 2670 (1958).

(8) Infrared analyses were conducted by Miss D. M. Robins and her staff, mass spectra were obtained by Dr. John H. Norman and his staff, n.m.r. spectra were obtained and interpreted by Dr. R. E. Williams and his staff and elemental analyses were conducted by Miss Alice M. Shimer. All melting points are uncorrected.

(9) The infrared spectrum of this compound was first reported by D. Mann and S. Karlan, Reaction Motors, Inc., Olin Mathieson Chemical Corporation, MCC-1023-TR-189, December 6, 1955.

(10) The spectrum reported by Mann and Karlan[9] was of the crude compound, m.p. 72–74°.

1511, 1550. Sample III showed these new bands in addition to those of Sample II (cm.$^{-1}$): 687, 864, 924, 1000. The quantities of material available were too small for further characterization.

Iodination of 2-Iododecaborane.—A mixture of 1.00 g. (4.03 mmoles) of 2-iododecaborane, m.p. 113–116°, and 1.05 g. (4.13 mmoles) of iodine was heated in a sealed tube at 110–120° for 24 hr. A sample of the crude product was saved for quantitative infrared analysis. The tube was opened and the product was removed. Recrystallization from benzene gave 0.225 g. of yellow plates, m.p. 259–262°. The m.p. of these crystals when mixed with authentic 2,4-diiododecaborane was not depressed.

The mother liquor was evaporated to dryness and the yellow solid was recrystallized from heptane to give 0.165 g. of a powder, m.p. 135–145°. Repeated crystallization from heptane or hexane raised the m.p. to 142–145°. Except for augmented bands due to III, the infrared spectrum was identical to that of IV.

Iodination of 5-Iododecaborane (II).—A mixture of 2.54 g. (10.2 mmoles) of 5-iododecaborane, m.p. 69–79°, and 2.62 g. (10.3 mmoles) of iodine was heated in a 300 ml. sealed tube at 110–120° for 25 hr. Recrystallization of the product from benzene gave 0.195 g. of III, m.p. 257–259°, and after evaporation of some solvent a second crystallate was obtained consisting of 0.112 g. of 2,4-diiododecaborane (III), m.p. 244–253°. Evaporation of the benzene to dryness and recrystallization of the residue from heptane gave 1.90 g. of a yellow solid, m.p. 128–135°. Several additional recrystallizations from hexane raised the m.p. to 144–147°. The infrared spectrum of this and of IV were identical except for bands attributable to III.

Quantitative Infrared Analyses for Product Distribution.—The extinction coefficients were calculated for the 932, 796 and 687 cm.$^{-1}$ bands for III and for the 920, 824, 804 and 723 cm.$^{-1}$ bands for IV. Six synthetic mixtures were prepared and examined. The error found was 4.8 ± 2.2%. Only the 950 cm.$^{-1}$ band for I and the 813 cm.$^{-1}$ band for II were useful. The error on seven synthetic mixtures was 6.8± 4.8%. Samples containing very low concentrations of any isomer generally gave much higher errors.

Tracer Experiments. Preparation of Deuterated Decaboranes.[11]—A solution of 6.1 g. of decaborane in 75 ml. of ether was shaken briefly with 40 ml. of 99.5% deuterium oxide (Stuart Oxygen Co.). The ethereal solution was dried quickly over anhydrous magnesium sulfate and evaporated to dryness. Decomposition due to hydrolysis was noted throughout the experiment. Sublimation gave 5.55 g. of *μ,μ',μ'',μ'''-tetradeuteriodecaborane* (VI) with a presumed deuterium content of 95% of the bridge positions.

These later manipulations were all carried out in a vacuum line. Dioxane previously dried over sodium ribbon was distilled into a tube coated with a sodium mirror. After standing overnight the specially dried dioxane was distilled to a tube containing approximately 1 g. of μ,μ',μ'',μ'''-tetradeuteriodecaborane (VI). After standing at room temperature for 72 hr., the dioxane was removed by distillation without warming. About 30 hr. were required for the distillation. The solid was removed from the tube with anhydrous ether. The ethereal solution was evaporated to dryness in vacuum and the solid residue was sublimed at high vacuum and low temperature to give 0.520 g. of 5,7,8,10,μ,μ',μ'',μ'''-octadeuterodecaborane[5] (V) theoretically containing 47.5% of deuterium in the eight positions.

In a separate experiment, a sample of 129 mg. of VI was heated in a sealed tube at 110° for one week. The infrared spectrum of the product indicated that equilibration of the 5, 7, 8, 10 and bridge positions had occurred to a greater extent than in dioxane. The n.m.r. spectrum indicated a similar stereospecificity.

Iodination of VI.—A mixture of 64 mg. (0.508 mmoles) of VI and 130 mg. (0.512 mmoles) of iodine was heated at 110° in a 30 ml. sealed tube equipped with a break-off tip for 24 hr. The gas produced (hydrogen iodide and deuterium iodide) was transferred with the aid of a vacuum line to another sealed tube with a break-off tip in which a few drops of mercury had been placed. After heating at 200° for 6.5 hr. the tube was opened and the hydrogen–deuterium mixture was analyzed with a mass spectrometer. The H_2, HD, D_2 peak heights of 3150, 53.6 and 0.4 respectively indicated that 0.8% of the mixture consisted of deuterium atoms.

Reaction of VI with Hydrogen Iodide.—Hydrogen iodide was generated by the reaction of 134 mg. (1.09 mmoles) of decaborane with 275 mg. (1.08 mmoles) of iodine at 110° for 24 hr. The hydrogen iodide formed was transferred to another sealed tube which already contained 90 mg. (0.714 mmole) of VI and the tube was heated at 110° for 24 hr. The hydrogen iodide then was transferred to a third sealed tube containing some mercury and converted to hydrogen at 200° for 6.5 hr. The mass spectral peak heights for H_2, HD and D_2 of 2535, 53.3 and 0.5 respectively indicated a deuterium atom content of 1.1%.

Iodination of V.—A mixture of 103 mg. (0.817 mmole) of V from the dioxane rearrangement and 203 mg. (0.80 mmole) of iodine was heated in a sealed tube at 110° for 24 hr. The gas produced was transferred to another tube containing mercury and was converted to hydrogen at 200° for 5 hr. The mass spectral peak heights for H_2, HD and D_2 of 3820, 963 and 63.2 respectively indicated a deuterium atom content of 11.2%. The expected value was 16.6%.

Results and Discussion

The method of iodination of decaborane reported by Stock[2] consisted of heating decaborane and either two moles or a large excess of iodine in a sealed tube. Shortly after the beginning of this investigation of the iodination of decaborane, R. Schaeffer[3] mentioned the use of iodine monochloride as an iodinating agent. These are the only methods mentioned in the open literature. In order to be consistent in the work reported here, modifications of the method of Stock[2] using varying ratios of iodine and decaborane were employed and all iodinations were performed under essentially the same conditions. When equimolar quantities of iodine and decaborane were used, the product consisted essentially of a mixture of two isomers of iododecaborane. 2-Iododecaborane[7] (I), m.p. 117–119°, was isolated by crystallization of the crude mixture from heptane. This compound was identified by means of the n.m.r. spectrum. The heptane soluble material consisted essentially of a second isomer of iododecaborane (II) as determined by both the infrared and the n.m.r. spectra. However, a very careful and tedious purification procedure was necessary to obtain monoclinic[12] crystals, space group P2$_1$/c with eight molecules per unit cell, m.p. 98.5–100°. Infrared spectrophotometry indicated that this substance was not a new isomer but the low melting iododecaborane, freer of the high melting isomer than had been obtained previously. The disappearance of I during the purification procedure was followed by the disappearance of bands at 950 and at 922 cm.$^{-1}$. Subsequent quantitative infrared analysis demonstrated that the original product of the reaction of equimolar quantities of iodine and decaborane consisted of 65% of I and 35% of II.

Iodination of I gave Stock's[2] diiododecaborane (III). Since R. Schaeffer[3] had shown that this isomer was the 2,4-diiododecaborane, I has now been chemically related to III and is 2-iododecaborane. Previously R. Schaeffer[7] had also assigned the same structure to I on the basis of n.m.r. spectroscopy, which in the case of 2-substituted decaboranes is a simpler method. For substitution in other positions, however, the n.m.r. spectra led to confusion.

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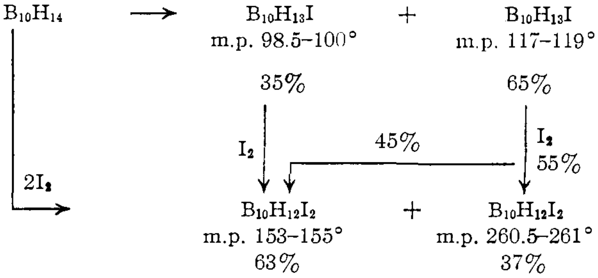
(11) M. F. Hawthorne and J. J. Miller, THIS JOURNAL, **80**, 754 (1958).

(12) We are indebted to Professor J. L. Hoard of Cornell University for this crystal determination.

In addition to III, a new isomer (IV) was obtained in only a slightly smaller in hand yield. Subsequent quantitative infrared analysis showed that 45% of the original reaction product was IV. The remainder of the reaction product was III.

Iodination of crude II, which contained a small amount of I, gave essentially IV and a small amount of III. Clearly then the positions of the iodine atom in II and of one of the iodine atoms in IV are identical.

In view of the observation that iodination of 2-iododecaborane gave a new diiododecaborane in relatively large amounts, it became interesting to see whether this isomer were actually formed during diiodination of decaborane itself. Non-formation of IV under these conditions would at this point have indeed been surprising. According to infrared analysis 63% of the product mixture was the new diiododecaborane. The rest was III. Without the aid of infrared spectrophotometry and without being suspicious of its presence, however, the isomer would have been easily missed due to the difficulty of separating it from III.



The Structure of the Low Melting Isomers (II and IV).—The problem of choosing the position of the iodine atom in the low melting isomers remains a challenging one. R. Schaeffer[7] with careful consideration of other possibilities tentatively guessed that the iodine atom might be in the 5 position on the basis of the n.m.r. spectrum.[13]

Recently results of Hawthorne and Miller[11] and Shapiro, Lustig and Williams[5] have made possible techniques by which the position of the iodine atom in question could be established within the limits of certainty dictated by the novelty of the chemistry.

Hawthorne and Miller[11] found that decaborane could be deuterated in the bridge positions with deuterium oxide in dioxane. Shapiro, Lustig and Williams[5] have found that upon "aging" a solution of bridge-deuterated decaborane in dry dioxane, a slow rearrangement occurred whereby deuterium atoms were equilibrated between the bridge positions and the 5, 7, 8 and 10 positions. The fate of the deuterium atoms was followed by means of n.m.r. spectroscopy. Since, in this particular case, the reaction appears to be quite clean and involves all four equivalent positions, the n.m.r. spectrum is interpreted easily and more confidence may be held in this interpretation than in the previously mentioned instances.

Then, if the iodine atom in II is in the 5 position, iodination of *5,7,8,10,μ,μ′,μ′′,μ′′′-tetradeuteriodecaborane* (*V*) should give deuterium iodide as one of the products. If deuterium iodide is not observed, then the iodine atom is in the 1 or the 6 position.

In a modification of Hawthorne and Miller's[11] method *μ,μ′,μ′′,μ′′′-tetradeuteriodecaborane* (*VI*) with the bridge positions containing 95% of deuterium was prepared by shaking decaborane in ether with deuterium oxide. Equilibration of the deuterium atoms in the bridge positions and the hydrogen atoms in the 5, 7, 8 and 10 positions was accomplished according to Shapiro's[5] procedure. Subsequently it was found that this equilibration could be effected more simply by heating the decaborane in a sealed tube just above its melting point. The latter method is just as stereospecific as the "aging" method according to the n.m.r. spectrum.

To establish the non-involvement of the bridge hydrogen atoms during iodination, VI was treated under the usual reaction conditions with iodine and with hydrogen iodide. The hydrogen iodide produced during iodination was converted to hydrogen by heating with mercury and the hydrogen was analyzed for deuterium content with the mass spectrometer. Iodination of VI gave hydrogen iodide containing 0.8% of deuterium iodide and reaction of VI with hydrogen iodide gave back hydrogen iodide containing 1.1% of deuterium iodide. This demonstrated that the bridges would be involved in a reaction with iodine and with hydrogen iodide to only a minute extent.

Iodination of V gave hydrogen iodide containing 11.2% of deuterium iodide. If there was no isotope effect, and if, in the preparation of V, equilibration was complete, then 16.6% of the hydrogen iodide formed should be deuterium iodide, *i.e.*, fraction DI formed = the fraction of D in 5, 7, 8 and 10 positions times the fraction of 5 isomer formed in reaction. An isotope effect whereby a protonated position would be more readily substituted by iodine would lower the expected value and incomplete equilibration of the bridges and the 5, 7, 8 and 10 positions would also lower the expected value. A study now in progress shows that the latter is the primary cause. Consideration of these possibilities tends to bring the expected and observed values in better agreement. Nevertheless, that so much deuterium has been obtained indicates that the iodine atom in II and one of the iodine atoms in IV are in the 5, 7, 8 or 10 position.

According to Lipscomb's[6] early analysis of the decaborane molecule, the 5, 7, 8 and 10 positions were the most positive. These, therefore, should not be susceptible to electrophilic attack. However, the earlier analysis did not take the hydridic nature of the bridge hydrogen atoms into account. Apparently, a more recent, not yet fully described analysis,[14,15] taking these hydridic hydrogens into account, finds that the 6 and 9 positions are most positive. This new interpretation and the results reported here are more in accord with the assignment of a neutral or small negative charge to the 5, 7, 8 and 10 positions. They can then be con-

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(13) In our own laboratories, an assignment of the 1 or 6 position on the basis of the same spectrum was preferred. It is apparent that deciphering the n.m.r. spectra for the 1, 3, 6, 9 and 5, 7, 8, 10 positions is still a very difficult and questionable task.

(14) W. N. Lipscomb, "Recent Studies of the Boron Hydrides," AEC Publication NP 6912.

(15) J. van der M. Reddy and W. N. Lipscomb, THIS JOURNAL, **81**, 754 (1959).

sidered as susceptible to electrophilic attack to some extent. These results are also consistent with the assignment of the bands in the n.m.r. spectrum.[7,16,17]

The question of formation of other isomers of diiododecaborane arises at this point. Provided that the presence of the first iodine atom does not influence the placement of the second iodine atom, six isomers are expected from the diiodination of decaborane. Three of these, the 5,7-, the 5,8- and the 5,10-isomers are each expected in only 3% of the total yield and therefore were missed easily. The 2,4-isomer by the same token is expected in 31% of the total yield which is fairly consistent with the experimentally obtained value of 37%. The other two isomers, the 2,5- and the 2,8-, are each expected in about 30% of the total yield. Apparently only one of these isomers was observed.

If the other isomer is not present or is present in much smaller quantities than expected, then it would suggest that the presence of one iodine atom would influence the placement of the second atom, and, intuitively at least, the isomer observed may be considered to be 2,8-diiododecaborane in equal admixture with its enantiomorph. On the other hand, if the properties of the two expected isomers were quite similar then one could easily have been missed even in the quantitative infrared analysis.

Small amounts of several substances were actually obtained with new bands in their infrared spectra, but these were not characterized further.

Acknowledgments.—Besides those whose names are mentioned in various footnotes, I am indebted to Professor A. W. Laubengayer, Dr. D. J. Mangold and the late Professor G. W. Schaeffer for advice and encouragement.

NIAGARA FALLS, NEW YORK

[16] R. E. Williams and I. Shapiro, *J. Chem. Phys.*, **29**, 677 (1958).

[17] NOTE ADDED IN PROOF.—Since this paper was prepared, additional evidence has been obtained supporting the proposition that the four-fold position is susceptible to electrophilic attack. Iodination by iodine and aluminum chloride, *i.e.*, by $I^{\oplus}$, gave the same ratio of iododecaborane isomers,[18] and reaction of decaborane with deuterium chloride and aluminum chloride gave what is apparently 2,4,5,7,8,10-hexadeuteriodecaborane.[19]

[18] M. Hillman, *J. Inorg. Nucl. Chem.*, in press.

[19] J. A. Dupont and M. F. Hawthorne, THIS JOURNAL, **81**, 4998 (1959).

[CONTRIBUTION FROM THE PROCTER & GAMBLE COMPANY, MIAMI VALLEY LABORATORIES]

Dilute Solution Condensation during Hydrolytic Degradation of Imidophosphates at 60°

BY O. T. QUIMBY, A. NARATH AND F. H. LOHMAN

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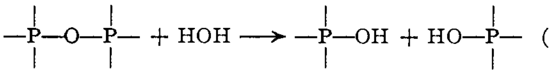
The ultimate product from acid hydrolysis of dilute solutions of these phosphorus-nitrogen compounds, like that of the analogous oxylinked phosphates, is very largely the mono- or orthophosphate. However, during imide degradation appreciable concentrations of new P–O–P links are formed *via* a condensation of the amide intermediates through the elimination of an ammonium ion. Hydrolysis of trimetaphosphimate ion at *p*H 3.5 furnishes a striking example of this condensation for a large part of the phosphorus can be recovered at intermediate stages in the form of diimidotrimetaphosphate, *i.e.*, a ring ion with an oxy link in place of one of the imide links. Imide links are usually less stable than oxy links in acid solutions but attain a comparable or greater stability in sufficiently alkaline solution. Imidotrimetaphosphate behaves exceptionally at *p*H 3.5 where the oxy links break faster than the imide link.

Introduction

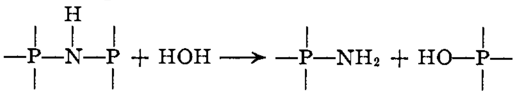
When condensed phosphates (P in the V oxidation state) suffer hydrolytic degradation in dilute aqueous solutions, there is but one over-all reaction involved, namely



$$-\overset{|}{\underset{|}{\text{P}}}-\text{O}-\overset{|}{\underset{|}{\text{P}}}- + \text{HOH} \longrightarrow -\overset{|}{\underset{|}{\text{P}}}-\text{OH} + \text{HO}-\overset{|}{\underset{|}{\text{P}}}- \quad (1)$$

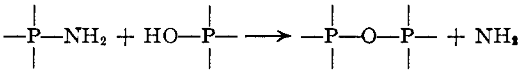
It is essentially irreversible, for if continued long enough, practically all of the phosphorus ends up as orthophosphate. Reaction 1 is reversed if crystalline acid phosphates are heated at 200° or higher.

When imide groups replace the oxy bridge in condensed phosphates, hydrolytic degradation presumably first acts to produce amides[1] as indicated by the equation



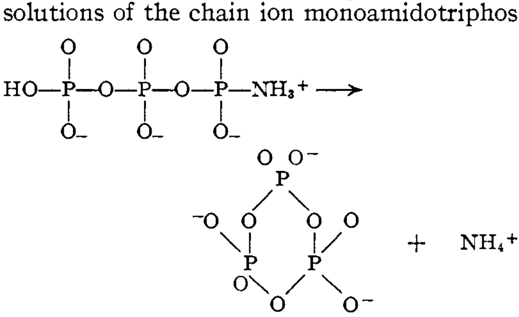
$$-\overset{|}{\underset{|}{\text{P}}}-\overset{\text{H}}{\overset{|}{\text{N}}}-\overset{|}{\underset{|}{\text{P}}} + \text{HOH} \longrightarrow -\overset{|}{\underset{|}{\text{P}}}-\text{NH}_2 + \text{HO}-\overset{|}{\underset{|}{\text{P}}}- \quad (2)$$

In acidic or mildly alkaline solutions this is not the end of the matter, for the amide may yield P–O–P links[2] by elimination of ammonia



$$-\overset{|}{\underset{|}{\text{P}}}-\text{NH}_2 + \text{HO}-\overset{|}{\underset{|}{\text{P}}}- \longrightarrow -\overset{|}{\underset{|}{\text{P}}}-\text{O}-\overset{|}{\underset{|}{\text{P}}}- + \text{NH}_3 \quad (3)$$

A striking example of amide condensation to form new P–O–P links occurs upon acidifidation of solutions of the chain ion monoamidotriphosphate[3]



(4)

At a *p*H of 3–4 amidotriphosphate is quickly and almost completely converted to trimetaphosphate at room temperature. The mild acid hydrolysis of trimetaphosphimate briefly described previously[2]

[1] H. N. Stokes, *Am.Chem. J.*, **18**, 629 (1896).

[2] A. Narath, F. H. Lohman and O. T. Quimby, THIS JOURNAL, **78**, 4493 (1956); the generality of reaction 3 is now well substantiated by other investigators, *e.g.*, V. M. Clark, G. W. Kirby and A. Todd, *J. Chem. Soc.*, 1497 (1957); R. W. Chambers, J. G. Moffatt and H. G. Khorana, THIS JOURNAL, **79**, 4240 (1957).

[3] O. T. Quimby and T. J. Flautt, *Z. anorg. allgem. Chem.*, **296**, 220 (1958).