of triethylamine in 100 ml. of benzene with stirring. The solution was heated slowly to reflux and kept refluxing for 24 hr. After cooling to 20°, the precipitate was removed and recrystallized from 250 ml. of toluene. An amount of 17.0 g. (57%) of pure XXI was collected, m.p. 157–158° (with polymerization).

Anal. Calcd. for $C_{10}H_{23}N_{10}P_3$: C, 31.95; H, 6.12; N, 37.25. Found: C, 32.12; H, 6.89; N, 37.46.

The solvent used in the preparation contained 4.2 g. of a compound which melted and immediately polymerized at 128–130°.

A similar reaction was performed in $CHCl_3$, affording less pure XXII.

2,2,4,4,6-Pentakis(1-aziridinyl)6-methylmercaptocyclotriphosphaza-1,3,5-triene (XXII).—An amount of 2.5 g. of metallic sodium was added in small portions to a solution of 5.2 g. of methanethiol in 100 ml. of methanol at 0–10° with stirring. To the clear solution 38.0 g. of powderized VI was added in small portions. The temperature rose from 24 to 34°. Stirring was continued overnight, then 4.5 g. of a white precipitate (mainly NaCl) was removed by filtration and the filtrate was freed from the solvent. The remaining oil was extracted eight times, each time with 250 ml. of boiling *n*-heptane. After cooling, heptane was decanted and the oily residues were composited by dissolving in ether; 2.5 g. of a white insoluble solid was removed by filtration and the filtrate freed from ether. After vacuum storage for 3 days, the oil had turned into a partially crystallized mass. The oily part of this material was removed by extraction with ether, leaving 8 g. of white crystals undissolved. The latter product was combined with the previously obtained 2.5 g. of ether-insoluble material and recrystallized three times from *n*-heptane, yielding 1.0 g. of XXII in the form of shiny needles, m.p. 106.5–107.5°.

Anal. Calcd. for $C_{11}H_{23}N_8P_3S$: C, 33.7; H, 5.9; N, 28.6; S, 8.16. Found: C, 34.26; H, 6.79; N, 26.99; S, 8.31.

2,2,4,4,6-Pentakis(1-aziridinyl)6-methoxycyclotriphosphaza-1,3,5-triene (XXIII).—A solution of 3.0 g. of $NaOCH_3$ in 20 ml. of methanol was added dropwise with stirring to a slurry of 19 g. of VI in 100 ml. of methanol. The reaction mixture was stirred overnight at 25° and then refluxed for 20 hr. Sodium chloride (2.0 g.) was removed by filtration and the filtrate was concentrated, leaving 20 g. of a white solid which was recrystallized from 20 ml. of toluene, yielding pure XXIII, m.p. 121–123°. After two additional recrystallizations, 6.6 g., m.p. 125–126°, was obtained.

Anal. Calcd. for $C_{11}H_{23}N_8OP_3$: C, 35.1; H, 6.16; N, 29.8; P, 24.7. Found: C, 35.02; H, 6.23; N, 29.5; P, 24.72.

2,2,4,4-Tetrakis(1-aziridinyl)6,6-bis(methoxy)cyclotriphosphaza-1,3,5-triene (XXIV).—To a slurry of 14.4 g. of V in 75 ml. of methanol was added a solution of 5.0 g. of $NaOCH_3$ in 30 ml. of methanol. The temperature increased from 24 to 28° and the PN compound went slowly into solution. After 22 hr. of refluxing, the reaction mixture yielded 3.4 g. of NaCl and 16.0 g. of a white crystalline product. Fractional recrystallization from heptane yielded 3.4 g. of pure XXIV, m.p. 119–120°.

Anal. Calcd. for $C_{10}H_{22}N_7O_2P_3$: C, 32.95; H, 6.03; N, 26.85. Found: C, 33.00; H, 6.08; N, 26.73.

N.m.r. Spectra.—The H^1 spectra were obtained from samples in deuteriochloroform solution by means of a Varian A-60 spectrometer. The chemical shifts were obtained using a Varian Associates 19.3-Mc. V-4311 radiofrequency unit with the suitable adjustment in the magnetic field to enable one to obtain phosphorus resonance spectra. The chemical shifts were measured using the side-band technique with 85% phosphoric acid as the external standard.

The spin-decoupling experiments were done by means of an NMR Specialties heteronuclear decoupler,[12] equipped with modules for irradiating protons while observing the phosphorus spectrum. The reverse procedure was accomplished by using the 60-Mc. V-4311 unit while irradiating nitrogen or phosphorus. In those cases where the phosphorus spectrum was AB_2,[13,14] the chemical shifts and coupling constants were obtained in the manner described.

Acknowledgment.—The authors wish to thank Dr. R. Rittner and Mr. R. Culmo for performing the microanalyses.

[12] NMR Specialties, New Kensington, Pa.

[13] J. D. Roberts, "Analysis of Spin-Spin Splitting in NMR," W. A. Benjamin, Inc., New York, N. Y., 1961, pp. 65–71.

[14] P. L. Corio, *Chem. Rev.*, **60**, 380 (1960).

CONTRIBUTION FROM THE CHEMICALS DIVISION AND THE ORGANICS DIVISION,
OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT

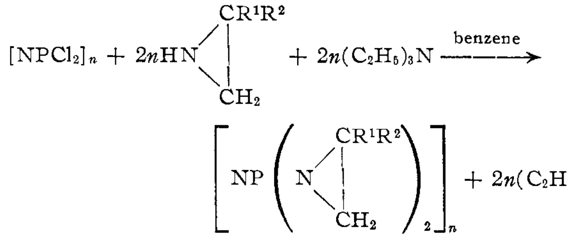
Syntheses and Reactions of 2,2,4,4,6,6-Hexakis(1-aziridinyl)-cyclotriphosphaza-1,3,5-triene and Related Compounds

BY RUDI RÄTZ, EHRENFRIED KOBER, CHRISTOPH GRUNDMANN,[1] AND GERHARD OTTMANN

Received June 4, 1963

Procedures for the synthesis of 2,2,4,4,6,6-hexakis(1-aziridinyl)cyclotriphosphaza-1,3,5-triene (I), 2,2,4,4,6,6,8,8-octakis(1-aziridinyl)cyclotetraphosphaza-1,3,5,7-tetraene (II), and some homologs are described. Compound I forms electron-transfer complexes with transition metal salts such as $AgNO_3$, $CuSO_4$, $ZnCl_2$, and others. A series of novel compounds has been prepared from I, utilizing the susceptibility of the ethylenimine ring to attack by acidic reagents.

The complete aminolysis of cyclic tri- and tetrameric phosphonitrilic chlorides (III and IV, respectively) by means of ethylenimine and some of its homologs had been achieved in our laboratories as early as 1954 using aromatic hydrocarbons as reaction media and triethylamine as acid scavenger.[2]

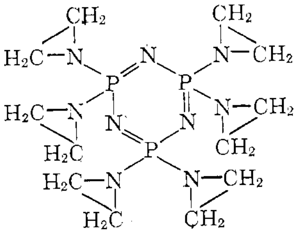


In the case of ethylenimine, 2,2,4,4,6,6-hexakis(1-aziridinyl)cyclotriphosphaza-1,3,5-triene (I) and 2,2,4,4,6,-

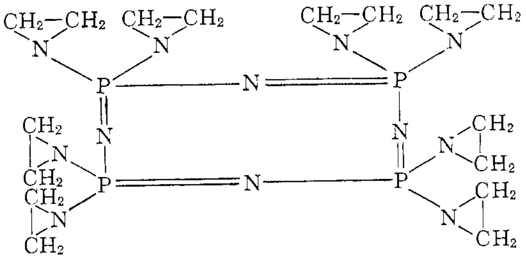
[1] Mellon Institute, Pittsburgh, Pa.

[2] R. F. W. Rätz and C. J. Grundmann, U. S. Patent 2,858,306 (October 28, 1958); R. F. W. Rätz, "A Contribution to the Chemistry of Cyclic Phosphonitrilic Compounds," Gordon Research Conference for Inorganic Chemistry, New Hampton, N. H., Aug., 1960.

6,8,8-octakis(1-aziridinyl)cyclotetraphosphaza-1,3,5,7-tetraene (II)[3] were obtained in high purity when the reaction mixture, after filtration of the precipitated triethylamine hydrochloride, was allowed to stand for several days.



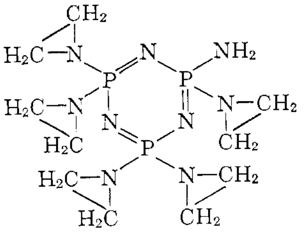
I



II

Compound I has recently attracted much attention, since it was found to be very effective in sterilizing both male and female house flies as well as many other insects. The entomological literature on compound I, tested mainly under the designation "Apholate," is rapidly growing.[4]

Two methods adaptable to large scale synthesis of I have been developed. The first of these methods is characterized by the replacement of the aromatic hydrocarbon by chloroform as solvent and of triethylamine by ammonia as hydrogen chloride acceptor. The progress of the reaction is indicated by separation of the ammonium chloride formed. I stays in solution. 2,2,4,4,6-Pentakis(1-aziridinyl)-6-amidocyclotriphosphaza-1,3,5-triene (V) was isolated as the sole by-product. The biological screening of compound V also revealed a strong radiomimetric activity, comparable with that of I.[5]



V

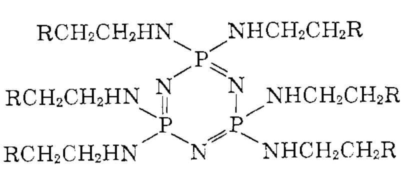
The second method, especially useful for the preparation of large quantities of I, utilizes a heterogeneous system with small amounts of benzene as solvent and aqueous alkali as hydrogen chloride acceptor. It is rather remarkable that these conditions promote the formation of pure I in excellent yields without the formation of appreciable amounts of trimetaphosphimate anion.[6]

The reactivity of compound I is mainly a function of the aziridinyl rings which tend to open easily without affecting the phosphorus–nitrogen ring system. I is a weak base as shown by titration and forms a crystalline picrate.

Hydrogen chloride in chloroform solution opens all six aziridinyl rings of I. 2,2,4,4,6,6-Hexakis(N-β-chloroethylamido)cyclotriphosphaza-1,3,5-triene (VI) is first formed as its hydrochloride; treatment of the salt with aqueous alkali gives the free base VI. Compound VI is stable at ambient temperature over extended periods of time, but forms a transparent resin at elevated temperatures. Attempted reaction of VI with aliphatic amines resulted in its recovery.

Reaction of I with sulfurous acid resulted in the formation of 2,2,4,4,6,6-hexakis(N-β-sulfoethylamido)-cyclotriphosphaza-1,3,5-triene (VII), which is water-soluble; I and hydrogen sulfide gave 2,2,4,4,6,6-hexakis-(N-β-mercaptoethylamido)cyclotriphosphaza-1,3,5-triene (VIII), which is water-insoluble.

Reaction of I with benzenethiol and benzoic acid, respectively, in a mole ratio of 1:6 yielded 2 2,4,4,6,6-hexakis(N-β-thiophenylethylamido)cyclotriphosphaza-1,3,5-triene (IX) and 2,2,4,4,6,6-hexakis(N-β-benzoyloxyethylamido)cyclotriphosphaza-1,3,5-triene (X), respectively, which are ether-soluble, almost colorless oils. Reaction of I with benzenethiol or benzoic acid in a mole ratio higher than 1:6 resulted always in the formation of IX and X, besides unreacted I. The isolation of compounds containing N-β-thiophenylethylamido or N-β-benzoyloxyethylamido groups besides intact aziridinyl rings was not achieved.



VI, R = Cl
VII, R = OSO_2H
VIII, R = SH
IX, R = SC_6H_5
X, R = $\mathrm{O\underset{\underset{O}{\|}}{C}C_6H_5}$

The retention of the cyclotriphosphaza-1,3,5-triene ring in VI, VII, VIII, IX, and X is evident by the presence of the strong infrared absorption in the range 1185–1200 cm.$^{-1}$, which is attributed to P_3N_3 ring vibration.[7] All other absorptions in the infrared spectra are also in full agreement with the postulated structures (Table I).

---

(3) In the cited patent compounds, I and II are named tri- and tetrameric bis(ethylenimido)phosphonitrile. Another possible designation, *e.g.*, for I, is 2,2,4,4,6,6-hexahydro-2,2,4,4,6,6-hexakis(1-aziridinyl)1,3,5,2,4,6-triazatriphosphorine.

(4) (a) For references see G. C. LaBrecque, *J. Econ. Entomology*, **54**, 684 (1961); H. K. Gouck, D. M. Meifert, and J. B. Gahan, *ibid.*, **56**, 445 (1963). (b) The name "Apholate" for compound I was selected by the U. S. Department of Agriculture.

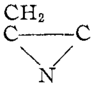
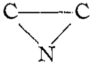
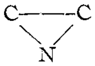
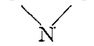
(5) Biological screening results to be published elsewhere.

(6) A comprehensive discussion of this method will be the subject of a separate paper by G. Ottmann, R. Alexander, and E. Kober, to be published elsewhere.

(7) R. A. Shaw, *Chem. Ind.* (London), 54 (1959), and references cited therein.

TABLE I

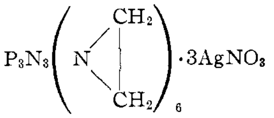
INFRARED SPECTRA[a]; MAIN ABSORPTION PEAKS IN CM.$^{-1}$

Compd. I	Assignment[b]	Compd. V	Assignment[c]	Compd. IX	Assignment[d]	Compd. X	Assignment[d]
3100 3000	CH_2	3420 3300	NH_2–	3410	–NH–	3430	–NH–
				3080	Aromatic =CH	3215	
1435	CH_2	3100 3000	CH_2	2950	CH_2	3100	Aromatic =CH
1260							
		1545	NH_2–	1580 1470	Phenyl ring	2890	CH_2
						1720	C=O
1200	P_3N_3 ring	1480	Not assigned				
1145	Not assigned	1430	CH_2	1430	C_6H_5S–	1600 1490	Phenyl ring
1080	Not assigned	1255		1385	S–CH_2		
				1190	P_3N_3 ring	1445	CH_2
939		1190	P_3N_3 ring	1085	Not assigned	1265	C–O–ester
						1185	P_3N_3 ring
885 850 705	Not assigned	1155	Not assigned	737 688	Phenyl ring	1100 1065 1025 960 782	Not assigned
		1080	Not assigned				
		937					
		870 847 707	Not assigned			708	Phenyl ring

[a] Determined with a Perkin-Elmer Infracord Model 137 on sodium chloride disks. [b] In CCl_4. [c] Smear in Nujol–Fluorolube. Liquid phase smear.

The molecule of I is an electron-rich species. Attachment of aziridinyl groups to the already electron-rich cyclotriphosphazatriene ring gives rise to additional unshared electron pairs. The formation of so-called "electron-transfer complexes" was observed when I was allowed to react with transition metal salts.[8] Silver nitrate, copper sulfate, and zinc, cobalt, and chromium chlorides gave precipitates with I from aqueous solution.

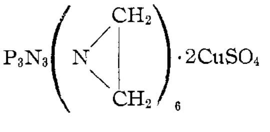
The silver nitrate complex of the composition



$$P_3N_3\left(N\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right)_6\cdot 3AgNO_3$$

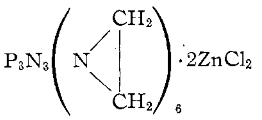
is a crystalline, shining white salt which had turned slightly yellow after 3 hr. storage at room temperature and deep brown after several days. Proof for the retention of the six aziridinyl rings as well as of the six-membered phosphorus–nitrogen ring was obtained by the reaction of an aqueous suspension of the silver salt with the calculated amount of an aqueous solution of sodium sulfide. Separation of the silver sulfide formed, chloroform extraction of the aqueous filtrate, and removal of the chloroform resulted in the recovery of 90% of I, m.p. 154°.

The I–copper sulfate complex is a light blue powder, whereas the I–zinc chloride complex is colorless. Their compositions were found to be



$$P_3N_3\left(N\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right)_6\cdot 2CuSO_4$$

and



$$P_3N_3\left(N\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right)_6\cdot 2ZnCl_2$$

Experimental[9]

The mixture of cyclic $(PNCl_2)_x$ oligomers (Hooker Chemical Corporation) was separated into $(PNCl_2)_3$ (III) and $(PNCl_2)_4$ (IV) by vacuum distillation using a Claisen flask with sausage receiver. Crude III (530 g.), thus obtained, was subjected to recrystallization from acetonitrile (1330 ml.) to give 495 g. of pure III, m.p. 113.5–114.5°.

Preparation of I in Chloroform in the Presence of Ammonia.—Chloroform (800 ml.) in a 5-l., three-necked flask, equipped with a power stirrer, gas inlet tube, and double-jacketed condenser, was saturated with ammonia gas at 0°. The gas inlet tube was then replaced by a 500-ml. dropping funnel. After addition of 136.5 g. of freshly distilled ethylenimine (5% excess over 3 moles), a solution of 174.0 g. of III (0.5 mole) in 500 ml. of chloroform was added dropwise over a period of 2 hr., avoiding contact of the droplets with the flask wall. Cooling was maintained at 5° during and for 4 hr. after the addition. After passing in ammonia at room temperature for 15 min., the mixture was allowed to stand for 3.5 days at room temperature. The calculated amount of 160.5 g. of ammonium chloride was removed by filtration. Evaporation of the chloroform from the clear and colorless filtrate at 40° (14 mm.) gave an almost colorless residue which amounted to 166.5 g. of powdery material after washing with 400 ml. of ether. Two recrystallizations from 1240-ml. portions of carbon tetrachloride resulted in 135 g. (70%) of colorless crystals, m.p. 154° (clear melt). The product was free of chlorine and its infrared spectrum did not show NH_2 absorption.

1,1,3,3,5-Pentakis(1-aziridinyl)5-amidocyclotriphosphaza-1,3,5-triene (V).—Ligroin (20% by volume) was added to the carbon tetrachloride mother liquor. The solution was evaporated to approximately 65% of its original volume and kept at 0° overnight to give hard crusty crystals (17.5 g.), m.p. 132–133° (from dimethylacetamide). The compound was free of chlorine and completely water-soluble.

Anal. Calcd. for $C_{10}H_{22}P_3N_9$: C, 33.25; H, 6.14; N, 34.90; P, 25.72. Found: C, 33.31, 33.69; H, 6.20, 6.25; N, 35.22, 35.31; P, 25.62, 25.55.

The infrared spectrum of this compound (Table I) is in agreement with structure V. The aqueous solution of V formed a white insoluble complex with $AgNO_3$, similar to that of I.

2,2,4,4,6,6,8,8-Octakis(1-aziridinyl)cyclotetraphosphaza-1,3,5,-7-tetraene (II).—A solution of 46.4 g. of IV in 250 ml. of dry ben-

---

[8] T. Moeller and S. G. Kokalis, *J. Inorg. Nucl. Chem.*, **25**, 881 (1963).

[9] All melting points were determined on the plate of a Fisher-Johns block at a heating rate of approximately 6°/min.

zene was added dropwise with stirring to a solution of 50 g. of ethylenimine and 100 g. of triethylamine in 80 ml. of dry benzene. After 24 hr. at 30°, the formed triethylamine hydrochloride was filtered. After cooling to 15°, crystals (II) precipitated which were collected on a Büchner funnel. The filtrate was concentrated to 150 ml. and gave, on standing at room temperature, an additional amount of II; yield 41 g. (79.5%); m.p. 262° (from *n*-heptane). The melting point of this compound can only be determined by using a preheated plate (255°) of a Fisher-Johns apparatus. Starting the melting point determination at room temperature leads to polymerization of the product.

Anal. Calcd. for $C_{16}H_{32}N_{12}P_4$: C, 37.21; H, 6.24; N, 32.55; P, 24.00. Found: C, 36.98; H, 6.48; N, 32.43; P, 24.05.

2,2,4,4,6,6-Hexakis[1-(2-methylaziridinyl)]cyclotriphosphaza-1,3,5-triene.—To a solution of 8 g. of dry triethylamine and 5 g. of 2-methylethylenimine in 50 ml. of dry benzene, a solution of 3.48 g. of III in 20 ml. of benzene was added dropwise with stirring. The slightly exothermic reaction was moderated by keeping the flask in an ice–water bath. Stirring was continued for 3 hr. After standing at room temperature for 24 hr., the almost quantitatively formed triethylamine hydrochloride was removed by filtration. The solvent was distilled from the filtrate and the oily residue was extracted with 30 ml. of cold petroleum ether. Evaporation of the petroleum ether resulted in a clear, almost colorless oil; yield 4.0 g., or 93.3% of theory; $n^{25}\mathrm{D}$ 1.5071. The crude product decomposed on attempted distillation under high vacuum. The analytical values are in fair agreement for 2,2,4,4,6,6-hexakis[1(2-methylaziridinyl)]cyclotriphosphaza-1,3,-5-triene.

Anal. Calcd. for $C_{18}H_{36}N_9P_3$: C, 45.85; H, 7.70; N, 26.74. Found: C, 44.75; H, 8.13; N, 25.26.

2,2,4,4,6,6-Hexakis[1-(2,2-dimethylaziridinyl)]cyclotriphosphaza-1,3,5-triene.—A solution of 3.48 g. of III in 20 ml. of benzene was added dropwise with stirring to a solution of 8 g. of triethylamine and 5.3 g. of 2,2-dimethylethylenimine in 70 ml. of dry benzene. The slightly exothermic reaction was moderated by external cooling with ice–water. After standing for 30 hr., the almost quantitative amount of triethylamine hydrochloride was removed by filtration. The solvent was evaporated *in vacuo* and the oily residue kept at 5 mm. and room temperature for 2 hr. After extraction of the residue with 30 ml. of petroleum ether and removing the solvent under vacuum, a clear oil was obtained. This oil is insoluble in water, but easily soluble in ether, ethanol, and hydrocarbons; yield 4.5 g. or 95% of the theory; $n^{25}\mathrm{D}$ 1.5110. Crystallization could not be induced. Attempted high vacuum distillation resulted in decomposition. Phosphorus and chlorine analysis of the crude material indicate 2,2,4,4,6,6-hexakis[1-(2,2-dimethylaziridinyl)]cyclophosphaza-1,3,5-triene.

Anal. Calcd. for $C_{24}H_{48}N_9P_3$: P, 17.51; Cl, 0.0. Found: P, 16.74; Cl, 0.0.

2,2,4,4,6,6-Hexakis[1-(2-*p*-anisyl)aziridinyl]cyclotriphosphaza-1,3,5-triene.—A solution of 6.3 g. of III in 25 ml. of toluene was added dropwise, with stirring, to a solution of 16.2 g. of 2-anisylaziridine and 11.0 g. of triethylamine in 75 ml. of toluene at 30–35°. The exothermic reaction required cooling. After standing for 15 hr., the triethylamine hydrochloride formed was removed by filtration and the toluene by distillation *in vacuo* at temperatures not exceeding 60°. The remaining oil was extracted with ether and the ether extract dried over NaOH pellets. The ether was removed by distillation and the remaining oil heated *in vacuo* at 100° for 8 hr. to result in 13 g. (yield 70%) of product; a clear, slightly yellow-colored glass-like solid.

Anal. Calcd. for $C_{54}H_{60}N_9P_3O_6$: C, 64.37; H, 5.96; N, 12.51; P, 9.22. Found: C, 62.72; H, 5.84; N, 12.21; P, 9.20.

Electron-Transfer Complexes of I with Transition Metal Salts. (a) **Complex with Silver Nitrate.**—A solution of 5.313 g. of I (m.p. 152–153°) in 20 ml. of water was mixed with a solution of 7.0 g. of silver nitrate in 25 ml. of water. Precipitation of a colorless crystalline precipitate was induced by scratching. The crystals were filtered and washed with 25 ml. of acetone to give 10 g. of shining white salt. After standing for 2 hr. at ambient temperature without light protection, the complex started to turn from slight yellow to ocher and finally to brown (48 hr.). Analysis was obtained for a freshly prepared sample.

Anal. Calcd. for $C_{12}H_{24}N_9P_3 \cdot 3AgNO_3$: C, 16.07; H, 2.70; N, 18.74; P, 10.36. Found: C, 16.60, 16.61; H, 2.50, 2.40; N, 18.91, 18.91; P, 11.00, 11.00.

Recovery of I from Its Silver Complex.—A solution of 4.1 g. of sodium sulfide monohydrate in 20 ml. of water was added dropwise to a suspension of 10 g. of the $I \cdot 3AgNO_3$ complex which had been suspended in 25 ml. of distilled water with shaking and external ice cooling. After addition was complete, the mixture was allowed to stand for 15 min. at room temperature. On filtering, 5.25 g. of silver sulfide was collected; the theoretical amount is 5.10 g. The aqueous filtrate was twice extracted with 50-ml. portions of chloroform; the chloroform extracts were combined and finally dried with a small amount of sodium sulfate. Evaporation of the clear filtrate at reduced pressure resulted in 4.1 g. (76%) of a colorless, crystalline residue, m.p. 154.5° without prior recrystallization. A mixture melting point of the residue with an authentic sample of I and its infrared spectrum demonstrated the identity of both materials.

(b) **Complex with Copper Sulfate.**—The amount of 3.87 g. of I (m.p. 153°, 0.01 mole) was dissolved in 6 ml. of distilled water and mixed with a solution of 7.5 g. of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 30 ml. of water. After standing for 20 min., the mixture formed a solid cake which was broken by addition of 20 ml. of water. The solid was collected on a Büchner funnel and again dispersed in 50-ml. portions of acetone. Vacuum drying over P_4O_{10} resulted in a faint bluish green powder; yield of $I \cdot 2CuSO_4$ 5.3 g. (75%).

Anal. Calcd. for $C_{12}H_{24}N_9P_3 \cdot 2CuSO_4$: N, 17.88. Found: N, 18.11, 18.24.

(c) **Complex with Zinc Chloride.**—Addition of a solution of 3.87 g. of I (m.p. 153°, 0.01 mole) in 15 ml. of water to a solution of 4.1 g. of zinc chloride in 10 ml. of water resulted, after 10 min. at room temperature, in the precipitation of $I \cdot 3ZnCl_2$ in the form of a colorless crystal cake; 5.8 g. (73%) after filtration.

Anal. Calcd. for $C_{12}H_{24}N_9P_3 \cdot 3ZnCl_2$: C, 18.12; H, 3.02; N, 15.83. Found: C, 19.26; H, 4.22; N, 16.49.

Reaction of I with Picric Acid.—The amount of 1 g. of I was dissolved in 10 ml. of ethanol and an excess of an ethanolic solution of picric acid added in one portion. A crystalline, yellow precipitate separated at once, m.p. 234–236° dec.

Anal. Calcd. for $C_{30}H_{33}N_{18}O_{21}P_3$: C, 33.53; H, 3.10; N, 23.46; P, 8.65. Found: C, 33.93; H, 3.21; N, 23.19; P, 8.91.

Ring-Opening Reactions of I. 2,2,4,4,6,6-Hexakis(2-chloroethylamido)cyclotriphosphaza-1,3,5-triene (VI).—A slow stream of hydrogen chloride was passed into a solution of 70.0 g. of I in 400 ml. of chloroform. External cooling with ice–water was required in order to moderate the exothermic reaction. When hydrogen chloride was no longer absorbed, the reaction mixture was purged with nitrogen and the solvent finally removed *in vacuo* at a temperature not exceeding 30°. The completely dry residue (118 g.) was dissolved in water and a 30% aqueous solution of sodium hydroxide was slowly added with external cooling. The oily precipitate was extracted with ether, the extract dried over sodium sulfate, and, after filtration, the solvent was removed from the filtrate by evaporation to dryness. The residue obtained was recrystallized from 120 ml. of benzene. Traces of polymeric material formed during the recrystallization step can be removed by dissolving VI in dry ether and regenerating it by evaporation of the filtered solution *in vacuo;* yield 62 g. (56.5%), m.p. 82–82.5°.

Anal. Calcd. for $C_{12}H_{30}Cl_6N_9P_3$: C, 23.78; H, 4.99; N, 20.80; P, 15.33; Cl, 35.10. Found: C, 24.05; H, 5.04; N, 20.0; P, 15.3; Cl, 35.27.

2,2,4,4,6,6-Hexakis(N-β-sulfoethylamido)cyclophosphaza-1,3,5-triene (VII).—A solution of 1 g. of I in 10 ml. of water was saturated with sulfur dioxide. The exothermic reaction was moderated by external cooling with ice–water. The water was evaporated from the clear solution at reduced pressure. The residue was dried over phosphorus pentoxide to give a transparent, colorless resin. Treatment with diethyl ether or ethanol did not induce crystallization. Structure VII is supported by phosphorus and nitrogen analysis, by its water solubility, and by strong infrared absorption at ~1220 cm.$^{-1}$ which is due to the P_3N_3 ring vibration.[7]

Anal. Calcd. for $C_{12}H_{36}N_9O_{18}P_3S_6$: N, 14.22; P, 10.56. Found: N, 14.11; P, 10.51.

2,2,4,4,6,6-Hexakis(N-β-mercaptoethylamido)cyclotriphosphaza-1,3,5-triene (VIII).—To a solution of 1 g. of I in 25 ml. of absolute ethanol, dry hydrogen sulfide was passed in until a crystalline colorless reaction product began to separate. The mixture was allowed to stand overnight; the solid formed (1.0 g.), m.p. 290° dec., was isolated by filtration. No solvent could be found for recrystallization of these crystals. Phosphorus and nitrogen values as well as the powerful absorption peak in the infrared spectrum at approximately 1220 cm.$^{-1}$ support structure VIII.[7]

Anal. Calcd. for $C_{12}H_{36}N_9P_3S_6$: N, 21.30; P, 15.70. Found: N, 20.99; P, 14.89.

2,2,4,4,6,6-Hexakis(N-β-thiophenylethylamido)cyclotriphosphaza-1,3,5-triene (IX).—A mixture of 3.87 g. of I (m.p. 153°, 0.01 mole) with 6.7 g. of benzenethiol (0.06 mole) was kept at 0° for about 1 hr. until solution was complete. The almost colorless highly viscous liquid reaction product was treated with two portions of 20 ml. of petroleum ether to remove unreacted benzenethiol. Crystallization could not be induced by treatment with various solvents or by refrigeration of a concentrated solution in carbon tetrachloride. Purification was achieved by precipitating the product from its solution in carbon tetrachloride with petroleum ether, dissolving the oil thus obtained in a small amount of ether, and again reprecipitating the oil by addition of petroleum ether. After decantation, the product was kept at 0.1 mm. pressure at 80° for 2 hr. to give a colorless viscous oil, $n^{30}D$ 1.6462.

Anal. Calcd. for $C_{48}H_{60}N_9P_3S_6$: C, 54.99; H, 5.77; N, 12.03; P, 8.86; S, 18.35. Found: C, 55.50; H, 6.50; N, 12.45; P, 8.90.

The infrared spectrum of this compound (Table I) is in agreement with structure IX.

2,2,4,4,6,6-Hexakis(N-β-benzoyloxyethylamido)cyclotriphosphaza-1,3,5-triene (X).—A solution of 3.87 g. of I (m.p. 153°, 0.01 mole) and 7.327 g. of benzoic acid (0.06 mole) in 100 ml. of chloroform was allowed to stand at ambient temperature for 1 week. The solvent was removed by vacuum distillation from the still clear and colorless solution. A highly viscous, colorless oil (12 g., calculated amount 11.2 g.) was obtained as a residue, which did not crystallize on treatment with various solvents or prolonged standing. Purification was attempted by dissolving the product in carbon tetrachloride and washing the solution several times with aqueous sodium bicarbonate. After drying over sodium sulfate, petroleum ether was added to the filtrate to result in precipitation of an oil. Decantation and removal of the adhering solvent at 80° (0.1 mm.) gave a colorless, extremely viscous oil. The infrared spectrum of this compound (Table I) is in agreement with structure X.

CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY,
CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MISSOURI

Exchange Reactions and Nuclear Magnetic Resonance Analysis of Some Organomercury Compounds[1]

BY MARVIN D. RAUSCH[2] AND JOHN R. VAN WAZER

Received November 7, 1963

The equilibrium compositions and reaction kinetics of several exchange reactions involving organomercury systems have been determined by means of proton n.m.r. spectroscopy. In systems involving either dimethylmercury or dibenzylmercury and mercuric chloride, bromide, or iodide, the corresponding organomercuric halide is the only product detectable at equilibrium, indicating a highly nonrandom exchange. The relative rates of reaction of dimethylmercury with mercuric halides in methanol at 36° decrease in the order $HgCl_2 > HgBr_2 > HgI_2$, although the relative rates in dioxane are in the order $HgBr_2 > HgCl_2 > HgI_2$. Dimethylmercury and diphenylmercury undergo an exchange reaction at 150° to produce an essentially random or statistical mixture of these mercurials and methylphenylmercury; disproportionation of the latter unsymmetrical compound at 100° produces the same result. Dibenzylmercury likewise undergoes exchange reactions with dimethylmercury and diphenylmercury on heating, although concomitant decomposition to bibenzyl and metallic mercury does not permit the equilibrium compositions to be ascertained. The proton n.m.r. spectra of a variety of organomercury compounds in solution have been determined, and many of these exhibit spin–spin coupling between Hg^{199} and adjacent protons. Exchange reactions involving bis(perfluoromethyl)mercury and bis(perfluorophenyl)mercury have been studied by means of F^{19} n.m.r.

Introduction

Nuclear magnetic resonance (n.m.r.) spectroscopy has proved to be a highly useful tool for the examination of chemical equilibria, since this technique permits the analysis of various species present without disruption of the conditions required for equilibrium.[3] It was of interest to determine if H^1 and F^{19} n.m.r. could be used to determine chemical equilibria and reaction kinetics in systems involving organomercury compounds. Since only a limited amount of information is presently available concerning the n.m.r. spectra of mercurials, a number of such spectra have been recorded and are examined in this paper.

Experimental

Materials.—Dimethylmercury and dibenzylmercury were obtained from Metallomer Laboratories, and diphenylmercury was obtained from Distillation Products Industries. Bis(perfluoromethyl)mercury and bis(perfluorophenyl)mercury were prepared

---

[1] Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963.

[2] Department of Chemistry, University of Massachusetts, Amherst, Mass.

[3] J. R. Van Wazer, *Am. Scientist*, **50**, 450 (1962).