CONTRIBUTION FROM THE ORGANICS DIVISION, THE CHEMICALS DIVISION, AND THE CENTRAL ANALYTICAL DEPARTMENT
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# (1-Aziridinyl)cyclotriphosphaza-1,3,5-trienes

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Described are (1) $P_3N_3Cl_3$(aziridinyl)$_3$, (2) the complete series $P_3N_3$(aziridinyl)$_{6-n}$(dimethylamino)$_n$, of which only $P_3N_3$(aziridinyl)$_4$(dimethylamino)$_2$ had been synthesized before, and (3) a number of compounds formed by the reaction of pentakis(1-aziridinyl)chlorocyclotriphosphaza-1,3,5-trienes with nucleophilic reagents. Evidence was obtained for the substitution pattern of these and related compounds by n.m.r.

2,2,4,4,6,6-Hexakis(1-aziridinyl)cyclotriphosphaza-1,3,5-triene (I) was synthesized as early as 1954 in our laboratories.[1] Recently, Clapp and co-workers described the preparation of some (1-aziridinyl)chlorophosphonitriles (II, III, V, and VI) from $(PNCl_2)_3$ and ethylenimine and established a geminal substitution pattern for the formation of the bis and tetrakis derivatives (III, V) by n.m.r. spectra on the $P^{31}$ nucleus.[2]

The formation of substantial amounts of unidentified oily or waxy by-products in the preparation of III and V from $(PNCl_2)_3$ and ethylenimine suggested the possibility that isomers of III and V were formed by a nongeminal substitution pattern.[3] Attempts to isolate any defined compound from these oils failed because of the complexity of the mixtures. In order to simplify the composition of the reaction mixtures, we allowed compounds II, III, and V, respectively, to react with only one mole of ethylenimine in the presence of triethylamine. This stepwise approach resulted in the preparation of the unknown 2,2,4-tris(1-aziridinyl)-4,6,6-trichlorocyclotriphosphaza-1,3,5-triene (IV) from III and in the conversion of II, IV, and V to their next higher homologs. Compound IV was finally also synthesized from $(PNCl_2)_3$ and ethylenimine (in the presence of triethylamine) in a 1:3 molar ratio. Besides IV, a second compound, m.p. 172°, was isolated which also has the composition of a tris(1-aziridinyl)trichlorocyclotriphosphaza-1,3,5-triene and which forms a tris-(1-aziridinyl)tris(dimethylamino)cyclotriphosphaza-1,3,5-triene, m.p. 178.5–180°, upon its reaction with dimethylamine. The structures of both compounds have not been elucidated yet.

Reaction of compounds II, III, IV, V, and VI, respectively, with dimethylamine resulted, in each case, in complete substitution of the chlorine atoms to give compounds VII, VIII, IX, X, and XI, of which only X has been reported.[2] Stepwise aminolysis of III gave 2,2-bis(1-aziridinyl)4,6-bis(dimethylamino)4,6-dichlorocyclotriphosphaza-1,3,5-triene (XII), which was also obtained[2] by allowing 2,4-bis(dimethylamino)-2,4,6,6-tetrachlorocyclotriphosphaza-1,3,5-triene (XIII) to react with ethylenimine.

A surprising unreactivity of the remaining two chlorine atoms in XVI toward ethylenimine was similarly experienced in attempts to synthesize isomers of compounds VIII and IX. Thus, the reaction of 2,4,6-trichloro-2,4,6-tris(dimethylamino)cyclotriphosphaza-1,3,5-triene (XIV) with excess ethylenimine resulted in the replacement of only one chlorine atom to give 2-(1-aziridinyl)2,4,6-tris(dimethylamino)4,6-dichlorocyclotriphosphaza-1,3,5-triene (XVI), while 2,4-dichloro-2,4,6,6-tetrakis(dimethylamino)cyclotriphosphaza-1,3,5-triene (XV) did not react at all, despite rather drastic reaction conditions in both cases. Surprisingly, the remaining two chlorine atoms of compounds XII and XVI could be substituted for aziridinyl groups when the crude reaction mixtures of XII and XVI were freed from solvent, triethylamine hydrochloride, excessive ethylenimine, and triethylamine and then heated with fresh reagents. Within a few hours, the calculated amounts of triethylamine hydrochloride had formed, indicating complete substitution. 2,2,4,6-Tetrakis-(1-aziridinyl)4,6-bis(dimethylamino)cyclotriphosphaza-1,3,5-triene (XVII) (an isomer of X) and 2,4,6-tris(1-aziridinyl)2,4,6-tris(dimethylamino)cyclotriphosphaza-1,3,5-triene (XVIII) (an isomer of IX) were isolated from the reaction mixtures. While the difficulty in substituting the last two halogens in XII, XVI, and XV might be partly explained by low nucleophilic strength of ethylenimine, we have no plausible explanation for the repeatedly observed promoting effect of fresh reactants on the progress of the reaction.

Compound VI is the first pentakis-substituted derivative of $(PNCl_2)_3$ reported.[2] However, the difficulties encountered in substituting the last two chlorines in XII, XVI, and XV by ethylenimine, as well as the fact that both halogens were substituted if reaction occurred, commanded further investigations to prove the existence of 2,2,4,4,6-pentakis(1-aziridinyl)6-chlorocyclotriphosphaza-1,3,5-triene (VI). First evidence for the structure of VI was already obtained by the reaction of VI with dimethylamine which formed compound XI. Additional evidence was furnished by the reactions of VI with other nucleophilic reagents. Pure

(1) R. Rätz and C. Grundmann, U. S. Patent 2,858,306 (Oct. 28, 1958); see also R. Rätz, E. Kober, C. Grundmann, and G. Ottmann, *Inorg. Chem.*, **3**, 757 (1964).

(2) Y. Kobayashi, L. A. Chasin, and L. B. Clapp, *ibid.*, **2**, 212 (1963).

(3) Russian investigators[4] reported melting points for three isomers of V which would be compatible with geminal and nongeminal substituted products. The Russian workers, however, neither identified the three isomers nor gave experimental details or analyses.

(4) A. A. Kropacheva and L. E. Mukhina, *Zh. Obshch. Khim.*, **31**, 2437 (1961).

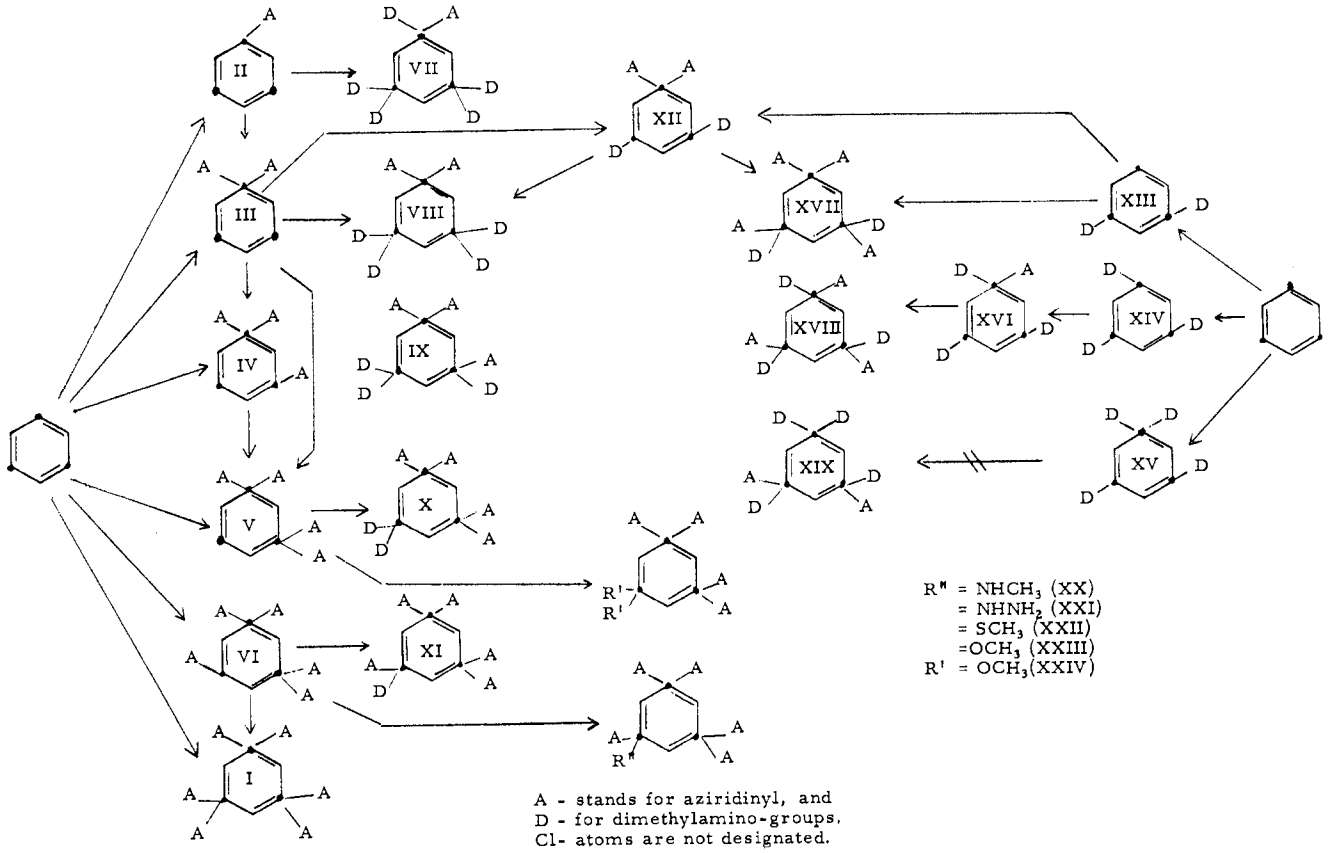


Fig. 1.—Aminolysis of $(PNCl_2)_3$ by aziridine, aziridine–dimethylamine, and dimethylamine–aziridine.

2,2,4,4,6-pentakis(1-aziridinyl)6-methylaminocyclotriphosphaza-1,3,5-triene (XX) and 2,2,4,4,6-pentakis(1-aziridinyl)6-hydrazinocyclotriphosphaza-1,3,5-triene (XXI) were obtained in yields of 61 and 57% from VI and methylamine and hydrazine, respectively. Considerable difficulties were encountered in the preparation of 2,2,4,4,6-pentakis(1-aziridinyl)6-methylmercaptocyclotriphosphaza-1,3,5-triene (XXII), which was finally obtained from VI and sodium methylthiolate in a very poor yield and unsatisfactory purity. In contrast, none of these difficulties was experienced in the corresponding methoxy series. Thus, pure 2,2,4,4,6-pentakis(1-aziridinyl)6-methoxycyclotriphosphaza-1,3,5-triene (XXIII) and 2,2,4,4-tetrakis(1-aziridinyl)6,6-bis(methoxy)cyclotriphosphaza-1,3,5-triene (XXIV) were synthesized by treating VI and V, respectively, with one and two moles, respectively, of sodium methoxide.

In Fig. 1 we have indicated by arrows the routes by which the compounds presented in this work were synthesized. Final conclusive evidence for the position of their substituents and, thereby, for the substitution pattern shown in Fig. 1 was established by n.m.r. spectroscopy.

Most of the compounds described in this article possess potent insect sterilizing and other attractive biological properties. The discussion of these results will be published elsewhere.

The study of cyclotriphosphaza-1,3,5-trienes by $P^{31}$ and $H^1$ n.m.r. spectroscopy[2,5-8] has received some attention with respect to the substitution scheme of amines with various cyclotriphosphaza-1,3,5-trienes. In this paper we are reporting the proton–phosphorus coupling constants of these various cyclotriphosphaza-1,3,5-trienes as well as the phosphorus and proton data of the new pentakis(1-aziridinyl)cyclotriphosphaza-triene derivatives. In addition, a technique is described in which $P^{31}$ chemical shift data might be obtained from the spectrum. This involves the irradiation of the proton while viewing the $P^{31}$ spectrum, and as indicated in Fig. 2 the assignment of the $P^{31}$ chemical shifts might be easily obtained. Since the spectrum does not appear to be first order, the chemical shifts for the phosphorus atoms are line 3 and the mean of lines 5 + 7.

(1-Aziridinyl)pentachlorocyclotriphosphaza-1,3,5-triene (II) has a proton spectrum consisting of a doublet centered at 142 c.p.s. from tetramethylsilane with a phosphorus–proton coupling of 22 c.p.s. (Table I).

The proton decoupled phosphorus resonance spectrum (Fig. 2) yielded a characteristic $AB_2$ spectrum,[9] from which the chemical shifts were obtained. The bis(1-aziridinyl)tetrachlorocyclotriphosphaza-1,3,5-tri-

(5) M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. allgem Chem.*, **302**, 103 (1959).

(6) K. John, T. Moeller, and L. F. Audrieth, *J. Am. Chem. Soc.*, **82**, 5616 (1960).

(7) S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 872 (1961).

(8) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 249 (1962), and pertinent references cited therein.

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 123–128.

ene (III) proton spectrum consisted of a doublet centered at 133 c.p.s. with a coupling constant of 17.5 c.p.s. It is interesting to note that the $J_{P-H}$ decreased as the phosphorus atom was disubstituted. The coupling constant for hexakis(1-aziridinyl)cyclotriphosphaza-1,3,5-triene is 16 c.p.s. The proton chemical shifts and the coupling constants for IV, V, and VI are shown in Table I.

TABLE I

PROTON CHEMICAL SHIFTS OF (1-AZIRIDINYL)CHLOROCYCLOTRIPHOSPHAZA-1,3,5-TRIENES RELATIVE TO TMS IN C.P.S.

| | | $\delta$ | | | $J_{P-H}$ |
|---|---|---|---|---|---|
| II | $(PN)_3Cl_5(NC_2H_4)$ | 142 | | | 22 |
| III | $(PN)_3Cl_4(NC_2H_4)_2$ | 133 | | | 17.5 |
| IV | $(PN)_3Cl_3(NC_2H_4)_3$ | 136 | 132 | 129 | 22.0, 18.0, 17.5 |
| V | $(PN)_3Cl_2(NC_2H_4)_4$ | | 128 | | 18.0 |
| VI | $(PN)_3Cl(NC_2H_4)_5$ | 133 | 128 | | 22, 17.5 |
| I | $(PN)_3(NC_2H_4)_6$ | | 125 | | 16 |

The proton spectrum of pentakis(1-aziridinyl)chlorocyclotriphosphaza-1,3,5-triene (VI) consisted of two overlapping doublets with an intensity ratio of 4:1, the high-field doublet being due to the pairwise substituted phosphorus atoms. A feature of the phosphorus spectrum was the chemical shift of the phosphorus atom containing the chlorine, the resonance occurring at −42.0 p.p.m., while the other phosphorus resonance was at 37.0 p.p.m. The electron density about the chlorine–aziridinyl substituted phosphorus atom has decreased, and, although this is qualitatively attributed to changes in the p-bonding of the phosphorus, the reason for the anomaly is not obvious from the data. Quite possibly steric effects may cause changes in resonance contributions, bringing about a chlorine with more negative character. This is unique for VI because the $P^{31}$ spectra of the other pentakis(1-aziridinyl) derivatives (Table II) do not exhibit this phenomenon. The proton and phosphorus chemical shifts of various pentakis(1-aziridinyl)cyclotriphosphazatriene derivatives are compiled in Table II.

TABLE II

PROTON CHEMICAL SHIFTS OF THE PENTAKIS(1-AZIRIDINYL)-CYCLOTRIPHOSPHAZATRIENE DERIVATIVES (C.P.S.)

| | | $\delta$ $NHCH_3$ | $\delta$ $(NC_2H_4)$ | $J_{P-H}$ $NHCH_3$ | $J_{P-H}$ $(NC_2H_4)$ |
|---|---|---|---|---|---|
| XX | $(PN)_3(NC_2H_4)_5NHCH_3$ | 152 | 124, 122, 118 | 13 | 16 |
| | | $OCH_3$ | | $OCH_3$ | |
| XXIII | $(PN)_3(NC_2H_4)_5OCH_3$ | 224 | 125, 122 | 11 | 16 |
| XXI | $(PN)_3(NC_2H_4)_5NHNH_2$ | | 124, 122 | | 16 |
| | | $OCH_3$ | | | |
| XXIV | $(PN)_3(NC_2H_4)_4(OCH_3)_2$ | 218 | 124 | 12 | 16.5 |

| | | Phosphorus Chemical Shifts (p.p.m.) | | |
|---|---|---|---|---|
| | | $P(NC_2H_4)_2$ | $P(NC_2H_4)X$ | $PX_2$ |
| XX | $(PN)_3(NC_2H_4)_5NHCH_3$ | 37.3 | 29.7 | ... |
| XXIII | $(PN)_3(NC_2H_4)_5OCH_3$ | 38.2 | 29.6 | ... |
| XXI | $(PN)_3(NC_2H_4)_5NHNH_2$ | 37.6 | 30.6 | ... |
| XXIV | $(PN)_3(NC_2H_4)_4(OCH_3)_2$ | 38.0 | ... | 20.1 |

The proton resonance spectral data for various (1-aziridinyl)dimethylaminocyclotriphosphaza-1,3,5-trienes and two (1-aziridinyl)dimethylaminocyclotriphosphaza-1,3,5-trienes are shown in Tables III and IV.

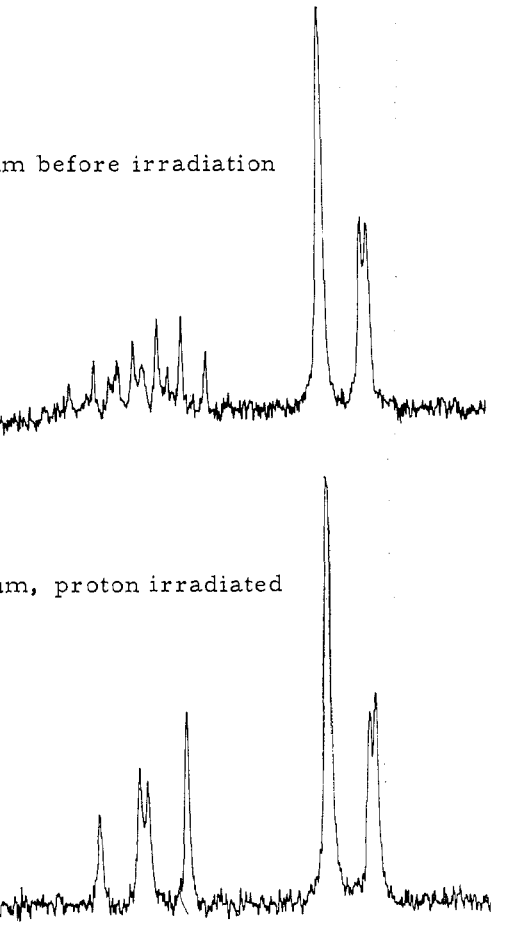


Fig. 2.—Decoupled n.m.r. spectrum of 2-(1-aziridinyl)2,4,4,6,6-pentachlorocyclotriphosphaza-1,3,5-triene.

TABLE III

PROTON CHEMICAL SHIFTS OF (1-AZIRIDINYL)DIMETHYLAMINOCYCLOTRIPHOSPHAZA-1,3,5-TRIENES RELATIVE TO TMS IN C.P.S.[a]

| | | $\delta$ $N(CH_3)_2$ | $\delta$ $NC_2H_4$ | $J_{P-H}$[b] $N(CH_3)_2$ | $J_{P-H}$ $NC_2H_4$ |
|---|---|---|---|---|---|
| XI | $(PN)_3(NC_2H_4)_5N(CH_3)_2$ | 161 | 122, 116 | 10 | 17.5 |
| XVII | $(PN)_3(NC_2H_4)_4[N(CH_3)_2]_2$ | 160.5 | 122, 114 | 11 | 17, 18 |
| X | $(PN)_3(NC_2H_4)_4[N(CH_3)_2]_2$ | 165 | 122 ... | 11 | 17 |
| XVIII | $(PN)_3(NC_2H_4)_3[N(CH_3)_2]_3$ | 161 | ... 114 | 11 | 17.5 |
| VIII | $(PN)_3(NC_2H_4)_2[N(CH_3)_2]_4$ | 156 | 122 ... | 9.5 | 17.5 |
| VII | $(PN)_3NC_2H_4[N(CH_3)_2]_5$ | 162, 157 | ... 114 | 11 9.5 | 17.0 |
| | | 156 | | 9.5 | |

[a] Midpoint of the doublets in cycles per second. [b] One coupling constant is reported if they are identical for each doublet.

TABLE IV

PROTON CHEMICAL SHIFTS OF (1-AZIRIDINYL)DIMETHYLAMINOCHLOROCYCLOTRIPHOSPHAZA-1,3,5-TRIENES RELATIVE TO TMS IN C.P.S.

| | | $\delta$ $N(CH_3)_2$ | $\delta$ $NC_2H_4$ | $J_{P-H}$ | |
|---|---|---|---|---|---|
| XII | $(PN)_3(NC_2H_4)_2Cl_2[N(CH_3)_2]_2$ | 158 | 128 | 13.5 | 17.5 |
| XVI | $(PN)_3(NC_2H_4)Cl_2[N(CH_3)_2]_3$ | 159 | 128[a] | | |

[a] Unresolved broad resonance line.

An indication of some differences in the relative geometry of the substituents is noted in asymmetric molecules with odd number of substituents, *e.g.*, for 2-(1-aziridinyl)2,4,4,6,6-pentakis(dimethylamino)cyclotriphosphaza-1,3,5-triene (VII), the proton spectrum exhibits three doublets. Although the differences are *ca.*

1.0 c.p.s., this is attributed to differences in the relative geometry of the dimethylamino groups. The phosphorus coupling constants in a system combining alternating nitrogen and phosphorus atoms is in the range of 30–40 c.p.s. Another feature of the proton spectrum is the appearance of a broad peak which seemed to indicate some secondary coupling. The phosphorus irradiated proton spectrum demonstrated this might be the case. Small coupling exists with the other phosphorus atoms and was not, as originally assumed, due to nitrogen coupling.[10]

## Experimental[11]

**2,2,4-Tris(1-aziridinyl)4,6,6-trichlorocyclotriphosphaza-1,3,5-triene (IV).** (a) **From $(PNCl_2)_3$.**—A solution of 12.9 g. (0.3 mole) of aziridine and 30.3 g. (0.3 mole) of triethylamine in 250 ml. of toluene was added dropwise over a period of 4 hr. to a stirred solution of 34.8 g. (0.1 mole) of $(PNCl_2)_3$ in 500 ml. of toluene at a temperature of 5–10°. After an additional 3 hr. of stirring at 20–25°, the mixture was filtered and 39.9 g. (0.29 mole) of triethylamine hydrochloride was collected. The filtrate was slowly concentrated *in vacuo* at 35° to approximately 10% of its original volume. After several days crystallization started at room temperature, and it was allowed to continue for 2 weeks. The semisolid product was placed on a porous plate to facilitate the removal of the oily portion. The remaining crystals (12.1 g.) were recrystallized from pentane and $CCl_4$ with the aid of some charcoal; yield 5.51 g. (15%) of IV, m.p. 68–70°.

*Anal.* Calcd. for $C_6H_{12}Cl_3N_6P_3$: C, 19.7; H, 3.3; Cl, 29.0; N, 22.9. Found: C, 20.1; H, 3.7; Cl, 28.5; N, 23.1.

(b) **From III.**—A solution of 4.3 g. (0.1 mole) of aziridine and 10.1 g. (0.1 mole) of triethylamine in 50 ml. of benzene was added dropwise to a stirred solution of 36.1 g. (0.1 mole) of III in 250 ml. of benzene. Thereby, the reaction temperature rose from 24 to 27° and was then cooled to and maintained at 25° for 16 hr. Triethylamine hydrochloride (13.9 g., 0.102 mole) was removed by filtration and the filtrate was freed from solvent. The remaining viscous oil was dissolved in 15 ml. of hot $CCl_4$. Upon standing, 12 g. of waxy crystals had precipitated. Recrystallization from *n*-hexane and $CCl_4$ afforded 4.1 g. of IV, m.p. 69–70°.

*Anal.* Calcd. for $C_6H_{12}Cl_3N_6P_3$: C, 19.7; H, 3.3; Cl, 29.0; N, 22.9; P, 25.3. Found: C, 19.25; H, 3.45; Cl, 29.21; N, 23.74; P, 24.7.

**2,2-Bis(1-aziridinyl)4,4,6,6-tetrachlorocyclotriphosphaza-1,3,5-triene (III) from II.**—Amounts of 7.7 g. of II, 0.9 g. of aziridine, and 2.0 g. of triethylamine were allowed to react under conditions similar to those of the previous experiment, yielding 3.9 g. of III, m.p. 104–105°.

**2,2,4,4-Tetrakis(1-aziridinyl)6,6-dichlorocyclotriphosphaza-1,3,5-triene (V) from IV.**—A 1.98-g. (39%) yield of V, m.p. 130–131°, was obtained from the reaction of 5.0 g. of IV, 0.59 g. of aziridine, and 1.4 g. of triethylamine in toluene under conditions described for the preparation of III and IV. V was recrystallized from $CCl_4$.

**2-(1-Aziridinyl)2,4,4,6,6-pentakis(dimethylamino)cyclotriphosphaza-1,3,5-triene (VII).**—An amount of 15.3 g. of II was dissolved in 100 ml. of benzene and a solution of 19.4 g. of dimethylamine in 50 ml. of benzene was added over a period of 75 min. at 20–25°. After standing for 3 days at room temperature and for 15 hr. at 50–55°, dimethylamine hydrochloride (17.2 g.) was collected. An amount of 16 g. of reaction product remained after the removal of benzene *in vacuo* at room temperature. The waxy residue was recrystallized from 12 ml. of hexane and the precipitate was dried on a porous plate. Vacuum sublimation (90–100° bath temperature) and one final recrystallization from dimethylformamide rendered 3.7 g. of the pure compound, m.p. 80–80.5°.

*Anal.* Calcd. for $C_{12}H_{34}N_9P_3$: C, 36.3; H, 8.6; N, 31.8. Found: C, 36.08; H, 8.0; N, 32.2.

**2,2-Bis(1-aziridinyl)4,4,6,6-tetrakis(dimethylamino)cyclotriphosphaza-1,3,5-triene (VIII).**—A solution of 18 g. of anhydrous dimethylamine in 300 ml. of ether was added dropwise to a solution of 25 g. of III (m.p. 105–106°) in 200 ml. of ether over a period of 30 min. at a temperature of 5 to 10°. After the addition was completed, the ice bath was removed and stirring continued for an additional 4 hr. Dimethylamine hydrochloride (11.7 g.) was filtered off and the filtrate freed from ether. The residue was dissolved in 200 ml. of benzene and 28 g. of dimethylamine was added. This mixture was heated in an autoclave for 3 hr. at 80°. An additional amount of 10.2 g. of dimethylamine hydrochloride was separated and the solution was concentrated to dryness. The residue (26.6 g. of crude product) was recrystallized threefold from 35 ml., 30 ml., and 25 ml. of *n*-hexane; yield 9.2 g. of pure VIII, m.p. 93°.

*Anal.* Calcd. for $C_{12}H_{32}N_9P_3$: C, 36.5; H, 6.52; N, 31.9; Cl, 0. Found: C, 36.31; H, 6.52; N, 31.89; Cl, 0.09.

**2,2,4,4,6-Pentakis(1-aziridinyl)6-dimethylaminocyclotriphosphaza-1,3,5-triene (XI).**—To a solution of 5.6 g. of VI in 100 ml. of benzene was added a solution consisting of 1.2 g. of dimethylamine, 4.0 g. of triethylamine, and 25 ml. of benzene within 10 min. Precipitation began 15 min. after addition and continued slowly during the next 24 hr. Only 55% of the triethylamine hydrochloride expected had separated, while the other 45% remained in solution. After 6 days of standing, the reaction mixture was worked up similarly to the procedures given in the other examples. The final purification–recrystallization from *n*-heptane rendered 2.9 g. (51.5%) of pure XI, m.p. 116.5–117.5°.

*Anal.* Calcd. for $C_{12}H_{28}N_9P_3$: C, 37.1; H, 6.74; N, 32.4. Found: C, 37.22; H, 6.45; N, 32.09.

**2,4,6-Tris-(1-aziridinyl)2,4,6-tris(dimethylamino)cyclotriphosphaza-1,3,5-triene (XVIII).**—A solution of 18.7 g. of 2,4,6-tris(dimethylamino)2,4,6-trichlorocyclotriphosphaza-1,3,5-triene[5] in 50 ml. of toluene was added dropwise, with stirring, to a solution of 9.7 g. of aziridine and 22.75 g. of triethylamine in 100 ml. of toluene. The reaction is exothermic, causing a temperature increase from 25 to 38°. After stirring at room temperature for 18 hr., an amount of 8.3 g. of triethylamine hydrochloride was removed by filtration. The filtrate was concentrated *in vacuo* until no toluene or triethylamine was left. The oily residue was treated with fresh aziridine (9.7 g.), triethylamine (22.75 g.), and toluene (150 ml.) for 2 hr. at 50–55°. An additional amount of 13.5 g. of triethylamine hydrochloride had formed and was removed by filtration. Upon concentration *in vacuo* the filtrate yielded an oil which crystallized to about 50% after several days. After removing the oily part by means of a porous plate, 8.35 g. of crystalline material was attained. Two crystallizations from *n*-pentane (35 ml.) afforded 5.5 g. of XVIII, m.p. 83–84°.

*Anal.* Calcd. for $C_{12}H_{30}N_9P_3$: C, 36.65; H, 7.65; N, 32.1. Found: C, 35.68; H, 7.92; N, 32.08.

**2,2,4,4,6-Pentakis(1-aziridinyl)6-methylaminocyclotriphosphaza-1,3,5-triene (XX).**—A solution of 4.5 g. of methylamine in 50 ml. of chloroform was added with stirring to a solution of 25 g. of VI in 75 ml. of $CHCl_3$. The slow precipitation of methylamine hydrochloride was completed after 48 hr.; 4.2 g. of the hydrochloride was removed by filtration. The residue left upon solvent removal was recrystallized from 100 ml. of $CCl_4$ and twice from 500 ml. of *n*-heptane; yield 15.1 g. (61% of the theory) of XX, m.p. 128–129.5°.

*Anal.* Calcd. for $C_{11}H_{24}N_9P_3$: C, 35.2; H, 6.45; N, 33.6. Found: C, 35.26; H, 6.85; N, 33.55.

**2,2,4,4,6-Pentakis(1-aziridinyl)6-hydrazinocyclotriphosphaza-1,3,5-triene (XXI).**—A solution of 30.2 g. of VI in 400 ml. of benzene was added to 3.2 g. of anhydrous hydrazine and 8.5 g.

(10) Since the same phenomenon is seen in the 2,2,4,4,6,6-hexakis(1-aziridinyl)cyclotriphosphazatriene, the interpretation due to secondary $P^{31}$ coupling is unsatisfactory in this case. The data suggest either polymer formation or the possibility of isomers being present in the material.

(11) Melting points were determined in a modified Thiele apparatus and are not corrected.

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).

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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

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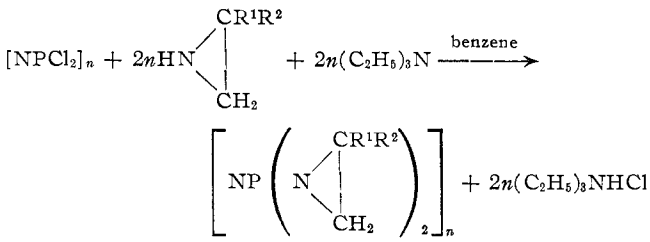
Procedures for the synthesis of 2,2,4,4,6,6-hexakis(1-aziridinyl)cyclotriphosphaza-1,3,5-triene (I), 2,2,4,4,6,6,8,8-octakis(1-aziridinyl)cyclotetraphosphaza-1,3,5,7-tetraene (II), and some homologs are described. Compound I forms electron-transfer complexes with transition metal salts such as $AgNO_3$, $CuSO_4$, $ZnCl_2$, 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]

(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.




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,-