mediate, it redistributes rapidly to $(C_2H_5)_2Mg$ and MgH_2.

It was observed that when the ratio of $(C_2H_5)_2Mg$:AlH_3 exceeds 1:1.5, a precipitate of $Mg(AlH_4)_2$ forms immediately. It would appear then that any $HMgAlH_4$ formed at the 3:5 ratio ($(C_2H_5)_2Mg$:AlH_3) quickly redistributes in a way represented by eq 24 or 25.

$$2HMgAlH_4 \longrightarrow MgH_2 + Mg(AlH_4)_2 \qquad (24)$$

$$3HMgAlH_4 + 2(C_2H_5)_3Al \longrightarrow Mg(AlH_4)_2 + HMgAl(C_2H_5)_2H_2 + (C_2H_5)_3Al \qquad (25)$$

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Notes

CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY,
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Preparation of Cyclo-1,3,5-tri-μ-dimethylamino-2,4-bis(dimethylalumino)-6-dihydridoborane[1]

BY R. E. HALL AND E. P. SCHRAM*

Received March 30, 1970

The chemistry of $B_3Al_3[N(CH_3)_2]_7H_5$ is under investigation including alkylation by aluminum trimethyl, $[Al(CH_3)_3]_2$.[2,3] In order to understand the results associated with this complicated reaction, it proved necessary to investigate the reaction of $[Al(CH_3)_3]_2$ with dimethylaminoborane, $[(CH_3)_2NBH_2]_2$, and bis (dimethylaminoborane), $[(CH_3)_2N]_2BH$. This latter reaction is reported herein, and the former will be reported in the near future.

Preparation and Characterization of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.—Treatment of $[Al(CH_3)_3]_2$ with excess $HB[N(CH_3)_2]_2$ results in the formation of a white crystalline solid which readily sublimes at 50° *in vacuo*. This material is very soluble in pentane and benzene and inflames upon exposure to the atmosphere. The analytical data, summarized in Table I, are consistent with the formulation $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$, in which the nine total valencies of boron plus aluminum are satisfied by the total sum of H, CH_3, and $N(CH_3)_2$ moieties. The hydrolysis of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$ is summarized by

TABLE I
ANALYTICAL DATA FOR $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$

	% Al	% B	% $N(CH_3)_2$	% CH_3 (hydrolyzable)	% hydride	Mol wt
Calcd	20.82	4.17	51.02	23.1	0.77	259.1
Found	20.15	4.11	51.17	23.9	0.75	224

$$Al_2B[N(CH_3)_2]_3(CH_3)_4H_2 + 9H_2O \longrightarrow 2Al(OH)_3 + B(OH)_3 + 3HN(CH_3)_2 + 4CH_4 + 2H_2 \qquad (1)$$

Nuclear Magnetic Resonance Studies.—The ^1H nmr spectrum of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$ (500-cps sweep width), Figure 1A, consists of three singlets at +0.79, −2.28, and −2.39 ppm from TMS in the area ratios 2:2:1. The high-field peak, +0.79 ppm, is assigned to terminal methyl groups bonded to aluminum as in $[(CH_3)_2AlN(CH_3)_2]_2$, δ +0.56 ppm.[4] The fact that the +0.79-ppm absorption is sharp and not temperature dependent, in the range +30 to −61°, indicates these methyl groups are equivalent. The field position of the other absorptions, −2.28 and −2.39 ppm, indicate resonances due to $N(CH_3)_2$ groups bonded to boron or aluminum in two slightly different environments in the ratio 2:1. Expansion of this region of the nmr spectrum (250-cps sweep width), Figure 1B, clearly indicates these same two singlets. A proton signal, associated with the BH_2 moiety, is not expected to be observable because of splitting by B, $I = {}^3/_2$, and quadrupole broadening.

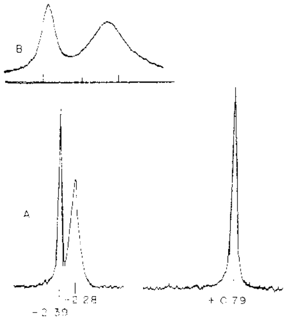

Figure 1.—The ^1H nmr spectrum of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.

The B^{11} nmr spectrum, Figure 2, is a well-defined 1:2:1 triplet, with J_{BH} = 108 ± 3 cps, centered at +17.7 ppm from $B(OCH_3)_3$ (−0.4 ppm from $BF_3 \cdot O(C_2H_5)_2$). The ratio of the absorptions indicates the presence of two equivalent terminal hydrogens bonded to B, while the field position indicates four-coordinate boron, *e.g.*, as in $[H_2BN(CH_3)_2]_2$, δ −4.6 ppm from $BF_3 \cdot O(C_2H_5)_2$, J_{BH} = 116 cps.[5]

Infrared Assignments.—The solid-state infrared spec-

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* To whom correspondence should be addressed.

(1) Work carried out by R. E. Hall for partial fulfillment of the Ph.D. degree, The Ohio State University, 1969.

(2) R. E. Hall and E. P. Schram, *Inorg. Chem.*, **8**, 270 (1969).

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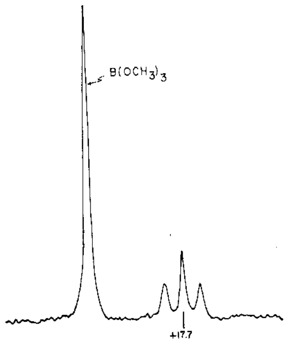

Figure 2.—The ^{11}B nmr spectrum of $Al_2B[(CH_3)_2]_3(CH_3)_4H_2$.

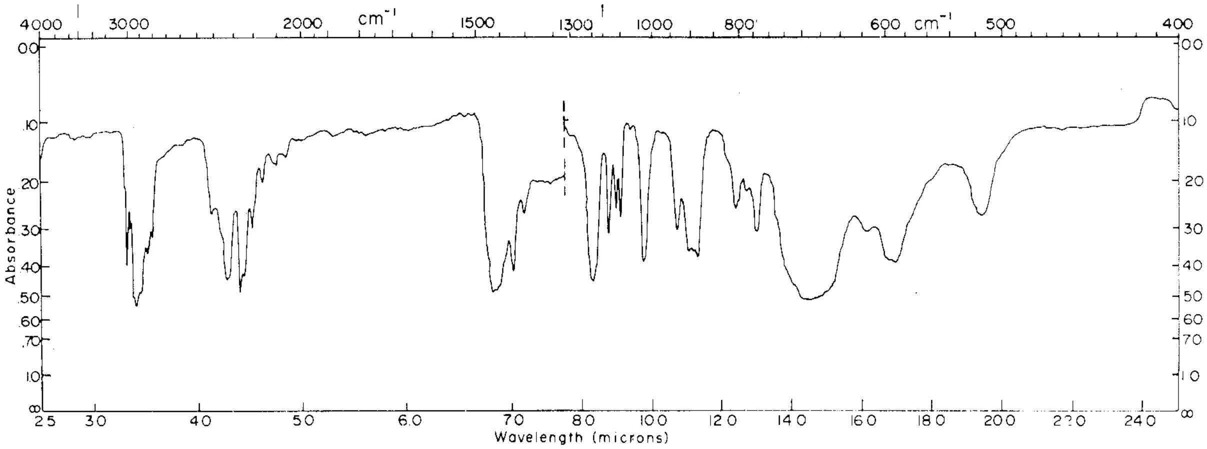

Figure 3.—Solid-state infrared spectrum of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.

trum of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$, Figure 3, summarized in Table II, includes two strong well-defined absorptions at 2331 and 2268 cm^{-1} which are interpreted to indicate the presence of a BH_2 group as in $[H_2BN(CH_3)_2]_2$, 2447 and 2369 cm^{-1}.[6] The absorptions at 1468, 1456, 1427, and 1406 cm^{-1}, common to aminoalanes and -boranes, are assigned to δ_{CH_3} modes. The absorptions at 1202 and 1112 cm^{-1}, observed in the spectrum of $[(CH_3)_2AlN(CH_3)_2]_2$ at 1202 and 1128 cm^{-1}, are assigned to ρ_{CH_3} modes. The strong bands at 1139 and 929 cm^{-1} are assigned to the δ_{CH_2} in- and out-of-plane modes by comparison with the 1156- and 964-cm^{-1} bands of $[H_2BN(CH_3)_2]_2$; the band at 1098 cm^{-1} is most likely due to a ν_{BN} mode.[7] The $\nu_{as}(NC_2)$ and $\nu_s(NC_2)$ bridge modes are assigned to the absorptions at 1024 and 887 cm^{-1} by reference to the same assignments in $[(CH_3)_2AlN(CH_3)_2]_2$ at 1049 and 918 cm^{-1}. Similarly, the absorptions at 690 and 590 cm^{-1} have been assigned to the ν_{as}(Al–C) and ν_s(Al–C) modes by comparison with the spectra of $[(CH_3)_2AlN(CH_3)_2]_2$, 714 and 576 cm^{-1}, and $[Al(CH_3)_3]_2$, 696 and 564 cm^{-1}.[7] The strong absorption at 769 cm^{-1} in $[Al(CH_3)_3]_2$, is assigned to a terminal CH_3 wag for terminal methyl bonded to aluminum. The band at 515 cm^{-1} appears to be due to the ν_{Al-N} bridge mode found at 509 cm^{-1} $[(CH_3)_2AlN(CH_3)_2]_2$.

TABLE II
INFRARED FREQUENCIES AND TENTATIVE
ASSIGNMENTS FOR $Al_2B[N(CH_3)_2]_3(CH_3)_4H_3$[a]

Freq, cm^{-1} (±5 cm^{-1})	Tentative assignment	Freq, cm^{-1} (±5 cm^{-1})	Tentative assignment
3003 s		1098 m	ν(B–N)
2924 vs			
2882 s, sh	ν(C–H)	1024 vs	$\nu_{as}(NC_2$ bridge)
2841 s, sh			
2793 s, sh		929 s	$\delta(BH_2$ out of plane)
2415 s, sh		905 vs	$\nu_s(NC_2$ bridge)
2364 s, sh		887 vs	
2331 vs			
2268 vs			
		823 w, sh	
2247 vs, sh	ν(B–H)	806 s	
2208 s		787 m	
2160 w			
2105 w		769 vs	Terminal Al–CH_3 wag
1468 vs		690 vs	ν_{as}(Al–C)
1456 vs	$\delta(CH_3)$		
1427 vs		621 m	
1406 m		590 vs	ν_s(Al–C)
1202 vs	$\rho(CH_3)$		
		515 s	ν(Al–N bridge)
1139 s	$\delta(BH_2$ in plane)		
1112 m	$\rho(CH_3)$		

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; v, very; w, weak; sh, shoulder.

The infrared spectrum allows one to draw the following conclusions concerning the nature of bonding in $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$: (1) the presence of a terminal BH_2 moiety, (2) the presence of bridging $N(CH_3)_2$ groups bonded to boron and aluminum, (3) the presence of terminal methyl groups bonded to aluminum, (4) the absence of terminal $N(CH_3)_2$ groups bonded to boron due to the absence of ν_{B-N} frequencies at *ca.* 1530 and 1409 cm^{-1},[8] (5) the absence of terminal $N(CH_3)_2$ groups bonded to aluminum based on the absence of ν_{NC_2} frequencies at *ca.* 1165 and 905 cm^{-1}, (6) the absence of terminal hydrogens bonded to aluminum due to the absence of a broad absorption at *ca.* 1800 cm^{-1},[9] (7) the absence of B–H–B or Al–H–B bridging based on the

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[6] W. C. Price, R. Fraser, T. Robinson, and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, **9**, 131 (1950).

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absence of absorptions at *ca.* 1600 and 2031 cm^{-1},[10,11] and (8) the absence of terminal methyl groups bonded to boron as indicated by the absence of absorptions at *ca.* 1150 and 675 cm^{-1} which are assigned to the ν_{as}(B–C) and ν_s(B–C) modes. Furthermore, the absence of the $\delta(CH_3)$ mode frequency at *ca.* 1300 cm^{-1}, which is common to all methylboranes, indicates the absence of a terminal methyl bonded to boron; no other aminoborane absorptions occur in this region.[12]

Proposed Structure for $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.—The structure of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$ must include four-coordinate BH_2 moieties, bridging $N(CH_3)_2$ groups in two different environments in the ratio of 2:1, and equivalent methyl groups bonded to aluminum. The most probable structure is the six-membered heterocyclic ring shown in Figure 4. This structure is similar to the chair form of cyclohexane and contains tetrahedral boron bonded to two terminal hydrogens and incorporates bridging $N(CH_3)_2$ groups in two slightly different environments in the ratio of 2:1. There are four terminal methyl groups bonded to the aluminum atoms, all in equivalent positions, thereby accounting for the 2:2:1 area ratios in the ^1H nmr spectrum.

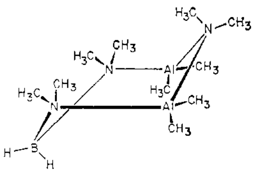

Figure 4.—Proposed structure for $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.

Probable Reaction Scheme for the Preparation of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.—Treatment of $[(CH_3)_2N]_2BH$ with $[Al(CH_3)_3]_2$ results in the isolation of large quantities of $(CH_3)_2BN(CH_3)_2$ and trace quantities of $(CH_3)HBN(CH_3)_2$, $[H_2BN(CH_3)_2]_2$, and $[(CH_3)_2AlN(CH_3)_2]_2$. From these data the following reaction route for the synthesis of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$ is proposed

$$[(CH_3)_3Al]_2 + 2HB[N(CH_3)_2]_2 \xrightarrow{25°} 2(CH_3)HBN(CH_3)_2 + 2(CH_3)_2AlN(CH_3)_2 \quad (2)$$

$$2(CH_3)HBN(CH_3)_2 \xrightarrow{25°} H_2BN(CH_3)_2 + (CH_3)_2BN(CH_3)_2 \quad (3)$$

$$H_2BN(CH_3)_2 + 2(CH_3)_2AlN(CH_3)_2 \xrightarrow{25°} Al_2B[N(CH_3)_2]_3(CH_3)_4H_2 \quad (4)$$

The reaction represented by eq 2 involves the alkylation of $HB[N(CH_3)_2]_2$ affording $CH_3(H)BN(CH_3)_2$ which has been shown to reorganize according to eq 3 to afford $H_2BN(CH_3)_2$.[13] This latter material readily dimerizes as does $(CH_3)_2NAl(CH_3)_2$ produced by the reaction represented by eq 2. Equation 4 represents the *in situ* intermolecular coordination of two monomeric units of $(CH_3)_2NAl(CH_3)_2$ and $H_2BN(CH_3)_2$. An alternate reaction mechanism based on cleavage of the amino-bridged species, $H_2BN(CH_3)_2$, seems unlikely because $[H_2BN(CH_3)_2]_2$ does not afford $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$ when treated with $[(CH_3)_2AlN(CH_3)_2]_2$.

Experimental Section

Apparatus and Procedures.—Equipment, techniques, and analytical methods have been previously described.[2,4] The ^1H nmr spectra were obtained with Varian Associates instruments A-60 (60 MHz) in benzene and toluene at 30 and −61°, respectively, while the ^{11}B spectrum was obtained at 32.1 MHz with an HA-100.

Reagents.—Bis(dimethylamino)borane was synthesized by hydrogenation of bis(dimethylamino)chloroborane with lithium hydride following the procedure of Noth, *et al.*[11] The products were fractionated through traps maintained at −30.6, −78, and −196°. The bis(dimethylamino)borane, collected at −78°, had a vapor tension of 7.9 Torr at 0.0° and 30.8 Torr at 23.2°, lit. values[15] 7.9 and 30.8 Torr, respectively. Trimethylaluminum, obtained from Ethyl Corp., was fractionated through a trap maintained at −22.9° into a −45.2° trap and the trimethylaluminum retained at −45.2° had a vapor tension of 8.9 Torr at 20°.

Preparation of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.—Trimethylaluminum, 20.8 mmol, was condensed onto 26.0 mmol of bis(dimethylamino)borane, $HB[N(CH_3)_2]_2$, contained in a 50-ml reaction bulb. A low volatile white solid formed during the 12 hr the solution was stirred at room temperature. Volatile dimethylaminoborane, $[H_2BN(CH_3)_2]_2$, dimethylaminomethylborane, $(CH_3)HBN(CH_3)_2$, dimethylaminodimethylborane, $(CH_3)_2BN(CH_3)_2$, dimethylaminodimethylalane, $[(CH_3)_2AlN(CH_3)_2]_2$, and excess $HB[N(CH_3)_2]_2$ were distilled from the reaction vessel which was maintained at 0°. These volatile components were separated by fractional condensations. The trace quality of $[H_2BN(CN_3)_2]_2$ was identified by its ^{11}B nmr spectrum which consists of a triplet centered at −4.7 ppm from $BF_3 \cdot O(C_2H_5)$, lit. value[5] δ −4.6 ppm. The $(CH_3)HBN(CH_3)_2$ was identified by its vapor tension, 31.2 Torr at 30°, 13.4 Torr at −45°, and 0.8 Torr at −78°, lit.[13] values 34.3, 13.2, and 0.8 Torr, respectively, and by comparison of its infrared spectrum with that of an authentic sample of $(CH_3)HBN(CH_3)_2$. A small doublet in the ^{11}B nmr spectrum centered at approximately −30.5 ppm from $BF_3 \cdot O(C_2H_5)_2$ was attributed to $(CH_3)HBN(CH_3]_2$. The ^{11}B nmr spectrum of the volatile products also contained a large singlet at −44.6 ppm from $BF_3.O(C_2H_5)_2$ which can be attributed to $(CH_3)_2BN(CH_3)_2$, δ −44.6 ppm.[14] The infrared spectrum and vapor tension of an isolated sample of the latter material, 53.3 Torr at 0°, 13.3 Torr at −22.9°, and 2.8 Torr at −45°, compared favorably with that of an authentic sample of $(CH_3)_2BN(CH_3)_2$, 54.8, 15.0, and 3.3 Torr, respectively.[15] Excess $HB[N(CH_3)_2]_2$ was identified by comparison of its infrared spectrum with that of a known sample; the ^{11}B nmr spectrum of the volitile products also contained a doublet, J_{BH} = 133 cps, centered at −28.4 ppm from $BF_3.O(C_2H_5)_2$ which was attributed to $HB[N(CH_3)_2]_2$, δ −28.6 ppm, J_{BH} = 132 cps.[16,17]

Purification and Characterization of $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.—The white solid residue from the reaction of $[Al(CH_3)_3]_2$ with $HB[N(CH_3)_2]_2$ was sublimed at 50° to a cold-water condenser with continual pumping to remove traces of $[(CH_3)_2AlN(CH_3)_2]_2$ which has a vapor tension of *ca.* 0.1 Torr at 20°. The infrared spectrum of the white solid is shown in Figure 3 and summarized in Table II. The ^1H nmr spectrum consists of three sharp singlets at +0.79, −2.28, and −2.39 ppm from TMS in the area ratios of 2:2:1 as shown in Figure 1. The ^{11}B nmr spectrum is a sharp triplet centered at −0.4 ppm from $BF_3 \cdot O(C_2H_5)_2$ with J_{BH} = 108 ± 3 cps, Figure 2. The isopiestic molecular weight was obtained by equilibrating 9.771 ml of cyclopentane between 0.295 mmol of azobenzene and 80.1 mg of the white solid for 18

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(10) R. C. Lord and E. Nielson, *J. Chem. Phys.*, **19**, 1 (1951).

(11) W. C. Price, *ibid.*, **17**, 1044 (1949).

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days at 25°. At equilibrium the azobenzene bulb contained 4.419 ml of cyclopentane and the sample bulb 5.346 ml of cyclopentane which results in an experimental molecular weight of 224.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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Synthesis of Optically Active 1,1-Dichloro-*trans*-3,5-bis(4-methylphenyl)-3,5-diphenylcyclotriphosphazatriene

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OTTO ZECK, AND S. SAHURI

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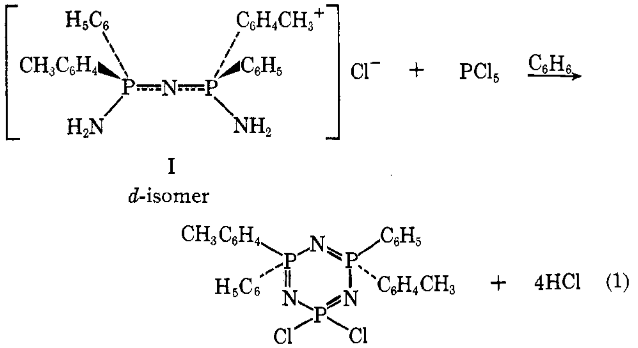
Numerous examples of cyclotriphosphazenes which possess the necessary asymmetry to exhibit optical isomerism have been reported, but no optical isomers have been isolated.[1] Because phosphazenes are neutral molecules, resolution of the racemic mixture presents a formidable experimental problem. By using an optically active phosphazenylphosphonium salt (I) in a cyclization reaction (eq 1), we have circumvented the difficult problem of resolving a neutral phosphazene and prepared the first optically active cyclotriphosphazatriene, *d*-1,1-dichloro-*trans*-3,5-bis(4-methylphenyl)-3,5-diphenylcyclotriphosphazatriene.



I

d-isomer

d-trans isomer
$[\alpha]^{32}{}_{5461}$ +4.2° (*c* 1.2
in methanol)

The general procedure for the synthesis of the optically active [amido(4-methylphenyl)phenylphosphazenyl]amido(4-methylphenyl)phenylphosphonium chloride (I) is outlined in eq 2–5. The final step in the synthesis of I is an adaptation of the method of Bezman and Smalley for the synthesis of $[(C_6H_5)_4P_2N_3H_4]Cl$.[4] In addition to the *dl* pair, the meso form is also possible.

$$CH_3C_6H_4NH_2 + HNO_2 \xrightarrow{H_2O} \xrightarrow{HBF_4} [CH_3C_6H_4N_2^+][BF_4^-] \quad (2)^2$$

$$[CH_3C_6H_4N_2^+][BF_4^-] + C_6H_5PCl_2 \xrightarrow[i\text{-}C_3H_7OAC]{Cu_2Br_2} \xrightarrow{Al} CH_3C_6H_4P(C_6H_5)Cl \quad (3)^3$$

$$(CH_3C_6H_4)P(C_6H_5)Cl + Cl_2 \xrightarrow[HCCl_3]{CCl_4\text{ or}} (CH_3C_6H_4)P(C_6H_5)Cl_3 \quad (4)$$

$$2(CH_3C_6H_4)P(C_6H_5)Cl_3 + 8NH_3 \xrightarrow{HCCl_3} \text{racemic mixture of I} + 5NH_4Cl \quad (5)$$

The racemic mixture of I was resolved in methanol by standard techniques with silver α-bromo-*d*-camphor-π-sulfonate monohydrate as the resolving agent. Colorless crystals of the diastereomer $[l\text{-}(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4][d\text{-}C_{10}H_{14}OBrSO_3]$ separated from the solution upon addition of 2-propanol and cooling. The diastereomer was twice recrystallized from methanol–2-propanol solution to give a sample, mp 201–202°, with a specific rotation $[\alpha]^{28}{}_{5461}$ +52.9° (*c* 1.90 in methanol). A slightly impure sample of the d^+,d^- diastereomer had a specific rotation $[\alpha]^{28}{}_{5461}$ +50.0° (*c* 1.64 in methanol).

The diastereomers were converted to the respective chloride salts by passing them through a chloride-exchange column. The $l\text{-}[(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$ sample, recrystallized from chloroform–ether, had a melting point of 215–218.5° and a specific rotation of $[\alpha]^{28}{}_{5461}$ −4.3° (*c* 1.43 in methanol). For the dextrorotatory phosphonium chloride, mp 215–218°, the $[\alpha]^{28}{}_{5461}$ is +4.7° (*c* 0.971 in methanol).

Experimental Section

Reagents.—Technical grade dichlorophenylphosphine (Victor) was used without further purification. Benzene was dried over sodium and fractionally distilled. The constant-boiling fraction was retained. All other organic solvents were used without further purification.

Elemental Analyses.—All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Physical and Spectroscopic Measurements.—Infrared spectral measurements were made on a Beckman Model IR-8 or IR-10 spectrophotometer. A Bendix-Ericsson ETL-NPL automatic polarimeter, Type 143A, with filtered mercury light source, was used for the measurement of specific rotations. The concentration of solute in grams per 100 ml of solution is given in parentheses after the value of the specific rotation. Molecular weight determinations were made by Galbraith Laboratories, Knoxville, Tenn., on a vapor pressure osmometer.

Synthesis of [Amido(4-methylphenyl)phenylphosphazenyl]-amido(4-methylphenyl)phenylphosphonium chloride (I).—The compound 4-methylphenyldiazonium tetrafluoroborate, dec pt 108°, was prepared in 49% yield according to the method of Roe.[2] The diazonium salt was used to prepare (4-methylphenyl)phenylchlorophosphine, bp 130–135° (4–5 mm), 23% yield, by the method of Quin and Montgomery.[3]

To a solution of 23.3 g (0.0993 mol) of (4-methylphenyl)phenylchlorophosphine in 700 ml of pure chloroform was added an excess of chlorine gas (Matheson). After removing the unreacted chlorine with a nitrogen purge, an excess of anhydrous ammonia was then added to the solution containing the phosphorane, and the ammonium chloride which precipitated was removed by filtration. Treatment of the chloroform filtrate with diethyl ether resulted in the precipitation of 9.00 g (38% yield) of $[(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$, mp 215–218°, which was removed by filtration. *Anal.* Calcd for $C_{26}H_{28}N_3ClP_2$:

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* To whom correspondence should be addressed.

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