

theoretically possible to determine equilibrium constants from intensity measurements, we find the intensity perplexingly sensitive to experimental conditions (*vide infra*) and also we have not been able to isolate solvent-coordinated species; accordingly, such studies have not been pursued as yet.

Although our data are readily explained in terms of the formation of a solvent-coordinated species $\text{SPtCl}_2(\text{CO})$ with a lower frequency $\nu_{\text{C}=\text{O}}$, the formation of a dimer and resulting *trans* to *cis* isomerization cannot be completely ruled out. It is known that strong *trans*-directing groups facilitate dimer formation⁸ and such a dimer could be the precursor to a *cis* isomer.⁹ However, the platinum carbonyl dimer $(\text{PtCl}_2\text{CO})_2$ has been reported to have $\nu_{\text{C}=\text{O}}$ at 2152 cm^{-1} in mull¹⁰ and such a high-frequency band has not been observed in our solution work.

Finally, certain difficulties with respect to the determination of spectra of these complexes were encountered and should be mentioned. When the complexes were milled with halocarbon oil, the resulting spectra were erratic. The extent of mulling and grinding seemed to affect the spectra. The spectra showed broad and split bands in many cases. Solution spectra of the pyridine complexes taken in KBr cells and NaCl cells differed. Although the values of $\nu_{\text{C}=\text{O}}$ and the effect of *Z* were similar in each type of cell, the relative intensities of the two carbonyl bands were affected, the low-frequency band increasing and the high-frequency band decreasing in intensity in changing from NaCl to KBr cells. The KBr pellet technique also gave erratic results possibly because of bromide incorporation into the complex.¹¹

Acknowledgment.—We are pleased to acknowledge the assistance of Thomas Atkins and partial support from the Petroleum Research Fund, National Science Foundation, and Standard Oil of Ohio. We also wish to thank Engelhard Industries for a generous supply of platinum.

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The Reactions of Triethylaluminum with Some Hydrazinophosphorus Compounds

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Received September 20, 1968

The reactions of organoaluminum compounds with some hydrazines,^{1,2} biphosphines,³ and aminophosphines³ have resulted in formation of adducts in which

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the aluminum atom is believed to be pentacoordinate by virtue of its attachment to two adjacent electron donor centers. The various hydrazinophosphines afford a variety of possibilities for such "pentacoordination," since such compounds contain adjacent nitrogen atoms as well as phosphorus and nitrogen atoms in adjacent positions. We were, therefore, interested in examining the products of the reactions of aluminum triethyl with 2,3,5,6,7,8-hexamethyl-2,3,5,6,7,8-hexaaza-1,4-diphosphabicyclo[2.2.2]octane, with 2,3,5,6-tetramethyl-2,3,5,6-tetraaza-1,4-diphenyl-1,4-diphosphacyclohexane, and with 1,2-bis(diphenylphosphino)-1,2-dimethylhydrazine. These products have been prepared and studied, and the results are reported below.

Experimental Section

Materials.—Toluene, hexane, benzene, and petroleum ether (bp 20–40°) were obtained as reagent grade materials and were dried and stored over calcium hydride. Triethylaluminum was obtained from the Ethyl Corp. and was distilled under nitrogen at 66° (0.4 mm). Phosphorus trichloride, obtained from the J. T. Baker Chemical Co., was used as received. Diphenylchlorophosphine and phenyldichlorophosphine were obtained from the Victor Chemical Co. These reagents were distilled under nitrogen and fractions boiling at 212–214° (760 mm) and 110° (0.5 mm), respectively, were kept for use. 1,2-Dimethylhydrazine dihydrochloride, obtained from the Aldrich Chemical Co. was used as obtained. Dimethylamine was obtained from the Matheson Co. Inc. Tris(dimethylamino)phosphine was prepared by the reaction of dimethylamine with phosphorus trichloride according to standard procedure.⁴ The 2,3,5,6,7,8-hexamethyl-2,3,5,6,7,8-hexaaza-1,4-diphosphabicyclo[2.2.2]octane, $\text{P}[(\text{CH}_3)_2\text{NN}(\text{CH}_3)]_2\text{P}$, was synthesized by the method of Payne, Nöth, and Henniger.⁵

General Methods.—Triethylaluminum, phosphines, and hydrazinophosphorus compounds were handled in an atmosphere of nitrogen. A Vacuum Atmospheres Model HE-43 inert-atmosphere box equipped with a Model HE-93B Dri-Train or a typical high-vacuum line was used for manipulation and storage of all reagents. Infrared spectra were obtained using a Beckman IR-10 spectrophotometer. The proton magnetic resonance spectra were recorded using a Varian A-60A nmr spectrometer. Tetramethylsilane was used as an internal reference when it was possible and as an external reference in all other cases. The phosphorus nuclear magnetic resonance spectra were obtained using a Varian high-resolution spectrometer, Model V-4300-2, equipped with a field homogeneity control, magnet insulation, and field stabilizer. These spectra were recorded at 19.3 Mc using 85% phosphoric acid as an external reference. Fine splitting was not observed on some of the ³¹P spectra since the sample tubes could not be spun. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of 1,2-Bis(diphenylphosphino)-1,2-dimethylhydrazine.—The $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2\text{P}(\text{C}_6\text{H}_5)_2$ was prepared as follows. 1,2-Dimethylhydrazine (2.58 g, 0.0431 mol) was added to a solution of diphenylchlorophosphine (19.1 g, 0.107 mol) in 200 ml of benzene. The solution was stirred as the hydrazine was added. The resulting mixture was allowed to stand for 12 hr. The mixture was then filtered and the solvent was removed under vacuum to yield 16.8 g of a clear liquid. This liquid was crystallized by dissolving it in boiling hexane and allowing the solution to cool. The resulting white crystals were filtered; after drying, they melted at 82–84°. The yield of

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recrystallized material was 10.1 g (56% of theory based on the amount of hydrazine used).

The infrared spectrum obtained for Kel-F and Nujol mulls of the solid supported between KBr disks contains peaks at 3040 (m), 2960 (w), 2905 (w), 2780 (w), 1940 (vw), 1870 (vw), 1800 (vw), 1750 (vw), 1645 (vw), 1575 (w), 1460 (m), 1455 (sh), 1425 (s), 1305 (m), 1220 (m), 1175 (m), 1150 (s), 1100 (sh), 1080 (s), 1060 (s), 1020 (m), 990 (m), 960 (m), 530 (s), 490 (s), 480 (s), and 440 (s) cm^{-1} .

The ^1H nmr spectrum obtained using C_6D_6 as a solvent and tetramethylsilane as an internal standard consists of a complex peak at τ 2.61 (average) assigned to phenyl protons and a distorted triplet at τ 7.32 ($J = 1.0$ cps) assigned to methyl protons. These peaks are in the ratio of 3.37:1.00. The ^{31}P nmr spectrum exhibits a single peak at -62.5 ppm relative to 85% phosphoric acid.

Anal. Calcd for $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_3)\text{NN}(\text{CH}_3)_2\text{P}(\text{C}_6\text{H}_5)_2$: C, 72.88; H, 6.12; P, 14.45; N, 6.55. Found: C, 72.82; H, 6.20; P, 14.21; N, 6.41.

Preparation of 2,3,5,6-tetramethyl-2,3,5,6-tetraaza-1,4-diphenyl-1,4-diphosphacyclohexane.—A benzene solution of phenyldichlorophosphine (35.7 g, 0.161 mol) and a benzene solution of 1,2-dimethylhydrazine (9.10 g, 0.149 mol) were added simultaneously over a period of 6 hr to a stirred solution of 100 ml of triethylamine (72.3 g, 0.716 mol) in 1200 ml of benzene. The resulting mixture was allowed to stand 48 hr and then filtered. After the solvent was evaporated, a mixture of white crystals and yellow oil remained. This mixture was dissolved in hot benzene and allowed to cool. A crystalline product resulted which melted at $222\text{--}223^\circ$ after drying. The molecular weight determined cryoscopically in benzene was 332 (calculated for $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2$, 333). The yield of product was 3.77 g of recrystallized material (15% of theory based on the amount of hydrazine used).

The infrared spectrum obtained for Kel-F and Nujol mulls of the solid contains peaks at 3060 (w), 3040 (w), 2960 (m), 2920 (m), 2880 (m), 2850 (m), 2780 (w), 1960 (w), 1900 (w), 1830 (w), 1735 (w), 1675 (w), 1580 (w), 1560 (w), 1460 (m), 1430 (s), 1400 (w), 1300 (w), 1215 (sh), 1200 (m), 1175 (w), 1140 (m), 1115 (m), 1090 (s), 710 (vs), 680 (w), 670 (sh), 615 (w), 590 (m), 570 (s), 490 (s), and 430 (s) cm^{-1} .

The ^1H nmr spectrum obtained using CDCl_3 as a solvent and tetramethylsilane as an internal standard consists of a complex peak at τ 2.44 (average) assigned to phenyl protons and a doublet at τ 6.96 ($J = 14.5$ cps) assigned to methyl protons. These peaks are in a ratio of 1.00:1.22. The ^{31}P nmr spectrum exhibits a single peak at -29.9 ppm relative to 85% phosphoric acid.

Anal. Calcd for $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2$: C, 57.83; H, 6.67; P, 18.64; N, 16.86. Found: C, 58.00; H, 6.78; P, 18.46; N, 16.64.

The Reaction of $\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}$ with $\text{Al}_2(\text{C}_2\text{H}_5)_6$.—In a typical reaction, $\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}$ (0.66 g, 2.8 mmol) was added to a toluene solution of $\text{Al}_2(\text{C}_2\text{H}_5)_6$ (0.64 g, 2.8 mmol) at -78° . The resulting mixture was stirred at room temperature for 2 hr. The solid material dissolved as the temperature approached room temperature. The toluene was distilled out of the reaction flask on the vacuum line leaving a white solid. After recrystallization from hexane, this solid melted at $153\text{--}155^\circ$.

The infrared spectrum obtained for a Nujol mull of the adduct consists of peaks at 2780 (s), 2700 (m), 1400 (m), 1300 (sh), 1220 (w), 1180 (s), 1085 (m), 1040 (m), 970 (m), 920 (s), 770 (m), 755 (sh), 715 (w), 640 (s), 590 (s), 495 (m), and 475 (sh) cm^{-1} .

The ^1H nmr spectrum obtained using C_6D_6 as a solvent and tetramethylsilane as an external standard consists of a doublet which encloses a broad peak at τ 7.95 ($J = 14.7$ cps) assigned to the methyl protons as well as a triplet at τ 9.23 ($J = 7.6$ cps) and a quartet at τ 10.37 ($J = 7.6$ cps) assigned to the ethyl protons. These peaks are in the ratio 3.0:3.2:2.0. The ^{31}P nmr spectrum consisted of a single peak at -11.8 ppm relative to 85% phosphoric acid.

Anal. Calcd for $\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P} \cdot [\text{Al}(\text{C}_2\text{H}_5)_3]_2$: C, 46.54;

H, 10.41; N, 18.09; P, 13.34; Al, 11.62. Found: C, 46.30; H, 10.67; N, 17.81; P, 13.13; Al, 11.87.

This reaction was also carried out with 2:1 and 2:3 mole ratios of $\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}$ to $\text{Al}_2(\text{C}_2\text{H}_5)_6$. Both reactions resulted in isolation of the adduct described above.

The Reaction of $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2$ with $\text{Al}_2(\text{C}_2\text{H}_5)_6$.—In the same manner as described above, $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2$ was allowed to react with $\text{Al}_2(\text{C}_2\text{H}_5)_6$ in 2:1, 1:1, and 2:3 mole ratios. In each case, $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2 \cdot [\text{Al}(\text{C}_2\text{H}_5)_3]_2$ was isolated. This solid, after recrystallization from hexane, melted at $181\text{--}184^\circ$.

The infrared spectrum obtained for a Nujol mull of the solid contains peaks at 3090 (w), 3070 (w), 2800 (m), 2730 (w), 1980 (vw), 1920 (vw), 1835 (vw), 1790 (vw), 1580 (vw), 1445 (s), 1415 (m), 1305 (w), 1235 (m), 1185 (m), 1145 (w), 1115 (sh), 1105 (m), 1095 (m), 1030 (w), 990 (sh), 965 (s), 950 (s), 920 (w), 850 (w), 770 (s), 750 (vs), 710 (s), 640 (s), 625 (sh), 610 (m), 570 (s), 495 (s), and 440 (m) cm^{-1} .

The ^1H nmr spectrum obtained using C_6D_6 as a solvent and tetramethylsilane as an external reference consists of a complex peak at τ 2.54 (average) assigned to phenyl protons, a doublet at τ 7.02 ($J = 13.0$ cps) assigned to methyl protons on nitrogen as well as a triplet at τ 8.75 ($J = 7.7$ cps), and a quartet at τ 9.86 ($J = 7.7$ cps) assigned to the ethyl protons. These peaks are in the ratios 1.00:1.19:1.78:1.10. The ^{31}P nmr spectrum consisted of a single peak at -79.2 ppm relative to 85% phosphoric acid.

Anal. Calcd for $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2 \cdot [\text{Al}(\text{C}_2\text{H}_5)_3]_2$: C, 59.96; H, 9.35; N, 10.00; P, 11.05; Al, 9.64. Found: C, 59.65; H, 9.03; N, 10.33; P, 11.56; Al, 9.27.

The Reaction of $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2$ with $\text{Al}_2(\text{C}_2\text{H}_5)_6$.—Using the same technique as described above, $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2$ was allowed to react with $\text{Al}_2(\text{C}_2\text{H}_5)_6$ in 1:1 and 2:3 mole ratios. In each case, $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2 \cdot [\text{Al}(\text{C}_2\text{H}_5)_3]_2$ was isolated. This compound melted at $79\text{--}80^\circ$ after recrystallization from hexane.

The infrared spectrum obtained as Kel-F and Nujol mulls of the solid contains peaks at 2910 (m), 2880 (m), 2850 (m), 1475 (w), 1430 (m), 1400 (vw), 1360 (vw), 1310 (w), 1225 (w), 1180 (w), 1090 (s), 1025 (m), 995 (w), 965 (w), 950 (m), 920 (sh), 840 (vw), 745 (s), 730 (s), 695 (s), 645 (s), 635 (sh), 620 (s), 540 (s), 510 (m), and 465 (m) cm^{-1} .

The ^1H nmr spectrum obtained using C_6D_6 as a solvent and tetramethylsilane as an external reference contains a complex peak at τ 2.60 (average) assigned to phenyl protons, a distorted triplet at τ 7.40 ($J = 6.5$ cps) assigned to methyl protons as well as a triplet at τ 8.70 ($J = 7.9$ cps) and a quartet at τ 9.65 ($J = 7.9$ cps) assigned to the ethyl protons. These peaks are in the ratios 3.59:1.00:3.33:2.00. The ^{31}P nmr spectrum consisted of a single peak at -61.2 ppm relative to 85% phosphoric acid.

Anal. Calcd for $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2 \cdot [\text{Al}(\text{C}_2\text{H}_5)_3]_2$: C, 69.49; H, 8.59; N, 4.27; P, 9.43; Al, 8.21. Found: C, 69.90; H, 8.25; N, 4.59; P, 9.44; Al, 8.30.

When this reaction was carried out with a 2:1 mole ratio of $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2$ to $\text{Al}_2(\text{C}_2\text{H}_5)_6$, an oil resulted. Attempts at crystallization of this oil were unsuccessful. The ^{31}P nmr spectrum of this oil consists of a single peak at -61.8 ppm relative to phosphoric acid. The ^1H nmr spectrum of the oil is similar to that observed for the 2:1 adduct described above, except for the difference in the area ratios of the peaks.

Discussion

The preparation of $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)_2$ illustrates that the general synthesis of hydrazinophosphorus compounds by the reaction of chlorophosphines with hydrazines can be extended to cyclic compounds. Assuming staggered methyl groups on the hydrazino bridges, there are two possible geometrical

isomers of this compound in which the phenyl groups are *cis* or *trans* relative to each other. The relatively sharp melting point and the single methyl doublet observed in the ^1H nmr spectrum indicate this material is probably not a mixture of isomers.

The doublet assigned to the methyl protons observed in the ^1H nmr spectrum of $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)_2\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)$ is in contrast to the distorted triplets assigned to the methyl groups of $\text{P}[(\text{CH}_3)_2\text{NN}(\text{CH}_3)]_3\text{P}^5$ and $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)_2\text{NN}(\text{CH}_3)]\text{P}(\text{C}_6\text{H}_5)_2$. The observed "triplets" may be explained by virtual coupling if the phosphorus nuclei are strongly coupled. Molecular models of $\text{P}[(\text{CH}_3)_2\text{NN}(\text{CH}_3)]_3\text{P}$ and $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)_2\text{NN}(\text{CH}_3)]\text{P}(\text{C}_6\text{H}_5)_2$ indicate the ^{31}P nuclei are or could be in close proximity. Therefore, strong phosphorus-phosphorus coupling could occur through a mechanism not involving the bonding system as well as through the bonds. The fact that only a doublet is observed for the methyl protons of $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)_2\text{NN}(\text{CH}_3)]_2\text{P}(\text{C}_6\text{H}_5)$ can be explained by the fact that the bond angles may not be such as to allow coupling of the protons with both ^{31}P nuclei. The effect that bond angles may have on the phenomenon of virtual coupling has been observed in the ^1H nmr spectra of some transition metal complexes having phosphine ligands. Virtual coupling was observed in *trans*-square-planar, octahedral, and trigonal-bipyramidal complexes, but not in *cis* isomers of these complexes.^{6,7} Alternatively, direct coupling could explain the observed triplets if the coupling constants of the two ^{31}P nuclei are nearly the same relative to the given methyl group. In this case, an overlap of peaks would result in the formation of a triplet.

When the hydrazinophosphorus compounds were allowed to react with triethylaluminum in 1:1, 2:1, and 3:1 mole ratios, only adducts having a 2:1 mole ratio of $\text{Al}(\text{C}_2\text{H}_5)_3$ to the hydrazinophosphorus compound were isolated. The stoichiometry of these adducts and the fact that these adducts exhibit single peaks for methyl groups on the nitrogen atoms in the ^1H nmr spectrum and single peaks for phosphorus in the ^{31}P nmr spectrum suggest that aluminum is bonded to phosphorus and is tetracoordinate. It should be noted that in the case of benzene solutions of $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)_2\text{NN}(\text{CH}_3)]\text{P}(\text{C}_6\text{H}_5)_2$ and $(\text{C}_6\text{H}_5)_2\text{P}[(\text{CH}_3)_2\text{NN}(\text{CH}_3)]\text{P}(\text{C}_6\text{H}_5)_2 \cdot [\text{Al}(\text{C}_2\text{H}_5)_3]_2$ single peaks at -62.5 and -61.2 ppm are observed in the ^{31}P nmr spectrum. The fact that these peaks have nearly the same shift suggests that there is a large degree of dissociation of this adduct in benzene solution. Also, the fact that the peaks observed in the ^1H nmr spectra were nearly independent of the concentration of triethylaluminum supports this supposition. In this case, therefore, the nmr data probably do not indicate the bonding of the solid adduct.

Acknowledgments.—The authors thank Dr. Wallace S. Brey, Jr., for his help in obtaining the phosphorus nuclear magnetic resonance spectra and for his assistance

in interpreting nuclear magnetic resonance data. We thank Dr. Donald F. Clemens for his suggestions. We acknowledge the National Science Foundation for partial support of this work through Grant No. NSF-GP-7863 with the University of Florida.

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The Reactions of Some Tri-*n*-alkylphosphines with Some Chlorophosphines

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Received September 30, 1968

Relatively little attention has been paid until very recently to the reaction of trialkylphosphines with chlorophosphines. Recent work in this laboratory^{1,2} and in others³⁻⁶ has indicated that reactions of tertiary alkylphosphines with halophosphines or haloarsines result in either (1) adduct formation or (2) halogen abstraction with the concurrent formation of P-P or As-As bonds and dihalophosphoranes. The objective of the present study was systematically to investigate a number of reactions of the above type in order to determine which reaction, if either, is the generation reaction, to investigate the possibility of extending the synthetic method of chlorine abstraction by tertiary phosphines to new systems, and to investigate the possible relationship of the chlorine-abstraction behavior of tertiary phosphines to adduct or phosphonium halide formation.

Experimental Section

Reagents.—Triethylphosphine and diethylchlorophosphine were obtained from K & K Laboratories. Methylchlorophosphine was obtained from the FMC Co. and was distilled at $79-83^\circ$. Tri-*n*-butylphosphine was obtained from the Carlisle Chemical Works, Inc., and the fraction boiling at 40° (0.05 mm) was retained for use. Tri-*n*-octylphosphine was obtained from the Matheson Coleman and Bell Co. Bis(dimethylamino)chlorophosphine was prepared by the method of Evleth, *et al.*⁷ Tri-*n*-propylphosphine was prepared in a manner similar to that reported by Davies, *et al.*^{8,9} Dimethylchlorophosphine was prepared by the method of Parshall.¹⁰

Procedures.—A Vacuum Atmospheres Model HE-43 inert-atmosphere box equipped with a Model HE-93B Dri-Train was used for manipulation and storage of all reagents. All solvents were dried and stored over calcium hydride except acetonitrile. Acetonitrile was distilled from phosphorus(V) oxide. Infrared spectra were obtained using a Beckman IR-10 spectrophotom-

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