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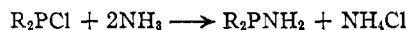
The Reactions of Diphenylchlorophosphine with Gaseous Ammonia and Chloramine and with Hydrazinium Chloride

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The reaction of diphenylchlorophosphine with ammonia and chloramine in tetrachloroethane yields $[(C_6H_5)_2PN]_3 \cdot 3Cl_2CHCHCl_2$ and a compound to which the formula $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$ (or its tautomer) may be assigned. The former readily loses tetrachloroethane to yield $[(C_6H_5)_2PN]_3$, and the latter on pyrolysis is converted to $[(C_6H_5)_2PN]_3$ and $[(C_6H_5)_2PN]_4$ in high yields. In absence of solvent diphenylchlorophosphine reacts with hydrazine dihydrochloride or with hydrazine monohydrochloride to give considerable yields of $[(C_6H_5)_2PN]_3$ and $[(C_6H_5)_2PN]_4$. In tetrachloroethane diphenylchlorophosphine reacts with hydrazine monohydrochloride to give $[(C_6H_5)_2PN]_3$ and a compound to which the formula $(C_6H_5)_2P(Cl)=N-P(=NH)(C_6H_5)_2$ has been tentatively assigned. This compound on pyrolysis gives $[(C_6H_5)_2PN]_3$ and $[(C_6H_5)_2PN]_4$ in high yields.

The recently established series of reactions involving the use of the gaseous mixture of ammonia and chloramine produced by the Sisler-Mattair process¹ in synthesizing a variety of phosphorus-nitrogen derivatives² led us to consider the possible use of this product in the formation of phosphonitriles. If a disubstituted monochlorophosphine is used as starting material, ammonolysis should yield the corresponding aminophosphine.



Further, it should be possible to oxidize the aminophosphine thus produced to the corresponding phosphonitrile monomer which then would polymerize.



Since chloramine is known to be an oxidizing agent of considerable strength, it might be expected that both of these steps would occur when the chlorophosphine is treated with the ammonia-chloramine mixture. Furthermore, since it has been shown that, under appropriate conditions in the liquid phase, ammonia and chloramine combine to form hydrazine monohydrochloride,³ it might be expected that the reaction of diphenylchlorophosphine with hydrazine monohydrochloride would yield a similar result. This communication reports the results of an experimental study

having as its objective the testing of these two hypotheses.

The reaction of gaseous ammonia and chloramine with diphenylchlorophosphine in tetrachloroethane solution, and the reactions of diphenylchlorophosphine with hydrazine monohydrochloride and with hydrazine dihydrochloride in the absence of solvent as well as suspended in tetrachloroethane have been investigated.

Experimental

Materials.—Diphenylchlorophosphine was obtained from the Victor Chemical Works and used as obtained. Hydrazine monohydrochloride and hydrazine dihydrochloride were obtained from the Olin Mathieson Chemical Corp. Tetrachloroethane (Reagent Grade) was obtained from the Fisher Scientific Company.

The gaseous mixture of chloramine and ammonia was produced by the gas phase reaction of chlorine with an excess of ammonia in a generator of the type described by Sisler and Omietanski.⁴ The flow rates specified in this reference were used.

Elementary analyses reported in this paper were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. All melting points listed are uncorrected.

Reaction of Diphenylchlorophosphine with Ammonia and Chloramine.—The following is a description of a typical experiment. The effluent gas from the chloramine generator⁴ was bubbled for 40 min. through a solution of 8.00 g. (0.036 mole) of diphenylchlorophosphine in about 100 ml. of tetrachloroethane. This treatment was sufficient to provide a considerable molar excess of chloramine introduced into the reaction system. The reaction vessel was heated externally by an infrared lamp. This, combined with the heat of the reaction, raised the temperature of the reaction mixture to reflux. At the end of the experiment, the solid reaction products were filtered under an

(1) H. Sisler, F. Neth, R. Drago, and D. Yaney, *J. Am. Chem. Soc.*, **76**, 3908 (1954).

(2) H. Sisler, A. Sarkis, H. Ahuja, R. Drago, and N. Smith, *ibid.*, **81**, 2982 (1959); H. Sisler, H. Ahuja, and N. Smith, *J. Org. Chem.*, **26**, 1819 (1961).

(3) F. Collier, H. Sisler, J. Calvert, and F. Hurley, *J. Am. Chem. Soc.*, **81**, 6177 (1959).

(4) H. H. Sisler and G. Omietanski, *Inorganic Syntheses*, **5**, 91 (1957).

atmosphere of dry nitrogen and washed with two 100-ml. portions of tetrachloroethane. The combined filtrate and washings were evaporated at reduced pressure yielding a light brown solid (4.0 g.) melting at 236–237°. Recrystallization from methanol raised the melting point to 240°. This substance is identified below as compound II. The solid obtained in the original reaction was extracted with two 100-ml. portions of benzene leaving an ammonium chloride residue. Reduction of the volume of the benzene extract through evaporation yielded 1.6 g. of a crystalline solid melting at 114° and identified below as compound I. The results of a series of these experiments using varying concentrations of diphenylchlorophosphine in the original solution are summarized in Table I. Reaction times and amounts of chloramine were kept constant.

TABLE I

$(C_6H_5)_2P_2Cl_2$ (g.)	$Cl_2CHCHCl_2$ (ml.)	Yield of Compound I		Yield of Compound II	
		(g.)	(%) ^a	(g.)	(%) ^b
8.0	90	1.3	10	4.2	51
11.5	90	3.4	18	5.6	47.5
11.5	90	3.3	17	6.0	50
15.6	90	6.2	23

^a Based on the assumption that compound I is $[(C_6H_5)_2PN]_3 \cdot 3Cl_2CHCHCl_2$. ^b Based on the assumption that compound II is $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$.

Identification of Compound I.—*Anal.* Found: C, 46.14; H, 3.51; P, 8.84; N, 4.39; Cl, 37.54. Calcd. for $[(C_6H_5)_2PN]_3 \cdot 3Cl_2CHCHCl_2$: C, 45.81; H, 3.30; P, 8.44; N, 3.82; Cl, 38.64. Compound I, either on standing or on being pumped at reduced pressure, loses tetrachloroethane quantitatively and yields a powder which melts at 228–229°. *Anal.* Found: C, 72.46; H, 4.95; N, 7.29; P, 15.61; mol. wt., 571. Calcd. for $[(C_6H_5)_2PN]_3$: C, 72.35; H, 5.06; N, 7.03; P, 15.55; mol. wt., 598. The infrared spectrum of this product was identical with that of an authentic sample of the diphenylphosphonitrilic trimer. The melting points recorded in the literature for the diphenylphosphonitrilic trimer are 228° and 230–232°.

A sample of diphenylphosphonitrilic trimer was added to a solution of tetrachloroethane in benzene and a product crystallized which was shown by its infrared spectrum and melting point to be identical with compound I.

We may conclude, therefore, that compound I is an adduct of the diphenylphosphonitrilic trimer with tetrachloroethane corresponding to the formula $[(C_6H_5)_2PN]_3 \cdot 3Cl_2CHCHCl_2$. The 1.6 g. of this compound obtained in the experiment described above corresponds to 12% yield based upon the diphenylchlorophosphine used. The data in Table I show that by the use of more concentrated solutions of diphenylchlorophosphine as starting material this yield can be increased considerably.

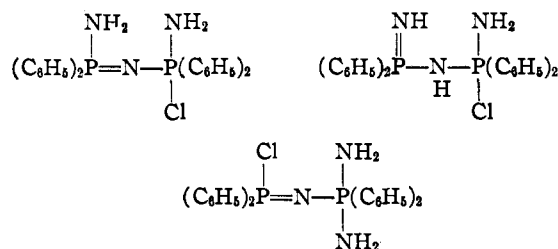
Identification of Compound II. *Anal.* Found: C, 63.75; H, 4.98; P, 13.60; N, 9.41; Cl, 8.50. Calcd. for $C_{24}H_{24}P_2N_2Cl$: C, 63.79; H, 5.35; P, 13.71; N, 9.30; Cl, 7.85. Bezman and Smalley⁵ had treated diphenylphosphorus trichloride with ammonia and obtained a white, crystalline compound which melted at 245.0–246.5° and which gave analysis in accord with the formula $C_{24}H_{24}P_2N_2Cl$. The molecular weight was determined by them and

(5) Bezman and Smalley, *Chem. & Ind.* (London), 839 (1960).

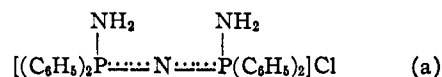
also found to agree with this formula. The infrared spectrum of our compound II was determined and compared in detail with the spectrum of Bezman and Smalley's compound kindly furnished to us by Dr. Bezman; the two are identical. Our spectrum has bands at 3185 and 3085 cm^{-1} attributable, respectively, to monosubstituted phenyl and to NH, bands at 1440 and 996 cm^{-1} attributable to P-phenyl bonds, and a band at 1250 cm^{-1} attributable to the P=N—P linkage. The spectrum also contains two bands at 936 and 971 cm^{-1} which may indicate the P-N(H)—P grouping.⁶ The nuclear magnetic resonance spectrum of compound II was run at 19.3 Mc. in a Varian high resolution spectrometer. A single peak for phosphorus was observed corresponding to a chemical shift of 20.3 p.p.m. to low field in comparison to 85% phosphoric acid as an external standard.

The hydrogen nuclear magnetic resonance spectrum was run at 60.0 Mc. and two peaks obtained, one complex peak in the benzene region and another broad single peak with a chemical shift of 1.3 p.p.m. to high field from benzene. The ratio of the respective areas under the two peaks was approximately 5 to 1.

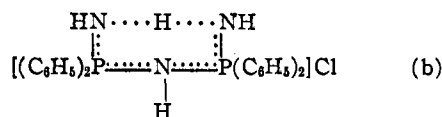
Bezman and Smalley had suggested these possible structures for the compound



All of these, however, may be eliminated on the basis of the single phosphorus peak in the nuclear magnetic resonance spectrum. We believe that phosphonium chloride structures are more appropriate in view of the known facts concerning this substance. Two such structures⁷ in which the phosphorus atoms are equivalent may be written



and its tautomer



In structure (a) the pi bond is distributed over both bonds in the P—N—P group and in structure (b) all the P—N bonds have some multiple bond character, and one proton is held in a hydrogen bond between two nitrogen atoms. Both these structures are in accord with the fact that the chlorine is readily replaced by a varied group of complex anions to give other salt-like derivatives. If, indeed, the 936 or 971 cm^{-1} band in the infrared spectrum is attributable to a

(6) E. Steger, *Chem. Ber.*, **94**, 266 (1961).

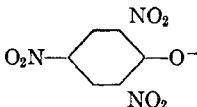
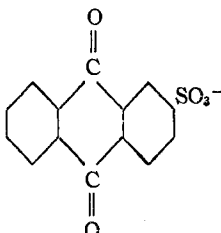
(7) An ammonium type structure $[(C_6H_5)_2P(NH)NH_2P(NH)(C_6H_5)_2]Cl$ was suggested as a possibility by one of the referees, but may be eliminated by the proton n.m.r. data as well as the fact that the P—⁺NH₂—P group should be sufficiently acidic to transfer protons to the P=NH groups.

P-(NH)-P group, structure (b) is to be preferred.

The hydrogen nuclear magnetic resonance spectrum favors structure (a), unless an unreasonably high rate of exchange among the various protons in (b) is assumed. On the basis of any of these formulations the yield of compound II obtained in several experiments averages about 50% based upon the diphenylchlorophosphine used (see Table I).

Formation of Derivatives of Compound II.—Three derivatives of compound II were prepared by metathesis with picric acid, potassium hexafluorophosphate, and sodium anthraquinone- β -sulfonate in aqueous ethanolic solutions. Nitrogen analyses and melting points for the resulting salts are given in Table II.

TABLE II
DERIVATIVES OF THE TYPE
[(C₆H₅)₂P(NH₂)NP(NH₂)(C₆H₅)₂]X

X ⁻	Empirical formula	Analysis % N calcd.: found:	Melt- ing point, °C.
PF ₆ ⁻	C ₂₄ H ₂₄ N ₃ P ₃ F ₆	7.49 7.48	153- 154
	C ₃₀ H ₂₆ N ₆ P ₂ O ₇	13.04 12.83	147
	C ₃₈ H ₃₁ N ₃ P ₂ SO ₃	5.97 5.82	218

When compound II is recrystallized from chloroform, it forms, as Bezman and Smalley have indicated,⁵ a chloroform adduct. We have analyzed this adduct and found it to be a 1:1 compound. *Anal.* Found: C, 52.46; H, 4.14; P, 11.15; N, 6.77; Cl, 24.60. Calcd. for [(C₆H₅)₂P(NH₂)NP(NH₂)(C₆H₅)₂]Cl·CHCl₃: C, 52.56; H, 4.41; P, 10.85; N, 7.36; Cl, 24.83. Since this adduct dissociates below its melting point it melts at the same temperature as compound II. This adduct also is broken down to the free compound II by recrystallization from methanol.

Pyrolysis of Compound II.—In a typical experiment 3.12 g. (0.0069 mole) of compound II was heated at 260–265° for 3 hr. and the resulting dark colored residue treated with 150 ml. of boiling benzene. The volume of the resulting benzene solution was reduced to approximately 60 ml. and 1.52 g. of a crystalline solid melting at 315–316° was obtained. This melting point plus the infrared spectrum of the material showed that it was the diphenylphosphonitrile tetramer [(C₆H₅)₂PN]₄ (literature value of m.p. for [(C₆H₅)₂PN]₄ 320–321°). This corresponds to a 55.4% yield based upon compound II. Further concentration of the mother liquor yielded a second crop of crystals (0.8 g.) which melted at 226–229° and which had the same infrared spectrum as diphenylphosphonitrile trimer (literature value of m.p. for [(C₆H₅)₂PN]₃ 230–232°). This cor-

responds to 29.0% yield based on compound II. Thus the pyrolysis of compound II at 260–265° for 3 hr. produces the diphenylphosphonitrile trimer and tetramer in a gross yield of not less than 85%.

Reaction of Diphenylchlorophosphine with Hydrazine Dihydrochloride and Hydrazine Monohydrochloride in the Absence of Solvent.—In a typical experiment a mixture of 1.7 g. (0.008 mole) of diphenylchlorophosphine and 1.1 g. (0.01 mole) of hydrazine dihydrochloride was heated in a semimicro sublimation apparatus at 245–250° for a period of 48 hr. During the early part of this period there was a vigorous evolution of hydrogen chloride gas. At the end of the period the pressure was reduced to 0.5 mm. for a 4-hr. period. The solid sublimate obtained was identified as a mixture of ammonium chloride and diphenylphosphinic acid. The residue (0.6 g.) melted at 310–312°. Upon recrystallization from benzene the m.p. was raised to 318.5–319.5°. The infrared spectrum of the product agreed with that of the diphenylphosphonitrile tetramer. A mixture of an authentic sample of [(C₆H₅)₂PN]₄ with the product melted at 318.5–319.5°. Thus, the product of the reaction is shown to be diphenylphosphonitrile. The amount of product obtained corresponds to 40% yield based on the diphenylchlorophosphine.

Under similar conditions the reaction of diphenylchlorophosphine (4.25 g., 0.02 mole) and hydrazine monohydrochloride (2.7 g., 0.04 mole) was carried out. Fractional crystallization in benzene of the residue from the sublimation of the reaction product yielded 1.1 g. (yield, 28%) of diphenylphosphonitrile tetramer and 0.5 g. (yield, 13%) of diphenylphosphonitrile trimer.

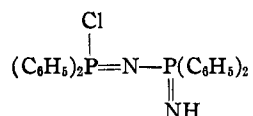
Reaction of Diphenylchlorophosphine with Hydrazine Monohydrochloride in Tetrachloroethane.—In a typical experiment a solution of 22.1 g. (0.1 mole) of diphenylchlorophosphine in 50 ml. of *sym*-tetrachloroethane was added dropwise with continuous stirring to a refluxing suspension of 7.0 g. (0.1 mole) of hydrazine monohydrochloride in 60 ml. of *sym*-tetrachloroethane. After stirring at reflux temperature for 45 hr., the solids in the reaction mixture were filtered off and washed with benzene and ethyl ether. The solid residue was extracted with boiling benzene leaving as residue ammonium chloride. White granular crystals (m.p. 222–225°) separated as the benzene solution cooled (wt. 3.2 g.). Repeated recrystallization from benzene raised the melting point to 229–230°. The infrared spectrum and the melting point of a mixture of the product with an authentic sample of diphenylphosphonitrile trimer confirmed the fact that the product was diphenylphosphonitrile trimer.

Evaporation of the filtrate yielded a gummy residue which upon recrystallization from benzene yielded a further 7.5 g. of white, granular crystals of diphenylphosphonitrile trimer. The identity of this crop of crystals was established by melting point, mixed melting point, and infrared spectroscopy. The total yield of trimer corresponds to 54% of theory.

The mother liquor from the above recrystallization was evaporated on the steam bath. The residue was dissolved in acetone and treated with "Nuchar." On standing, 3.3 g. of a white crystalline product melting over the range 217–229° separated. Repeated recrystallization yielded a white, granular product (denoted below as compound III) melting sharply at 268° with decomposition.

Identification of Compound III.—The infrared spectrum of compound III showed the characteristic P=N—P band at 1260 cm^{-1} and the P-phenyl bands at 1440 and 1000 cm^{-1} . There was no evidence of the P-NH—P band. *Anal.* Found: C, 66.69; H, 5.02; N, 6.26; P, 14.15; Cl, 7.88; mol. wt., 446. Calcd. for $\text{C}_{24}\text{H}_{21}\text{ClN}_2\text{P}_2$: C, 66.64; H, 4.88; N, 6.46; P, 14.28; Cl, 7.95; mol. wt., 434.

The nuclear magnetic resonance spectrum of compound III was run at 19.3 Mc. using a Varian high resolution spectrometer. Two peaks for phosphorus corresponding to chemical shifts of 15.0 and 27.5 p.p.m. to low field in comparison to an 85% phosphoric acid solution as standard were obtained. The analysis, molecular weight, infrared spectrum, and nuclear magnetic resonance spectrum of compound III may be rationalized in terms of the structural formula



Other resonance forms also might be considered as making a contribution to the structure. It will be noted that this formula differs by one nitrogen atom and three hydrogen atoms from that of compound II obtained in the diphenylchlorophosphine-ammonia-chloramine reaction. Mixed melting points of the compounds II and III clearly demonstrated that they are different species. Assuming the above formula, compound III was obtained in 15% yield based on the diphenylchlorophosphine starting material.

Pyrolysis of Compound III.—A 1.0 g. sample of compound III was heated at 250–255° under 1 mm. pressure for a period of 10 hr. yielding 0.8 g. of a white, crystalline sublimate. Fractional crystallization of this sublimate from benzene yielded diphenylphosphonitrile trimer and tetramer in a weight ratio of 5:1, respectively. Each of these products was identified by its infrared spectrum, its melting point, and by mixed melting points with authentic samples of the trimer and tetramer. The combined amounts of trimer and tetramer correspond to approximately 87% yield based on compound III.

Discussion

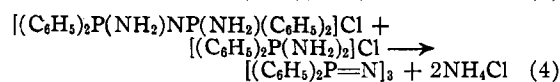
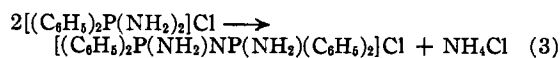
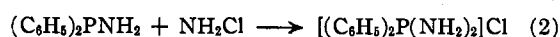
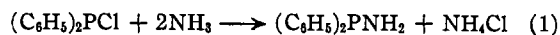
The experiments described above show that diphenylphosphonitrilic trimer can be prepared by the reaction of diphenylchlorophosphine with the gaseous mixture of ammonia and chloramine, and further that the compound



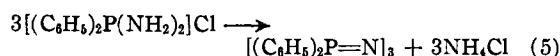
is formed in the reaction. Further, it was shown that this compound is identical with the intermediate obtained by Bezman and Smalley in the $(\text{C}_6\text{H}_5)_2\text{PCl}_3\text{-NH}_3$ reaction.

By means of pyrolysis of this compound the total yield of diphenylphosphonitrile trimer can be greatly increased and a considerable amount of the tetramer obtained.

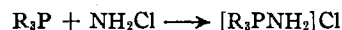
We are far from being able to state with certainty a mechanism for this reaction. However, the following series of steps seems reasonable



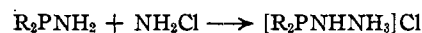
or



In support of this mechanism it may be pointed out that diphenylchlorophosphine undergoes rapid and complete ammonolysis in liquid ammonia and in solutions of ammonia in inert solvents. Crude $(\text{C}_6\text{H}_5)_2\text{PNH}_2$ mixed with some $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})(\text{OH})$ has been obtained in good yields from the $(\text{C}_6\text{H}_5)_2\text{PCl-NH}_3$ reaction in chloroform. Thus, step 1 has been established. Furthermore, the well established chloramination of tertiary phosphines²



lends credibility to step 2 of the mechanism. The alternative reaction



is not an attractive assumption in view of the established fact that quaternization of aminophosphines has been shown to occur on the phosphorus atom.⁸

The trimer crystallizes from tetrachloroethane as the adduct $[(\text{C}_6\text{H}_5)_2\text{P}=\text{N}]_3 \cdot 3\text{Cl}_2\text{CHCHCl}_2$. The postulated mechanism explains the formation of compound II and corresponds to the fact that only trimer (no tetramer) is obtained from the reaction in tetrachloroethane. Compound II can be made to undergo further condensation to yield both diphenylphosphonitrile trimer and tetramer but this reaction occurs only under pyrolytic conditions above the melting point (240°) of compound II. Compound II has been shown to be quite stable in refluxing tetrachloroethane. The reactive intermediate in the reaction in tetrachloroethane solution thus is assumed to be diaminodiphenylphosphonium chloride $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)_2]\text{Cl}$ (or the diaminodiphenylphosphonium ion, $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)_2]^+$). The fact that a mixture of trimer and compound II rather than one or the other is obtained in the reaction presumably results from the competition of steps 3 and 4 or 5 for the diaminodiphenylphosphonium chloride intermediate.

The fact that compound II may be pyrolyzed to give tetramer as well as trimer offers at least

(8) H. Sisler and N. Smith, *J. Org. Chem.*, in press.

the formal possibility of forming higher cyclic or linear polymeric phosphonitriles under pyrolytic conditions.

One of the most interesting aspects of this work lies in the fact that it provides a well-substantiated instance of molecular addition compound formation by a phosphonitrilic species. If we assume that the compound $[(C_6H_5)_2PN]_3 \cdot 3Cl_2CHCHCl_2$ is formed through electron pair donor-acceptor interaction, one must conclude that the phosphonitrile trimer is acting as electron acceptor for one would not expect tetrachloroethane to play this role under the circumstances of this experiment. However, in the absence of X-ray data discussion of the structure of this compound is purely speculative.

The results of these studies demonstrate conclusively that diphenylphosphonitrile trimer or tetramer may be obtained in considerable yields by the reaction of diphenylchlorophosphine with hydrazine monohydrochloride or dihydrochloride in the absence of solvent or suspended in tetrachloroethane. It is interesting to note that in those reactions carried out in tetrachloroethane as a solvent and which, hence, were run at temperatures not greatly in excess of 145° , only trimer plus compound III was obtained—no tetramer. However, in the reactions in absence of solvent in which the temperature was held in the range of

$245\text{--}250^\circ$ the product was preponderantly tetramer though we are not able to say definitely that compound III is not formed in these reactions. Thus, there is a parallelism between the reactions of diphenylchlorophosphine with ammonia plus chloramine and the reaction with hydrazine hydrochloride.

The assumption that compound III is an intermediate in the reaction of diphenylchlorophosphine with hydrazine hydrochloride in tetrachloroethane analogous to the function of compound II in the corresponding ammonia-chloramine reaction is certainly an attractive speculation. The fact that compound III differs from compound II by one molecule of ammonia is not too surprising when it is considered that compound II is formed in the presence of an excess of ammonia, whereas compound III is formed under acidic conditions—hydrogen chloride is liberated during the reaction.

Acknowledgments.—We are pleased to acknowledge the support of much of this research by W. R. Grace and Company through a contract with the University of Florida. We also would like to express our gratitude to Professor Wallace S. Brey, Jr., of the Department of Chemistry of the University of Florida, under whose direction the nuclear magnetic resonance spectra were determined and interpreted.