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Positional and *cis–trans* N-Methylaminotriphosphonitriles. The Use of H^1 Nuclear Magnetic Resonance in Configurational Analysis

By C. T. Ford, F. E. Dickson, and I. I. Bezman

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Through aminolysis with methylamine, phenylation with benzene in the presence of aluminum chloride, and a combination of both, a series of derivatives of trimeric phosphonitrilic chloride has been made. H^1 nuclear magnetic resonance spectra were obtained for these compounds and used to determine both their positional and *cis-trans* configurations. The structural analysis is based on consideration of the number of chemical environments and the values of the coupling constants.

I. Introduction

We have previously shown[1] that H^1 nuclear magnetic resonance spectra can be used to determine the positional and *cis–trans* configurations of a number of N,N-dimethylaminotriphosphonitriles. The procedure was then applied to an analysis of selected comparable N-methylamino compounds and the results are presented herein. These are in substantial agreement with the earlier findings and indicate that aminolysis of trimeric phosphonitrilic chloride, $(NPCl_2)_3$, with methylamine proceeds in a manner similar to that when dimethylamine is used, *i.e.*, the chlorines are replaced nongeminally. It was also found that treatment of $P_3N_3Cl_4(NHCH_3)_2$, in which the $-NHCH_3$ groups are attached to separate phosphorus atoms, with benzene in the presence of aluminum chloride will give replacement of the chlorine atoms in the $\equiv P(Cl)(NHCH_3)$ groups by phenyls; the $\equiv PCl_2$ group is unaffected. The apparent coupling constants,[1] J'_{PH}, for the methyl protons in the groups $\equiv P(NHCH_3)_2$, $\equiv P(Cl)(NHCH_3)$, and $\equiv P(C_6H_5)(NHCH_3)$ were found to be 13.0, 18.5, and 13.7 c.p.s., respectively. These are similar to the J'_{PH} values for the comparable groups, $\equiv P[N(CH_3)_2]_2$, $\equiv P(Cl)[N(CH_3)_2]$, and $\equiv P(C_6H_5)[N(CH_3)_2]$, 11.8, 17.5, and 12.8 c.p.s., which we reported previously.

II. Experimental

Using $(NPCl_2)_3$ as a starting material and carrying out aminolysis with methylamine, phenylation with benzene in the presence of $AlCl_3$, and a combination of both, various derivatives were made as shown in Charts I–III.

The specific configurations as shown for the compounds capable of existing in isomeric forms are based, for the most part, on proton magnetic resonance spectra; these are discussed separately.

Benzene, diethyl ether, and petroleum ether (b.p. 30–60°) were dried over freshly extruded sodium wire. Chloroform was dried overnight over molecular sieves 4A. Trimeric phosphonitrilic chloride, $(NPCl_2)_3$, purchased commercially, was recrystallized to constant melting point from petroleum ether before use.

Chart I
Aminochlorotriphosphonitriles

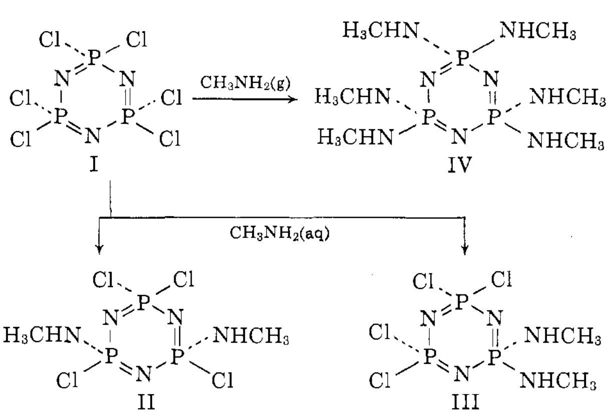


Chart II
Derivative Obtained by Aminolysis
of Diphenyltetrachlorotriphosphonitrile

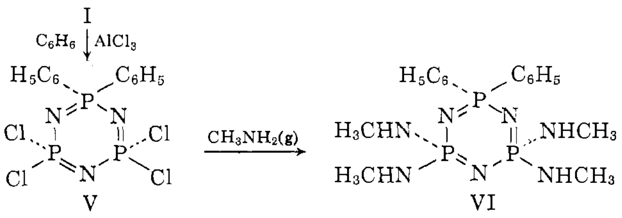
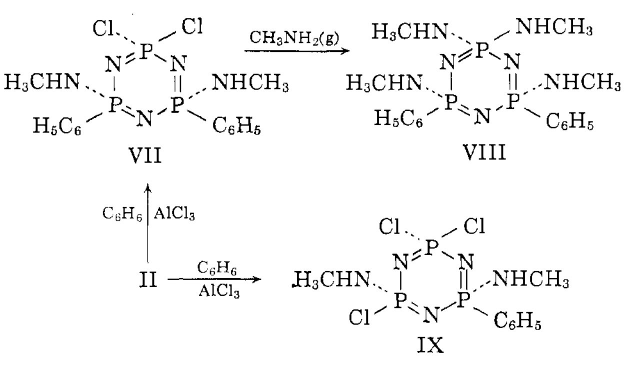


Chart III
Arylation and Aminolysis Derivatives
of Bis-N-methylaminotetrachlorotriphosphonitrile



Aminochlorotriphosphonitriles. $P_3N_3Cl_4(NHCH_3)_2$ (II and III).—To a solution of 0.06 mole of $(NPCl_2)_3$ in 80 ml. of $(C_2H_5)_2O$ in a pressure flask was added a 30% aqueous solution of CH_3NH_2 in a 1:4.3 $(NPCl_2)_3$:CH_3NH_2 mole ratio. The flask was stoppered and shaken for 5 min. An exothermic reaction occurred. After phase separation, the organic phase was dried over calcium sulfate, filtered, and evaporated to dryness under vacuum, taking care to avoid heating the products. Extraction of the solids

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(1) C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 177 (1964).

with petroleum ether and recrystallization from the same solvent gave III in 0.5% yield, m.p. 131°. The petroleum ether insoluble portion was recrystallized once from $(C_2H_5)_2O$ to give II in approximately 70% yield, m.p. 99° (lit. m.p. 85[2] and 100–100.5°[3]). *Anal.* Calcd. for $C_2H_8Cl_4N_5P_3$: C, 7.13; H, 2.39; Cl, 42.10; N, 20.79; P, 27.59. Found (compound III, m.p. 131°): C, 7.37; H, 2.65; Cl, 41.66; N, 20.84; P, 27.78. Found (compound II, m.p. 99°): C, 7.14; H, 2.41; Cl, 42.05; N, 20.63; P, 27.84.

$P_3N_3(NHCH_3)_6$ (IV).—A solution of 0.03 mole of $(NPCl_2)_3$ in 200 ml. of $(C_2H_5)_2O$ was cooled in an ice bath and saturated with anhydrous, gaseous CH_3NH_2 while being stirred constantly. The mixture was brought slowly to room temperature and held there for 4 hr. Amine addition was continued during the entire operation, which lasted about 8 hr. The total amount of amine bubbled through the solution was 2.5 moles. Excess amine was removed by purging with N_2. At the end of the reaction no $(C_2H_5)_2O$-soluble material was present. Removal and extraction of the solids with hot $CHCl_3$ and recrystallization from the same solvent gave IV in 60% yield, m.p. 259°, in agreement with the literature value of 258°.[2,4] *Anal.* Calcd. for $C_6H_{24}N_9P_3$: C, 22.86; H, 7.67; N, 39.99; P, 29.48. Found: C, 23.14; H, 7.74; N, 40.30; P, 29.65.

Phenylaminotriphosphonitriles. $P_3N_3Cl_4(C_6H_5)_2$ (V).—A solution of 0.26 mole of $(NPCl_2)_3$ and 1.05 moles of anhydrous $AlCl_3$ in 400 ml. of C_6H_6 was refluxed for 7 days, then cooled and treated slowly with water until HCl evolution ceased. The C_6H_6 layer was washed twice with water, dried over calcium sulfate, and filtered, and the filtrate was evaporated to dryness leaving an oily material. Fractional crystallization of the oil with petroleum ether and recrystallization from the same solvent gave V in 60% yield, m.p. 97° (lit.[5,6] m.p. 95°). Degradative hydrolysis gave diphenylphosphinic acid, confirming the geminal configuration of the phenyl groups.

$P_3N_3(C_6H_5)_2(NHCH_3)_4$ (VI).—Gaseous CH_3NH_2, 1.5 moles, was bubbled into 0.05 mole of V in 200 ml. of refluxing C_6H_6 for 8 hr. Excess CH_3NH_2 was removed by purging with N_2. By-product $CH_3NH_2 \cdot HCl$ was removed by filtering the warm solution. The filtrate was evaporated to dryness. Recrystallization of the residue from C_6H_6 gave VI in 85% yield, m.p. 178° (lit.[6,7] m.p. 174°). *Anal.* Calcd. for $C_{16}H_{26}N_7P_3$: C, 46.94; H, 6.40; N, 23.95; P, 22.70. Found: C, 47.09; H, 6.63; N, 24.00; P, 22.61.

$P_3N_3Cl_2(C_6H_5)_2(NHCH_3)_2$ (VII).—A solution of 0.044 mole of II and 0.17 mole of anhydrous $AlCl_3$ in 200 ml. of C_6H_6 was refluxed for 6 days and processed as in the preparation of V. The oil crystallized slowly from a mixture of $(C_2H_5)_2O$ and petroleum ether. Recrystallization from the same solvent mixture gave VII in 20% yield, m.p. 145°. A solution of 0.044 mole of II and 0.10 mole of anhydrous $AlCl_3$ refluxed for 6 days also gave VII but in 12% yield. The nongeminal position of the phenyl groups was established by hydrolytic degradation to phenylphosphonic acid and confirmed by the proton resonance data. *Anal.* Calcd. for $C_{14}H_{18}Cl_2N_5P_3$: C, 40.02; H, 4.32; Cl, 16.88; N, 16.67; P, 22.12. Found: C, 40.07; H, 4.41; Cl, 17.04; N, 16.79; P, 22.47.

$P_3N_3(C_6H_5)_2(NHCH_3)_4$ (VIII).—Gaseous CH_3NH_2, 1.1 moles, was bubbled into 0.03 mole of VII in 150 ml. of refluxing C_6H_6 for 8 hr. Excess CH_3NH_2 was removed by purging with N_2. By-product $CH_3NH_2 \cdot HCl$ was removed by filtration. The filtrate was evaporated to dryness. Recrystallization from C_6H_6 gave VIII in 63% yield, m.p. 125°. *Anal.* Calcd. for $C_{16}H_{26}N_7P_3$: C, 46.94; H, 6.40; N, 23.95; P, 22.70. Found: C, 46.37; H, 6.56; N, 23.30; P, 21.88.

$P_3N_3Cl_3C_6H_5(NHCH_3)_2$ (IX).—A solution of 0.044 mole of II and 0.088 mole of anhydrous $AlCl_3$ in 200 ml. of C_6H_6 was refluxed for 3 days and processed as in the preparation of V. Crystallization of the oil from $(C_2H_5)_2O$–petroleum ether and recrystallization from the same solvent mixture gave IX in 6% yield, m.p. 138°. Starting material (II), 10%, was also recovered unreacted. *Anal.* Calcd. for $C_8H_{13}Cl_3N_5P_3$: C, 25.38; H, 3.46; Cl, 28.10; N, 18.50; P, 24.55. Found: C, 25.41; H, 3.71; Cl, 27.76; N, 18.69; P, 24.75.

Table I gives the principal characterizing infrared absorption peaks for the various compounds. All absorptions are strong.

TABLE I

PRINCIPAL CHARACTERISTIC INFRARED ABSORPTION PEAKS (CM.$^{-1}$)

Compd.	Formula	P=N stretch[a]	P–C_6H_5[b]
II	$P_3N_3Cl_4(NHCH_3)_2$	1210, 1200	
III	$P_3N_3Cl_4(NHCH_3)_2$	1225, 1170	
IV	$P_3N_3(NHCH_3)_6$	1180	
VI	$P_3N_3(C_6H_5)_2(NHCH_3)_4$	1190	1440
VII	$P_3N_3Cl_2(C_6H_5)_2(NHCH_3)_2$	1205, 1170	1440
VIII	$P_3N_3(C_6H_5)_2(NHCH_3)_4$	1190, 1170	1440
IX	$P_3N_3Cl_3C_6H_5(NHCH_3)_2$	1205, 1180	1440

[a] L. W. Daasch, *J. Am. Chem. Soc.*, **76**, 3403 (1954). [b] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

III. Proton Magnetic Resonance

Proton magnetic resonance spectra were obtained for 20% solutions in $CDCl_3$ on a Varian Model A-60 spectrometer. Chemical shift measurements were made from tetramethylsilane as an internal reference. The spectra of this series of monomethylaminotriphosphonitriles are similar to those of the dimethylaminotriphosphonitriles.[1] In each case, however, an additional resonance, characteristic of the NH protons, was observed. These resonances were broad and diffuse and did not significantly contribute to the interpretation of the spectra. (The integrals were consistent with the proposed structures.) The N-methyl proton resonance spectrum contains a doublet for each $-NHCH_3$ group in a particular chemical environment in the molecule. By environment is meant the nuclei in close proximity to the $-NHCH_3$ group. The groups attached to the other phosphorus atoms and on the same side of the ring comprise one influence. A second effect is associated with the influence of the group attached to the phosphorus atom bearing the $-NHCH_3$ group.

The apparent coupling constant, J'_{PH}, ranges from about 12 to 19 c.p.s. and is dependent on the nature of the second substituent bonded directly to the phosphorus carrying the $-NHCH_3$. The data in Table I indicate that the $\equiv P(Cl)(NHCH_3)$, $\equiv P(C_6H_5)(NHCH_3)$, and $\equiv P(NHCH_3)_2$ groups are characterized by J'_{PH} values of about 18.5, 13.7, and 13.1 c.p.s., respectively. Thus the coupling constants indicate the group attached to the phosphorus atoms and the number of doublets indicates different sets of environments. The J'_{PH} values, along with consideration of the number of doublets in the spectra and a decoupling experiment, have enabled delineation of both positional and *cis–trans* isomerism.

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

[3] H. Bode, K. Butow, and G. Lienau, *Ber.*, **81**, 547 (1948).

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

[5] H. Bode and H. Bach, *Ber.*, **75B**, 215 (1942)

[6] M. Becke-Goehring and K. John, *Z. anorg. allgem. Chem.*, **304**, 126 (1960).

[7] M. Becke-Goehring and K. John, *Angew. Chem.*, **70**, 657 (1958).

Compounds II, III, and IV were obtained from starting material, I, through the action of methylamine. Compounds II and III, with different melting points, are isomers. The n.m.r. spectra of all three of these compounds show one doublet structure each with J'_{PH} = 18.9, 13.4, and 12.8 c.p.s., respectively, due to coupling to the neighboring phosphorus atom.

Because compound IV has unambiguously only the $\equiv$P(NHCH$_3$)$_2$ grouping, the single observed coupling constant, J'_{PH} = 12.8 c.p.s., is established as characteristic of this grouping.

The compound $P_3N_3Cl_4(NHCH_3)_2$ can exist in three isomeric forms: one in which both –NHCH$_3$ groups are attached to the same phosphorus, and two in which the –NHCH$_3$ groups are attached to different phosphorus atoms, the difference between these being *cis* and *trans* configurations. Sequential replacement of chlorine by strongly basic amines such as $(CH_3)_2NH$ and CH_3NH_2 has been established[1,2,4] as occurring in a nongeminal pattern. The single observed coupling constant, J'_{PH} = 18.9 c.p.s., for compound II is substantially different from that established for the $\equiv$P(NHCH$_3$)$_2$ grouping; this both indicates the nongeminal location of the –NHCH$_3$ groups and establishes J'_{PH} = 18.9 c.p.s. for the $\equiv$P(Cl)(NHCH$_3$) grouping. The spectrum is not sufficient to establish the *cis* or *trans* configuration.

TABLE II

PROTON MAGNETIC RESONANCE DATA

Compound		No. of doublets	J'_{PH} for $\equiv$P(X)(NHCH$_3$), c.p.s.			Chemical shift, p.p.m.
No.	Formula		X = Cl	X = NHCH$_3$	X = C$_6$H$_5$	
II	$P_3N_3Cl_4(NHCH_3)_2$	1	18.9			2.62
III	$P_3N_3Cl_4(NHCH_3)_2$	1		13.4		2.62
IV	$P_3N_3(NHCH_3)_6$	1		12.8		2.57
VI	$P_3N_3(C_6H_5)_2(NHCH_3)_4$	1		13.0		2.52
VII	$P_3N_3Cl_2(C_6H_5)_2(NHCH_3)_2$	1			13.4	2.67
VIII	$P_3N_3(C_6H_5)_2(NHCH_3)_4$	1[a]		13.0		2.62
IX	$P_3N_3Cl_3C_6H_5(NHCH_3)_2$	2	18.2		14.0	2.70, 2.63

[a] Although only one doublet was observed in the normal spectrum, the decoupled spectrum indicated that three were present.

It might be expected that compound III is the other nongeminal isomer; however, the J'_{PH} value of 13.4 c.p.s. observed for it shows that it is the geminally-substituted isomer. Although this is an apparent exception to the normal substitution pattern, it should be noted that compound III was isolated only in 0.5% yield while compound II was obtained in 70% yield.

In compound VI, made from compound V in which the C$_6$H$_5$ groups are known[5] to be attached to the same phosphorus, the four –NHCH$_3$ groups must be equivalent and appear only in the $\equiv$P(NHCH$_3$)$_2$ grouping. The spectrum shows only one doublet with J'_{PH} = 13.0 c.p.s., in accord with the J'_{PH} value of 12.8 c.p.s. observed for the same grouping in compound IV.

The treatment of compound II with benzene in the presence of AlCl$_3$ results in replacement of two Cl atoms by C$_6$H$_5$ groups. The replacement is nongeminal, in sharp contrast with the geminal substitution observed when the reaction is carried out with $(NPCl_2)_3$ and in accord with that previously observed and reported[1] when carried out with $P_3N_3Cl_4[N(CH_3)_2]_2$, in which the –N(CH$_3$)$_2$ groups are attached to different phosphorus atoms. The nongeminal location of the C$_6$H$_5$ groups in compound VII was proved by hydrolytic degradation and isolation of phenylphosphonic acid rather than diphenylphosphinic acid.

The spectrum of compound VII exhibits one doublet with J'_{PH} = 13.4 c.p.s. This finding and the isolation of phenylphosphonic acid on hydrolysis of the compound are sufficient to establish that each C$_6$H$_5$ group is present in a $\equiv$P(C$_6$H$_5$)(NHCH$_3$) grouping. If one C$_6$H$_5$ were held in the $\equiv$P(C$_6$H$_5$)(Cl) grouping, two doublets would appear in the spectrum with at least one having J'_{PH} = 18.9 c.p.s. It is not possible to assign *cis* and *trans* configuration.

Compound VIII was obtained from VII by further treatment with CH$_3$NH$_2$ and serves as an illustration of some difficulties of interpretation which may be encountered when chemical shifts for different environments have approximately the same value. In compound VIII, there should be present one $\equiv$P(NHCH$_3$)$_2$ and two $\equiv$P(C$_6$H$_5$)(NHCH$_3$) groupings. The J'_{PH} values for these groupings were established as 12.8 c.p.s. (compound IV) and 13.0 c.p.s. (compound VI) for the former and 13.4 c.p.s. (compound VII) for the latter. The observed spectrum for compound VIII showed only one rather ambiguous doublet typically broadened and complicated by long range phosphorus coupling[8] with J'_{PH} = 13.0 c.p.s. For this to be authentically only one doublet and not a composite of several resonances with only a small chemical shift difference, all –NHCH$_3$ groups in compound VIII would have to be equivalent. This would mean that a C$_6$H$_5$ group had migrated so that in compound VIII the –NHCH$_3$ groups are located in two $\equiv$P(NHCH$_3$)$_2$ groupings, *i.e.*, that compounds VI and VIII are identical. This is obviously not so because they have different melting points. The difference was confirmed by further investigation.

Assuming that the observed resonance is actually two or more resonances separated by a small, unobservable chemical shift difference and that the –NHCH$_3$ groups are, indeed, located in $\equiv$P(NHCH$_3$)$_2$ and $\equiv$P(C$_6$H$_5$)(NHCH$_3$) groupings, two possibilities exist. If the C$_6$H$_5$ groups are in a *trans* configuration, two doublets should be present in a 1:1 area ratio, each

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[8] R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, **2**, 377 (1963).

representing an equal number (six) of methyl protons. If the C_6H_5 groups are in a *cis* configuration, there would be three $-NHCH_3$ environments and three doublets in a 2:1:1 area ratio. Each $-NHCH_3$ group in the two $\equiv P(C_6H_5)(NHCH_3)$ groupings would be equivalent and account for six methyl protons. The $-NHCH_3$ groups in the single $\equiv P(NHCH_3)_2$ group would be in different environments and account for three methyl protons each.

In order to clarify the interpretation of this spectrum, a decoupling experiment was performed. The n.m.r. sample was irradiated at the Larmor frequency of the phosphorus nuclei (24.28 Mc.) while the n.m.r. spectrum of the protons was observed. When completely decoupled, the spectrum revealed two singlets separated only by 3.5 c.p.s. and in the ratio of 3:1. Only the *cis* compound (2:1:1) could give this ratio, the similarity in the methyl proton environments accounting for the inability to separate completely the three singlets. The existence of more than one singlet confirmed that the C_6H_5 groups were still attached to different phosphorus atoms.

Since compound VIII was obtained from compound VII, which was originally obtained from compound II, it appears that, assuming no rearrangement during reaction, compound II and compound VII are also in *cis* configurations.

Compound IX, also obtained from compound II, showed two doublets in its n.m.r. spectrum with coupling constants, J'_{PH}, of 18.2 and 14.0 c.p.s. The value of these coupling constants is consistent with the interpretation that the $-NHCH_3$ groups are located in $\equiv P(Cl)(NHCH_3)$ and $\equiv P(C_6H_5)(NHCH_3)$ groupings. The n.m.r. spectrum does not differentiate *cis–trans* isomers but, again assuming no rearrangement during reaction, the $-NHCH_3$ groups remain *cis* to each other.

Chemical shift data for each individual compound have not been considered as a deciding factor in determining the configuration. Chemical shift data can only be presumed accurate when each solution is made up to exactly the same concentration even though concentration dependence may be slight. Chemical shift values for n.m.r. absorptions within the same spectrum, however, can be compared since no concentration effect will be noted. It is not to be inferred, in any case, that the chemical shift data could not be used as supporting evidence of our above conclusions.

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CONTRIBUTION FROM MONSANTO COMPANY
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Nuclear Magnetic Resonance Study of Equilibrated Methyl Polyarsenites and Related Families of Compounds

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With heating to effect dissolution, arsenious oxide may be dissolved in trimethyl arsenite or tris(dimethylamino)arsine to give homogeneous liquids. The solutions in tris(dimethylamino)arsine show a great increase in viscosity with increasing arsenious oxide content beyond the composition of 1 mole of As_2O_3 per mole of $As[N(CH_3)_2]_3$. Arsenious sulfide could be similarly dissolved in tris(dimethylamino)arsine but to lesser amounts, with no more than 0.5 mole of As_2S_3 per mole of $As[N(CH_3)_2]_3$ in solution at 150°. All attempts to dissolve arsenious sulfide in trimethyl arsenite, arsenic trichloride, or arsenic trifluoride were unsuccessful. Proton nuclear magnetic resonance (n.m.r.) showed that the dissolution of arsenious oxide in either trimethyl arsenite or tris(dimethylamino)arsine—as well as the dissolution of arsenious sulfide in tris(dimethylamino)arsine—is accompanied by scrambling reactions whereby a family of compounds is formed.

Introduction

This paper is a continuation of the study[1] of families of compounds based on triply connected arsenic with bridging oxygen atoms. However, in the work reported here, H^1 nuclear magnetic resonance (n.m.r.) was used instead of the F^{19} n.m.r. employed in the previous paper. At the time this work was started, there seemed to be no literature on the chemistry described herein except for a short note.[2] After this work was completed, a paper[2] describing ebullioscopic measurements on trimethyl arsenite as a solvent for arsenious oxide appeared in print. Although the ebullioscopic data showed too much scatter to be interpreted in detail, these measurements are not inconsistent with the findings given below.

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[1] J. R. Van Wazer, K. Moedritzer, and D. W. Matula, *J. Am. Chem. Soc.*, **86**, 807 (1964).

[2] E. Thilo and P. Flögel, *Z. anorg. allgem. Chem.*, **329**, 244 (1964). Also see *Angew. Chem.*, **69**, 754 (1957).