equivalent to those obtained from eq. 8

$$\tau = A/2\pi(\nu_1 - \nu_2) \qquad (9)$$

where A is a constant[9] ranging from 0.5 to 10, and ν_1 and ν_2 are the frequencies in c.p.s. of the neighboring lines. It was assumed that $A = \sqrt{2}$ when the saddle between a neighboring pair of peaks barely disappeared. The data obtained by use of eq. 8 and 9 are reported in Fig. 2. We found that treatment of any of the single resonances by eq. 8 or pairs of neighboring resonances by eq. 9 gave data which fitted on a single line for a given composition in the AsF_3–As_2O_3 system. Thus, within better than an order of magnitude, the rates of exchange between the various structural units are the same. This exchange may involve fluorine for fluorine and/or fluorine for bridging oxygen. However, exchange of oxygen solely for oxygen cannot lead to the observed n.m.r. spectra since the *neso* peak would not broaden with this kind of exchange but instead there would simply be coalescence of the end peaks with each other and the middle peaks with each other.

Discussion

The gel point has been calculated to occur at R = 1.485 assuming that the macromolecules do not contain small rings. This R-value is probably near the true gel point since an appreciable tendency for the formation of small rings would give unduly high values in Table I for the n.m.r. resonance peak at 8.6 p.p.m. (especially for R-values $\geq$ *ca.* 1.5, there should be some simple molecules based on small rings). Since flow is found for R-values considerably smaller than 1.485, it would appear that the flow process—at least in the more viscous systems—involves the making and breaking of As–O–As linkages.

It is interesting to note that for R = 2.0, the activation energy for viscous flow calculated from eq. 4 is 4.11 kcal. as compared to the approximate value of 4.3 kcal. for the activation energy for the fluorine exchange measured by n.m.r. (see Fig. 2). Likewise, for the composition corresponding to R = 1.25, the activation energy for flow is 9.06 kcal. as compared to 9.5 kcal. for the fluorine exchange. These results probably mean that the energy barrier for flow is the same as that for the observed exchange involving fluorine atoms.

The AsF_3–As_2O_3 system studied here represents an interesting intermediate case where the rate of reorganization is so fast that one could not hope to separate individual species at room temperature. However, these species have a reasonably long lifetime and there is no question as to their existence. This system is roughly halfway between the very stable molecules based on C–C linkages and the extremely rapidly reorganizing association polymers linked together by hydrogen bonds; *e.g.*, water and glycerol.

Since the equilibrium constants for reorganization in the AsF_3–As_2O_3 system are close to random, this means that a number of the smaller branched molecules will be present in relatively large amounts in equilibrium with the other species for R-values in the neighborhood of 1.5–2.0. Thus, the "isotetra" molecule based on three ends and one branch is calculated[4] to be present to the amount of 1.1% and the "isopenta" molecule based on three ends, a middle, and a branch to correspond to 1.4% of the total arsenic in the mixture of polyarsenous oxyfluoride molecules with an R-value of 1.74.

Acknowledgment.—We wish to thank Claude H. Dungan for running the many F^{19} n.m.r. spectra involved in this study and Allan W. Dickinson for the necessary computer runs.

[Contribution from Monsanto Chemical Co., Central Research Department, St. Louis, Mo.]

Exchange of Parts between Molecules at Equilibrium. III. Nonrandom Redistribution of Dialkylamino Groups and Halogens on Triply Connected Phosphorus

By J. R. Van Wazer and Ludwig Maier[1]

Received July 11, 1963

Ligand-interchange reactions were carried out between PCl_3 and $P[N(C_2H_5)_2]_3$, PCl_3 and $PCl[N(CH_3)_2]_2$, CH_3PCl_2 and $CH_3P[N(CH_3)_2]_2$ or $CH_3P[N(C_2H_5)_2]_2$, CH_3PBr_2 and $CH_3P[N(CH_3)_2]_2$, $CH_3P[N(C_2H_5)_2]_2$ and PCl_3, and between CH_3PCl_2 and $P[N(C_2H_5)_2]_3$. In all cases, the equilibrium constant for disproportionation of the intermediate compounds obtained by exchanging halogens and dialkylamino groups was found to be so small that it could not be detected within experimental error ($K < 5 \times 10^{-4}$) from the stoichiometry of the reaction products. However, from calorimetric measurements of the enthalpy of the disproportionation reaction, the equilibrium constants were calculated on the assumption that the entropy consists only of the entropy of mixing. The heat of formation of bis-(diethylamino)-chlorophosphine was found to be −76 kcal./mole and of diethylaminodichlorophosphine −77 kcal./mole. The exchange of chlorine and dialkylamino groups between triply connected phosphorus atoms represents the unusual case corresponding to a large enthalpy for a redistribution reaction.

Introduction

Although this series is primarily concerned with the elucidation of families of compounds, a few papers will be devoted to the scrambling reactions of *neso* molecules when such studies give important information concerning exchange of parts between molecules. In this paper such work is reported.

In single-phase equilibrium reactions in which two or more different types of substituents undergo exchange between a given kind of central atom or moiety, there is no bond-energy contribution to the free energy of the exchange reactions since the total number of bonds between the various pairs of bonded atoms remains constant. Thus, to the same approximation that constant bond energies,[2] electronegativities, and, where appropriate, *a priori* assignments of π-bond contributions to the enthalpy[3] may be used to calculate the heat of a reaction, it is expected that the enthalpy of a scrambling reaction will be zero. This paper presents information concerning a system in which there is a large enthalpy contribution to the free energy which causes the scrambling equilibria to be extremely nonrandom. Although a considerable amount of information is available on reorganization of substit-

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[1] On leave of absence during 1960 from Monsanto Research S. A., Zurich.

[2] *E.g.*, M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

[3] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 28–34; also Chapter 12.

uents between phosphorus compounds, all previously known scrambling reactions involving *neso* phosphorus have exhibited only small deviations from randomness.[4] This is also true for all adequately studied families of compounds based on phosphorus in the backbones, except for the polyphosphates.[5]

Experimental Operations

The phosphorus trichloride used in this study was redistilled from the Monsanto commercial-grade product. Tris-(diethylamino)-phosphine was prepared from phosphorus trichloride and diethylamine by standard procedures.[6] The new compound methylbis-(dimethylamino)-phosphine was made according to the general procedure one of us has published elsewhere.[7] The diethylamino derivative was prepared in a similar manner. For comparison purposes, bis-(dimethylamino)-chlorophosphine was made according to the technique described in a patent.[8] The two new compounds $CH_3P[N(C_2H_5)_2]_2$ and $CH_3PCl[N(C_2H_5)_2]$ have b.p. 78° (5 mm.) and 182° (740 mm.), respectively.

In the equilibrium studies, weighed amounts of the two reagents were combined in a tube which was cooled in liquid nitrogen. After sealing the tube, it was then warmed up to room temperature, and disproportionation equilibrium was found to have been achieved as soon as the temperature was stabilized and a nuclear magnetic resonance (n.m.r.) measurement could be made. When the reagents were artlessly combined at room temperature, the reaction was extremely rapid with almost explosive spattering. However, when the chlorine compound was carefully floated upon the amino compound, the tube could be sealed with inappreciable reaction. Upon shaking such a sealed tube, the reaction occurred immediately, with considerable evolution of heat. In this case, the same equilibrium values were obtained as were achieved by combining the reagents while very cold. From these procedures, the half-life for the disproportionation reaction was estimated to be less than 30 sec. at 25°.

The P^{31} n.m.r. technique was the same as described elsewhere.[9] The chemical shifts for the various compounds studied in this investigation are given in Table I.

TABLE I

P^{31} N.M.R. CHEMICAL SHIFTS

	P.p.m.[a]		P.p.m.[a]
$P[N(CH_3)_2]_3$	−123[b]	$CH_3P[N(CH_3)_2]_2$	−86
$P[N(C_2H_5)_2]_3$	−119[c]	$CH_3P[N(C_2H_5)_2]_2$	−80
$PCl[N(CH_3)_2]_2$	−160	$CH_3PCl[N(CH_3)_2]$	−151
$PCl[N(C_2H_5)_2]_2$	−154	$CH_3PBr[N(CH_3)_2]$	−161
$PCl_2[N(CH_3)_2]$	−166	$CH_3PCl[N(C_2H_5)_2]$	−143
$PCl_2[N(C_2H_5)_2]$	−163		

[a] Measured to ±1 p.p.m. on liquid samples by the tube-interchange technique. [b] Reported value = −122 ± 2 p.p.m.[10] [c] Reported value = −118 ± 3 p.p.m.[10]

The heats of several of the reactions were measured in a calorimeter constructed from a 1-l. dewar flask, with electrical heating for calibration. Several cc. of one reagent was placed in one arm of a glass vessel having the shape of an inverted U and the desired stoichiometric amount of the other reagent was placed in the other arm. After the U-shaped vessel was sealed and brought to equilibrium in the water bath within the calorimeter, it was turned upside down so as to mix the reagents. The resulting increase in temperature (in the range of 1–2°) of the water in the calorimeter was read with a Beckmann thermometer.

Equilibrium Measurements

Exchange on Three Sites.—When phosphorus trichloride, PCl_3, and tris-(diethylamino)-phosphine, $P[N(C_2H_5)_2]_3$, are combined in a 2:1 mole ratio, only a single nuclear magnetic resonance peak is observed and, when they are combined in a 1:2 ratio, another single peak is seen. Assignment of these two peaks to diethylaminodichlorophosphine, $PCl_2[N(C_2H_5)_2]$, and to bis-(diethylamino)-chlorophosphine, $PCl[N(C_2H_5)_2]_2$, respectively, is borne out by the facts that ratios other than 2:1 or 1:2 show only the two resonance peaks as presented in Table II and that upon isolation of the products, the observed boiling points agreed with the literature values. This means that equilibrium constants for disproportionation of the two intermediate products are less than 5 × 10^{-4}, according to the equation

$$K = [PX_3][PXZ_2]/[PX_2Z]^2 \qquad (1)$$

A check experiment was carried out by combining phosphorus trichloride with pure bis-(diethylamino)-chlorophosphine made by the technique of Burg and Wagner,[8] and, in this case, a 1:1 molar ratio also gave a 100% yield of diethylaminodichlorophosphine.

Exchange on Two Sites.—A similar type of reaction occurs for the monomethylphosphine derivatives. Since redistribution reactions involving P–C bonds are extremely slow even at high temperatures, a monomethylphosphine derivative acts as if it had only two exchangeable substituent sites instead of the three normally associated with triply connected phosphorus. Then when methyldichlorophosphine, CH_3PCl_2, is mixed with methylbis-(dimethylamino)-phosphine, $CH_3P[N(CH_3)_2]_2$, the intermediate compound, dimethylaminomethylchlorophosphine, $CH_3PCl[N(CH_3)_2]$, is produced in 100% yield from a 1:1 mixture of the starting materials, as shown in Table II. Similarly, only one intermediate product was found when methyldibromophosphine was combined with methylbis-(dimethylamino)-phosphine.

TABLE II

EQUILIBRIUM DATA

System: PCl_3–$P[N(C_2H_5)_2]_3$

Initial mole % of PCl_3	Percentage of total phosphorus as PCl_3	$PCl_2[N(C_2H_5)_2]$	$PCl[N(C_2H_5)_2]_2$	$P[N(C_2H_5)_2]_3$
100	100.0	0	0	0
91.3	25.1	74.9	0	0
83.0	52.0	48.0	0	0
66.7	0	100	0	0
64.0	0	92.4	7.6	0
48.8	0	47.9	52.1	0
34.8	0	4.0	96.0	0
17.3	0	0	51.5	48.5
0.0	0	0	0	100.0

System: CH_3PCl_2–$CH_3P[N(C_2H_5)_2]_2$

Initial mole % of CH_3PCl_2	Percentage of total phosphorus as CH_3PCl_2	$CH_3PCl[N(C_2H_5)_2]$	$CH_3P[N(C_2H_5)_2]_2$
100.0	100.0	0	0
85.0	72.3	27.7	0
71.2	42.9	57.1	0
62.1	35.2	64.8	0
52.0	4.0	96.0	0
36.8	0	74.3	25.7
24.6	0	49.0	51.0
16.5	0	32.7	67.3
0.0	0	0	100.0

Since the equilibrium constants having the form of eq. 1 have all been found to be zero within experimental error when the exchanging substituents are dialkylamino groups and halogen atoms, it was thought desirable to investigate the situation where substituents were transferred between phosphines with three exchangeable substituent sites and monomethylphosphines with two exchangeable substituent sites. Typical data are shown in Fig. 1 and 2. Figure 1

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(4) *E.g.*, L. C. D. Groenweghe and J. H. Payne, *J. Am. Chem. Soc.*, **81**, 6357 (1959); E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *ibid.*, **81**, 6363 (1960); E. Schwarzmann and J. R. Van Wazer, *ibid.*, **81**, 6366 (1960).

(5) J. R. Van Wazer and C. F. Callis, "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press, Inc., New York, N. Y., 1962, Chapter 2.

(6) A. Michaelis, *Ann. Chem. Liebigs*, **326**, 154 (1903).

(7) L. Maier, *Angew. Chem.*, **71**, 574 (1959).

(8) A. B. Burg and R. I. Wagner, U. S. Patent 2,934,564 (1960).

(9) K. Moedritzer, G. M. Burch, J. R. Van Wazer, and H. K. Hofmeister, *Inorg. Chem.*, **2**, 1152 (1963).

(10) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

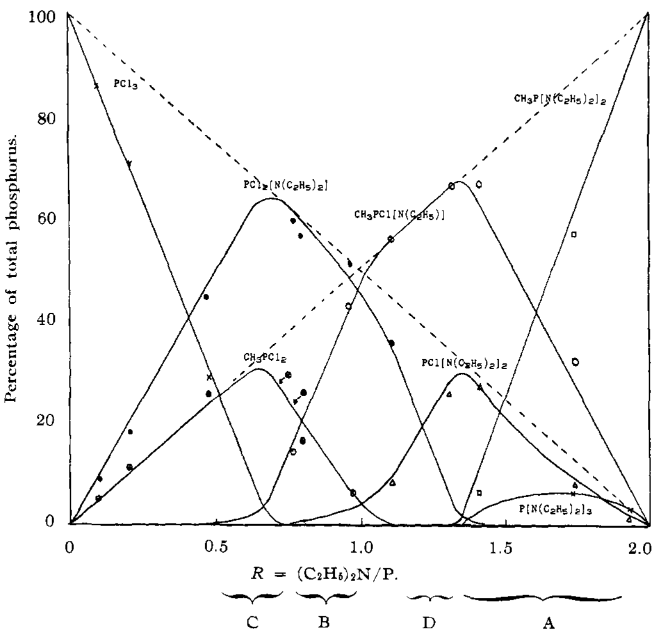

Fig. 1.—Equilibrium at 25° in the system $CH_3P[N(C_2H_5)_2]_2$–PCl_3. The curves in this figure were calculated on the basis that $K_1 = 4 \times 10^{-8}$, $K_2 = 4 \times 10^{-7}$, $K_3 = 1 \times 10^{-10}$, and $K_4 = 1.42$.

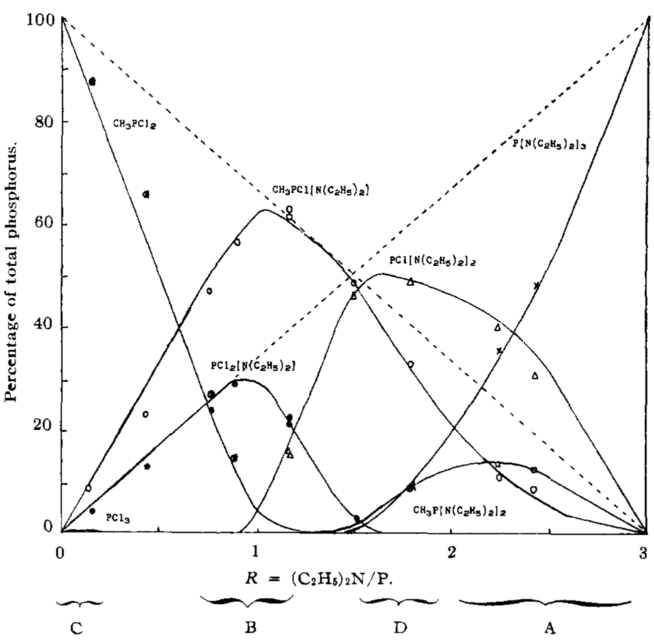

Fig. 2.—Equilibrium at 25° in the system CH_3PCl_2–$P[N(C_2H_5)_2]_3$. The curves in this figure were calculated on the basis that $K_1 = 4 \times 10^{-8}$, $K_2 = 4 \times 10^{-7}$, $K_3 = 1 \times 10^{-10}$, and $K_4 = 1.42$.

deals with the exchange of methylbis-(diethylamino)-phosphine with phosphorus trichloride, and Fig. 2 with the exchange of methyldichlorophosphine with tris-(diethylamino)-phosphine.

In this system, there are four equilibrium constants

$$K_1 = [PCl[N(C_2H_5)_2]_2][PCl_3]/[PCl_2[N(C_2H_5)_2]]^2 \quad (2)$$

$$K_2 = [PCl_2[N(C_2H_5)_2]][P[N(C_2H_5)_2]_3]/[PCl[N(C_2H_5)_2]_2]^2 \quad (3)$$

$$K_3 = [CH_3P[N(C_2H_5)_2]_2][CH_3PCl_2]/[CH_3PCl[N(C_2H_5)]]^2 \quad (4)$$

$$K_4 = [PCl[N(C_2H_5)_2]_2][CH_3P[N(C_2H_5)_2]_2]/[P[N(C_2H_5)_2]_3][CH_3PCl[N(C_2H_5)_2]] \quad (5)$$

The constant K_4 was evaluated to be 1.42 ± 0.05 from those regions marked A at the left-hand side of Fig. 3 and 4, where four species co-exist. These are the only two places in Fig. 1 and 2 where there is a sufficient number of compounds (the four species of eq. 5) to evaluate a constant of the form of K_4. At the regions of composition marked B, C, and D, values of $K_4(K_2/K_3)$, $K_4(K_1K_2/K_3)$, and K_4K_2, respectively, could have been evaluated from the data if measurable quantities of four compounds had been experimentally observed. Although this was not the case, empirical extrapolations of the data in these regions showed that K_1 and K_2 must be less than about 10^{-4} and K_3 less than about 10^{-6}.

Enthalpy Data.—Two measurements of the heat of the reaction shown in eq. 6 gave −8.27 and −8.58 kcal., whereas two measurements for the reaction of eq. 7 gave −8.71 and −9.53 kcal. For eq. 8, the two values were 6.60 and 6.20 kcal. Only one measurement was made for eq. 9, since an insufficient amount of reagents was available to make a replicate determination. The average value for the heat of each reaction is:

$$^2/_3P[N(C_2H_5)_2]_3 + {^1/_3}PCl_3 \longrightarrow 1[(C_2H_5)_2N]_2PCl,\ \Delta H = -8.5 \text{ kcal.} \quad (6)$$

$$^1/_3P[N(C_2H_5)_2]_3 + {^2/_3}PCl_3 \longrightarrow 1[(C_2H_5)_2N]PCl_2,\ \Delta H = -9.0 \text{ kcal.} \quad (7)$$

$$^1/_2CH_3P[N(C_2H_5)_2]_2 + {^1/_2}CH_3PCl_2 \longrightarrow 1CH_3P[N(C_2H_5)_2]Cl,\ \Delta H = -6.4 \text{ kcal.} \quad (8)$$

$$^1/_2[(C_2H_5)N]_2PCl + {^1/_2}PCl_3 \longrightarrow 1[(C_2H_5)_2N]PCl_2,\ \Delta H = -5 \text{ kcal.} \quad (9)$$

As calculated from eq. 6 and 7, ΔH for eq. 9 is −4.8 kcal.

The enthalpies of reaction of eq. 6, 7, and 8 may be used to show that $\Delta H = +4.8$, +4.0, and +6.4 kcal. per mole of product for the chemical reactions represented by eq. 2, 3, and 4, respectively. On the assumption that the entropies of these three reactions correspond only to random interchange, the equilibrium constants may be evaluated from

$$(-RT/\alpha) \ln K \approx \Delta H - (RT/\alpha) \ln K_{\text{rand}} \quad (10)$$

where α is the appropriate factor to cause ΔH to refer to 1 mole.

On this basis, $K_1 = 4 \times 10^{-8}$, $K_2 = 4 \times 10^{-7}$, and $K_3 = 1 \times 10^{-10}$. The curves shown in Fig. 1 and 2 were calculated on an IBM-704 computer from these values and $K_4 = 1.42$, using a direct trial-and-error procedure minimizing the sum-of-the-squares discrepancies.

Since the heats of formation of phosphorus trichloride[11] and tris-(diethylamino)-phosphine[12] are known to be −68.6 and −66.8 kcal./mole, respectively, the heats of formation of the intermediate compounds can be calculated. For bis-(diethylamino)-chlorophosphine, $PCl[N(C_2H_5)_2]_2$, $\Delta H_f = -76$ kcal./mole, and for diethylaminodichlorophosphine, $PCl_2[N(C_2H_5)_2]$, $\Delta H_f = -77$ kcal./mole. From the data given here, one may also show that the heat of formation of CH_3PCl_2 is 3.2 kcal. more positive than that of $CH_3P[N(C_2H_5)_2]_2$.

Discussion

These studies demonstrate the use of a "systems-interaction" equilibrium constant (eq. 5) to relate two systems of compounds undergoing scrambling of substituents. Such "systems-interaction" constants are applicable in all cases where there are two or more experimentally distinguishable central atoms or moieties exchanging substituents. The unusual shape of the curves in Fig. 1 and 2 should be noted. We think that, from the shape of such curves and from careful investigation of the species present in the

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[11] W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall. Inc., New York, N. Y., 1952.

[12] P. A. Fowell and C. T. Mortimer, *J. Chem. Soc.*, 2913 (1959).

critical regions (such as the ones labeled A, B, C, and D in these figures), more accurate information can be obtained about nonrandom reorganization equilibria by mixing compounds based on different central atoms (*e.g.*, MX_n with QZ_p) than by mixing two different compounds based on the same central atom (*e.g.*, MX_n with MZ_n).

The rapid and highly nonrandom equilibration exhibited by the systems investigated here is probably attributable to considerable rehybridization of the electronic orbitals of the phosphorus when a chlorine atom is substituted by an amino group or *vice versa*. The problem does not seem to be one of steric hindrance, since bis-(dialkylamino)-chlorophosphine and dialkylaminodichlorophosphine would not be expected to be equally efficacious in relieving any strain assumed to exist in phosphorus trichloride and/or tris-(diethylamino)-phosphine. It is interesting to note that, in the system studied here and the related nonrandom systems[13] PCl_3–$P(OC_2H_5)_3$ and $P(OC_6H_5)_3$–$P[N(C_2H_5)_2]_3$, the change in P^{31} n.m.r. chemical shifts when going from one to another in a series of compounds obtained by substituent interchange is nonlinear. In a number of cases where random sorting of substituents is observed at equilibrium, the chemical shifts generally vary linearly from compound to neighboring compound.

Acknowledgment.—We are indebted to Allan W. Dickinson for computing the curves shown in the figures.

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(13) E. Fluck and J. R. Van Wazer, *Z. anorg. allgem. Chem.*, **307**, 113 (1961).

[Contribution from Monsanto Chemical Company, Central Research Department, St. Louis, Missouri]

Exchange of Parts between Molecules at Equilibrium. IV. The New Family of Poly(fluoroarsenous methylimides)

By Marvin D. Rausch, John R. Van Wazer, and Kurt Moedritzer

Received October 8, 1963

Dissolution of the cage compound, $As_4(NCH_3)_6$, in arsenic trifluoride gives homogeneous liquids which, by H^1 and F^{19} n.m.r., are seen to be made up of several structural entities. Interpretation of the proton n.m.r. data in terms of methylimino bridges between various combinations of end, middle, and branch structure-building units leads to the conclusion that interchange between halogens and bridging methylimino groups on the arsenic atoms is quite nonrandom, with the mixed species (the end and middle units) having relatively large negative heats of formation from the *neso* and branch units. The data also show that ring structures are not present in appreciable amounts throughout the composition region ranging from AsF_3 to an average over-all stoichiometry around $As_6F_8(NCH_3)_5$ in the AsF_3–$As_2(NCH_3)_3$ system. Within this composition range, the molecules are predominantly straight chains.

Polyatomic molecules based on backbones other than chains of carbon atoms often undergo exchange of parts between different molecules or within the same molecule at the temperatures involved in standard laboratory operations.[1] This means that the usual synthetic procedures give equilibrium distributions of the variously sized and shaped molecules which can be formed. In order to synthesize new families of compounds in which the higher molecular weight molecules are amenable to study (*i.e.*, they are not insoluble, amorphous, network polymers), one must find systems in which the end (monofunctional) and middle (difunctional) molecule building units occur at equilibrium in quantities greater than that expected from random sorting of the molecular parts exhibiting various functionalities. When middles and ends predominate, there will be composition regions in which the molecules are large but not sufficiently tied together by cross linking through branch units to form an infinite network (*i.e.*, the system will not be beyond the "gel point").

In previous studies[2] on *neso*[3] compounds, we found that scrambling of amino groups with halogens on arsenic gave essentially quantitative yields of the mixed molecules at their respective stoichiometric compositions. It was therefore reasoned that exchange of a bridging nitrogen atom with halogens should lead to systems involving long straight chain molecules at the over-all composition corresponding to a halogen–arsenic mole ratio slightly greater than unity. This paper describes the use of n.m.r. in elucidating the structures of the molecules present in the previously unknown system AsF_3–$As_2(NCH_3)_3$.

Experimental

Materials.—Arsenic trifluoride was obtained from the Chemicals Procurement Laboratories, Inc. Tetraarsenic hexamethylimide, $As_4(NCH_3)_6$, was prepared from arsenic trichloride and methylamine according to the directions[4] of its discoverers. Dry reagent grade toluene was employed when a solvent was used.

Equilibration.—Depending on the equilibrium composition desired, from 0.2 g. to 2.0 g. of tetraarsenic hexamethylimide and from 3.3 g. to 0.2 g. of arsenic trifluoride were accurately weighed into 5 mm. i.d. thick-walled Pyrex tubes which had previously been kept in an oven to remove sorbed water and then flushed with pure, dry nitrogen. The tubes were sealed and then heated for 8 hr. at 130°. The contents of each tube were completely homogeneous under these conditions. After heating, the tubes were rapidly cooled to 0°. They were opened and were carefully warmed until the contents were again homogeneous. A portion of the contents was transferred directly into a precision-bore, thin-walled n.m.r. tube. The remaining material was dissolved in three parts of toluene and the resulting solution transferred into another n.m.r. tube. It was subsequently found that equilibrium was attained immediately upon dissolution of the $As_4(NCH_3)_6$.

Analytical Procedures.—Proton n.m.r. spectra were obtained on a Varian Model A-60 spectrometer, at 36° and a frequency of 60.000 Mc., generally using a sweep rate of 0.5 c.p.s. at the smallest available sweep width (50 cycles for full scan). As compared to the neat liquid, the toluene solution of a given equilibrium mixture generally provided much better resolution of the individual peaks. Moreover, the over-all spectra of the diluted and undiluted samples were similar, showing identical peak areas in those cases where the resolution with the neat liquid was adequate for area measurement ($R \equiv$ the F/As mole ratio > 1.5). As the proportion of $As_2(NCH_3)_3$ in the AsF_3–$As_2(NCH_3)_3$ mixtures was increased, the viscosity of the neat liquids rose precipitously so that, for an over-all composition less than that corresponding to the mole ratio $R \equiv F/As = 1.9$, some peaks could not be resolved, and below $R = 1.5$ all peaks had coalesced into a single broad hump. Upon combining $As_2(NCH_3)_3$ with AsF_3, the number of proton resonances gradually increased from

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(1) J. R. Van Wazer, *Am. Scientist*, **50**, 450 (1962).

(2) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139 (1964).

(3) The *neso* molecule is the smallest member of a family of compounds, being a central atom or moiety surrounded by monofunctional substituents. In the case of the system introduced herein, the *neso* compound is arsenic trifluoride.

(4) H. Noth and H. J. Vetter, *Naturwissenschaften*, **48**, 553 (1961).