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.

Acknowledgment.—This work was carried out for the Armstrong Cork Co., Lancaster, Pa., to whom we are indebted for long-term financial support. We also appreciate the generosity of NMR Specialties, Inc., New Kensington, Pa., for making the n.m.r. measurements.

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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).

Experimental

Reagents.—The tris(dimethylamino)arsine was prepared according to the procedure published[3] by one of us and the trimethyl arsenite was made by the technique described in a previously published related paper.[4] The arsenious sulfide was purchased from Bios Laboratories.

Considerable effort was put into obtaining appropriate samples of arsenious oxide. A C.P. product from Fisher Scientific was found to give intolerable line broadening in the proton n.m.r. spectra of the arsenious oxide reaction products, as compared to an analytical standard sample from the National Bureau of Standards. Presumably the line broadening is due to paramagnetic impurities or trace amounts of a powerful catalyst for subsequent interchange. A second standard sample from the Bureau of Standards gave considerable line broadening so that a number of their standard samples had to be tested. It was found that Standard Samples No. 83b and c gave good spectra in the final product but that somewhat better resolution was obtained by using arsenious oxide which we made from hydrolysis of carefully redistilled arsenic trichloride.

Scrambling Studies.—Dissolution of the arsenious oxide or sulfide in the appropriate *neso*[5] compound was achieved by heating in sealed glass tubes in a furnace equipped with a rotating tube holder so that the solid was continuously tumbled about in the liquid. In the system $As(OCH_3)_3$–As_2O_3, it was found that 12 hr. at 80° was sufficient to dissolve the arsenious oxide for values of the over-all composition corresponding to $R \equiv CH_3O/As$ between 2 and 3. Likewise, 10 hr. at 120° was needed for complete dissolution with $1.5 \leq R < 2$, and 4 hr. at 200° for $1 \leq R < 1.5$. In a similar manner, 8 hr. or less at 120° was seen to be sufficient for complete dissolution of the arsenious oxide in tris(dimethylamino)arsine for values of $R \equiv (CH_3)_2N/As$ between 1.5 and 3. After 8 hr. at 150°, complete dissolution was effected for $1.0 \leq R < 1.25$; but 8 hr. at 175° was needed for $0.5 \leq R < 1$.

All of the arsenious trisulfide dissolved in tris(dimethylamino)arsine within 12 hr. at 120° for $1.6 \leq R \equiv (CH_3)_2N/As \leq 3$. For $1 \leq R \leq 1.5$, dissolution was not complete in this time but the remaining solid was seen to have converted from the yellow, powdered As_2S_3 to large bright red, plate-like crystals which were shown to be AsS (realgar) by X-ray diffraction powder patterns. It is very probable that the realgar was in equilibrium with the liquid phase, since such a liquid–solid equilibrium offers a mechanism for its crystal growth.

Quantitative analyses were carried out by proton n.m.r. according to the techniques described previously,[4] except that the peak areas were integrated by the cut-and-weigh technique.[1]

The Family of Methyl Polyarsenites

N.m.r. Assignments.—In the case of the $As(OCH_3)_3$ *vs.* As_2O_3 system, cursory inspection of the spectra (three of which are reproduced in Figure 1) showed three prominent maxima plus a smaller one on the tail of the downfield maximum. The first of these maxima was a sharp peak which appeared in the range of −3.57 to −3.65 p.p.m. (with respect to tetramethylsilane), depending on the over-all composition, and which diminished monotonically with decreasing values of $R \equiv CH_3O/As$. It was readily assigned to the *neso* compound since the n.m.r. spectra of pure $As(OCH_3)_3$ showed only this single peak. The second maximum was several times broader than the *neso* peak and, in the neat liquid, appeared around 0.04 p.p.m. downfield from the *neso* peak. The third maximum was very broad, centering at a point around 0.11 p.p.m. downfield from the *neso* peak and tailing off around −0.22 p.p.m. from the *neso* peak. A 1:1 dilution with carbon tetrachloride did not affect the general shape of the maxima except to move them together by a small amount. Careful inspection and comparison of the spectra for the various over-all compositions showed that for some R values, the maximum immediately downfield from the *neso* peak could be partially resolved into two overlapping resonances. In a similar manner, the coalesced signals centering around 0.11 p.p.m. downfield from the *neso* compound were shown to consist of four (or perhaps more) greatly overlapping resonances. The areas of the first group of two resonances and of the second group of about four were independently estimated by three different persons prior to any calculation or interpretation.

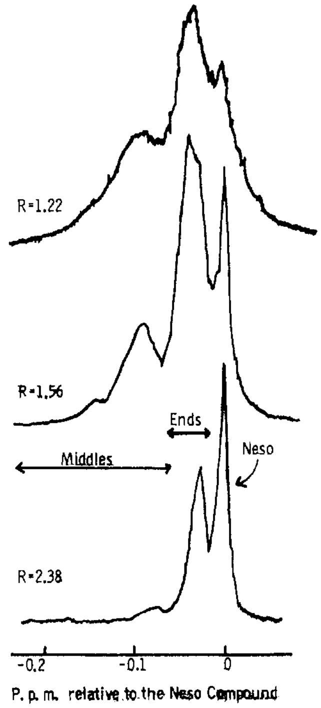

Figure 1.—N.m.r. spectra at 25° for various over-all compositions denoted by the parameter $R \equiv CH_3O/As$ in the family of methyl polyarsenites. The three spectra shown were obtained at different amplitudes: 5.00×, 3.20×, and 1.25× reading from the top to the bottom spectrum.

It seems logical to assign the more-or-less coalesced resonance pair at *ca.* −0.04 p.p.m. (ref. *neso*) to end groups. The very broad mass of resonances centering around −0.11 p.p.m. (ref. *neso*) is assigned to middle groups. The relative area of the first was found to maximize at $R = 2$ and that of the second to increase gradually over the investigated range from $R = 2.8$ to 0.9 as expected for these building units.

Equilibrium between Structure-Building Units.—As in prior investigations,[1] the treatment is centered on the building units (based on a single arsenic atom) which make up the various molecules in the family of methyl polyarsenites. The relative amounts of *neso* molecules, $(CH_3O)_3As$; end groups, $(CH_3O)_2AsO_{1/2}$–;

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[3] K. Moedritzer, *Chem. Ber.*, **92**, 3627 (1959).

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

[5] The word "*neso*" refers to the smallest molecule in a family of compounds. It has been employed for a number of years in silicate chemistry; *e.g.*, see G. W. Morey, "Encyclopedia of Chemical Technology," R. E. Kirk and D. Othmer, Ed., Interscience Publishers, New York, N. Y., 1st Ed., 1954, Vol. XII, p. 280.

TABLE I

N.M.R. DATA ON EQUILIBRATED MIXTURES OF METHYL POLYARSENITES AT 37°
(IN PERCENTAGE OF TOTAL HYDROGEN)

$R = (CH_3O)/As$						
From ingredients	By n.m.r.	*neso*	Total ends	End–end molecule (approx. values)	Total middles	Estd. % of total middles and total branches in rings
2.79	2.62	77 (86.5)[a]	21 (13.0)	18 (11.5)	2 (0.5)	1
2.59	2.36	64 (74.0)	30 (24.3)	35 (18.6)	6 (1.7)	11
2.38	2.31	58 (62.2)	36 (33.8)	31 (22.1) [23.9][b]	6 (4.0)	12
2.19	2.19	50 (51.8)	42 (41.1)	32 (22.6) [25.4]	8 (7.1)	16
1.99	2.07	44 (42.6)	45 (46.4)	33 (21.2) [26.9]	11 (11.0)	24
1.77	Branches present	36 (33.4)	47 (50.2)	26 (18.1) [23.0]	18 (16.4)	33
1.56		24 (25.8)	50 (51.6)	19 (14.5) [21.1]	26 (22.6)	44
1.436		25 (21.7)	46 (51.6)	20 (12.2) [20.0]	29 (26.7)	51
1.216		25 (15.5)	44 (49.8)	19 (8.4) [18.0]	31 (34.7)	64
0.987		16 (10.2)	43 (45.6)	17 (5.1) [19.4]	41 (44.2)	83

[a] Values in parentheses are calculated on the assumption that the system is ring-free and has $K_1 = 0.29$ and $K_2 = 0.36$. [b] Values in brackets are calculated on the assumption of rings as indicated in the last column of this table.

and middle groups, $(CH_3O)As(O_{1/2}-)_2$ were obtained from the n.m.r. resonances. Then the amounts of branches were calculated from material balances. As expected, no branches were found for $R >$ *ca.* 1.8, and the relative amount of branches then increased monotonically with decreasing R value. In those cases where there were no branch groups, the calculated R value matched the value obtained from the ingredients, as shown in Table I.

The data of Table I were employed to calculate[6] equilibrium constants between the various building units, thereby obtaining the following values.

$$K_1 = [nesos][\text{total middles}]/[\text{ends}]^2 = 0.36 \qquad (1)$$

$$K_2 = [\text{branches}][\text{ends}]/[\text{total middles}]^2 = 0.29 \qquad (2)$$

The standard deviations computed from the weighted distributions[6] of each constant were found to be 0.21 for K_1 and 0.15 for K_2. Such large deviations probably mean that ring molecules are present in the system since equilibrium constants of the form of K_1 and K_2 are only theoretically applicable to the ring-free molecules.[7] Nevertheless, these values of the equilibrium constant are close to those expected for ideal random sorting of methoxyl groups with the bridging oxygen atoms; *i.e.*, $K_1 = K_2 = 0.333$ in the random case. It is interesting to note that exchange of substituents in the family of polyphosphoric esters is quite far from random,[8] with $K_1 = 0.02$ and $K_2 = 0.06$. Equilibria in the esters of condensed oxy acids (such as the polyarsenite esters discussed in this paper and the polyphosphate esters of ref. 8) represent an exchange of an alkoxy substituent for a substituent consisting of the bridging oxygen atom connected to the neighboring central atom of the oxy acid. Thus, it is not surprising to find that exchange of methoxyl groups for "arsenoxyl" moieties, –OAs<, is close to random. The problem lies in developing an explanation for the nonrandom exchange of alkoxyl groups for the "phosphoryloxyl" moieties, –OP(O)<.

Analysis of N.m.r. Spectral Details.—Since, under the conditions of highest resolution, two end-group as well as four or more middle-group resonances could be distinguished, an attempt was made to estimate the amount of rings from the qualitative information obtained from the n.m.r. fine structure. It was apparent that the end-group resonance lying closest to the *neso* peak was due to the end–end molecule, with the remaining end-group resonance being attributable to all ends which are bonded to middles. If an appreciable amount of the middle and branch groups is used up in

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(6) L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

(7) D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, **41**, 3105 (1964).

(8) E. Schwarzmann and J. R. Van Wazer, *J. Am. Chem. Soc.*, **83**, 365 (1961).

rings, the end–end molecule will be present to larger amounts than calculated for random sorting[1,9] of the end, middle, and branch groups into molecules on the assumption that there were no rings. From this type of calculation and fitting of all of the end and middle peaks,[1] we have estimated that the rings build up gradually from a few per cent in the neighborhood of $R = 2$ to *ca.* 70% at $R = 1$. However, the poor resolution of the individual n.m.r. peak makes these calculations no more than a rough approximation.

Physical Properties.—Although clear liquids having R values lying between 1.0 and 1.5 could be prepared at 120°, it was found that these compositions precipitated a mixture of crystalline and amorphous As_2O_3 upon standing at room temperature. At $R \equiv CH_3O/As = 1.0$, precipitation occurred immediately upon cooling, but at $R = 1.5$, several minutes elapsed before the precipitate started to form. Upon long standing, a small amount of precipitate formed for R values as high as *ca.* 1.8.

Since the rate of crystallization was speeded up by shearing of the liquid, viscosity measurements could not be made for $R < 1.2$. At this composition, the viscosity was in the neighborhood of 0.3 poise—about tenfold more viscous than the *neso* compound. However, inspection of the heated tubes at 200° indicated that the room-temperature viscosity—if it could be measured—would increase rather rapidly in the neighborhood of $R = 1$.

Dilution with carbon tetrachloride also caused precipitation of crystalline As_2O_3 at the lower R values. Although the *neso* compound ($R = 3.0$) appeared to be miscible with carbon tetrachloride, immediate precipitation started to occur at a 1:2 dilution for R in the neighborhood of 1.7.

The theoretical gel point[1] (assuming no rings and random sorting of ends, middles, and branches into molecules) comes at $R = 1.5$ for the $As(OCH_3)_3$ *vs.* As_2O_3 system. However, this composition is about as fluid as the *neso* compound at room temperature. This indicates either that considerable rings are to be found in the various kinds and sizes of molecules present at that composition or that the mechanism of flow is greatly dependent on scrambling of the constituent molecules. Presumably both factors are operative.

Formation of crystalline As_2O_3 from this equilibrated system is not surprising, since the liquid is undergoing rapid exchange of parts between molecules. Therefore, precipitation of the most insoluble solid form merely results in shifting the system of equilibria toward that species until the over-all composition of the liquid, as measured by the R value, represents the collection of molecules in which the molecule(s) found in the precipitate correspond to its solubility constant. The fact that the "solubility" of As_2O_3 increases with temperature and decreases with lowering R values and greater dilution, as shown by our crude experiments, is subject to qualitative interpretation: First, since the scrambling equilibrium is close to random and since there is no reason to believe that the sorting of structure-building units into molecules is highly nonrandom, the temperature dependence of solubility must be attributed almost wholly to the heat of crystallization of the As_4O_6 molecule. Furthermore, the lessening solubility with decreasing R value indicates that, for $R = ca.\ 1.8$, the concentration of the As_4O_6 at equilibrium in this system builds up to the solubility limit so that, at lower R values, precipitates are formed. The fact that dilution causes precipitation is in accord with the following ideas: (a) As the reorganizing molecules are separated, an exchange of parts occurs more frequently by intra- rather than intermolecular processes, and (b) this will lead to an increase[7] in the proportion of the small-sized and ring-containing molecules, including bird-cage structures such as As_4O_6.

Reorganization Rates.—By adding trimethyl arsenite to several of the previously equilibrated compositions and immediately running the n.m.r. spectra, it could be shown that exchange of substituents in this system is so fast that equilibrium is reached within 3 min. at 37°. An n.m.r. study at varying temperature of the compositions for which $R = 1.99$ and 1.56 showed that cooling down to −15° sharpened the n.m.r. peaks and that heating caused the peaks to coalesce around 60°, with the coalesced peak becoming sharper as the temperature was raised to 120°. By applying the proper equations,[4] the average lifetime for exchange could be calculated from these measurements, and the results are shown in Figure 2. The activation energy of the over-all exchange process was found to be in the range of 2 to 3 kcal./mole for $R \equiv CH_3O/As = 1.99$ and 4 kcal./mole for $R = 1.56$.

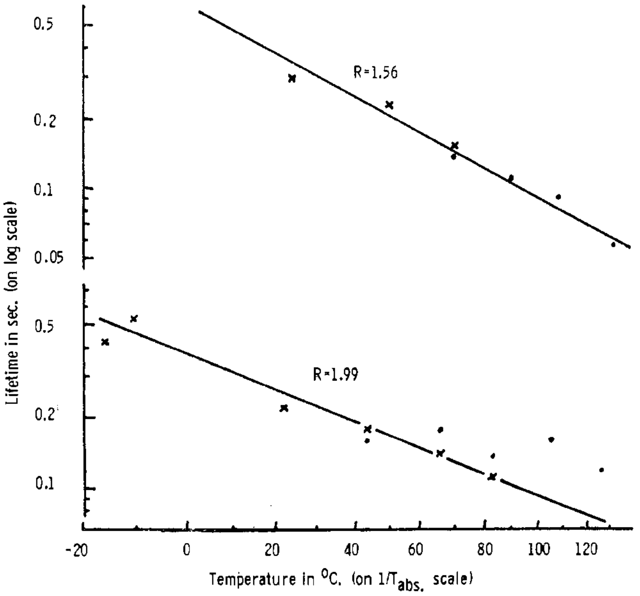

Figure 2.—Variation with temperature of the rate of exchange of methoxyl groups between chemically different sites in two methyl polyarsenite compositions. The crosses denote values estimated from saddle-shaped spectra and the dots from the width of coalesced peaks.[4]

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(9) K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 802 (1964).

The Family of Polyarsenious Oxydimethylamides

Interpretation of N.m.r. Peaks.—As illustrated by the three examples in Figure 3, the n.m.r. spectrum obtained on the system $As[N(CH_3)_2]_3$ *vs.* As_2O_3 was complicated, with poor resolution of the individual peaks at values of $R \equiv (CH_3)_2N/As$ below *ca.* 1.3. In all, approximately fifteen individual resonances were observed. Of these, the resonance at −2.55 p.p.m. (ref. tetramethylsilane) was readily identified as the *neso* compound. Another resonance at −2.15 p.p.m. (ref. tetramethylsilane) (omitted from Figure 3) was shown to correspond to trimethylamine which, it should be noted, forms in these mixtures even upon such gentle treatment as shaking the samples for about 1 week at room temperature. There was another prominent resonance at 0.14 p.p.m. downfield from the resonance of the *neso* peak (corresponding to 4–6% of the total hydrogen) which was shown to be an as-yet-unidentified hydrogen-containing by-product of the scrambling reactions. The presence of about 9% (an average value) of the total hydrogen as trimethylamine corresponds to 3% as methylimino bridges, on the assumption that the trimethylamine is produced by simple switching of methyl groups and arsenic atoms on some of the nitrogens. This side reaction necessitates that the n.m.r. spectrum will show some dimethylamino as well as methylimino resonances of the system[10] $As[N(CH_3)_2]_3$ *vs.* $As_2(NCH_3)_3$. By deducting the areas corresponding to the n.m.r. peaks of trimethylamine and the unidentified by-product and assuming the division of the spectrum into regions corresponding to *neso*, end, and middle groups, as indicated in Figure 3, it was estimated that $K_1 \approx 0.2$ and $K_2 \approx 4$, with the constants defined as in eq. 1 and 2. These values are presented as approximations because of the complications due to two types of bridges between arsenic atoms. For this reason, a detailed analysis of the spectra is not reported here. Although considerable effort was expended on such an analysis, it will remain untrustworthy until the pure individual systems $As[N(CH_3)_2]_3$ *vs.* $As_2(NCH_3)_3$ and $As[N(CH_3)_2]_3$ *vs.* As_2O_3 have individually received detailed analysis.

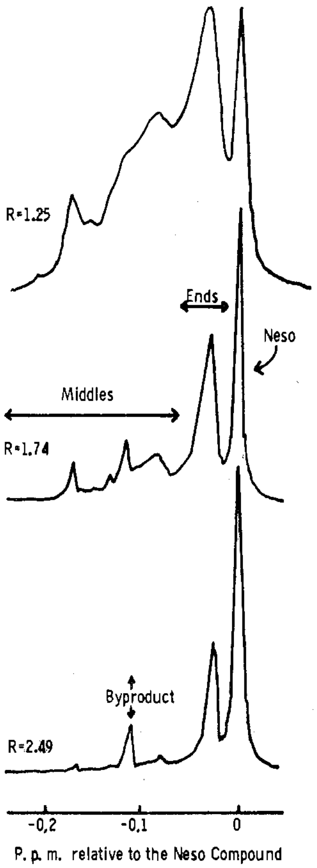

Figure 3.—Three n.m.r. spectra corresponding to different compositions in the family of polyarsenious oxydimethylamides. The spectrum for $R = 1.25$ was taken at an amplitude setting of 63×, whereas that for $R = 1.74$ was taken at 12.5× and that for $R = 2.49$ at 8×.

Physical Data and Reorganization Rates.—Except for the fact that As_2O_3 does not readily precipitate from the $As[N(CH_3)_2]_3$ *vs.* As_2O_3 system, the physical properties of this system are similar to those of the $As(OCH_3)_3$ *vs.* As_2O_3 system. For the polyarsenious oxydimethylamides, viscosity measurements could be made at room temperature for R values as low as 0.88. The viscosity at this value was found to be 6 poises and to be 2 poises at $R = 0.95$. The rapid rise in room-temperature viscosity with decreasing R values seems to start around $R = 1$.

Investigation of reorganization rates in this system was carried out in the same way as for the $As(OCH_3)_3$ *vs.* As_2O_3 system, except that there was no appreciable change in the n.m.r. spectra with temperature in the range of +15 to +130°. Again, mixing of the *neso* compound with several equilibrated mixtures showed equilibrium to be achieved in less than 3 min.

At temperatures up to 130°, there was no systematic variation in the peak width at half-height for the *neso* compound in compositions for which $R = 1.25$ and 2.00. In both cases, the *neso* peak was well-resolved and exhibited a narrow width in the range of 0.5 to 0.7 c.p.s. The various resonances corresponding to the end and middle groups appeared to be slightly better resolved at 100° than at any other temperature in the range of 15 to 130°. If this slight sharpening of the spectrum of the end and middle groups is real, it is probably attributable to localized loss of freedom of motion of certain ends and especially middles (*i.e.*, a locally high viscosity). This should cause broadening at temperatures below 100°, with a very small amount of exchange broadening between ends and middles (but not including the *neso* compound) showing up above 100°. From these findings, we estimate that the average lifetime of a building unit in this system with respect to exchange is greater than 1 sec. at all temperatures measured and is less than 200 sec. at 37°.

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(10) For related systems exhibiting methylimino bridges, see M. D. Rausch, J. R. Van Wazer, and K. Moedritzer, *J. Am. Chem. Soc.*, **86**, 814 (1964); J. R. Van Wazer, K. Moedritzer, and M. D. Rausch, *J. Chem. Phys.*, in press.

Systems Prepared from Arsenious Sulfide

Attempts to dissolve arsenious sulfide in trimethyl arsenite, arsenic trichloride, and arsenic trifluoride were unsuccessful although a considerably longer time was used in trying to effect these dissolutions than was needed to dissolve arsenious sulfide in tris(dimethylamino)arsine. It is also noteworthy that the equilibrium precipitate in the $As[N(CH_3)_2]_3$ *vs.* As_2S_3 system is realgar, AsS, rather than the As_2S_3 starting material; although in the case of the $As(OCH_3)_3$ *vs.* As_2S_3, $AsCl_3$ *vs.* As_2S_3, and AsF_3 *vs.* As_2S_3 systems, the As_2S_3 remained in the form of the yellow powder originally added to the sealed tubes in which equilibration was attempted.

N.m.r. study of the $As[N(CH_3)_2]_3$ *vs.* As_2S_3 system showed a number of different peaks in the composition range $2.8 \geq R \equiv (CH_3)_2N/As \geq 1.6$. Careful inspection of the spectrum indicated that there were at least eleven separate methyl-containing species present in the reorganized liquid. Furthermore, it seemed quite probable that the n.m.r. peaks represented two classes of structure-building units since there were two distinct clumps of peaks in the n.m.r. spectra.

Because of the precipitation of realgar and the great difficulties encountered in finally reaching a successful interpretation of data obtained in a previous study[11] dealing with the system $SP(SC_4H_9)_3$ *vs.* P_2S_5, no attempt was made to carry out a quantitative interpretation of the n.m.r. spectra obtained for the $As[N(CH_3)_2]_3$ *vs.* As_2S_3 system. However, it seems reasonable to conclude from the formation of realgar that there is some formation of S–S linkages (and hence of As–As bonds) at equilibrium in this system. In the system involving P_2S_5,[11] we were fortunate to find a difference in the rate between the exchange of substituents around the phosphorus atoms and the formation of S–S linkages so that a metastable substituent-exchange equilibrium was established. In the more labile arsenic systems, such good luck might not pertain.

Rationale.—The fact that arsenious sulfide remained unchanged upon heating with trimethyl arsenite, arsenic trichloride, and arsenic trifluoride under conditions where realgar formed in the $As[N(CH_3)_2]_3$ *vs.* As_2S_3 system gives support to the idea that the equilibria between the various structure-building units in the methoxyl and halogen systems are such that ends and middles are present in only trace amounts; *i.e.*, K_1 and K_2 of eq. 1 and 2 are very large. Of course, the alternative explanation of merely very slow dissolution of the As_2S_3 cannot be ruled out. The formation of realgar also indicates that sulfur atoms in equilibrated mixtures may play roles other than acting as monatomic bridges between arsenic atoms. These ideas are in accord with our previous quantitative study[11] of the $SP(SC_4H_9)_3$ *vs.* P_2S_5 system, where it was found that the end groups were present to considerably lesser amounts than expected for random interchange of the monofunctional and bridging substituents on the phosphorus, and that the phosphorus sulfides which precipitated from equilibrated mixtures had an S/P mole ratio considerably smaller than the value of $^5/_2$ corresponding to P_2S_5.

Acknowledgment.—We wish to thank David Matula for an analysis of the n.m.r. spectra of the $As[N(CH_3)_2]_3$ *vs.* As_2O_3 system, Elizabeth Van Wazer for the n.m.r. peak-area measurements, and Claude Dungan for the high-temperature n.m.r. spectra.

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[11] L. Maier and J. R. Van Wazer, *J. Am. Chem. Soc.*, **84**, 3054 (1962).