hexadiene)iridium(I)[43] by Krogmann's procedure.[8] Hayter's procedure was used in the preparation of the $[HM_2(CO)_{10}]^-$ anions.[7] Aqueous solutions of $M_3[HCo(CN)_5]$ were prepared by reducing solutions of $[Co(CN)_5]^{3-}$ with hydrogen, sodium borohydride, or 1% sodium amalgam.[13]

$K_3[HRh(CN)_5]$. Solid bis(*cis,cis*-1,5-cyclooctadiene)-μ-dichlorodirhodium(I) (0.10 g, 0.4 mmol) was added to a boiling solution of potassium cyanide (0.26 g, 4.0 mmol) in 5 ml of degassed absolute methyl alcohol. The red-purple mixture was gently refluxed for 10 min and then cooled to room temperature. The resulting white crystalline precipitate was separated by filtration, washed with cold methyl alcohol, and dried under vacuum (0.126 g, 90% yield).

Anal. Calcd for $K_3[HRh(CN)_5]H_2O$: C, 16.26; H, 0.86; N, 18.97. Found: C, 16.12; H, 0.66; N, 18.71.

This material gave the same nmr spectrum as that prepared using the procedure of Krogmann.[12]

***cis*-$HMn(CO)_4P(C_6H_5)_3$** was prepared by a modification of a literature procedure.[44] Manganese pentacarbonyl hydride (~0.20 g, 1 mmol) was distilled under vacuum into a liquid nitrogen cooled Schlenck tube containing a solution of triphenylphosphine (0.26 g, 1 mmol) in dry, degassed diethyl ether (3 ml). The mixture was warmed to room temperature and stirred until carbon monoxide evolution ceased (~5 hr). From time to time the evolved gas was pumped out of the tube. Evaporation of the resulting yellow solution under reduced pressure and recrystallization of the product from boiling toluene afforded 0.3 g of pale yellow crystals, mp 137° (under nitrogen) (lit.[45] mp 137.5°); ir (cyclohexane) 2060 (vs), 1985 (vs), 1970 (vs), 1960 (vs), 1940 (vw) cm^{-1}.

Anal. Calcd for $C_{22}H_{16}O_4MnP$: C, 61.21; H, 3.74. Found: C, 61.80; H, 4.01.

Acknowledgments. We are indebted to our colleague Alan Davison for a gift of $HMn(CO)_5$ and for helpful discussions concerning the interpretation of the data reported in this paper, to Dr. Frank Weigert and Professor J. D. Roberts (California Institute of Technology) for the ^{13}C spectrum of $HMn(CO)_5$, and to H. L. Mitchell for extensive assistance in obtaining nmr spectra.

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Linear and Cyclic Permethylpolyarsines

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Abstract: At room temperature, molecules in the family of fully methyl-substituted polyarsines undergo exchange reactions through the making and breaking of As–As bonds while the C–As bonds remain perfectly stable. As a result, mixtures of tetramethyldiarsine with arsenomethane react to form equilibrium mixtures of molecules in which the diarsine and cyclic pentameric arsenomethane predominate because of the relatively large value of the pertinent ring–chain equilibrium constants. This equilibrium has been studied by proton nuclear magnetic resonance (nmr) of the methyl groups bonded to the arsenic. In addition, nmr and mass spectrometric studies have been carried out on the neat, yellow, liquid form of pure arsenomethane. The data have been interpreted to mean that liquid arsenomethane consists primarily of a cyclic pentamer exhibiting a single detectable conformation.

In spite of the fact that cacodyl (tetramethyldiarsine) was the first organometallic compound[4] to be synthesized and that the earliest work in this area was published over 200 years ago,[5] the literature on the peralkyl- or perarylarsines is small. Although this may be due in some part to the toxicity of these compounds, the major reason for the paucity of literature has probably been the lack of appropriate experimental methods. Since nuclear magnetic resonance (nmr) appeared to be particularly suited for a study of the permethylpolyarsines, the work reported here was undertaken to shed more light on this ancient area of chemistry.

Experimental Section

Reagents. Arsenomethane, $(CH_3As)_n$, was prepared by treating sodium methylarsenate with hypophosphorous acid.[6] The oily product was washed with dilute NaOH and water and then distilled under high vacuum. It was found to persist as a clear yellow liquid[7] for several months at room temperature if air and light are excluded.

Tetramethyldiarsine, $(CH_3)_2AsAs(CH_3)_2$, was made in a similar manner by reducing cacodylic acid with an excess of hypophosphorous acid.[8] The reaction is exothermic; hence the solution of cacodylic acid in water had to be added slowly. The reaction was carried out under argon. The lower phase was dried with $CaSO_4$ and fractionated. The liquid going over at 158° was redistilled to give a product showing a single sharp nmr peak at −1.06 ppm (internally referenced to tetramethylsilane).

Most of the reactions studied herein were carried out in sealed-glass nmr tubes so that there was no gain or loss of material in the system.

Physical Measurements. The nmr measurements were made with a Varian A-60 spectrometer equipped with a V-604 variable-temperature controller. The reference standard was tetramethylsilane added to the samples, with downfield shifts being given a negative sign. The nmr peaks were determined by cutting and weighing, as well as with a Du Pont curve resolver. Viscosities were measured in a dry-nitrogen-filled drybox on a Haake Rotovisco instrument, using the plate-cone attachment and calibrating with Bureau of Standards oils. The mass spectra were obtained on a CEC 21-104 medium-resolution rapid-scan spectrometer, in some cases with the liquid sample being contained in a capillary tube inserted into the vacuum chamber close to the point of ionization. In other experiments, the sample was completely volatilized into a 3-l. glass-sampling system. Using a moderate value for the ac-

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celeration voltage (800 V), the ionizing potential was varied downward from 70 to 4 eV.

Results and Conclusions

Reactions and Exchange Lives. When dimethylbromoarsine is added to a benzene solution of tetramethyldiarsine, coalescence of the nmr peaks is observed, with the shift of the coalesced peak ranging from that of the diarsine to that of the dimethylbromoarsine in accord with the relative proportions of these ingredients. At 35°, the peak width corresponds to a lifetime for exchange of As–As with As–Br bonds of *ca.* 10^{-3} sec in a 10 vol % solution. Dimethylbromoarsine catalyzes formation of the brownish red solid modification[4] from the liquid form of arsenomethane.

When arsenomethane and tetramethyldiarsine are combined in various proportions at room temperature, a bright red precipitate is seen to form immediately. For large proportions of the diarsine, the precipitate dissolves in a few minutes at room temperature to give a clear yellowish solution which was found to remain free of precipitation (according to studies lasting several months at temperatures up to 100°). In the composition region corresponding to approximately equimolar amounts of arsenic being donated by the two reagents, the red precipitate can only be caused to disappear by heating at 100° for a few minutes. When the arsenomethane predominates, the precipitate formed upon mixing cannot be caused to redissolve but instead changes color from red to brown upon standing at room temperature or, more rapidly, with heating. Reaction products having values of $R \equiv CH_3/As$ over-all mole ratio ≤ 1.3 always contain suspended precipitate and finally convert completely to a dark brown solid, the X-ray diffraction pattern of which indicates the presence of both crystalline and amorphous constituents, with the crystalline material being identical with the "dark-colored modification"[4] of arsenomethane. Line broadening in the nmr, coupled with visual observation, show that in this composition region ($R \leq 1.3$), the viscosity of the liquid phase increases rapidly upon mixing the fluid diarsine with the relatively viscous arsenomethane.

From the observed temperature dependence of the nmr line shapes, it was calculated that the mean exchange time for tetramethyldiarsine in an equilibrium mixture for which $R = \sim 1.5$ was about 0.3 sec at 150°, with an activation energy for exchange of 12 ± 3 kcal. About the same values were obtained for arsenomethane in this reaction-product mixture, whereas the nmr peaks assigned to end and middle groups present in chain molecules larger than the diarsine exhibited line broadening which indicated that exchange of parts between these chain molecules is about two or three times faster, under the same conditions, than the exchange life for the diarsine or arsenomethane molecules. It should also be noted that the middle groups in pure arsenomethane showed an exchange rate at a given temperature which was slower by a factor of *ca.* 10 than that for arsenomethane in the equilibrium mixtures. However, the activation energies for exchange did not differ greatly between the pure arsenomethane and the mixtures.

The exchange-rate measurements referred to in the preceding paragraph as well as the unchanging nmr patterns of the samples consisting of single-phase liquids show that the fluid mixtures made from various proportions of tetramethyldiarsine with arsenomethane reach equilibrium within a few minutes at room temperature. However this equilibrium, which involves the making and breaking of As–As bonds, is metastable with respect to substituent-exchange processes based on C–As bond scission. Samples held at high temperatures for long periods of time formed a black precipitate, presumably of more-or-less pure elemental arsenic. Nmr of the resulting liquid phase showed that, as the black precipitate formed and increased in volume, first end groups and then trimethylarsine appeared in the liquid, as would be expected for exchange of methyl groups through the making and breaking of C–As bonds in addition to the generally more rapid making and breaking of As–As bonds. Thus, after 90 hr at 180°, the spectrum of what was originally pure arsenomethane exhibited 17.3% of the total As as end groups and 1.5% as trimethylarsine. Under the more extreme condition of 4 hr at 250°, the resulting liquid phase consisted of 99.5% of the total As as $(CH_3)_3As$, with the remainder corresponding to $(CH_3)_2AsAs(CH_3)_2$.

The Nmr Triplet of Arsenomethane.[9,10] In addition to some small upfield peaks, the nmr spectrum of the neat-liquid form of arsenomethane shows three major resonances exhibiting a 2:2:1 area ratio appearing at (A) −1.66, (B) −1.63, and (C) −1.61 ppm. The chemical shifts of the three peaks of arsenomethane are relatively independent of the concentration in carbon disulfide but are quite dependent in benzene so that the A, B, and C peaks change places with each other upon dilution. At about 50 vol % of benzene, the A and C peaks are exactly superimposed so that the spectrum exhibits a 3:2 area ratio, with peak B at −1.62 and A + C at −1.59 ppm. At large dilutions, the B:C:A = 2:1:2 spectrum can be extrapolated to shifts in the neighborhood of (A) −1.38, (B) −1.45, and (C) −1.42 ppm.

The A:B:C nmr pattern showed no variation of the 2:2:1 area relationship with rather large changes in either temperature or dilution, with either carbon disulfide or benzene. This is shown for benzene in Table I.

Table I. Relative Areas of the Three Major Nmr Peaks of Arsenomethane

Dilution by vol	Temp, °C	Areas relative to area of B = 1.00 A	C
0	35	0.97	0.58
0	60	1.00	0.54
0	90	0.96	0.70
0	120	0.93	0.48
0	150	0.87	0.46
0.25	35		0.56[a]
1.0	35		1.50[b]
2.6	35	0.92	0.49
4.9	35	0.98	0.49
11.5	35	1.03	0.50
24.0	35	1.00	0.48

[a] At the position of the B resonance, superposition of peaks A and B gave a peak area set equal to 2.00. [b] Resonance C is a superposition of the A and C resonances with the area of *B* = 1.00.

Since an equilibrium between different sized rings must be volume dependent and since small rings are ex-

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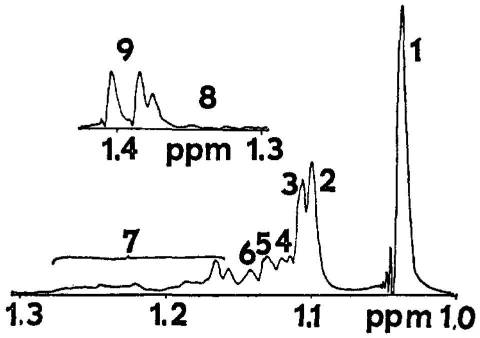
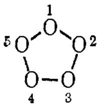


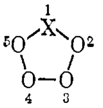
Figure 1. Nmr pattern of the product from reaction of arsenomethane and cacodyl, for an over-all CH_3/As mole ratio of 1.48. Resonance 1 is $(CH_3)_2AsAs(CH_3)_2$; resonance 2, the end groups of $(CH_3)_2AsAs(CH_3)As(CH_3)_2$; and resonance 5, its middle group; resonances 3, 4, and 6 correspond to end groups for $j = 4$, 5, and ≥ 6 in $(CH_3)_2As[As(CH_3)]_{j-1}CH_3$. All other resonances are $CH_3As<$ middle groups, corresponding to long chains for resonance 7, and the minor and predominant pentameric cyclics for resonances 8 and 9, respectively.

pected[11] to exhibit heats of formation which vary considerably with ring size, we interpret this invariance to mean that the three resonances rather surprisingly correspond to only one size of cyclic molecule. Moreover, if there are several configurations of this molecule, they must differ in energy by either a small or a very large amount.

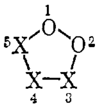
Reported colligative measurements[12] indicate an average of a pentamer in solution. A cyclic pentamer will exhibit five configurations, which are separated from each other by energy barriers which are probably high compared to the barriers for the various twistings available within each configuration. These five may be represented as follows, with X and O standing for CH_3 groups oriented respectively above or below the puckered ring.



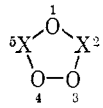
I



II



III



IV

Presumably the nmr chemical shift of a given methyl group in a pentameric ring is determined by the relative "above" or "below" orientations of the other methyl groups in the ring, with the pair of nearest neighbor groups having more effect than the two remaining ones. If we refer only to the pair of nearest neighbors, we see that configuration I corresponds to five of the (OOO) nearest neighbor arrangements; II to two (OOO), two (OOX), and one (XOX); III to one (OOO) and four (OOX); and IV to two (OOX) and three (XOX). Based on a statistical probability[13] of 1 for I as compared to 5 for each of the other structures, we see that the assumption that all four structures have the same energy leads to a 1:2:1 rather than a 2:2:1 nmr pattern. This reasoning leads us to postulate that the three major nmr peaks belong to only one configuration, with the observed nmr pattern being attributable to the effects of the relative orientation of the other methyl groups in the ring with the given methyl group.

On the assumption that right- and left-handed enantiomeric rings will exhibit the same chemical shift, configurations II, III, and IV may be expected each to show the observed 2:2:1 nmr pattern. Configuration IV corresponds to the atomic arrangements in the yellow crystals as determined by X-ray diffraction.[14] However, it is not apparent why one configuration should be greatly preferred over the others.

In addition to the three major peaks, the nmr spectrum of arsenomethane exhibits several smaller peaks which are upfield of the major ones. These represent 4.7% of total As at room temperature. The relative total area of these peaks was found to increase reversibly with rise in temperature so that, at 180°, they correspond to about 18% of total As. Since the relative areas of these peaks showed no discernible dilution dependence, it is reasonable to assign them to other configurations of the pentameric ring. The equilibrium constant between the predominant pentamer and the other pentameric rings equals

$$K_{5,5}{}^{00} = \frac{[(CH_3As)_{\text{predom}}]}{[(CH_3As)_5]} = 22.2 \pm 0.8 \text{ at } 35° \qquad (1)$$

with a reaction enthalpy of $\Delta H = \sim 2.5$ kcal.

The most upfield resonance in this series of small peaks is very broad, with upfield tailing, and represents ~0.5% of the total As. From comparison with the spectra of equilibrated mixtures of arsenomethane with tetramethyldiarsine, this resonance has been ascribed to CH_3As groups in long-chain polymers.

The Family of Permethylpolyarsines. As exemplified by Figure 1, mixtures of tetramethyldiarsine with arsenomethane exhibit a complex nmr pattern. This pattern is characterized by the fact that for all ratios of the ingredients the nmr peaks characteristic of the unreacted reagents are found to correspond to a preponderance of the total CH_3. Since the kinetic studies showed these mixtures to be at equilibrium, this means that the ring–chain equilibria of eq 2 must be shifted toward the right.

$$\underset{i\text{-mer chain}}{CH_3[As(CH_3)]_iCH_3} \rightleftharpoons \underset{(i-x)\text{-mer chain}}{CH_3[As(CH_3)]_{i-x}CH_3} + \underset{x\text{-mer ring}}{[As(CH_3)]_x} \qquad (2)$$

On the assumption that the heat of insertion of a CH_3As group into a permethylpolyarsine chain is independent of the chain length, we have the following form for the ring–chain equilibrium constant of eq 2

$$(K^0{}_{\text{mol}})_x = \frac{[x\text{-mer ring}][(i-x)\text{-mer chain}]}{[i\text{-mer chain}]} = \frac{[CH_3As \text{ in } x\text{-mer rings}]}{xV} \left[\frac{[(CH_3)_2As][2[CH_3As \text{ in chains}]}{2[CH_3As \text{ in chains}]}\right]^x \qquad (3)$$

where V is the over-all molar volume of the arsenic compounds in liters/mole. From eq 3 and 1, we can readily calculate with a computer the equilibrium constants which will give best fit to the observed nmr peaks. For $x = 5$, these constants on a molecular basis[15] are $(K^0{}_{\text{mol}})_{5,\text{predom}} = 90$ moles/l. and $K_{5,5}{}^{00} = 22.2$. The theoretically calculated peak areas (in parentheses) cor-

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responding to these equilibrium constants are compared in Table II with the experimental values.

Table II. Nmr Data for Reactions of Arsenomethane with Tetramethyldiarsine at 35°

$R \equiv$ CH_3/As	Percentage of total CH_3 as					
	ee	e*m*	*e*m*e*	*m*m*m*	(m)$_5$	(m)$_5'$
1.35	20.6	26.5	5.1	18.2	28.2	1.3
	(21.9)[a]	(29.8)	(3.2)	(14.5)	(28.7)	(1.3)
1.41	28.7	30.7	4.7	16.4	20.0	0.7
	(25.9)	(32.0)	(3.6)	(14.3)	(22.7)	(1.0)
1.47	33.0	30.5	4.6	15.9	15.1	0.6
	(30.1)	(33.3)	(4.0)	(13.7)	(17.4)	(0.8)
1.55	39.1	31.1	4.7	15.2	9.8	0.1
	(36.4)	(34.5)	(4.4)	(12.4)	(11.5)	(0.5)
1.57	42.8	30.3	4.6	13.1	9.1	
	(37.8)	(34.6)	(4.5)	(12.1)	(10.6)	(0.3)
1.65	48.0	31.1	3.9	11.6	5.3	
	(45.1)	(33.8)	(4.8)	(10.0)	(6.0)	(0.1)
1.70	52.6	29.6	4.1	9.2	4.5	
	(49.4)	(32.7)	(4.9)	(8.7)	(4.2)	
1.77	60.2	27.9	2.4	7.9	1.5	
	(58.1)	(29.2)	(4.8)	(6.1)	(1.7)	
1.88	76.8	19.3	1.5	2.2	0.1	
	(74.2)	(19.5)	(3.6)	(2.3)	(0.2)	

[a] Values in parentheses are calculated with a computer program written by L. C. D. Groenweghe, assuming that $(K^0_{mol})_5 = 90$ moles/l. and $K_{5,5}^{00} = 22.2$.

Other Physical Measurements. The viscosity of neat arsenomethane is 0.38 P at 25°, with an activation energy for flow of 8 kcal. From the relationship[16] representing the effect of a nonreactive solvent (the cyclic arsenomethanes) on the viscosity of polymer melts, we have estimated from the measured viscosity and the percentage of chain molecules *calculated* for $R = 1.000$ from the ring–chain constants that the viscosity of the chains free of the cyclics in the neat liquid is *ca.* 150 P. From the relationship[17] of the viscosity of short-chain polymer melts to their molecular weights, this viscosity was seen to be commensurate with an average of several hundred arsenic atoms per chain.

Mass spectra of the vapor volatilized from the surface of liquid arsenomethane exhibit only one peak of the type which increases in relative intensity with lowering of the ionization voltage. This parent-ion peak appears at a mass number of 450, which corresponds to 5 × CH_3As. At low ionization voltages, the only peaks which are observed correspond to 5 × CH_3As, this mass with either one or two CH_3 groups abstracted, and 3 × CH_3As. At high ionization voltages, the spectra are, of course, complex and the largest mass peak which was detected corresponds to 7 × CH_3As minus a CH_3 group. We infer from the spectra that, in the liquid phase, there are trace amounts of the molecules for which $n = 7$ and 6 in the formula $(CH_3As)_n$, with a predominant amount of $(CH_3As)_5$ and perhaps some $(CH_3As)_3$ but no $(CH_3As)_4$.

When the arsenomethane was volatilized into a glass bulb at *ca.* 0.1 μ pressure, there were two parent ions corresponding to 4 × CH_3As and 5 × CH_3As. The mass spectral data indicate that, in the dilute gas, there are appreciable amounts of the three- and four-membered cyclic molecules, as well as the pentamer. In all of the spectra, the peaks corresponding to multiples of CH_3As are relatively large, probably because scission of a ring structure into an equiatomic chain absorbs electron-collision energy which would otherwise result in fragmentation.

Discussion

Before the equilibrium character of this system was recognized by us, abortive attempts were carried out in our laboratory to prepare isolates of such short-chain compounds as pentamethyltriarsine. When methyldibromoarsine and dimethylbromoarsine were combined in the proper ratio and treated with various metals such as K, Li, and Hg to effect condensation, tetramethyldiarsine was generally observed to be the major component in the liquid phase which accompanied the ubiquitous reddish precipitate. From the preceding results, it should be obvious that even if pentamethyltriarsine were prepared, it would convert in a matter of seconds at room temperature to the equilibrium mixture corresponding to $R = 5/3 = 1.67$ which, as shown in Table II, consists predominantly of tetramethyldiarsine. The *a priori* assumption made in the two recent nmr studies[9,10] of arsenomethane (which appeared after this paper had been written) that the liquid consists of a pentameric ring is naive since melting of this kind of labile compound may lead to very different molecular structures in the liquid as compared to the crystal.

The ideas[18,19] presented by Kraft concerned with polyarsines are reasonably sound except for the neglect of the rapid exchange of parts between the molecules and the ring–chain equilibria. Since ring–chain equilibrium constants are to a first approximation independent of the terminal groups of the chain, the ring–chain equilibrium constants given in eq 1 and 3 must apply to the work of Kraft and Katyshkina.[19]

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