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# The Formation of Unsymmetric Diarsines from the Reaction of Aminoarsines and Secondary Organoarsines

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## Abstract

The reaction of $Me_2AsNMe_2$ with $Ph_2AsH$ yields $Ph_2AsAsMe_2$, $Me_2AsAsMe_2$, $Ph_2AsAsPh_2$ and $Me_2NH$. The course of the reaction was studied over a range of temperatures and concentrations in toluene-$d_8$ solution using $^1H$ and $^{13}C$ NMR spectroscopy. The NMR data indicate the initial formation of $Me_2NH$ and $Ph_2AsAsMe_2$. The diarsine subsequently undergoes symmetrization to give a mixture of the unsymmetric diarsine and the two symmetric diarsines. All attempts to isolate $Ph_2AsAsMe_2$ were unsuccessful. Exchange processes involving the >AsN</>NH and >AsAs</>AsAs< systems are very influential in determining the overall rate of reaction. Equilibrium constants were determined for the $Me_2AsAsMe_2/Ph_2AsAsPh_2$ and $Et_2AsAsEt_2/Ph_2AsAsPh_2$ systems. The results are compared with those of the analogous $Me_2AsH/Me_2AsNMe_2$ system.

## Introduction

Our studies on the $Me_2AsNMe_2/Me_2AsH$ [1], $Me_2AsNMe_2/MeAsH_2$ [2] and $Me_2AsNMe_2/Et_2AsAsEt_2$ [3] systems demonstrated that the lability of the As–N, As–As and As–H bonds leads to exchange reactions involving H–, $Me_2As$–, $Me_2N$– and/or MeAs< units. These exchange processes influence the overall rate of reaction and/or the equilibrium product distribution. These investigations led to new and convenient synthetic routes to symmetric diarsines [1] and cyclic polyarsines [4].

Previous reports concerning the characterization of unsymmetric diarsines are limited to those for $(CF_3)_2AsAsMe_2$ [5, 6]. Recently, we noted that the reaction of $Me_2AsNMe_2$ with $Et_2AsAsEt_2$ yields the unsymmetric diarsine, $Me_2AsAsEt_2$, in solution [3]. Thus, we have undertaken a detailed study of several reaction systems, which lead to the formation of unsymmetric diarsines in solution via $R_2As$-exchange processes to gain an understanding of the influence that various substituents may have on the lability of the As–As bond and the potential isolation of unsymmetric diarsines.

In this paper, we describe our results related to the formation of $Ph_2AsAsMe_2$ from the reaction of $Me_2AsNMe_2$ with $Ph_2AsH$. The course of the reaction was studied by $^1H$ and $^{13}C$ NMR spectroscopy as a function of reactant concentration, temperature and time. Those factors that significantly influence the rate of formation of $Ph_2AsAsMe_2$ and its equilibrium concentration are discussed. We also describe NMR studies of potential exchange reactions involving the >AsN</>NH, >AsN</>AsH, >AsN</>AsAs<, >AsAs</>AsH, and >AsAs</>AsAs< systems.

## Experimental

Standard high-vacuum-line techniques and a Vacuum Atmospheres Model HE-43 Dri-lab equipped with a Model HE-493 Dri-Train were used for storing and handling of all compounds. Toluene-$d_8$ and $Me_4Si$ were purchased from Aldrich Chemical Company and were stored over molecular sieves. $Me_2NH$ (Matheson Gas Products) was dried over sodium metal and was distilled on the vacuum line prior to use. $Me_2AsAsMe_2$ (60 °C/25 torr) [1], $Et_2AsAsEt_2$ (185 °C) [1, 7], $Ph_2AsAsPh_2$ (melting point (m.p.) 129–130 °C) [8], $Me_2AsCl$ (106 °C) [9], $Et_2AsCl$ (73–76 °C/73 torr) [10], $Me_2AsH$ (36 °C) [11], $Ph_2AsH$ (160 °C/10 torr) [12] and $Me_2AsNMe_2$ (108 °C) [13] were synthesized by previously reported methods. $Ph_2AsNMe_2$ (111–114 °C/1.0 torr) was synthesized by the reaction of $Ph_2AsCl$ with $Me_2NH$ using a procedure [13] analogous to that reported for $Me_2AsNMe_2$. The purity of all compounds was checked by NMR spectroscopy. The reaction mixtures were protected from exposure to light. The NMR tubes were carefully washed in a non-acid medium to prevent any possible acid-catalyzed exchange.

$^1H$ and $^{13}C$ NMR spectra were recorded on a Nicolet 300 MHz multinuclear FT NMR spectrometer operating at 300.1 and 75.4 MHz, respectively, using tetramethylsilane as an internal reference.

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The $^1$H NMR peaks were integrated with respect to a constant integration value for the TMS signal throughout a study. Reactant concentrations as a function of time in the $Me_2AsNMe_2/Ph_2AsH$ and $Me_2AsNMe_2/Me_2AsH$ systems were determined by the integration of the $^1$H NMR $Ph_2AsH$ and $Me_2AsH$ resonances, respectively. The overall rate of reaction $k_2$ (l mol$^{-1}$ min$^{-1}$) was determined from the slope of a plot of the reciprocal of the reactant concentration *versus* time (1:1 stoichiometry) and the corresponding correlation coefficients, $r$, are given in the text. See spectral data below for all NMR assignments.

### *Synthesis of $Me_2AsAsMe_2$ and $Ph_2AsAsPh_2$ from the Reaction of $Me_2AsNMe_2$ with $Ph_2AsH$*

A 20.0 mmol (4.60 g) sample of $Ph_2AsH$ was condensed onto approximately 20 ml of a toluene solution containing 20.0 mmol (2.98 g) of $Me_2AsNMe_2$ at $-196$ °C by using standard vacuum line techniques. The mixture was warmed slowly to $-25$ °C and stirred for 2 days. The toluene and dimethylamine were removed under reduced pressure in the vacuum line. The resulting white solid was washed with pet-ether (40–60 °C) and recrystallized from a chloroform–pet-ether mixture [yield 3.2 g (69%); $Ph_2AsAsPh_2$, m.p. 129–130 °C] [8]. Vacuum distillation of the filtrate gave 1.5 g $Me_2AsAsMe_2$ (71%) at 60 °C/25 torr [1]. The diarsines were characterized by $^1$H and $^{13}$C NMR spectroscopy [1].

### *Reactions of $Me_2AsNMe_2$ with $Ph_2AsH$ and $Me_2AsH$; $Me_2AsAsMe_2$ with $Ph_2AsH$; and $Ph_2AsAsPh_2$ with $Me_2AsH$, $Me_2AsAsMe_2$ and $Me_2AsNMe_2$*

The reactions of $Me_2AsNMe_2$ with equimolar amounts of $Ph_2AsH$ (1.32, 0.75 or 0.50 mmol) and $Me_2AsH$ (0.75 or 0.50 mmol); $Me_2AsAsMe_2$ (0.50 mmol) with $Ph_2AsH$ (0.50 mmol); and $Ph_2AsAsPh_2$ (0.25 mmol) with $Me_2AsH$ (0.25 mmol), $Me_2AsAsMe_2$ (0.25 mmol) and $Me_2AsNMe_2$ (0.25 mmol) were carried out in toluene-d$_8$ using the following procedure. The appropriate amount of the less volatile compound and a drop of TMS were dissolved in enough toluene-d$_8$ in an NMR tube (10 mm × 22.5 cm, Pyrex) equipped with a greaseless vacuum stopcock. The tube was degassed using standard vacuum line techniques. At liquid nitrogen temperatures, an equimolar amount of the more volatile compound was condensed into the NMR tube. The total volume of the solution was maintained at 4.0 ml. The tube was sealed, agitated gently at $-95$ °C (toluene slush), and inserted into the precooled ($-90$ °C) probe of the NMR spectrometer. The reaction was then followed at selected temperatures by recording the $^1$H and $^{13}$C NMR spectra as a function of time. We restricted our study to a maximum temperature of $-10$ °C due to the low boiling $Me_2NH$. The reaction of $Me_2AsNMe_2$ with $Ph_2AsH$ carried out with more than 0.75 mmol of each reactant resulted in the precipitation of $Ph_2AsAsPh_2$.

### *Reactions of $Ph_2AsAsPh_2$ with $R_2AsAsR_2$*

Equimolar amounts of $Ph_2AsAsPh_2$ and $R_2AsAsR_2$ (R = Me, Et) (0.50 mmol of each reactant) were dissolved in enough toluene-d$_8$ at room temperature to give a total solution volume of 4.0 ml. The reaction was monitored by $^1$H NMR spectroscopy until equilibrium had been reached. The equilibrium constant, $K_{eq}$, was calculated for the reaction $Ph_4As_2 + R_4As_2 \rightleftharpoons 2Ph_2AsAsR_2$ by using the $^1$H NMR peak intensities for the reactants and the products.

### *NMR Data*

The following is a list of $^1$H and $^{13}$C NMR spectral data [$\delta$, ppm (TMS)] in toluene-d$_8$ solution at $-10$ °C that were determined independently on synthesized compounds. The unsymmetric diarsine data were obtained from the solution equilibria studies.

#### *$^1$H NMR Data*

$Me_2AsNMe_2$: 0.79 ($Me_2As$), 2.42 ($Me_2N$). $Ph_2AsH$: [14] 4.84 (AsH), 6.97–7.01 (C-3, 5; C-4; m), 7.32–7.35 (C-2,6; m). $Ph_2AsAsMe_2$: 0.94 (MeAs), 6.94–7.09 (C-3,5; C-4; m), 7.51 (C-2,6; m). $Ph_2AsAsPh_2$: 6.95–6.99 (C-3,5; C-4; m), 7.40–7.44 (C-2,6; m). $Me_2AsAsMe_2$: 0.96. $Me_2NH$: 2.17 ($Me_2N$), 0.21 (NH). $Me_2AsH$: 0.77 ($Me_2As$, d, $^3J_{HH}$ = 7.0 Hz), 2.39 (AsH, septet, $^3J_{HH}$ = 6.9 Hz). $Et_2AsAsEt_2$: 1.16 ($CH_3CH_2As$, t), 1.54 ($CH_3\mathbf{CH_2}As$, m). $Me_2AsAsEt_2$: [3] 1.02 ($Me_2As$), 1.16 ($CH_3CH_2As$, t), 1.53 ($CH_3\mathbf{CH_2}As$, m). $Ph_2AsAsEt_2$: 1.05 ($CH_3CH_2As$, t), 1.53 ($CH_3CH_2As$, m). 6.92–7.12 (C-3,5; C-4; m), 7.59 (C-2,6; m). $Ph_2AsNMe_2$: 2.50 ($Me_2N$), 7.10–7.16 (C-3,5; C-4 m), 7.44–7.47 (C-2, 6; m).

#### *$^{13}$C NMR Data*

$Me_2AsNMe_2$: 9.70 ($Me_2As$, $^1J_{CH}$ = 130.6 Hz), 41.92 ($Me_2N$, $^1J_{CH}$ = 132.7 Hz). $Ph_2AsH$: [14] 128.2 (C-4), 128.9 (C-3,5), 134.9 (C-2,6), 136.9 (C-1). $Ph_2AsAsMe_2$: 7.0 ($Me_2As$), 128.3 (C-4), 128.8 (C-3,5), 134.4 (C-2,6), 139.6 (C-1). $Ph_2AsAsPh_2$: 128.4 (C-4), 128.8 (C-3,5), 134.9 (C-2,6), 139.1 (C-1). $Me_2AsAsMe_2$: 5.94 ($^1J_{CH}$ = 132.6 Hz). $Me_2NH$: 38.87 ($^1J_{CH}$ = 131.9 Hz). $Me_2AsH$: 1.43 ($^1J_{CH}$ = 132.5 Hz). $Et_2AsAsEt_2$: 12.80 ($\mathbf{CH_3}CH_2As$, $^1J_{CH}$ = 125.8 Hz), 14.63 ($CH_3\mathbf{CH_2}As$, $^1J_{CH}$ = 132.4 Hz). $Me_2AsAsEt_2$: [3] 6.16 (MeAs, $^1J_{CH}$ = 132.7 Hz), 12.61 ($\mathbf{CH_3}CH_2As$, $^1J_{CH}$ = 125.6 Hz), 15.28 ($CH_3\mathbf{CH_2}As$, $^1J_{CH}$ = 132.3 Hz). $Ph_2AsAsEt_2$: 12.41 ($\mathbf{CH_3}CH_2As$), 15.96 ($CH_3\mathbf{CH_2}As$), 128.3 (C-4), 128.8 (C-3,5), 134.7 (C-2,6), 139.5 (C-1)).

$Ph_2AsNMe_2$: 43.40 ($Me_2N$), 140.8 (C-1), 133.2 (C-2, 6), 128.9 (C-3, 5), 128.2 (C-6).

## Results and Discussion

The reaction of an equimolar mixture of $Me_2AsNMe_2$ and $Ph_2AsH$ (0.125 M) in toluene-$d_8$ was monitored by $^1H$ and $^{13}C$ NMR spectroscopy as a function of temperature and time. The $^1H$ NMR spectra at −80 °C consist of very low intensity peaks assignable to $Ph_2AsAsMe_2$, $Ph_2AsAsPh_2$, $Me_2AsAsMe_2$ and $Me_2NH$ and high intensity resonances corresponding to the reactants. After raising the temperature to −60 °C, the peaks associated with $Ph_2AsAsMe_2$ and $Me_2NH$ increased, peaks assigned to $Me_2AsNMe_2$ and $Ph_2AsH$ decreased, and peaks attributed to $Me_2AsAsMe_2$ and $Ph_2AsAsPh_2$ increased slightly in intensity. At −40 °C, the $Me_2N$–signals (2.4 and 2.17 ppm) broadened because of slow $Me_2N$ exchange between $Me_2AsNMe_2$ and $Me_2NH$ [1, 15]. Increased conversion of $Me_2AsNMe_2$ and $Ph_2AsH$ to $Ph_2AsAsMe_2$, $Me_2AsAsMe_2$, $Ph_2AsAsPh_2$ and $Me_2NH$ occurred upon raising the temperature to −25 °C ($CCl_4$ slush). As more $Me_2AsNMe_2$ was consumed, the $Me_2N$– $^1H$ NMR peaks narrowed. After 3 days at −25 °C the $^1H$ NMR intensity data indicated complete consumption of the reactants and a resulting equilibrium mixture containing 32% $Ph_2AsAsMe_2$, 9% $Me_2AsAsMe_2$, 9% $Ph_2AsAsPh_2$ and 50% $Me_2NH$ and a trace amount of $Me_2AsH$.

These results suggest that $Me_2AsNMe_2$ reacts completely with $Ph_2AsH$ to yield $Ph_2AsAsMe_2$ and $Me_2NH$ (eqn. (1)). $Me_2NH$ undergoes $Me_2N$– moiety exchange with $Me_2AsNMe_2$ (eqn. (2)). This exchange process has been shown to be both temperature and concentration dependent [1, 15] and is important in influencing the overall reaction kinetics (discussed below).

$$Me_2AsNMe_2 + Ph_2AsH \longrightarrow Ph_2AsAsMe_2 + Me_2NH \qquad (1)$$

$$Me_2AsNMe_2 + Me_2NH \rightleftharpoons Me_2AsNMe_2 + Me_2NH \qquad (2)$$

The $Ph_2AsAsMe_2$ produced via eqn. (1) undergoes symmetrization to $Me_2AsAsMe_2$ and $Ph_2AsAsPh_2$ (eqn. (3)). This reaction is important in influencing both the overall reaction kinetics as well as yield of unsymmetric diarsine (discussed below).

$$2Ph_2AsAsMe_2 \rightleftharpoons Me_2AsAsMe_2 + Ph_2AsAsPh_2 \qquad (3)$$

The observation of a trace amount of $Me_2AsH$ in the $Ph_2AsH/Me_2AsNMe_2$ equilibrium mixture suggests that >AsAs</>AsH exchange reactions (eqns. (4) and (5)) could occur. Because of the previously established lability of the As–N, As–As, and As–H bonds, other reactions are also possible [1–4] (eqns. (6) and (7)).

$$Ph_2AsAsMe_2 + Ph_2AsH \rightleftharpoons Ph_2AsAsPh_2 + Me_2AsH \qquad (4)$$

$$Me_2AsAsMe_2 + Ph_2AsH \rightleftharpoons Ph_2AsAsMe_2 + Me_2AsH \qquad (5)$$

$$Me_2AsH + Me_2AsNMe_2 \longrightarrow Me_2AsAsMe_2 + Me_2NH \qquad (6)$$

$$Ph_2AsAsPh_2 + Me_2AsNMe_2 \rightleftharpoons Ph_2AsAsMe_2 + Ph_2AsNMe_2 \qquad (7)$$

The relative importance of the reactions represented by eqns. (3)–(7) was investigated independently to determine the relative rate and extent of these as they influence the course of the initial $Ph_2AsH/Me_2AsNMe_2$ reaction.

The symmetrization process (eqn. (3)) was investigated by following the reaction of $Me_2AsAsMe_2$ with $Ph_2AsAsPh_2$. The NMR data of an equimolar mixture of $Me_2AsAsMe_2$ and $Ph_2AsAsPh_2$ in toluene-$d_8$ (0.125 M) at −25 °C indicated a facile exchange to yield within 50 min an equilibrium mixture containing 64% $Ph_2AsAsMe_2$, 18% $Me_2AsAsMe_2$ and 18% $Ph_2AsAsPh_2$. To determine the influence that the organic group on arsenic has on the equilibrium composition, we also studied the exchange reactions of $Et_2AsAsEt_2$ with $Ph_2AsAsPh_2$ and $Me_2AsAsMe_2$ in toluene-$d_8$ at 24 °C. All exchange reactions reached equilibrium within 30 min of mixing. The equilibrium constants are 4.0 (50% $Me_2AsAsEt_2$)*, 12.6, and 13.8 (65% $Ph_2AsAsEt_2$) for the $Me_2AsAsMe_2/Et_2AsAsEt_2$, $Ph_2AsAsPh_2/Me_2AsAsMe_2$, and $Ph_2AsAsPh_2/Et_2AsAsEt_2$ systems, respectively at 24° (see 'Experimental' for NMR data and $K_{eq}$ definition). An equilibrium constant of 4.0 is predicted based on probability considerations. However, substitution of a phenyl group for a methyl or ethyl group shifts the equilibrium towards the unsymmetric diarsine. These data are consistent with those from previous studies on exchange reactions involving similar P–As [16, 17], As–Sb [16], and As–N [3] systems.

The reaction represented by eqn. (4) was studied by following the reaction of $Me_2AsH$ with $Ph_2AsAsPh_2$ at −10 °C, because $Ph_2AsAsMe_2$ cannot be isolated from solution. The reaction could only be studied at a lower concentration (0.0625 M in each reactant) because of the low solubility of $Ph_2AsAsPh_2$. The NMR spectra indicated facile exchange

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*The $K_{eq}$ value should have been listed as 4.0 in ref. 3.

with only a limited formation of $Ph_2AsAsMe_2$ and $Ph_2AsH$. At equilibrium, 5% $Ph_2AsAsMe_2$, 5% $Ph_2AsH$, 45% $Ph_2AsAsPh_2$ and 45% $Me_2AsH$ were detected in the reaction mixture.

The NMR spectra of the $Ph_2AsH/Me_2AsAsMe_2$ reaction mixture (eqn. (5)) indicated no reaction at −80 °C. However, at −25 °C, very low intensity peaks corresponding to $Ph_2AsAsMe_2$ and $Me_2AsH$ were noted. After 30 min, resonances due to $Ph_2AsAsMe_2$ were also noted. The reaction reached equilibrium after 27 days at −25 °C with 34% $Ph_2AsAsMe_2$, 21% $Me_2AsAsMe_2$, 7% $Ph_2AsAsPh_2$, 24% $Me_2AsH$ and 14% $Ph_2AsH$ in the reaction mixture.

The reaction represented by eqn. (6) has been previously reported [1]. $Me_2AsH$ reacts with $Me_2AsNMe_2$ to yield $Me_2AsAsMe_2$ and $Me_2NH$ over the temperature and concentration conditions of this study.

The possibility of reaction between $Ph_2AsAsPh_2$ and $Me_2AsNMe_2$ (eqn. (7)) was studied at −10 °C. The NMR spectral data of an equimolar mixture indicated no reaction after 7 h. A slow reaction did occur at 24 °C to yield after 15 days a mixture containing 6% $Ph_2AsAsMe_2$, 6% $Ph_2AsNMe_2$, 44% $Me_2AsNMe_2$ and 44% $Ph_2AsAsPh_2$.

Although the reactions represented by eqns. (4)–(6) appear to be of minor importance in the $Me_2AsNMe_2/Ph_2AsH$ system at −25 °C, they are of slightly greater importance at higher reactant concentrations and temperatures. For example, an investigation of the $Ph_2AsH/Me_2AsNMe_2$ reaction at 0.330 M concentration and −10 °C indicated the initial formation and then consumption of $Me_2AsH$ as proposed in eqns. (4)–(6). At −10 °C, resonances were observed initially due to $Ph_2AsAsMe_2$, $Me_2AsAsMe_2$, $Ph_2AsAsPh_2$ and $Me_2NH$. The $^1H$ NMR peaks assigned to the $Me_2N$– moieties of $Me_2AsNMe_2$ and $Me_2NH$ were considerably broadened due to $Me_2N$– exchange. After 5 min, low intensity peaks attributed to $Me_2AsH$ appeared. With time, the intensities of the $Me_2AsH$, $Ph_2AsAsMe_2$, $Me_2AsAsMe_2$ and $Ph_2AsAsPh_2$ peaks (eqns. (1) and (3)) increased, the widths of the $Me_2N$– $^1H$ NMR lines narrowed, and the intensities of the $Ph_2AsH$ peaks decreased. After 4 h, a trace amount of $Ph_2AsAsPh_2$ had precipitated in the NMR tube. Although all the $Ph_2AsH$ had been consumed within 18 h, some $Me_2AsNMe_2$ remained. After 48 h, all the $Me_2AsH$, as well as the $Me_2AsNMe_2$, was consumed to give a mixture of $Ph_2AsAsMe_2$, $Ph_2AsAsPh_2$, $Me_2AsAsMe_2$ and $Me_2NH$.

The relatively rapid consumption of $Ph_2AsH$ and observed formation of $Me_2AsH$ at −10 °C, as compared to −25 °C, can be attributed to the greater significance of the reactions represented by eqns. (4) and (5) at higher temperature and concentration. This is followed by the irreversible reaction of $Me_2AsNMe_2$ with $Me_2AsH$ (eqn. (6)).

The synthesis of $Ph_2AsAsMe_2$ was attempted by reacting equimolar amounts of $Me_2AsNMe_2$ with $Ph_2AsH$ at −25 °C in toluene. All attempts to isolate $Ph_2AsAsMe_2$ by removal of solvent and $Me_2NH$ under reduced pressure resulted in the complete conversion to $Ph_2AsAsPh_2$ and $Me_2AsAsMe_2$.

The kinetics of the $Me_2AsNMe_2/Ph_2AsH$ reaction were studied at −10 and −25 °C and 0.125 and 0.188 M initial reactant concentrations (1:1 stoichiometry). Although the linearity of the plots of $[Ph_2AsH]^{-1}$ *versus* time at a given temperature and concentration indicates that the reaction is second order, the rate constant appears to be an averaged value for the combined reactions (eqns. (1), (2) and (3)) rather than being specific for the initial step (eqn. (1)). As expected, the rate constant increases with increasing temperature. However, at a given temperature the apparent second order rate constant decreases with increasing initial reactant concentration although the $[Ph_2AsH]^{-1}$ *versus* time plots are linear. For example, at −25 °C, $k_2$ (l $mol^{-1}$ $min^{-1}$) = 0.012 ($r$ = 0.992) at 0.188 M, while $k_2$ = 0.020 ($r$ = 0.093) at 0.125 M. Similarly at −10 °C, $k_2$ = 0.035 ($r$ = 0.997) at 0.188 M and 0.040 ($r$ = 0.997) at 0.125 M. This variation of rate constant with concentration suggests that when the competing symmetrization (eqn. (2)) and transamination (eqn. (3)) reactions are considered, the overall rate of the reaction is more complex than second order.

In an attempt to establish the relative importance of the competing transamination and symmetrization reactions, the $Me_2AsNMe_2/Me_2AsH$ system [1] was studied at the same concentrations and temperatures as those for the $Me_2AsNMe_2/Ph_2AsH$ system. Significant curvature in the second order rate constant plot of $[Me_2AsH]^{-1}$ *versus* time was observed after one half-life. Therefore, the transamination process is very significant in slowing down the overall rate of reaction in the $Me_2AsNMe_2/Me_2AsH$ system when there is no possibility of a symmetrization reaction. However, in the $Me_2AsNMe_2/Ph_2AsH$ system, the transamination reaction becomes less significant in slowing down the initial step, because the symmetrization process (eqn. (3)) promotes the initial step of the reaction (eqn. (1)) which involves consumption of $Ph_2AsH$.

Thus, the reaction of $Me_2AsNMe_2$ with $Ph_2AsH$ to yield $Ph_2AsAsMe_2$ involves competing facile exchange equilibria, primarily transamination (eqn. (2)) and symmetrization (eqn. (3)), and these processes contribute significantly to the overall rate of reaction. The reactions represented by eqns. (4)–(7) appear to be of minor importance in influencing the rate of formation and overall yield of the unsymmetric diarsine at −25 °C. This can be substantiated by the fact that the ratio of the percentage distributions of $Ph_2AsAsMe_2$, $Me_2AsAsMe_2$

and $Ph_2AsAsPh_2$ at equilibrium in the $Ph_2AsH/Me_2AsNMe_2$ system (eqn. (1)) is the same as the ratio observed for the independently studied $Ph_2AsAsPh_2/Me_2AsAsMe_2$ system (eqn. (3)). These exchange reactions are assumed to involve the formation of a concerted, four-centered activated intermediate that undergoes bond dissociation and formation processes to give the various exchange products observed in the reaction mixture [18].

Preliminary investigations of analogous reactions involving >AsN< and >PH bonded compounds indicate the formation of phosphinoarsines. The reaction of $Me_2AsNMe_2$ with $Ph_2PH$ in toluene-$d_8$ solution yields $Ph_2PAsMe_2$ and $Me_2NH$. $Ph_2PAsMe_2$ then undergoes symmetrization to yield $Ph_2PPPh_2$ and $Me_2AsAsMe_2$. The >AsN</>PH and >AsAs</>PP< systems are currently being studied to obtain kinetic and thermodynamic data and to relate these data with those obtained from the >AsN</>AsH and >AsAs</>AsAs< systems.

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